

Experimental Assessment and Enhancement of Planar Laser-Induced Fluorescence Measurements of Nitric Oxide in an Inverse Diffusion Flame

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LIST OF SYMBOLS

English Symbols

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
A_L	Cross sectional area of laser beam	cm^2
$A_{L,\text{sat}}$	Saturation cross sectional area	cm^2
A_N	Net spontaneous emission rate coefficient	s^{-1}
$A_{N,F}$	Spectrally filtered net spontaneous emission rate coefficient	s^{-1}
$A_{vv'}$	Spontaneous band emission rate coefficient	s^{-1}
bkg	Background emission image	counts
B	Environmental emission	photons
B_{lu}	Einstein B coefficient for absorption from level l to level u	$\text{cm}^2 \cdot \text{cm}^{-1} / \text{J}$
B_{ul}	Einstein B coefficient for stimulated emission from level u to level l	$\text{cm}^2 \cdot \text{cm}^{-1} / \text{J}$
$\tilde{B}_{lu}$	Einstein B coefficient for absorption from level l to level u	$\text{cm}^3 \cdot \text{cm}^{-1} / \text{J} \cdot \text{s}$
$\tilde{B}_{ul}$	Einstein B coefficient for stimulated emission from level u to level l	$\text{cm}^3 \cdot \text{cm}^{-1} / \text{J} \cdot \text{s}$
C_B	Concentration of the NO standard gas	ppm
C_D	Digital equivalent fluorescence signal	counts

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
C_p	Total photons collected at the ICCD entrance per pixel	photons
$C_{p,ss}$	Steady state solution for C_p	photons
$C_{p,ssd}$	Deviation from steady state solution for C_p	photons
$C_{p,f}$	Spectrally filtered photons collected at the ICCD entrance per pixel	photons
$C_{p,t}$	Total (not spectrally filtered) photons collected at the ICCD entrance per pixel	photons
CF^{LSF}	LSF calibration factor	ppm/V
CF^{PLIF}	PLIF calibration factor	ppm/counts
dnr	Dark and readout noise image	counts
D_R	Doped [NO] relative to calibration flame reactants	ppm
D_P	Doped [NO] relative to calibration flame products	ppm
E_L	Laser energy per pulse	mJ/pulse
E_p	Fluorescence photon emission event	photons/cm ³ ·sr
EINO	NO emission index	g NO/kg fuel
EINO _x	NO _x emission index	g NO _x /kg fuel
$f_B(T)$	Boltzmann fraction	--
$F(v)$	Spectral filter function of collection optics	--
F^v	Normalized spectral fluence	J/cm ² ·cm ⁻¹
FWHM	Full width at half maximum	ns or cm ⁻¹
g	Degeneracy	--
G	ICCD gain	--

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
ima	Total signal image	counts
$I_v(\nu, t)$	Spectral irradiance	$\text{W}/\text{cm}^2 \cdot \text{cm}^{-1}$
I_v°	Normalized spectral irradiance	$\text{W}/\text{cm}^2 \cdot \text{cm}^{-1}$
I_v^{sat}	Saturation spectral irradiance	$\text{W}/\text{cm}^2 \cdot \text{cm}^{-1}$
I°	Normalized irradiance	W/cm^2
IM	Image	counts
K^{LSF}	Grouped constants in the LSF equation	$\text{V} \cdot \text{cm}^3/\text{photons}$
K^{LIF}	Grouped constants in the LIF equation	$\text{cm}^3 \cdot \text{cm}^2 \cdot \text{cm}^{-1}/\text{J}$
lib	Laser-induced background image	counts
L	Fraction of doped NO lost due to flame-front destruction	--
$L_L(\nu)$	Laser spectral lineshape function	--
L°	Laser spectral profile normalizing constant	--
LSD	Laser sheet deviation image	counts
M	Magnification of collection optics	--
MW	Molecular weight	g/gmole
n	Number of moles	moles
N	Number density	cm^{-3}
N_A	Avogadro's number	molecules/kgmole
N_l	Number density of lower laser-coupled level	cm^{-3}
N_u	Number density of upper laser-coupled level	cm^{-3}
N_l°	Initial number density of lower laser-coupled level	cm^{-3}

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
N_T	Total number density	cm^{-3}
$N_{T,RT}$	Total concentration relative to the temperature of the calibration flame	relative ppm
$N_{T,RT,RQ}$	Total concentration relative to the temperature and electronic quenching rate of the calibration flame	relative ppm
Ni1	Intermediate image	counts
Ni2	Corrected [NO] image	counts
P	Pressure	kPa
P_L	Integrated power	W
Q_e	Electronic quenching rate coefficient	s^{-1}
Q_i	Photoionization rate coefficient	s^{-1}
Q_p	Predissociation rate coefficient	s^{-1}
R	ICCD responsivity	counts/photon
R_L	Repetition rate of laser	Hz
R_u	Universal gas constant	$\text{kPa}\cdot\text{cm}^3/\text{kgmole}\cdot\text{K}$
snu	Sheet nonuniformity image	counts
S_D	Fluorescence signal	counts
t_G	ICCD gate width	ns
t_o	ICCD gate delay	ns
t_w	ICCD wait time	s
T	Temperature	K
$T_L(t)$	Laser temporal profile	--

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
T°	Temporal profile normalizing constant	--
TR	Transmission ratio	--
v'	Vibrational quantum number of upper level	--
v''	Vibrational quantum number of lower level	--
V_C	Collection volume per pixel	cm^3
$\dot{V}$	Volumetric Flow Rate	SLPM
$\dot{V}R$	Volumetric Flow Rate Ratio	--
W_{lu}	Absorption rate coefficient	s^{-1}
W_{ul}	Stimulated emission rate coefficient	s^{-1}
x	Transverse dimension of collection volume perpendicular to laser k vector	cm
x'	Pixel dimension perpendicular to laser k vector	cm
$[X]_{\text{ND}}$	Concentration of species X in number density	cm^{-3}
$[X]_{\text{ppm}}$	Concentration of species X in parts per million	cm^3/cm^3
y	Longitudinal dimension of collection volume	cm
Y_A°	Absorption spectral profile normalizing constant	$1/\text{cm}^{-1}$
$Y_A(v)$	Absorption spectral lineshape function	$1/\text{cm}^{-1}$
$Y_E(v)$	Emission spectral lineshape function	$1/\text{cm}^{-1}$
$Y_{\text{EN}}(v)$	Net emission spectral lineshape function	$1/\text{cm}^{-1}$
z	Transverse dimension of collection volume parallel to laser k vector	cm
z'	Pixel dimension parallel to laser k vector	cm

Greek Symbols

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
β	Inverse of the transition lifetime	s^{-1}
γ	Lower to upper level degeneracy ratio plus unity	--
Γ_{luL}	Spectral overlap fraction	--
δX	Absolute uncertainty in the parameter X	(X)
ϵX	Relative uncertainty in the parameter X	--
η	Surface loss factor for collection optics	--
θ	Jet impingement angle relative to chimney wall normal	degrees
λ	Wavelength	nm
ν	Frequency	cm^{-1}
ν_{em}	Emission frequency	cm^{-1}
ν_{ex}	Excitation frequency	cm^{-1}
ν_o	Center frequency	cm^{-1}
$\Delta \nu_L$	Laser linewidth (FWHM)	cm^{-1}
$\Delta \nu_A$	Absorption linewidth (FWHM)	cm^{-1}
Δt_L	Laser temporal width (FWHM)	ns
τ	Temporal profile normalizing time	ns
Υ^ν	Effective fluorescence coefficient	$cm^2 \cdot cm^{-1} / J$
Υ_I^ν	Effective interference coefficient	$cm^2 \cdot cm^{-1} / J$
ϕ	Equivalence ratio	--
ϕ_o	Overall equivalence ratio	--

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
Φ	Fluorescence yield	--
Ω	Solid angle of collection optics	sr

approximately 50% in the quantitative nature of the PLIF measurements, and results in concentration images that are nominally as quantitative as a single LSF point measurement. Furthermore, these experimentally-based PLIF correction procedures can be applied to other species, including radicals, for which no experimental data are available from which to implement numerically-based PLIF enhancement procedures.

CHAPTER 1

INTRODUCTION

1.1 Background

Planar laser-induced fluorescence (PLIF) is a nonintrusive optical diagnostic tool for making measurements of temperature, pressure, velocity or concentration. The primary advantage of PLIF over other fluorescence-based diagnostics is that it provides two-dimensional, spatially resolved data, i.e., an image of the measured parameter. PLIF measurements achieve high temporal and spatial resolution via the use of pulsed lasers and intensified-charge-coupled-device (ICCD) detectors, respectively. Because of this high temporal and spatial resolution, PLIF concentration measurements are immediately quantitative in time and space. However, obtaining a quantitative species concentration image from a raw PLIF image requires correcting that image for errors associated with variations in the Boltzmann fraction, the overlap fraction and the electronic quenching rate coefficient. These measurement parameters depend to varying degrees on the local temperature, pressure, major-species concentrations, and their associated electronic quenching cross-sections. Of the three measurement parameters, correcting for the influence of variations in the electronic quenching rate coefficient is the most difficult, and represents the primary limitation to realizing quantitative PLIF imaging of species concentrations (Hanson et al., 1990). Because of this difficulty, PLIF concentration imaging is most often used as a qualitative diagnostic.

Recent improvements in both the measurement of electronic quenching cross-sections at flame temperatures (Drake and Ratcliffe, 1993) and the modeling of electronic quenching rate coefficients (Paul et al., 1993) allow for improved PLIF concentration images. These improvements can be used to implement numerically-based correction

schemes (Paul et al., 1994) which enhance the quantitative nature of PLIF concentration images. However, in addition to electronic quenching cross-sections for the major species, these advanced correction schemes require spatially-resolved measurements of the major-species concentrations. Although such measurements can be made in reacting flows (e.g., Carter and Barlow, 1994), they require extensive if not unique experimental resources. Moreover, the requisite major-species electronic quenching cross-sections have been measured for only a limited number of probe species. Hence, the general implementation of numerically-based correction schemes for PLIF measurements would require a significant lead time for cross-section measurements and model validation. Consequently, the applicability of numerically-based correction schemes is limited both in terms of the number of researchers with the resources necessary for their implementation, as well as the number of probe species for which they may be implemented.

1.2 Content of Report

The objectives of this study are: (1) to experimentally assess the quantitative nature of uncorrected PLIF measurements of nitric oxide (NO) concentration ([NO]); (2) to develop experimentally-based procedures for enhancing the quantitative nature of PLIF [NO] images; and (3) to experimentally evaluate the effectiveness of the proposed experimentally-based PLIF enhancement procedures.

The study is performed by making PLIF measurements of [NO] in an atmospheric pressure $\text{C}_2\text{H}_6/\text{O}_2/\text{N}_2$ inverse diffusion flame (IDF). NO is an environmentally-important species because of its role in the production of photochemical smog and in the destruction of stratospheric ozone. The primary basis for using an IDF is that it provides a very harsh environment for implementation of PLIF concentration imaging. This is due to the accompanying wide range of temperatures, stoichiometries and major-species concentrations. Hence, the IDF provides a worst-case scenario for PLIF assessment and enhancement. However, since the extent of knowledge concerning IDFs is so limited, these measurements also further the IDF-knowledge data base.

In the following chapter, a chemiluminescent-based study of NO formation in a laboratory-scale, staged-air burner is presented. Staged-air combustion is a combustion

scheme for low-NO emissions incorporating inverse diffusion flames. This is a practical study applicable to the industrial furnace community, and was used to gain an initial knowledge of IDFs (Partridge and Laurendeau, 1995b).

The PLIF literature is reviewed in Chapter 3, including a basic discussion of the measurement theory. The review generally covers PLIF temperature, pressure and velocity measurements with an emphasis on quantitative PLIF concentration measurements. Fluorescence theory, including linear PLIF as well as laser-saturated fluorescence (LSF), is rigorously developed in Chapter 4. This chapter includes the development of a novel formulation of the overlap fraction which affords a clear physical description of the spectral interaction between laser radiation and an absorption line (Partridge and Laurendeau, 1995a). Chapter 5 is a detailed presentation of the experimental apparatus used for making LSF and PLIF measurements of [NO] in the IDF. The PLIF/LSF laboratory was developed during the course of this work and has the capability of permitting separate or simultaneous PLIF and/or LSF measurements in a variety of atmospheric pressure flame environments. This chapter includes work concerning the development of optimum concentration and tuning curves for two new research-grade laser dyes which were used in subsequent experiments (Partridge et al., 1994). Chapter 5 also includes the presentation of a unique axial inverse-diffusion-flame burner (AIDF) which we developed for use in the PLIF studies. In addition to producing IDFs, this burner has been used for normal-diffusion-flame and partially-premixed-flame studies in our laboratory.

In Chapter 6 we present an experimental assessment of O₂ interferences on fluorescence-based measurements of [NO] in atmospheric and high-pressure environments. Optimum excitation and detection schemes are determined for both narrow-band (i.e., LSF) and broad-band (i.e., PLIF) detection strategies applicable to fluorescence-based measurements. These optimum measurement schemes are determined based on excitation and detection scans in uncooled, fuel-lean methane flames with nitrogen and argon dilution. Five candidate filtering schemes are assessed for broad-band detection measurements, and assessment parameters are formulated to evaluate the

influence of various excitation/filter combinations on interference rejection and the detection limit.

The PLIF assessment, including the development and evaluation of experimentally-based PLIF enhancement procedures, is presented in Chapter 7. Correction of PLIF images for the influences of the Boltzmann and overlap fractions is relatively straightforward compared to that for the electronic quenching rate coefficient. Moreover, the influences of the Boltzmann and overlap fractions are accounted for in the experimentally-based enhancement procedures. Hence, the quantitative nature of the uncorrected and experimentally-enhanced PLIF images are assessed relative to the degradation due to only the electronic quenching rate coefficient. The PLIF images of [NO] are assessed by comparison to an array of LSF point measurements. Experimentally-based PLIF correction procedures which use one or more of the LSF point measurements as secondary inputs are developed for various general test environments. These experimentally-based procedures are assessed using the same array of LSF point measurements. The conclusions and recommendations for future PLIF development and application are presented in Chapter 8.

CHAPTER 2

CHEMILUMINESCENT MEASUREMENTS OF NITRIC OXIDE FORMATION BY INVERSE DIFFUSION FLAMES IN STAGED-AIR BURNERS

2.1 Introduction

To characterize NO formation by inverse diffusion flames (IDFs), initial measurements were made by using a chemiluminescence-based probe-sampling technique. This technique was used to make integrated [NO] measurements in the post-flame region of a staged-air combustor for various operating conditions. In addition to elucidating the dependence of NO formation on combustor operating parameters, this study suggested regions within the IDF where NO formation is maximized. Moreover, this initial study was useful for evaluating the utility of the staged-air combustor in investigations to assess the quantitative nature of PLIF [NO] imaging and to develop and evaluate experimentally-based PLIF enhancement procedures. The results of this work were reported by Partridge and Laurendeau (1995b).

The detrimental effects of nitric oxide emissions has prompted the need for less polluting combustion strategies. Staged-air combustion is a candidate technique for producing ultra-low- NO_x burners for furnaces (Garg, 1994). This approach retains the practical and safety benefits of non-premixed combustion while minimizing the residence time of the combustion gases in high temperature stoichiometric zones where NO_x formation is high (Correa, 1992). In a staged-air burner, secondary air is added, in an annular manner or by discrete jets, downstream of a primary fuel-rich combustion zone (Garg, 1994; Babcock and Wilcox, 1978). The secondary air used to drive the combustion from fuel-rich to fuel-lean creates IDFs. Clausen (1991) has reviewed the IDF literature and discusses differences in the physics of IDF and normal diffusion flame

(NDF) combustion. Compared to NDFs, IDFs are cooler and require one tenth the entrainment for a given equivalence ratio (Clausing, 1991). How these differences influence NO_x formation has yet to be investigated.

To minimize NO_x formation in burners via staged-air combustion, a fundamental investigation of NO_x formation by IDFs is required. The present chapter uses chemiluminescent analysis of exhaust gases to investigate bulk NO and NO_x emissions through the IDF driven transition from fuel-rich ($\phi=1.55$) to overall fuel-lean ($\phi_o=0.5$) combustion for a range of discrete jet configurations (diameter and impingement angle). This strategy can be used to identify the significant parameters for minimizing NO formation in a staged-air burner, and to identify global NO trends in the rich-to-lean transition.

2.2 Experimental Apparatus

A schematic of the staged-air burner is shown in Fig. 2.1. The apparatus is the same as that described by Clausing (1991). Primary fuel-rich ($\phi=1.55$) ethane/air combustion was provided by a 2.5 cm square, low-density, Hencken flat-flame burner. The Hencken burner was fitted with a chimney to isolate the combustion products for approximately 30 cm downstream of the burner surface. We estimated the primary combustion temperature to be approximately 1800 K and measured an average primary combustion exhaust temperature, at the rake position, of 913 K. Each of the two stainless steel side walls of the chimney had a round stainless steel tube passing through its longitudinal centerline, approximately 2.5 cm from the burner surface, and tilted vertically in the downstream direction ($\theta=45^\circ$ or 70° w.r.t. the chimney wall normal). Air injected through these tubes reacted with the fuel-rich primary combustion products forming IDFs. The chimney walls with 70° jets could accommodate 2.16 mm and 4.57 mm I.D. jet tubes (1/8 and 1/4 in. O.D., respectively) while those with 45° jets could accommodate 2.16 mm, 4.57 mm and 7.75 mm I.D. jet tubes (1/8, 1/4 and 3/8 in. O.D., respectively). This provided five unique burner configurations. The front chimney wall was quartz to allow observation of the flames while the back wall was stainless steel. All construction

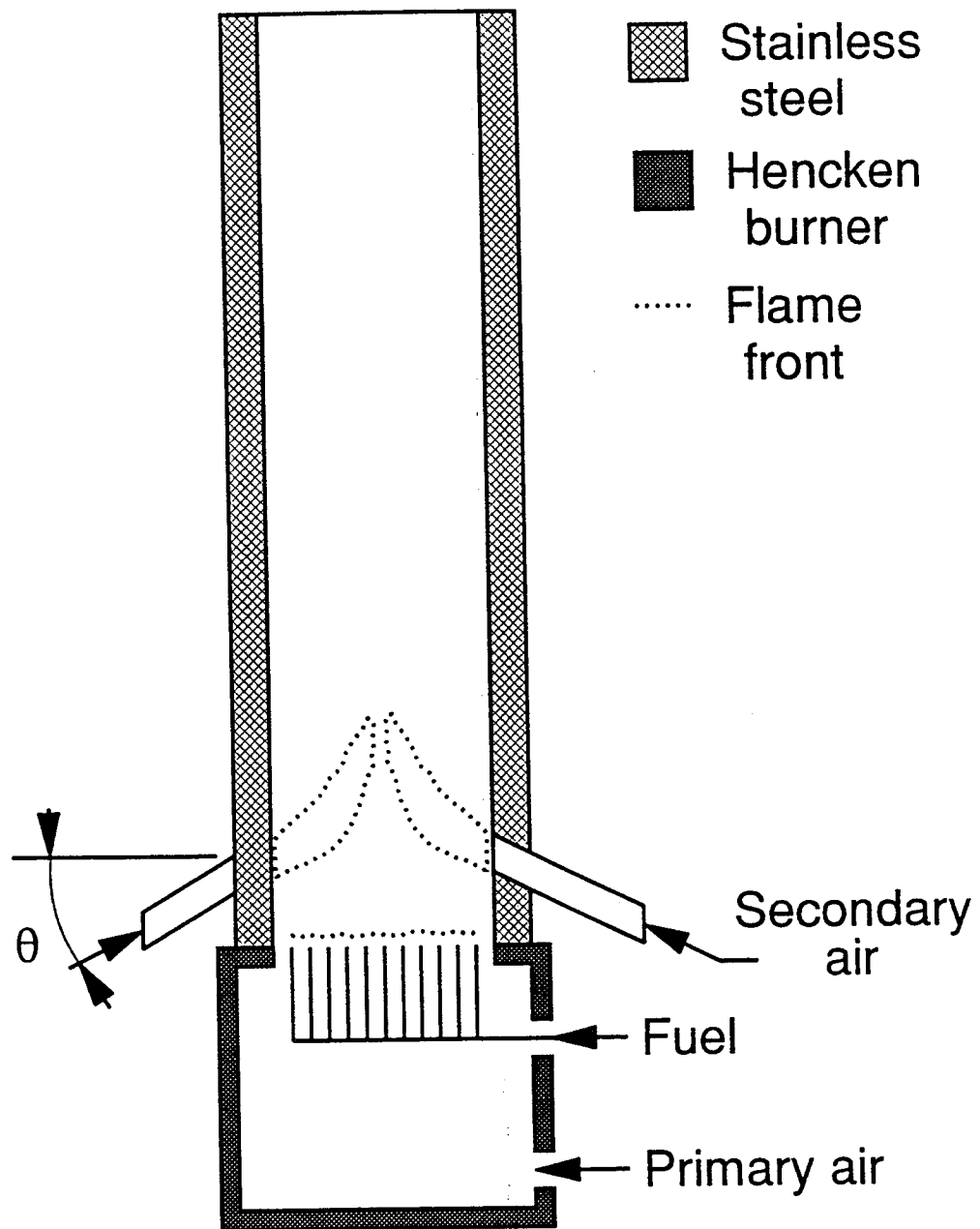


Figure 2.1 Schematic of the staged-air burner.

interfaces were sealed either with graphite gasket material and clamping pressure or with high temperature cement to prevent leakage.

All gas volume flow rates supplied to the burner were determined by rotameter readings. Each rotameter was supplied with a sufficiently high regulated pressure to ensure choked flow across the needle valve downstream of the rotameter tube. The rotameters were calibrated under normal operating conditions using a dry test meter and converted to standard conditions. The primary and secondary (jet) air were compressed on-site from the atmosphere and dried using three in-line chambers filled with a hydrophilic material (Dry Rite).

2.3 Sampling/Analyzer System

In this study, a two-dimensional rake was used to spatially average the exhaust from the burner assembly. Novel probe designs have been investigated by Drake et al. (1987) which freeze all chemical reactions and which can be used for quantitative *in situ* species analysis near the reaction zone. Because the present work samples the exhaust well away from the high temperature flame front, a rake design to freeze reactions was not necessary. The rake was fabricated from loosely-coiled, blinded 1/8" O.D. stainless steel tubing with radial sampling slots. The rake was positioned approximately 38 mm inside the chimney exhaust, and the rake sample to exhaust volumetric flow ratio was maintained at less than 0.06 throughout the experiments. These two considerations ensured that the sample was from the exhaust and not from the room air.

A schematic of the sampling system is shown in Fig. 2.2. Considerations pertinent to chemiluminescent sampling system design and error have been investigated elsewhere (e.g., Matthews et al., 1977; Tidonna et al., 1988; Zabielski et al., 1984). The sampling system used in this investigation was heat traced and instrumented with thermocouples to control and monitor the sample gas temperature. Resistance heaters maintained the exhaust sample above its dew point. Vacuum line pressures prior to exhaust gas dilution provided additional guard against condensation. The exhaust sample was sufficiently diluted with preheated dry nitrogen to ensure that the dew point at atmospheric conditions was below the ambient temperature. The mixture was drawn through a mixing can by a

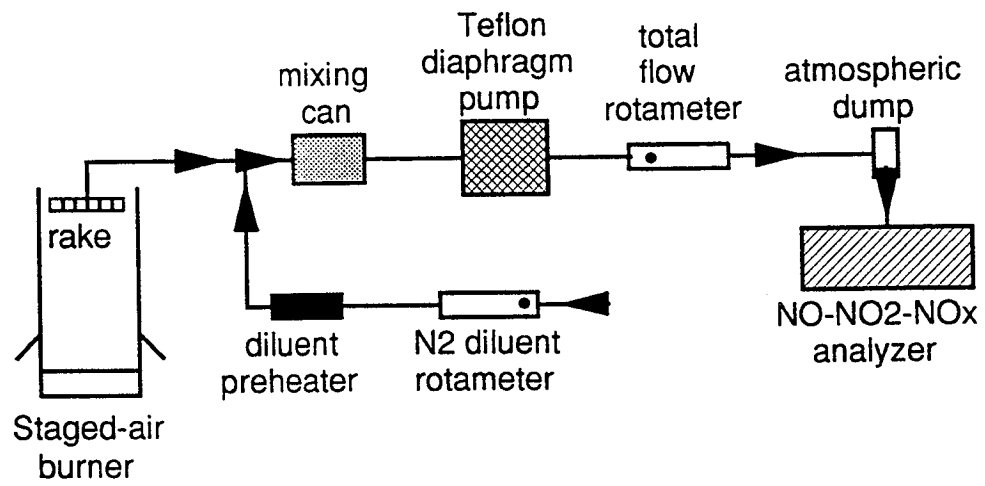


Figure 2.2 Exhaust gas sampling and dilution system.

teflon-diaphragm pump (Thomas model 2737CM39 TFEL). Rotameters, calibrated at operating conditions, were used to determine the volumetric flow rates of the diluent and total exhaust/diluent mixture. From these values, the volumetric sampling rate of the rake could be determined.

The mixture was sampled by a Thermo Environmental Instruments Model 42 chemiluminescence NO-NO₂-NO_x analyzer. The NO measurement scheme is based upon standard NO-O₃ kinetics (Clyne et al., 1964). By mixing ozone (O₃) with the sample, all NO is converted to electronically excited NO₂. The electronically excited NO₂ relaxes via radiative decay or collisional quenching. A thermoelectrically cooled photomultiplier tube (PMT) is used to monitor the chemically-induced radiation. The PMT signal is proportional to the NO concentration in the reaction chamber. Quenching or non-radiative de-excitation is minimized by operating the reaction chamber at low pressures. To measure total NO_x, the sample is diverted to a converter prior to entering the reaction chamber. In the high temperature (~325 °C) molybdenum converter, any NO₂ in the sample is converted to NO via $3\text{NO}_2 + \text{Mo} \rightarrow 3\text{NO} + \text{MoO}_3$. The PMT signal from this converted sample, once in the reaction chamber, is proportional to the total NO_x. By alternately removing and inserting the converter in the flow path, the NO and NO_x concentrations can be measured. The NO₂ concentration is then determined internally as the difference in the two signals.

2.4 Experimental Procedure

A sequence of NO, NO₂ and NO_x measurements was taken at nine stoichiometries, from overall fuel-rich to overall fuel-lean, in five burner configurations. Variations in burner configuration were implemented by changing the secondary-air-jet diameter and/or impingement angle. Prior to taking NO_x data, the burner and sampling systems were allowed to reach a steady-state operating temperature. Existence of this steady state condition was verified by temporally monitoring the various thermocouple ports. During this warm up period, the NO_x analyzer's zero and span were set using standard gases.

Each experimental run consisted of measuring NO, NO₂ and NO_x concentrations in the diluted exhaust at nine uniformly spaced, overall equivalence ratios from 1.55 to

0.50, as tabulated in Table 2.1. The overall equivalence ratio was defined as that which would result from premixed combustion with the ethane and net air (primary plus secondary) for a given case. The primary C_2H_6 /air combustion was maintained constant at $\phi=1.55$ and a total volumetric flow rate of 12.0 SLPM. The overall equivalence ratio was incrementally driven to 0.50 by increasing the volumetric flow rate of the secondary-jet air from zero to 23.0 SLPM. This produced maximum ambient-condition Reynolds numbers of 22700, 10700, and 6330 for the 2.16 mm, 4.57 mm and 7.75 mm I.D. jets, respectively. Steady-state operation at each overall equivalence ratio was specified as that point at which the NO_x reading was within approximately 3% of the 5-minute average.

The burner assembly was actively monitored to ensure that the chimney had no leaks, which would compromise the overall equivalence ratio. Following each experimental run, the NO_x analyzer was exposed to the zero and span gases to ensure that the integrity of the calibration had been maintained. The maximum drift in the zero and span calibration was 0.001 ppm and 1.5%, respectively.

Concentration values, in parts per million (V/V), displayed by the NO_x analyzer were pre-processed internally using factors determined by the zero and span calibration procedure. Post processing of the data was used to account for nitrogen dilution of the rake sample, to reference all runs to a well-defined control case, and to convert to an emission index basis. The dilution correction factor consisted of the ratio of the total (sample plus diluent) to rake volumetric flow rate and was determined independently for each data point to account for fluctuations in the sample pump rate. This correction was applied to the concentration values displayed by the NO_x analyzer using

$$NO_j = \frac{\dot{V}_T}{\dot{V}_T - \dot{V}_D} NO_{j,d} , \quad (2.1)$$

where NO_j is the exhaust concentration (of NO, NO_2 or NO_x), $NO_{j,d}$ is the displayed concentration, $\dot{V}_T$ is the total volumetric flow rate, and $\dot{V}_D$ is the diluent volumetric flow rate.

Table 2.1. Calculated molecular weights of the undiluted exhaust mixture at the nine overall equivalence ratios investigated.

ϕ_o	M_T
1.55	25.22
1.41	25.88
1.27	26.59
1.13	27.36
1.00	28.12
0.87	28.21
0.74	28.30
0.61	28.39
0.50	28.47

For each burner configuration, the $\phi=1.55$ case consisted of primary combustion only (no secondary air) and thus served as a control for referencing the individual measurements. At this fuel-rich equivalence ratio, little or no oxygen is available following combustion to oxidize the NO to NO₂. Thus, the NO and NO_x values were expected to be equivalent, within the uncertainty of the measurements. This was verified by our experimental results. The control reference value was chosen as the average of the combined NO and NO_x results from the five control cases ($\phi=1.55$), and was found to be 58.7 ppm with a sample standard deviation of 2.3 ppm. Referencing was applied at each overall equivalence ratio of a given configuration by using

$$NO_{j,r} = NO_j - (NO_{j,c} - 58.7) , \quad (2.2)$$

where $NO_{j,r}$ is the reference-corrected exhaust concentration, NO_j is obtained from Eq. (2.1) and $NO_{j,c}$ is the control concentration for the specific burner configuration.

Expressing concentrations in terms of an emission index eliminates the dilution effects associated with the excess air required to drive the combustion to overall fuel-lean conditions. The conversion of concentration values from parts per million (V/V) to an emission index (g NO_j/kg fuel) is accomplished via

$$EINO_j = \frac{MW_{NO_2} NO_{j,r}}{MW_T(\phi_o) 1000} \left[1 + \frac{16.66 MW_A}{\phi_o MW_F} \right] , \quad (2.3)$$

where MW_{NO_2} , $MW_T(\phi_o)$, MW_A and MW_F are the molecular weights of NO₂, the undiluted exhaust mixture, air and ethane, respectively, and ϕ_o is the overall equivalence ratio. Notice that this formulation follows the standard procedure of using the molecular weight of NO₂ for all emission index calculations. The molecular weight of the undiluted sample was determined at each overall equivalence ratio based on the equilibrium composition of ethane/air combustion at the specified stoichiometry and 1000 K. Table 2.1 lists the nine overall equivalence ratios investigated, along with the calculated undiluted sample molecular weight at each overall equivalence ratio.

No corrections were applied to account for differences in the quenching of the electronically excited NO_2 during normal operation relative to that existing during calibration. The exhaust sample was diluted approximately 11 to 1 with nitrogen and hence viscosity differences (Zabieliski et al., 1984) between the diluted sample and the calibration gas were expected to be minimal. Using quenching theory (Matthews et al., 1977) and calculated equilibrium exhaust concentrations, the maximum quenching error was estimated to be $\pm 5\%$. The reaction chamber pressure was monitored and found to be constant at 579.1 ± 5.1 mm Hg Vac. (22.8 ± 0.2 in. Hg Vac.) throughout all experiments.

2.5 Results

Initial experimental investigations were conducted to determine the experimental repeatability and to evaluate the influence of interfering effects on the measured data. An emission index uncertainty, due to the finite experimental repeatability, was formulated using the standard deviation ($\sigma=2.3$ ppm) in the dilution corrected NO and NO_x concentrations over the five control runs mentioned previously. Assuming 2σ (95% confidence limit) uncertainty in the dilution corrected readings and propagating this value through Eqs. (2.2) and (2.3), the absolute uncertainty in the emission index is found to be

$$\delta E_{\text{INO}_j} = \frac{2.3 (8)^{1/2} E_{\text{INO}_j}}{\text{NO}_{j,r}} \quad (2.4)$$

Equation (2.4) gives an average uncertainty in the emission index of approximately 10%.

The interfering effect of primary concern was the interaction between the relatively cool chimney walls and the IDFs, and the potential influence of this interaction on NO_x formation. Direct contact between the IDF-front and the chimney walls lowers the peak temperature in the contact region. The thermal NO_x mechanism, which dominates in non-premixed combustion (i.e., IDFs and NDFs), has a rate which increases with temperature and which is particularly temperature sensitive (Correa, 1992). Hence, if wall effects are significant, they would be expected to decrease NO_x formation.

To investigate the magnitude of possible wall effects, results from burner configurations with varying degrees of IDF/wall interaction were compared. In separate experimental runs using one and two 1/8" O.D. jets at 70°, the single jet configuration was observed to have more wall/jet contact for $\phi_o > 1$. However, in this overall equivalence ratio range, the single jet configuration produced slightly larger EINO_x . Although the difference in the EINO_x between the two configurations was within the calculated uncertainty, the results were repeatable. This behavior contradicts the expected EINO_x trends resulting from wall interfering effects. Similar results were found in a second investigation which compared two 1/8" O.D. jets at 70° and 45°, for which the 45° configuration was observed to have a higher degree of wall/jet interaction. These two studies both indicate that any wall interfering effects are not observable in our experimental investigation.

Figure 2.3 shows the EINO and EINO_x results for two 1/8" O.D. 70° jets. The trends of Fig. 2.3 are generally representative of the results from other burner configurations. Since the motivation is to investigate the process of driving primary fuel-rich combustion to overall fuel-lean via secondary air injection, the data are typically read from high to low overall equivalence ratios or from right to left in Figs. 2.3, 2.4 and 2.5. The NO and NO_x results are equivalent in the overall fuel-rich region with the EINO and EINO_x curves diverging in the overall fuel-lean region as more oxygen is available to oxidize the NO to NO_2 . The EINO_x gradually increases as the combustion is driven away from the control case ($\phi = 1.55$), experiences a large increase near overall stoichiometric conditions, and reaches an approximate plateau by $\phi_o \approx 0.9$.

Results from two 1/8" and two 1/4" O.D. 70° jets are compared in Fig. 2.4. Although error bars are shown for only one curve, the error at a given overall equivalence ratio applies to both EINO_x curves. The EINO_x curves follow the same general trends as in Fig. 2.3, and are equivalent within error limits except at $\phi_o = 1.13$. Ultimately, the NO_x concentration at the extreme overall fuel-lean stoichiometry or $\phi_o = 0.50$ is the figure of merit for any burner configuration. At this limit, Fig. 2.4 indicates no substantial difference between the 1/8" and 1/4" O.D. jets. Similar results are obtained for two 1/8",

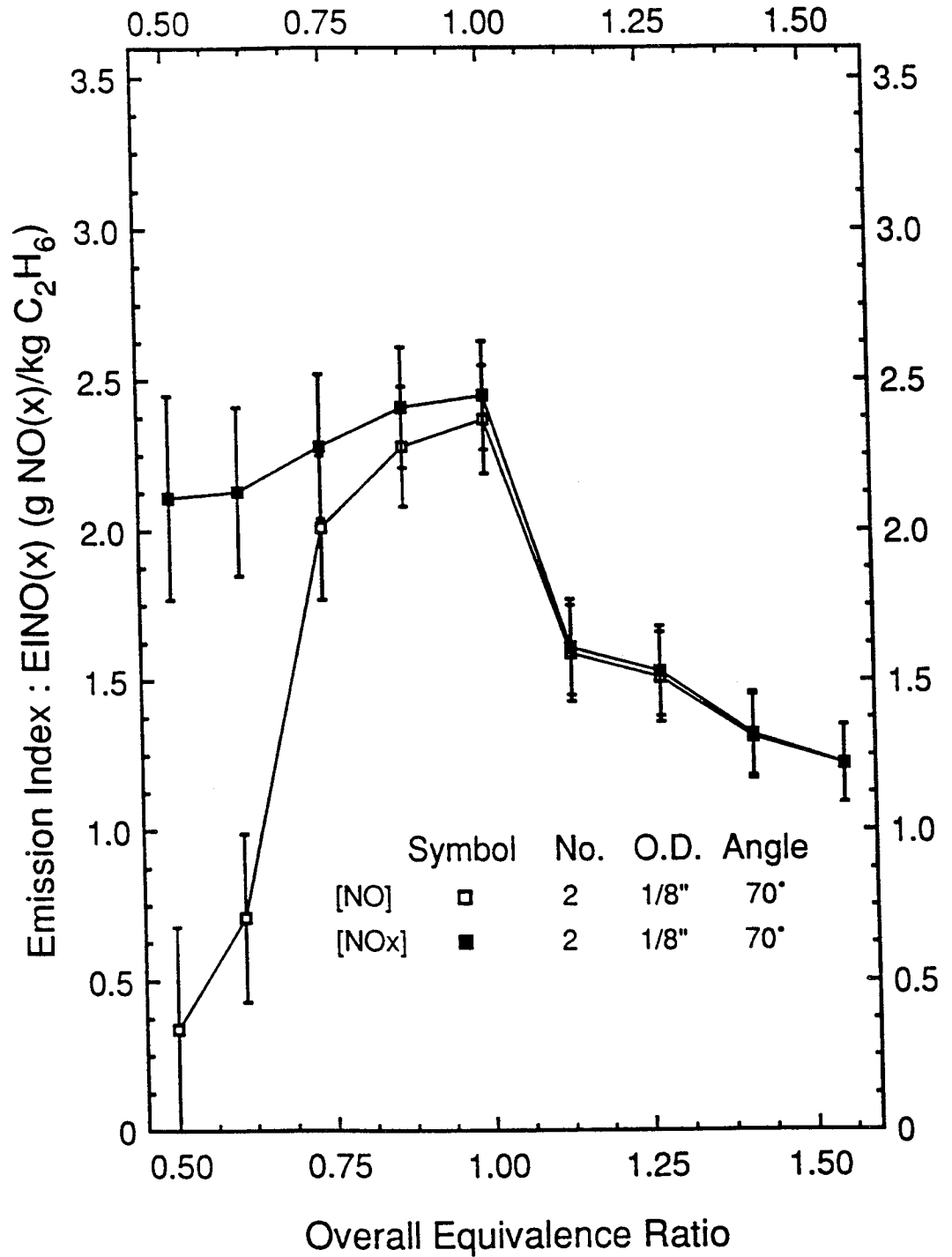


Figure 2.3 NO and NO_x emission indices from experimental runs using two 1/8" O.D. jets at 70° from the chimney wall normal. The general trends are characteristic of results from other burner configurations.

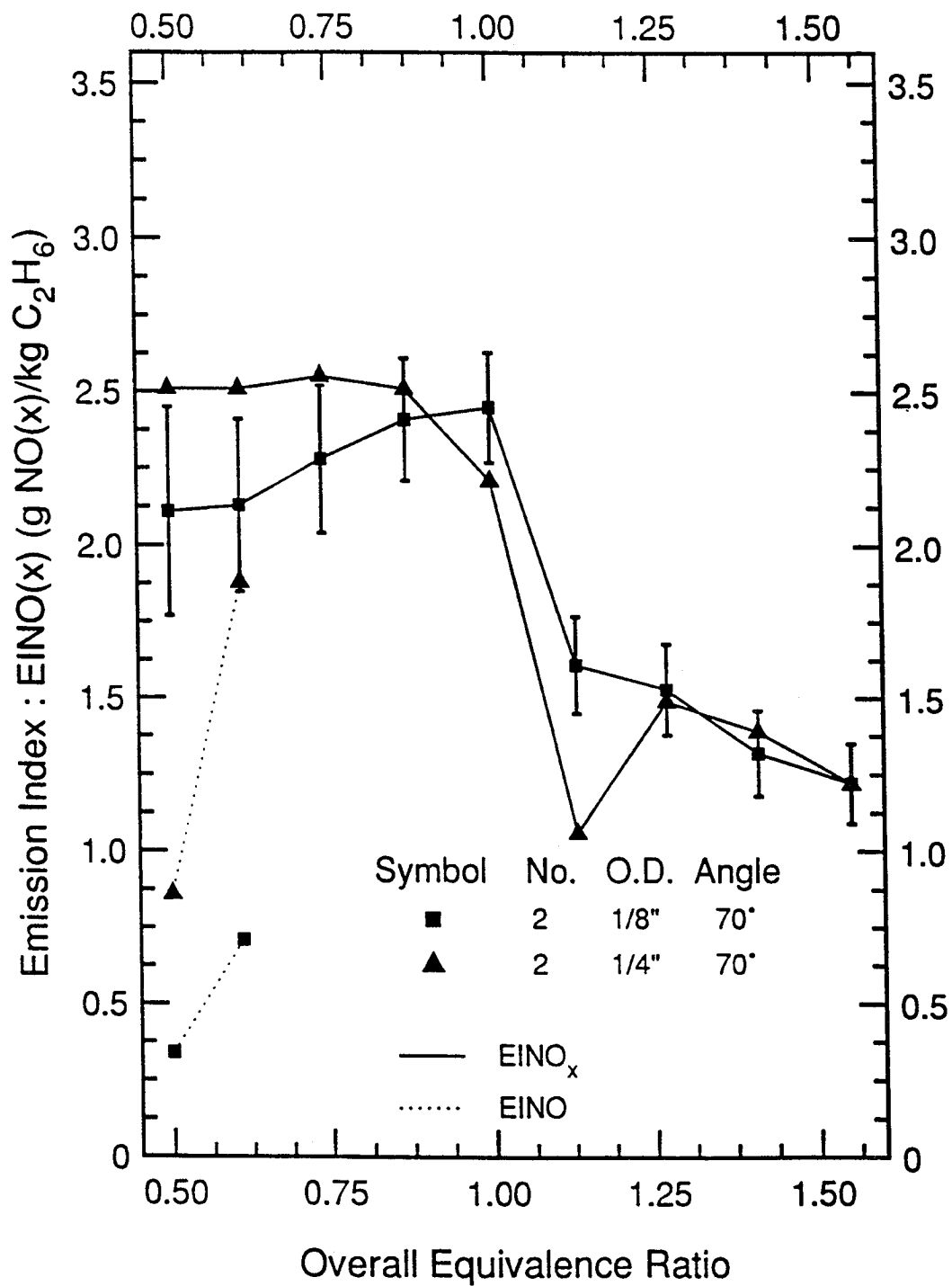


Figure 2.4 NO_x emission indices from experimental runs using two 1/8" and two 1/4" O.D. jets at 70° from the chimney wall normal. EINO values are shown for overall equivalence ratios of 0.50 and 0.61.

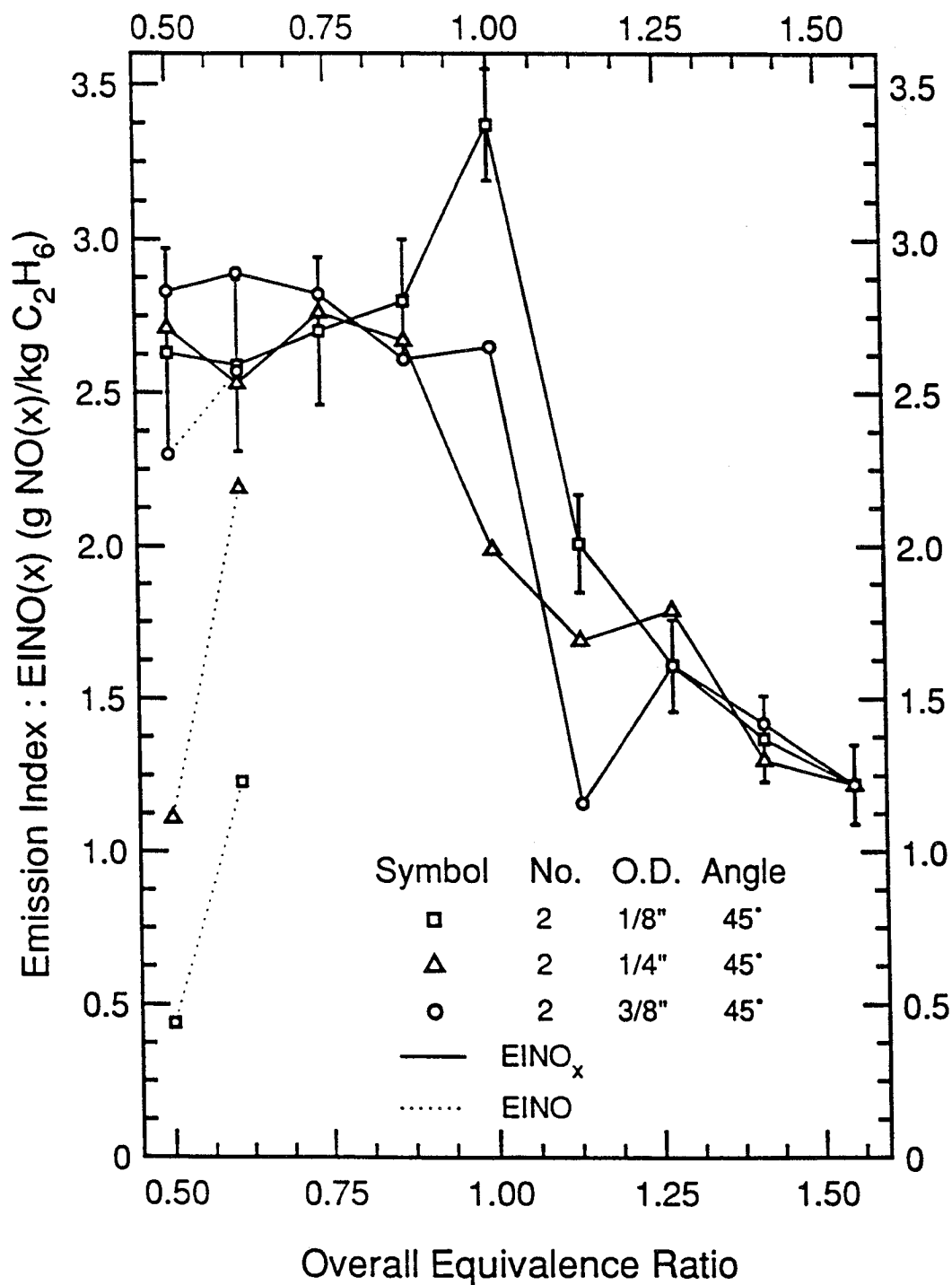


Figure 2.5

NO_x emission indices from experimental runs using two 1/8", two 1/4" and two 3/8" O.D. jets at 45° from the chimney wall normal. EINO values are shown for overall equivalence ratios of 0.50 and 0.61.

two 1/4" and two 3/8" O.D. 45° jets as shown in Fig. 2.5. The full data for the five combustor configurations is tabulated in Appendix A.

Figures 2.4 and 2.5 also show the EINO data at overall equivalence ratios of 0.61 and 0.50. These results indicate that the NO oxidation rate increases with decreasing jet diameter. This burner-geometry-specific behavior indicates that the oxidation of NO is occurring in the burner and not in the sample line. These EINO and EINO_x results demonstrate that although the value of EINO_x may be relatively constant, the NO produced at the flame front is oxidized to NO₂ to greater degrees by smaller jets. This enhanced conversion of NO to NO₂ by the smaller jets indicates more rapid mixing of the secondary air and primary combustion products (Tidona et al., 1988).

2.6 Discussion

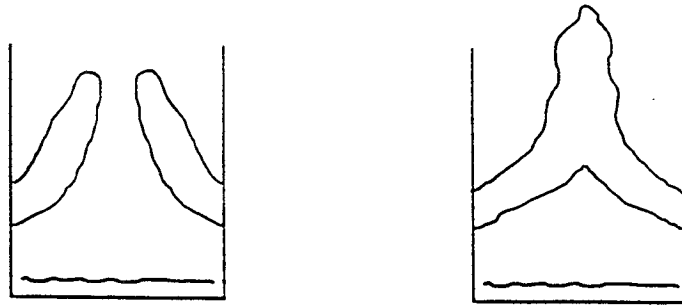
Figures 2.4 and 2.5 show that jet diameter, and hence initial jet velocity, does not significantly influence NO and hence NO_x formation in the fuel-lean driven limit ($\phi_o=0.5$). Recall that the volumetric flow rate of the secondary-air at a given overall equivalence ratio (e.g., $\phi_o=0.5$) is a constant, independent of the diameter of the air jets used in a specific burner configuration. Hence, initial jet velocity scales inversely with jet diameter squared. Therefore, it is apparent from our results that NO formation must occur at a point in the burner where there is little direct influence of the initial jet velocity.

The work of Turns and Myhr (1991) suggests that the majority of NO in NDFs is formed in large homogeneous eddies at the flame tip. This location in the flame should produce large amounts of NO because of the near overall stoichiometric conditions, high temperatures and large residence times (the time required for a stoichiometric mixture to pass through the visible flame) (Turns and Myhr, 1991). The flame tip also corresponds to a position along the NDF where the initial fuel-jet velocity has minimal direct influence. This NDF behavior is consistent with our IDF results described earlier. Thus, it appears that IDF and NDF behavior are similar with respect to the lack of a direct correlation between NO formation and initial jet velocity. Moreover, any apparent correlation between NO formation and initial jet velocity may actually be occurring through some secondary parameter(s) such as the mixing rate and/or the residence time.

Although our results indicate no significant direct influence of jet diameter on NO_x emissions (at $\phi_o=0.50$), a secondary influence of jet diameter with respect to the mixing between secondary air and primary products has been observed. Systematic changes in the EINO_x vs. ϕ_o slope (Figs. 2.4 and 2.5), corresponding with the transition to different mixing regimes, indicate that mixing is an important parameter in optimizing the staged-air combustion process. This is evident from a comparison of the EINO_x results and the flame structure at each overall equivalence ratio for the individual configurations. In our work, several unique flow regimes were observed and are depicted in Fig. 2.6: (1) laminar separate or combined jets; (2) combined jets with a fluctuating plume transitioning to apparently turbulent conditions; and (3) post-impingement turbulent mixing of jet air and primary products with varying degrees of observable stoichiometric sheets. The onset and degree of mixing for each flow regime is unique to each burner configuration. This is reflected in the details of the EINO_x curves in Figs. 2.4 and 2.5. Specific examples of the relationship between mixing and EINO_x are given below.

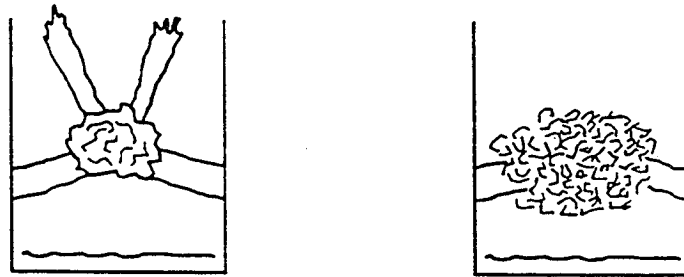
For the two 1/8" O.D. 70° jets (Fig. 2.4), although mutual jet impingement occurs at $\phi_o=1.27$, the jet flow is laminar in appearance for $\phi_o \geq 1.13$. Hence, the slope of the EINO_x curve is approximately constant through this flow regime. For the same configuration, the flow appears increasingly turbulent from $\phi_o=1.00$ to $\phi_o=0.50$, where the EINO_x curve has reached a plateau. The existence of an approximate EINO_x plateau in apparently turbulent flow regimes was observed to be characteristic of all burner configurations.

The two 1/8" O.D. 45° jets (Fig. 2.5) were laminar for $\phi_o \geq 1.13$ and turbulent appearing for $\phi_o \leq 0.87$. The EINO_x results for this configuration are similar to those at 70° but show a more pronounced EINO_x peak at $\phi_o=1.00$. At $\phi_o=1.00$, the 1/8" O.D. 45° combined-jet plume exhibited oscillations with overall laminar behavior, while that at 70° exhibited a turbulent appearing jet plume. Hence, the enhanced mixing in the 70° jet configuration apparently corresponds to a lower EINO_x .



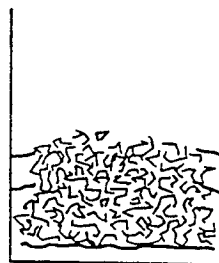
$$1 < \phi_0 < 1.5$$

- Overall laminar behavior
- Possibility of slight low-frequency oscillations



$$0.61 \leq \phi_0 \leq 1$$

- Turbulent jet mixing



$$\phi_0 < 0.61$$

- Recirculation of secondary products back into primary combustion region

Figure 2.6 Typical IDF structure regimes.

For the two 1/4" O.D. 45° jets (Fig. 2.5), the reduction in slope from $\phi_o=1.27$ to $\phi_o=1.13$ and the less significant $EINO_x$ increase from $\phi_o=1.13$ to $\phi_o=1.00$ are coincident with an increasing radial spread of the combined-jet plume, although the overall flow remains laminar in appearance. The radial spread of the plume is caused by significant jet radial velocity, which enhances air/products mixing. Hence, $EINO_x$ is again observed to decrease with enhanced mixing. The two 3/8" O.D. 45° jets (Fig. 2.5) were laminar through $\phi_o=0.87$ and mutually impinged at $\phi_o=1.00$. Although these jets were distinct and laminar for $1.00 < \phi_o < 1.55$, they began to oscillate at $\phi_o=1.13$ which is coincident with a change in the $EINO_x$ slope in Fig. 2.5.

Although the results discussed above indicate that enhanced mixing reduces $EINO_x$, there appears to be a mixing limit beyond which $EINO_x$ tends to increase. We have observed that secondary-air-jet velocities sufficient to penetrate the burner centerline cause recirculation of the secondary combustion products into the primary zone and a corresponding increase in the predicted NO_x concentration in the exhaust. With all 1/8" and 1/4" O.D. jets (i.e., for both 70° and 45°), turbulent jet mixing is established by $\phi_o=0.61$. Increasing the secondary-air flow to achieve an overall equivalence ratio of 0.50 produces some degree of recirculation of secondary products back towards the primary combustion zone (see Fig. 2.6). Notice from Figs. 2.4 and 2.5 that the $EINO_x$ curve tends to increase from $\phi_o=0.61$ to $\phi_o=0.50$, and that the effect is greater for the 45° jets. In fact, it was observed that the 45° jets exhibited a greater degree of recirculation at $\phi_o=0.50$ compared to the 70° jets. Hence, mixing sufficient to cause recirculation apparently increases the NO_x emissions in a manner related to the degree of recirculation. Such recirculation back into the primary zone may actually reduce the equivalence ratio of the primary combustion. For primary combustion closer to stoichiometric (relative to $\phi=1.55$), an increase in both the primary combustion temperature and the NO_x emissions would be expected. Even if the secondary products do not recirculate all the way back into the primary zone, higher NO_x emissions would be expected. This could arise from the increased residence time of the secondary air in the higher temperature regions near the primary combustion zone.

The observations above have addressed the influence of mixing between the secondary air and the primary products on NO_x emissions. Although mixing is the observable parameter, secondary phenomena resulting from enhanced mixing are clearly the more fundamental factors influencing NO_x formation. These could be changes in the local temperature, residence time and/or creation of localized partially premixed zones. In general, enhanced mixing was observed to reduce the apparent total area of stoichiometric sheets, and to broaden or blur the flame front. At the extreme overall fuel-lean stoichiometry, the IDFs create a zone of apparently uniform combustion similar in appearance to premixed combustion. Because our purpose was to map the global NO_x trends through the primary fuel-rich to overall fuel-lean transition, detailed geometric shapes and dimensions of the IDFs in the burner, which might aid in estimating residence time and degree of premixing, were not recorded. Moreover, inferring detailed flame structure from global NO_x measurements is impossible (Turns and Myhr, 1991).

2.7 Conclusions on Chemiluminescent Measurements

We have investigated NO_x formation in the stoichiometry-transition region of a staged-air burner, for a range of secondary-air jet configurations. No substantial difference in EINO_x at the most overall fuel-lean stoichiometry ($\phi_o=0.5$) was found for our 1/8", 1/4" and 3/8" O.D. secondary-air jet configurations. This indicates that at this extreme overall fuel-lean stoichiometry, NO is formed at locations in the burner where the initial jet velocity is of little direct consequence. Significant formation of NO in turbulent eddies resulting from vigorous mixing of the secondary-air jets and primary combustion products, as suggested by the work of Turns and Myhr (1991), is consistent with this conclusion and implies that residence time may be the controlling parameter for NO formation. In the transition from fuel-rich to fuel-lean, we observed a strong relationship between EINO_x and the degree of mixing of the secondary air and primary combustion products. In general, enhanced mixing reduces the EINO_x growth trends and the EINO_x vs ϕ_o curves plateau when turbulent mixing conditions exist within the burner. However, the EINO_x tends to increase when vigorous mixing causes the secondary combustion products to recirculate to the primary combustion zone.

CHAPTER 3

PREVIOUS PLIF MEASUREMENTS

3.1 Overview of the PLIF Technique

Planar laser-induced fluorescence (PLIF) is a nonintrusive optical diagnostic tool for making temporally and spatially resolved measurements of a probed species' temperature, pressure, velocity or concentration. In general, PLIF involves exciting a spatially extended volume of a specific probed species from a lower laser-coupled level in its ground electronic state to an upper laser-coupled level in some excited electronic state via laser irradiation. Subsequently, a portion of the fluorescence emitted as the probed molecule relaxes back to its ground electronic state is collected, spatially discretized and detected. Through detailed knowledge of both the spectral characteristics of the laser and the probed species, and the dynamics of the molecular excitation/relaxation process, the collected fluorescence signal may be related to the variable of interest. Specific examples of the application of PLIF for measurement of the different flow parameters listed above are discussed in the following sections. The theory of PLIF is discussed in greater detail in Chapter 4 and the specific experimental apparatus used for the PLIF and LSF experiments is described in Chapter 5.

3.1.1 General PLIF Experimental Configuration

A typical PLIF setup is shown schematically in Fig. 3.1. The UV radiation required for excitation of molecules to an upper electronic state is generated by a tunable pulsed laser system, possibly incorporating nonlinear mixing processes. A long focal-length spherical lens and a cylindrical lens are used to form the UV radiation into a thin sheet of proper orientation within the test environment. The spherical lens is selected to

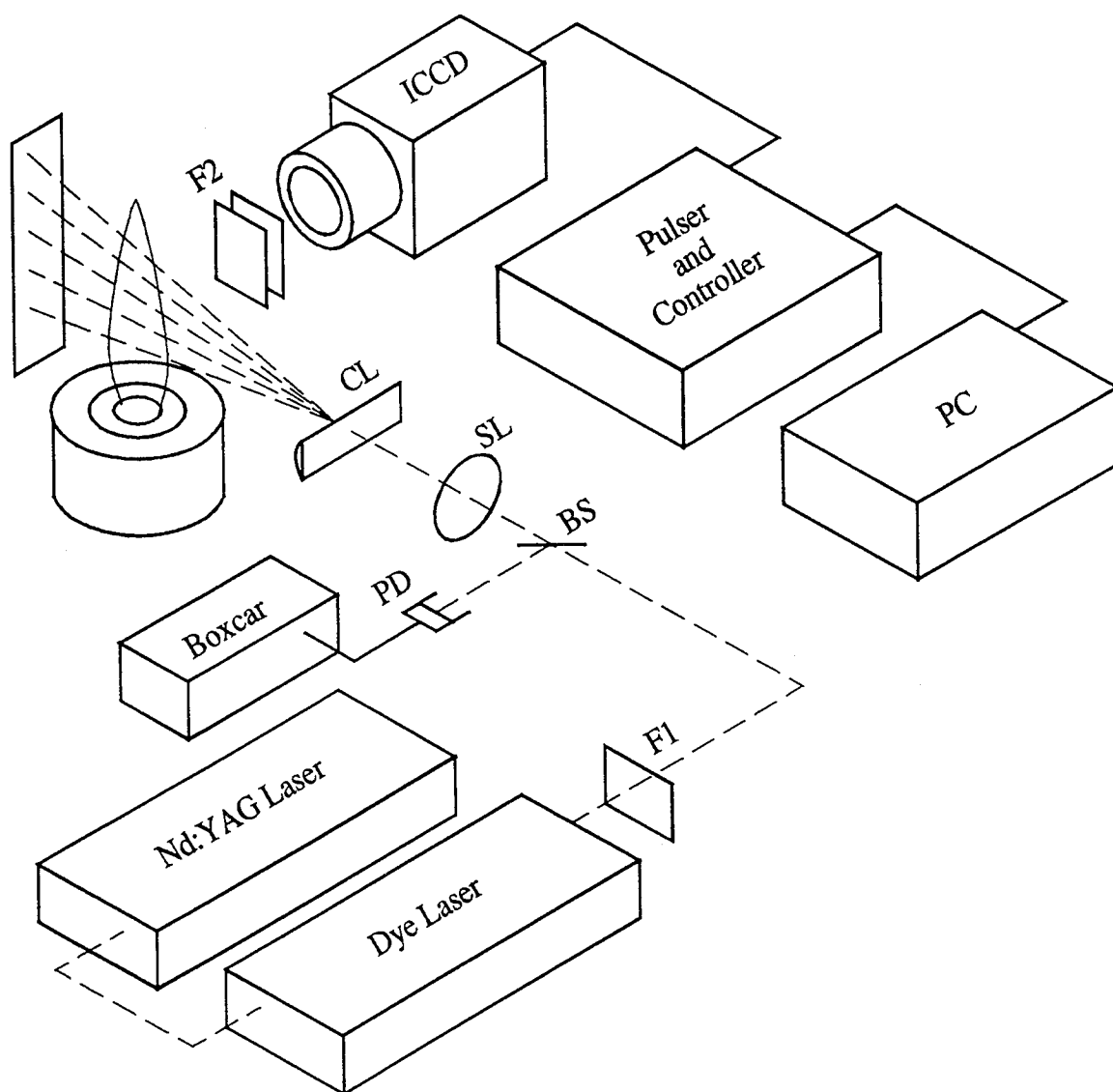


Figure 3.1 Schematic of PLIF facility. F1 and F2 represent filters, BS represents a beam splitter, SL and CL represent spherical and cylindrical lenses, respectively, PD represents a photodiode, and ICCD represents the intensified charge coupled device.

produce the desired sheet thickness and Rayleigh range. Assuming proper spectral tuning and sufficient irradiance of the laser system, any molecule of the probed species in the volume defined by the laser sheet will be electronically excited and will subsequently fluoresce isotropically as it relaxes back to its ground electronic state. A portion of this fluorescence is collected, typically in a direction normal to the laser sheet, spectrally filtered, and imaged onto the front surface of a gated intensified charge coupled device (ICCD). The ICCD's intensifier imposes a temporal gate on and imparts a gain to the fluorescence signal without destroying its spatial integrity. This spectrally and temporally filtered and amplified fluorescence signal is spatially resolved and detected by a charge-coupled-device (CCD) array. The spatial extent of the collection volume per pixel in the plane of the laser sheet corresponds to the size of a CCD pixel projected back through the ICCD and collection optics onto the laser sheet. Temporal gating of the ICCD, readout and A/D conversion of the 2-D fluorescence signal is implemented and coordinated by a PC-interfaced camera controller and pulser system.

3.1.2 General ICCD Description

The ICCD is the primary component of the experimental setup that is unique to PLIF. A schematic of a proximity-focused ICCD is shown in Fig. 3.2. The type of particle, photons or electrons, which comprises the signal in different portions of the camera is also indicated in Fig. 3.2.

Photons from the probe volume are collected by a lens and focused onto the front surface of the image intensifier, which is coated with a photocathodic material. The incident photons cause the ejection of electrons from the back side of the photocathode, which are accelerated towards the microchannel plate (MCP) image intensifier by a potential field applied across the intermediate gap. The point spread function on the front surface of the MCP corresponding to each emission sight on the photocathode is minimized by the large potential between the two components. The point spread function is further minimized by minimizing the gap between the individual intensifier components (e.g., the photocathode and MCP). ICCDs which use this type of inter-component focusing are referred to as proximity focused ICCDs.

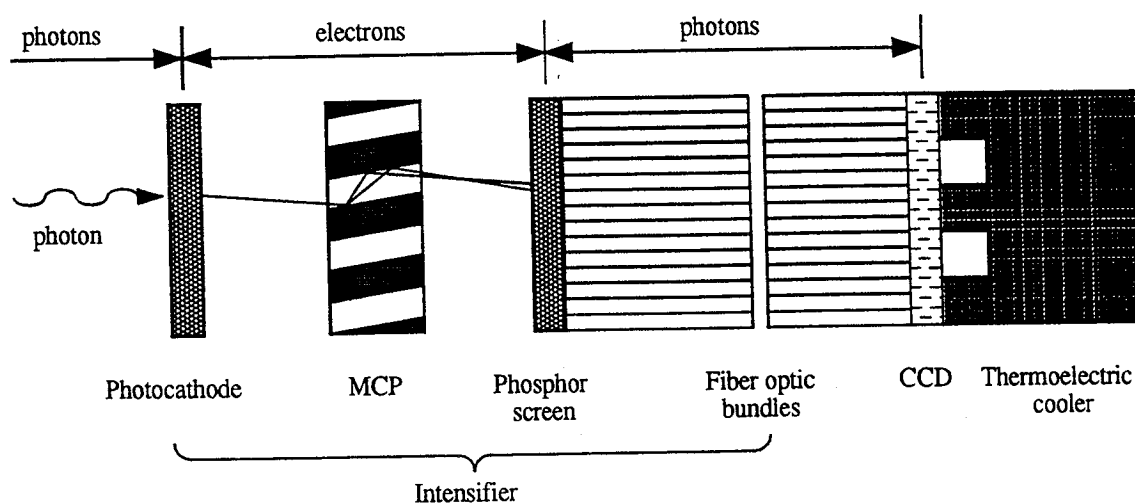


Figure 3.2 Schematic of the major components of the ICCD camera. The intensifier as well as the signal basis in the various regions of the ICCD are indicated.

The MCP amplifies the image of weakly irradiating objects to a level which may be detected by the camera sensor without destroying the spatial integrity of the unintensified image. In depth discussion of MCPs is provided in the literature (e.g., Wiza, 1979; Ruggieri, 1972; Torr, 1985; Eberhardt, 1979). The MCP is a surfaced-charged disk perforated with small holes or microchannels, whose interior is coated with a dynode material. The microchannels are oriented 5 degrees from the direction of bulk electron motion (Greathouse, 1991) so that an electron will collide with the channel walls soon after entering the microchannel. Such a collision causes several secondary electrons to be ejected from the collision site. Each of these secondary electrons subsequently collides with the channel walls producing tertiary electrons and so on. The degree of amplification or gain is controlled by a variable potential across the MCP. Microchannel plates can provide electron multiplications on the order of 10^4 to 10^7 (Wiza, 1979).

The electrons leaving the MCP are accelerated across a second potential field and subsequently collide with an aluminum-coated phosphor screen. The potential field minimizes the spread function across the gap and provides additional system gain via the increased kinetic energy imparted to the electrons which is in turn transferred to the phosphor screen. The small gap between these two intensifier components further minimizes the point spread function through proximity focusing. The phosphor screen converts the electrons to photons within the spectral bandwidth of the CCD. An aluminum screen provides a constant potential over the phosphor surface to create the conduction band necessary for operation and serves as a mirror to increase the surface efficiency by redirecting photons emitted back towards the MCP toward the output of the intensifier (Csorba, 1985).

The photons exiting the intensifier are guided, via a fiber-optic bundle, to the CCD detector array. Two distinct fiber bundles are used because the phosphor screen and detector are manufactured as separate units, each mounted on the end of a fiber bundle. To reduce cross talk between adjacent fibers, the gap between the two fiber bundles is minimized. To minimize signal loss due to surface reflections at the fiber ends, this gap is filled with a refractive index matching epoxy (Nir, 1991). The CCD is composed of an array of pixels which allows the signal to be discretized into a two-dimensional image.

The description of the camera as a proximity-focused type refers to the method used to couple the components of the intensifier. For proximity-focused devices, the spatial integrity of the signal is maintained by placing adjacent components in close proximity to one another. Alternate coupling methods include electromagnetic and electrostatic optical coupling. Such devices are for photoelectrons the corollary of lenses for photons. While the latter two coupling methods can provide better resolution, proximity focusing provides uniform spatial resolution across the field of view (Freeman, 1973). Hence, proximity-focused image intensifiers do not suffer from geometric aberrations (Csorba, 1985).

3.1.3 General PLIF Theory

The relationship between the different measured parameters (e.g., concentration, temperature, pressure) and the fluorescence signal is unique to each measured parameter. However, the most fundamental relationship between the various parameters is provided by the equation describing LIF or PLIF concentration measurements. Hence, this relationship is described in a general manner below to clarify the different PLIF measurement techniques reviewed in the later sections of this chapter. The equation for the fluorescence signal in volts (or digital counts on a per-pixel basis for PLIF measurements) is formulated as

$$S_D = (V_C f_B N_T) \left(\Gamma_{lu,L} B_{lu} I_v^o \right) \Phi \left(\eta \frac{\Omega}{4\pi} \right) G R \Delta t_L \quad (3.1)$$

where

$$\Phi = \frac{A_{N,F}}{A_N + Q_e + W_{lu} + W_{ul} + Q_p}, \quad (3.1a)$$

and

S_D : Measured fluorescence signal

V_C : Collection volume

f_B	Boltzmann fraction of lower laser-coupled level
N_T	Total number density of probe species
$\Gamma_{lu,L}$	Overlap fraction
B_{lu}	Einstein B coefficient for absorption from level l to level u
I_v^o	Normalized laser spectral irradiance
Φ	Fluorescence yield
η	Collection optics efficiency factor
Ω	Solid angle subtended by the collection optics
G	ICCD gain
R	CCD responsivity
Δt_L	Temporal FWHM of the laser pulse
$A_{N,F}$	Spectrally filtered net spontaneous emission rate coefficient
A_N	Net spontaneous emission rate coefficient
Q_e	Quenching rate coefficient
Q_P	Predissociation rate coefficient.
W_{lu}	Absorption rate coefficient
W_{ul}	Stimulated emission rate coefficient

The individual terms in Eq. (3.1) have been grouped in a manner that provides a clear physical interpretation of the actions represented by the individual groups. Moreover, the groups have been arranged from left to right in the natural order that the fluorescence measurement progresses. The first parenthetical term in Eq. (3.1) is the number of probe molecules in the lower laser-coupled level. This is fraction of the total number of probe molecules which are available for excitation. The second parenthetical term in Eq. (3.1) is the probability per unit time that one of the available molecules will absorb a laser photon and become electronically excited. Hence, following this second parenthetical term, a fraction of the total number of probed molecules has become electronically excited and has the potential to fluoresce.

The fluorescence yield represents the probability that one of the electronically excited probe molecules will relax to the ground electronic state by spontaneously emitting

a fluorescence photon within the spectral bandwidth of the detection system. This fraction reflects the fact that spectral filtering is applied to the total fluorescence signal and that radiative as well as nonradiative (e.g., spontaneous emission and quenching, respectively) decay paths are available to the excited molecule. In the linear fluorescence regime and in the absence of predissociation, the fluorescence yield essentially reduces to $A_{N,F}/(A_N+Q_e)$ so that the fluorescence signal is adversely affected by the quenching rate coefficient.

The third parenthetical term in Eq. (3.1) represents the net efficiency of the collection optics. This term accounts for both reflection losses as well as the fact that only a fraction of the isotropically emitted fluorescence is captured (due to the finite solid angle of the collection optics). Following this third parenthetical term, a fraction of the fluorescence emitted by the electronically excited probe molecules has been captured. This captured fluorescence is then passed through an optical amplifier where it receives a gain, G . The amplified signal is then detected with a given spectral responsivity, R . The detection process in Eq. (3.1) produces a time varying voltage or charge (depending on whether a PMT or ICCD detector is used). This time varying signal is then integrated over a specific gate time to produce the final measured fluorescence signal. Using Eq. (3.1), the total number density of the probed species, N_T , can be determined via a PLIF measurement of S_D provided the remaining unknown parameters can be either calculated or calibrated.

Investigation of the different terms of Eq. (3.1) suggests possible schemes for PLIF measurements of temperature, velocity and pressure. For a given experimental setup (i.e., constant optical and timing parameters) and total number density of probe molecules, all of the terms in Eq. (3.1) are constants except for f_B , $\Gamma_{lu,L}$ and Q_e . The Boltzmann fraction, f_B , varies in a known manner with temperature. The degree and type of variation with temperature is unique to the lower laser-coupled level chosen for excitation. The overlap fraction, $\Gamma_{lu,L}$, varies with changes in the spectral lineshape(s) of the absorption transition and/or the laser. Changes in velocity and pressure produce varying degrees of Doppler and pressure shift, respectively, in the absorption spectral profile (Demtroder, 1988). Hence, variations in these parameters will, in turn, produce changes in the overlap fraction. The electronic quenching rate coefficient varies with temperature, pressure and

major-species concentrations. Detailed knowledge of the relation between the variable of interest (i.e., temperature, pressure or velocity) and the Boltzmann fraction and/or overlap fraction can be used in conjunction with Eq. (3.1) to relate the PLIF signal to the variable of choice. Often ratiometric techniques can be used to allow cancellation of terms in Eq. (3.1) that are constant for a given set of experiments. Specific examples of different PLIF measurement schemes are given in the following review of the pertinent literature.

3.2 Review of Literature

Since its conception in the early 1980s, PLIF has grown to become a powerful and widely used diagnostic technique. The PLIF diagnostic technique evolved naturally out of early imaging research based on Raman- (Hartley, 1974; Webber, 1979), Mie- (Long, 1979) and Rayleigh- (Escoda, 1983) scattering and 1-D LIF research by Alden et al. (1982). Planar imaging was originally proposed by Hartley (1974), who made planar Raman-scattering measurements and termed the process Ramanography. Two-dimensional LIF based measurements were made by Miles et al. (1978). However, in this work, the dye laser was simply expanded into a larger diameter beam and evidently not formed into a planar sheet. The first PLIF work involved imaging of OH in a flame and was independently reported by Dyer and Crosley (1982) and Kychakoff et al. (1982). In addition to its use in species imaging, PLIF has been employed for temperature and velocity imaging. General reviews of PLIF have been provided by Alden and Svanberg (1984), Hanson (1986) and Hanson et al. (1990). In the following sections, the pertinent references and basic concepts underlying the different PLIF diagnostics techniques are discussed. More rigorous discussion of selected topics which provide the foundation for the specific PLIF and LSF experiments performed here is given in later chapters.

3.2.1 PLIF Temperature Measurements

The theory behind PLIF thermometric measurements is the same as that developed for point LIF. Laurendeau (1988) gives a review of thermometric measurements from a theoretical and historical perspective. Thermometric PLIF measurement schemes may be generally classified as monochromatic or bichromatic (two-line). Monochromatic methods

employ a single laser. Bichromatic methods require two lasers in order to simultaneously excite two distinct molecular rovibronic transitions. In temporally stable environments (e.g., laminar flows), it is possible to employ bichromatic methods with a single laser by systematically tuning the laser to the individual transitions.

In bichromatic PLIF thermometric measurements, the ratio of the fluorescence resulting from two distinct excitation schemes is formed pixel-by-pixel. If the two excitation schemes are chosen such that the upper laser-coupled level is the same, then the fluorescence yields (Stern-Vollmer factors) are identical (Eckbreth, 1988). Hence, as evident from Eq. (3.1), the signal ratio becomes a sole function of temperature through the ratio of the temperature-dependent Boltzmann fractions for the two lower laser-coupled levels of interest.

Monochromatic PLIF thermometry is based on either the thermally-assisted fluorescence (THAF) or the absolute fluorescence (ABF) methods. In THAF-based techniques, the temperature is related to the ratio of the fluorescence signals from the laser-excited level and from another higher level collisionally coupled to the laser-excited level. Implementation of this method requires detailed knowledge of the collisional dynamics which occur in the excited level (Laurendeau, 1988). In ABF-based techniques, the field of interest is uniformly doped and the fluorescence is monitored from a single rovibronic transition. The temperature-independent terms in Eq. (3.1) (i.e., all terms except f_B , Γ_{uL} and Φ) are determined through calibration. The temperature field may then be determined from the fluorescence field by assuming a known dependence of the Boltzmann fraction, the overlap fraction and the quenching rate coefficient on temperature.

Spatially resolved one-dimensional temperature measurements were first demonstrated by Alden et al. (1983). The two-line LIF technique was implemented, using visible radiation from a dye laser to excite indium (In) which had been seeded into a methane/air flame.

Seitzman et al. (1985) demonstrated a self-calibrating monochromatic PLIF technique for two-dimensional ABF mapping of temperature fields in high temperature environments. In this work, approximately 2000 ppm of NO was doped into a lean

premixed CH_4/air flame and excited via the $Q_1(22)$ line of the $\gamma(0,0)$ band. If the quenching cross-section is independent of temperature, the quenching rate coefficient can be assumed to be proportional to $T^{1/2}$ through its dependence on the mean molecular speed. With this assumption and through modeling of the Boltzmann fraction, relative temperatures were determined from the relative fluorescence signal. The $Q_1(22)$ line produced a fluorescence signal which peaked at 740 K and subsequently dropped monotonically with increasing temperature. Hence, self-calibration was effected by pinning the maximum relative temperature at 740 K. The estimated accuracy of this PLIF technique was ± 100 to ± 200 K (i.e., 27% error for the worst case).

Hartfield et al. (1991) presented a PLIF thermometric technique similar to that of Seitzman et al. (1985), but which could be applied at low temperatures (i.e., 100 to 300 K). In this work, iodine was doped into the flow through a Mach-2 nozzle. Theory predicted a fluorescence signal which varied nonmonotonically with temperature and peaked at approximately 10 K. Since the temperature at the theoretical signal peak was below that observed in the experiment, self-calibration could not be implemented. Hence, relative temperatures were calibrated based on that at the nozzle exit found from a Navier-Stokes calculation. Compared to the calculated temperature field, their PLIF temperature field showed a maximum deviation of $\pm 2\%$.

Through the use of two lasers and two cameras, the two-line PLIF thermometric technique has been demonstrated by Paul et al. (1990) and McMillin et al. (1994). Using this twin experimental system and probing the $R_1(3)$ and $Q_1(10)$ lines of the $\gamma(1,0)$ band of OH, Paul et al. (1990) were able to obtain temperature measurements of approximately 2000 K $\pm 10\%$ by averaging over 40 laser shots. McMillin et al. (1994) demonstrated the complimentary nature of OH and NO PLIF thermometry in an investigation of a scramjet model. The concentration of the doped NO was approximately 0.1 to 1% (1,000 to 10,000 ppm).

3.2.2 PLIF Velocity and Pressure Measurements

PLIF velocity and pressure measurements are based on changes in the absorption line-shape function of a probed molecule under the influence of variations in velocity,

temperature and pressure. In general, the absorption line-shape function is Doppler-shifted by velocity, Doppler-broadened (Gaussian) by temperature, and collisionally broadened (Lorentzian) and shifted by pressure (Demtroder, 1988). These influences on the absorption line-shape function and consequently on the fluorescence signal via the overlap fraction of Eq. (3.1) provide a diagnostics path for velocity and pressure measurements.

The possibility of using a fluorescence based Doppler-shift measurement to determine gas velocity was first proposed by Measures (1968). The measurement strategy involved seeding a flow with a molecule which could be excited by a visible, narrow-bandwidth (with respect to the absorption linewidth) laser. The Doppler-shift could be determined by tuning the laser over the shifted absorption line and comparing the spectrally resolved fluorescence to static cell measurements. By probing the flow in two different directions, the velocity vector along each propagation direction could be determined from the resulting spectrally resolved fluorescence. Miles (1975) demonstrated the experimental realization of this technique by making velocity and qualitative pressure measurements in a nonreacting flow. Miles et al. (1978) used photographs to spatially resolve the fluorescence from a sodium-seeded, hypersonic nonreacting helium flow so as to make velocity and pressure measurements. The photographs of the fluorescence at each tuning position of a narrow bandwidth laser highlighted those regions of the flow with a specific velocity component. Although this work used a large diameter beam rather than a sheet for excitation, it evidently represents the first two-dimensional, LIF-based imaging measurement.

Hiller et al. (1986) presented velocity and pressure measurements in a 300 ppm iodine-seeded, nonreacting flow using a narrow bandwidth, cw dual-frequency, non-scanning technique. This method is based on positioning two laser frequencies in the 'linear portion' of one wing of the absorption line and measuring the Doppler shift (through its relation to the measured fluorescence signal) relative to a reference value. The method requires collecting four fluorescence images to resolve two velocity components, determine the reference value, and evaluate the slope of the 'linear portion' of the absorption wing. Three of the four images are taken with the laser at a fixed frequency by

probing the field in three independent directions. The fourth image is taken at a shifted laser frequency but in one of the three previously probed directions. Because only four images are required, this method greatly reduces the data collection time and storage demands compared to spectral scanning methods. The velocity method is self-calibrating and, through the use of ratiometric techniques, eliminates the need to measure the electronic quenching rate coefficient and number density. Moreover, the data inherently give pressure, through the normalized wing slope, if the Voigt-broadening parameter of the absorption line is in a specified range (Hiller, 1988). When within the specified range, this method of determining pressure does not require an independent temperature measurement. In contrast, pressure diagnostic techniques based on pressure-shifting of the absorption-line center require such a temperature measurement.

Paul et al. (1989) demonstrated the use of broadband pulsed lasers for the non-scanning technique. Their work presented velocity and pressure measurements in a 5000-ppm NO doped nonreacting supersonic flow. The use of broadband pulsed lasers was a significant advancement in the utility of this technique. By using a broadband source, the governing bandwidth becomes that of the laser, thus eliminating the need for a fourth image (required in the method presented by Hiller et al., 1986). The use of pulsed lasers increases the temporal resolution of the measurement to the order of the laser pulse width (~ 10 ns). Because pulsed laser radiation can be efficiently mixed to the UV, the possibility of probing naturally occurring species in reacting flows is realized by this method. This provided a path for implementing velocity diagnostics in reacting environments for which seeding can be problematic. Recognizing this, Paul and Hanson (1990) demonstrated implementation of velocity diagnostics based on the Doppler-shift by mapping the velocity in a high pressure H_2 /air diffusion flame using only the naturally present OH as the probed species.

3.2.3 PLIF Species Measurements

The theory for PLIF concentration measurements is similar to that developed for linear LIF with broadband detection. The basic measurement technique involves exciting a specific rovibronic transition of a probe molecule (seeded or naturally occurring) and

determining the probed molecule concentration from the resulting broadband fluorescence. Unlike ratiometric techniques, the fluorescence signal from this single line method retains its dependence on the fluorescence yield (and therefore the electronic quenching rate coefficient). Hence, the local fluorescence signal depends on the local probe molecule number density, Boltzmann fraction, overlap fraction and electronic quenching rate coefficient. Furthermore, the Boltzmann fraction depends on the local temperature, the overlap fraction depends on the local temperature and pressure, and the electronic quenching rate coefficient depends on the local temperature, pressure and composition. This enhanced dependence of the fluorescence signal complicates determination of probed species concentrations from PLIF images. The difficulty in accurately determining the local electronic quenching rate coefficient, particularly in reacting environments, is the primary limitation to realizing quantitative PLIF concentration imaging (Hanson et al., 1990).

Useful fundamental information can be obtained from uncorrected, uncalibrated PLIF 'concentration' images. Because of the species specificity of LIF, raw PLIF images can be used to identify reaction zones (Drake et al., 1991), mixing regimes and large-scale structures of flows. For instance, qualitative PLIF imaging of pollutant formation in a combustor can be used to determine optimum operating parameters (Versluis et al., 1992).

One approach for mitigating the influence of a spatially varying electronic quenching rate coefficient is to choose an excitation scheme such that the product of the fluorescence yield and Boltzmann fraction is approximately constant. The electronic quenching rate coefficient displays a $T^{-1/2}$ temperature variation through its dependence on the product of quenching partner number density and mean molecular velocity. Consequently, the fluorescence yield displays a $T^{1/2}$ temperature variation, as evident from Eq. (3.1a). Hence, if an excitation scheme is chosen such that the Boltzmann fraction of the lower laser-coupled level displays a $T^{-1/2}$ temperature dependence, then according to Eq. (3.1), the temperature dependence of the fluorescence signal will approximately cancel (assuming constant quenching cross-sections throughout the image field). Implementation of such a PLIF excitation scheme in an isobaric environment produces approximate concentration maps.

Kychakoff et al. (1984a) demonstrated this technique for measuring [NO] in NO-doped premixed methane/air flames. The $R_1(16)$ line of the (0,0) band (at ~ 225.6 nm) was used for the temperature range 500 K to 2000 K, and the $Q_1(35)$ line (at ~ 224.5 nm) was used for the temperature range 1100 K to 2400 K. These excitation schemes produced a constant product of fluorescence yield and Boltzmann fraction to within 10% over the specified temperature ranges. The minimum doping level used by Kychakoff et al. (1984a) was 350 ppm NO. Barlow and Collignon (1991) have also used this technique to make spatially resolved point-wise OH concentration measurements in a nonpremixed methane/air flame. The uncorrected (for quenching or Boltzmann fraction temperature variations) OH profiles were calibrated relative to the peak [OH] determined by a separate measurement using a combined absorption/fluorescence technique. Their work demonstrated that through optimum excitation scheme selection, the error in measured [OH] could be less than 10% of the peak [OH].

An alternate approach to account for spatial variations in the electronic quenching rate coefficient is to calculate its value using previously measured cross-section data and measured temperatures. Clearly, this may only be implemented for well characterized probe molecules and environments. Quenching cross-section data are available only to a limited extent and often not at flame temperatures. Formulating relationships for scaling quenching cross-sections measured at room temperature to flame temperatures can be rather arbitrary and is a significant source of uncertainty in this method (Drake and Pitz, 1985). Nevertheless, Allen et al. (1990) have used this technique to measure [OH] in a reacting flow. Their work used two lines and two cameras to simultaneously measure the temperature and [OH] field. Because of the limited cross-section data at flame temperatures, they estimated their calculated quenching rate coefficients to be correct to within a factor of two.

Planar laser-induced predissociative fluorescence (PLI(P)F) is a possible technique for minimizing the difficulties associated with a spatially variable electronic quenching rate coefficient. In this method, an excitation scheme is chosen such that the upper laser-coupled level has a sufficiently large predissociative rate coefficient Q_p (e.g., 10^{-10} s^{-1} (Seitzman and Hanson, 1993)) such that it becomes the dominant term in the denominator

of the fluorescence yield. Under these conditions, the fluorescence yield becomes a constant, $\Phi \approx A_{N,F}/Q_P$, independent of concentration, temperature and usually pressure (Hanson et al., 1990). Arnold et al. (1990) have demonstrated the use of this technique for OH concentration imaging in nonpremixed flames. In that work, the concentration maps were not calibrated to obtain absolute concentration values. A major drawback to this technique is that the signal levels can be very low. This is due to the small fluorescence yield (to negate quenching, the predissociative rate coefficient must be approximately ten times the electronic quenching rate coefficient) and to the fact that predissociation destroys the probe molecule, thereby limiting the number of excitation/fluorescence cycles per molecule to one (Schafer et al., 1991).

Battles et al. (1994) have made PLIF measurements of [NO] in the burnt-gas region of a laminar, premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flame at pressures up to 10.2 atm. Their measurement scheme used five overlapping NO lines for excitation and UG5 colored-glass filters for fluorescence detection. The measurements were calibrated via a sampling probe and chemiluminescent analyzer measurements. The influence of the electronic quenching rate coefficient was corrected via a numerically-based correction scheme using major-species concentrations based on a completely reacted mixture at the appropriate stoichiometry. Based on a PLIF image averaged over 100 laser shots and a measured signal-to-noise ratio of 3.3 at a measured [NO] of 480 ppm, they calculated a 10.2-atm detection limit of ~44 ppm when using 2-by-2 pixel binning. With greater laser irradiance and through use of faster collection optics, they estimate that the 10.2-atm detection limit could be reduced to ~1 ppm. The authors found that high-temperature O_2 can produce serious interferences in fluorescence-based measurements of [NO]. Moreover, they concluded that detection filtering schemes other than use of UG5 may be more effective in mitigating O_2 interferences.

3.3 State of PLIF Concentration Measurements

The primary utility of PLIF concentration imaging remains its ability to image relative species distributions in a plane, rather than providing quantitative field concentrations (Kychakoff et al., 1983). Nevertheless, this does not detract from the

utility of PLIF as a highly effective research tool. Because PLIF images are immediately quantitative in space and time (due to the high temporal and spatial resolution of pulsed lasers and ICCD cameras, respectively), qualitative species images may be used to effectively identify zones of species localization, shock wave positions, and flame front locations (Hanson et al., 1990).

The major experimental considerations limiting or pertinent to the realization of quantitative PLIF were identified in the early spatially resolved LIF works (Alden et al., 1982; Dyer and Crosley, 1982; Kychakoff et al., 1982). These considerations are: (1) spatial cut-off frequency of the imaging system which defines the range-of-scales which can be faithfully resolved by the PLIF image; (2) selection of imaging optics parameters (e.g., $f/\#$ and magnification) which best balance spatial resolution and signal level considerations; (3) image corrections implemented via post processing to account for nonuniformities in experimental parameters such as pixel responsivity and offset, and laser sheet intensity; and (4) spatial variation in the fluorescence yield due to that in the electronic quenching rate coefficient. These and other considerations not specific to PLIF are generally discussed by Seitzman et al. (1990). In the past seven years, much effort has been dedicated to quantifying the effect of these experimental considerations. The work to characterize imaging optics and camera parameters (e.g., Hertz et al., 1988; Paul and Hanson, 1990; Paul, 1991) plus post processing image corrections (e.g., van Cruyningen et al., 1990) has been a significant step towards realizing quantitative PLIF.

Spatial variations in the electronic quenching rate coefficient continue to hinder PLIF measurements of absolute species concentrations in reacting environments. The magnitude of the error resulting from spatial variations in quenching (e.g., Drake and Pitz, 1985; Barlow and Collignon, 1991) and the selection of excitation/detection schemes which minimize the influence of quenching (Allen et al., 1993; Seitzman and Hanson, 1993) have been investigated. Planar laser-induced predissociative fluorescence can make the effect of electronic quenching insignificant, but PLI(P)F is applicable only to a limited number of species (Hanson et al., 1990).

Recently, much effort has been devoted to obtaining more quantitative PLIF and broad-band LIF concentration measurements in harsh environments. These include high-

pressure (Battles et al., 1994), non-premixed turbulent (Carter and Barlow, 1994) and liquid-fuel spray (Allen et al., 1995) flame environments. Use of an overlap fraction (Partridge and Laurendeau, 1995a) in the fluorescence modeling and data reduction process enhances the quantitative nature of the concentration measurements in such harsh environments. The quantitative nature of such measurements is further enhanced by careful selection of the calibration conditions (Reisel et al., 1995). Application of PLIF in such environments has also required a significant reevaluation of the influence of potential interferences and of the effectiveness of candidate filtering schemes (Battles et al., 1994; Allen et al., 1995). These works demonstrate the advancement of PLIF to a more quantitative and realistic measurement arena.

Of particular significance are improvements associated with correcting for the effects of variations in the electronic quenching rate coefficient on fluorescence-based measurements. Measurements of electronic quenching cross-sections at flame temperatures (Drake and Ratcliffe, 1993) for selected probe species has eliminated the uncertainty associated with scaling such quantities to flame temperatures. Furthermore, improvements in techniques for modeling of the electronic quenching rate coefficient (Paul et al., 1993) have improved the utility of numerically-based PLIF correction schemes (Paul et al., 1994). Despite such work, numerically-based schemes for enhancing the quantitative nature of PLIF concentration measurements are extremely limited. Most significant is the fact that they can be implemented only for studies on probe species whose electronic quenching cross-sections have been painstakingly measured. Such measurements have been made only for a limited number of molecules and would require considerable lead time to make for new species of interest. The utility of numerically-based correction schemes is further limited by the extensive experimental and computational resources necessary for their implementation. For instance, spatially resolved concentration measurements are required for all major species. Despite the potential of this technique, numerically-based correction procedures are not broadly applicable because the resources necessary for their implementation are not broadly available.

Experimentally-based procedures for enhancing the quantitative nature of PLIF concentration images may provide the diagnostic community with a more broadly applicable and sufficiently-quantitative PLIF diagnostic. Such correction procedures use selective, directly-measured and highly quantitative secondary point measurements to enhance the quantitative nature of a PLIF concentration image. The number of secondary measurements required depends on the density and magnitude of error gradients in the PLIF image due to variations in the electronic quenching rate coefficient, the extent of existing knowledge concerning the error gradients in the test environment, and the required accuracy of the results. Experimentally-based PLIF correction procedures also eliminate the need for extensive resources which so greatly limits the applicability of numerically-based techniques. Because experimentally-based techniques do not require secondary measurements of the relevant electronic quenching cross-sections, the technique is immediately applicable to new species of interest including radicals. Moreover, because experimentally-based techniques do not require measurements of local major-species concentrations, the experimental resources necessary for its implementation are greatly reduced compared to that required for numerically-based techniques. Hence, experimentally-based techniques provide great potential for realizing broadly applicable and sufficiently quantitative PLIF concentration measurements.

CHAPTER 4

FLUORESCENCE THEORY : APPLICATIONS TO PLIF MEASUREMENTS OF NO

In this chapter, the theory describing laser excitation, molecular fluorescence and fluorescence collection is formulated to provide a general relation between the laser spectral irradiance and the molecular number density within the probed volume. With this general theory developed, the specific cases of linear and saturated fluorescence are investigated, along with the requirements for saturation.

The fluorescence theory is developed in a general form because of the nature of planar fluorescence imaging. Point LIF or LSF measurements most often employ both short spectral and temporal gates (via monochromators and gated integrators). Consequently, steady-state fluorescence in a well-defined spectral range can be collected, thereby simplifying theoretical considerations. PLIF signals are collected spectrally broadband and with wide temporal gates (>18 ns). Hence, fluorescence transients are integrated, along with the steady-state fluorescence signal, during the temporal gate of the ICCD. Moreover, because PLIF uses spectrally broadband detection, the spectral responses of both the collection-optics filtering and camera systems must be incorporated into the PLIF theory. Two differences between the theory developed in this chapter and more traditional fluorescence theory are that: (1) the spectral width of the laser pulse is not assumed to be much narrower or broader than that of the absorption line; and (2) the fluorescence signal is not assumed to be comprised of a single wavelength.

4.1 Spectral and Temporal Profile Considerations

Because of different broadening mechanisms (e.g., see Demtroder, 1988), laser and molecular lines are not delta functions, but rather have characteristic spectral profiles. These spectral profiles reflect the fraction of the total response of each system at a given wavelength. For example, the laser spectral profile describes the spectral distribution of the total pulse power around a central wavelength (e.g., 1064 nm for Nd:YAG). The degree of interaction between laser radiation and a probed molecule is a function of both the position of the individual line centers and the relative distribution of the two profiles. Hence, lineshape functions which describe these distributions must be formulated.

The laser has a characteristic temporal pulse shape which describes the temporal distribution of the net energy per pulse. In gated detection, the integrated fluorescence signal depends on the temporal overlap between the detector (camera) gate and the fluorescence temporal profile. The temporal pulse shape of the fluorescence signal reflects that of the laser modified by various spectroscopic parameters of the probed molecule and environment. Hence, fluorescence theory requires a temporal description of the laser pulse.

4.1.1 Laser Pulse Description

Our injection-seeded laser system produces a temporal pulse which has been measured to be approximately Gaussian. The spectral profile of the laser is modeled as Lorentzian. The spectral irradiance of the laser may be represented by a normalized spectral irradiance, I_v^o , and independent temporal and spectral distribution functions, $T_L(t)$ and $L_L(v)$, so that

$$I_v(v,t) = I_v^o T_L(t) L_L(v) , \quad (4.1)$$

where

$$I_v^o = \frac{1}{\Delta v_L \Delta t_L} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} I_v(v,t) dv dt . \quad (4.1a)$$

The normalized spectral irradiance defined by Eq. (4.1a) demonstrates how the spectral and temporal FWHMs (Δt_L and $\Delta \nu_L$) of the laser are used to normalize the spectrally and temporally integrated value of the spectral irradiance, $I_\nu(\nu, t)$.

The normalized spectral irradiance is defined so as to be determined from experimental measurements of the laser cross-sectional area (A_L), temporal and spectral FWHMs, integrated power (P_L), and repetition rate (R_L), via

$$I_\nu^\circ = \frac{P_L}{A_L R_L \Delta \nu_L \Delta t_L} = \frac{E_L}{A_L \Delta \nu_L \Delta t_L}, \quad (4.2)$$

where $E_L = P_L/R_L$ is the laser energy per pulse. The formulation in Eq. (4.2) assumes uniform spatial, spectral and temporal responses for the power meter which integrates in the three specified dimensions. The temporal distribution of the laser, $T_L(t)$, is described by a Gaussian function normalized to its temporal FWHM, so that

$$T_L(t) = T^\circ e^{-\left(\frac{t-t_0}{\tau}\right)^2}, \quad (4.3)$$

where

$$T^\circ = 2\sqrt{\frac{\ln 2}{\pi}} \quad (4.3a)$$

$$\tau = \frac{\Delta t_L}{2\sqrt{\ln 2}} \quad (4.3b)$$

and

$$\int_{-\infty}^{+\infty} T_L(t) dt = \Delta t_L. \quad (4.3c)$$

The variable t_0 in Eq. (4.3) represents the time corresponding to the temporal peak of the laser pulse. Equation (4.3c) demonstrates how the temporal profile of the laser is normalized to Δt_L , rather than to unity, so as to be consistent with the definition of I_v^0 as indicated in Eq. (4.1a). Similarly, the spectral distribution of the laser, $L_L(v)$, is described by a Lorentzian normalized to its spectral FWHM, so that

$$L_L(v) = L^0 \left[1 + \left(\frac{2(v-v_0)}{\Delta v_L} \right)^2 \right]^{-1}, \quad (4.4)$$

where

$$L^0 = \frac{2}{\pi} \quad (4.4a)$$

$$\int_{-\infty}^{+\infty} L_L(v) dv = \Delta v_L \quad (4.4b)$$

and v_0 is the spectral position of the laser line center. Again, the normalization is consistent with the definition of I_v^0 in Eq. (4.1a).

Using Eqs. (4.1), (4.2), (4.3) and (4.4), the purely mathematical laser spectral irradiance may be defined in terms of physically measurable parameters. The formulation of Eqs. (4.1) through (4.4) was specifically designed to provide this link between modeling and experiment. Moreover, it is the mathematical and physical consistency between Eq. (4.1) and Eqs. (4.2), (4.3) and (4.4) that dictates use of these unique normalization procedures. Specifically, normalization of the laser distribution functions to unity (Gross et al., 1987) would destroy the link between experiment and modeling. From the definitions presented above, it is clear that integration of the laser spectral irradiance over all times and frequencies results in the laser energy flux per pulse, i.e., $P_L/A_L R_L$ (J/cm²). Moreover, integration of this quantity over all space results in the laser energy per pulse,

i.e., $E_L = P_L / R_L$ (J). Hence, there should be no misunderstanding concerning normalization to the individual FWHMs rather than to unity.

4.1.2 Absorption and Emission Lineshape Descriptions

The spectral lineshape function for absorption by the probed species, $Y_A(\nu)$, is assumed to be a normalized Gaussian, as characteristic of Doppler-broadened spectral lines. This function is actually a Voigt profile with the lineshape parameters chosen to reflect the contributions from homogeneous and inhomogeneous broadening. However, a Gaussian function will suffice for the current presentation. This function modifies the Einstein coefficient for absorption, B_{lu} , which is a spectroscopic constant for a given transition regardless of its FWHM. Hence, each Einstein B-coefficient tabulated in the literature represents an infinite spectral integration of the product of the B-coefficient and the absorption lineshape function. This, in turn, indicates that the spectral lineshape function for absorption should be normalized to unity. Thus, the result becomes

$$Y_A(\nu) = Y_A^o e^{-\left[\frac{2 \sqrt{\ln 2} (\nu - \nu_o)}{\Delta \nu_A} \right]^2}, \quad (4.5)$$

where

$$Y_A^o = \frac{2}{\Delta \nu_A} \sqrt{\frac{\ln 2}{\pi}} \quad (4.5a)$$

and

$$\int_{-\infty}^{+\infty} Y_A(\nu) d\nu = 1. \quad (4.5b)$$

In Eq. (4.5), ν_o and $\Delta \nu_A$ represent the line center and FWHM of the absorption line, respectively. Because stimulated emission involves the same two laser-coupled molecular

energy levels associated with the absorption process, the lineshape function for stimulated emission is equivalent to that of Eq. (4.5).

Spontaneous emission transitions also have finite spectral widths and hence each requires a unique lineshape function to modify its Einstein A-coefficient. The formulation of emission lineshape functions assumes the use of net A-coefficients for each vibrational band and therefore requires one emission lineshape function for each of these band transitions. Each net A-coefficient is denoted as $A_{v,v'}$ and its transition lineshape function is denoted as $Y_{E(v,v')}(v_{v,v'}^0, v)$ where $v_{v,v'}^0$ indicates the center frequency. This lineshape function should be normalized to unity. Although the spontaneous emission lineshape function is recognized to exist, its functional form is not explicitly given here, as such detailed knowledge is not required.

4.1.3 Formulation of the Spectral Overlap Integral

As laser-induced fluorescence measurements become increasingly quantitative, inclusion of an overlap term to account for variations in the absorption lineshape with temperature and pressure has become increasingly common (Lee et al., 1993; Battles et al., 1994; Carter and Barlow, 1994; Paul and Dee, 1994). The overlap term is also referred to as the overlap factor or the overlap integral. The overlap term is typically defined as the spectral integration of the product of the spectral distribution functions of the laser and the absorption transitions, each normalized to unity when individually spectrally integrated (Gross et al., 1987). This definition results in an overlap term, g , which has units of inverse wave number ($1/\text{cm}^{-1}$). Through subtle changes to the modeling of the laser spectral irradiance, we have produced a novel overlap fraction, Γ_{luL} , that is dimensionless and may be physically interpreted as the ratio of the total photon absorption rate (s^{-1}) in the actual broadened system to that which exists in the monochromatic limit (Partridge and Laurendeau, 1995). This interpretation is more physically meaningful compared with that of the traditional overlap term, which has a vague physical meaning.

The spectral overlap integral is a function which describes the spectrally distributed interaction between laser radiation and an absorption transition. The spectral overlap fraction, Γ_{luL} , is the value of the spectral overlap integral for a given absorption transition,

l-u, and laser, L. This fraction represents the loss from optimum (maximum) interaction due to both detuning of the center frequencies and the different spectral distributions of the laser radiation and absorption transition. For instance, the overlap fraction reflects the fact that although the laser may have a nonzero spectral irradiance in a frequency interval Δv , little to no absorption of that radiation by the probe species may occur if Δv is situated in a wing of the absorption profile or completely off-line. In fact, the overlap fraction will be less than unity even when the two line centers are coincident. It is the variation in the overlap fraction that accounts for the variation in fluorescence signal as the laser is tuned through a spectral line during an excitation scan. The dimensionless overlap fraction is realized via the unique normalization of the laser spectral distribution function described by Eq. (4.4). The overlap fraction may be evaluated numerically given the laser and absorption spectral lineshape functions and FWHMs. The result is

$$\begin{aligned}\Gamma_{lu,L} &= \int_{-\infty}^{+\infty} Y_A(v) L_L(v) dv \\ &= Y_A^o L^o \int_{-\infty}^{+\infty} \exp\left\{-\left[\frac{2\sqrt{\ln 2}(v-v_o)}{\Delta v_A}\right]^2\right\} \left[1 + \left(\frac{2(v-v_o)}{\Delta v_L}\right)^2\right]^{-1} dv .\end{aligned}\quad (4.6)$$

The second portion of Eq. (4.6) shows the form of the overlap integral for a laser and absorption line with Lorentzian and Gaussian spectral profiles, respectively, assuming alignment of the line centers (v_o) of the two profiles. Moreover, it is clear from Eq. (4.6) that this unique formulation produces a dimensionless overlap fraction.

The importance of the overlap fraction can be assessed by considering the spectral absorption rate, $B_{lu} I_v(v,t) Y_A(v)$. When Eq. (4.1) is used, at any given spectral position, v_j , the absorption rate becomes $B_{lu} I_v^o T_L(t) Y_A(v_j) L_L(v_j)$ so that the total photon absorption rate can be represented by the spectral integral of this function, or $B_{lu} I_v^o T_L(t) \Gamma_{lu,L}$. Thus, the total photon absorption rate in a broadened system is less than that for a monochromatic laser interacting with a monochromatic absorption line for which $\Gamma_{lu,L}=1$.

In fact, even in the unlikely condition that the laser and absorption transition have identically broadened profiles that are spectrally aligned, the total absorption rate will be a fraction (equal to the overlap fraction) of the absorption rate in the monochromatic limit. For instance, if the two constituents have spectrally aligned Gaussian profiles, this fraction may be shown to be approximately 0.664. Hence, our definition of the overlap fraction represents the ratio of the total photon absorption rate in the actual broadened system to that which would exist in the monochromatic limit. This simple but highly useful view of the overlap fraction is only possible if it is a dimensionless parameter, as provided by our formulation.

The more common overlap term g ($1/\text{cm}^{-1}$) is also defined by Eq. (4.6), but with a laser spectral distribution function, L_L^* ($1/\text{cm}^{-1}$), normalized to unity via use of $L^{o*} = 2/(\pi \cdot \Delta \nu_L)$ in place of Eq. (4.4a) (Gross et al., 1987). Hence, the dimensionless overlap fraction is related to the dimensional overlap term by $\Gamma_{luL} = \Delta \nu_L \cdot g$. Thus, in equations that relate the fluorescence signal to the probed species number density, which have been developed with the dimensional overlap term g (e.g., Eq. 1 of Paul and Dee, 1994), the resultant grouping $\Delta \nu_L \cdot g$ may be collapsed to a single dimensionless parameter Γ_{luL} .

A program to numerically evaluate the overlap integral was developed to determine its value under different laser operating conditions. The program utilizes the symmetry of the individual and combined spectral lineshapes by evaluating only one side of the overlap integral and doubling the result. Spectral integration out to four times the larger of the two FWHMs using a step size of 0.0001 cm^{-1} was sufficient to capture approximately 100% of the Gaussian (absorption) lineshape and 97% of the Lorentzian (laser) lineshape. This is expected and demonstrates the significance of the wings of the Lorentzian profile. Nevertheless, the overlap fraction was constant to at least five decimal places for a variation in the integration range from two to 10 times the larger FWHM. To check the program, the overlap fraction for two identical Gaussian lineshape functions was determined using the program and compared to a calculated solution. The numerical result agreed with the exact solution to at least five decimal places.

The overlap fraction has been numerically evaluated for a range of laser spectral FWHMs assuming Lorentzian and Gaussian lineshapes for the laser irradiance and absorption transition, respectively. Generation of UV radiation for excitation of NO via a Nd:YAG pumped, dye-laser system involves sum frequency mixing of the Nd:YAG fundamental with the second harmonic of the dye laser. Hence, the bandwidth of this UV radiation is a function of the bandwidths of both the dye and Nd:YAG lasers. The bandwidth of the dye laser has been found to depend only on the selected order of its diffraction grating. The bandwidth of the Nd:YAG laser depends on whether it is operated in the unseeded mode, with an inter-cavity etalon, or in the injection seeded mode. Hence, the bandwidth of the mixed UV radiation is a function only of the Nd:YAG laser's mode of operation. Although the bandwidth of the mixed radiation has not been measured experimentally, Spectra-Physics estimates the FWHMs to be approximately 1.15 cm^{-1} for the unseeded mode, 0.35 cm^{-1} when using the inter-cavity etalon and 0.15 cm^{-1} for operation with injection seeding (Spectra-Physics, 1992). The spectral FWHM of the NO transition was taken to be 0.4 cm^{-1} at atmospheric pressure (Reisel, 1993b). The results of the numerical calculation of the overlap fraction for these three modes of operation are tabulated in Table 4.1. The overlap fraction was calculated to be approximately 0.59, 0.42 and 0.26, for the unseeded mode, operation with the inter-cavity etalon and for the injection seeded mode, respectively. This indicates that the coupling efficiency between the available laser irradiance and the absorption line is highest for operation of the Nd:YAG laser in the unseeded mode.

4.2 Applicability of Rate Equation Analysis

The interaction of laser radiation with the probe molecule is most rigorously described by the density matrix methodology. However, in particular circumstances it can be shown that the disparity of time scales (collision rate vs. absorption rate) involved in the interaction causes the density matrix equations to reduce to the more common rate equations (Milonni and Eberly, 1988). Daily (1977) has investigated the specific circumstances under which a rate equation analysis is appropriate. His work indicates that the rate equations are applicable when the rise time of the laser pulse is long compared to

Table 4.1 Numerical evaluation of the overlap fraction $\Gamma_{lu,L}$ for a Lorentzian laser lineshape of FWHM $\Delta\nu_L$ and a Gaussian absorption lineshape of FWHM $\Delta\nu_A$.

Mode	$\Delta\nu_A$ (cm ⁻¹)	$\Delta\nu_L$ (cm ⁻¹)	$\Gamma_{lu,L}$
Seeded	0.40	0.15	0.26
ICE	0.40	0.35	0.42
Unseeded	0.40	1.15	0.59

the collisional decay time (10^{-10} to 10^{-11} s). Since the laser system used for the present PLIF imaging work has a rise time of approximately 5 ns, the rate equation analysis is applicable to these studies.

4.3 Model for Molecular Dynamics

A schematic of the relevant molecular excitation and relaxation processes is shown in Fig. 4.1. The lower (l) and upper (u) laser-coupled levels correspond to a specific rotational level within a specific vibrational level of the ground and first excited electronic states of the molecule, respectively. Because of this rotational, vibrational and electronic level specificity, transitions between such levels are termed rovibronic transitions. Although only vibrational and electronic levels are indicated in Fig. 4.1, each vibrational level is understood to be composed of a manifold of rotational levels. The rate coefficients for absorption and stimulated emission are indicated by W_{lu} and W_{ul} , respectively. A second radiative de-excitation path is spontaneous emission which is characterized by isotropic emission of incoherent radiation at frequencies corresponding to the energy differences between the upper laser-coupled level and the available rovibronic levels in the ground electronic state. The net rate coefficient for spontaneous emission between specific vibrational bands is indicated by $A_{v'v''}$, where v' and v'' denote the vibrational quantum numbers of the upper and lower levels, respectively. Nonradiative de-excitation processes are electronic quenching, photoionization and predissociation which are assigned the rate coefficients Q_e , Q_i and Q_p , respectively. Photoionization and predissociation have been successfully used to perform quenching-independent, controlled-loss spectroscopy (Salmon and Laurendeau, 1987; Arnold et al., 1990) but will not be considered here.

4.3.1 Rate Equation Description of Molecular Dynamics

The molecular dynamics can be modeled as a two-level system which assumes that the vibrational energy transfer rates in the lower electronic level are fast compared to the rates shown in Fig. 4.1. With this assumption, the rate of change of population in the upper laser-coupled level may be formulated as

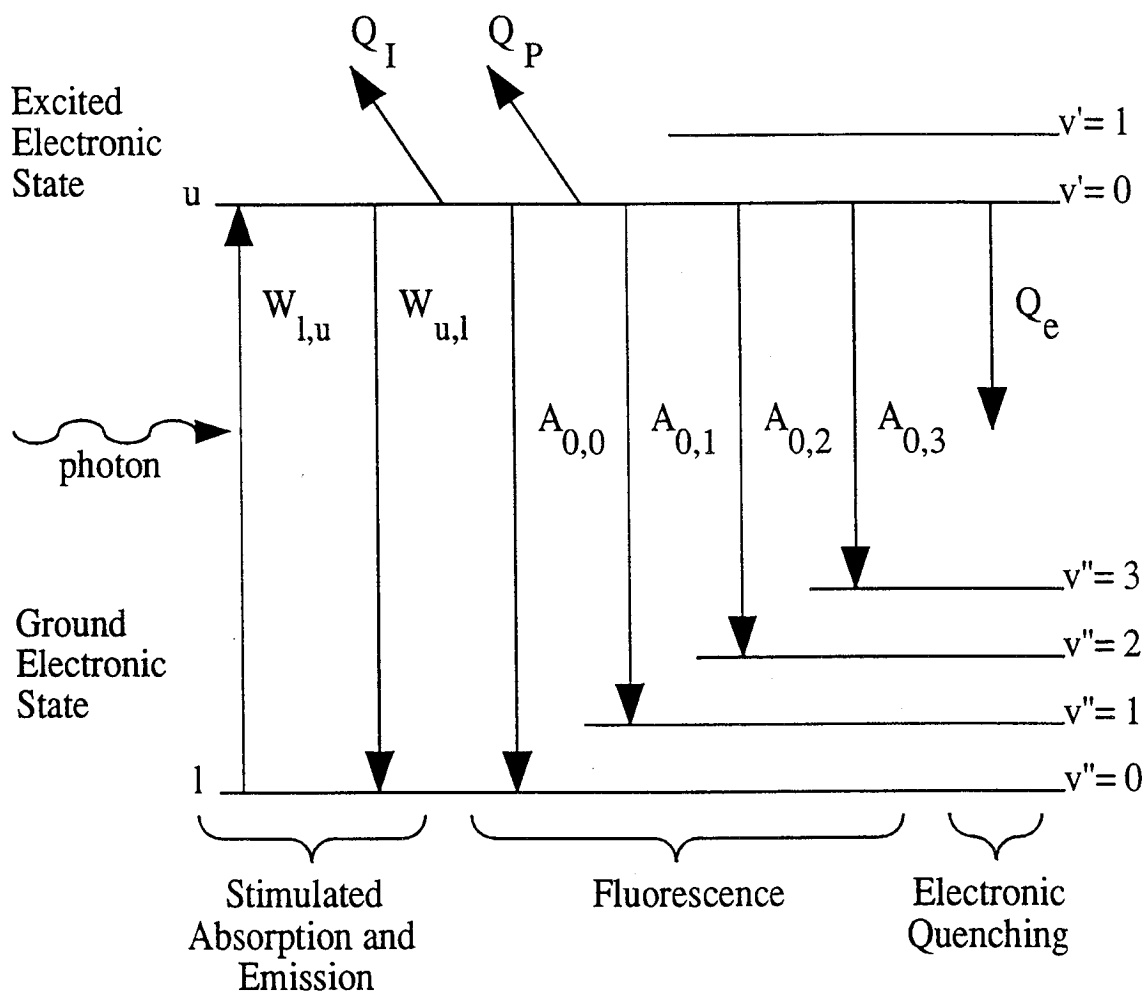


Figure 4.1 Schematic of molecular dynamics. The upper and lower laser-coupled levels are labeled u and l , respectively. Vibrational quantum numbers in the upper and lower electronic states are indicated as v' and v'' , respectively. The absorption and stimulated emission rate coefficients are labeled $W_{l,u}$ and $W_{u,l}$, respectively. The spontaneous emission rate coefficients for specific band transitions are indicated by $A_{v',v''}$. The rate coefficients for electronic quenching, photoionization and predissociation are labeled Q_e , Q_I and Q_P , respectively.

$$\frac{dN_u}{dt} = N_l W_{lu} - N_u [W_{ul} + Q_P + Q_I + A_N + Q_e] , \quad (4.7)$$

where

$$A_N = \sum_{v''} A_{v',v''} \quad (4.8)$$

represents a net rate coefficient for spontaneous emission from the upper laser-coupled level to all the rovibronic levels in the ground electronic state. With the definition of a net spontaneous emission rate coefficient as formulated in Eq. (4.8), it becomes useful to define a net emission lineshape function. This function operates on A_N in the same manner as discussed in Section 4.1.2 for the individual band transitions, i.e.,

$$Y_{EN}(v) = \frac{\sum_{v''} A_{v',v''} Y_{E(v',v'')}(v_{v',v''}^o, v)}{A_N} . \quad (4.9)$$

The populations of the upper and lower levels of the two-level model obey the typical population conditions (Laurendeau and Goldsmith, 1989):

$$\begin{aligned} N_u(t=0) &= 0 \\ N_l(t) + N_u(t) &= N_l^o = N_l(t=0) . \end{aligned} \quad (4.10)$$

The first condition of Eq. (4.10) implies that at typical flame temperatures insufficient energy is available to cause an initial electronic excitation of the probed molecule. The second condition of Eq. (4.10) indicates conservation of the initial population of the lower laser-coupled level. This implies that the rates of population transfer from the laser-coupled levels of the two-level model to other unspecified levels are equal to rates of population transfer from these unspecified levels back into the laser-coupled levels. This

is often satisfied for fast rotational and vibrational transfer rates, particularly in the ground electronic state.

Solving Eq. (4.7) for the population in the upper laser-coupled level is complicated by the temporal dependence of the absorption and stimulated emission rate coefficients, W_{lu} and W_{ul} , respectively. These rate coefficients obtain temporal dependence through their relation to the laser spectral irradiance, $I_\nu(\nu, t)$. However, for a molecular system with a response time much smaller than any temporal variations in the laser spectral irradiance, the population distribution reaches a pseudo steady-state value at each temporal interval. For such a disparity of time scales, the excited state population, N_u , should follow the temporal variations in the rate coefficients, W_{lu} and W_{ul} , as discussed in Section 4.3.3.

The response time of the molecular system may be investigated by observing its response to a step-irradiance input. With such an input, the absorption and stimulated emission rate coefficients become constants. For such a condition, the time-dependent population of the upper laser-coupled level (molecules/cm³) is found to be

$$N_u(t) = W_{lu} N_l^o \beta^{-1} [1 - e^{-\beta t}] , \quad (4.11)$$

where

$$\beta = W_{lu} + W_{ul} + A_N + Q_e = \gamma W_{lu} + A_N + Q_e . \quad (4.11a)$$

The relation $g_l W_{lu} = g_u W_{ul}$ has been used to define the variable $\gamma = 1 + g_l/g_u$ in Eq. (4.11a); the possible effects of photoionization and predissociation have been neglected. The variable β is recognized to be the inverse time constant for this first order system. The time constant is maximized for the case of linear fluorescence, in which case $\beta \approx Q_e$. Using the value for the electronic quenching rate coefficient listed in Table 4.2, $\beta^{-1} \approx 1.7$ ns for this case, which indicates that it takes approximately 5 ns (i.e., $3 \beta^{-1}$) for the upper-level population to reach 95% of its steady-state value, $W_{lu} N_l^o \beta^{-1}$.

A realistic laser pulse provides a more gradual input compared to a step input. However, with a typical laser pulse temporal FWHM of 8 ns, the time constant for the

Table 4.2

Typical values for different spectroscopic parameters: Excitation of the $Q_{22}(26.5)$ line of the $\gamma(0,0)$ band of NO with detection in the $\gamma(0,1)$ and higher bands. The net spontaneous emission rate coefficient was obtained from Piper and Cowles (1986), the electronic quenching rate coefficient was obtained from Reisel (1993b), and the values for the variable γ and the Einstein B coefficient were obtained from Reisel et al. (1992).

$$A_N = 4.59 \times 10^{-3} \text{ ns}^{-1}$$

$$Q_e = 0.6 \text{ ns}^{-1}$$

$$\gamma = 2$$

$$B_{lu} = 310.86 \text{ cm}^2\text{cm}^{-1}/\text{J}$$

simple case discussed above is not short enough to immediately justify the desired disparity of time scales. This indicates that a significant portion of the fluorescence, through each pulsed fluorescence event, may occur under non-steady conditions. Typically, a qualitative PLIF analysis assumes the fluorescence rate to be at steady-state throughout the laser pulse. Clearly, any deviation from the steady-state condition during the laser pulse must be quantified if quantitative information is to be extracted from PLIF images. This requires solving Eq. (4.7) with time-dependent absorption and stimulated emission rate coefficients using numerical techniques. Any significant unsteady response should cause the temporal distribution of the fluorescence signal to deviate from that of the laser pulse. The fluorescence signal was experimentally observed to temporally follow the laser pulse. Hence, the response time of the molecular system is assumed to be sufficiently fast so as to allow the transient term in Eq. (4.11) to be neglected. In this limit, the time dependent population of the upper laser-coupled level, $N_u(t)$, becomes $W_{lu}(t)N_l^0/\beta(t)$ with the time dependence of β arising from the spectral irradiance via the absorption rate coefficient, W_{lu} .

4.3.2 Photon Emission Rate for Fluorescence

A fluorescence photon is emitted from the probe volume each time an electronically excited molecule relaxes to the ground electronic state via spontaneous emission. Since an electronically excited molecule can relax to a number of vibrational levels, each with a manifold of rotational levels, the fluorescence has a finite spectral bandwidth characteristic of the different relaxation paths available. Use of the net spontaneous emission rate coefficient, as defined by Eq. (4.8), accounts for all possible relaxation paths. As mentioned in the preceding section, fluorescence is an isotropic process and hence, the photons are uniformly emitted into 4π steradians. With these considerations, the photon emission rate (photons/cm³·sr·s) for fluorescence may be formulated as

$$\frac{dE_P}{dt} = \frac{1}{4\pi} N_u(t) A_N . \quad (4.12)$$

4.3.3 Photon Collection Rate Per Pixel

The photon collection rate per pixel at the entrance face (photocathode) of the ICCD is influenced by the collection optics through their effect on the collection efficiency and the collection volume. Spectral filtering of the fluorescence is addressed in a later section. Moreover, the point spread function of the ICCD is assumed to be a delta function (i.e., pixel dimensions projected back through the ICCD onto the photocathode are exact spatial duplicates).

Because the collection optics subtend a finite solid angle relative to the probe volume, only a fraction of the total isotropically emitted fluorescence is captured and focused onto the ICCD. Defining the solid angle subtended by the collection optics as Ω , the fraction of the total fluorescence photons which are collected is $\Omega/4\pi$. This fraction is further reduced by reflection losses at each optical surface in the collection optics system. A general optical loss factor η is defined to account for these reflection losses.

For a given photon emission rate, dE_p/dt , and a given collection optics system, the total number of photons intercepted by each pixel is dictated by the extent of the collection volume corresponding to each pixel. The spatial extent of the pixel collection volume normal to the optical axis of the collection optics (i.e., in the plane of the laser sheet) is dictated by the dimensions of each pixel and the collection optics magnification. Assuming a negligible point spread function for the ICCD, the CCD pixel dimensions, y' and z' , project back through the intensifier to produce exact spatial duplicates on the entrance face (i.e., photocathode) of the ICCD. These pixel dimensions, y' and z' , on the photocathode are then related to those in the laser sheet via the collection optics magnification. For a given magnification, M , the transverse spatial extent of the collection volume, y and z , may be expressed as $y=y'/M$ and $z=z'/M$. The longitudinal spatial extent of the collection volume, x , is dictated by the thickness of the laser sheet. The unfiltered photon collection rate per pixel at the entrance face of the ICCD, $dC_{p,T}/dt$ (photons/s), may now be determined by integrating the photon emission rate over the pixel collection volume. Including the optical loss factors (Ω and η), we obtain

$$\begin{aligned}
\frac{dC_{P,T}}{dt} &= \eta \Omega \int_0^z \int_0^y \int_0^x \frac{dE_P}{dt} dx dy dz \\
&= \eta \Omega \frac{dE_P}{dt} \int_0^z \int_0^y \int_0^x dx dy dz = \eta \Omega \frac{dE_P}{dt} V_C \\
&= \eta \frac{\Omega}{4\pi} V_C N_l^o W_{lu}(t) \beta(t)^{-1} A_N
\end{aligned} \tag{4.13}$$

where we have employed Eqs. (4.11) and (4.12) with the steady-state approximation. Since the CCD pixel is the minimum spatial sampling interval, spatial fluctuations in the field within the projected pixel dimensions are unresolved. Hence, the photon emission rate must be assumed to be some average over the pixel collection volume and may therefore be taken outside the spatial integration in Eq. (4.13).

The total number density (N_T) of the probed species is typically of greater interest than the number density in the lower laser-coupled level, N_l^o . The Boltzmann fraction, $f_B(T)$, relates these two number densities via

$$f_B(T) = \frac{N_l^o}{N_T} . \tag{4.14}$$

Equation (4.14) emphasizes the temperature dependence of the population distribution of the probe species in the ground electronic state. The absorption and stimulated emission rate coefficients, W_{lu} and W_{ul} , are typically expressed in terms of the Einstein B-coefficients and the laser spectral irradiance, e.g.,

$$W_{ij}(t) = (\tilde{B}_{ij} / c) I_v(t) = B_{ij} I_v(t) \tag{4.15}$$

for a monochromatic laser interacting with a monochromatic absorption line. The total photon collection rate (i.e., photons/s) for monochromatic conditions may now be obtained by substituting Eqs. (4.14) and (4.15) into Eq. (4.13) to obtain

$$\frac{dC_{P,T}}{dt} = \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T B_{lu} I_v(t) \beta(t)^{-1} A_N. \quad (4.16)$$

Generalization of this expression to account for spectral broadening is presented in the following section.

4.3.4 Inclusion of Spectral and Temporal Dependence

Before any spectral and temporal gates may be applied to the photon collection rate of Eq. (4.16), the spectral and temporal dependence must be clarified using the relations developed in Section 4.1. Substituting the shape functions for the laser and spectral lines from Eqs. (4.1) to (4.5) and Eq. (4.9) into Eq. (4.16) gives the most general form of the photon collection rate. However, by introducing the excitation and emission spectral dependencies into Eq. (4.16), the total photon collection rate is expressed per unit excitation frequency interval and per unit emission frequency interval. Thus, the appropriate units are photons/($s \cdot \text{cm}_{\text{ex}}^{-1} \cdot \text{cm}_{\text{em}}^{-1}$), where $\text{cm}_{\text{ex}}^{-1}$ represents the excitation frequency interval and $\text{cm}_{\text{em}}^{-1}$ represents the emission frequency interval. Making these substitutions, we obtain

$$\frac{d^3 C_{P,T}}{dv_{\text{ex}} dv_{\text{em}} dt} = \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T B_{lu} Y_A(v_{\text{ex}}) I_v^o T_L(t) L_L(v_{\text{ex}}) \beta(t)^{-1} A_N Y_{EN}(v_{\text{em}}) \quad (4.17)$$

where subscripts have been added to differentiate dependencies on excitation frequency, v_{ex} , from dependencies on emission frequency, v_{em} . Integrating Eq. (4.17) over all excitation frequencies and using Eq. (4.6), we obtain

$$\frac{d^2 C_{P,T}}{dv_{\text{em}} dt} = \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \Gamma_{lu,L} B_{lu} I_v^o T_L(t) \beta(t)^{-1} A_N Y_{EN}(v_{\text{em}}) \quad (4.18)$$

where

$$\beta(t) = \gamma \Gamma_{luL} B_{lu} I_v^o T_L(t) + A_N + Q_e \quad (4.18a)$$

results from a similar integration of Eq. (4.11a) over all excitation and emission frequencies and using Eqs. (4.9) and (4.15). Equation (4.18) represents the fluorescence collection rate per unit emission frequency interval (i.e., photons/(s·cm_{em}⁻¹)) in a form suitable for the application of spectral (emission) and temporal gates. Equation (4.18) is a generally applicable equation which assumes only steady-state fluorescence and excitation via a single isolated spectral line.

4.3.5 Application of Spectral Filters

High-pass spectral filters are typically incorporated in the collection optics system for planar imaging experiments to reject both Rayleigh and Mie scattering at the laser wavelength. For point measurement techniques, this spectral filtering is achieved via use of a monochromator. As demonstrated in Chapter 6, colored-glass spectral filters do not produce a perfect spectral gate but rather have some characteristic transmission vs. frequency profile. This profile may be obtained from the filter manufacturer or may be measured experimentally by monitoring the transmission of scattered radiation from a tuned laser. Since each filter combination will produce a different spectral profile, a specific form cannot be assumed. Rather, a spectral filter function, $F(\nu)$, is accepted as having been determined such that it describes the transmission ($F(\nu)=1$ for 100% transmission) of the filter system as a function of frequency. This spectral distribution function is not normalized but rather acts as a weighting function.

The collection rate of filtered fluorescence photons, $dC_{p,F}/dt$ (photons/s), may be determined by applying the spectral filter function to the total photon collection rate per unit emission frequency interval and integrating over all emission frequencies. Thus, using Eq. (4.18),

$$\begin{aligned}
\frac{dC_{P,F}}{dt} &= \int_{-\infty}^{+\infty} \frac{d^2C_{P,T}}{dv_{em}dt} F(v_{em}) dv_{em} \\
&= \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \Gamma_{lu,L} B_{lu} I_v^o T_L(t) \beta(t)^{-1} A_N \int_{-\infty}^{+\infty} Y_{EN}(v_{em}) F(v_{em}) dv_{em} \quad (4.19) \\
&= \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \Phi(t) \Gamma_{lu,L} B_{lu} I_v^o T_L(t) ,
\end{aligned}$$

where

$$\Phi(t) = \beta(t)^{-1} A_N \int_{-\infty}^{+\infty} Y_{EN}(v_{em}) F(v_{em}) dv_{em} = \beta(t)^{-1} A_{N,F} . \quad (4.19a)$$

The fluorescence yield (Φ) as defined in Eq. (4.19a) is the probability that the absorption of a pump (laser) photon will result in emission of a fluorescence photon within the spectral bandwidth of the collection optics (Allen et al., 1993). Notice that the fluorescence yield is specific to a given excitation scheme through its dependance on the Einstein B-coefficient (an excitation variable) and a given detection scheme via its dependance on the spectral filter function (a detection variable).

4.3.6 Amplification and Digital Conversion by the ICCD

In terms of fluorescence theory, the ICCD may be considered to be a device for amplifying, temporally gating or integrating, and converting the fluorescence signal. During the time that the camera is gated on, the fluorescence signal is amplified by the intensifier and integrated on the CCD array. This integrated signal array is then converted to a digital array for storage on a PC. Although the actual sequence of events is amplification, integration and conversion, it is mathematically equivalent to amplify and convert the filtered photon collection rate from Eq. (4.19) and then to apply temporal

integration. This is the approach taken here so that the camera's effect on the signal may be isolated.

In the process of passing the fluorescence signal through the camera system to be stored as a digital signal (counts), spectrally and spatially dependent amplification and noise are imparted to the signal. The spectral variation in the amplification may be experimentally measured by scanning a scattering source (laser) over the range of signal wavelengths and recording the spectral pixel responsivity. This provides a pixel specific spectral-amplification filter which can be applied to the photon signal in a manner similar to Eq. (4.19). Many of the noise contributions to the signal are repeatable for a given detection clocking scheme and may thus be measured separately and subtracted off as described in Appendix D. The dark noise, which results from thermal or Johnson noise integrated over the readout cycle (i.e., $R_L^{-1} \times [\text{number of on-chip integrations}]$), is repeatable and hence subtractable for a given readout cycle and chip temperature. Readout of the CCD array produces a fixed pattern noise which is constant as long as the readout rate of the camera is constant (Simpson, 1979). All of the repeatable noise sources may be combined into a single noise image which may be subtracted from the fluorescence image via post processing. A significant amount of work has been devoted to quantification of and correction for camera noise sources (e.g., van Cruyningen et al., 1990). Hence, such techniques will be accepted and thus camera noise will be taken as zero in the present discussion. Ultimately, signal contributions from such noise sources are accounted for as described in Appendix D.

The ICCD functions as a photon-to-digital signal converter with pixel-specific gain, G , and response, R (counts/photon), functions. Hence, the digital fluorescence rate, dC_D/dt (counts/s), may be determined as the product of the filtered fluorescence collection rate (photons/s) from Eq. (4.19) and $G \cdot R$, so that

$$\begin{aligned} \frac{dC_D}{dt} &= G R \frac{dC_{PF}}{dt} \\ &= G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \Phi(t) \Gamma_{luL} B_{lu} I_v^o T_L(t) . \end{aligned} \quad (4.20)$$

A direct relationship between the experimentally obtained digital fluorescence signal, C_D , and the probed species number density, N_T , may be obtained by integrating Eq. (4.20) over the temporal gate of the ICCD. However, execution of this integration is simplified if the fluorescence is in either the linear or saturated regime. Hence, the following section recasts Eq. (4.20) in terms of the saturation spectral irradiance. After the digital fluorescence signal rate is recast in this most general form, the specific cases of linear and saturated fluorescence can be investigated.

4.3.7 Formulation Using the Saturation Spectral Irradiance

The inverse transition lifetime (Eq. 4.18a) may be expanded in the equation for the fluorescence yield (Eq. 4.19a) and the result may be rearranged as follows:

$$\begin{aligned}
 \Phi(t) &= \frac{A_{N,F}}{\beta(t)} = \frac{A_{N,F}}{\gamma \Gamma_{lu,L} B_{lu} I_v^o T_L(t) + A_N + Q_e} \\
 &= \frac{A_{N,F}}{\gamma \Gamma_{lu,L} B_{lu} I_v^o T_L(t)} \frac{1}{1 + \frac{A_N + Q_e}{\gamma \Gamma_{lu,L} B_{lu} I_v^o T_L(t)}} \\
 &= \frac{A_{N,F}}{\gamma \Gamma_{lu,L} B_{lu} I_v^o T_L(t)} \left[1 + \frac{I_v^{sat}}{I_v^o T_L(t)} \right]^{-1}
 \end{aligned} \tag{4.21}$$

where

$$I_v^{sat} = \frac{A_N + Q_e}{\gamma \Gamma_{lu,L} B_{lu}} . \tag{4.21a}$$

The saturation spectral irradiance, I_v^{sat} , defined in Eq. (4.21a) differs from the standard definition (e.g., see Eckbreth, 1988) in that it uses the net spontaneous emission rate coefficient and includes the overlap fraction. Equation (4.21) may be substituted into Eq. (4.20) to express the digital fluorescence rate in terms of the saturation irradiance, i.e.,

$$\frac{dC_D}{dt} = G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \frac{A_{N,F}}{\gamma} \left[1 + \frac{I_v^{\text{sat}}}{I_v^o T_L(t)} \right]^{-1}. \quad (4.22)$$

Because the laser spectral irradiance is a function of time, the spectral irradiance ratio, $I_v^{\text{sat}}/I_v^o T_L(t)$, in Eq. (4.22) will vary through the laser pulse. The limiting cases of linear and saturated fluorescence exist in the limits of the bracketed term in Eq. (4.22). These limits are driven by variations in the spectral irradiance ratio and are investigated in the following sections.

4.4 Linear Fluorescence

In the limit that $I_v^o T_L(t) \ll I_v^{\text{sat}}$, the bracketed term in Eq. (4.22) reduces to $I_v^o T_L(t)/I_v^{\text{sat}}$. In this linear fluorescence limit, the digital fluorescence rate reduces to

$$\begin{aligned} \frac{dC_D^{LN}}{dt} &= G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \frac{A_{N,F}}{\gamma} \frac{I_v^o T_L(t)}{I_v^{\text{sat}}} \\ &= G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \Gamma_{lu,L} B_{lu} \Phi^{LN} I_v^o T_L(t), \end{aligned} \quad (4.23)$$

where we have used Eq. (4.21a), and

$$\Phi^{LN} = \frac{A_{N,F}}{A_N + Q_e} \quad (4.23a)$$

is the fluorescence yield in the linear fluorescence limit. Notice that the right hand side of Eq. (4.23) is linear with respect to the laser spectral irradiance, as characteristic of linear fluorescence processes.

Integration of Eq. (4.23) over the temporal gate width, t_G , produces the desired relation between the probed species number density and the digital signal in the linear fluorescence limit. Using Eq. (4.3c), we obtain

$$\begin{aligned}
 C_D^{LN} &= \int_0^{t_G} \frac{dC_D^{LN}}{dt} dt \\
 &= G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \Gamma_{lu,L} B_{lu} \Phi^{LN} I_v^o \int_0^{t_G} T_L(t) dt \\
 &= G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \Gamma_{lu,L} B_{lu} \Phi^{LN} I_v^o \Delta t_L
 \end{aligned} \tag{4.24}$$

when

$$t_G \geq \frac{3\Delta t_L}{\sqrt{\ln 2}}. \tag{4.25}$$

If the condition on the gate width specified by Eq. (4.25) is satisfied, then the temporal integral in Eq. (4.24) reduces essentially to Δt_L . Recall from Eq. (4.3a) that the temporal profile of the laser is normalized to the FWHM for infinite integration. However, expanding the integral and evaluating via the error function (Ozisik, 1980), one can show that more than 99.99% of the total profile is captured if Eq. (4.25) is satisfied. Equation (4.24) can be inverted to determine the probed species number density, N_T , from the digital fluorescence signal, C_D^{LN} , as long as the fluorescence is in the linear regime throughout the laser pulse.

4.5 Saturated Fluorescence

If sufficient laser irradiance is available, quenching-independent species concentration measurements are possible via saturated fluorescence. Spatially extended saturated fluorescence measurements of OH have been demonstrated along a line (Alden et al., 1982) and in two dimensions (Schafer et al., 1991). These one- and two-dimensional LSF investigations incorporated a frequency-doubled Nd:YAG-pumped dye laser at ~ 283 nm with ~ 20 mJ/pulse, and a tunable XeCl excimer laser at ~ 308 nm with ~ 250 mJ/pulse, respectively. Excitation of NO around 226 nm via a Nd:YAG-pumped dye laser requires an additional nonlinear process which further reduces the laser output. By formulating theory describing saturated fluorescence, estimates can be made concerning the ability to perform spatially extended saturated fluorescence measurements of NO. Moreover, it allows identification of those laser parameters (seeded vs. unseeded) which maximize the potential for saturation. The final general equation describing measured fluorescence signals under saturated conditions may also be reduced further to describe point LSF measurements of [NO].

4.5.1 Saturated Fluorescence Theory

In the limit that $I_v^\circ T_L(t) \gg I_v^{\text{sat}}$, the bracketed term in Eq. (4.22) reduces to unity and the fluorescence is said to be saturated. In this saturated fluorescence limit, the digital fluorescence rate reduces to

$$\frac{dC_D^{\text{SAT}}}{dt} = G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \frac{A_{NF}}{\gamma} . \quad (4.26)$$

Equation (4.26) demonstrates that the saturated fluorescence rate is independent of both the laser spectral irradiance and the electronic quenching rate coefficient. Such independence, particularly for the electronic quenching rate coefficient, is the primary hallmark of saturated fluorescence measurements.

Although the right-hand side of Eq. (4.26) indicates that the saturated digital signal rate is independent of time, care must be taken to apply this expression only when the

transition is fully saturated. As mentioned previously, the irradiance ratio in Eq. (4.22) varies through the laser pulse. This variation complicates saturated fluorescence measurements with wide temporal gates, i.e., $t_G > \Delta t_L$, because although the transition may be saturated at the peak of the laser pulse, there is always some portion of the temporal wings where $I_v^o T_L(t) \ll I_v^{sat}$ so that the fluorescence signal displays linear and partially saturated behavior. Hence, in a saturated imaging experiment, the wide temporal gates associated with planar imaging will integrate over temporal regimes for which the fluorescence is linear, partially saturated and saturated. We can, for example, investigate the situation where the transition is fully saturated for a time t_s centered about t_o in a strongly collisional environment. Assuming the fluorescence to be either fully saturated or fully linear, and using Eqs. (4.23) and (4.26) for the appropriate temporal regimes, we obtain

$$\begin{aligned}
 C_D &= \int_0^{t_G} \frac{dC_D}{dt} dt = 2 \int_{t_o}^{t_o + \frac{t_s}{2}} \frac{dC_D^{SAT}}{dt} dt + 2 \int_{t_o + \frac{t_s}{2}}^{t_G} \frac{dC_D^{LIN}}{dt} dt \\
 &= G R \eta \frac{\Omega}{4\pi} V_C f_B(T) N_T \frac{A_{N,F}}{\gamma} \left[t_s + 2 \frac{I_v^o}{I_v^{sat}} \int_{t_o + \frac{t_s}{2}}^{t_G} T_L(t) dt \right], \tag{4.27}
 \end{aligned}$$

where the symmetry of the temporal profile has been exploited, as well as Eqs. (4.21a) and (4.23a). The terms preceding the bracketed terms in Eq. (4.27) are common to signals from both the saturated and linear fluorescence regimes. The first term in the brackets of Eq. (4.27), t_s , accounts for the portion of the integrated signal due to saturated fluorescence. This term indicates that for the time t_s , the laser spectral irradiance is sufficiently large for the transition to be considered fully saturated. The second or additive term in the brackets of Eq. (4.27) accounts for the linear fluorescence in the rising and

falling wings of the laser pulse. In the limit that t_s goes to zero, Eq. (4.27) reduces to Eq. (4.24) for linear fluorescence.

Equation (4.27) demonstrates the difficulty in making laser-saturated fluorescence (LSF) measurements with wide temporal gates. For point LSF measurements, the temporal gate of the system, $t_{G,LSF}$, can be made sufficiently small and positioned so that only fluorescence at saturated conditions is collected. With such a configuration, Eq. (4.26) may be integrated over $t_{G,LSF}$ so that the result is equivalent to replacing the bracketed term in Eq. (4.27) with $t_{G,LSF}$. This condition was satisfied for the LSF point measurements of [NO] in Chapter 7 via use of a 500-ps temporal gate. With wide temporal gates, Eq. (4.27) indicates that a portion of the signal is always due to linear fluorescence. By increasing the normalized spectral irradiance of the laser, I_v^0 , the time at which the spectral irradiance ratio, $I_v^{sat}/I_v^0 T_L(t)$, of Eq. (4.22) becomes sufficiently small so that the transition may be considered saturated can be made to occur earlier in the laser pulse. In this manner, t_s may be increased via I_v^0 . However, the irradiance ratio, I_v^0/I_v^{sat} , in Eq. (4.27) indicates that the significance of the temporal wings of the laser pulse, and thus the contribution from linear fluorescence increases linearly with I_v^0 . Hence, Eq. (4.27) shows that it is impossible to obtain fully saturated fluorescence measurements with wide temporal gates.

Although Eq. (4.27) indicates that it is not possible to drive the linear portion of the fluorescence signal to insignificant levels, it does indicate a unique relationship between the different components of the signal. Specifically, the transition may be considered to be sufficiently saturated above some particular irradiance ratio (IR). With this value determined, t_s is specified for a given I_v^0 through the temporal distribution via $I_v^0 T_L(t_s) = IR \cdot I_v^{sat}$. Through this relation, Eq. (4.27) becomes a function of a single variable, t_s or I_v^0 . The integration may then be evaluated numerically at different levels of laser irradiance to assess the relative contributions to the total signal from the different components. This, in turn, would indicate the relative sensitivity to the experimental parameters, e.g., the electronic quenching rate coefficient. By employing such an approximate relationship between the different signal contributions as afforded by Eq.

(4.27), a pathway is provided for exploring the utility of temporally-integrated, saturated-imaging measurements.

4.5.2 Influence of Laser Parameters

The influence of the Nd:YAG laser's mode of operation (injection seeded, inter-cavity etalon or unseeded) on the overlap fraction was discussed in Section 4.1.3. Operation of the laser system in the different modes changes both the bandwidth and the energy per pulse of the mixed UV radiation. Hence, each mode of operation has unique values of the laser bandwidth, energy per pulse and overlap fraction. These variables affect the laser spectral irradiance and/or the saturation irradiance, and hence influence the ability to saturate. To maximize the potential for saturation, the optimum mode of operation of the laser system must be identified.

The degree of saturation is increased by maximizing the spectral irradiance ratio, I_v^o / I_v^{sat} . Thus, the optimal mode of laser system operation for saturated fluorescence measurements is that which maximizes this irradiance ratio. The only variables in Eq. (4.22) which change with the laser system's mode of operation are the normalized laser spectral irradiance and the saturation irradiance. Thus, the ratio of the irradiances may be expanded to reveal the dependance on the appropriate variables by using Eqs. (4.2) and (4.21a), i.e.,

$$\frac{I_v^o}{I_v^{sat}} = \frac{E_L}{A_L \Delta \nu_L \Delta t_L} \frac{\Gamma_{luL} \gamma B_{lu}}{A_N + Q_e} = \frac{\gamma B_{lu}}{A_L \Delta t_L (A_N + Q_e)} \left[\frac{E_L \Gamma_{luL}}{\Delta \nu_L} \right]. \quad (4.28)$$

In Eq. (4.28), the variables which change with the laser system's mode of operation have been isolated in the square brackets on the right-hand side. Hence, the mode of operation which maximizes the ratio $R_I = E_L \Gamma_{luL} / \Delta \nu_L$ will most effectively saturate the NO transition. The variations in Γ_{luL} and $\Delta \nu_L$ were summarized in Table 4.1. The energy per pulse of the mixed UV beam has been conservatively measured (i.e., with a sufficiently divergent dye laser beam so as to produce a strong lock on the nonlinear crystal's active angle tuning mechanisms in the WEX-2C, as described in Chapter 5) with the Nd:YAG laser in the

injection seeded and unseeded modes; the resulting values are 8 mJ/pulse and 5 mJ/pulse, respectively. Although the laser system used with the planar imaging facility is not currently equipped with an inter-cavity etalon (ICE), it is configured to accept an ICE if needed. The energy per pulse expected for Nd:YAG operation with an ICE is estimated to be 6.5 mJ/pulse. The values of the individual variables and the resulting ratio R_1 for operation of the laser system in the different modes are summarized in Table 4.3. These results make it clear that saturation is most probable with the laser system operating in the injection seeded mode.

4.5.3 Spatially Extended Saturation

Saturated fluorescence has been successfully used to measure NO concentrations at a point in an atmospheric pressure flame (e.g., see Reisel et al., 1993a). With sufficient UV laser power, saturated fluorescence is possible in extended areas such as along a line or in a sheet. Such spatially extended saturation has been demonstrated for OH along a line using a Nd:YAG-pumped dye-laser system near 283 nm (Alden et al., 1982) and in a sheet using an excimer laser near 308 nm (Schafer et al., 1991). Excitation of NO near 226 nm using a Nd:YAG-pumped dye laser requires an additional nonlinear mixing process, relative to generation of UV radiation for OH excitation, and consequently reduces the beam power.

As discussed in Section 4.5.2, the degree of saturation is proportional to the ratio of the laser to saturation spectral irradiances. As this ratio goes to infinity, the transition becomes fully saturated. However, realistically this ratio is set by the maximum available laser spectral irradiance (via the maximum power per pulse and the minimum achievable focus spot size) and the experimentally acceptable deviation from saturation (with consequent sensitivity to variations in the electronic quenching rate coefficient and laser spectral irradiance). For point measurements, the first criterion is used to set the irradiance ratio although it is not typically evaluated explicitly. For spatially extended measurements, the quantitateness of the measurement may be sacrificed to obtain partially quantitative information over a finite area. In such a case, the second criterion is used to set the irradiance ratio based on the accepted sensitivity to environmental

Table 4.3 Evaluation of the ratio $R_I = E_L \Gamma_{luL} / \Delta \nu_L$ for the different modes of laser operation. Maximization of the ratio R_I indicates the mode of operation for which saturation is most probable.

Mode	Γ_{luL}	$\Delta \nu_L$ (cm ⁻¹)	E_L (mJ/pulse)	R_I (mJ/pulse cm ⁻¹)
Seeded	0.26	0.15	8.00	13.87
ICE	0.42	0.35	6.50	7.80
Unseeded	0.59	1.15	5.00	2.56

conditions. In practice, this ratio would probably not be evaluated but rather would be extracted from relative experimental measurements. To predict the extended spatial range that may be saturated, the variation in the degree of saturation with irradiance ratio must be investigated as well as the magnitude of achievable laser UV spectral irradiance relative to the calculated saturation irradiance.

As indicated by Eq. (4.22), the degree of saturation (DOS) is determined by the quantity $(1 + I_v^{\text{sat}}/I_v^0 T_L(t))^{-1}$ which goes to unity in the saturated limit. Hence, the variation in the DOS with relative laser spectral irradiance may be observed by plotting this quantity vs. the irradiance ratio. The DOS for $T(t)=1$ and a range of irradiance ratios is shown in Fig. 4.2, which displays the expected trends. The DOS-slope curve reflects the variation in the slope of the DOS with irradiance ratio. In the limit of full saturation, the DOS-slope curve goes to zero indicating the observed independence of the saturated fluorescence signal, C_D , to variations in the laser irradiance. Figure 4.2 demonstrates that full saturation is approached asymptotically and that the major nonlinear DOS growth occurs for $0.5 < I_v^0/I_v^{\text{sat}} < 6$. The primary value of Fig. 4.2 is that it indicates the order of magnitude of I_v^0/I_v^{sat} required for saturation. Based on Fig. 4.2, a minimum value of the normalized laser spectral irradiance for full saturation may be chosen as $10(I_v^{\text{sat}})$.

The saturation irradiance defined in Eq. (4.21a) may be calculated for operation of the laser in the seeded (most optimum) mode by using the appropriate value of the overlap fraction calculated in Section 4.1.3, estimating the value for the electronic quenching rate coefficient, and obtaining the remaining spectroscopic data from the literature. Employing the values of the different parameters in Table 4.2, the saturation irradiance for the $Q_{22}(26.5)$ line of the $\gamma(0,0)$ band of NO is calculated to be $3.74 \times 10^6 \text{ W/cm}^2 \cdot \text{cm}^{-1}$. Therefore, using the minimum saturation criterion defined above requires that $I_v^0 > 10(I_v^{\text{sat}}) = 3.74 \times 10^7 \text{ W/cm}^2 \cdot \text{cm}^{-1}$. Since operation of the injected seeded laser system at a given repetition rate fixes the spectral and temporal FWHMs and the energy per pulse, the cross-sectional area of the laser beam (A_L) may be expanded (i.e., formed into a sheet) up to the point where the chosen saturation criterion ($I_v^0 > 10(I_v^{\text{sat}})$) is just satisfied. Taking the seeded laser parameters to be $\Delta t_L = 8 \text{ ns}$, $\Delta \nu_L = 0.15 \text{ cm}^{-1}$ and $E_L = 8 \text{ mJ/pulse}$ and using Eq. (4.2), the chosen saturation criterion provides that $A_L < E_L / (10 \Delta t_L \Delta \nu_L I_v^{\text{sat}}) = 0.178 \text{ cm}^2 =$

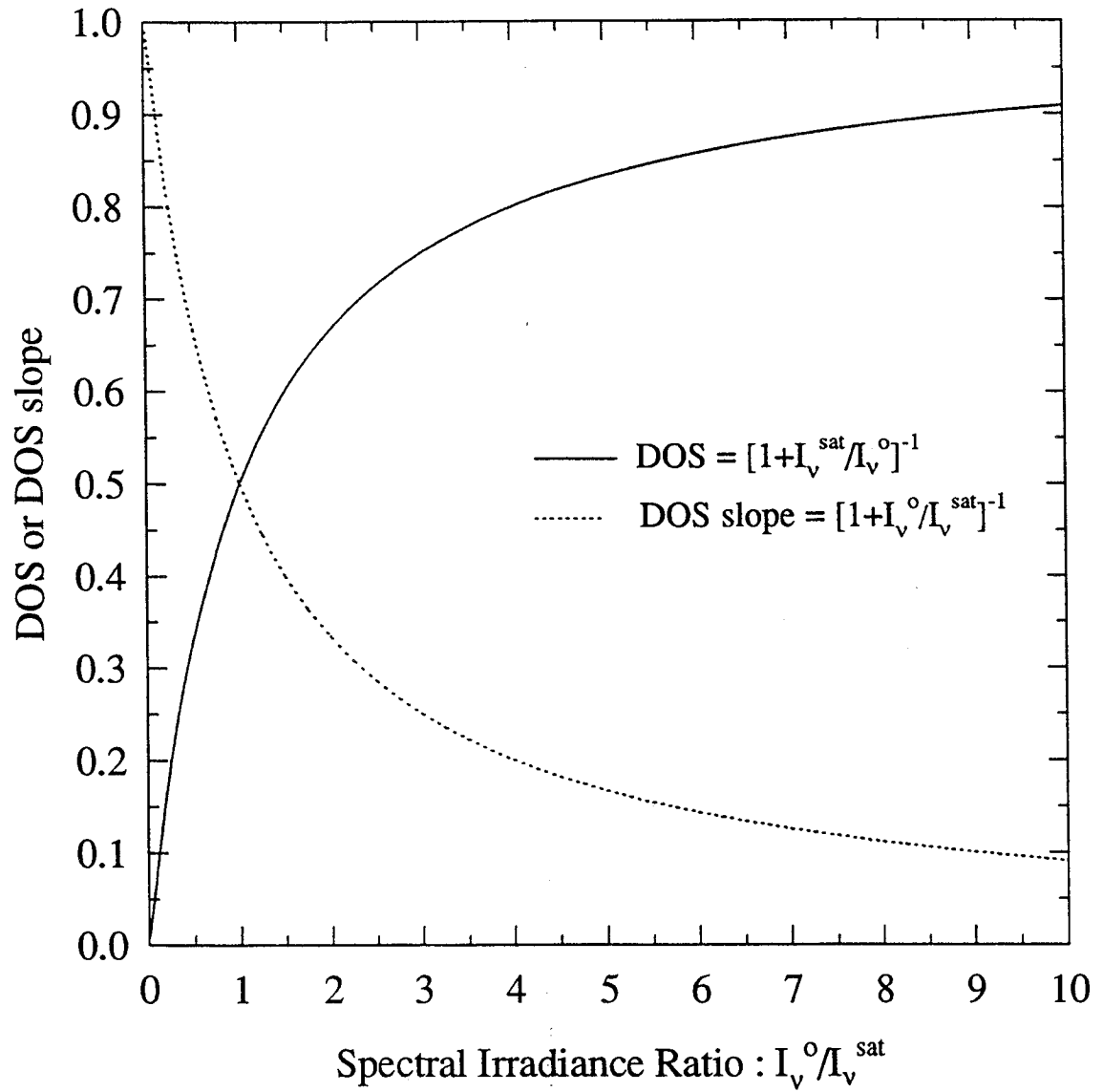


Figure 4.2 Degree of saturation (DOS) vs. irradiance ratio. The DOS is the theoretical saturation curve : $DOS = [1 + (I_v^{sat} / I_v^o)]^{-1}$. The DOS-slope curve is the slope of the DOS : $DOS \text{ slope} = [1 + (I_v^o / I_v^{sat})]^{-1}$.

$17.8 \text{ mm}^2 = A_{L,\text{sat}}/10$. For a laser sheet with a thickness of 0.5 mm, this would correspond to a height of $35.6 \text{ mm} = 3.56 \text{ cm}$. Although this value represents the maximum sheet height which would just satisfy the saturation criterion, it does indicate that spatially extended saturation of NO is possible. However, no consideration has yet been given to reflection losses at optical surfaces.

An alternate method for assessing the ability to saturate an extended area is to choose the desired area and to compare this area to the saturation area ($A_{L,\text{sat}}$) defined above, noticing that the chosen saturation criterion may be written as $10 < I_v^o / I_v^{\text{sat}} = A_{L,\text{sat}} / A_L$. For a laser sheet $0.5 \text{ mm} \times 5 \text{ mm}$, $A_L = 2.5 \text{ mm}^2$ and $I_v^o / I_v^{\text{sat}} = 178 / 2.5 = 71.2$ which is greater than the accepted value of 10. If the optical train contains two mirrors and two lenses (6 surfaces total) and there is a 4% loss at each surface, only approximately 78% of the laser irradiance arrives at the probe volume, resulting in $I_v^o / I_v^{\text{sat}} = 0.78(71.2) = 55.5 > 10$. For saturation of a line with a 0.5 mm diameter beam ($A_L \approx 0.2 \text{ mm}^2$), including the estimated optical losses, $I_v^o / I_v^{\text{sat}} = 0.78(178 / 0.2) \approx 694 > 10$. These results again indicate that spatially extended saturation of NO is possible at the temporal peak of the laser pulse.

To implement saturated imaging, an experimental technique must be developed to quantitatively assess the degree of saturation. Specifically, two images at different laser powers are not sufficient to quantitatively assess the degree of saturation. For LSF point measurements, the saturation curve (Section C.1) provides a means of quantitatively assessing the degree of saturation. For one-dimensional saturated imaging (i.e., along the axis, z , of a loosely focused laser beam) the degree of saturation could be assessed from a saturation surface. The axes of such a saturation surface would be space (i.e., z), relative fluorescence signal, and relative laser power. Hence, the saturation surface would contain the traditional saturation curve for each point along the focused laser (i.e., each point along z). In practice, spatial wing effects could be minimized by using sufficient magnification and monitoring only signals from the pixels of the ICCD corresponding to the central portion of the focused laser. Quantitatively assessing the degree of saturation in a two-dimensional saturated imaging experiment would be further complicated by the existence of two spatial dimensions. Specifically, four dimensional information (i.e., y , z , relative fluorescence signal, and relative laser power) is even more difficult to analyze.

Nevertheless, for such experiments, a modified saturation surface could be generated, for example, by collapsing the variations in relative fluorescence signal and relative laser power into a single variable (e.g., the slope of these two variables) that goes to zero in the saturated limit. Hence, a saturation surface or modified saturation surface provides an experimental technique for quantitatively assessing the degree of saturation in saturated-imaging measurements.

A saturation surface was generated to evaluate the possibility of one-dimensional saturated imaging of NO in the AIDF burner described in Section 5.7. This experiment used the optical setup described for the LSF experiments in Chapter 5. The maximum laser power used for the experiment corresponded to ~ 7 mJ/pulse out of the FA in Fig. 5.4. This laser power is much greater than the ~ 3.65 mJ/pulse required to saturate the $Q_2(26.5)$ transition of NO (see Sections 5.2.2 and C.3). Neutral density filters were used to impose 13 levels of attenuation ranging from 100% to 0.4% transmission. Hence, the range of laser powers investigated should have produced varying degrees of saturation. The magnification of the ICCD collection optics was ~ 0.46 , which produced a per-pixel resolution in the laser of $50\text{ }\mu\text{m}$. This spatial resolution should be sufficient to minimize laser wing effects. An image was taken for each level of attenuation by integrating 500 shots on chip and using the minimum 18-ns temporal gate width of the ICCD. To generate the saturation surface, we used the fluorescence signals from the row of pixels corresponding to the center of the loosely focused laser. The saturation surface was built up image by image to provide a one-dimensional, spatially-resolved indication of the variation in fluorescence signal with relative laser power.

The saturation surface resulting from the one-dimensional saturated imaging experiment displayed nominally linear behavior over the entire range of laser powers investigated. This result was predicted by Eq. (4.27) and is due to the wide temporal gate width of the ICCD relative to the temporal FWHM of the laser. Specifically, the linear fluorescence in the temporal wings of the laser pulse dominated the combined linear-fluorescence, partially-saturated-fluorescence and saturated-fluorescence signals integrated over the gate width of the camera. Hence, although spatially extended saturation is possible with Nd:YAG-pumped dye-laser systems, the relatively wide temporal gate

widths of ICCDs prevent realization of saturated imaging (with such laser systems). However, this indicates that saturated imaging is ICCD-technology limited. Currently, ICCDs with 5-ns gate widths are common (e.g., second generation image intensifiers from DEP, Delft Instruments, Netherlands; the 4-Quik-05 ICCD from Stanford Computer Optics Inc., Palo Alto, CA). This is a profound improvement compared to the 18-ns gate width of the ICCD used and represents a 72% reduction in the ICCD temporal gate width over the past ~6 years. However, this improved gate width is still not sufficient for saturated imaging with ~8-ns temporal FWHM lasers. As for point LSF measurements, saturated imaging with such laser systems will require ICCD temporal gate widths on the order of 500 ps.

CHAPTER 5

EXPERIMENTAL APPARATUS

The PLIF/LSF facility used in the fluorescence measurements includes the following: (1) a pulsed laser system for creating the requisite UV radiation; (2) excitation optics for attenuating, focusing, spatially shaping, and directing the laser pulse; (3) detection systems which include the fluorescence-collecting and spectral-filtering optics as well as the detector elements; (4) an overlap reference system for adjusting and monitoring the spectral overlap between the laser and the NO excitation line; (5) a data acquisition system for sampling the various photodiode and PMT signals; (6) unique triggering systems for temporally synchronizing the point or image data acquisition with the radiation event; and (7) an axial inverse-diffusion flame burner with associated flow-delivery and translation systems. The details of the PLIF/LSF facility's configuration, operation, and performance are described in this chapter.

5.1 Laser System

5.1.1 Laser Operation

The UV radiation required for NO excitation was generated using a Quanta-Ray GCR-4 Nd:YAG laser, a PDL-3 dye laser, and a WEX-2C wavelength extender. The Nd:YAG laser incorporated a model 6300 injection seeder to force single longitudinal mode operation. The Nd:YAG fundamental (1064 nm) was frequency doubled (to 532 nm) via angle-tuned, type II phase matching within a KD*P crystal housed in a temperature stabilized oven. The two crossed-polarized and concentric beams were spatially separated using a dichroic harmonic separator model DHS-2. The vertically-polarized Nd:YAG second harmonic was used to pump the PDL-3, which was configured

for longitudinal amplifier pumping via the delay line and operated without the optional preamplifier. An appropriate dye mixture was used to generate visible radiation at approximately 574 nm. The PDL oscillator grating drive was modified to incorporate a 100-to-1 gear reducer (Bayside Controls Inc. model NE23-100, Port Washington, NY) and a 200 step-per-revolution stepper motor (SLO-SYN DC model MO61-LS08-E). This provided a minimum spectral step resolution of ~ 0.0012 nm/step in the fifth-order PDL fundamental.

The vertically-polarized dye fundamental was frequency doubled ($\lambda_D/2 \approx 287$ nm) via angle-tuned, type I phase matching within another KD*P crystal using the CM-1 module of the WEX-2C wavelength extender. All crystal modules of the WEX-2C were equipped with feedback control units to actively optimize the phase matching angles during scanning of the PDL and to account for variations in temperature. The horizontally-polarized residual Nd:YAG fundamental was frequency mixed with the dye second harmonic via angle-tuned, type I phase matching within a third KD*P crystal using the CM-2 module of the WEX-2C to produce a vertically-polarized mixed beam at ~ 226 nm ($\lambda_M \approx 1/(287^{-1} + 1064^{-1})$). The four concentric beams (1064, 574, 287, 226 nm) were dispersed using a Pellin-Broca prism, and the mixed beam exited the WEX vertically polarized.

The Nd:YAG laser typically produced pulsed 532-nm radiation with an ~ 9 -ns temporal FWHM and ~ 552 and ~ 516 mJ/pulse in the unseeded and seeded modes, respectively. Experiments were performed to further investigate the influence of injection seeding on the spectral and temporal characteristics of the pulsed radiation from the laser system.

A qualitative measurement of the pulsed radiation bandwidth was made based on the Airy distribution pattern created by a solid etalon. The radiation was diverged using a negative lens, passed through a solid etalon with a free-spectral range (FSR) of ~ 0.98 cm^{-1} and a reflectivity finesse (F_s) of ~ 19 , and projected onto a screen to magnify the image of the resulting spatial distribution. It can be shown that the instrument bandwidth of the etalon is FSR/F_s (cm^{-1}) while the measured bandwidth is $w \cdot \text{FSR}/s$ (cm^{-1}), where w is the width of an Airy distribution ring and s is the ring spacing; the bandwidth of the incident

radiation is equal to the difference in the measured and instrument bandwidths (i.e., $w \cdot \text{FSR}/s - \text{FSR}/F_s$) (Demtroder, 1988). These calculations neglect the surface and wedge finesse of the etalon. The ring width and spacing of the Airy distribution pattern were measured using a laboratory ruler. Although this was a rather crude measurement, it was useful in demonstrating the effectiveness and in evaluating the performance of the injection seeding unit. Clearly, the accuracy of this measurement could be greatly improved via the use of an optimized etalon and a high density linear array.

The bandwidth of the 532 radiation was measured to be $\sim 0.33 \text{ cm}^{-1}$ with the seeder off and $\sim 0.08 \text{ cm}^{-1}$ with the seeder on. The manufacturer specifications for the bandwidth of the 1064-nm radiation are less than 1.0 and 0.003 cm^{-1} for unseeded and seeded Nd:YAG operation, respectively (Spectra Physics, 1991). Nonlinear frequency doubling and mixing processes reduce the bandwidth of the radiation, and thus, the bandwidth of the 532-nm radiation should be less than the manufacturer specifications. The difference in our results and the manufacturer specifications are at least partially due to the limitations of our experimental technique. Nevertheless, our qualitative numbers indicate an order of magnitude reduction in the bandwidth of the 532-nm radiation with injection seeding compared to unseeded operation.

We also measured the influence of injection seeding on the temporal repeatability and shape of the 532-nm radiation. For this investigation, we used a fast photodiode (Electro-Optics Technology model ET-2000, Traverse City, MI) and an analog storage oscilloscope (Tektronix model 7834, Beaverton, OR). In the unseeded mode, the 532-nm pulse was temporally multimodal about a nominal Gaussian appearing distribution. Moreover, the temporal multimodal nature of this unseeded pulse varied drastically from pulse to pulse. This is characteristic of multimode Nd:YAG operation where the dominance of the different longitudinal modes varies from pulse to pulse. In contrast, the 532-nm radiation pulse with injection seeding was temporally smooth with a single mode, and was repeatable from pulse to pulse.

The influence of injection seeding within the Nd:YAG on the bandwidth of the PDL fundamental radiation was also investigated using the same etalon-based technique described above. The bandwidth of the PDL-fundamental radiation was measured (at

560 nm) to be $\sim 0.048 \text{ cm}^{-1}$. This value was found to be independent of the seeding condition of the Nd:YAG pump laser, i.e., the bandwidth of the PDL is set by the dispersion optics of its oscillator. Although injection seeding did not affect the PDL pulse characteristics, it does influence those of the mixed UV beam used as a spectroscopic probe. This is because the Nd:YAG fundamental, whose characteristics are drastically influenced by injection seeding as apparent from the 532-nm results, is used to generate the UV mixed beam. Hence, injection seeded operation is preferred since it (1) improves the temporal repeatability and shape of the laser radiation by eliminating longitudinal mode competition in the Nd:YAG laser, and (2) improves the efficiency of the nonlinear mixing processes in CM-2 of the WEX-2C by reducing the bandwidth of the Nd:YAG fundamental.

5.1.2 Pyrromethene Laser Dye Development

Excitation of the $\gamma(0,0)$ band of NO requires UV radiation around 225.5 nm (Reisel et al., 1992). For Nd:YAG-pumped dye-laser systems, such radiation is produced by sum frequency mixing the second harmonic of the dye fundamental with the Nd:YAG fundamental. Because of the squared dependence of the mixed beam irradiance on that of the dye fundamental, via the nonlinear frequency-doubling process, increasing the dye-laser irradiance would result in a significant enhancement of the mixed beam's irradiance. Such an enhancement would increase the signal-to-noise ratio in linear fluorescence measurements of NO concentration. This would benefit both planar imaging work, for which the beam is expanded into a sheet, and also point fluorescence measurements at high pressure, for which pressure broadening and subsequent blending of adjacent spectral lines precludes saturated fluorescence measurements (Reisel and Laurendeau, 1994). Because of these potential benefits, we investigated methods for increasing the irradiance of the dye fundamental at the wavelength for NO excitation. This work was performed in conjunction with C.C. Johnson and R.N. Steppel (Exciton Inc., Dayton, OH), and the results were reported by Partridge et al. (1994).

Fluorescence measurements of NO require dye fundamental radiation around 572.5 nm. Unfortunately, this wavelength falls between the energy output maxima of

Rhodamine 590 (R-590) and Rhodamine 610 (R-610), which are at 560 nm and 582 nm, respectively. Previously, to obtain 572.5-nm radiation, we used a mixture of R-590 perchlorate and R-610 perchlorate in methanol, in both the oscillator (osc.) and amplifier (amp.) dye cells, and achieved a dye laser conversion efficiency of approximately 24%. We investigated base shifting a standard mixture of R-610 perchlorate in methanol, using a saturated base solution of potassium hydroxide in ethanol. For this base shifting experiment, the base solution was added dropwise to the dye solutions to maximize the power at the desired wavelength. However, this produced a conversion efficiency of only 18% at 572.5 nm. In an effort to increase our conversion efficiency at the desired wavelength and based on the previous successes of pyrromethene-BF₂ complexes, we investigated the performance of two new laser dyes, Pyrromethene 580 (PM-580) and Pyrromethene 597 (PM-597) (Exciton, Inc., Dayton, OH).

Recent reports indicate that pyrromethene-BF₂ complexes have demonstrated remarkable performance as laser dyes. When the complexes were incorporated in a polymer matrix, conversion efficiencies exceeding 80% were reported (Hermes et al., 1993; Hermes, 1994). When the complexes were used in jet-stream dye lasers, conversion efficiencies on the order of 35% for cw operation (Guggenheimer et al., 1993, using Pyrromethene 556 in ethylene glycol) and 47.5% for subpicosecond pulse generation (O'Neil, 1993, using Pyrromethene 567 in PPH) were attained. These large efficiencies motivated us to investigate the performance of the new laser dyes PM-580 and PM-597 for nanosecond pulse generation at 10 Hz using a commercial Nd:YAG-pumped dye-laser system.

PM-580, or 1,3,5,7,8-pentamethyl-2,6-di-n-butylpyrromethene-difluoroborate complex, is structurally similar to PM-597, or 1,3,5,7,8-pentamethyl-2,6-di-t-butylpyrromethene-difluoroborate complex. Both dyes have a molecular weight of 374.32. Spectrally, both PM-580 and PM-597 absorb well at 532 nm and their absorption maxima in ethanol are at 518 nm and 525 nm, respectively. The molar absorptivity of PM-580 at 518 nm is 7.59×10^4 liters $\cdot$ mol⁻¹ $\cdot$ cm⁻¹; for PM-597, it is 6.58×10^4 liters $\cdot$ mol⁻¹ $\cdot$ cm⁻¹ at 525 nm. PM-580 and PM-597 are only slightly soluble in methanol; room temperature saturation is at approximately 8.5×10^{-4} M and 1.0×10^{-3} M, respectively. However,

sufficient solubility is available in ethanol for both dyes when using second-harmonic Nd:YAG pumping due to their relatively high molar absorptivities and high fluorescence quantum yields.

The laser system used in this investigation incorporated a Quanta-Ray GCR-4 Nd:YAG laser equipped with a model 6300 injection seeder and a PDL-3 dye laser (Spectra-Physics Lasers, Mountain View, CA). For all data reported here, the Nd:YAG laser was operated at a 10 Hz repetition rate and in the injection seeded mode. This provided a 532-nm second harmonic pump beam with 500 mJ/pulse, a measured bandwidth of 0.08 cm^{-1} and a temporal FWHM of $\sim 9\text{ ns}$. The PDL-3 was operated using the oscillator, amplifier and amplifier pump delay line and configured for longitudinal amplifier pumping. The preamplifier of the PDL-3 was not used. The PDL-3 grating was operated in fifth order and was spectrally calibrated using a separate NO excitation scan.

During the experiments, the energy in the pump beam was monitored by a photodiode and was found to be constant to approximately $\pm 1.5\%$. The dye laser beam was monitored by a volume absorbing disc calorimeter and an analog indicator (Sciencetech models 38-0101 and 361, Boulder, CO). To obtain the tuning curves in terms of conversion efficiency for the individual dyes, we subtracted the amplified spontaneous emission (ASE) in the wings of the spectral profiles of the individual dyes as a spectrally flat background from the appropriate curve and divided the result by the nominal 500 mJ/pulse energy of the pump beam. This should provide a conservative indication of the conversion efficiencies since the ASE is at its maximum in the wings of the spectral profiles (Enright, 1994).

The PM-580 was dissolved in 100% ethanol (absolute); the solubility was found to be greater than $1.1 \times 10^{-3}\text{ M}$ (400 mg/liter). The optimum oscillator concentration was determined empirically by operating the PDL with the oscillator alone and systematically adding small amounts of a concentrate solution to the oscillator solution as it circulated until the output power was maximized. The amplifier was subsequently installed into the system, and its optimum concentration was determined in a similar manner. Small samples of these optimized solutions were taken prior to operation of the laser system for any experiment, and the concentrations were determined by UV-visible spectrometry. The

optimum oscillator concentration was found to be $8.6 \times 10^{-4} \pm 1.5 \times 10^{-5}$ M, and the optimum amplifier concentration was found to be $1.2 \times 10^{-4} \pm 1.5 \times 10^{-5}$ M.

The tuning curve for the optimum concentrations of PM-580 is shown in Fig. 5.1 along with that for a standard mixture of R-590 in methanol (Spectra-Physics 1989, 2.2×10^{-4} M (osc.) and 3.2×10^{-5} M (amp.)). The tuning curve for PM-580 is spectrally broad with a peak conversion efficiency of approximately 38% at 552 nm. In fact, the curve is spectrally broader and more efficient than R-590, which has long been the efficiency standard for dye-laser systems. The half-life of PM-580 was linearly extrapolated to be approximately 47 hr/liter (i.e., hours of continuous operation required for the dye-laser output power to drop to half its initial value with 1 liter of osc. solution and 1 liter of amp. solution) or 850 kJ/liter for operation at 10 Hz with 500 mJ/pulse pump energy. At the target wavelength for NO excitation, the PM-580 mixture provides approximately 23% conversion efficiency.

The PM-597 was dissolved in 100% ethanol (absolute); the solubility was found to be greater than 1.1×10^{-3} M (400 mg/liter). The oscillator and amplifier concentrations were optimized as described for PM-580. These concentrations were determined by UV-visible spectrometry to be $4.2 \times 10^{-4} \pm 1.5 \times 10^{-5}$ M (osc.) and $6.0 \times 10^{-5} \pm 1.5 \times 10^{-5}$ M (amp.). However, we suggest using a PM-597 amp. concentration towards the upper limit of the uncertainty range and diluting if necessary.

The tuning curve for the optimum concentrations of PM-597 is shown in Fig. 5.2 along with that for a standard mixture of R-610 in methanol (Spectra-Physics 1989, 2.1×10^{-4} M (osc.) and 3.1×10^{-5} M (amp.)). The tuning curve for PM-597 is spectrally broad with a peak conversion efficiency of approximately 32% at 571 nm. This curve is spectrally broader and more efficient than that for R-610. The half-life of PM-597 was linearly extrapolated to be approximately 14 hr/liter or 255 kJ/liter. At the target wavelength for NO excitation, the PM-597 mixture provides approximately 31% conversion efficiency. This is significantly better than the 24% efficiency obtained with the R-590/R-610 mixture which we have used for NO excitation in the past.

The tuning curves of Figs. 5.1 and 5.2 indicate that at the target wavelength of approximately 572.5 nm, PM-597 provides better conversion efficiency compared to PM-

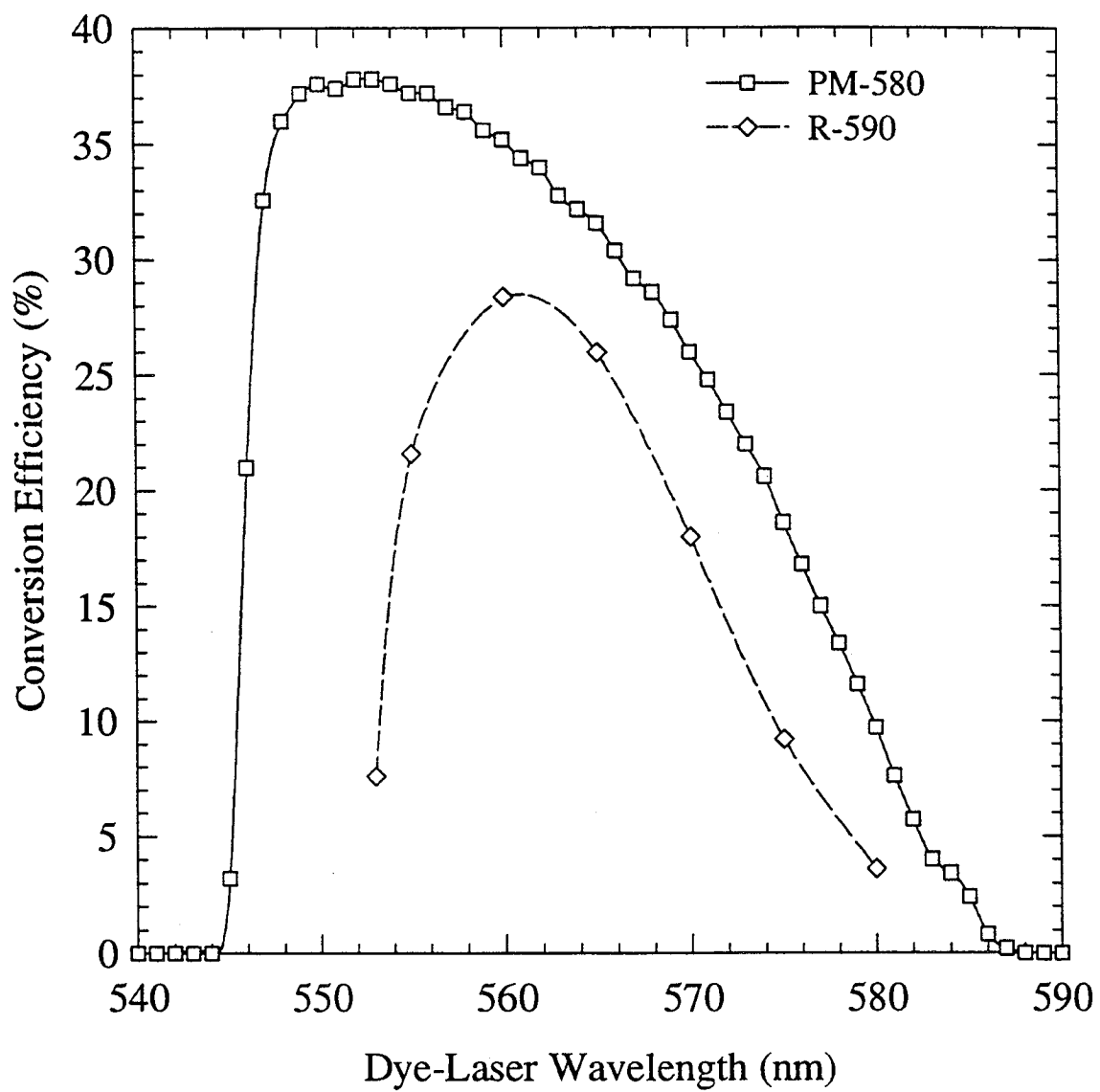


Figure 5.1 Spectral tuning curves for PM-580 and R-590 (Spectra-Physics 1989).

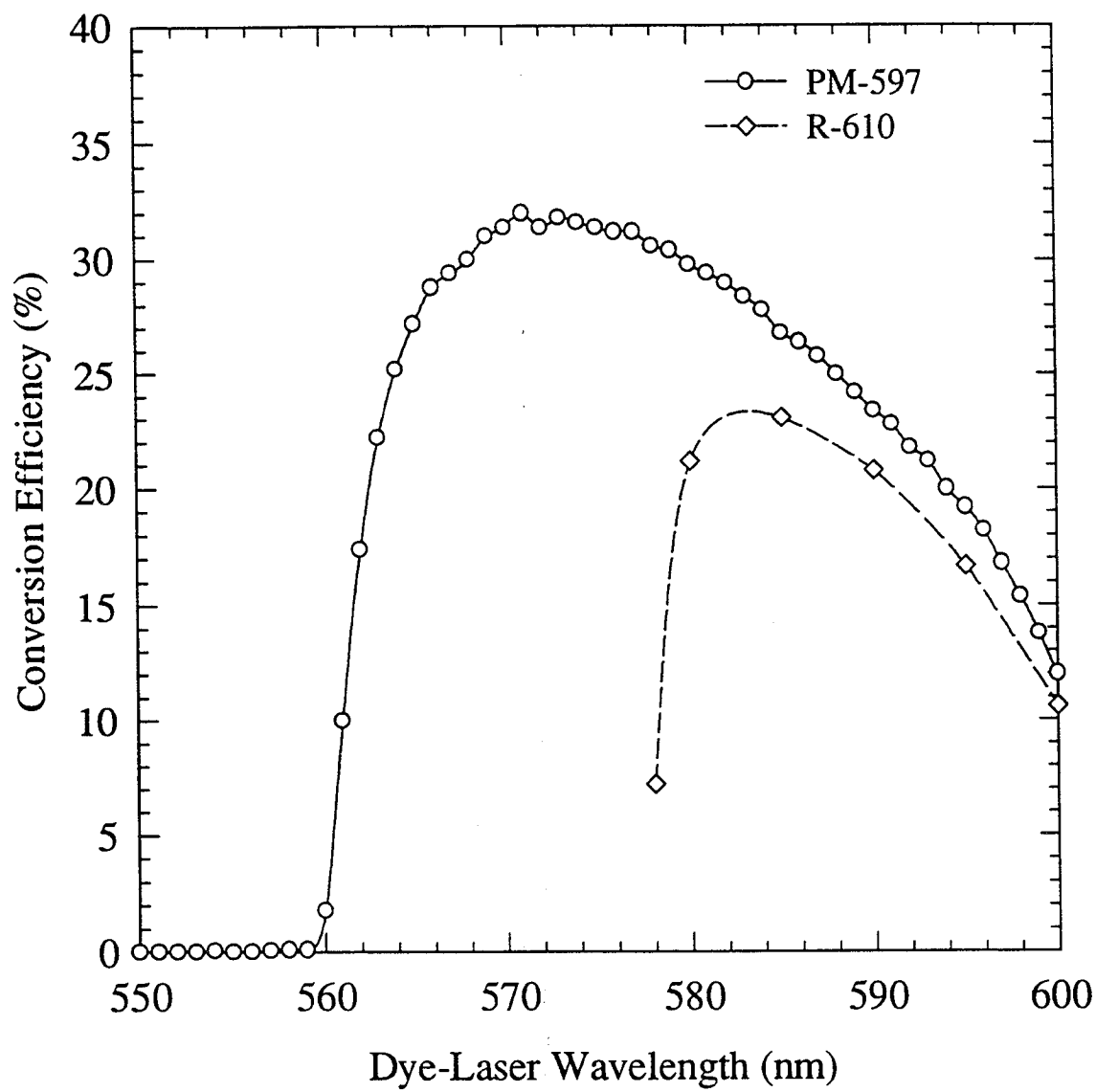


Figure 5.2 Spectral tuning curves for PM-597 and R-610 (Spectra-Physics 1989).

580. However, the peak efficiency of PM-580 is greater than that of PM-597. This is reasonable as the fluorescence quantum yield for PM-580 is 0.90 (Boyer et al., 1993), while that for PM-597 is 0.77 (Boyer et al., 1991). Hence, we investigated operation of the laser system with the 8.6×10^{-4} M solution of PM-580 in the oscillator and the 6.0×10^{-5} M solution of PM-597 in the amplifier. The tuning curve for operation of the PDL-3 with this combination of dyes is shown in Fig. 5.3. For reference, Fig. 5.3 also contains the tuning curves for the single-dye operations from Figs. 5.1 and 5.2. This PM-580(osc.)/PM-597(amp.) tuning curve has a peak efficiency of approximately 31% at 569 nm. The conversion efficiency at the target wavelength for NO excitation is much better than that obtained with the R-590/R-610 mixture but is slightly less than that for PM-597 operation. However, the oscillator's PM-580 solution used for this PM-580(osc.)/PM-597(amp.) spectral scan was the same solution used to investigate the tuning curve and lifetime of PM-580 alone. Based on the performance of this aged dye, it is possible that operation with an oscillator solution of fresh PM-580 and an amplifier solution of PM-597 may provide the optimum conversion efficiency for NO excitation.

In summary, Pyrromethene 580 and Pyrromethene 597 demonstrate excellent performance in Nd:YAG-pumped dye-laser systems, providing peak conversion efficiencies of 38% at 552 nm and 32% at 571 nm, respectively. These new dyes provide spectrally broader lasing and higher conversion efficiencies compared to R-590 and R-610; moreover, they can efficiently perform in the spectral region between the tuning maxima of R-590 and R-610. The stability of these dyes has been found to be good at the high pump powers used. Although the stability of the R-590/R-610 mixture was not quantified, it appears to be more stable than the pyrromethene dyes investigated. These dyes provide 31% conversion efficiency near 572.5 nm, which is the wavelength required for fluorescence studies of NO via excitation in the (0,0) band. This efficiency is a significant improvement over the 24% conversion efficiency achieved in the past with an R-590/R-610 mixture and should enhance the signal-to-noise ratio in linear fluorescence measurements of NO concentration.

Although the conversion efficiency of PM-580 is not as high as that of PM-597, it produced UV-irradiance levels sufficient for both the PLIF and LSF experiments.

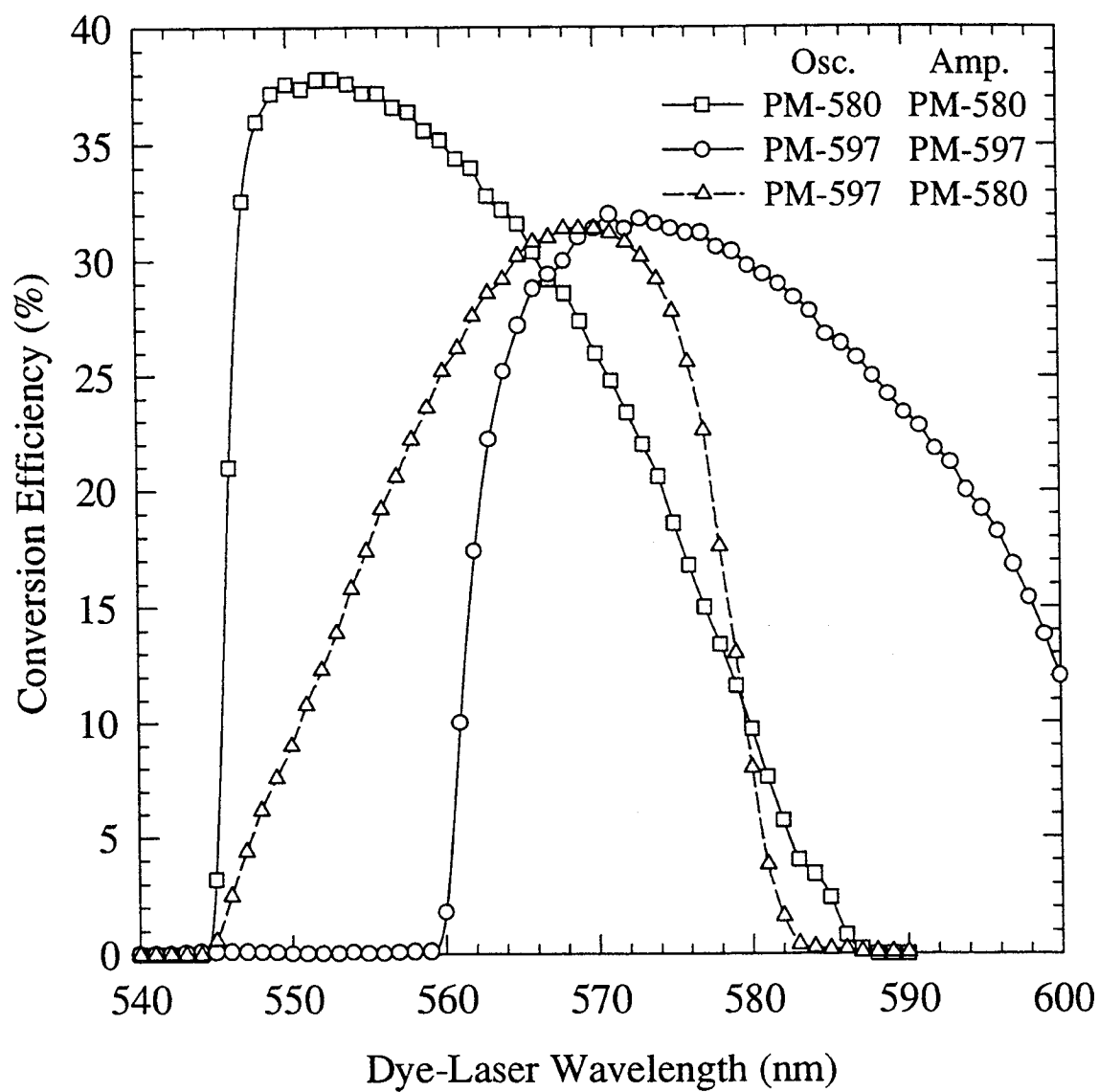


Figure 5.3 Spectral tuning curves for PM-580, PM-597 and a combination of using PM-580 in the oscillator and PM-597 in the amplifier.

Moreover, PM-580 provided significantly longer lifetimes compared to PM-597.

Although the conversion efficiency of PM-580 is similar to that of the R590/R610 mixture used in the past, use of PM-580 simplifies (1) dye preparation and (2) dye concentration optimization. Hence, PM-580 laser dye was used for all of the PLIF and LSF experiments. For future experiments with a more uniform laser sheet, the greater conversion efficiency of PM-597 will be useful for enhancing the measurement SNR.

5.2 Excitation Optics

The excitation optics include optical elements for attenuating, focusing, spatially shaping, and directing the laser pulse. In addition to optical elements that are common to the PLIF and LSF experiments, there are excitation optical elements that are PLIF and LSF specific. These are described in the following sections.

5.2.1 Common Excitation Optics

The optical elements that are common to both the PLIF and LSF experiments are evident in Fig. 5.4 which is a schematic diagram of the experimental apparatus used for the LSF experiments. The UV radiation exits the WEX vertically polarized and is directed using dichroic mirrors (CVI model KRF-1037-0). A Fresnel attenuator (FA) is used to provide any necessary gross attenuation of the UV beam. Fused-silica splitter plates (SP) are used to split off small portions of the beam for power monitoring via photodiodes (PD) and for use with the overlap reference system (ORS). The ORS is described separately in section 5.4. Several diaphragm apertures, A, are used to block scattering and reflections. A Rochon prism (RP) is used to provide high resolution and continuous attenuation of the vertically polarized beam. The remaining optical elements are specific to the LSF experiment.

5.2.1.1 Fresnel Attenuator

The FA consists of two 50-mm square fused-silica plates (Melles Griot model 03FNQ002) mounted on individual rotation stages (Newport model RSP-1). Operation of the FA is based on the Fresnel equations (Born and Wolf, 1980) and hence provides the

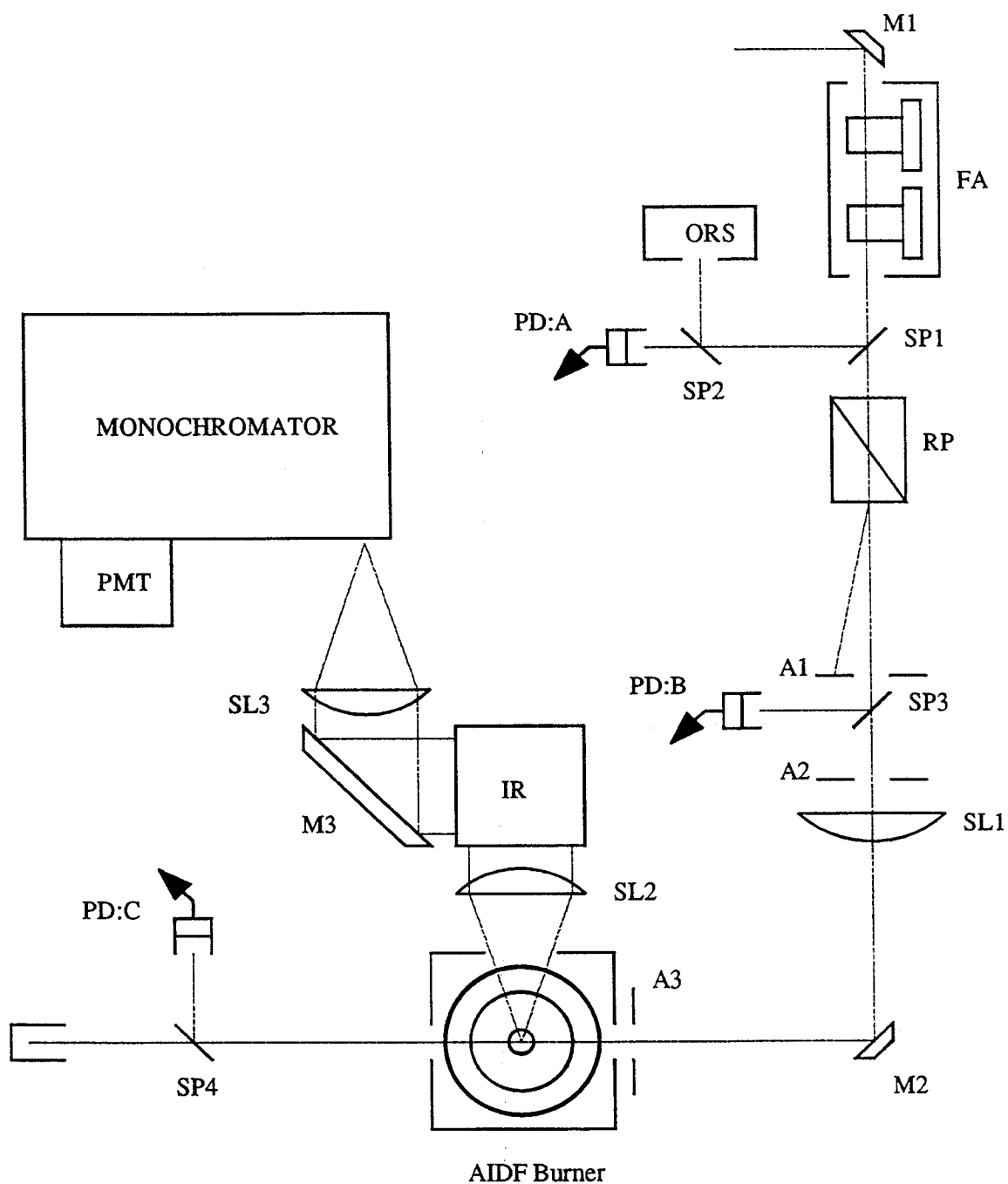


Figure 5.4 Schematic diagram of the experimental apparatus used for the LSF experiments. M : mirror, FA : Fresnel attenuator, SP : splitter plate, A : aperture diaphragm, PD : photodiode, RP : Rochon prism, ORS : overlap reference system, SL : spherical lens, AIDF : axial inverse-diffusion flame burner, IR : image rotator.

widest dynamic range of attenuation with the vertically-polarized beam if rotated about a horizontal axis. Using this configuration with a two-plate system, the FA provided over an order of magnitude of UV beam attenuation. Moreover, by rotating the two plates of the FA system in approximately equal but opposite angles, the individual displacements induced on the beam by each plate could be approximately counteracted.

5.2.1.2 Rochon Prism

The RP (Karl Lambrecht Corp. model MFRV-9) is composed of two birefringent magnesium fluoride (MgF_2) prisms which are optically contacted with their optical axes oriented mutually normal (Wood, 1988). The UV radiation passing through the RP is divided into an ordinary beam which traverses the prism undeviated, and an extraordinary beam which is deviated by ~ 5.1 degrees from the undeviated ordinary beam. By rotating the RP about the axis of the undeviated beam, the fraction which appears ordinary to the prism may be continuously varied from unity to zero; corresponding with such an adjustment, the fraction which appears extraordinary varies from zero to unity, respectively. To provide controlled rotation of the RP, it was housed in a rotary stage (Newport model 481-A). A diaphragm aperture, A2, was appropriately positioned to block the deviated (extraordinary) beam, and to pass the undeviated (ordinary) beam. In this way, the energy of the undeviated beam may be continuously attenuated.

The RP was calibrated over a range of angular positions by monitoring the integrated laser power before and after the RP using photodiodes PD:A and PD:B, respectively. The angular position of the RP was determined by reading the vernier scale on the translation stage. The RP calibration curve is shown in Fig. 5.5, which demonstrates the continuous and approximately cosinusoidal variation in transmission between the maxima and minima at $\sim 185^\circ$ and $\sim 275^\circ$, respectively. Figure 5.5 demonstrates the enhanced benefits of the RP compared to the used of discrete attenuation plates and Fresnel-based attenuation devices (such as the FA described in section 5.2.1.1). Compared to discrete plates, the RP provides continuous selectable attenuation; compared to Fresnel-based attenuators whose total maximum dynamic range covers only an $\sim 34^\circ$ range (Born and Wolf, 1980), the RP provides significantly better control in setting a

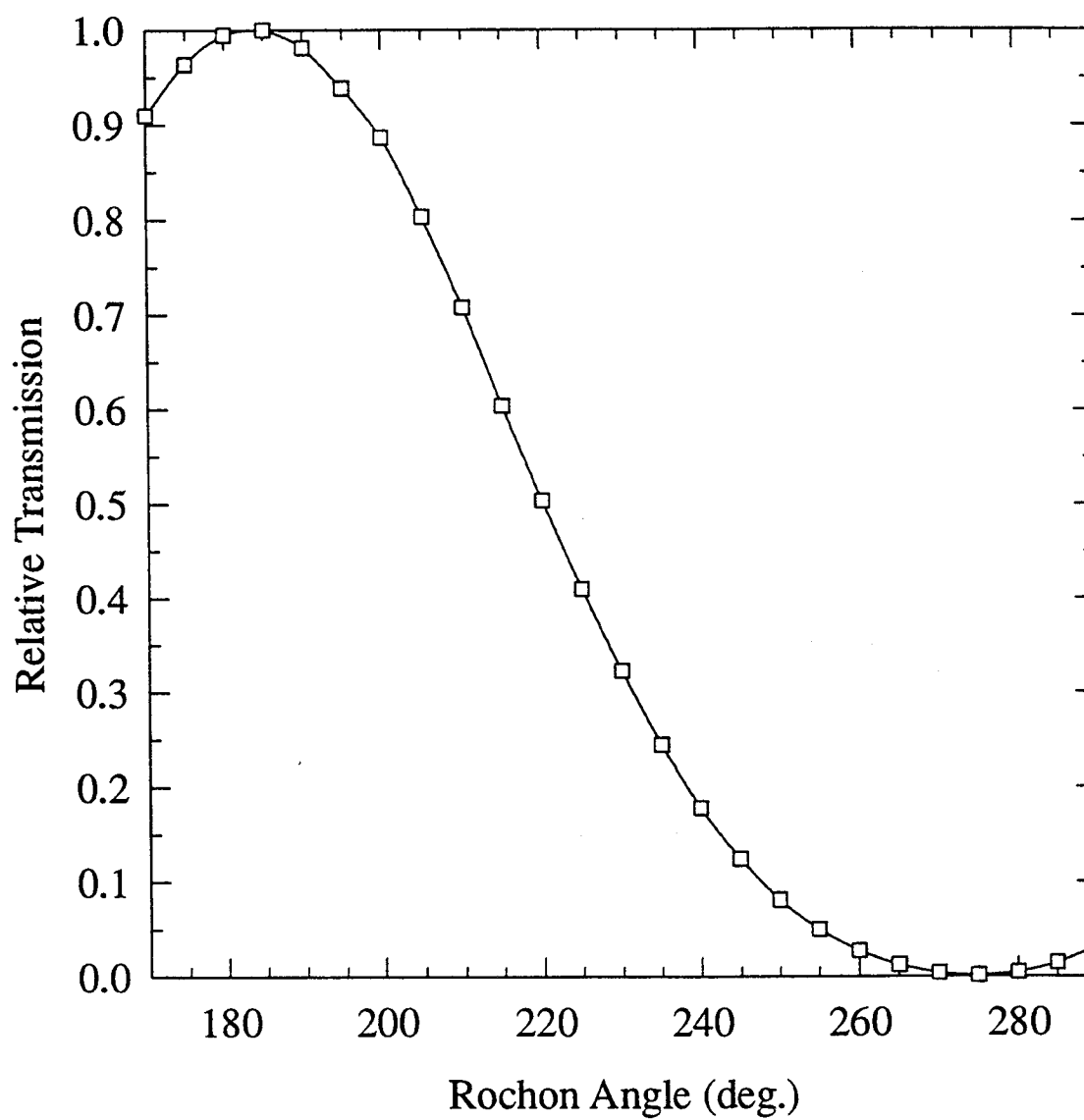


Figure 5.5 Rochon prism calibration curve.

desired attenuation. Figure 5.5 indicates that the RP provides controlled attenuation of the UV radiation over three decades of dynamic range.

5.2.2 LSF Specific Excitation Optics

A schematic diagram of the experimental apparatus used for the LSF experiments was shown in Fig. 5.4. The LSF specific excitation optics are the apertures (A2 and A3) and the spherical lens (SL1) used to produce the desired beam characteristics in the probe volume. A diaphragm aperture, A2, was used to limit the diameter of the laser input to SL1 to ~ 6 mm. A 1000-mm focal length fused-silica spherical lens (Newport model SPX034), SL1, was used to focus the laser beam into the probe volume. This combination produced a calculated waist diameter and Rayleigh range of ~ 50 μm and ~ 8 mm, respectively. A diaphragm aperture, A3, was positioned just prior to the burner facility (described in Section 5.7) to eliminate forward scattering and off-axis focusing in the probe volume. The net system transmission of the optical elements after the FA and before SP4 was measured using a power meter (Coherent model FM with detector head model LM-P10i) to be $\sim 16\%$. This allowed the desired irradiance in the probe volume to be related to that exiting the FA.

To measure the waist diameter of the focused radiation, a razor blade was displaced through the beam in steps of ~ 10 μm , using the burner translation system. Photodiode PD:C (Fig. 5.4) was used to monitor the beam energy as a function of razor blade position, and was corrected for fluctuations in laser power via the signal from PD:B (Fig. 5.4). The results of this experiment are shown in Fig. 5.6, which indicates a beam diameter of ~ 180 μm based on the 90% and 10% relative signal levels. Multiple runs of this experiment indicated a beam diameter of ~ 180 μm to ~ 213 μm .

5.2.3 PLIF Specific Excitation Optics

Figure 5.7 shows a schematic diagram of the experimental apparatus used for the PLIF experiments. To form the laser radiation into a vertically-oriented sheet, a spherical lens (SL1) was used to generate the desired sheet thickness and Rayleigh range, two cylindrical lenses (CL1 and CL2) were used to vertically expand and collimate the beam,

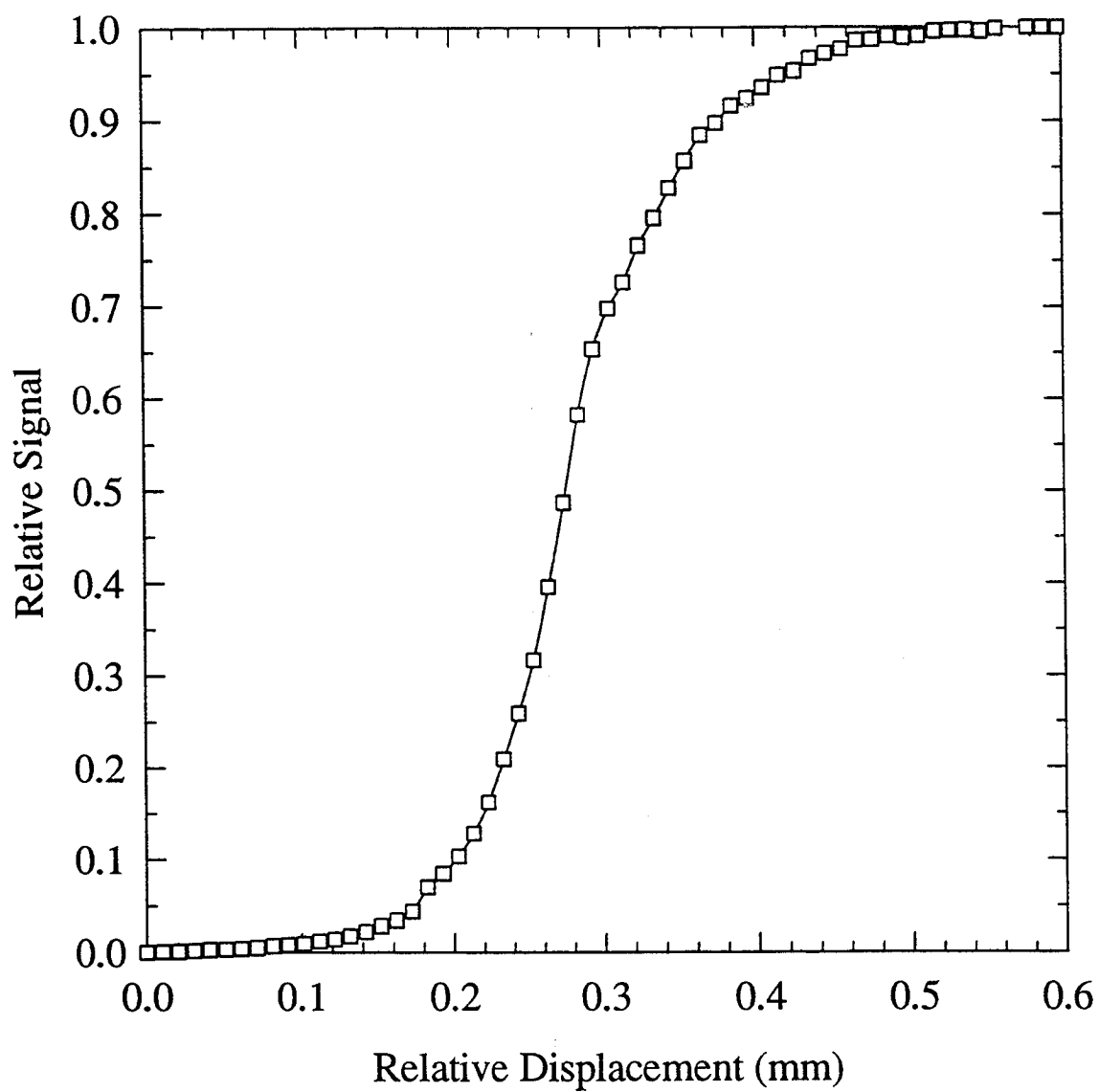


Figure 5.6 Profile of the UV laser beam used for the LSF measurements.

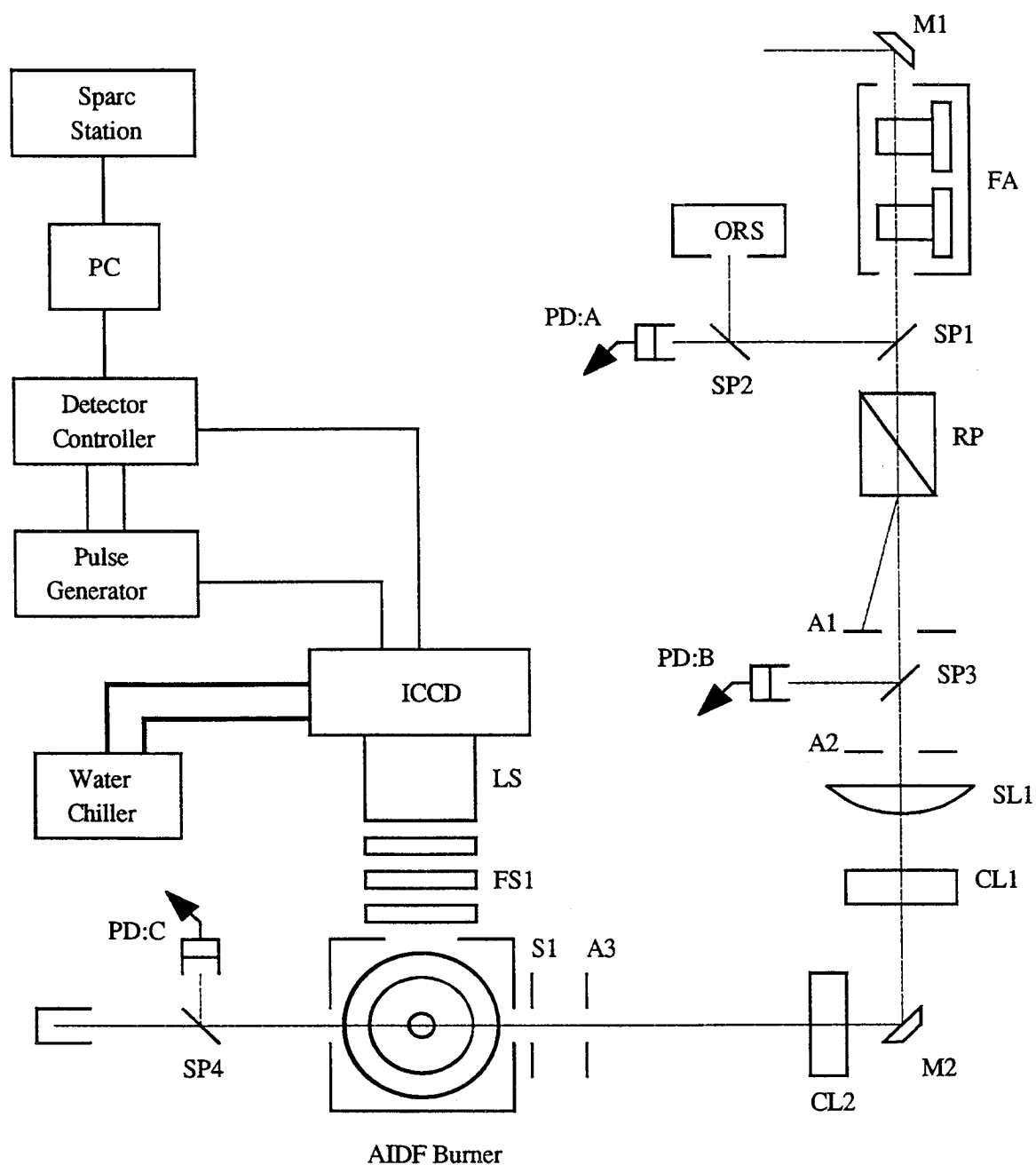


Figure 5.7 Schematic diagram of the experimental apparatus used for the PLIF experiments. M : mirror, FA : Fresnel attenuator, SP : splitter plate, A : aperture diaphragm, PD : photodiode, RP : Rochon prism, ORS : overlap reference system, CL : cylindrical lens, SL : spherical lens, AIDF : axial inverse-diffusion flame burner, S : slit, FS : filter stack, LS : lens system, ICCD : intensified charge-coupled device.

and an aperture/slit assembly (A3 and S1, respectively) were used to clip the wings of the sheet. Aperture A2 and spherical lens SL1 of Fig. 5.7 were used in the same configuration described in Section 5.2.2. CL1 and CL2 (Newport model CSX025 and CVI model PLCX-40.0-25.4-76.3-UV, respectively) were fused-silica cylindrical lenses with focal lengths of 25.4 mm and 150 mm, respectively. S1 was fabricated from two razor blades and a 50-mm diameter lens holder (Newport model LH2-200R), and provided an ~ 524 - μm wide vertically-oriented slit. The net system transmission of the optical elements after the FA and before SP4 was measured to be $\sim 7.1\%$.

The sheet thickness was measured by scanning a vertically oriented razor blade through the laser sheet at the position of the focus of SL1 (i.e., above the center of the AIDF burner). To reduce the effects from the razor blade and the laser sheet not being exactly parallel, an 84- μm wide horizontally-oriented slit was positioned just after S1 and aligned with the center line of the laser sheet. The razor blade was manually scanned using a translation stage (Newport model 420) and the relative position was determined from a dial indicator reading (Starrett model 25-881J, 2-cm range with 0.01 mm graduations). At each position through the scan, the integrated irradiance was measured by PD:C, and the signal from PD:B was used to correct for fluctuations in the laser power. Figure 5.8 shows the results of the experiment and indicates a sheet thickness of ~ 400 μm based on the 90% and 10% relative signal levels. Multiple runs of this experiment indicated sheet thickness values ranging from ~ 370 μm to ~ 440 μm .

5.3 Detection Systems

The detection systems include elements to collect, filter, amplify and register the fluorescence signal. The detection system used for the LSF experiments includes a monochromator which is capable of providing a spectral resolution on the order of 0.01 nm (ISA, 1994). Due to the high spectral selectivity afforded by monochromators, such detection systems are referred to as narrow-band (NB) detection schemes. In contrast, the detection system used for the PLIF experiments achieves spectral selectivity via the use of color-glass (CG) and/or interference filters. Such filters have unique spectral transmission profiles with typical FWHM values of 20 to 170 nm. Moreover, CG filters often have

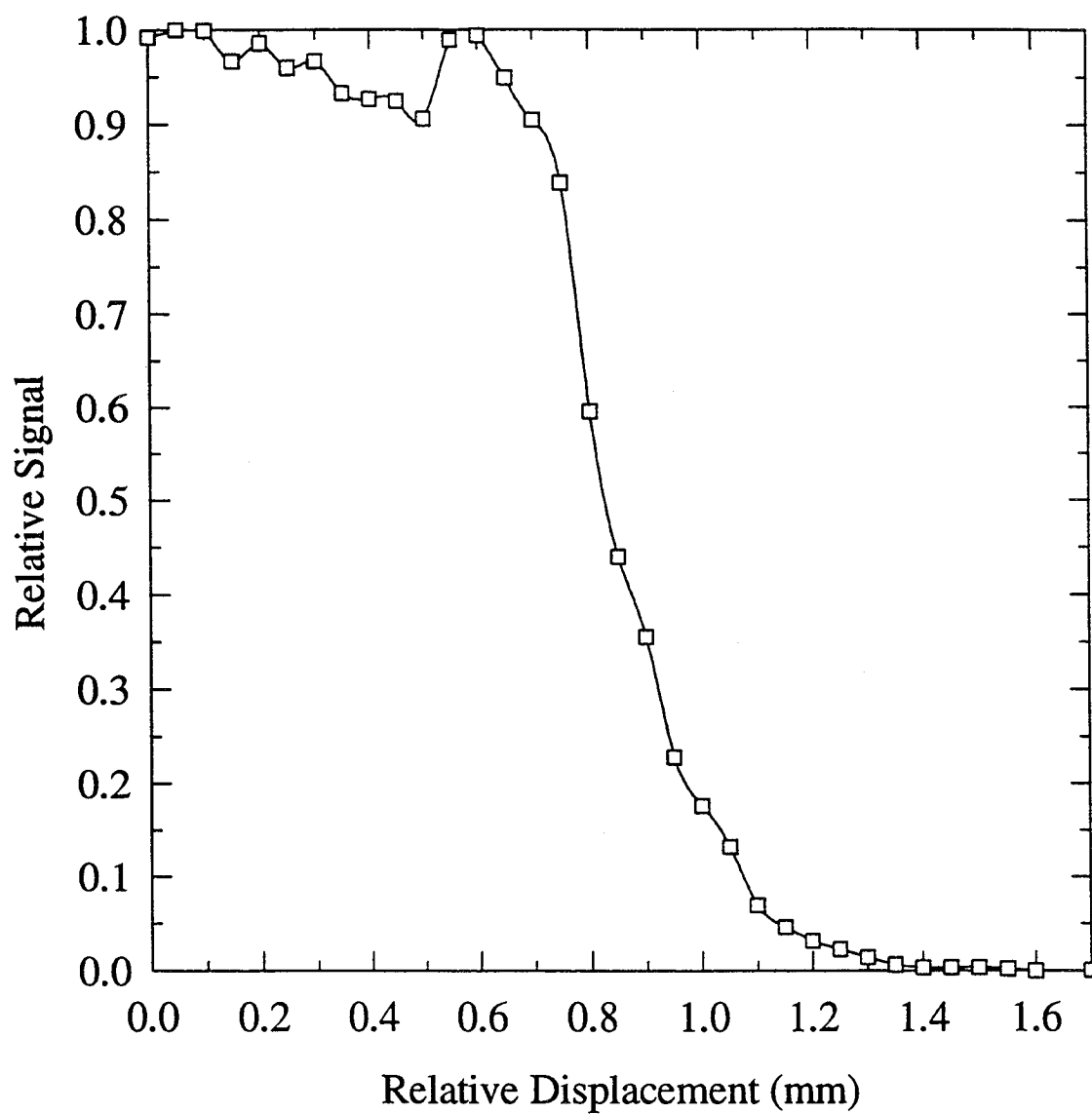


Figure 5.8 Profile of the UV laser sheet used for the PLIF measurements.

bimodal distributions which exacerbate the spectral selectivity issue. Because of the high bandwidth, and hence relatively low spectral selectivity, of the spectral filtering techniques used with the PLIF experiments, such detection schemes are referred to as broad-band (BB) detection schemes. NB and BB detection schemes and their optimization are discussed thoroughly in Chapter 6. The detection system elements that are common and specific to the LSF and PLIF experiments are described in the following sections.

5.3.1 Common Detection Elements

Photodiode based detectors (i.e., PD:A, PD:B, and PD:C of Figs. 5.4 and 5.7) are common to both the LSF and PLIF experiments, and are used to actively monitor shot-to-shot fluctuations and laser attenuation (e.g., by the RP). These detectors are also used to measure the beam diameter and sheet thickness, as well as to determine the vertical zero position of the burner. The photodiode detectors used incorporated PIN silicon photodiodes with high UV sensitivity (Hamamatsu model S1722-02) in circuits designed for ultra-high speed light detection (i.e., application no. 9 described in Hamamatsu, 1991). These photodiode detector circuits were internally 50- Ω terminated and used a 102-V bias voltage. The photodiode detectors were housed in small boxes to minimize the influence of ambient lighting; UV opal diffusers (Oriel model 48110) were also incorporated to minimize the effects of beam steering. Operation was confined to the linear range of the photodiode detector by attenuating the split-off beam, prior to the housing, via combinations of neutral-density (ND) and color-glass (CG) filters (Schott model UG5). The signals from the photodiodes were temporally integrated over a 12-ns gate centered at the temporal peak of the pulse using a Stanford Research Systems gated integrator and boxcar averager (SR250 as described in Section 5.5).

The linear range of the photodiode detectors was experimentally measured using PD:B. At the time this experiment was performed, the RP had not been procured. Instead, an ND-filter wheel (New Focus model 5215) which occupied the position of the RP in Figs. 5.4 and 5.7 was used to provide discrete attenuation of the laser beam. To initially estimate the linear range of the PD, its temporal response was monitored using a digital oscilloscope (Hewlett Packard model 54502A) as a function of laser power.

Saturation of PD:B was clearly revealed by a deformation of the trailing edge of the temporal pulse and a corresponding increase in the measured temporal FWHM. For laser powers sufficient to produce peak signal levels of approximately less than 9 V, no pulse shape deformation was observed and the measured FWHM was nominally ~ 9 ns. However, as the maximum input signal to the gated integrator/boxcar averager is 2 V, the PD input must be sufficiently attenuated (via CG and/or ND filters) so that the peak pulse voltage from the PD is less than this value. This 2-V peak signal level is well within the linear range observed via the oscilloscope temporal pulse traces. As a more quantitative means of measuring the linear range of the PD, the integrated laser irradiance was measured, at 13 levels of attenuation, by both PD:B and a power meter (Scientech model 361 with surface absorbing disc calorimeter model 36-0001) positioned between A2 and SP3 in Fig. 5.4. The radiation input to PD:B was sufficiently attenuated via ND and UG5 CG filters so that the peak voltage was always less than 2 V, and the signal was integrated by a gated SR250 data acquisition unit. The results of this experiment are shown in Fig. 5.9, which indicate that the photodiode systems provided an approximately linear response for over two decades of dynamic range.

5.3.2 LSF Specific Detection Elements

Figure 5.4 shows a schematic representation of the NB detection system used for the LSF experiments. In the NB detection system the fluorescence was captured using a system of collection optics, spectrally filtered using a monochromator, and spectrally integrated and amplified using a PMT. A portion of the signal from the PMT was temporally integrated by the data acquisition system described in Section 5.5. The elements of the LSF detection system are described in the following sections.

5.3.2.1 Collection Optics

A portion of the isotropically emitted fluorescence was captured and collimated by a 50-mm diameter, 254-mm focal length, fused silica spherical lens (CVI model PLCX-50.8-130.8-UV) which is represented by SL2 in Fig. 5.4. The collimated fluorescence was rotated and directed by an image rotator, IR, and a 76-mm diameter mirror M3 (CVI

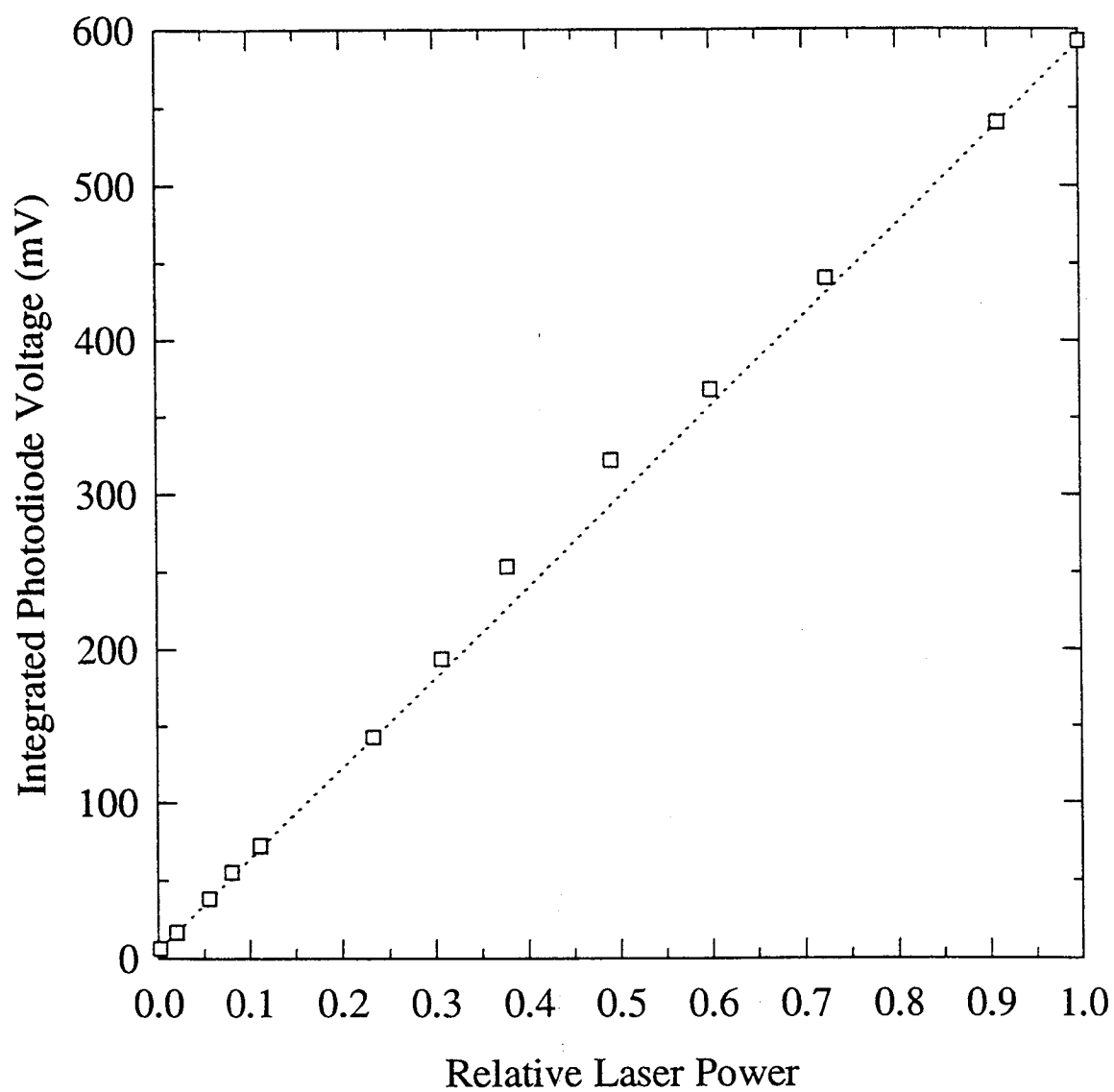


Figure 5.9 Linearity of the photodiode systems.

model PAUV-PM-3050-C). IR is composed of two mirrors identical to M3 and rotates the fluorescence image so that it is aligned parallel to the vertical entrance slit of the monochromator. A second lens SL3, identical to SL2, was used to focus the fluorescence signal onto the entrance slit of the monochromator.

SL2 and SL3 were specified to produce the desired system magnification and f-number ($f/\#$). Because SL2 and SL3 are identical, the collection optics system has a magnification of unity. Hence, the monochromator slit settings project back through the collection optics system to produce a collection volume with lateral dimensions equal to those of the slit. Although SL3 was a 50-mm diameter optic, it was housed in a lens holder (Newport model LH2-200R) which reduced the clear aperture to ~ 43 mm, resulting in a system f-number of $f/5.9$. This closely matches the $f/6.0$ of the 3/4-m monochromator used for the LSF experiments (ISA, 1994), and hence optimizes the throughput and theoretical spectral resolution of the NB detection system. Using these collection optics with the 51-mm diameter AIDF burner (described in Section 5.7), fluorescence may be sampled without vignetting ~ 2.2 mm above the burner surface.

5.3.2.2 Monochromator

A 3/4-m monochromator (Spex model 1700) was used in the LSF experiments to spectrally filter the fluorescence and interfering signals. The entrance slit incorporated both a stepped diaphragm (2, 5, and 10 mm tall) and three Hartmann diaphragm settings (1 mm tall) to limit the collection volume along the axis of the laser beam. A 110-mm x 110-mm, 1200-groove/mm holographic grating with a 250-nm blaze angle was used in first order to provide a dispersion of 1.1 nm/mm (ISA, 1994) at the exit slit. The monochromator grating drive was modified to incorporate a 50-to-1 gear reducer (Bayside Controls Inc. model NE23-050, Port Washington, NY) and a 200 step-per-revolution stepper motor (SLO-SYN DC model MO61-LS02-E). This provided a minimum spectral step resolution of ~ 0.0003 nm/step in first order. The monochromator was aligned and calibrated using the mercury lines at 435.83 nm in first and second order (871.67 nm in second order) and 546.07 nm in first order (Weast, 1984). The monochromator was spectrally calibrated to produce a scan error of less than ~ 0.03 nm

over the 435.83-nm to 871.67-nm spectral range. By spectrally scanning the monochromator over the Rayleigh scattered signal for radiation appropriate for excitation of the $Q_2(26.5)$ line of NO, the correction to the monochromator dial reading was determined to be ~ 28.28 nm (the correction based on the visible mercury lines was ~ 28.35 nm). Thus, if the actual wavelength is λ , and the dial reading is DIAL, then $\lambda \approx \text{DIAL} + 28.28$ nm.

The entrance- and exit-slit settings were selected to minimize integration of linear fluorescence in the spatial wings of the laser beam, and to minimize the integration of interfering signals. Detection schemes which minimize integration of interferences in fluorescence studies are discussed in detail in Chapter 6. For all of the LSF experiments, the entrance slit was 68- μm wide by 1-mm tall (Hartmann setting no. 2). This defines a probe volume which is 68- μm wide along the radius of the laser beam and 1-mm long along the axis of the laser beam, whose image is vertically centered on the monochromator entrance slit. With the ~ 213 - μm diameter beam (Section 5.2.2), this slit setting spatially integrates only the center $\sim 32\%$ of the beam, hence minimizing fluorescence wing effects. However, this collection scheme is still sensitive to depth-of-field wing effects as for previous NB detection system measurements (Reisel et al., 1993; Carter et al., 1992).

A 1.818-mm wide exit slit was used in all LSF experiments so as to spectrally integrate over a 2-nm region of the fluorescence spectrum. A greater signal-to-noise ratio could have been obtained by integrating a larger region of the fluorescence spectrum (e.g., possibly up to 3 nm as discussed in Chapter 6). However, considering the 8-mm wide window of the PMT and its PMT housing (see Section 5.3.2.3), the limiting aperture for a 2.727-mm wide slit (i.e., the slit setting for integration of a 3-nm region of the fluorescence spectrum) could be the PMT window rather than the monochromator exit slit. More detailed experiments would be required to determine the upper limit on the exit slit setting. Hence, a 2-nm region of the fluorescence spectrum was integrated so that the limiting aperture dictating the range of spectral integration by the PMT would clearly be the monochromator exit slit.

Although the monochromator was spectrally calibrated using visible mercury lines and Rayleigh scattering, as described above, detection scans were performed so that the

monochromator could be confidently centered on the $\gamma(0,1)$ band of NO. Figure 5.10 shows the resulting detection scans taken in a premixed, $\phi=0.8$ flame with three different levels of NO doping. In Fig. 5.10, the relative fluorescence signal is plotted against approximate wavelength which represents the corrected monochromator spectral dial reading (i.e., via $\lambda \approx \text{DIAL} + 28.28 \text{ nm}$). The fact that the relative fluorescence signal scales with doping level indicates that the signal is due to NO and not some interfering species (Reisel et al., 1993a). Moreover, it appears that at the UV wavelengths of interest for detection of NO in the $\gamma(0,1)$ band at $\sim 236.6 \text{ nm}$ (Piper and Cowles, 1986), the calculated monochromator correction is slightly low. For exact determination of this monochromator correction, high resolution detection scans would have to be taken from which the calibration factor could be determined using the known spectral locations of specific NO lines. Nevertheless, Fig. 5.10 is sufficient for setting the monochromator parameters for the LSF measurements of [NO]. To integrate a 2-nm region of the $\gamma(0,1)$ NO band, the exit slit width was set to 1.818 mm, as described above, and the grating was set to a spectral dial position of 207.50 (235.78 nm in Fig. 5.10). This results in an integration of the fluorescence signal over the spectral range of 234.78 nm to 236.78 nm in Fig. 5.10.

5.3.2.3 PMT Detector

A Hamamatsu R106UH-HA PMT was used for amplification and spectral integration of the fluorescence signal in the LSF experiments. This PMT is a third generation descendent of the 1P28B PMT which has been used in the past for OH (Carter et al., 1991) and NO (Reisel et al., 1993a) LSF studies. Compared to the 1P28B, the R106UH-HA PMT has $\sim 140\%$ more gain, less spectral variation in gain, and $\sim 500\%$ less dark noise (Hamamatsu, 1994). The PMT was mounted in a custom voltage divider circuit that distributed the 1000-V supply voltage, and which was optimized for temporal resolution of the fluorescence signal (Harris et al., 1976). This PMT and voltage divider system was enclosed in a light-tight housing which was attached to the monochromator exit slit housing and incorporated an $\sim 64\text{-mm}$ focal length fused-silica spherical lens for focusing the diverging radiation exiting the exit slit onto the 8-mm x 24-mm PMT

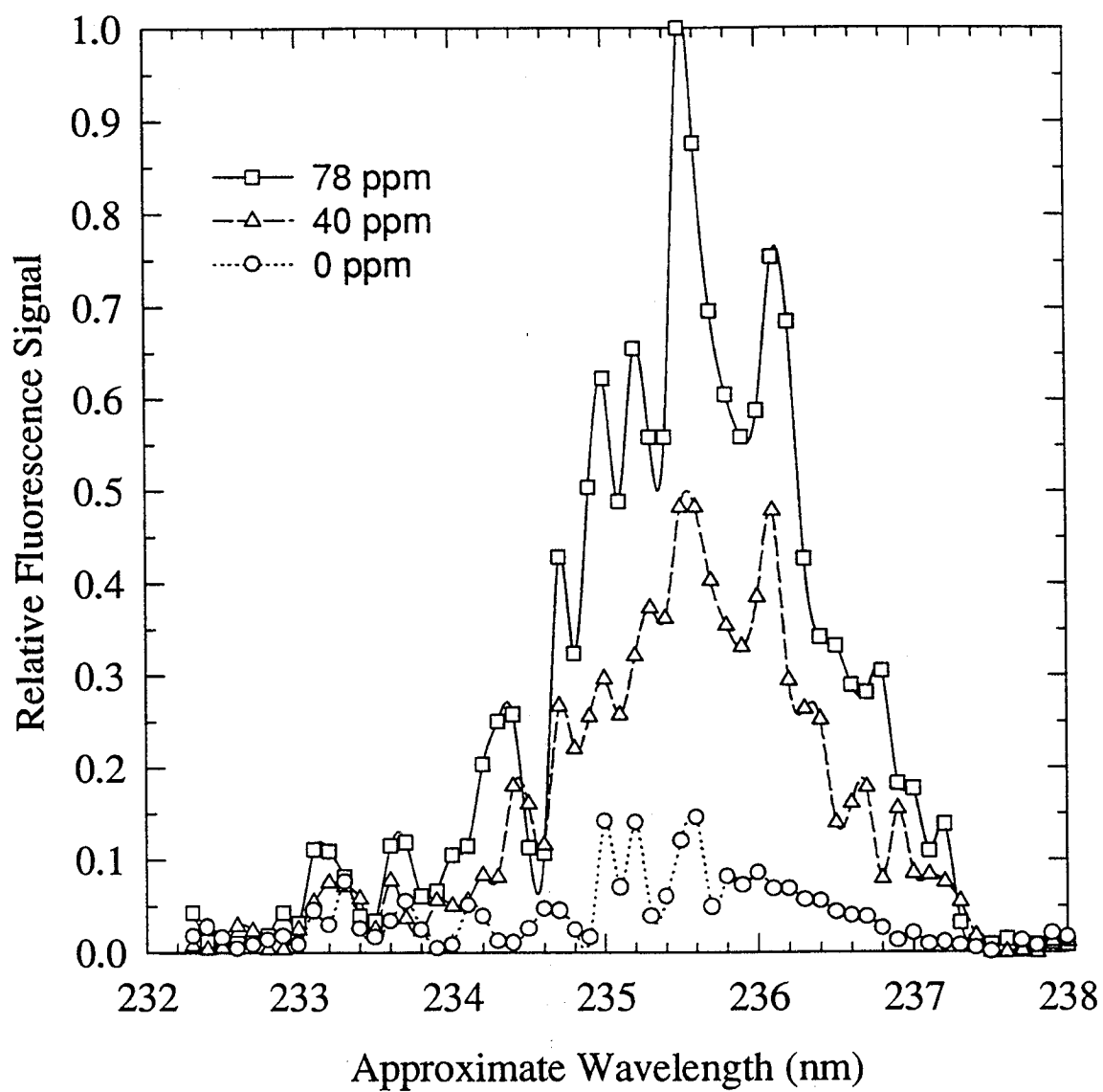


Figure 5.10 Detection scan over the spectral region containing the $\gamma(0,1)$ band of NO.

window. The LSF signal from the PMT was temporally integrated over a 500-ps gate centered at the temporal peak of the fluorescence pulse using a Stanford Research Systems fast sampler (SR255) and gate scanner (SR200) (see Section 5.5).

To measure the linear range of the R106UH-HA PMT, the Rayleigh scattering signal was measured at a range of relative laser powers using the experimental configuration described in Fig. 5.4. An ND-filter wheel was used in place of the RP (as discussed in Section 5.3.1) to provide thirteen discrete levels of attenuation. At each level of attenuation, PD:B was used to measure the relative laser power and PD:A was used to correct the signals from the PMT and PD:B for shot-to-shot fluctuations in laser power. The PD signals were integrated using gated SR250 integrator/boxcar averager units, as described in Section 5.5. The results of this experiment are shown in Fig. 5.11, which indicates that the PMT detector system provided a linear response over approximately three decades of dynamic range. Moreover, the maximum signal level was ~ 0.33 V. This indicated that the PMT detector system provided a linear response throughout the range of the fast sampler data acquisition unit for a sensitivity setting of 0.25 Vin/Vout, as used for all of the LSF experiments.

5.3.3 PLIF Specific Detection Elements

5.3.3.1 PLIF Equipment Description

The BB detection system used for the PLIF experiments is shown in schematic form in Fig. 5.7 and includes: (1) a filter stack (FS1) to spectrally filter the radiation signal, (2) a lens system (LS) for collecting and focusing a portion of the signal, (3) an intensified charge coupled device (ICCD) for spatially resolving, amplifying and registering the radiation signal, and (4) supporting equipment including a water chiller/circulator, pulse generator, detector controller, PC and Sparc station. The FS1 consisted of a wide-band interference filter spectrally centered at 250.0 nm with a 92-nm FWHM (Acton model 250-W-2S, i.e., filter no. 4 of Chapter 6) and 6 mm of UG5 CG filter. LS was an aberration-corrected, five fused-silica element, UV-Micro-Nikkor 105-mm focal length, f/4.5 lens (Nikon Corp., Melville, NY). The spectrally-filtered PLIF image was spatially amplified, discretized, and registered using a Princeton Instruments

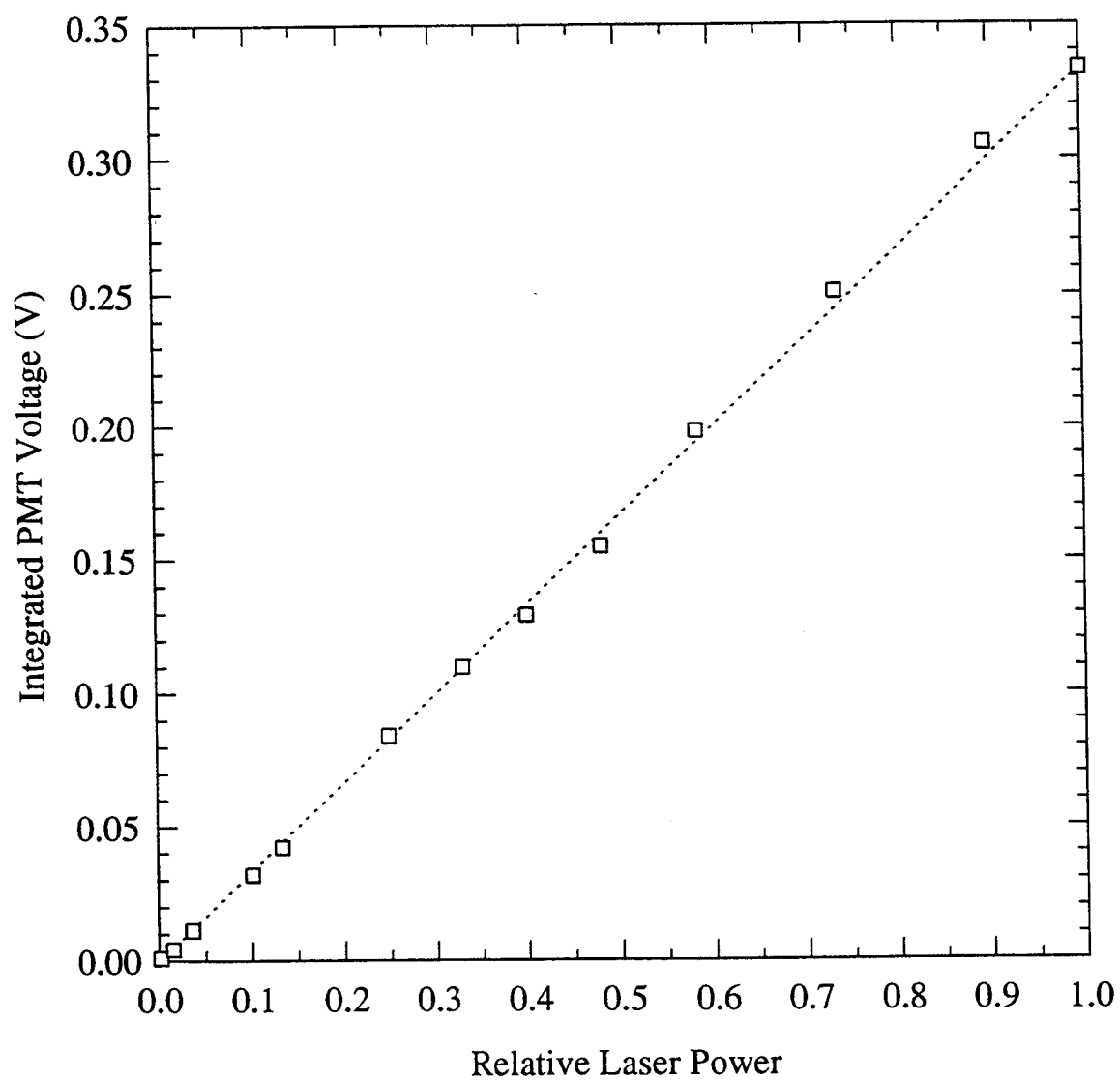


Figure 5.11 Linearity of the R106UH-HA PMT.

model ICCD-576TC-RG proximity focused ICCD detector (Princeton, NJ). The ICCD incorporated a 578 x 384 pixel charge-coupled device (CCD) (Thomson model CSF 7883) which has 23- μ m square pixels with transparent channel stops and greater than 14-bit dynamic range. The channel stops prevent blooming (i.e., spilling over of the charge from a saturated pixel to adjacent pixels), and having transparent channel stops provides 100% active area in the CCD. The ICCD thermoelectric (Peltier-effect) cooler was used in conjunction with an external water chiller/circulator (Lauda model RMT-6, Brinkmann Instruments, Westbury, NY) to reduce the temperature of the CCD to minimize thermal (Johnson) noise. With a water bath temperature of 20° C, the CCD could be thermoelectrically cooled to -20° C. A pulse generator (Princeton Instruments model FG-100) was used to provide a gate of the appropriate delay and width to the ICCD. The pulse generator was capable of providing a minimum gate width of 18 ns. All ICCD voltages, the Peltier cooler, and the CCD readout were controlled by a detector controller (Princeton Instruments model ST-130). The user interface to the ICCD system was provided by PC-based Princeton Instruments CSMA software (version 2.3A), and the images were stored via an Ethernet connection on a dedicated hard drive of the laboratory Sparc station. All image analysis and reduction was performed on the laboratory Sparc station using PV-WAVE version 5.0 software (Visual Numerics Inc., Boulder, CO).

5.3.3.2 ICCD Alignment and Specifications

Experimental procedures for aligning, focusing and determining the magnification of the ICCD as well as experiments to determine the linear operating range and minimum resolvable scale of the ICCD are described in this section. Routine procedures for operation of the ICCD are not discussed.

The LS was focused using a multiple star target (Rolyn Optics Co. Model 70.5020) and real-time feedback images from the ICCD system. The multiple star target consist of five stars with four arranged in a square and the fifth positioned in the center. Each star consists of alternating opaque and transparent wedges to form a circle. Such star targets are common focusing aids; for extreme out-of-focus conditions, they display contrast reversal (Goodman, 1968), i.e., the opaque regions appear transparent and the

transparent regions appear opaque. At near optimal focus the stars display a blur circle within which the individual wedges of alternating opacity are not resolvable and outside of which the individual wedges may be resolved. For focusing the camera, the star target was aligned in the plane of the laser sheet. With the laser off, the optimal focus was determined by using the image of the central star registered by the ICCD system as real-time feedback for adjusting the LS to minimize the blur circle. By using only a 128×128 pixel region of the CCD to image only the central star of the target, the frequency of the feedback is increased to a level sufficient for actively setting the focus (i.e., larger image areas reduce the camera framing rate). The outer stars of the target were used to orient the axis of the ICCD normal to the laser sheet. If this condition is not satisfied, then the central portion of the image will be in focus and the outer edges will be out of focus. Variations in the diameters of the blur circles in the vertical and horizontal directions indicate misalignment in pitch and yaw of the ICCD, respectively. By taking a full image, and validating that the diameter of the blur circles were approximately constant for all of the individual star targets, the camera axis was determined to be normal to the laser sheet.

To determine the magnification of the camera, a 50-mm square calibration target with a 1-mm grid on an opal-glass coated substrate (Klarmann Rulings Inc., Manchester, NH) was used. The magnification was determined as the ratio of the total length of the image corresponding to an integral number of grids (the pixel width is known to be $23 \mu\text{m}$) to the corresponding actual length of the imaged grid. For all PLIF experiments, the magnification was experimentally determined using this procedure to be ~ 0.42 . The magnification was determined independently along the two dimensions of the CCD and found to be equivalent. This value of $M \approx 0.42$ is close to the upper magnification limit possible using the UV-Nikkor lens alone. For higher levels of magnification, the UV-Nikkor lens may be used in conjunction with one or more lens extension rings (Nikon model PK-13). For zero, one and two extension rings at a given camera position, the magnification was determined to be 0.42, 0.68, and 0.95, respectively, and the field of view was $\sim 31.4 \times 20.9 \text{ mm}^2$, $\sim 19.5 \times 13.0 \text{ mm}^2$, and $\sim 14.0 \times 9.3 \text{ mm}^2$, respectively. Hence, the PLIF facility is capable of achieving magnifications larger than used in the

present study (e.g., for resolving small length scales in fluctuating flows or narrow probe-species production zones) but this clearly results in degradation of the field of view.

The linearity of the ICCD was experimentally measured by illuminating the ICCD with a diffused tungsten light source which was attenuated to different levels via calibrated neutral density (ND) filters. It would have been more appropriate to use an illumination source in a spectral range similar to that of the fluorescence to be measured (e.g., a spectrally filtered mercury lamp). However, such an illumination source was not available. The results of this experiment are shown in Fig. 5.12, which indicates that the response of the ICCD is linear over the range 165 to 10600 counts. Greater radiation levels or longer integration times would be required to investigate the upper limit (i.e., above 10600 counts) of the ICCD linear dynamic range. However, the signal levels of the PLIF experiments were always within the signal range indicated in Fig. 5.12.

The range of scales that may be faithfully resolved by an imaging system, and the degradation in resolution with increasing spatial frequency may be represented by the system's modulation transfer function (MTF) (Smith, 1990). The MTF is the real portion of the optical transfer function which is determined through Fourier analysis methods. Experimentally, the MTF is determined as the spatial-frequency resolved variation in the contrast or modulation of a sinusoidally varying irradiance distribution, where the contrast is defined as the ratio of the difference between the maximum and minimum signals to the sum of these signals (i.e., $\text{modulation} = (S_{\max} - S_{\min}) / (S_{\max} + S_{\min})$, where S is the signal level). Characteristically, the MTF decays with increasing spatial frequency, indicating a corresponding reduction in contrast (i.e., modulation) or resolution. One pertinent variable of the MTF curve is the spatial cutoff frequency, which is defined as the spatial frequency at which the MTF decays to zero or some appropriately small value. In theory, the spatial cutoff frequency should vary with the imaging lens aperture or $f/\#$ for a constant magnification (Goodman, 1968) and should be a maximum for a magnification of unity (Paul et al., 1990a).

An MTF-like variable was experimentally measured for a magnification of $M \approx 0.5$ at the extreme $f/\#$ values of the UV-Nikkor lens (i.e., $f/4.5$ and $f/32$) using a square wave irradiance distribution (MTF is formally defined for a sinusoidal irradiance distribution).

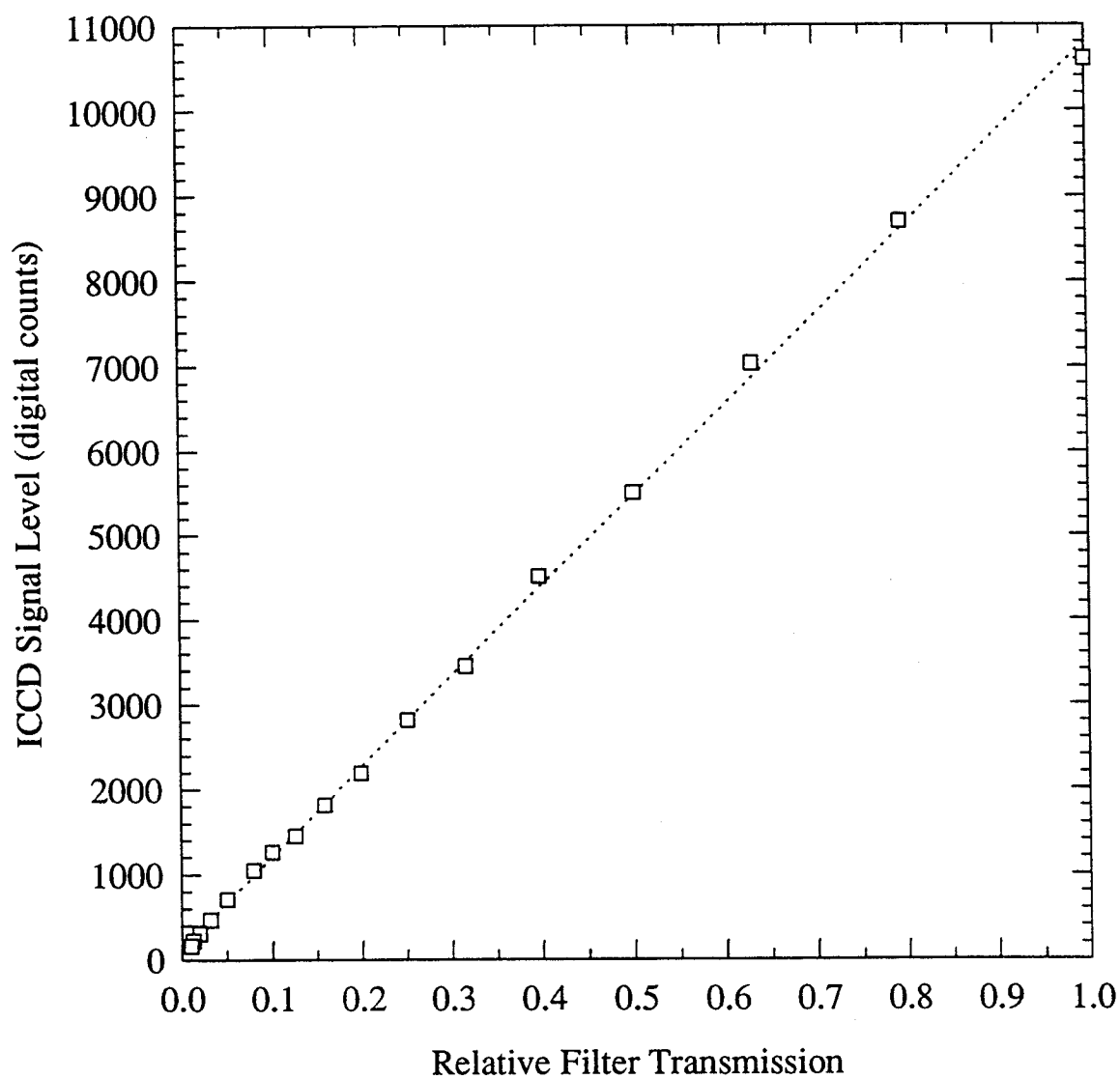


Figure 5.12 Linearity of the ICCD.

For this experiment, an NBS 1963A bar resolution target (Rolyn Optics Co. model 70.6010) was positioned in the plane of optimum focus and uniformly illuminated using a diffused tungsten light source. Images were taken of the target and the contrast was calculated (by averaging over four cycles for each spatial frequency) for each resolvable spatial frequency component of the resolution target. The spatial frequency components of the resolution target are specified in line pairs per millimeter (lp/mm), where a line pair is understood to be one high signal level (transparent) and one low signal level (opaque) bar pair. The results of this experiment for the two extreme $f/\#$ s investigated are shown in Fig. 5.13, which displays the characteristic profiles of an MTF curve. The curves would probably be smoother if the data at each spatial frequency had been numerically fit and if more averages had been taken (e.g., along the height of the resolution bars). However, these results are sufficient for estimating the spatial cutoff frequency of the ICCD system. The results indicate no difference in the MTF for the extreme lens $f/\#$ s. Therefore, the lens $f/\#$ could be adjusted to produce the desired signal level with no degradation of the spatial resolution. Based on Fig. 5.13, the spatial cutoff frequency may be estimated to be ~ 5 lp/mm, based on the 10% contrast level. This indicates a minimum resolvable scale of $\sim 100 \mu\text{m}$ (i.e., $(1 \text{ line pair}/2 \text{ lines}) \cdot (1 \text{ mm}/5 \text{ line pairs}) = 0.1 \text{ mm/line} = 100 \mu\text{m}$) in the plane of the laser sheet.

The measured spatial cutoff frequency is in good agreement with a separate Fourier analysis of the ICCD which did not include the lens and indicated a spatial cutoff frequency of ~ 5.6 lp/mm based on a magnification of 0.5. This agreement between experiment and theory indicates that the focusing procedure is rather good, since any focusing error would contribute to degrading the spatial cutoff frequency. Moreover, Fig. 5.13 indicates that the imaging system's MTF is effective at filtering spatial frequencies greater than the Nyquist frequencies of the ICCD's components. Recall that signals of frequency greater than the Nyquist frequency of a detector will be aliased by that detector. Therefore, if the system MTF was such that its cutoff frequency was greater than the Nyquist frequency of any ICCD component, there would be the potential for experiencing signal aliasing problems. The Nyquist frequency of the ICCD's MCP, fiber optic bundle, and CCD array are approximately 42, 84, and 20 lp/mm, respectively. Hence, since the

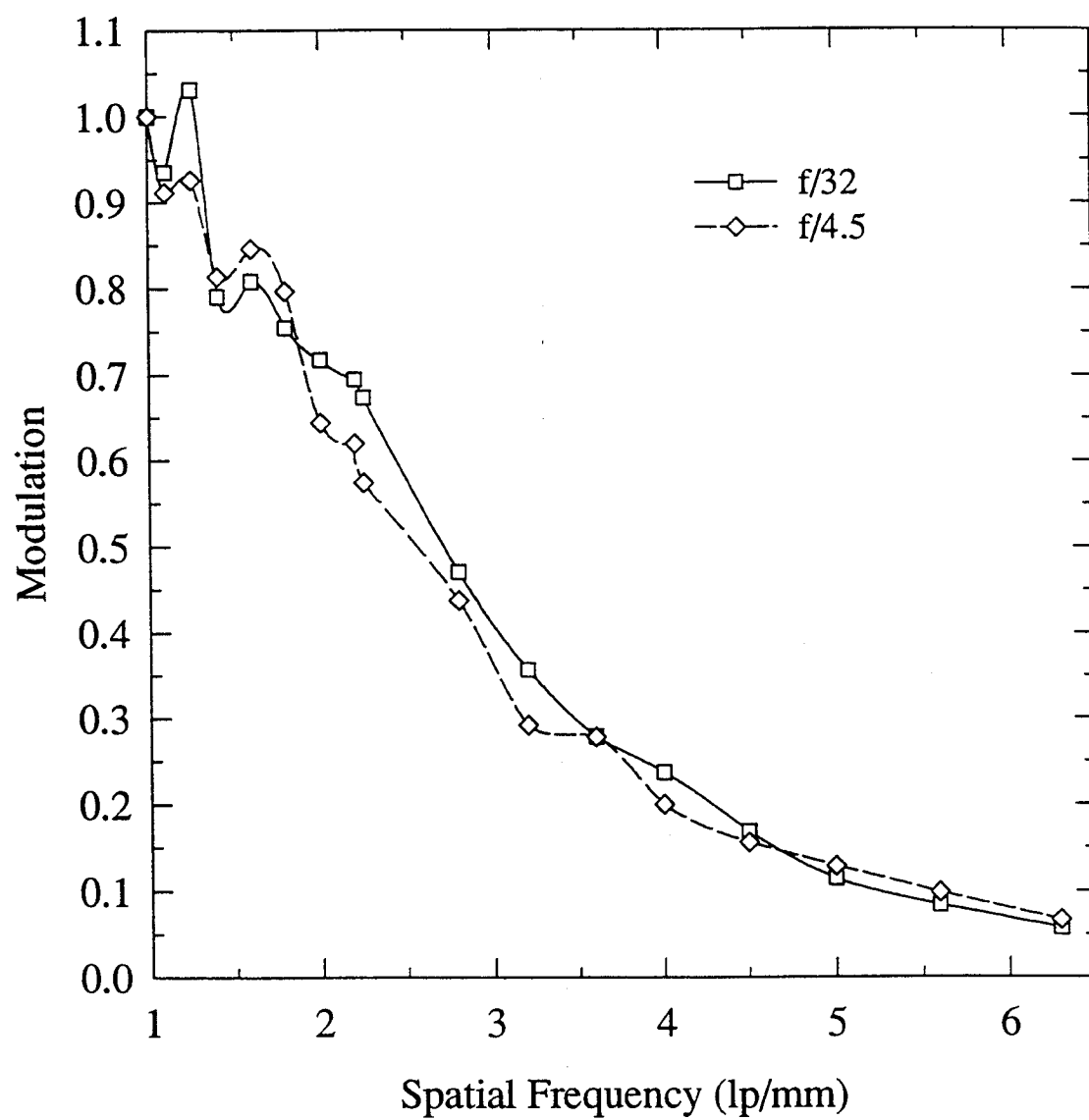


Figure 5.13 Spatial cut-off frequency of the imaging system.

system cutoff frequency is ~ 5 lp/mm, spatial frequencies greater than these Nyquist frequencies of the ICCD's components are filtered out by the system MTF. Therefore, there is no potential for aliasing signals that are within the spatial frequency bandwidth (i.e., 0 to ~ 5 lp/mm) of the detector, i.e., any spatial frequency that may be resolved by the ICCD.

5.4 Overlap Reference System

The overlap reference system (ORS) was used to set and monitor the spectral overlap of the laser radiation and the NO excitation line (i.e., $Q_2(26.5)$). To optimize the overlap between the frequency mixed radiation exiting the WEX and the $Q_2(26.5)$ NO line, the PDL oscillator grating was scanned (hence, indirectly spectrally scanning the frequency mixed radiation) until the NO-fluorescence signal measured by the BB-detection system was maximized. The overlap was routinely adjusted throughout an experiment to correct for drift in the laser wavelength.

A schematic representation of the ORS is shown in Fig. 5.14. The ORS was incorporated in both the LSF and PLIF experiments as evident from Figs. 5.4 and 5.7, and is composed of excitation optics, a burner to provide a hot NO source, and a BB detection system to detect any NO fluorescence induced by the tuned laser. A portion of the UV radiation was split off and focused by an ~ 600 mm, fused-silica spherical lens (SL4). To achieve excitation nominally in the linear fluorescence regime, the focus of SL4 was positioned ~ 130 mm behind the burner center and the beam was attenuated sufficiently using a (Fresnel-based) UV variable attenuator (Newport model 935-5), VA. The hot reference NO was created by a 2.5 cm square, low-density, Hencken flat-flame burner (Research Technologies, Pleasanton, CA) which was shielded to eliminate flickering in the secondary diffusion flame front. The Hencken burner was operated with ethane (C_2H_6) and an oxygen/nitrogen (O_2/N_2) mixture at a total volumetric flow rate of 11.2 SLPM and an overall equivalence ratio $\phi_o \approx 1.25$.

The collection and filtering optics (SL5, FS2, and SL6 of Fig. 5.14), and the PMT/slit/shutter assembly (PMT of Fig. 5.14) were housed in a light-tight container composed of a post and tubing structure and a thick felt skin. SL5 and SL6 were both 50-

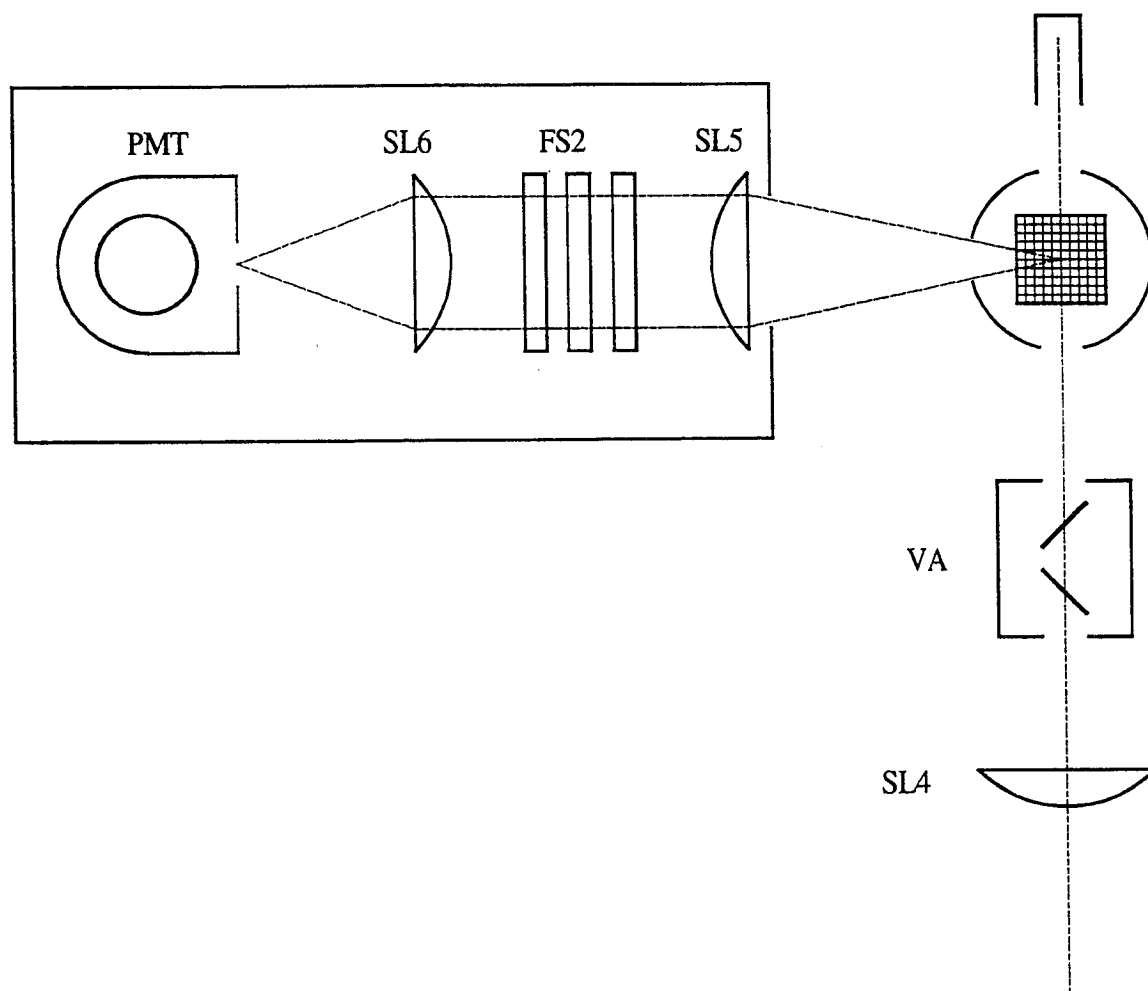


Figure 5.14 Schematic diagram of the overlap reference system.

mm diameter, 100-mm focal length, fused-silica, spherical lenses. The filter stack, FS2, was used to spectrally filter the fluorescence to minimize interfering signals (see specifically, Chapter 6) and to attenuate the fluorescence signal to within the linear range of the PMT. The FS2 consisted of a narrow-band interference filter spectrally centered on 259.5 nm with a 21-nm FWHM (Acton model 260-N-2S, i.e., filter no. 5 of Chapter 6) and 4 mm of UG5 CG filter. The radiation detector, PMT in Fig. 5.14, included a horizontally oriented slit/shutter assembly, a PMT (RCA 1P28B), a voltage-divider circuit (Hamamatsu E717-21) and a PMT housing (Oriel model 70680). The LIF signal from the PMT in the ORS was temporally integrated over a 30-ns gate centered at the temporal peak of the LIF pulse using a Stanford Research Systems gated integrator and boxcar averager (SR250) (see Section 5.5).

5.5 Data Acquisition System

Signals from the photodiodes, the ORS PMT and the monochromator PMT were sampled using equipment purchased from Stanford Research Systems. This system included three SR250 gated integrators/boxcar averagers and an SR255 fast sampler for sampling the various signals, an SR200 gate scanner for setting the gate position of the SR255, and an SR245 computer interface for transferring the integrated signals to a dedicated PC. Data transfer and storage were controlled via SR265 software which had been previously modified to interface with the stepper motor controller. Through this program, any one of the stepper motors driving the PDL grating, monochromator grating, or AIDF burner vertical or horizontal translation could be stepped. Hence, the SR245 program could be configured to automate the experimental procedure by coordinating the data collection, transfer, and storage and motor stepping processes. The remainder of this section describes the general application of the individual data acquisition system components used in the LSF and PLIF experiments. The specific triggering schemes for the LSF and PLIF experiments are described in Section 5.6.

The SR250 gated integrators/boxcar averagers were used to sample signals from the photodiodes and the ORS PMT. Because the minimum gate width of the SR250 is 2 ns, it is not capable of temporally isolating the saturated portion (i.e., the signal at the

temporal peak) of an LSF event, and hence cannot be used for LSF measurements. However, an SR250 was used to dampen out shot-to-shot fluctuations in the monochromator PMT signal from the SR255 when aligning the monochromator collection optics at the beginning of an experiment. The SR250 provides gate position and width control, signal amplification and filtering, as well as single shot or averaged results. The value of the output (single shot or averaged) is determined as the temporal integration of the signal within the gate, divided by the temporal gate width and times the gain (i.e., sensitivity) factor.

The SR255 fast sampler was configured for a fixed 500-ps gate width and used to sample the LSF signal from the monochromator PMT. The SR200 gate scanner was used to position the SR255 gate at the temporal peak of the LSF pulse, as determined via operation of the SR255/SR200 systems in the sampling-oscilloscope mode. Because the SR255 had been inoperable for an unknown amount of time, its gain and offset were calibrated per the manufacture's instructions (Stanford Research Systems, 1993) prior to any data acquisition.

5.6 Triggering System

Detailed triggering schemes were developed for the LSF and PLIF experiments to temporally synchronize the signals from the various detectors (i.e., photodiodes, ORS PMT, monochromator PMT, and ICCD) with the data acquisition events. Unique aspects of the governing theory or experimental equipment used for the LSF and PLIF experiments required each to have a unique triggering scheme. The primary difference between the two triggering schemes is the source of the master trigger. The two master triggering schemes are described below and the specific LSF and PLIF triggering schemes are discussed in the following sections.

The Quanta-Ray GCR-4 Nd:YAG laser offers several BNC outputs that may be used as a master trigger to temporally synchronize the data acquisition system with the various detector signals. The Q-switch sync. (QSS) and variable sync. (VS) positive-edge BNC outputs are based on an internal high voltage signal which triggers the Q-switch, thus producing pulsed radiation (1064 and 532 nm) nominally 50 ns after the trigger. The

QSS output is synchronized with the Q-switch high voltage trigger, and the VS output may be temporally varied over a range from 680 ns before to 1000 ns after the QSS. Because the QSS and VS are based on the Q-switch high voltage trigger, any jitter in this high voltage trigger will be propagated through to the QSS and VS outputs. The manufacturer specification for the jitter in the QSS for seeded operation is <1 ns (Spectra-Physics, 1991).

Another factor which influences the experimental synchronization is the unavoidable variation in build-up time (i.e., the time between the high voltage Q-switch trigger and the production of the radiation pulse). It was observed that a radiation pulse produced with seeded operation builds up approximately 10 ns earlier than one produced with unseeded operation. Although this 10-ns variation in build-up time is an approximate upper limit, there is always variation in the pulse build-up time; this is because the Nd:YAG laser is not simply seeded or unseeded, but rather seeded to a given degree or quality. Specifically, if the alignment of the seed laser optics with the Nd:YAG oscillator cavity is very good, then the quality of the injection seeding will be very high. Unfortunately, the quality of the injection seeding was observed to vary about this optimum value or possibly drift in one direction or another throughout an experiment; this caused a corresponding variation in the pulse build-up time. Hence, if the quality of the injection seeding drifts after the experiment has been temporally synchronized, the data acquisition gates may integrate only a portion or actually miss the signals from the detectors.

In summary, the two factors which cause variations in the time between the QSS and VS outputs and the generation of pulsed radiation are: (1) nominal jitter specified as <1 ns, and (2) variation in the quality of the injection seeding which will vary the build-up time by <10 ns. In general, the VS offers a high degree of flexibility in the initial production of the master trigger, but has a relatively high degree of temporal variation relative to the actual radiation pulse from shot to shot and over time (i.e., throughout an experiment).

An alternate technique is to trigger off the pulsed radiation itself. This bypasses any electronic variation in the Nd:YAG performance and offers zero jitter and variation in

the master trigger relative to the pulsed radiation. For implementation of this triggering scheme, a master photodiode (PD:M) was used which monitored scattered 532-nm radiation through the window of the Nd:YAG harmonics box. Although this triggering scheme offers zero temporal variation relative to the radiation pulse, it does not allow a broad variation in the initial generation of the master trigger pulse relative to the radiation pulse, as does the VS BNC output of the Nd:YAG laser.

5.6.1 LSF Specific Triggering system

For the LSF experiments, the fluorescence is in the saturated regime only at the temporal peak of the laser pulse. To either side of the temporal peak, the fluorescence is initially in a partially saturated regime and subsequently in the linear fluorescence regime for the majority of the temporal wings of the laser pulse. The LSF experiments used a 500-ps gate centered at the temporal peak of the laser pulse, as described in Section 5.5, so that only the fluorescence in the saturated regime would be temporally integrated by the data acquisition equipment. However, this data acquisition scheme requires that the 500-ps gate be temporally synchronized with the center of the LSF signal for every fluorescence event (i.e., from shot to shot). Hence, any jitter (i.e., shot-to-shot fluctuations) in the master trigger which coordinates this synchronization may cause the 500-ps gate to integrate some fluorescence outside the saturated fluorescence regime on certain fluorescence events. For this reason, the LSF experiments require a very stable (i.e., low jitter) master trigger. This in turn dictated the use of a triggering scheme based on the signal from PD:M as the master trigger.

The triggering scheme for the LSF experiments is shown in Fig. 5.15. The master trigger pulse from PD:M was divided by three 50- Ω voltage divider circuits (VD:A, VD:B, and VD:C). The outputs from the voltage divider circuits were used to trigger the three gated integrators/boxcar averagers (SR250:A, SR250:B, and SR250:C). The 50- Ω BUSY outputs of SR250:C and SR250:A were used to trigger the fast sampler (SR255) and the computer interface (SR245), respectively. The signals from PD:B, the ORS PMT and the monochromator PMT were input via 50-ft delay lines to the SIGNAL BNC input of SR250:B, SR250:A and SR255, respectively. During initial alignment of the

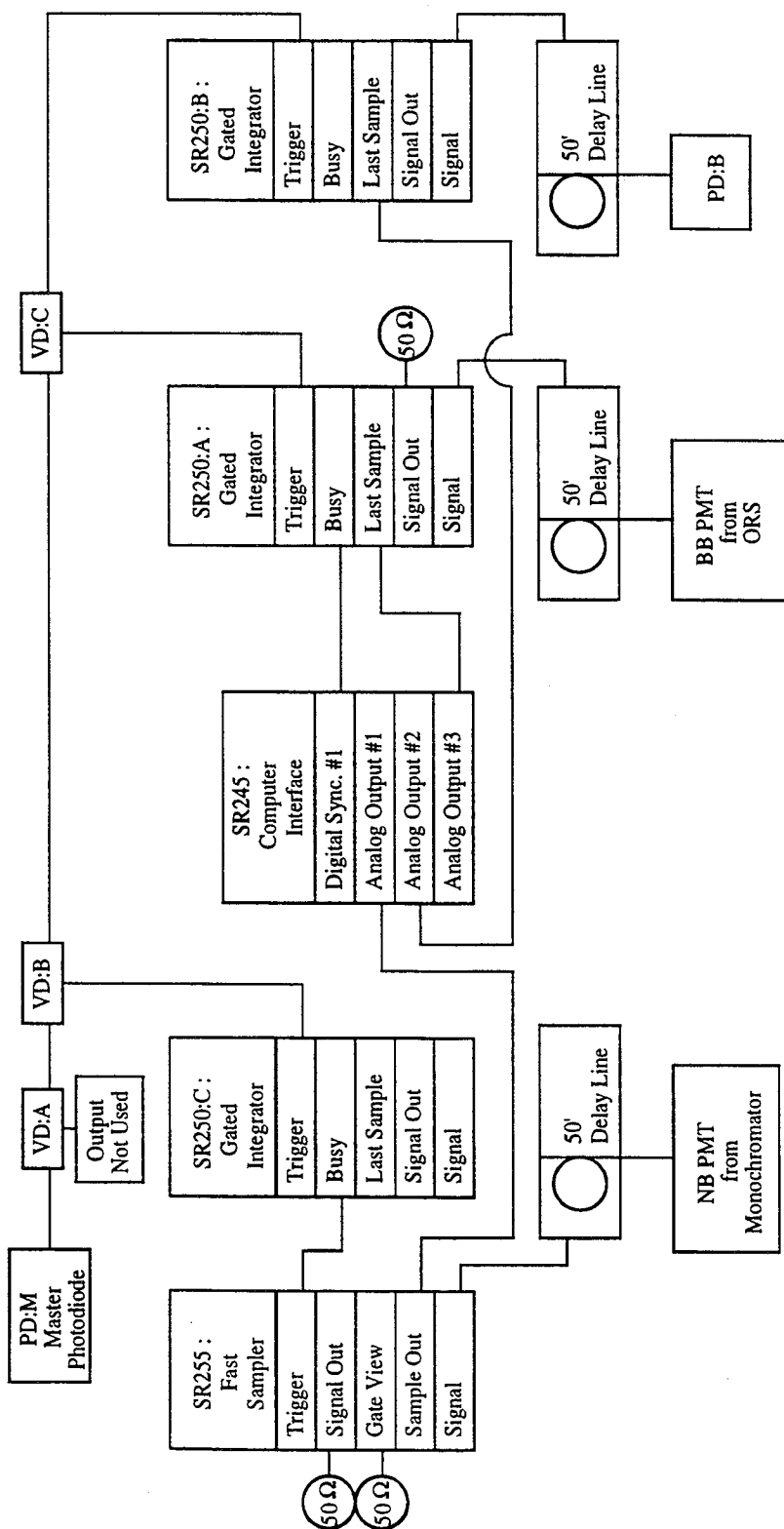


Figure 5.15 Schematic diagram of the triggering scheme for the LSF experiments.

monochromator collection optics, the SAMPLE OUT of the SR255 was input to SR250:C to dampen out shot-to-shot fluctuations as described in Section 5.5. Typically, the LAST SAMPLE BNC outputs of SR250:A and SR250:B and the SAMPLE OUT of the SR255 were connected to the analog outputs of the SR245 to allow storage of the shot-to-shot ORS, laser power, and LSF data on the PC.

5.6.2 PLIF Specific Triggering system

For the PLIF experiments, the ICCD must be temporally synchronized with the fluorescence pulse. Because of the inherent internal ~ 18 -ns delay of the pulse generator (FG-100), either the fluorescence signal must be optically delayed or the FG-100 must be pretriggered. The fluorescence signal may be optically delayed by increasing the distance traveled by the UV radiation (~ 1 ns/ft). However, this was not an option since the hardware was not available for such a delay line. Moreover, this scheme would increase losses in the excitation optics. Hence, pretriggering was the method used for overcoming the internal delay of the FG-100. Unfortunately, the PD:M master triggering scheme could not provide sufficient pretriggering. For this reason, the VS output from the Nd:YAG was used with the VS potentiometer adjusted to cause the VS output to occur 36 ns prior to the QSS. This scheme produces a trigger ~ 136 ns prior to that from PD:M, and was found to offer sufficient pretriggering for the ICCD system. To account for the relatively high degree of temporal variation in the VS relative to the radiation pulse, the ICCD gate width was set to 30 ns and temporally centered on the fluorescence event. This gate width was sufficient to negate any temporal drift in the fluorescence event relative to the ICCD gate due to the variability in the quality of the Nd:YAG injection seeding; moreover, this gate width approximately satisfies Eq. (4.25) for the ~ 9 -ns FWHM of the laser pulse. Nevertheless, the quality of the injection seeding was monitored throughout all PLIF experiments via the Q-switch build-up time output of the injection seeder.

In addition to the ICCD synchronization, the point data acquisition system (i.e., the Stanford Research system) had to be synchronized to the image acquisition system (i.e., the Princeton Instruments system). Specifically, a measure of the laser power (from

a PD:A) for the shots corresponding to the specific fluorescence events that were integrated on chip by the ICCD was needed to correct the images for fluctuations in laser power. Since the ICCD did not acquire data for each pulse of the laser system, a triggering scheme was required which would force the point measurement data acquisition system to acquire data only when the ICCD was gated. This was accomplished by using the FG-100 as a second-level triggering master to the SR250:C via the pulse monitor output of the FG-100. Although the pulse monitor output of the FG-100 was not recommended (by the manufacturer) for use as a triggering signal, this triggering scheme was found to be reliable.

While the ICCD does not acquire images for every laser pulse, pulse-to-pulse information was required in order to adjust both the WEX for maximum laser power and the PDL to optimize the overlap fraction between individual image acquisitions. This information was provided by the PD:B and ORS PMT detectors through SR250:A and SR250:B triggered via the PD:M master as described in Section 5.6.1. However, since these gated integrator/boxcar averager units were not synchronized with the ICCD system, the corresponding information could not be stored on the PC. Hence, although the ORS was monitored and adjusted throughout the PLIF experiments, it was not possible to store a record of its signal variation throughout the experiments. Laser power fluctuations were recorded and stored using PD:A and SR250:C as described above.

The triggering system for the PLIF experiments is shown in Fig. 5.16. The master trigger pulse from the VS was attenuated by a 10X, 50- Ω attenuator and used to trigger the pulse generator (FG-100). The trigger output from the FG-100 was used to synchronize the detector controller (ST-130); the NOT SCAN output from the ST-130 was used to prevent the FG-100 from gating the ICCD during readout of the CCD. The VARIABLE OUTPUT of the FG-100 was used to gate the ICCD, and the PULSE MONITOR of the FG-100 was used as a second-level triggering master to trigger the SR250:C. The SR250:C was used to monitor fluctuations in the laser power from PD:A via a 50-foot delay line, and the BUSY output was used to trigger the SR245 via its DIGITAL SYNC input #1. Shot-to-shot fluctuations corresponding to fluorescence

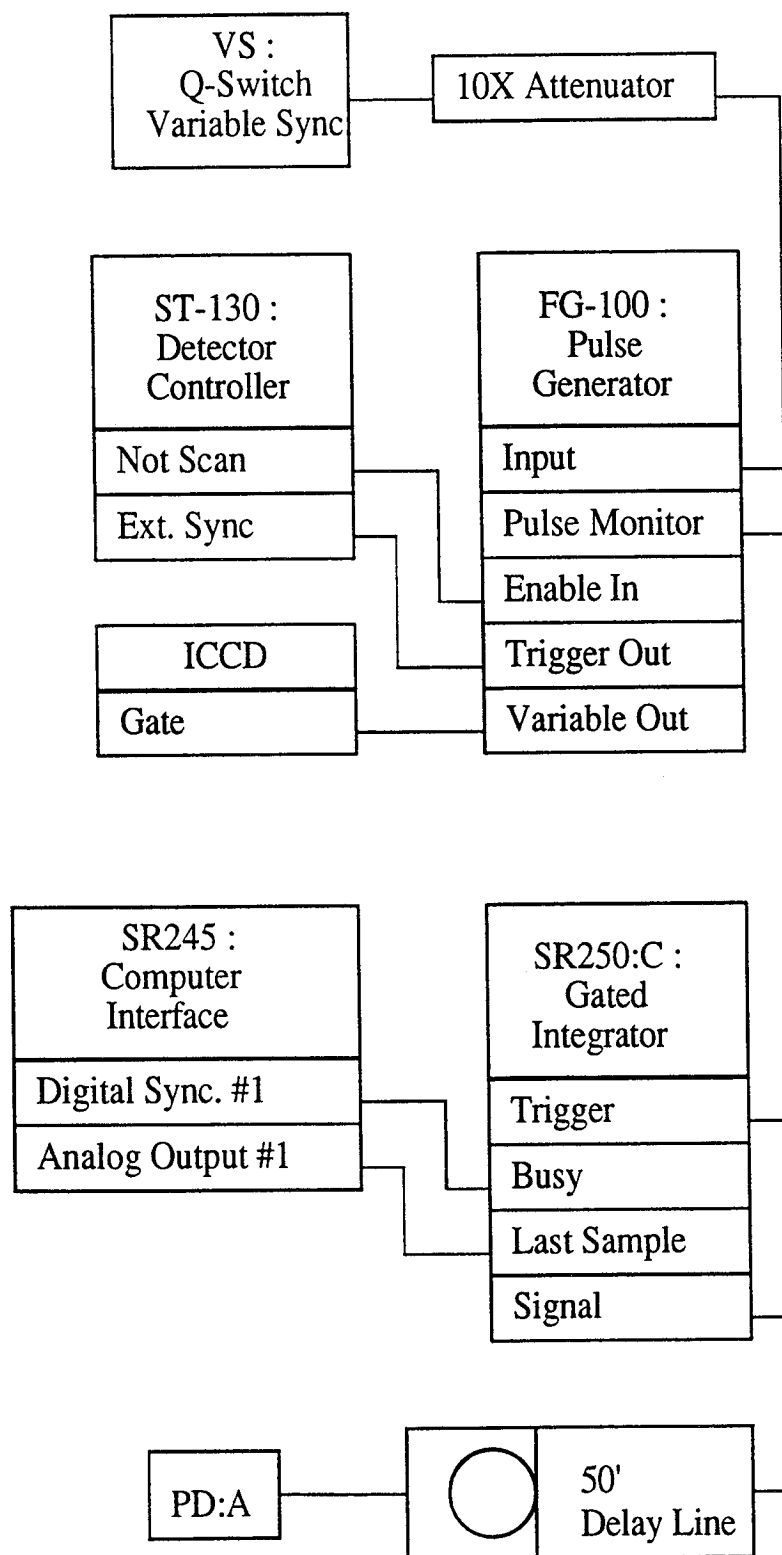


Figure 5.16 Schematic diagram of the triggering scheme for the PLIF experiments.

events integrated on chip by the ICCD were passed to the PC via the ANALOG OUTPUT #1 of the SR245.

5.7 AIDF Burner, Flow, and Translation

Qualitative PLIF measurements of NO were made in the JQC described in Chapter 2. For that investigation, the JQC chimney was modified to incorporate several 10-cm tall fused-silica wall sections to allow optical access to the combustor interior. Although trace NO levels were detected in the JQC, the geometry of the combustor produced several interfering effects which obscured the fundamental measurement assessment goal. The predominant difficulties associated with the JQC combustor were wall effects and surface scattering. The wall effects were related to the influence of the relatively cool chimney walls on both the base NO signal from the primary combustion, and on thermal-NO production at the IDF front when in contact with a chimney wall. Surface scattering from the entrance and exit chimney walls was imaged along with the fluorescence signal by the ICCD, and back scattering from the exit window provided additional excitation to the NO molecules near that side of the combustor. Although the majority of the surface scattering was masked by appropriate placement of apertures, the effect of the additional excitation resulting from the back scattering had to be corrected for via post processing. These real but rather secondary effects obscured the primary goal of the research which was to assess the quantitative nature of PLIF imaging of NO in an IDF.

To avoid the difficulties associated with PLIF imaging of NO in the JQC, a new axial IDF (AIDF) burner was designed and is shown in Fig. 5.17. The AIDF burner isolates a single IDF which is a fundamental component of the JQC NO reduction scheme. Because the AIDF burner isolated a single IDF within an argon guard, all of the secondary difficulties prominent in the JQC were eliminated. This provided an environment conducive to evaluating the quantitative nature of PLIF measurements of NO in the harsh environment of an IDF.

The AIDF burner consists of a central jet tube surrounded by two annular regions. A flat fuel-rich premixed $C_2H_6/O_2/N_2$ flame was stabilized on the surface of the inner

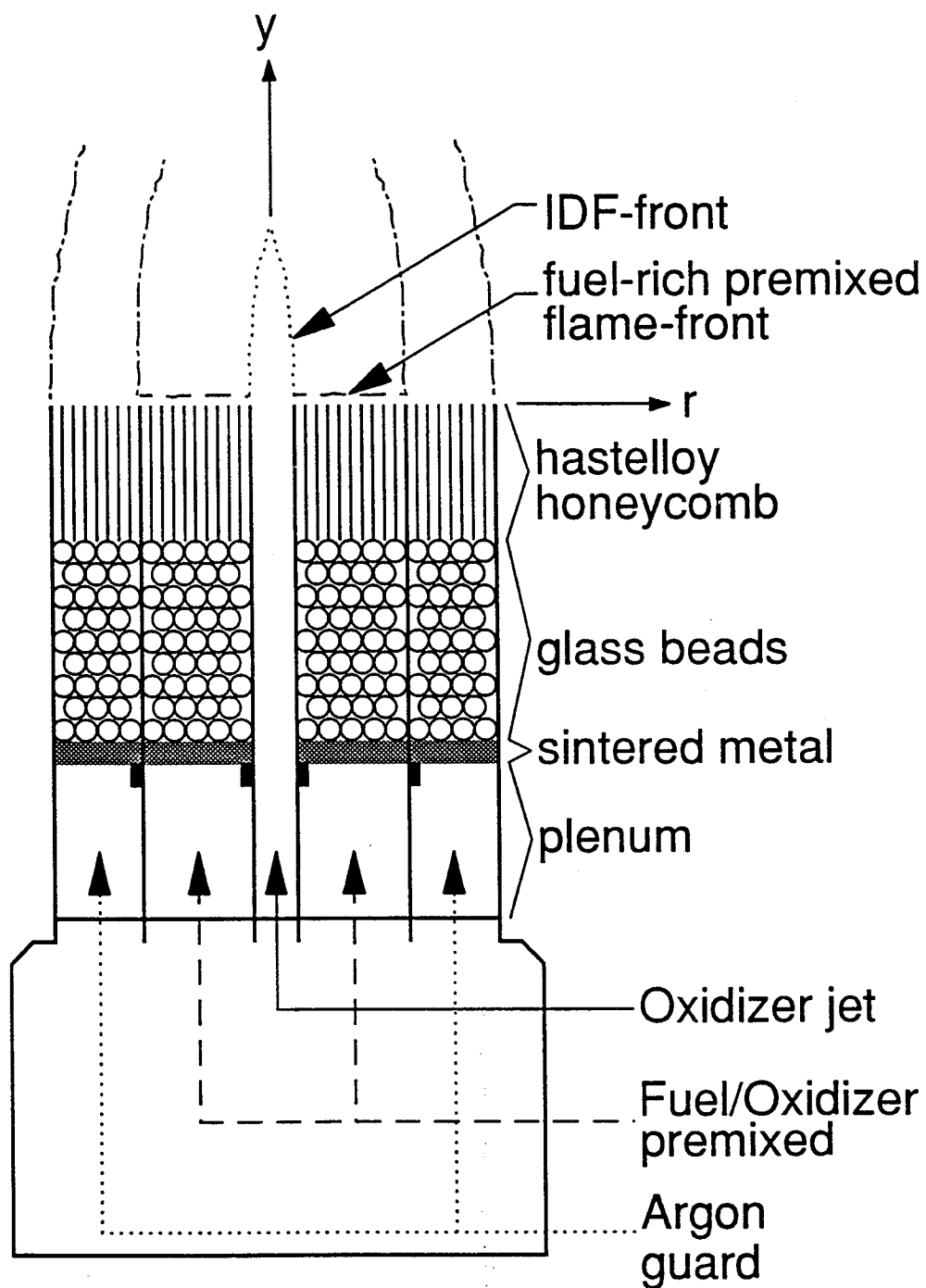


Figure 5.17 Schematic diagram of the AIDF burner.

annular region. This primary combustion was sheathed from the ambient air by an argon guard flowing through the outer annulus. An O_2/N_2 oxidizing mixture flowing through the central tube reacted with the fuel-rich primary combustion products creating a single AIDF. The AIDF burner was constructed of three 304 stainless steel (SS) tubes attached to an SS base using low-temperature silver solder. The inner, middle and outer tubes had outside diameters of 6.35 mm (0.25"), 25.4 mm (1.0"), and 50.8 mm (2.0"), respectively, and wall thicknesses of ~0.838 mm (0.033"), ~0.889 mm (0.035"), and ~2.79 mm (0.110"), respectively. Moreover, the inner diameter of the central tube was tapered at the exit end to provide a smooth transition at the air jet and primary combustion gas interface. An ~24.13 mm (0.95") tall plenum was provided at the base of the AIDF burner tubes to allow circumferential distribution of the gases. This plenum was created by sintered SS annular plugs supported by SS collars attached to the tubes with low-temperature silver solder. The two annular regions were filled with a 38.1 mm (1.5") deep bed of 1.5-mm diameter (model TG-1.5, Cataphote Inc., Jackson, MS) glass beads to insure uniformity of the gas mixture at the burner surface and to guard against burner flashback. In addition, the two annular regions housed ~19 mm (0.75") thick Hastelloy honeycomb (~0.787 mm (0.031") cell diameter, ~0.051 mm (0.002") thick Hastelloy stock; Kentucky Metals, New Albany, IN) sections which rested on the glass-bead bed and were flush with the surface of the AIDF burner. The Hastelloy honeycomb material straightened the annular flows and was able to withstand the high temperatures associated with the primary combustion stabilized just above the inner-annular surface. Moreover, all AIDF burner materials were specified so as to be impervious to the corrosive nature of NO gas (doped into the reactants during the calibration procedure) and to be inert with respect to all reactant gases.

The flows provided to the burner to create the AIDF were carefully chosen so as to match the velocities of the primary reactants and the oxidizing jet. Moreover, the dilution ratio of the oxidizer in the primary reactants was the same as that of the oxidizing jet; its value was also kept as close as possible to that of air so as to closely simulate industrial combustion processes. Attempts were also made to force the primary-combustion equivalence ratio as high as possible in order to make any IDF-front NO

production distinct. However, the stability limitations of the AIDF burner placed constraints on both the oxidizer dilution ratio and the upper equivalence ratio of the primary combustion. The AIDF studied used a dilution ratio of 3.9 and had a primary-combustion equivalence ratio of ~ 1.4 and an overall equivalence ratio of ~ 1.3 . This produced an AIDF whose inner and outer flame fronts, at the AIDF tip, were ~ 9 mm and ~ 13 mm above the burner surface, respectively. In other words, the IDF tip was ~ 4 mm thick and extended from ~ 9 mm to ~ 13 mm above the burner surface. The primary combustion used C_2H_6 , O_2 , and N_2 volumetric flow rates of 0.38, 0.94, and 3.68 SLPM, respectively. The oxidizing jet used O_2 , and N_2 volumetric flow rates of 0.06 and 0.24 SLPM, respectively. The argon guard did not have a matched velocity with the primary combustion reactants; its volumetric flow rate was set based on obtaining a desired guard height. An argon guard volumetric flow rate of 21.4 SLPM was found to reliably guard the AIDF over a distance up to 33 mm above the burner surface.

All gas volume flow rates supplied to the AIDF burner were determined by rotameter (Matheson Gas Products, series E Tube Cubes, Joliet, IL) readings. The individual rotameters were isolated from bottle pressure fluctuations by the bottle regulator and an instrument regulator (Prax Air, formerly Linde, model SG4820-60, Somerset, NJ) connected in series. The individual rotameter tube pressures were set to 50 psig via the appropriate instrument regulators. This regulated rotameter pressure was sufficient to ensure choked flow across the needle valve at the exit of the rotameters. This sonic condition at the needle valve isolated the rotameter tube environment from ambient pressure fluctuations. All rotameters were calibrated using either a dry test meter or a bubble meter (Alltech Associates, model 4047, Deerfield, IL) and converted to standard temperature and pressure conditions.

The AIDF burner was mounted on a custom translation system to provide vertical and radial (i.e., horizontal) translation (y and r directions, respectively, as defined in Fig. 5.17). The translation system was positioned so that the r-translation direction coincided with the axis of the focused laser beam or sheet. The individual translations were driven through stepper motor and gear head assemblies (similar to those described for the PDL and monochromator) coupled to a ball screw and an acme thread for the y- and r-direction

translations, respectively. The translation system provided a maximum translation range of ~200 mm (7.9") in the y direction and ~75 mm (3") in the r direction. The combined gear reduction and 200 step-per-revolution stepper motors provided a minimum translation step of ~0.0013 mm (0.00005") and ~0.0010 mm (0.00004") in the y and r directions, respectively. Translation was coordinated from the data acquisition PC via the modified Stanford Research Systems SR265 software as described in Section 5.5.

CHAPTER 6
EXPERIMENTAL ASSESSMENT OF O₂ INTERFERENCES
ON LIF MEASUREMENTS OF NO
IN HIGH-PRESSURE, LEAN PREMIXED FLAMES
USING NARROW-BAND AND BROAD-BAND DETECTION

In this chapter, we experimentally investigate the influence of O₂ interferences on LIF measurements of NO in lean methane-fueled flames at a range of pressures for both narrow-band and broad-band fluorescence detection. NO excitation schemes are identified which minimize O₂ interferences. The interference spectra, using different NO excitation schemes, are obtained from detection scans. Optimum excitation/detection schemes are then identified for narrow-band detection measurements of NO. To simulate broad-band detection experiments, five different filter combinations are numerically applied to the experimentally obtained detection scans. Filter assessment parameters are developed to judge the effectiveness of the different filtering schemes, and a methodology is established for evaluating broad-band excitation/detection strategies. Based on this work, optimum excitation/detection schemes are identified for broad-band detection measurements of NO.

6.1 Background

Laser-induced fluorescence (LIF) has been demonstrated to be a viable technique for making quantitative nitric oxide (NO) concentration measurements in combustion environments at a range of pressures (Reisel et al., 1993; Reisel and Laurendeau, 1994; Battles et al., 1994). Nitric oxide has a high density spectrum with band origins at approximately 226 nm, 236 nm, 247 nm, and 259 nm for the $\gamma(0,0)$, $\gamma(0,1)$, $\gamma(0,2)$, and

$\gamma(0,3)$ vibrational bands, respectively (Deézsi, 1958; Piper and Cowles, 1986), where the parenthetical band specifications, (v', v'') , indicate the upper and lower vibrational levels of a given band. Typically, for NO fluorescence studies, excitation occurs via a specific rovibronic line in the $\gamma(0,0)$ band followed by detection of the fluorescence from one or more of the higher order bands. Such a detection scheme provides good signal to noise ratio (SNR) by reducing scattering interferences within the $\gamma(0,0)$ band. However, quantitative LIF diagnostics require that we eliminate or account for other measurement interferences, such as secondary species Raman scattering, absorption and fluorescence. We have previously investigated the transportability of a calibration factor for quantitative LIF measurement of NO at high pressures (Reisel et al., 1995). Secondary species interferences are another major issue concerning quantitative LIF measurements and are the subject of this chapter.

The $B^3\Sigma_u^- - X^3\Sigma_g^-$ Schumann-Runge system of O_2 (175-535 nm) (Krupenie, 1972) represents a source of potential interference in NO fluorescence studies because of the density and spectral coincidence of its hot-band spectrum with that of NO. The 'hot-band' terminology has been adopted to refer to spectra that appear only at elevated (i.e., flame) temperatures due to Boltzmann redistribution into the upper vibrational levels of the ground electronic state. The Schumann-Runge system is the strongest band system of O_2 and has received considerable attention in the literature (Krupenie, 1972; Creek and Nicholls, 1975). The structure of the O_2 hot-band fluorescence spectrum consists of distinct features (i.e., obvious lines) with additional broad-band regions characteristic of many-lined spectra (Battles et al., 1994; Krupenie, 1972; Carter and Barlow, 1994). These high density broad-band regions occupy the various spectral regions between the distinct O_2 features. We will refer to these many-lined spectral regions as broad-band regions.

Absorption by the $v''=0$ band progression of the O_2 system, and subsequent predissociation, produces atmospheric opacity below 200 nm (Creek and Nicholls, 1975). At elevated temperatures, such as exist in combustion environments, Boltzmann redistribution populates higher vibrational levels of the ground electronic state of O_2 , hence activating the red-end (200 nm and above) portion of the Schumann-Runge system

(Goldsmith and Anderson, 1986). Spectrally resolved scans of the fluorescence from these O_2 hot bands reveal prominent features throughout the spectral regions occupied by the higher order NO bands normally used for LIF detection of NO (Goldsmith and Anderson, 1986; Wysong et al., 1989). The numerical work of Lee and Hanson (1986) demonstrates the temperature-induced activation of these O_2 hot bands. Their investigation indicates a ten order-of-magnitude increase in the line strengths of the hot bands for a temperature increase from 300 K to 2000 K (Lee and Hanson, 1986). Moreover, because the molecular dynamics of O_2 following excitation are limited by predissociation, any O_2 -originating interferences will be independent of pressure for a given O_2 number density (Wysong et al., 1989; Lee and Hanson, 1986). This characteristic could be particularly problematic for high-pressure NO measurements since, for a given NO number density, the NO fluorescence signal degrades with pressure due to pressure broadening, while that from O_2 interferences would remain constant (Goldsmith and Anderson, 1986). These issues demonstrate the strong potential for O_2 interferences during LIF studies of NO formation in flame environments.

Interference assessments are typically incorporated in fluorescence studies. Reisel et al. (1993) used detection scans with different NO doping conditions to identify potential interferences for their narrow-band LIF measurements of local NO concentration. Potential interferences were identified from N_2 , O_2 , and CO_2 Raman scattering and O_2 fluorescence. These interferences were easily eliminated by appropriate selection of the narrow-band detection bandwidth. Battles et al. (1994) used numerical modeling of the O_2 spectrum to identify an excitation scheme which minimized O_2 interferences for their broad-band PLIF measurements of NO. They chose an excitation scheme which employed five overlapping NO lines in the DC region of the O_2 spectrum as indicated by their synthetic O_2 spectrum generated at 1 atm and 2000 K.

Despite extensive studies of the O_2 spectrum, and investigations to minimize its influence on fluorescence measurements of NO, the interfering effect of O_2 on LIF NO measurements remains a significant concern. This concern arises from the variations in interference potential with changes in flame conditions and experimental configuration. In general, the four environmental and experimental parameters which influence the potential

for O_2 interference in LIF measurements of NO are temperature, pressure, excitation scheme, and broad-band vs. narrow-band detection. For example, Reisel et al. (1993) used narrow-band detection to measure NO in a low-temperature (~ 1700 K) premixed flame above a water-cooled burner. The narrow-band detection scheme provided precise control of the detection bandwidth, thus allowing the rejection of non-resonant interferences. Such interference rejection is more difficult in a broad-band detection scheme due to the degraded spectral selectivity of colored-glass (CG) filters.

In the broad-band work of Battles et al. (1994), some O_2 interference was observed despite use of a multiple-component NO excitation line in the broad-band region of the O_2 spectrum. These investigators used spectrally broad CG filtering (i.e., UG5) in their collection optics and concluded that other filters may be more effective in eliminating interferences. However, no assessment has been published concerning the effectiveness of specific filter combinations. Uncertainty in the anticipated influence of interferences is exacerbated by moving to high-pressure conditions. Here, the spectral modeling is less reliable and the potential exists for the appearance of new interference lines due to the onset of significant rotational (RET) or vibrational (VET) energy transfer (Allen, 1994).

In this chapter, we address the influence of O_2 interferences on LIF measurements of NO in high-temperature flames from 1 to 9 atm using different excitation and detection schemes. Uncooled fuel-lean flames were investigated as a worst case scenario since they maximize the O_2 hot band activation and provide an abundance of O_2 . Based on these results, optimum excitation and detection schemes are specified for LSF and PLIF measurements of NO.

6.2 Experimental Apparatus

The UV radiation required for NO and O_2 excitation in this study was generated using a Quanta-Ray DCR-3G Nd:YAG laser, a PDL-2 dye laser, and a WEX-1 wavelength extender. The second harmonic of the Nd:YAG-laser fundamental was used to pump the PDL-2, which was configured for longitudinal amplifier pumping and operated without the optional preamplifier. A dye mixture of R-590 perchlorate and R-610 perchlorate was used in both the oscillator and amplifier to generate visible radiation

at approximately 574 nm. The dye laser fundamental was frequency doubled and subsequently sum frequency mixed with the residual Nd:YAG fundamental (1064 nm), using two separate KD*P crystals, to produce the requisite UV radiation (~226 nm). The four concentric beams (1064, 574, 287, 226 nm) were dispersed using a Pellin-Broca prism. For these experiments, we typically generated mixed-beam energies of approximately 1 mJ/pulse.

A schematic of the optical system, excluding the laser system, is shown in Fig. 6.1. After exiting the WEX, small portions of the beam were twice split off and directed to UV-sensitive photodiodes (Hamamatsu S1722-02 UV). The first photodiode (PD:A) was used to trigger the detection electronics and the second (PD:B) was used to monitor the laser energy. A 1000-mm focal-length lens was used to focus the beam over the burner, producing a waist diameter of ~250 μm . The beam passed through a diaphragm aperture prior to the burner to minimize forward propagation of surface scattering.

The burner was housed in a high-pressure combustion facility consisting of a stainless-steel high-pressure vessel, a PC-interfaced mass-flow-control system for gas metering, and a PC-interfaced 2-D burner translation system to provide movement in a plane perpendicular to the direction of beam propagation. The high-pressure combustion facility has been described thoroughly elsewhere (Carter et al., 1989).

The narrow-band detection system consisted of the collection optics, a $\frac{1}{2}$ -m monochromator, and a photomultiplier tube (PMT). Fluorescence was collected normal to the laser beam and collimated by a 200-mm focal-length, fused-silica lens. A mirror system was used to rotate the image of the laser beam parallel to the vertical entrance slit of the monochromator. A 300-mm focal-length, fused-silica lens focused the collimated and rotated fluorescence onto the entrance slit of the monochromator. The $\frac{1}{2}$ -m monochromator was operated in first order using a 1200 line/mm grating blazed at 250 nm. The radiation passing through the exit slit was detected by an RCA 1P28B PMT. A custom PMT voltage divider was used that has been optimized for temporal resolution of the fluorescence signal (Harris, 1976).

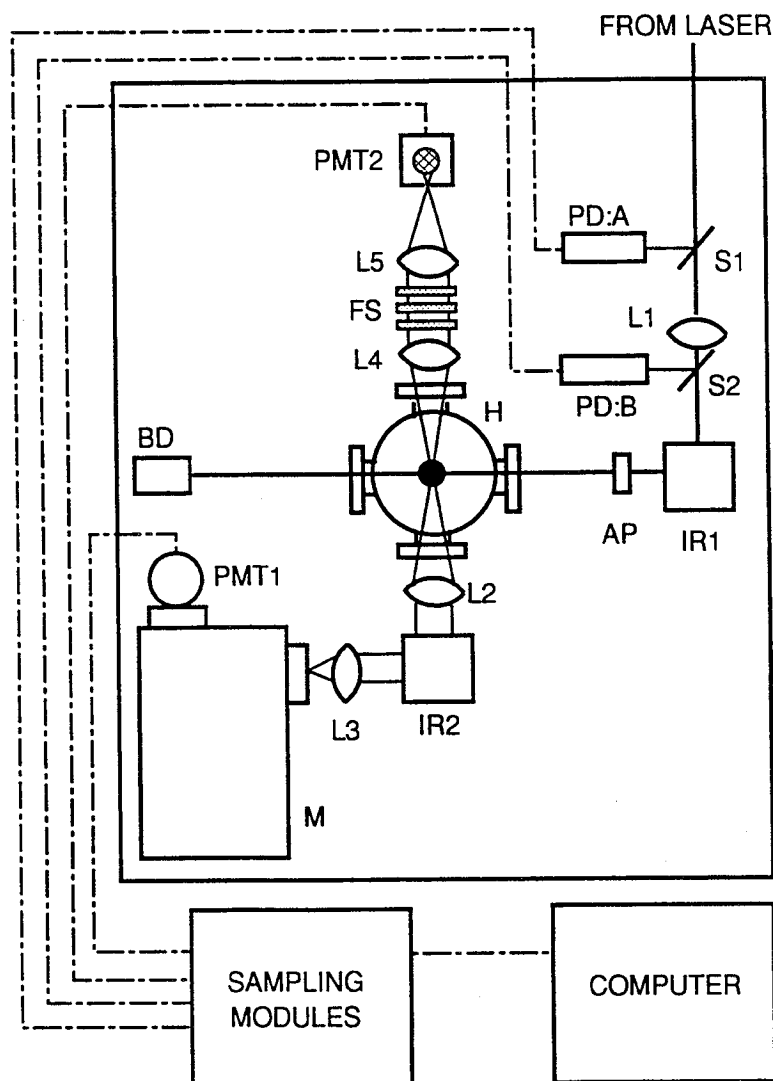


Figure 6.1 Schematic of the optical setup. The laser is directed to the probe volume using lens L1, image rotator IR1, aperture AP, and steered to a beam dump BD following the probe volume. Splitter plates S1 and S2 are used with photodiodes PD:A and PD:B to monitor the laser energy. The burner is housed in the high-pressure vessel H. The narrow-band detection system consists of lenses L2 and L3, an image rotator IR2, a 0.5 m monochromator M and a photomultiplier tube PMT1. The broad-band detection system consists of lenses L4 and L5, a filter stack FS for spectral filtering, and a slit/PMT assembly PMT2. Signals from the photon converting devices are monitored by PC interfaced sampling modules.

The broad-band detection system consisted of the collection optics, including any CG or neutral-density (ND) filters, a slit assembly and a PMT. Fluorescence was collected normal to the laser beam and directly opposite the narrow-band collection optics, and collimated by a 100-mm focal-length, fused-silica lens. When used, the CG or ND filters were inserted in the collimated fluorescence beam following the collection lens. The filtered fluorescence was focused onto a horizontally oriented slit assembly ($\sim 120\text{ }\mu\text{m}$) using a 100-mm focal-length, fused-silica lens. The radiation detector following the slit assembly consisted of an Oriel 70680 PMT housing, an RCA 1P28B PMT, and a Hamamatsu E717-21 voltage-divider circuit.

During detection scans from the $\text{CH}_4/\text{O}_2/\text{N}_2$ flames, the broad-band detection system was used to monitor and correct for any PDL drift. This was not possible in argon-diluted flames since the $\text{CH}_4/\text{O}_2/\text{Ar}$ flames produced no NO. During detection scans from $\text{CH}_4/\text{O}_2/\text{Ar}$ flames, the broad-band detection system was used in conjunction with an atmospheric-pressure reference flame to monitor and correct for any PDL drift. The atmospheric pressure reference flame used a small Méker burner supplied with natural gas. NO in this reference flame was excited using the unfocused UV mixed beam exiting the high-pressure vessel. Pressure shifting caused the central position of the NO excitation line in the high-pressure flame to be different from that in the atmospheric-pressure reference flame. Hence, when the laser radiation is spectrally aligned with a specific NO line at high-pressure, it will be at a specific location in the spectral wing of the same NO line at atmospheric pressure. Therefore, to lock the laser to the high-pressure NO line, we actively tuned the PDL so as to maintain a specific signal from the reference flame which was a specific fraction of the signal level at the peak of the NO line in the same flame. Ideally, the reference flame should be in a separate high-pressure vessel at the same pressure as that of the flame of interest. However, we found, through separate experimental investigations, that this indirect line-locking scheme was effective for monitoring and correcting any drift in the laser wavelength.

The signals from the laser-power monitoring photodiode as well as the broad-band and narrow-band PMTs were sampled using equipment purchased from Stanford Research Systems. SR250 gated integrators/boxcar averagers were used to integrate and average

the signals from the photodiode and the broad-band PMT. The narrow-band PMT signal was integrated using an SR255 fast sampler configured for a 500-ps gate, which was centered on the temporal peak of the fluorescence pulse using an SR200 gate scanner. This integrated narrow-band PMT signal was subsequently processed by a separate SR250 unit operating with a DC filter to allow averaging over consecutive fluorescence events. For all results reported here, the signals were averaged over 30 events. The three output voltages were digitized and stored for analysis on a PC via use of the SR245 computer interface module and the SR265 software package.

A custom 25-mm diameter burner with an 11-mm wide circumferential guard flow, manufactured by McKenna Products, Inc. (Pittsburgh, CA), was used throughout this study. This burner was described by Carter et al. (1989), but here the water-cooled burner section was replaced with an uncooled burner section. To accommodate the high burner surface temperatures associated with uncooled combustion, a porous alumina plug (65 pores per inch, 92% Al_2O_3 , 23-mm OD x 25-mm thick, with patented edge coat; Hi-Tech Ceramics Inc., Alfred, NY) was installed in the center 25-mm burner section. Mass flow controllers were used for gas metering. Stable $\text{CH}_4/\text{O}_2/\text{N}_2$ flat flames were obtained for the equivalence ratio range $0.63 \leq \phi \leq 0.66$ at pressures of 1 to 9 atm. Stable $\text{CH}_4/\text{O}_2/\text{Ar}$ flat flames were obtained for $0.54 \leq \phi \leq 0.55$ at pressures of 1 to 6 atm.

6.3 Selection of NO Excitation Line

At flame temperatures, the hot bands of the Schumann-Runge O_2 system display lines throughout the $\gamma(0,0)$ band of NO. This makes $\gamma(0,0)$ band excitation of NO without some degree of O_2 excitation difficult. The NO excitation scheme must be carefully selected so as to minimize O_2 excitation and therefore interference potential. Gross O_2 excitation may be avoided by exciting an NO line which is not resonant with a distinct O_2 feature. Unfortunately, the broad-band O_2 background extends throughout the $\gamma(0,0)$ band of NO, thus making some degree of O_2 excitation unavoidable regardless of line selection. The best one can do is to excite NO in the broad-band region of the O_2 spectrum between the distinct O_2 lines. The minimal O_2 interference resulting from such an optimal excitation scheme may then be subtracted off as a constant background (Battles

et al., 1994). This was the primary excitation-scheme criterion relative to minimization of interferences. Additional criteria imposed on NO excitation line selection were that the rovibronic line should be unique, isolated (i.e., no other lines within $\sim 1 \text{ cm}^{-1}$ at atmospheric pressure), and should also have a relatively temperature-insensitive Boltzmann fraction (Reisel et al., 1995).

Two NO lines were selected which satisfied the above criteria. To identify optimum lines for NO excitation, three general broad-band regions of the O_2 spectrum within the NO $\gamma(0,0)$ band were identified based on the work of Battles et al. (1994). These broad-band regions were in the spectral ranges 44318.38 cm^{-1} to 44305.62 cm^{-1} , 44251.70 cm^{-1} to 44228.22 cm^{-1} , and 44202.80 cm^{-1} to 44182.30 cm^{-1} . The specific NO lines within these O_2 broad-band regions were then identified using the tabulated data of Reisel et al. (1992). Lines with $15.5 \leq J'' \leq 30.5$ were favored since they are most likely to exhibit temperature insensitivity at typical flame temperatures. A synthetic spectrum program by Seitzman (1991) was used to generate the NO spectrum at 1750 K in the three broad-band regions. Based on this information, we identified five candidate NO lines, $P_2(23.5)$, $Q_2(16.5)$, $R_1(15.5)$, $Q_2(25.5)$ and $Q_2(26.5)$. The spectroscopic notation used to describe the NO lines is consistent with that described by Reisel et al. (1992). The $Q_2(26.5)$ line has been used in our previous LIF measurements of NO (Reisel et al., 1993; Reisel and Laurendeau, 1994). Figure 6.2 shows the variation in Boltzmann fraction from 1000 K to 2400 K for the five candidate lines. Clearly, the $Q_2(25.5)$ and the $Q_2(26.5)$ lines are the most temperature insensitive. Moreover, the Einstein B coefficients for the Q_2 lines are approximately twice those of the R_1 and P_2 lines (Reisel et al., 1992).

Excitation scans in lean $\text{CH}_4/\text{O}_2/\text{Ar}$ flames were taken over the spectral region covering the $Q_2(25.5)$ and the $Q_2(26.5)$ lines to verify that these selected NO excitation lines were within the broad-band regions of the O_2 spectrum. Both lines were found to reside in such regions, although this had not been obvious for the $Q_2(26.5)$ line from the numerical work of Battles et al. (1994). Based on these findings, we considered both $Q_2(25.5)$ and $Q_2(26.5)$ excitation of NO in the present study of O_2 interferences.

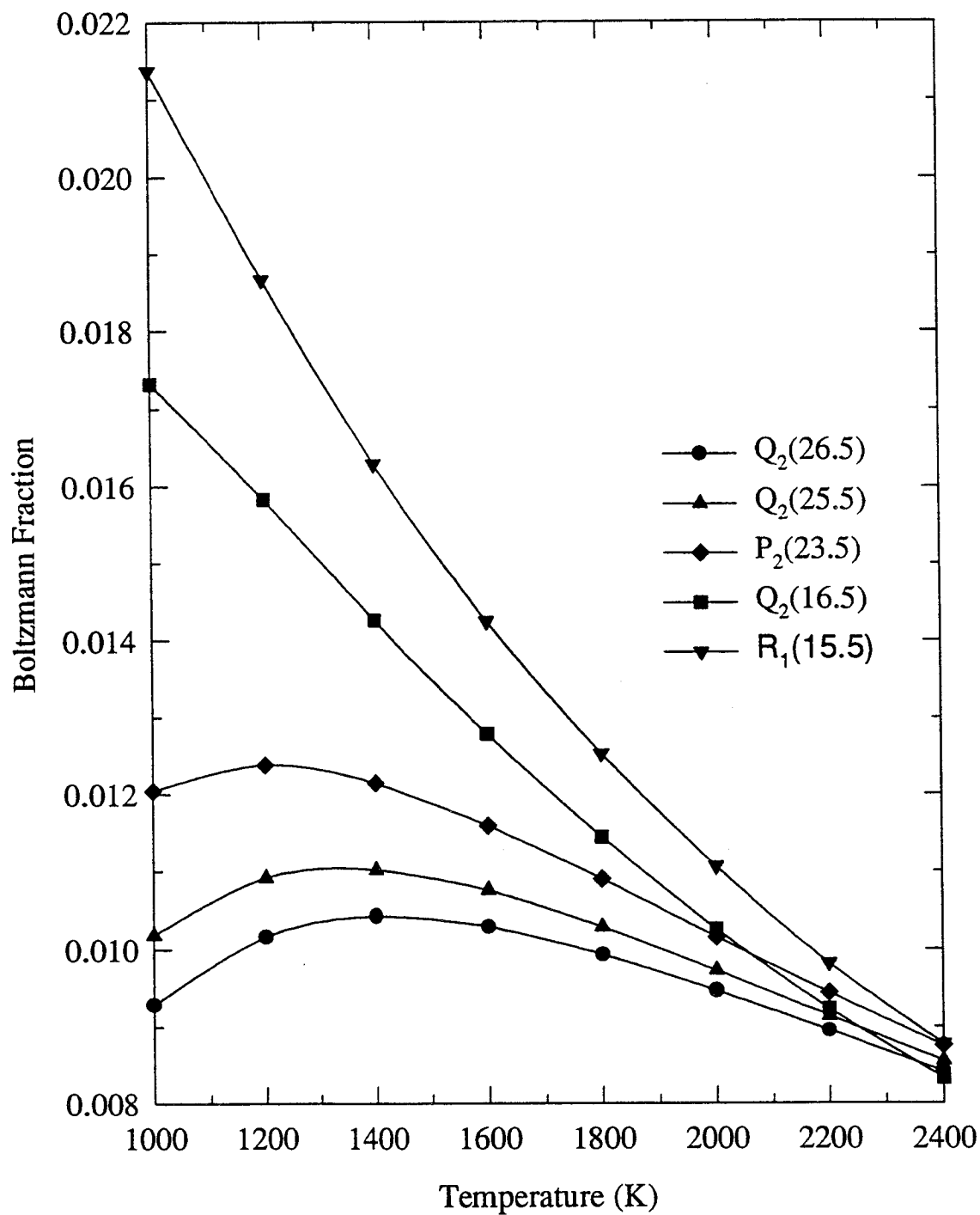


Figure 6.2 Temperature dependence of the Boltzmann fraction for candidate NO excitation lines.

6.4 Excitation Spectra

6.4.1 Experiments and Results

We have obtained excitation scans in $\text{CH}_4/\text{O}_2/\text{N}_2$ (nitrogen-diluted) and $\text{CH}_4/\text{O}_2/\text{Ar}$ (argon-diluted) flames over a range of pressures using both narrow-band and broad-band detection. The equivalence ratios (ϕ) of the nitrogen- and argon-diluted flames investigated were approximately 0.65 and 0.55, respectively. All flames used a dilution ratio of 3.76 and produced flame temperatures of approximately 100 K below the adiabatic flame temperature. Nitrogen-diluted flames were investigated at pressures of 1.0, 3.05, 6.1, and 9.15 atm. The argon-diluted flames were investigated at pressures of only 1.0, 3.05, and 6.1 atm due to flame stability limitations. For narrow-band detection, the monochromator was configured for an entrance slit of 120 μm x 10 mm (width x height) and an exit-slit width of 2.4 mm. This corresponds to a spectral bandwidth of ~ 3 nm, which was centered on the $\gamma(0,1)$ band of NO. The broad-band detection system used a 120- μm slit, 10 mm of UG5 CG filter and sufficient ND filtering to prevent saturation of the PMT. The excitation scans of the nitrogen-diluted flames using narrow-band and broad-band detection are shown in Figs. 6.3 and 6.4, respectively. The excitation scans of the argon-diluted flames using narrow-band and broad-band detection are shown in Figs. 6.5 and 6.6, respectively.

6.4.2 Spectral Identification

Several features of the NO and interference spectra are readily identifiable. The positions of the $\text{Q}_2(25.5)$ and $\text{Q}_2(26.5)$ NO lines are indicated in the excitation scans. These NO features are apparent in Figs. 6.3a and 6.4a, as is the remainder of the hot NO spectrum in the scanned region of Figs. 6.3a-6.3d. The distinct features at 225.53 nm in Figs. 6.5a-6.5c appear to be two resolved components of the $\text{P}^{0,3}(25)$ triplet lines of O_2 (Reisel et al., 1993; Wysong et al., 1989). In the spectroscopic notation used to describe the O_2 lines, the letter describes the branch (P or R), the superscript specifies the upper and lower vibrational levels involved (v', v''), and the parenthetical number specifies the lower level rotational quantum number (N''). The prominent features in the excitation scans using broad-band detection, Figs. 6.4 and 6.6, have been identified as the $\text{R}^{2,4}(23)$

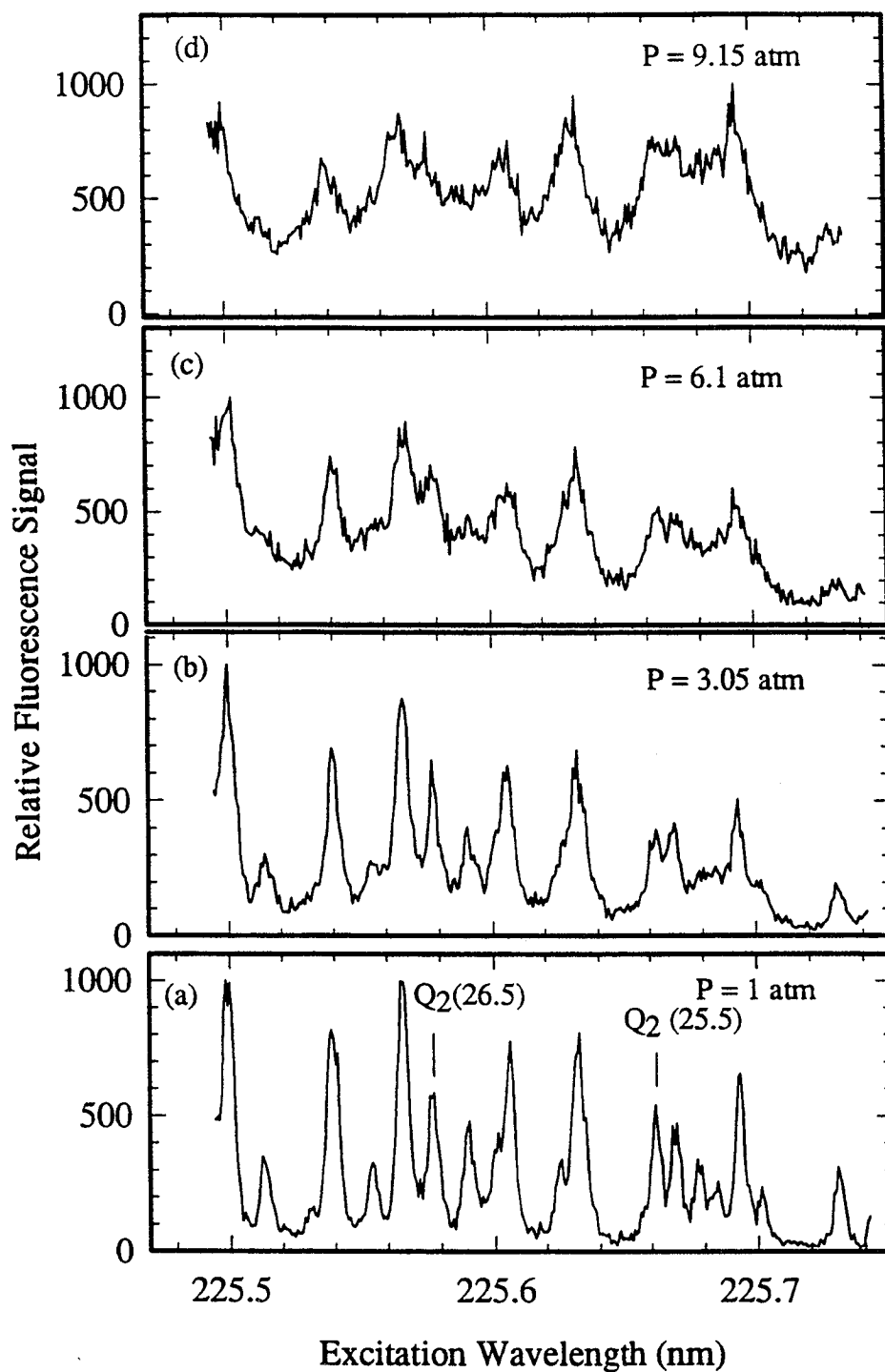


Figure 6.3 Excitation scans in a $\text{CH}_4/\text{O}_2/\text{N}_2$ flame at (a) 1.0 atm, (b) 3.05 atm, (c) 6.1 atm, and (d) 9.15 atm using narrow-band detection.

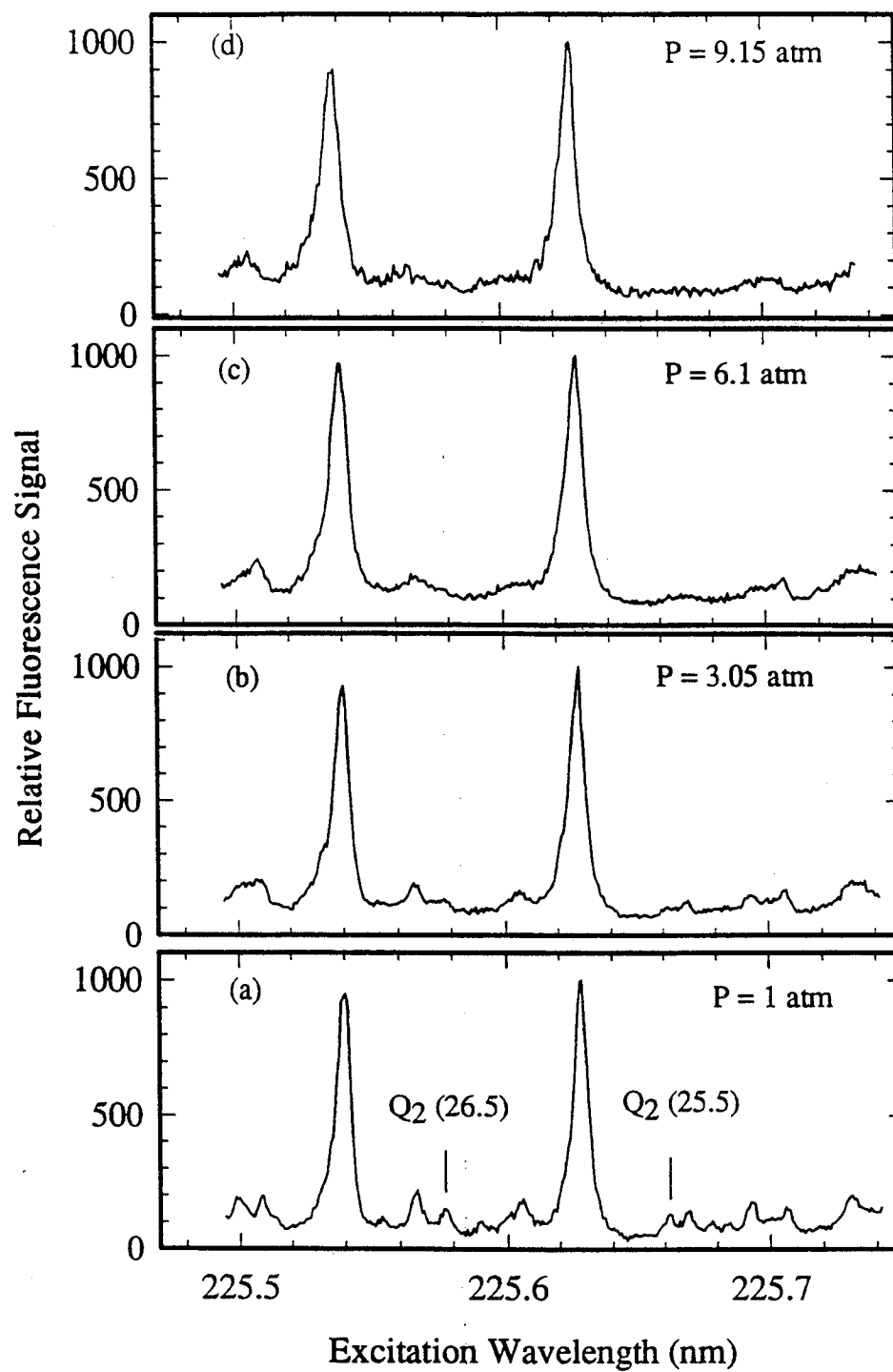


Figure 6.4 Excitation scans in a $\text{CH}_4/\text{O}_2/\text{N}_2$ flame at (a) 1.0 atm, (b) 3.05 atm, (c) 6.1 atm, and (d) 9.15 atm using broad-band detection.

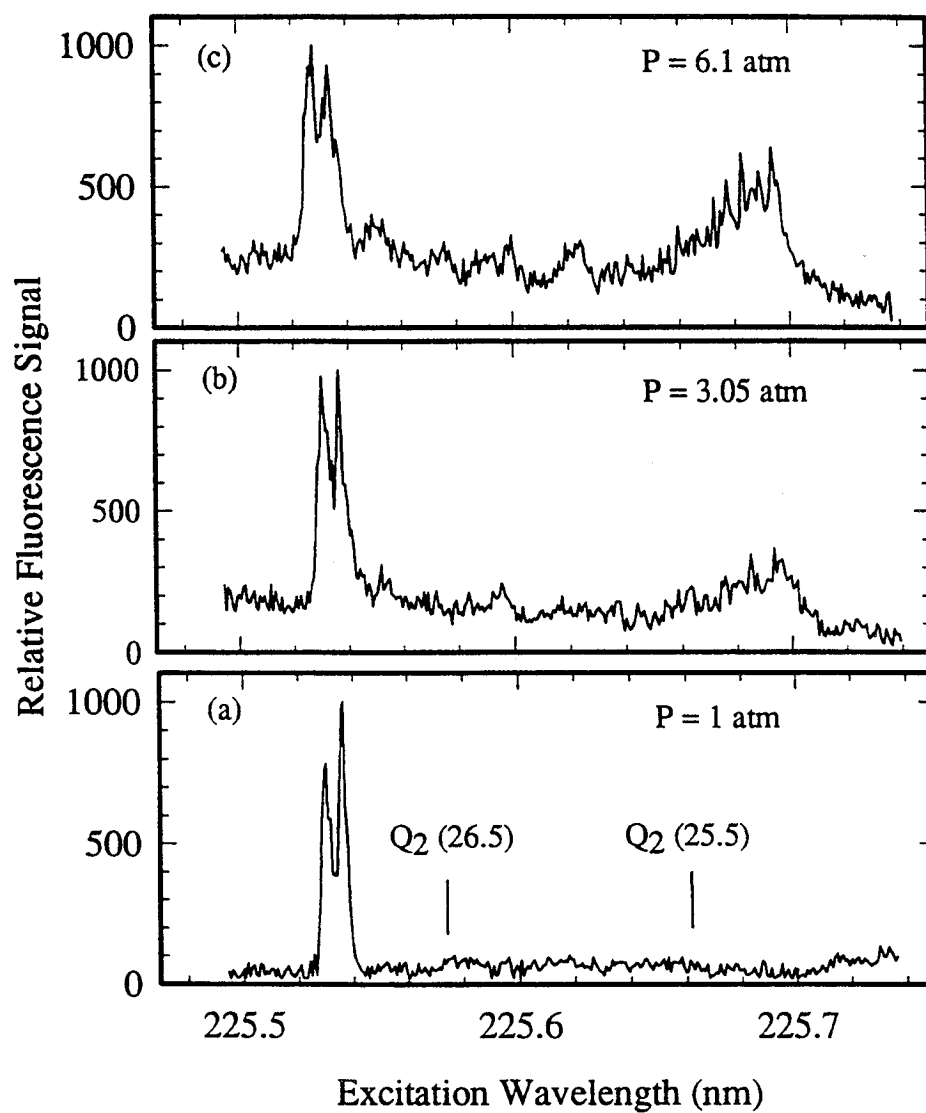


Figure 6.5 Excitation scans in a $\text{CH}_4/\text{O}_2/\text{Ar}$ flame at (a) 1.0 atm, (b) 3.05 atm, and (c) 6.1 atm using narrow-band detection.

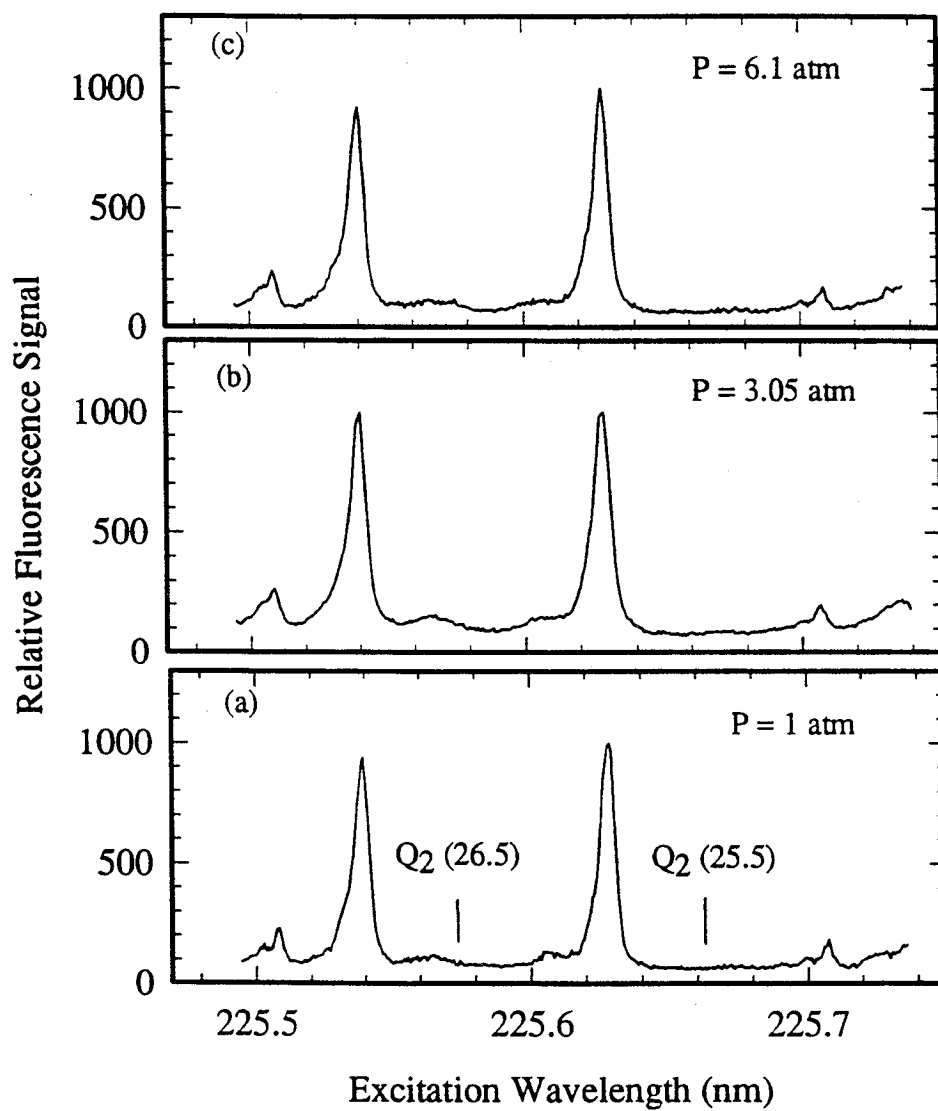


Figure 6.6 Excitation scans in a $\text{CH}_4/\text{O}_2/\text{Ar}$ flame at (a) 1.0 atm, (b) 3.05 atm, and (c) 6.1 atm using broad-band detection.

and $P^{2,4}(21)$ lines of O_2 (Wysong et al., 1989). The line positions of these and other O_2 features encountered in this study are tabulated in Table 6.1. These features are not observed with narrow-band detection.

6.4.3 Observations for Narrow-Band Detection

The NO lines in Fig. 6.3 display the expected influence of pressure broadening. Figure 6.5 indicates a similar positive scaling of the broad-band interference background with pressure. This interference is at least partially due to the broad-band region of the O_2 spectrum. The pressure dependence of the broad-band interference background is not a practical problem since LIF measurement parameters (e.g., calibration factors) are typically not transportable with changes in pressure (Reisel et al., 1995). Based on the results at 1 atm (Fig. 6.5a), the $Q_2(25.5)$ and $Q_2(26.5)$ NO lines both appear to reside in a broad-band portion of the interference spectrum. However, at higher pressures, Fig. 6.5 shows a relatively unstructured blue-shaded interference feature around 225.69 nm, whose magnitude apparently scales with pressure. This feature is likely to be problematic with a $Q_2(25.5)$ NO excitation scheme because it blends into this NO line at higher pressures. In contrast, the $Q_2(26.5)$ line resides in the broad-band region of the interference spectrum at all pressures investigated. Figure 6.3 demonstrates that, although they are evident in Fig. 6.5, the most prominent interference features are much weaker than the NO lines of interest.

6.4.4 Observations for Broad-Band Detection

Figure 6.6 indicates that, with broad-band detection, the broad-band region of the interference spectrum is independent of pressure. This interference region is again at least partially due to the broad-band portion of the O_2 spectrum. Figure 6.6 does not show the relatively unstructured feature that appears at higher pressures in Fig. 6.5. Apparently, this feature has been engulfed in the larger background of the broad-band detection system. Figure 6.4 indicates that for broad-band detection, the $Q_2(25.5)$ and $Q_2(26.5)$ NO lines are in the broad-band region of the interference spectrum at all observed pressures. This figure also clearly demonstrates the particular difficulties associated with

Table 6.1 Line positions in nanometers of the different O₂ lines encountered either in absorption or emission. The O₂ line specification notation is as described by Wysong et al. (1989). The R^{2,4}(23) and P^{2,4}(21) lines are apparent in the excitation scans using broad-band detection. The R^{4,4}(51) and R^{4,5}(15) lines are the O₂ excitation pathways which produce potential interferences with Q₂(25.5) excitation of NO, as is the R^{4,5}(13) line for Q₂(26.5) excitation of NO. However, these three O₂ lines are not apparent in the excitation scans. All other O₂ line positions listed are apparent in the detection scans of Figs. 6.7, 6.8, or 6.9.

O ₂ Line	Line position (nm)					
	n" = 4	n" = 5	n" = 6	n" = 7	n" = 8	n" = 9
R ^{2,n"} (23)	225.54					
P ^{2,n"} (21)	225.62	233.29	241.36	249.87	258.85	
R ^{2,n"} (19)		232.69	240.72	249.19	258.13	
R ^{4,n"} (13)		225.56	233.12	241.08	249.45	258.27
P ^{4,n"} (15)			233.55	241.53	249.93	258.78
R ^{4,n"} (51)	225.67	233.15	241.01	249.29	257.99	
P ^{4,n"} (53)		234.68	242.63	251.00	259.80	
R ^{4,n"} (15)		225.73	233.29	241.26	249.64	258.46
P ^{4,n"} (17)			233.78	241.77	250.18	259.04

interferences which have predissociative-limited dynamics. The major lines of the NO spectrum are clearly apparent above the interference background at 1 atm in Fig. 6.4a. However, as the pressure increases, the NO spectrum broadens and ultimately drops below the interference background.

Although the NO spectrum is not apparent at 6.1 and 9.15 atm in Fig. 6.4, this does not indicate that LIF measurements of NO at high pressures are impossible using broad-band detection. LIF measurements of NO up to 10 atm have been made elsewhere (Battles et al., 1994). If a lower laser power had been used to generate the excitation scans of Fig. 6.4, larger NO signal-to-interference ratios would probably have been attained (Reisel et al., 1993). At laser powers above that required to saturate NO, the NO fluorescence signal reaches a plateau and no longer increases with laser power. However, because the O₂ dynamics are limited by predissociation, interference from O₂ continues to increase with laser power. This effect is detrimental to the measurement SNR and should be given appropriate attention when designing the excitation scheme (Reisel et al., 1993; Carter 1994). Although some degree of saturation no doubt exists for our detection scans, these data are completely adequate for the present study.

6.5 Emission Spectra

6.5.1 Experiments and Results

We have obtained detection scans to characterize the emission spectra from nitrogen- and argon-diluted flames at 1 and 6.1 atm using both Q₂(25.5) and Q₂(26.5) excitation. The equivalence ratios of the nitrogen- and argon-diluted flames investigated were approximately 0.65 and 0.55, respectively, and a dilution ratio of 3.76 was used throughout. The detection scans covered the spectral range 232.5 nm to 266.1 nm in steps of 0.033 nm/bin, and hence incorporated the $\gamma(0,1)$, $\gamma(0,2)$, and $\gamma(0,3)$ bands of NO. The monochromator was operated in first order with an entrance slit of 120 μm x 20 mm and an exit slit width of 120 μm . The detection scans using the two excitation schemes in nitrogen- and argon-diluted flames are shown in Figs. 6.7 and 6.8, respectively.

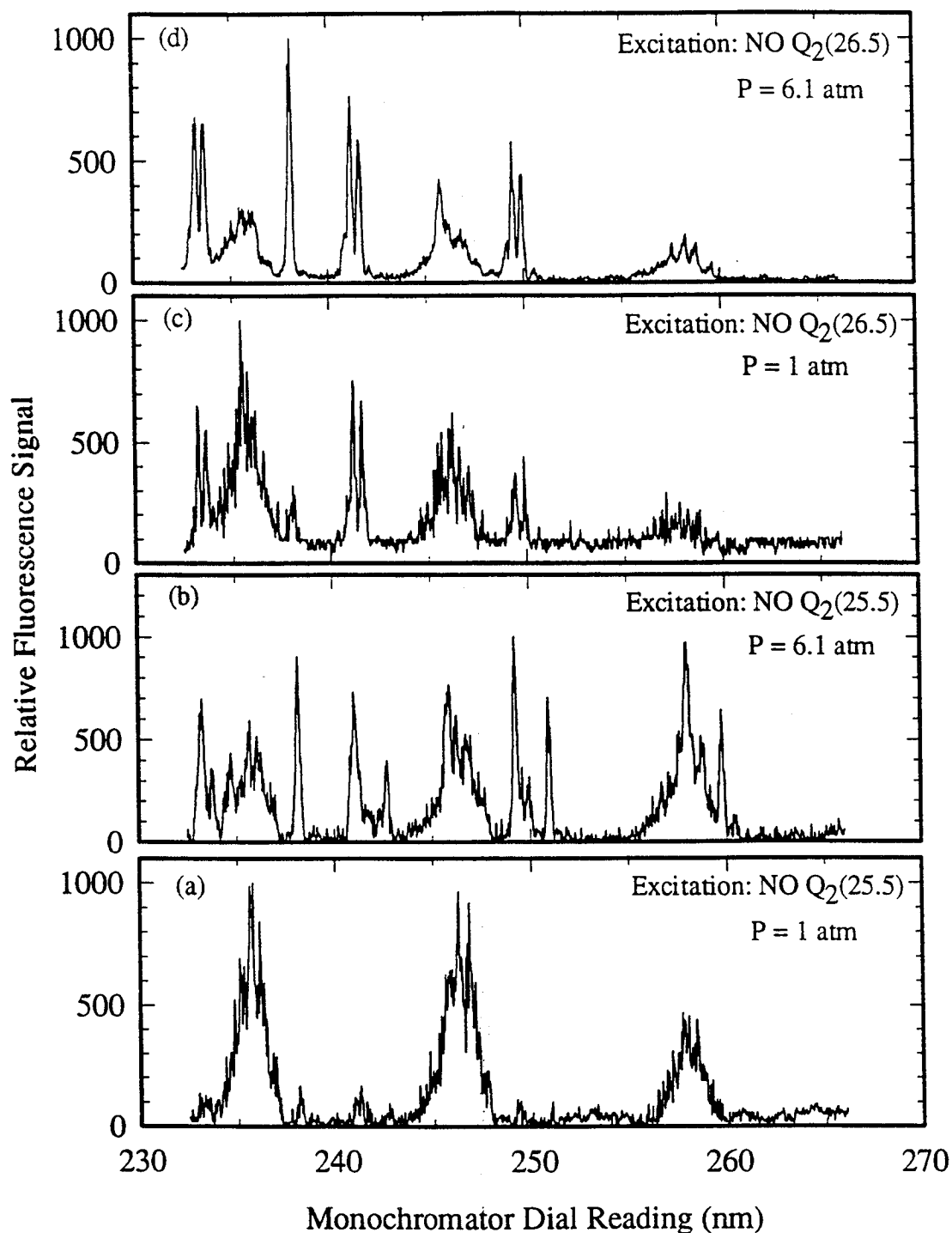


Figure 6.7 Detection scans in a CH₄/O₂/N₂ flame using the two candidate excitation schemes: Q₂(25.5) excitation at (a) 1.0 atm and (b) 6.1 atm; Q₂(26.5) excitation at (c) 1.0 atm and (d) 6.1 atm.

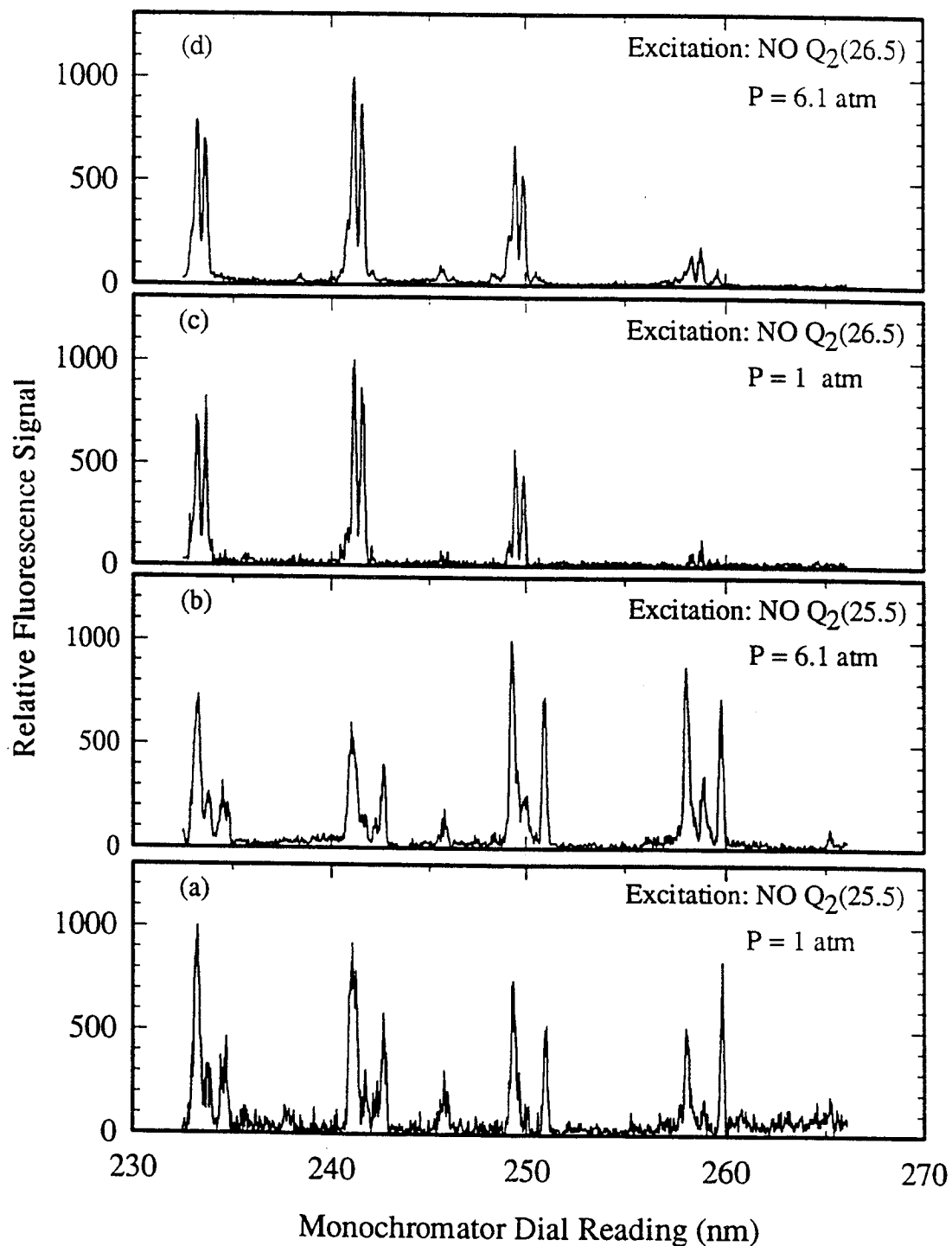


Figure 6.8 Detection scans in a $\text{CH}_4/\text{O}_2/\text{Ar}$ flame using the two candidate excitation schemes: $\text{Q}_2(25.5)$ excitation at (a) 1.0 atm and (b) 6.1 atm; $\text{Q}_2(26.5)$ excitation at (c) 1.0 atm and (d) 6.1 atm.

6.5.2 Spectral Identification

Before attempting to identify the interference spectra of Figs. 6.7 and 6.8, we performed experiments to characterize the behavior of the O_2 excitation and fluorescence process. Figure 6.9 is a detection scan in a nitrogen-diluted flame at 1 atm for direct excitation of the $P^{2,4}(21)$ transition of O_2 . Clearly, a line of the $\gamma(0,0)$ band of the high-density NO spectrum was also excited as evident from the observation of the $\gamma(0,1)$, $\gamma(0,2)$ and $\gamma(0,3)$ bands of NO in Fig. 6.9. This detection scan also reveals four sets of paired interferences which increase in magnitude with wavelength over the spectral region investigated. The magnitudes of the paired interferences approximately scale with those of the Franck-Condon factors (Albritton, 1972) for the $v'=2$ band system of O_2 . The paired nature of the interferences reflects the P and R splitting which is characteristic of O_2 (Herzberg, 1989). The appearance of individual P and R lines, rather than broader P and R manifolds, provides experimental validation that RET, and hence VET, is insignificant at 1 atm for $v'=2$ (Andresen, 1988). Since RET does not occur in O_2 , the spectroscopic selection rules ($N'=N''-1$ in the P branch, and $N'=N''+1$ in the R branch) mandate observation of the $P^{2,v''}(21)$ and $R^{2,v''}(19)$ lines for $v''>4$ in Fig. 6.9. In fact, the line positions observed in Fig. 6.9 match those of the predicted lines for $v''=5, 6, 7$, and 8 , based on a numerical spectrum simulation as listed in Table 6.1 (Creek and Nicholls, 1975).

The techniques outlined above were used to identify O_2 interferences observed in the detection scans with NO $Q_2(25.5)$ and $Q_2(26.5)$ excitation. Specifically, the paired-interference distribution provides clues to the actual band progression via comparison to tabulated Franck-Condon factors (Albritton, 1972). Moreover, the fact that RET does not occur in the excited state of O_2 greatly limits the pool of attributable transitions. If a $P^{v,v''}(N'')$ line of O_2 is excited, only $P^{v,v''+j}(N'')$ and $R^{v,v''+j}(N''-2)$ lines with $j=1,2,3,\dots$ will be observed; similarly, if an $R^{v,v''}(N'')$ line of O_2 is excited, only $P^{v,v''+j}(N''+2)$ and $R^{v,v''+j}(N'')$ lines with $j=1,2,3,\dots$ will be observed. For a given NO excitation scheme, candidate O_2 excitation lines may be identified by proximity to the excitation wavelength based on the numerical spectrum simulation for O_2 . Each candidate O_2 excitation line may be evaluated by comparing the line positions of the predicted emission spectrum, as governed by the

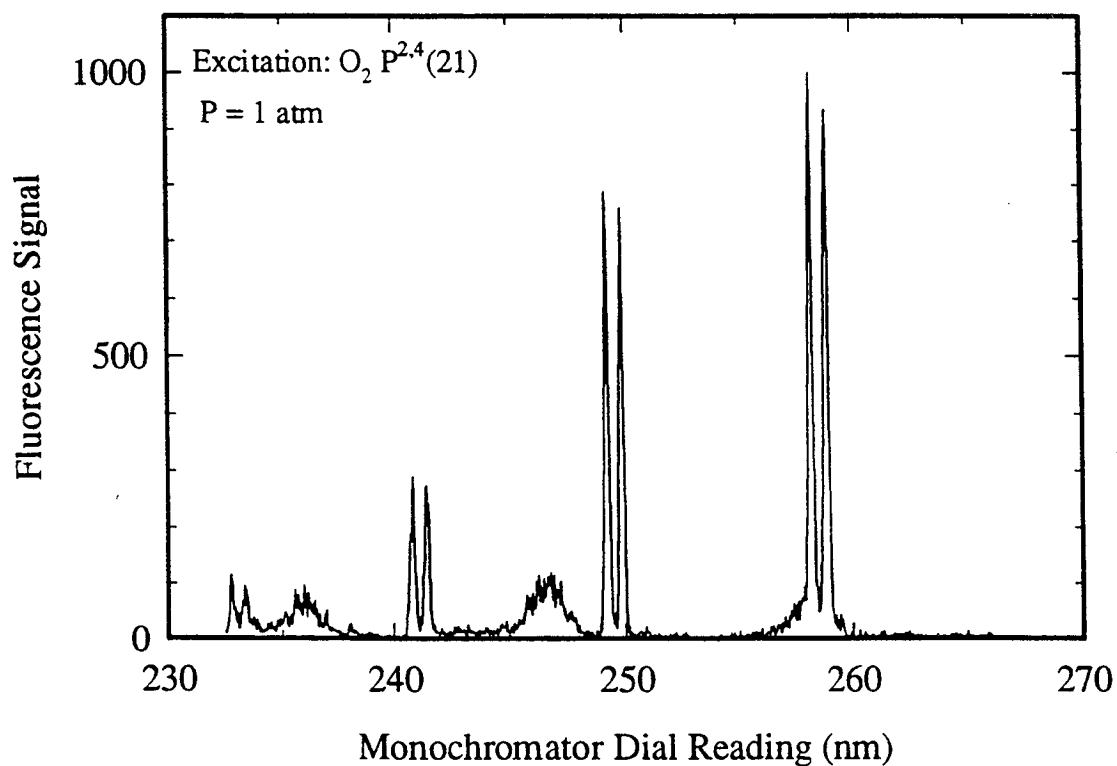


Figure 6.9 Detection scan in a CH₄/O₂/N₂ flame using O₂ P^{2,4}(21) excitation at 1.0 atm. The O₂ line positions observed in emission match those predicted based on the spectroscopic selection rules and insignificant RET in the excited state.

above rules and indicated by the spectrum simulation, to the actual interference spectrum observed in the detection scans for the specific excitation scheme. The relevant O_2 lines can then be identified by experimental and numerical coincidence in both the absorption and emission spectra.

The detection scans in Figs. 6.7 and 6.8 are presented on a relative fluorescence basis by normalizing the peak signal to 1000. The $\gamma(0,1)$, $\gamma(0,2)$, and $\gamma(0,3)$ bands of NO are readily apparent in Figs. 6.7a-6.7d at approximately 236, 246, and 258 nm, respectively. A strong N_2 Stokes Raman scattering signal is observed at ~ 238 nm (Eckbreth, 1988) in the nitrogen-flame detection scans of Fig. 6.7. This N_2 Raman signal was used to spectrally calibrate the individual detection scans using the excitation-specific Raman line position. Other Raman scattering lines observed are H_2O at ~ 246 nm (evident in Figs. 6.7b, 6.7d, 6.8a and 6.8b) and O_2 at ~ 234 nm (evident in Figs. 6.7b, 6.8a, and 6.8b). Notice that the H_2O Raman line resides within the $\gamma(0,2)$ band of NO. The remaining lines, most evident in Fig. 6.8, are due to O_2 fluorescence. The most prominent interferences resulting from $Q_2(25.5)$ excitation (Figs. 6.8a and 6.8b) are due to O_2 fluorescence in the $v'=4$ band progression activated through excitation of the $O_2 R^{4,4}(51)$ line (see Table 6.1). The interferences resulting from $Q_2(26.5)$ excitation (Figs. 6.8c and 6.8d) are due to O_2 fluorescence in the $v'=4$ band progression activated through excitation of the $O_2 R^{4,5}(13)$ line (see Table 6.1). The smaller interference features in Figs. 6.8a and 6.8b (@ 233.8, 241.7, 250.1, and 259.0 nm) are probably from O_2 fluorescence in the $v'=4$ band progression activated through excitation of the $O_2 R^{4,5}(15)$ line (see Table 6.1). The $R^{4,v'}(15)$ lines of this progression appear to be in the red wing of the $R^{4,v'}(51)$ lines resulting from $R^{4,4}(51)$ excitation. These $N''=15$ lines are believed to be less prominent than the $N''=51$ lines due to a degraded overlap fraction (Partridge and Laurendeau, 1995a) for the $R^{4,5}(15)$ line of O_2 . This provides a positive identification of the existence of O_2 interferences for LIF measurements of NO.

6.5.3 Observations

Figures 6.7 and 6.8 indicate that for $Q_2(26.5)$ excitation (c and d) the $\gamma(0,1)$ band of NO is free of structured interferences at 1.0 and 6.1 atm while $Q_2(25.5)$ excitation (a

and b) produces a structured interference in the blue wing of the $\gamma(0,1)$ band at the same pressures. Interferences are also observed within the $\gamma(0,2)$ and $\gamma(0,3)$ bands of NO for both excitation schemes and at all pressures. This indicates that the better excitation/detection scheme for narrow-band measurement of NO is excitation via the $Q_2(26.5)$ line followed by detection of a 2- to 3-nm region of the fluorescence spectrum centered on the $\gamma(0,1)$ band. The broad-band interference signal integrated by this optimum excitation/detection scheme could be subtracted as a pressure-specific background (Reisel et al., 1993; Reisel and Laurendeau, 1994; Reisel et al., 1995). In general, the background should be expected to vary spatially in a flame. However, in our studies of inverse diffusion flames, we found no measurable variation in background throughout this diverse environment. On the other hand, this scheme is sensitive to laser attenuation via O_2 absorption, which may be problematic in experiments with long path lengths such as in industrial scale burners.

Figure 6.8 shows that for both NO excitation schemes the same interferences occur at 1.0 and 6.1 atm. Thus, neither O_2 RET or VET become significant so that new interference lines do not appear at elevated pressures up to 6.1 atm. Hence, a broad-band detection filter combination selected at 1.0 atm is expected to be equally applicable at elevated pressures up to 6.1 atm. A detection scan in a nitrogen-diluted flame at 9 atm using $Q_2(26.5)$ excitation revealed no new interferences compared to the 1.0 and 6.1 atm results.

An optimum excitation/detection scheme for broad-band measurements is not readily apparent from the results of Figs. 6.7 and 6.8. In general, NO $Q_2(25.5)$ excitation produces a greater number of interferences. However, the peak values of the interferences resulting from $Q_2(26.5)$ excitation (as evident in the raw data) are greater than those resulting from $Q_2(25.5)$ excitation. Hence, a more detailed study is required to reveal whether it is better to spectrally integrate a larger number of interferences with small peak value or a fewer number of interferences with greater peak value. We have performed such a study by numerically applying different filter combinations to the detection scans of Figs. 6.7 and 6.8. The effectiveness of the different filter combinations with the two NO excitation schemes can be compared via one or more filter assessment parameters.

6.6 Broad-band Spectral Filter Evaluation

We have performed a numerical investigation to determine generally optimal excitation/filtering schemes for making LIF measurements of [NO] using broad-band detection. Such schemes should minimize the scattered signal at the pump wavelength, minimize the interference signal, and maximize transmission of the NO fluorescence signal. Unfortunately, due to the gross spectral selectivity of broad-band filters and the intimate intermingling of the O₂ and NO spectra, an ideal broad-band filter does not exist. Rather, excitation/filtering schemes must be selected based on their relative merit. The assessment parameters which were used to rank the excitation/filtering schemes and the method of calculating these parameters are described in the following subsections. These assessment parameters are then compared and excitation/detection schemes are specified for broad-band LIF measurements of NO under selected conditions.

6.6.1 Filter-Analysis Nomenclature

Five filter combinations were investigated at 1.0 and 6.1 atm using both Q₂(25.5) and Q₂(26.5) excitation. The five individual filters are described in Table 6.2 and their spectral transmission profiles from 220 to 300 nm are shown in Fig. 6.10. Filter 2 was considered in a two mirror configuration. As indicated by Fig 6.10, all four band-pass filters (i.e., filters 2-5) require some co-application of UG5 CG filtering to provide the blue-end cutoff necessary to minimize scattering at the pump wavelength (i.e., ~226 nm). All filters are referred to by number, as assigned in Table 6.2, regardless of the degree of UG5 co-filtering. In the analysis, excitation of NO via the Q₂(25.5) and Q₂(26.5) transitions are referred to as excitation schemes A and B, respectively, and the studies at 1.0 and 6.1 atm are referred to as 1 and 6, respectively. Hence, results using Q₂(25.5) excitation at 6.1 atm are referred to as A6. An indexing parameter *n* is used to indicate the degree of filtering; *n*=0 refers to the unfiltered or baseline condition. All assessment parameters are normalized to unity at *n*=0. For filter 1, the value of *n* refers to the thickness of UG5 in mm. For the remaining filters, *n*=1 refers to parameter results with no UG5 co-filtering, and *n*≥2 refers to co-application of *n*-1 mm of UG5. Hence, results

Table 6.2 Description of five filters investigated for reducing O₂ interferences. The assigned filter number, type, model, and base bandwidth are indicated. All band-pass filters were applied in conjunction with a varying number of 1-mm UG5 CG filters. The base bandwidth refers to the FWHM bandwidth of each band-pass filter without UG5 application.

Filter No.	Type	Model	Bandwidth
1	Colored Glass	Schott UG5	NA
2	Dichroic Mirror	Acton M248V + UG5	63 nm
3	Interference	Acton 240B + UG5	40 nm
4	Interference	Acton 250W + UG5	92 nm
5	Interference	Acton 260N + UG5	21 nm

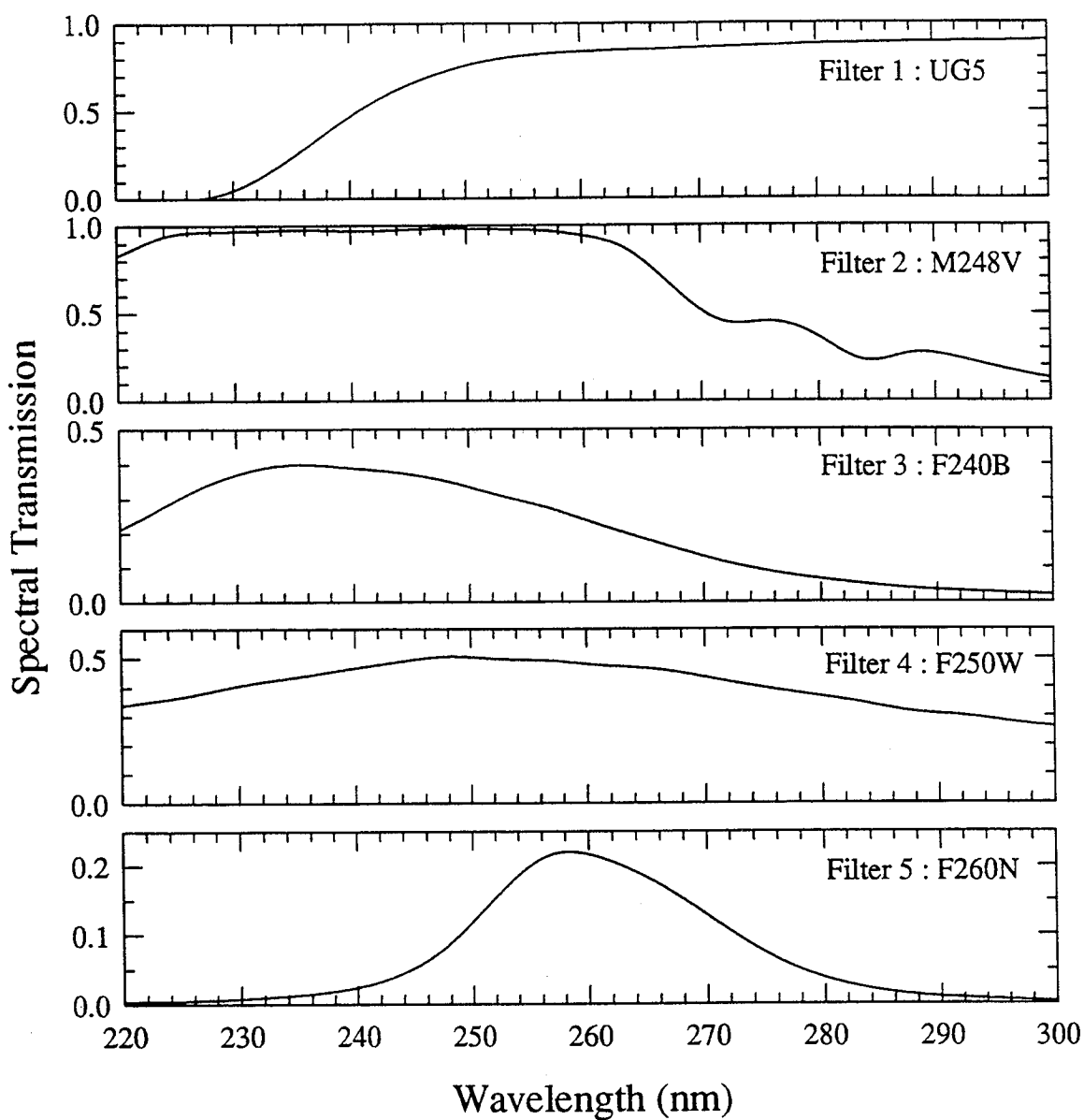


Figure 6.10 Spectral profiles for the five candidate filters considered for broad-band detection measurements of NO. Filter 1 is a UG5 colored-glass filter. Filter 2 is a two-element dichroic mirror system. The spectral transmission indicated for filter 2 is that of the mirror system which is equal to the square of the reflectivity of a single mirror. Filters 3, 4 and 5 are broad-bandwidth, wide-bandwidth and narrow-bandwidth interference filters, respectively.

using filter 4 with 7 mm of UG5 co-filtering and Q₂(25.5) excitation at 6.1 atm are referred to as 4₈A6.

6.6.2 Filter Assessment Criteria

The filtering schemes were assessed based on their effect on the signal-to-interference ratio (SIR), the degree of net signal transmission for the probed (i.e., NO) species (PST), and the scattering transmission (ST). The measured total signal (TS) is composed of the sum of the probe signal (PS) and the interfering signals (IS). Filter criteria are formulated based on knowledge of the individual PS and IS contributions.

A given filter is specified as having value, in terms of eliminating interferences, if it increases the SIR of the measurement relative to the unfiltered condition. The SIR is defined for a given filter, pressure and excitation scheme as

$$SIR_n = \frac{PS_n}{TS_n - PS_n}, \quad (6.1)$$

where $TS_n = PS_n + IS_n$ and the subscript n refers to the degree of filtering as described earlier. VALUE is a filter assessment parameter which indicates the relative SIR enhancement provided by that filter. The filter VALUE is formulated as

$$VALUE_n = \frac{SIR_n}{SIR_0} = \frac{PS_n}{PS_0} \cdot \frac{TS_0 - PS_0}{TS_n - PS_n}, \quad (6.2)$$

where the subscript 0 refers to the n=0 unfiltered condition. A filter has a VALUE which is greater (less) than unity if it enhances (degrades) the measurement SIR.

Attenuation of the probe fluorescence signal resulting from filter application influences the detection limit of the measurement. Hence, the filter PST must also be considered in assessing the merit of different filters. The filter PST is formulated as

$$PST_n = \frac{PS_n}{PS_0}. \quad (6.3)$$

Notice that the PST is normalized to unity for the unfiltered condition and will be less than or equal to unity for subsequent filter applications.

The ST is unique to each filter combination. We incorporate ST into our analysis by calculating the filter VALUE and PST for different levels of effective filter transmission at the pump wavelength (~226 nm in this study). The gaseous flame environments of interest here produce relatively little scattering (e.g., Rayleigh- relative to Mie-scattering signal). Hence, ST is not assigned as an explicit assessment parameter. In strongly scattering environments, such as in spray flames, the filter ST should be explicitly used as an assessment parameter (Allen, 1994). However, because Rayleigh scattering will exist to varying degrees (e.g., depending on whether the pump laser is vertically or horizontally polarized) we do consider discrete order-of-magnitude levels of ST in this study.

A global figure of merit (FOM) may be formulated by noting that the optimum filter seeks to simultaneously maximize both the VALUE and PST. However, this requires knowledge of the individual importance of the VALUE and PST in a given experiment, which can be modeled via appropriate weighting factors W_{VALUE} and W_{PST} , respectively. Assuming knowledge of the weighting factors, the FOM can be formulated as

$$FOM_n = VALUE^{W_{\text{VALUE}}} \cdot PST^{W_{\text{PST}}} \quad (6.4)$$

The magnitudes of the weighting factors are experiment specific. For example, in situations for which the probe species fluorescence signal is large (e.g., if the probe species is doped in high concentrations for temperature, pressure or velocity measurements), the appropriate values of W_{VALUE} and W_{PST} may be 1 and 0, respectively. In contrast, for situations where the probe species fluorescence signal is low (e.g., a study investigating the distribution of naturally occurring chemical species within a combustor), the appropriate values of W_{VALUE} and W_{PST} may be 0 and 1, respectively. However, intermediate values of the weighting factors are probably more applicable in most practical investigations.

6.6.3 Calculation of Filter Assessment Parameters

Calculation of the filter assessment parameters is based on the ability to separate the signal contributions due to NO and the various interferences (i.e., PS and IS), and also

knowledge of the spectral transmission profiles of each filter combination. The values of TS, PS and IS for the different excitation schemes and pressures investigated were determined from the experimental detection scans shown in Figs. 6.7 and 6.8. To determine TS_n for a given case, the numerically-filtered detection scan of the nitrogen-diluted flame was spectrally integrated over the entire range of the scan using the scan step size and trapezoidal-rule integration. This total signal is equivalent to that integrated by the PMT in a broad-band detection scheme, and includes signals from NO fluorescence as well as any unwanted interfering signals (i.e., O_2 fluorescence, and N_2 , O_2 and H_2O Raman scattering).

Information on the competing interference signals can be obtained from the detection scans in the argon-diluted flames. Calculation of IS and PS are less straightforward than TS since the N_2 Raman interference signal does not appear in the argon-diluted scans; moreover, the interference signals do not have the same absolute magnitudes in the nitrogen- and argon-diluted scans. However, if the N_2 Raman line did not exist, PS could be determined from the difference in TS and IS multiplied by an appropriate scale factor to account for the difference in the absolute magnitudes of the interferences in the two scans. This information, combined with the recognition that an insignificant level of NO fluorescence exists within the spectral range of the N_2 Raman line, provides a means for calculation of PS. Specifically, the nitrogen- and argon-diluted detection scans may be spectrally integrated with the N_2 Raman line skipped in the integration. Hence, IS and PS are calculated using a two-step integration consisting of two separate spectral integrations over two excitation-scheme-specific spectral regions on either side of the N_2 Raman line. This effectively removes the influence of the N_2 Raman line from the nitrogen-diluted detection scan.

Application of the two-step spectral integration to the detection scans from the nitrogen- and argon-diluted flames produced the parameters TS^* and IS, respectively. TS^* differs from TS as the latter is integrated over the entire spectral region of the nitrogen-diluted scan. IS includes the signal from all interferences in the argon-diluted scan less the N_2 Raman signal and the small amount of broad-band interference signal within the narrow spectral region skipped in the integration. To scale the interferences in the nitrogen- and

argon-diluted detection scans to the same absolute magnitude, the signal from an isolated interference was chosen as a reference. This scaling corrects the interference measurements for variations in the Boltzmann fraction due to the finite temperature difference between the nitrogen- and argon-diluted flames. For $Q_2(25.5)$ excitation, the $R^{47}(51)$ O_2 interference feature was used for referencing, while for $Q_2(26.5)$ excitation, the $R^{47}(13)$ O_2 interference feature was used for referencing. For each excitation scheme and pressure, a scale factor (SCALE) was determined as the ratio of the peak signals of the particular reference feature in the nitrogen- and argon-diluted detection scans. The total NO-attributable signal was then determined as

$$PS_n = TS_n^* - (SCALE \cdot IS_n) . \quad (6.5)$$

Because of the possible confusion associated with the scale factor, Eqs. (6.1) through (6.4) were formulated using only TS_n and PS_n . This method of calculating PS proved effective in accounting for all the O_2 -originating interferences. However, it did not completely account for the H_2O Raman interference signal. This is due to the differing equivalence ratios of the nitrogen- and argon-diluted flames and also to the unavoidable temperature difference in the two flames. However, we believe that this experimentally based accounting procedure is the most reliable technique available, and is certainly adequate for the filter assessment.

The spectral transmission profiles of the individual filters were obtained from the Schott optical glass filter catalog (Schott, 1991) for the UG5 CG filter and from manufacturer measurements for the various band-pass filters (Acton Research Corp., Acton, MA.). To obtain spectral transmission data of the same spectral step size as the detection scans, a cubic spline was fit to the available data and used for intermediate interpolation. This produced the requisite high-density spectral transmission profiles. To simulate different filter combinations, the appropriate high-density spectral transmission profiles were spectrally multiplied to produce an effective high-density spectral transmission profile.

To determine the filter assessment parameters, the effective high-density spectral transmission profile of each filter combination was applied to the nitrogen- and argon-

diluted detection scans. These numerically filtered detection scans were subsequently integrated to determine TS_n ; the two-step integration and Eq. (6.5) were used to determine PS_n . The filter VALUE and PST were then determined using TS_n and Eqs. (6.2) and (6.3), respectively. A copy of the program used to perform the analysis for filter 2 is included in Appendix B.

Since the experimental detection scans cover the spectral range 232.5 to 266.1 nm, our filter assessment only considers NO and interference signals in this spectral regime. A sufficient blue-end cutoff can be obtained for all of the candidate filtering schemes by appropriate co-application of UG5 CG filters. However, all of the candidate filtering schemes have some finite transmission in the spectral range above 266.1 nm. Hence, any NO or interference signals in this longer wavelength regime are not considered in the present analysis. However, the average transmission of the various band-pass filters relative to that of UG5 (filter 1) in the spectral range 265 nm to 300 nm is 1/68.0, 1/19.6, 1/15.2, and 1/2.6 for filters 5, 3, 2, and 4, respectively. These average relative transmissions are the same regardless of the required level of ST. Hence, filters 5, 3, 2, and 4 have 68.0, 19.6, 15.2, and 2.6 times better red-end cutoff, respectively, compared to that of UG5.

Another concern is the influence of chromatic aberration on the detection scans. Modeling the collection optics as thin lenses and the dispersion of each fused-silica lens with the Sellmeier equation (Smith, 1990), as recommended by the lens manufacturer (CVI, 1994), it may be shown that the image distance (i.e., the distance between L3 and the monochromator entrance slit in Fig. 6.1) varies by up to ~28 mm over the spectral range of the detection scans due to chromatic aberration. Specifically, at 232.5, 236.0 and 266.1 nm, the image distance is approximately 296, 299 and 324 mm, respectively. Because the collection optics were optimized at ~236 nm, as the monochromator is scanned away from this optimum wavelength the PMT integrates radiation that is misfocused. Monitoring such misfocused radiation results in an underprediction of the actual signal level as compared to radiation that is properly focused on the monochromator entrance slit. Hence, the effect of chromatic aberration is to spectrally filter the radiation in a manner similar to the application of the various filters in Table 6.2

and Fig. 6.10. This effect could have been minimized by the use of achromates in the collection optics.

The influence of chromatic aberration on the measured signal level was experimentally evaluated using NO fluorescence. With the collection optics optimized at ~ 236 nm, the measured signal level at ~ 258 nm was 64% of that with the focus optimized at this second wavelength. Hence, chromatic aberration effectively reduced the transmission of the narrow-band detection system by 36% at ~ 258 nm. To assess the influence of chromatic aberration on the procedure for evaluating the various broad-band excitation/filtering schemes, an inverse spectral filter was numerically applied to all detection scans. This filter was designed to counteract the influence of chromatic aberration, and was based on a triangular filter function centered on the $\gamma(0,1)$ band of NO and fit to the measured transmission data. Evaluation of the broad-band excitation/filtering schemes was performed with and without the chromatic-aberration filter. The ranking and selection of the various excitation/filtering schemes were found to be independent of chromatic aberration for the range of ST and pressures investigated.

Despite the above spectral limitations, our analysis can be used to successfully identify generally optimal excitation/detection schemes and certainly improved filtering techniques compared to that traditionally used for broad-band LIF measurements of NO (i.e., UG5). In addition, our analysis establishes a useful methodology for future evaluations of candidate broad-band excitation and filtering schemes.

6.6.4 Filter Assessment Results

Figures 6.11 and 6.12 show the VALUE and PST data, respectively, in graphical form for filter 2. The VALUE and PST trends for the other filter combinations are quite similar to those of filter 2. Hence, Figs. 6.11 and 6.12 suffice for demonstrating the influence of the degree of filtering on the filter assessment parameters.

Application of filter 2 produces VALUE magnitudes both greater and less than unity over the degree-of-filtering range investigated. However, the lower n values may not be useful as they do not provide sufficient scattering rejection. In particular, because our broad-band detection measurements of NO required an ST of $\sim 10^{-10}$, we consider ST

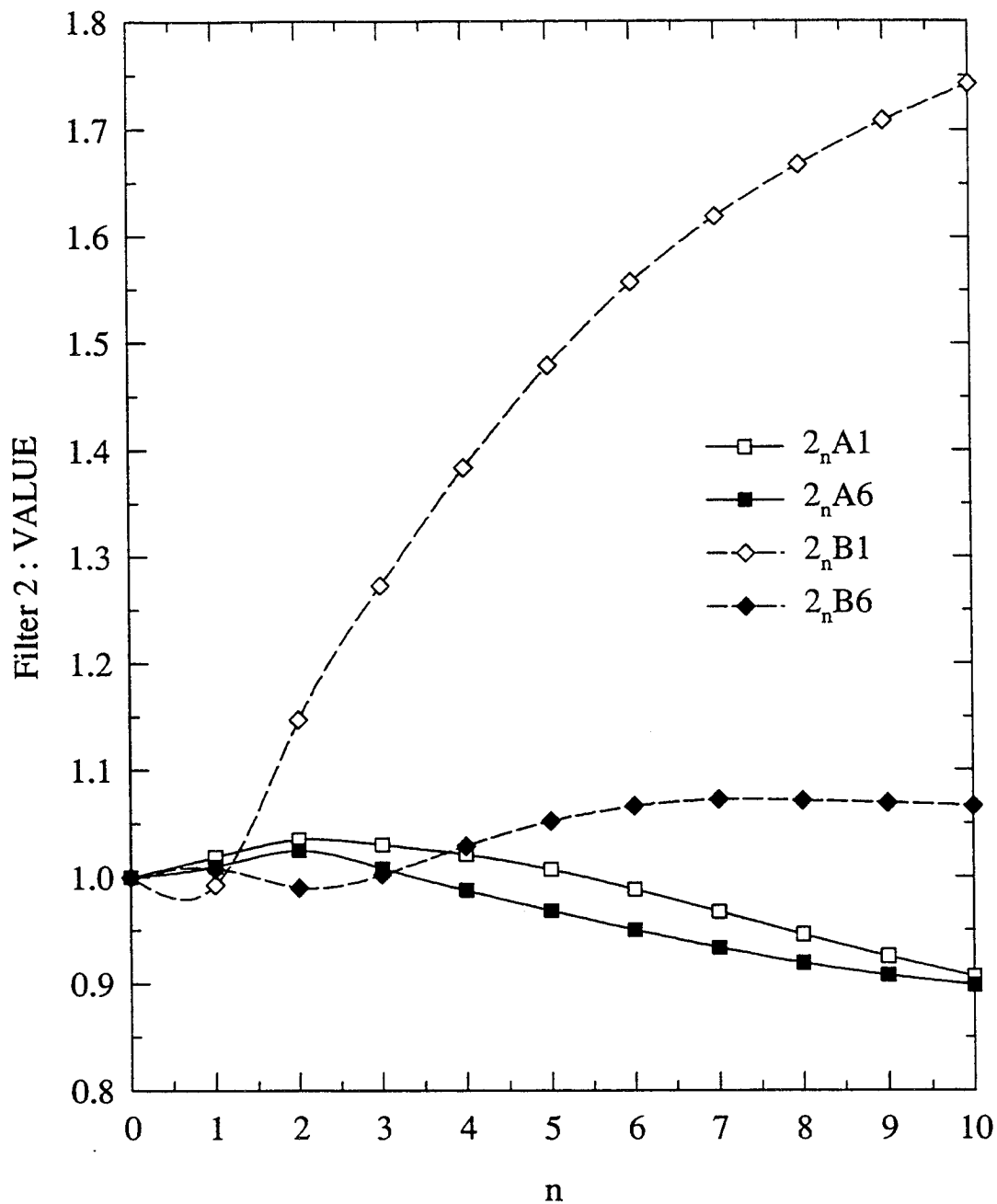


Figure 6.11 VALUE results for filter 2 combinations (i.e., two M248V dichroic mirrors with $n-1$ mm of UG5 co-filtering) using both $Q_2(25.5)$ (A) and $Q_2(26.5)$ (B) excitation at 1.0 (1) and 6.1 atm (6). Indexing term: $n=0$ refers to the unfiltered condition, $n=1$ refers to application of the two M248V mirrors alone, and $n \geq 2$ refers to $n-1$ mm of UG5 co-filtering.

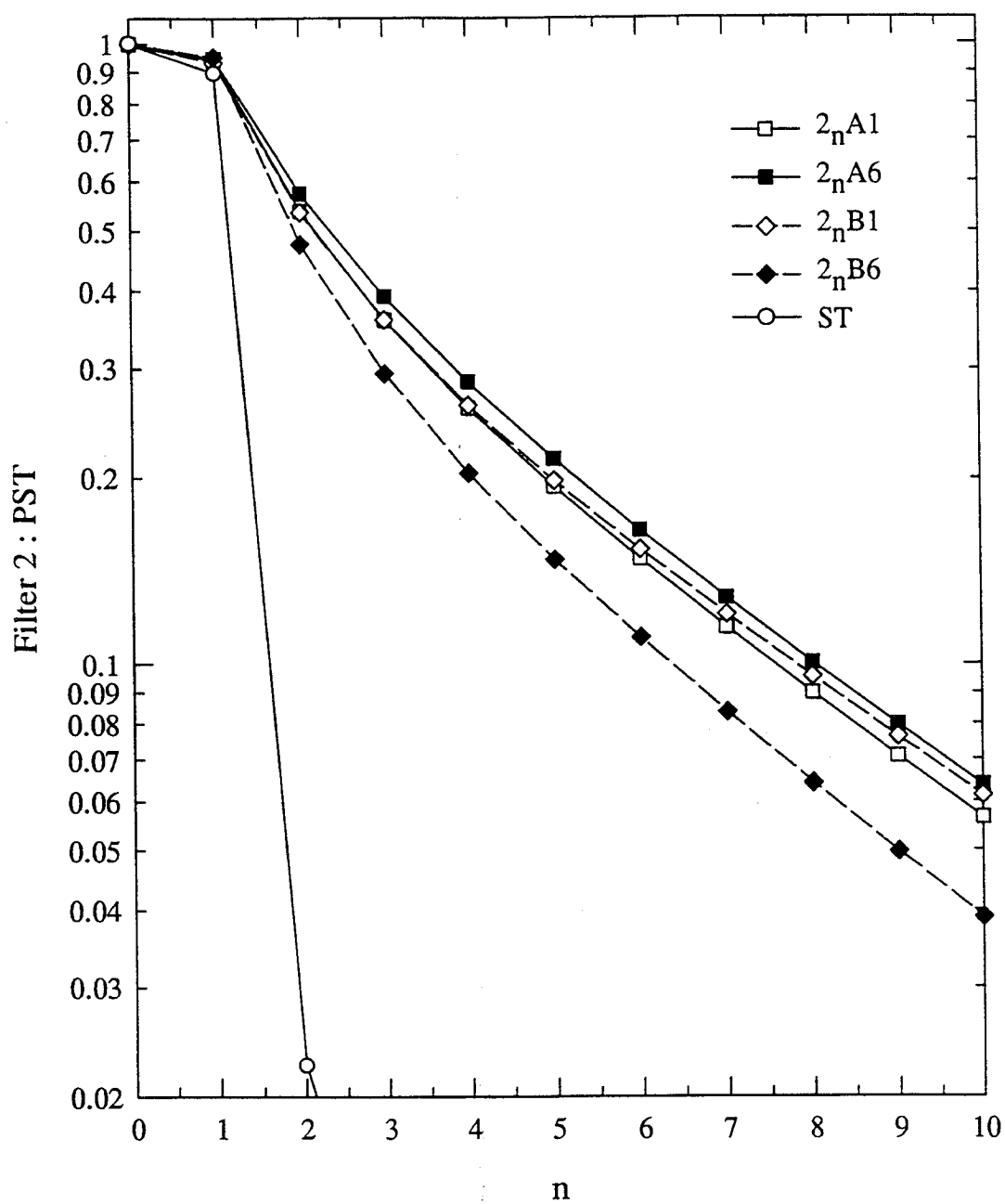


Figure 6.12 PST results for filter 2 combinations (i.e., two M248V dichroic mirrors with $n-1$ mm of UG5 co-filtering) using both $Q_2(25.5)$ (A) and $Q_2(26.5)$ (B) excitation at 1.0 (1) and 6.1 atm (6). Indexing term: $n=0$ refers to the unfiltered condition, $n=1$ refers to application of the two M248V mirrors alone, and $n \geq 2$ refers to $n-1$ mm of UG5 co-filtering. The ST, or effective filter transmission at the pump wavelength, is also shown.

levels of 10^{-7} , 10^{-10} and 10^{-13} (i.e., $n=5$, 7 and 9 for filter 2) to be experimentally feasible. Hence, these characteristic ST levels are used for assessment of the various excitation/filtering schemes. Using filter 2 at 1.0 atm, $Q_2(26.5)$ excitation (2_nB1) produces VALUE magnitudes greater than unity over the entire useful range, while $Q_2(25.5)$ excitation (2_nA1) provides enhanced VALUE only at the largest feasible ST level (i.e., $n=5$). Hence, using filter 2 at 1.0 atm, the SIR is optimized by use of $Q_2(26.5)$ excitation. Moreover, Fig. 6.11 indicates that the SIR increases with n for $Q_2(26.5)$ excitation in flames at 1.0 atm. For flames at 6.1 atm, the SIR is enhanced by $Q_2(26.5)$ excitation (2_nB6) and degraded by $Q_2(25.5)$ excitation (2_nA6) when using filter 2 in the useful ST range. These results clearly indicate that for broad-band detection measurements of NO using filtering scheme 2 at 1.0 and 6.1 atm, $Q_2(26.5)$ excitation is preferable since it minimizes the influence of interfering signals. Moreover, it is clear that with this filtering scheme $Q_2(25.5)$ excitation actually exacerbates the interference problem for both pressures and at all feasible ST levels except for 2_5A1 .

The effect of filter 2 on PST is shown in Fig. 6.12. As expected, for a given filter, the PST decreases with increasing degree of co-filtering. To maximize the probe signal, the minimum n required for sufficient scattering rejection should be used. Although Fig. 6.11 indicates that the filter VALUE increases with increasing n for $Q_2(26.5)$ excitation in flames at 1.0 atm, Fig. 6.12 indicates a monotonically decreasing PST with increasing n for this same excitation scheme and pressure. Hence, the VALUE cannot, in general, be used as the sole filter assessment parameter.

The various broad-band filters are ranked in terms of VALUE and PST, using the optimum excitation scheme and the three characteristic ST levels, for the 1.0 and 6.1 atm cases in Tables 6.3 and 6.4, respectively. The optimum excitation scheme selection and filter ranking from most to least optimum are based on maximizing the magnitude of the particular filter assessment parameter. The rank of a given filter is considerably different based on VALUE and PST. Moreover, the VALUE-based filter ranking differs considerably at 1.0 and 6.1 atm. This is one example of the experimental specificity of filter selection. Notice that the order of the PST-based ranking at both 1.0 and 6.1 atm decreases with decreasing filter bandwidth (see Table 6.2), except for filter 2. Although

Table 6.3 VALUE- and PST-based rank of the candidate excitation and broad-band filtering schemes at 1.0 atm for three experimentally feasible levels of scattering transmission at the pump wavelength (ST). The initial number in the notation refers to the filter as defined in Table 6.2. The subscript refers to the degree of filtering (n) where $n=0$ refers to the unfiltered condition, $n=1$ refers to application of the base filter with no co-filtering, and $n \geq 2$ refers to use of $n-1$ mm of UG5 co-filtering. The letter refers to the excitation scheme where A and B refer to excitation using $Q_2(25.5)$ and $Q_2(26.5)$ excitation, respectively. Higher VALUE-based rank indicates better interference rejection, while higher PST-based rank indicates greater NO-attributable signal level.

VALUE-Based Rank, 1.0 Atm					
ST	1st	2nd	3rd	4th	5th
1E-07	5 ₄ B	1 ₄ B	4 ₅ B	2 ₅ B	3 ₅ B
	1.733	1.502	1.501	1.479	1.402
1E-10	5 ₆ B	1 ₆ B	4 ₇ B	2 ₇ B	3 ₇ B
	1.817	1.643	1.636	1.619	1.552
1E-13	5 ₈ B	1 ₈ B	4 ₉ B	2 ₉ B	3 ₉ B
	1.879	1.732	1.723	1.709	1.648

PST-Based Rank, 1.0 Atm					
ST	1st	2nd	3rd	4th	5th
1E-07	1 ₄ B	2 ₅ B	4 ₅ B	3 ₅ B	5 ₄ B
	0.220	0.198	0.107	0.063	0.043
1E-10	1 ₆ B	2 ₇ B	4 ₇ B	3 ₇ B	5 ₆ B
	0.135	0.120	0.066	0.037	0.028
1E-13	1 ₈ B	2 ₉ B	4 ₉ B	3 ₉ B	5 ₈ B
	0.086	0.076	0.042	0.023	0.019

Table 6.4 VALUE- and PST-based rank of the candidate excitation and broad-band filtering schemes at 6.1 atm for three experimentally feasible levels of scattering transmission at the pump wavelength (ST). The PST-based rank is also given using the excitation scheme dictated by the VALUE-based rank. The initial number in the notation refers to the filter as defined in Table 6.2. The subscript refers to the degree of filtering (n) where n=0 refers to the unfiltered condition, n=1 refers to application of the base filter with no co-filtering, and n $\geq$ 2 refers to use of n-1 mm of UG5 co-filtering. The letter refers to the excitation scheme where A and B refer to excitation using Q₂(25.5) and Q₂(26.5) excitation, respectively. Higher VALUE-based rank indicates better interference rejection, while higher PST-based rank indicates greater NO-attributable signal level.

VALUE-Based Rank, 6.1 Atm					
ST	1st	2nd	3rd	4th	5th
1E-07	5 ₄ B	2 ₅ B	4 ₅ B	3 ₅ B	1 ₄ B
	1.072	1.052	1.048	1.046	1.043
1E-10	5 ₆ B	2 ₇ B	3 ₇ B	4 ₇ B	1 ₆ B
	1.084	1.072	1.070	1.062	1.060
1E-13	5 ₈ B	2 ₉ B	3 ₉ B	1 ₈ B	4 ₉ B
	1.093	1.069	1.065	1.056	1.056

PST-Based Rank, 6.1 Atm					
ST	1st	2nd	3rd	4th	5th
1E-07	1 ₄ A	2 ₅ A	4 ₅ A	3 ₅ A	5 ₄ A
	0.230	0.215	0.113	0.069	0.045
1E-10	1 ₆ A	2 ₇ A	4 ₇ A	3 ₇ A	5 ₆ A
	0.138	0.128	0.068	0.040	0.029
1E-13	1 ₈ A	2 ₉ A	4 ₉ A	3 ₉ A	5 ₈ A
	0.086	0.080	0.042	0.024	0.020

PST-Based Rank, 6.1 Atm with excitation scheme dictated by VALUE					
ST	1st	2nd	3rd	4th	5th
1E-07	1 ₄ B	2 ₅ B	4 ₅ B	3 ₅ B	5 ₄ B
	0.157	0.148	0.077	0.049	0.027
1E-10	1 ₆ B	2 ₇ B	4 ₇ B	3 ₇ B	5 ₆ B
	0.089	0.084	0.044	0.027	0.017
1E-13	1 ₈ B	2 ₉ B	4 ₉ B	3 ₉ B	5 ₈ B
	0.053	0.050	0.026	0.016	0.011

the bandwidth of filter 2 is less than that of filter 4, filter 2 is more top-hat shaped (as evident from Fig. 6.10) and hence, passes more net signal. Moreover, the PST-based filter ranking is the same at 1.0 and 6.1 atm.

At 1.0 atm $Q_2(26.5)$ excitation (B) produces greater VALUE and PST throughout the useful degree-of-filtering (i.e., ST) range. This indicates that of the two candidate excitation schemes, the $Q_2(26.5)$ line of NO provides both the best interference rejection and detection limit. Moreover, since this excitation scheme is universally favorable at this pressure, the broad-band filtering scheme may be chosen independently of the excitation scheme.

Filter selection for 1-atm experiments requires a compromise between VALUE and PST based on the relative importance of interference rejection and detection limit. This is another example of the experimental specificity of filter selection. Filter 5 provides the best VALUE (hence, the highest measurement SIR) but the lowest PST (hence, the highest detection limit). Therefore, filter 5 is not considered to be broadly applicable, particularly for broad-band LIF measurements of trace NO concentrations. Filter 3 is rejected based on its having both low VALUE and PST rank. Table 6.3 indicates that filters 1, 2 and 4 provide equivalent VALUE to less than ~2% at all ST levels. Hence, filters 1, 2 and 4 provide approximately equivalent interference rejection within the spectral range of this investigation. Although filter 1 provides the best PST-based rank, it does not provide good red-end cutoff, making it susceptible to interferences at wavelengths greater than that of the $\gamma(0,3)$ band of NO. Compared to filter 1, filter 2 provides an ~15.2 times better red-end cutoff with only ~12% loss in PST. Similarly, filter 4 provides an ~2.6 times better red-end cutoff, but with an ~82% loss in PST when compared to filter 1. Hence, both filters 2 and 4 provide good VALUE and red-end cutoff, but filter 2 provides significantly better PST. This indicates that in gaseous combustion environments at 1 atm, the generally optimal excitation/detection scheme for broad-band LIF measurements of NO is excitation via the $Q_2(26.5)$ line and detection filtering using a two M248V-mirror system and n-1 mm of UG5 CG filter, with the required ST dictating the value of n based on Table 6.3.

Table 6.4 indicates that, for flames at 6.1 atm, $Q_2(26.5)$ excitation (B) produces greater VALUE in the ST range considered, but $Q_2(25.5)$ excitation (A) produces greater PST. However, ranking the filtering schemes using the optimum VALUE-based excitation scheme indicates that the PST-based filter rank is independent of excitation scheme although the PST values resulting from excitation scheme B are ~36% less than those for excitation scheme A. Nevertheless, at 6.1 atm, only $Q_2(26.5)$ excitation produces VALUE magnitudes greater than unity over the useful degree-of-filtering range. Specifically, use of $Q_2(25.5)$ excitation exacerbates the interference problem. This was demonstrated for filter 2 in Fig. 6.11 and is true for all other candidate filter combinations. Therefore, we suggest selecting the 6.1-atm excitation scheme based on maximizing the VALUE for a particular filter combination. This basis for selection of the excitation scheme clearly places more emphasis on interference rejection than on the detection limit.

Based on Tables 6.3 and 6.4 it is apparent that the candidate filtering schemes are less effective in mitigating the interference problem at 6.1 atm as compared to 1.0 atm. Specifically, the average VALUE magnitude at 6.1 atm is ~35% less than that at 1.0 atm. Moreover, among the candidate filtering schemes, there is only an ~3% variation in VALUE at 6.1 atm as compared to ~18% at 1.0 atm. This indicates that the measurement SIR is relatively insensitive to the specific filtering scheme used at 6.1 atm. Hence, the 6.1-atm filtering scheme may be selected based primarily on PST and red-end cutoff. From Table 6.4, filter 2 appears to be an optimal filter choice since it provides both a high PST (only ~5.6% less than that for filter 1) and a good red-end cutoff. Hence, in gaseous combustion environments at 6.1 atm, the generally optimal excitation/detection scheme for broad-band LIF measurements of NO is excitation via the $Q_2(26.5)$ line and detection filtering using a two M248V-mirror system and n-1 mm of UG5 CG filter with the required ST dictating the value of n based on Table 6.4.

In addition to the two mirror configuration of filter 2, we also investigated one and four mirror configurations. The VALUE magnitudes provided by filter 2 in a one, two and four mirror configuration were found to be equivalent to within 2%. Moreover, use of a one and four mirror system provided an ~6% PST enhancement and an ~10% PST degradation, respectively, compared to the PST results for filter 2 in Table 6.3 (i.e., a two

mirror configuration). Use of one, two and four mirrors for filter 2 provides approximately 3.2, 15.2 and 547 times better red-end cutoff, respectively, compared to that of UG5 (filter 1). Recall that these values were 19.6, 2.6 and 68.0 for filters 3, 4 and 5, respectively. This indicates that use of a single mirror system would provide a red-end cutoff similar to that of filter 4, and a four mirror system could provide an excellent red-end cutoff. We chose a two mirror configuration for filter 2 as it provides a good combination of PST and red-end cutoff. In studies where detection limit is of less importance, a four mirror configuration for filter 2 could be used to provide a significantly enhanced red-end cutoff.

6.7 Conclusions on O₂ Interferences

We have investigated the influence of O₂ interferences on narrow-band and broad-band LIF measurements of NO in high temperature flames at 1.0 and 6.1 atm. Based on this work, we have identified optimal excitation/detection schemes which minimize O₂ interferences for different experimental and environmental conditions. The Q₂(25.5) and Q₂(26.5) lines of NO minimize inadvertent O₂ excitation because they reside in the broad-band region of the O₂ hot-band spectrum. Moreover, they simplify fluorescence data interpretation because they are unique and isolated lines which have relatively temperature-insensitive Boltzmann fractions. The optimum excitation/detection scheme for narrow-band LIF measurements of NO is excitation via the Q₂(26.5) line followed by detection of a 2- to 3-nm portion of the fluorescence spectrum centered on the $\gamma(0,1)$ band. The broad-band interference signal integrated by this excitation/detection scheme can be subtracted from the LIF signal as a pressure-specific background.

Our investigation of optimal broad-band LIF filtering techniques emphasizes the experimental and environmental specificity of excitation and filtering scheme selection. Interference rejection is both less efficient and less sensitive to the specific broad-band filtering scheme used at 6.1 atm as compared to that at 1.0 atm. Moreover, optimal broad-band excitation/filtering schemes will vary depending on the relative importance of SIR and the magnitude of the measured NO fluorescence signal. Nevertheless, our analysis suggests generally optimal excitation/filtering schemes for use with broad-band

LIF NO measurements in gaseous flames at 1.0 and 6.1 atm. For flames at both 1.0 and 6.1 atm, the generally optimal excitation/detection scheme for broad-band detection measurements of NO is excitation via the $Q_2(26.5)$ rovibronic transition and detection filtering using a two M248V-mirror system and sufficient UG5 CG filter for low ST.

We found that an F250W wide-bandwidth interference filter with sufficient UG5 co-filtering provided interference rejection comparable to that of the above optimal M248V/UG5 system at both 1.0 and 6.1 atm. However, this alternate filter resulted in an approximately 45% lower NO-attributable signal as compared to the M248V/UG5 system. Hence, an F250W/UG5 filtering system could be confidently used to provide interference rejection in studies for which the detection limit is of less importance. In such situations, the F250W/UG5 filtering system may be preferable since it is easier to implement compared to the M248V/UG5 system.

Because all of the candidate filters considered have finite transmission beyond the red-end of our experimental data, the current analysis can only be used to suggest generally optimal filtering schemes. However, the filters indicated by our analysis for the 1.0 and 6.1 atm broad-band LIF measurements of NO both have markedly better red-end cutoffs compared to UG5. Hence, these filters should be a clear improvement over UG5 filtering which has traditionally been used for broad-band LIF measurements of NO (e.g., Battles et al., 1994; McMillin et al., 1994; Paul et al., 1989). Future work should be directed towards generating an experimental database of relevant interferences at different temperatures and pressures, including the spectral region above 266 nm. With such a database, our methodology for evaluating broad-band excitation and filtering schemes could be used to conclusively identify optimum measurement schemes for a broad range of specific environmental conditions.

CHAPTER 7

NITRIC OXIDE CONCENTRATION MEASUREMENTS : PLIF ASSESSMENT AND ENHANCEMENT

PLIF and LSF measurements of NO concentration were made by using the experimental apparatus and the AIDF burner conditions described in Chapter 5. All measurements were made in a plane passing through the centerline of the AIDF. The optimum excitation and detection scheme for NB detection, identified in Chapter 6, was used for the LSF measurements. The PLIF measurements used excitation via the $Q_2(26.5)$ line of NO followed by detection filtering using an F250W wide-bandwidth interference filter with 6 mm of UG5 co-filtering. This alternate excitation and detection scheme for BB detection was used because it was more practical to implement and provided equivalent interference rejection compared to the optimum BB-detection measurement scheme identified in Chapter 6. All NO-fluorescence data were reduced, calibrated, and their uncertainties quantified using the procedures described in Appendices D, E, and F, respectively.

The LSF measurements of local [NO] relative to the calibration flame temperature, $N_{T,RT}$ (relative ppm), were determined using (Appendix E)

$$N_{T,RT} = CF^{LSF} C_D^{LSF}, \quad (7.1)$$

where CF^{LSF} (ppm/V) is the LSF calibration factor and C_D^{LSF} (V) is the NO-attributable signal. The total NO number density, $N_{T,ND}$, is related to $N_{T,RT}$ by

$$N_{TND} = \left[\frac{P_C N_A}{R_u T_C 10^6} \right] \left[\frac{f_{B,C}(T_C)}{f_B(T)} \right] N_{TJT} , \quad (7.2)$$

where P is the absolute pressure, T is the absolute temperature, R_u is the universal gas constant, N_A is Avogadro's number, f_B is the Boltzmann fraction of the lower laser-coupled level at the local temperature, and the subscript C indicates parameter values in the calibration flame. The bracketed terms in Eq. (7.2) correct the relative [NO] measurements of Eq. (7.1) for density and Boltzmann fraction effects due to the different conditions of the calibration and test environments (Appendix E). However, the PLIF measurements have the same dependence on the bracketed terms of Eq. (7.1) as the LSF measurements. Hence, the final LSF measurements of NO concentration in relative ppm were calculated using Eq. (7.1).

The PLIF measurements of local [NO] relative to the calibration flame temperature and quenching environment, $N_{T,RT,RQ}$ (relative ppm), were determined using (Appendix E)

$$N_{T,RT,RQ} = CF^{PLIF} Ni2 , \quad (7.3)$$

where CF^{PLIF} (ppm/counts) is the PLIF calibration factor and $Ni2$ (counts) is the NO-attributable signal for a given pixel. The image $Ni2$ results from the image analysis procedure (Appendix D) and has been corrected for dark and readout noise, laser-induced interferences, image-to-image irradiance fluctuations, as well as spatial nonuniformities in the laser-sheet fluence and both the ICCD gain and responsivity. The total NO number density, $N_{T,ND}$, is related to $N_{T,RT,RQ}$ by

$$N_{TND} = \left[\frac{P_C N_A}{R_u T_C 10^6} \right] \left[\frac{f_{B,C}(T_C)}{f_B(T)} \right] \left[\frac{\Phi_C^{LIN}}{\Phi^{LIN}} \right] N_{T,RT,RQ} , \quad (7.4)$$

where the first two bracketed terms are the same as described in Eq. (7.2), and the subscript C is again used to denote parameter values in the calibration environment. The

third bracketed term in Eq. (7.4) is the ratio of linear fluorescence yields, as defined by Eq. (4.23a), and accounts for variations in the electronic quenching rate coefficient between the calibration and AIDF environments. The final PLIF measurements of NO concentration in relative ppm were calculated using Eq. (7.3).

Based on Eqs. (7.2) and (7.4), it is clear that the LSF and PLIF measurements of relative [NO] (i.e., $N_{T,RT}$ and $N_{T,RT,RQ}$, respectively) differ only through local variations in the electronic quenching rate coefficient relative to the calibration flame. Hence, the quantitative nature of PLIF, as well as the proposed experimentally-based PLIF enhancement procedures, can be accurately assessed via the relative NO concentrations indicated by $N_{T,RT}$ and $N_{T,RT,RQ}$. Thus, the [NO] measurements presented in this chapter are on a relative ppm basis; i.e., the NO concentrations are calculated using Eq. (7.1) for the LSF measurements and Eq. (7.3) for the PLIF measurements. The LSF and PLIF measurements, the PLIF image assessment, and the experimentally-based procedures for enhancing the quantitative nature of PLIF imaging are discussed in the following sections.

7.1 LSF NO Concentration Measurements

A total of 290 LSF measurements of [NO] were made in the AIDF. These point measurements were made at 29 radial locations in 1-mm increments from -14 mm to +14 mm, and at 10 elevations from 3 mm to 15 mm above the burner surface. Since the outer flame tip of the AIDF was 13 mm above the burner surface (Section 5.7), the largest elevation captured the post-AIDF-tip region of the [NO] field. Pyrromethene-580 laser dye was used to provide a laser fluence of 19.3 mJ/mm²·pulse in the probe volume. Based on Appendix C, this laser fluence was sufficient for saturation of the NO transition. The LSF measurements were made using $Q_2(26.5)$ excitation followed by detection of a 2-nm range of the fluorescence spectrum centered on the $\gamma(0,1)$ band of NO (Section 5.3.2.2). Based on the projected entrance-slit size of the monochromator and the focused-beam thickness, the probe volume was approximately 1-mm long, 68- μ m tall, and 213- μ m thick. The NO-fluorescence signal at each point was determined as the average of 400 consecutive single-shot measurements. The detection limit of the LSF measurements was determined to be ~0.6 relative ppm (Section F.2).

The 290 LSF point measurements of [NO] in the AIDF are tabulated in Table H.1 of Appendix H, and shown in Fig. 7.1. The relative uncertainty for those data points with [NO] > 20 relative ppm is ~22%, which corresponds to a signal-to-noise ratio of ~4.5. The specific LSF uncertainties for each signal level are shown in Fig. F.1 of Appendix F and are tabulated in Table H.1 of Appendix H. From Fig. 7.1, it is apparent that the [NO] field above the fuel-rich annular combustion zone (i.e., $-9 \text{ mm} \leq r \leq -6 \text{ mm}$ and $6 \text{ mm} \leq r \leq 9 \text{ mm}$) is relatively flat with a nominal magnitude of ~54 relative ppm. The measured [NO] drops off in the oxidizer jet at heights $y \leq 9 \text{ mm}$ and in the argon guard flow. However, even at the lowest elevation (i.e., $y = 3 \text{ mm}$), the LSF measurements indicate that some NO has diffused into the oxidizer-jet centerline. This surprising result may arise from the effects of spatial integration due to the finite extent of the probe volume. Nevertheless, this NO diffusion effect is observed to increase with increasing height above the burner. No radial enhancement in [NO] is observed at these AIDF-front locations. However, Fig. 7.1 indicates some enhancement in NO production around the AIDF tip which extends from 9 mm to 13 mm above the burner surface (Section 5.7). At the inner edge of the AIDF tip ($y = 9 \text{ mm}$), the radial [NO] profile is observed to be relatively flat. However, enhanced NO formation is observed within the AIDF tip ($y = 11 \text{ mm}$), and is more prominent at the outer edge of and just above the AIDF tip ($y = 13\text{--}15 \text{ mm}$). This NO formation enhancement at the AIDF tip produces a peak [NO] of ~70 relative ppm. This enhanced NO formation is apparently due to the combination of high temperatures and high residence times associated with the AIDF tip, and is consistent with the conclusions of Chapter 2.

7.2 PLIF NO Concentration Measurements

The PLIF [NO] image spanned a radial range of -15 mm to $+15 \text{ mm}$, and an elevation range of 2.5 mm to 16 mm above the AIDF-burner surface. Hence, the PLIF [NO] image captured the post AIDF-tip region of the [NO] field. Pyrromethene-580 laser dye was used to provide an average laser-sheet fluence of $\sim 0.04 \text{ mJ/mm}^2\text{-pulse}$. Based on Appendix C, this laser fluence was well within the range necessary to ensure linear fluorescence throughout the laser sheet, even accounting for a 67% fluctuation in local

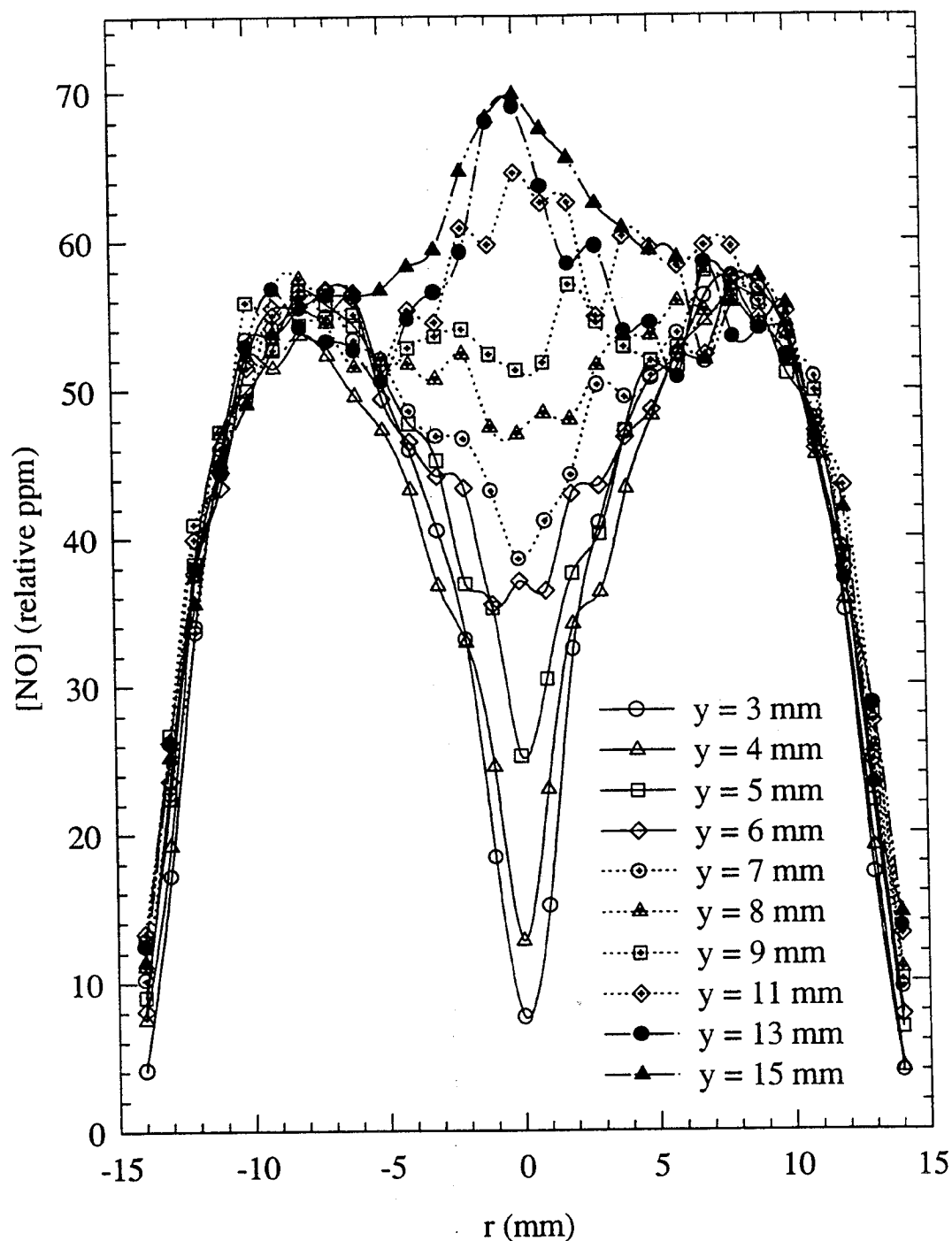


Figure 7.1 LSF measurements of [NO] in the AIDF. The LSF measurements are relative in terms of temperature; they have not been corrected for temperature effects (density and Boltzmann fraction) due to the temperature differences between the test and calibration environments.

fluence of the laser sheet. The PLIF measurements were made using $Q_2(26.5)$ excitation followed by BB detection incorporating a 250-W-2S wide-band interference filter with 6 mm of UG5 color-glass filter (Section 5.3.3). Based on the projected pixel size with an ~ 0.42 collection-optics magnification and a focused-sheet thickness of 400 μm , the per-pixel probe volume was approximately 56- μm square by 400- μm thick. For the PLIF [NO] imaging, a 30-ns gate was used, the ICCD gain was set to 9.16, and 1800 fluorescence events were integrated on chip. To reduce the dark noise, the CCD temperature was reduced to -20°C via the thermoelectric cooler. The PLIF [NO] images were corrected for dark and readout noise, flame luminosity, laser-induced background (i.e., interferences), and laser-sheet nonuniformity, as discussed in Sections D.2 and D.3. The detection limit for the PLIF measurements was determined to be ~ 1.5 relative ppm (Section F.3).

The PLIF image of [NO] in the AIDF is shown in Fig. 7.2 where the color bar indicates the [NO] in relative ppm. The relative uncertainty for those data points with [NO] > 20 relative ppm is $\sim 28\%$, which corresponds to a signal-to-noise ratio of ~ 3.6 . The specific PLIF uncertainties for each signal level are shown in Fig. F.3 of Appendix F. Compared to the 290 LSF measurements of Fig. 7.1, the PLIF image of Fig 7.2 represents 133,407 individual point [NO] measurements spaced every $\sim 56 \mu\text{m}$ in the image. The PLIF image displays the same general [NO] distribution as the LSF results but with ~ 18 times better spatial resolution. This two-dimensional imaging capability of PLIF demonstrates its major advantage over point-measurement techniques.

The horizontal structures in Fig. 7.2 are not due to the bulk distribution of the laser sheet (i.e., laser-sheet nonuniformities). The effects of such laser-sheet nonuniformities have been corrected for as described in Section D.2. The magnitude of the fluctuations associated with the horizontal structures in Fig. 7.2 is $\sim 20\%$; this is less than both the uncertainty of the PLIF measurements (i.e., $\sim 28\%$ as indicated in Appendix F) and the laser sheet nonuniformities (i.e., $\sim 67\%$ as indicated in Section C.2). Moreover, the spatial distribution of these horizontal structures is not spatially representative of the bulk laser-sheet nonuniformities. We believe that these structures are due to small fluctuations in the irradiance of the laser sheet that occur about the bulk laser-sheet nonuniformity

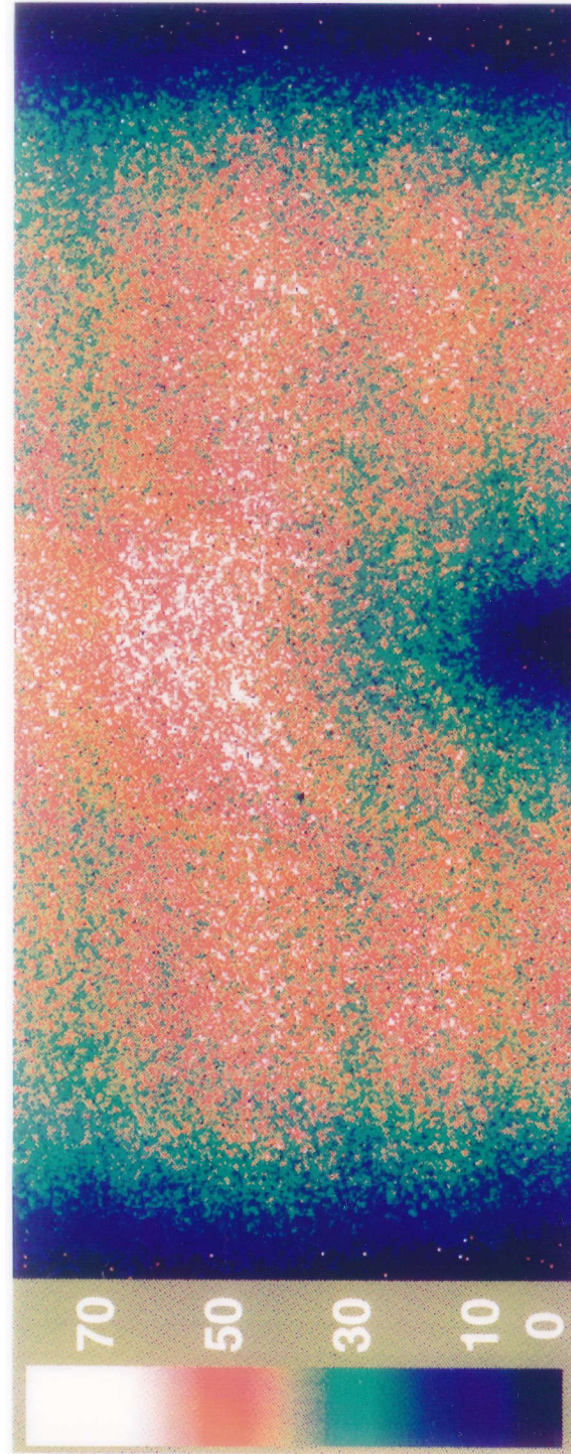


Figure 7.2 PLIF [NO] image in the AIDF. The color bar indicates the [NO] in relative ppm. The PLIF measurements are relative in terms of both temperature and electronic quenching; they have not been corrected for either temperature (density and Boltzmann fraction) or electronic quenching effects due to differences in both the temperature and the electronic quenching rate coefficient between the test and calibration environments.

throughout the PLIF experiment. The corrections for laser-sheet nonuniformity were implemented by using the images taken at the end of an experiment (i.e., IM12, IM13, IM14, and IM15 in Table D.1). Hence, the laser-sheet nonuniformities were characterized in the final ~20 minutes of the total 80-minute experiment. It is highly likely that small variations in the spatial profile of the laser occurred throughout the experiment and possibly even during the acquisition of images IM12 through IM15. Such fluctuations would be expected to produce errors in the final corrected PLIF image, as observed by the spatial structure in Fig. 7.2. The influence of these shot-to-shot and image-to-image fluctuations in the laser sheet could be accounted for if such fluctuations were actively monitored (e.g., with a linear photodiode array). Unfortunately, the resources necessary to actively monitor the spatial distribution of the laser sheet were not available during these experiments. However, such monitoring should be implemented in future PLIF measurements.

From Fig. 7.2, it is apparent that the [NO] field above the fuel-rich annular combustion zone is relatively flat with a nominal magnitude of ~48 relative ppm. The PLIF measured [NO] again drops off radially in the oxidizer jet and in the argon guard flow, with increasing NO diffusion into the oxidizer-jet centerline with increasing height above the burner surface. Moreover, although no enhancement in [NO] is observed at the radial AIDF-front locations, the localized [NO] enhancement near the AIDF tip is obvious.

7.3 PLIF Image Assessment

The quantitative nature of PLIF imaging in the AIDF was experimentally assessed by comparing the PLIF image of Fig. 7.2 to the 290 LSF point measurements of Fig. 7.1. To make the comparison, the PLIF image was sampled at locations corresponding to the spatial locations of the 290 LSF measurements. Moreover, at each sample location in the image, binning was employed to create a sample region 19-pixels long in the radial dimension by 1-pixel tall in the axial dimension. This corresponded to an area in the laser sheet ~1.06-mm long by ~56- μ m tall, which compares well with the area (1-mm long by 68- μ m tall) sampled by the LSF measurements. The program used to sample and bin the PLIF image at the 290 locations is provided in Appendix G. The binned PLIF data and

their associated uncertainties are tabulated in Table H.2 of Appendix H. Comparison of this binned PLIF data to the LSF data ensures no biasing of either data set due to different spatial-sampling areas.

The binned PLIF data are compared with the corresponding LSF point measurements, on an elevation-specific basis, in Figs. 7.3a, 7.3b and 7.3c. In these figures, the uncertainty bars are shown only for the LSF measurements. For reference, at an [NO] of ~50 relative ppm, for which the uncertainty in the LSF measurements is ~21% (Section F.2), the uncertainty in the PLIF data is ~28% (Section F.3). These figures demonstrate that the PLIF and LSF measurements display the same [NO] trends throughout the AIDF. Moreover, 84% of the binned PLIF data points are within the uncertainty of the LSF measurements (i.e., only 46 of the 290 PLIF measurements are outside the $\delta N_{T,RT}$ range of the LSF data). In fact for 99% of the data, the uncertainty bars of the binned PLIF and LSF data overlap (i.e., the uncertainty bars do not overlap at only two locations, (y,r), at (3,0) and (4,14)). These observations demonstrate that the quantitative nature of the PLIF measurements of [NO] is excellent when considering the harsh environment of the AIDF.

The quantitative nature of the PLIF image may be more critically assessed by evaluating the difference between the LSF and binned PLIF data. Recall that the PLIF and LSF measurements of relative [NO] should differ only through the influence of the electronic quenching rate coefficient. Hence, spatial variations in the difference between the two data sets will be due to spatial variations in only the electronic quenching rate coefficient plus data scatter within the uncertainty of each measurement. Figure 7.4 shows the spatial variation in the difference between the LSF and binned PLIF measurements normalized by the absolute uncertainty in the corresponding LSF measurement, i.e., $(N_{T,RT} - N_{T,RT,RQ}) / \delta N_{T,RT}$. Positive (i.e., enhanced) and negative (i.e., depressed) values of the normalized difference indicate an underprediction and overprediction of the [NO] by the PLIF measurements, respectively, relative to the LSF measurements. Data in Fig. 7.4 for which the absolute value of the normalized difference is less than unity indicates that the binned PLIF measurement is within the uncertainty of

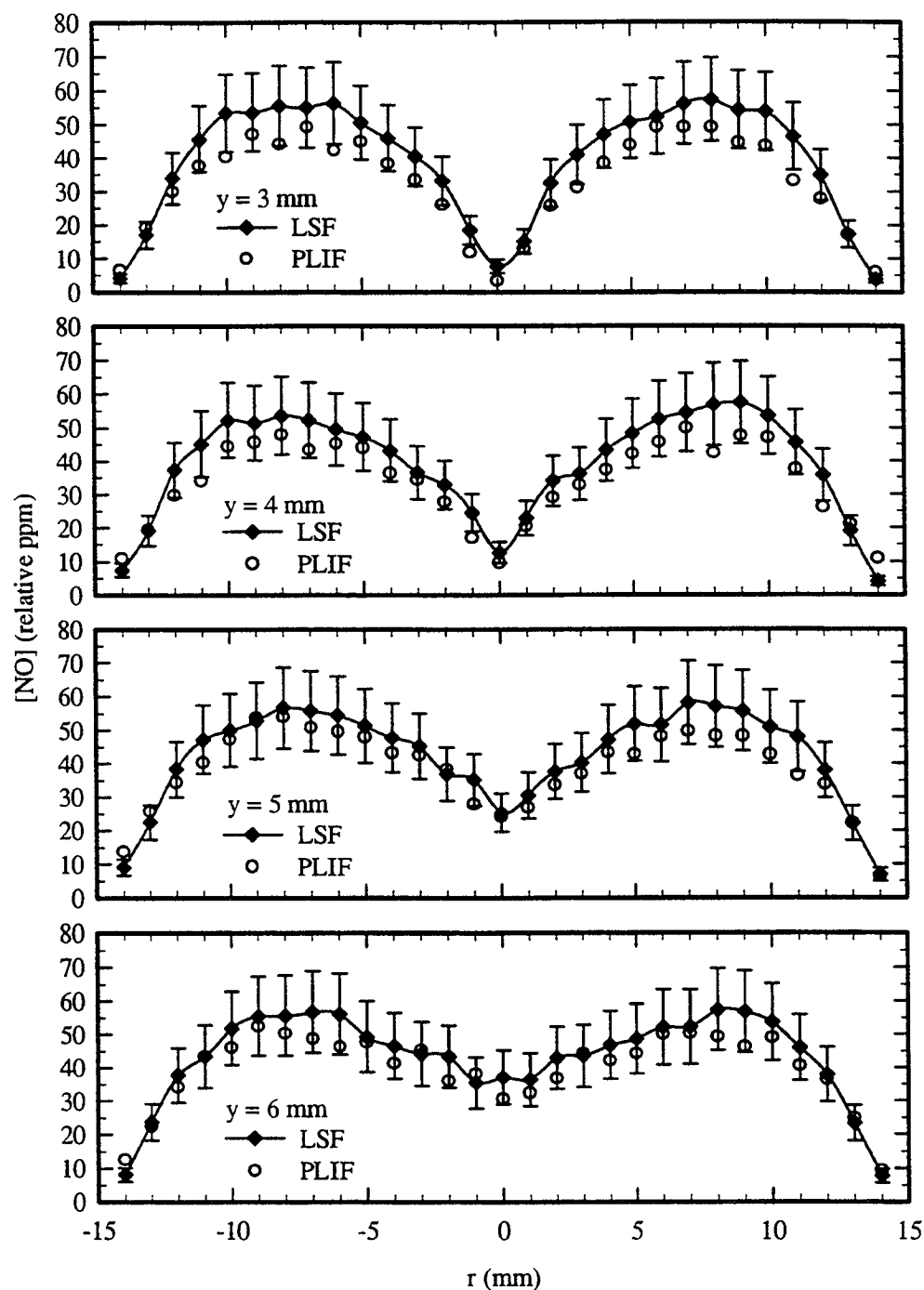


Figure 7.3a Comparison of the binned data from the PLIF image with the corresponding LSF point measurements. The PLIF and LSF data are compared at 29 radial locations and heights $y=3$ to 6 mm.

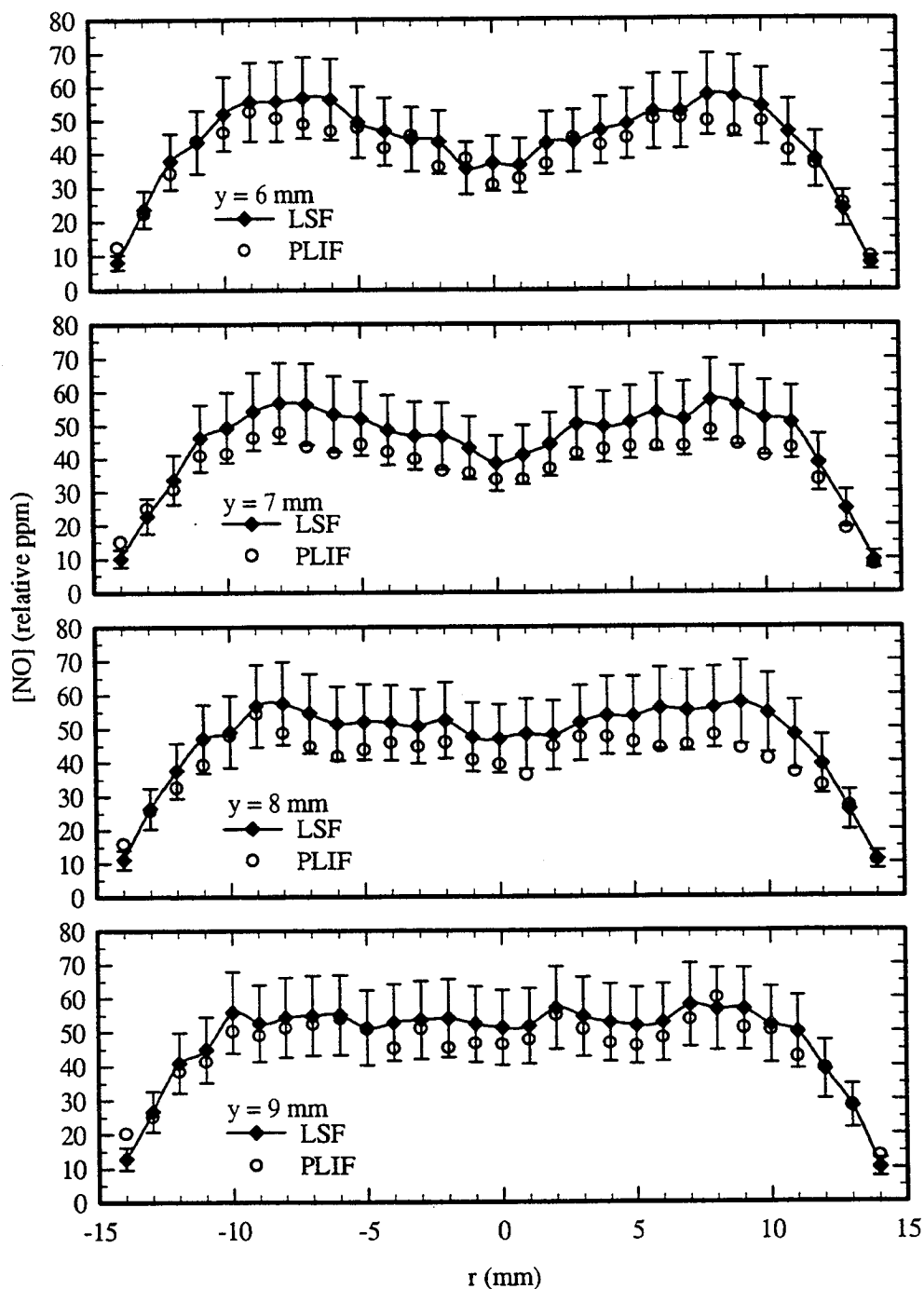


Figure 7.3b Comparison of the binned data from the PLIF image with the corresponding LSF point measurements. The PLIF and LSF data are compared at 29 radial locations and heights $y=6$ to 9 mm.

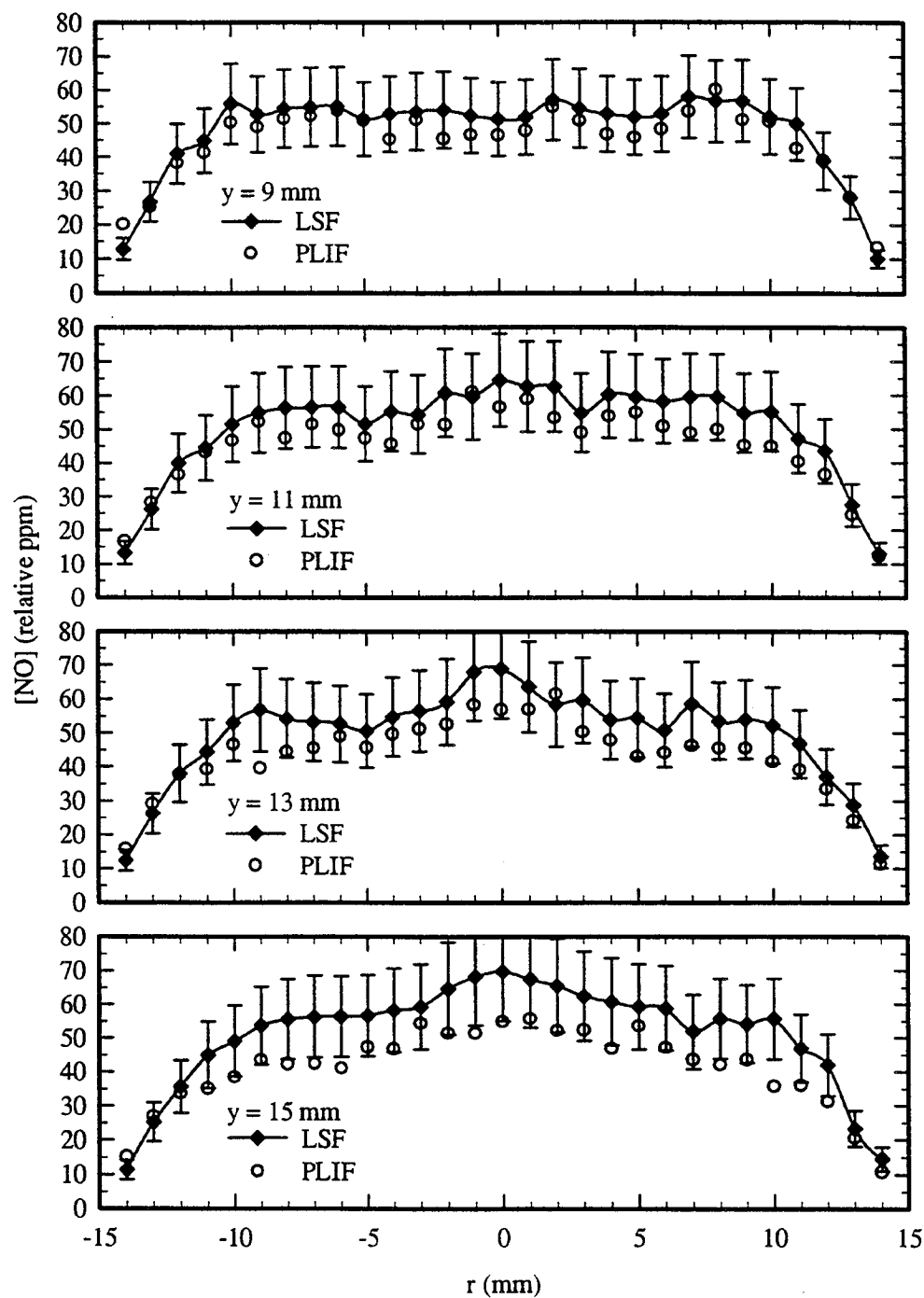


Figure 7.3c Comparison of the binned data from the PLIF image with the corresponding LSF point measurements. The PLIF and LSF data are compared at 29 radial locations and heights $y=9$ to 15 mm.

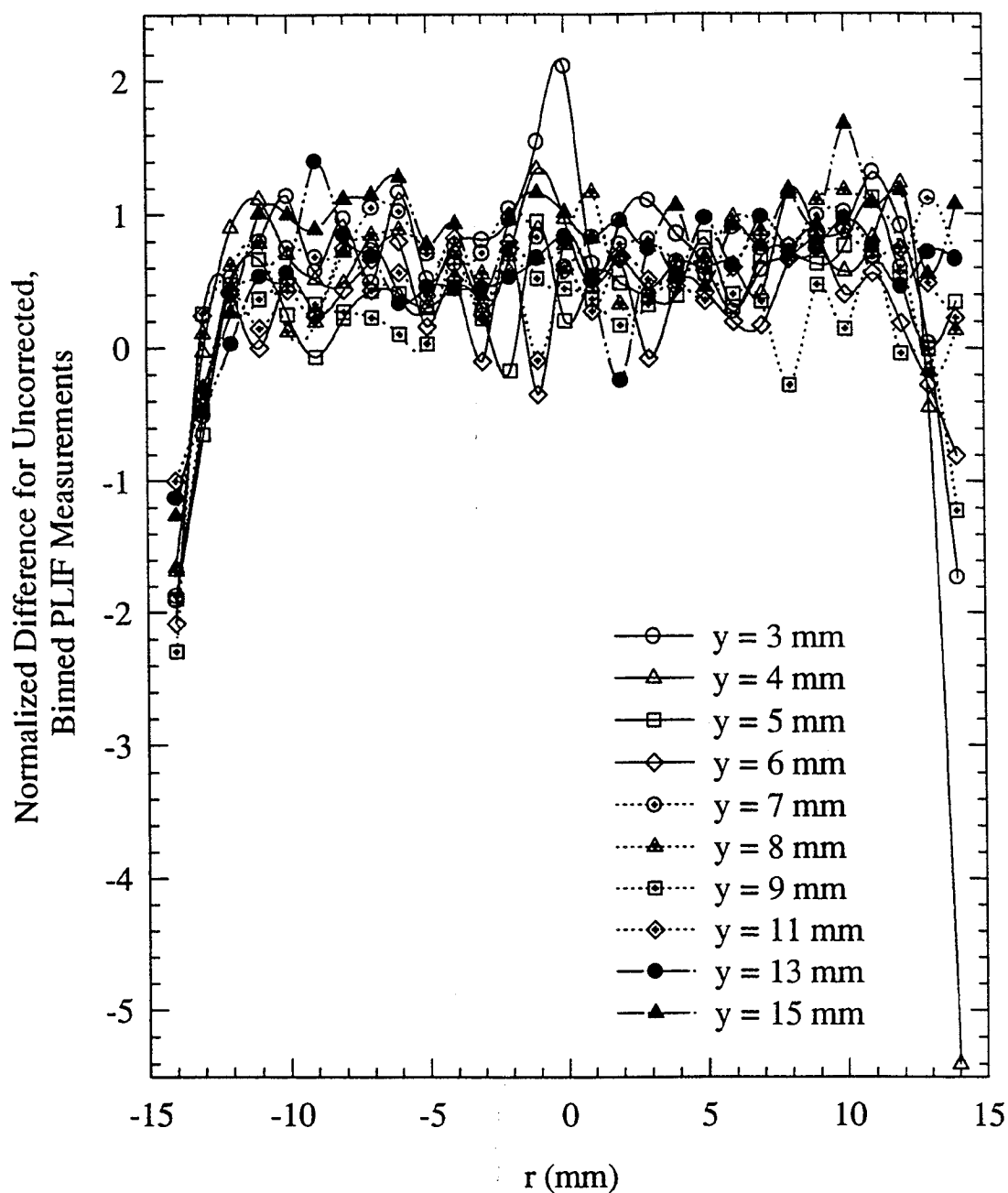


Figure 7.4 Difference in the binned PLIF and LSF data normalized by the absolute uncertainty in the corresponding LSF data. The normalized difference is defined as $(N_{T,RT} - N_{T,RT,RQ}) / \delta N_{T,RT}$, where $N_{T,RT}$ and $N_{T,RT,RQ}$ are the LSF and PLIF relative [NO] measurements, respectively, and $\delta N_{T,RT}$ is the absolute uncertainty in the LSF measurements.

the corresponding LSF measurement. The results in Fig. 7.4 confirm that 84% of the binned PLIF data points are within the uncertainty of the LSF measurements.

The normalized difference data of Fig. 7.4 display significant scatter attributable primarily to fluctuations in the individual measurements within their uncertainties. Errors in the PLIF measurements due to the influence of the electronic quenching rate coefficient are revealed in Fig. 7.4 by consistent trends in the normalized difference. The three consistent trends in Fig. 7.4 are : (1) a nominally uniform but enhanced normalized difference within the combustion region (i.e., $-12 \text{ mm} < r < +12 \text{ mm}$), (2) an enhanced normalized difference within the oxidizing jet at the lowest elevation (i.e., $y=3 \text{ mm}$), and (3) a depressed normalized difference at the interface between the combustion region and the argon guard flow. However, based on evaluating the results of five separate PLIF experiments, the only consistent trend in the normalized difference associated with the IDF was in the center of the oxidizing jet at the lowest elevation (i.e., at $(y,r) = (3,0)$). Specifically, a consistent normalized difference, beyond that described in (1) above, was not observed for $(y,r) = (3,-1)$ and $(y,r) = (3,1)$. Finally, the asymmetry of the normalized difference at the argon-guard interface is apparently due to an asymmetry of this interface about the AIDF centerline.

Figure 7.4 indicates that the PLIF measurements nominally underpredict $[\text{NO}]$ by $\sim 0.64 \cdot \delta N_{\text{T,RT}}$ within the AIDF (i.e., $-12 \text{ mm} < r < +12 \text{ mm}$), and tend towards overpredicting the $[\text{NO}]$ in the argon guard flow. The nominally uniform, enhanced normalized difference within the AIDF indicates a nominally uniform electronic quenching rate coefficient over the range of stoichiometries in the AIDF ($0 < \phi \leq 1.4$) and through the AIDF-front. Errors due to gradients in the electronic quenching rate coefficient are apparent at the coolest location in the oxidizing jet and at the argon guard flow interface. Experimentally-based procedures to correct the PLIF image for these errors are discussed in the following sections.

7.4 Experimentally-Based PLIF Enhancement Procedures

The quantitative nature of PLIF images may be enhanced by correcting for the influence of the electronic quenching rate coefficient. One method for making such

corrections is to implement numerically-based correction schemes (Paul et al., 1994). Such correction schemes rely on proper modeling of the electronic quenching rate coefficient, as generally described in Section E.2. These numerically-based correction schemes may be implemented given sufficient knowledge of the local temperature, as well as the local number density (Cheng et al., 1992) and quenching cross-sections (Drake and Ratcliffe, 1993) of the major species, and using established modeling techniques (Paul et al., 1993). However, the extensive experimental and numerical resources necessary to implement such a numerically-based correction scheme greatly limits its applicability.

An alternative method to enhance the quantitative nature of PLIF images is to implement experimentally-based correction schemes. Such correction schemes use selective, directly-measured and highly quantitative secondary measurements as input to the PLIF measurement. Specifically, for the PLIF image of Section 7.2, an experimentally-based correction scheme would use one or more LSF point measurements of [NO] to enhance the quantitative nature of the PLIF image. Implementation of such an experimentally-based correction scheme requires only the ability to make PLIF and LSF measurements, which is a significant reduction in the requisite resources as compared to the above numerically-based correction schemes. Hence, experimentally-based correction schemes should provide a more broadly applicable method for enhancing the quantitative nature of PLIF.

Implementation of experimentally-based enhancement schemes requires a compromise between obtaining the requisite image and the uncertainty (i.e., the quantitative nature) of the final measurements. For example, a highly quantitative two-dimensional image could be built up point by point from single-point LSF measurements. In contrast, PLIF provides instantaneous two-dimensional data, although with higher uncertainty. The goal of the proposed enhancement schemes is to combine the strengths of the LSF (quantitative measurements) and PLIF (imaging capability) techniques to obtain [NO] images (i.e., two-dimensional [NO] data) that are sufficiently quantitative for a specific application. The compromise between obtaining spatially extended measurements and uncertainty dictates the number of secondary LSF inputs to be used in

the experimentally-based PLIF enhancement scheme. In general, the number of secondary inputs should be minimized so as to just satisfy the relevant uncertainty criteria.

7.4.1 Single-Input PLIF Enhancement Procedure

The simplest experimentally-based correction scheme uses a single secondary LSF point measurement to enhance the quantitative nature of a PLIF image. In this scheme, the entire PLIF image is scaled based on one LSF point measurement and an associated PLIF measurement at the location in the image corresponding to the location of the LSF measurement. Specifically, each point in the image is multiplied by $N_{T,RT}(y_s, r_s)/N_{T,RT,RQ}(y_s, r_s)$, where (y_s, r_s) is the location corresponding to the secondary LSF point measurement. Clearly, this single-input, experimentally-based correction scheme cannot correct for error gradients in the PLIF image. However, this simple scheme can minimize the average error throughout the PLIF image. Hence, the optimal location, (y_s, r_s) , at which to make the secondary LSF point measurement should correspond to a location in the image where the error is equal to the average error.

The primary utility of this single-input PLIF enhancement scheme is to correct PLIF images in environments with negligible errors due to gradients in the electronic quenching rate coefficient, Q_e . Implementation of the single-input PLIF enhancement scheme for fields with Q_e gradients requires separate spatially resolved LSF measurements to determine the optimal location, (y_s, r_s) , at which to make the secondary LSF point measurement. Making such requisite LSF measurements defeats the purpose of the single-input PLIF enhancement scheme, which is to minimize the number of secondary LSF inputs. Moreover, once such extensive spatially resolved LSF measurements are made, more accurate experimentally-based PLIF enhancement schemes could easily be implemented, as described in Section 7.4.2.

In many situations, it is known that Q_e effects produce a gradient-free error offset throughout the PLIF image. For instance, Q_e gradients have been shown to be negligible for NO measurements in premixed flames over the range $0.6 \leq \phi \leq 1.6$ (Reisel et al., 1993) and were shown to be so in Section 7.3 throughout the combustion region of the AIDF (i.e., $-12 \text{ mm} < r < +12 \text{ mm}$) except for the lowest elevation at the oxidizing-jet

centerline. In such gradient-free environments, every point in the image field corresponds to the optimum scaling location, (y_s, r_s) , since the normalized difference surface in such an environment is flat to within the uncertainties in the individual measurements (as evident from Fig. 7.4). Hence, for a PLIF image in an environment with negligible Q_e gradients, the single-input, experimentally-based enhancement scheme may be implemented by simply choosing a convenient location for the secondary LSF point measurement.

The single-input, experimentally-based enhancement scheme has been implemented on the binned data from the PLIF image of Fig. 7.2 by using $(y_s, r_s) = (7, 7)$ as the conveniently chosen scaling location; i.e., each binned PLIF data point was multiplied by $N_{T,RT}(7,7)/N_{T,RT,RQ}(7,7)$. The normalized difference between these 290 single-input enhanced PLIF measurements and the corresponding LSF measurements was calculated as described in Section 7.3. The binned-PLIF measurements resulting from application of the single-input, experimentally-based enhancement scheme are tabulated in Table H.3 of Appendix H. The average absolute value of the normalized difference over various radial ranges is also tabulated in Table 7.1, and the resulting normalized-difference curves are shown in Fig. 7.5. It is clear from Fig. 7.5 that the single-input enhancement scheme has shifted the nominal normalized difference values closer to zero. The average error in the PLIF image may be assessed based on the average absolute value of the 290 normalized-difference data points. In fact, as indicated in Table 7.1, whereas the absolute value of the normalized difference for the 290 uncorrected measurements of Fig. 7.4 was ~ 0.68 , it is ~ 0.49 for the enhanced measurements of Fig. 7.5. This corresponds to a nominal $\sim 28\%$ enhancement in the quantitative nature of the PLIF image over the entire image field.

Since the single-input enhancement scheme is most applicable in Q_e gradient-free environments, its true utility should be assessed in the combustion region of the PLIF image (i.e., $-12 \text{ mm} < r < +12 \text{ mm}$). This is also the region of primary interest for studying NO formation by IDFs. Moreover, in this region, the binned data is 99.6% gradient free (i.e., only 1 out of 250 binned PLIF measurements displayed a consistent quenching gradient). As indicated in Table 7.1, the absolute value of the normalized difference for the single-input enhanced PLIF measurements in this region is ~ 0.33 . Compared to the corresponding ~ 0.65 value for the uncorrected binned PLIF

Table 7.1 Average absolute values of the normalized difference in the binned PLIF and LSF measurements over various radial ranges in the imaged environment. Average absolute values are given for the uncorrected, single-input enhanced and multiple-input enhanced PLIF data discussed in Sections 7.3, 7.4.1 and 7.4.2, respectively. The normalized difference is defined as $(N_{T,RT} - N_{T,RT,RQ})/\delta N_{T,RT}$, where $N_{T,RT}$ and $N_{T,RT,RQ}$ are the LSF and PLIF relative [NO] measurements, respectively, and $\delta N_{T,RT}$ is the absolute uncertainty in the LSF measurements.

	-14 mm to +14	-12 mm to +12	-14 mm to +12	-14 mm to -10
Uncorrected	0.68	0.65	0.67	0.73
Single-input Enhancement	0.49	0.33	0.44	0.98
Multiple-input Enhancement	0.41	0.34	0.34	0.27

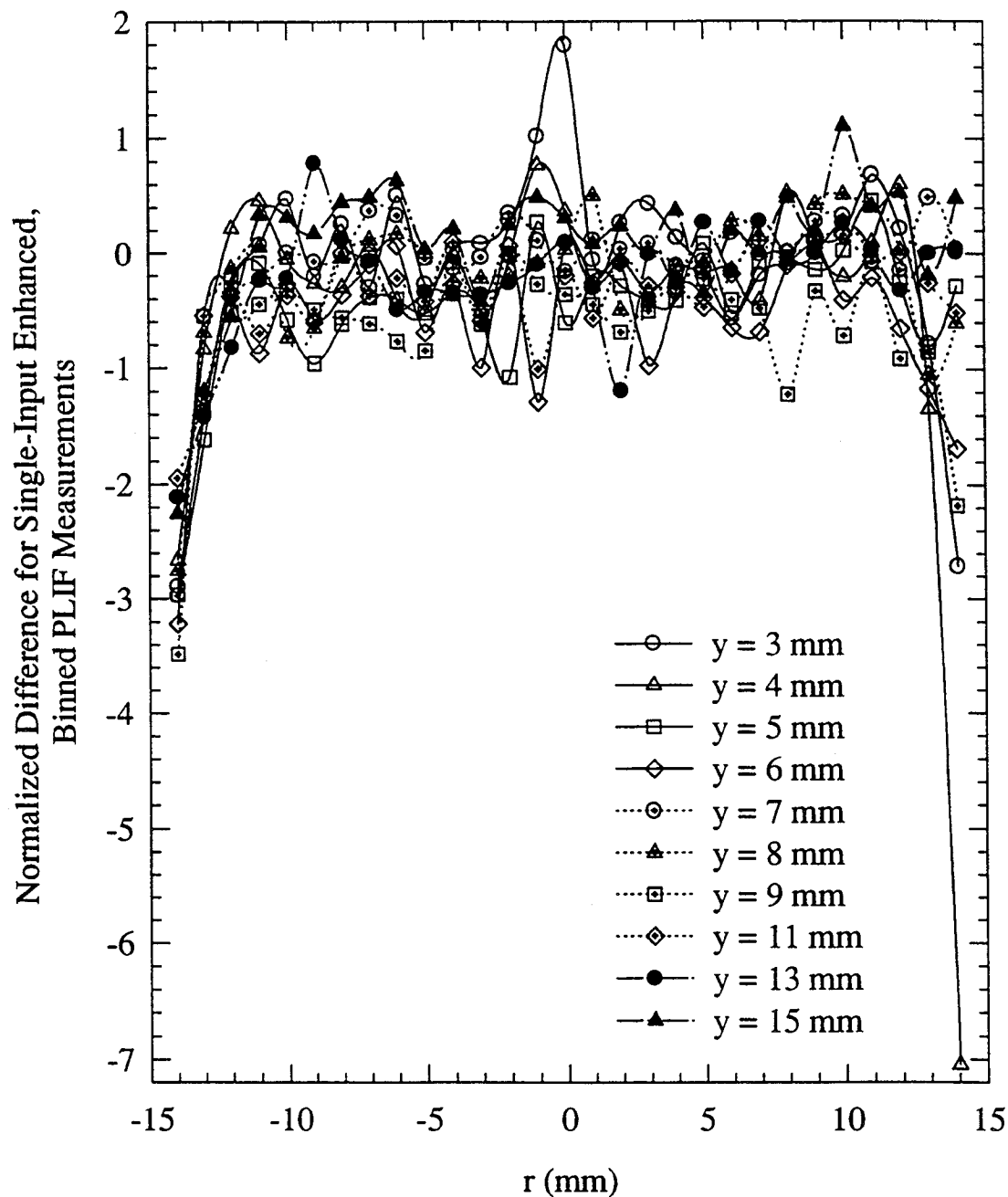


Figure 7.5 Difference in the binned PLIF measurements using the single-input, experimentally-based enhancement scheme and the LSF data, normalized by the absolute uncertainty in the corresponding LSF data. The normalized difference is defined as $(N_{T,RT} - N_{T,RT,RQ}) / \delta N_{T,RT}$, where $N_{T,RT}$ and $N_{T,RT,RQ}$ are the LSF and PLIF relative [NO] measurements, respectively, and $\delta N_{T,RT}$ is the absolute uncertainty in the LSF measurements.

measurements of Fig. 7.4, this represents an ~50% enhancement in the quantitative nature of the PLIF image over the specified region of the [NO] image. Moreover, application of the single-input enhancement scheme, in the specified range, has driven the number of binned PLIF measurements outside the $\delta N_{T,RT}$ range of the LSF measurements from 32 (12.8%) in Fig. 7.4 to only 8 (3.2%) in Fig. 7.5.

Although the above discussion indicates an ~50% enhancement in the quantitative nature of the PLIF image resulting from application of the single-input enhancement scheme, a more quantitative assessment may be obtained for the uncertainties in the resulting enhanced PLIF image. Specifically, the uncertainty in the enhanced PLIF image should be limited by the greater of either the precision of the PLIF measurement or the total uncertainty in the LSF measurement. The precision of the PLIF measurement is the significant uncertainty parameter since the division by $N_{T,RT,RQ}(y_s, r_s)$ during the single-input enhancement process effectively cancels the previous application of CF^{PLIF} and its associated accuracy. The resulting intermediate PLIF measurements are then recalibrated using the single-input LSF measurement via multiplication by $N_{T,RT}(y_s, r_s)$. Hence, as the LSF measurement is used as an effective calibration standard, its total uncertainty is of significance. Based on the analysis of Appendix F, the nominal precision of the PLIF measurements is ~18% and the nominal uncertainty in the LSF measurements is ~21%. This indicates that the single-input enhanced PLIF image is limited by the uncertainty in the LSF measurements and should be quantitative, over the specified range, to within ~21% based on a 95% confidence interval. The normalized differences for the single-input enhanced PLIF image in Fig. 7.5 support this conclusion as 96.8% of the 250 measurements in the combustion region are within the uncertainty of the LSF measurement. This demonstrates that in an environment that is relatively free of Q_e gradients, the single-input enhancement scheme produces PLIF images that are nominally as quantitative as a single LSF point measurement. This profound enhancement in the quantitative nature of PLIF imaging of [NO] was achieved through use of only a single secondary LSF point measurement.

7.4.2 Multiple-Input PLIF Enhancement Procedure

A more involved experimentally-based correction scheme uses multiple secondary LSF point measurements to correct errors in a PLIF image due to gradients in the electronic quenching rate coefficient. Through use of multiple secondary inputs, the quantitative nature of such a PLIF image may be enhanced beyond that achievable via single-input correction schemes. The multiple-input PLIF correction scheme uses multiple LSF measurements, of suitable density along the Q_e gradients, to properly correct the PLIF image. Often, such error gradients are approximately spatially constant over some finite region of the image (i.e., over a distance normal to the direction of the gradient). In such a situation, a single array of LSF measurements can be applied, over the corresponding finite range of the image, to correct for the errors resulting from the Q_e gradients. Hence, the number of secondary inputs used for implementation of a multiple-input PLIF enhancement scheme can be minimized by : (1) minimizing the number of LSF measurements used to resolve a Q_e gradient, and (2) applying a single LSF array over a finite region of the image to nominally correct for the error gradients in that region.

The multiple-input, experimentally-based enhancement scheme has been implemented on the binned data from the PLIF image of Fig. 7.2. From Fig. 7.4, it is apparent that the PLIF image has a error gradient in the range $-14 \text{ mm} \leq r \leq -10 \text{ mm}$ that is nominally uniform over the entire elevation range of the image. The LSF and binned PLIF measurements at a given elevation may be used to define this gradient (which is in the radial direction). Moreover, since the gradient is nominally uniform with elevation, the error-gradient correction defined by the LSF and PLIF measurements at a given elevation may be used to correct the corresponding gradients at all other elevations in the image.

To demonstrate the multiple-input correction scheme, the data at $y=7 \text{ mm}$ was used to define the error gradient. The multiple-input correction was implemented by applying a radial-location-specific correction to the binned image data. Specifically, each binned measurement, $N_{T,RT,RQ}(y,r)$, was multiplied by $N_{T,RT}(7,r)/N_{T,RT,RQ}(7,r)$. Similarly, to correct the entire image, a curve could be fit to the $N_{T,RT}(7,r)/N_{T,RT,RQ}(7,r)$ data and the resulting correction curve could then be applied on a radial-location-specific basis to the full 133,407 pixels of the PLIF image. Moreover, although the error gradients may be

uniform with elevation, extensive LSF data should be used once available. In other words, optimum enhancement of the full PLIF image would implement the multiple-input enhancement scheme using all 290 LSF point measurements. In this process, a given error gradient correction, $N_{T,RT}(y_j, r)/N_{T,RT,RQ}(y_j, r)$, would be applied over an elevation range in the image corresponding to $(y_{j-1} + (y_j - y_{j-1})/2) < y < (y_j + (y_{j+1} - y_j)/2)$; possibly, some matching rule could be implemented, via weighting factors, to match the error-gradient correction at the various interfaces (e.g., at $y_{j-1} + (y_j - y_{j-1})/2$). Nevertheless, use of a single error-gradient correction over the entire image can be used to demonstrate the utility of multiple-input, experimentally-based enhancement procedures. Such a procedure also demonstrates image enhancement with a limited number of secondary LSF inputs. Further minimization of the number of secondary LSF inputs necessary for the experimentally-based enhancement procedure is demonstrated in the following section.

The normalized difference between the 290 multiple-input enhanced PLIF measurements and the corresponding LSF measurements was calculated as described in Section 7.3. The binned-PLIF measurements resulting from application of the multiple-input, experimentally-based enhancement scheme are tabulated in Table H.4 of Appendix H. Moreover, the average absolute value of the normalized difference over various radial ranges is tabulated in Table 7.1 and the resulting normalized difference curves are shown in Fig. 7.6. Comparing Figs. 7.4 and 7.6, it is apparent that the multiple-input correction scheme is quite effective in mitigating the error gradient in the range $-14 \text{ mm} \leq r \leq -10 \text{ mm}$. Specifically, the error gradient in this range of the multiple-input, corrected measurements has collapsed to within the uncertainty of the LSF measurements. Moreover, the normalized error throughout the image has shifted closer to zero as compared to the uncorrected results of Fig. 7.4. The correction scheme is not as effective in the range $10 \text{ mm} \leq r \leq 14 \text{ mm}$ since the error gradients in this region of the image are not nominally uniform over the range of elevations investigated. Nevertheless, based on Table 7.1, the multiple-input correction scheme provides an ~40% enhancement in the quantitative nature of the PLIF measurements over the entire range of the image as compared to the uncorrected measurements. Moreover, application of the multiple-input enhancement scheme has driven the number of binned PLIF measurements outside the

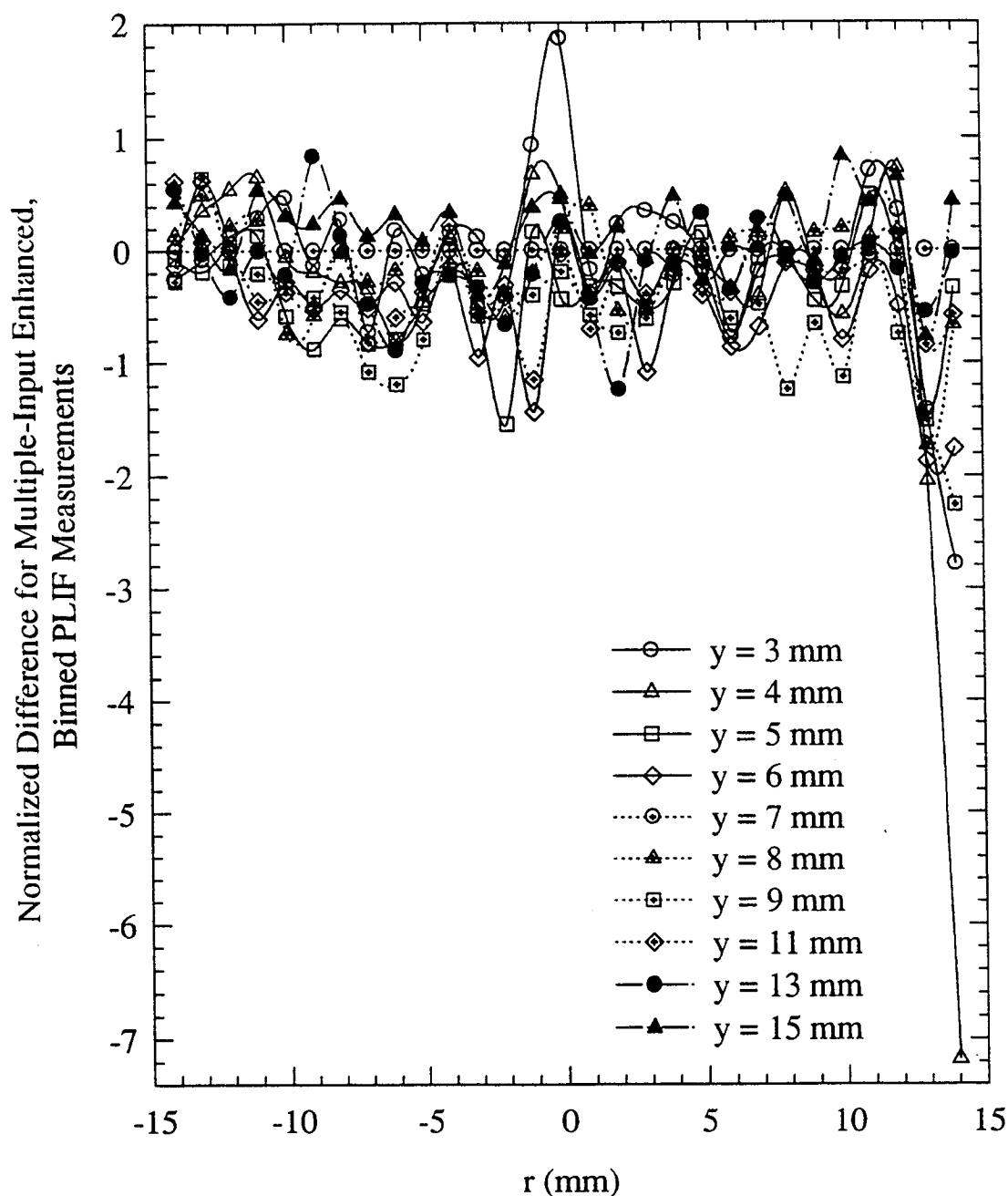


Figure 7.6 Difference in the binned PLIF measurements using the multiple-input, experimentally-based enhancement scheme and the LSF data, normalized by the absolute uncertainty in the corresponding LSF data. The normalized difference is defined as $(N_{T,RT} - N_{T,RT,RQ}) / \delta N_{T,RT}$, where $N_{T,RT}$ and $N_{T,RT,RQ}$ are the LSF and PLIF relative [NO] measurements, respectively, and $\delta N_{T,RT}$ is the absolute uncertainty in the LSF measurements.

$\delta N_{T,RT}$ range of the LSF measurement from 46 (15.8%) in Fig. 7.4 and 31 (10.7%) in Fig. 7.5, to 20 (6.9%) in Fig. 7.6. This demonstrates the enhanced benefit of the multiple-input correction scheme over the single-input correction scheme.

Based on the way the multiple-input correction scheme was implemented to arrive at the data of Fig. 7.6 (i.e., using a single elevation to characterize the error gradients at all elevations of the image), its true utility should be assessed by neglecting the error gradients at the positive radial locations. The error gradients at the positive radial locations could be mitigated by implementing the multiple-point correction scheme over several distinct elevation ranges in the imaged environment, as discussed earlier. Based on Table 7.1, the multiple-input correction scheme used provides ~50% enhancement in the quantitative nature of PLIF over the range $-14 \text{ mm} \leq r \leq +12 \text{ mm}$ (i.e., the full range less the error gradients at the positive radial locations). Moreover, in this radial range, the number of multiple-input enhanced PLIF measurements outside the $\delta N_{T,RT}$ range of the LSF measurement has been reduced from 41 (15.2%) in Fig. 7.4, to only 10 (3.7%) in Fig. 7.6. The effectiveness of the multiple-input correction scheme is even more pronounced in the immediate region of the error gradients (i.e., $-14 \text{ mm} \leq r \leq -10 \text{ mm}$). In this range, based on Table 7.1, the multiple-input correction scheme provides an ~63% enhancement to the quantitative nature of the PLIF measurements.

The uncertainty in the multiple-input corrected PLIF measurement should be limited by either the total uncertainty in the LSF measurements or the precision of the PLIF measurements, as discussed in Section 7.4.1. The enhanced PLIF image is again limited by the uncertainty in the LSF measurements. Over the range $-14 \text{ mm} \leq r \leq +12 \text{ mm}$, the multiple-input enhanced PLIF image should be quantitative to within ~21% based on a 95% confidence interval. This conclusion is supported by the data in Fig. 7.6 as, in the specified range, 96.3% of the 270 measurements are within the uncertainty of the LSF measurements. As discussed earlier, for images with nonuniform error gradients, the multiple-input enhancement scheme could be implemented over several distinct regions of the image. Nevertheless, these results demonstrate that in environments with Q_e gradients, the multiple-input enhancement scheme is capable of

producing PLIF images that are nominally as quantitative as a single LSF point measurement.

7.4.3 PLIF Enhancement Procedure Implementation

The number of secondary LSF measurements required for confident implementation of an experimentally-based PLIF enhancement procedure is directly related to the quantity of existing knowledge concerning the test environment. As mentioned earlier, the absolute minimum number of LSF measurements is required for implementation of a single-input enhancement scheme for PLIF measurements in environments with negligible Q_e gradients. However, this requires a rather extensive understanding of the test environment. It is more likely to expect that (1) little to no knowledge of the test environment exists, or (2) some knowledge exists of a test environment which has regions both with and without Q_e gradients. Implementation of experimentally-based enhancement procedures in such general circumstances is discussed in this section. Moreover, a minimal-input, experimentally-based enhancement procedure is discussed, which uses a minimum number of secondary LSF data for our PLIF measurements of [NO] in the AIDF.

The most involved implementation of an experimentally-based PLIF enhancement procedure would occur for measurements in a test environment concerning which little to no a-priori knowledge exists. In such a general situation, Q_e -induced error gradients would be assumed to exist, and one would anticipate using a multiple-input PLIF enhancement procedure. Hence, sufficient secondary LSF measurements would be required to characterize the PLIF error field (i.e., identify regions of constant and varying Q_e), resolve any error gradients, and assess the range of applicability of any error-gradient correction in a direction normal to the error gradient. Such a worst-case scenario is likely to require several hundred secondary LSF measurements for this error-field characterization. In fact, error-field characterization may require more secondary LSF measurements than are ultimately required for implementation of an experimentally-based enhancement procedure. For example, in the current study of NO formation in an AIDF, although 290 LSF measurements were used in conjunction with the PLIF image to

characterize the error-field, fewer secondary measurements were required to produce an enhanced PLIF image with an acceptable quantitative nature.

Implementation of experimentally-based enhancement procedures in uncharacterized environments requires many secondary LSF measurements. Moreover, even in well-characterized environments, implementation of a multiple-input enhancement scheme may require extensive secondary measurements in order to characterize and correct for error gradients. Once such extensive quantitative LSF data is available, an image could be generated by interpolation using only the LSF data. However, confidence in such results would not be as high as for results from a multiple-input enhanced PLIF image. This is because $[\text{NO}]$ gradients are not equivalent to Q_e gradients. This statement is clear from comparing Figs. 7.1 and 7.4 in the region of the oxidizing jet above $y=3$ mm. Moreover, as evident from Eq. (4.24), the sensitivity of PLIF to $[\text{NO}]$ and to the electronic quenching rate coefficient is not the same; specifically, PLIF is less sensitive to Q_e gradients. Hence, the data density necessary to resolve Q_e gradients is less than that required to resolve $[\text{NO}]$ gradients. This conclusion indicates that it is more experimentally efficient to use the combination of a PLIF image to provide spatial resolution and arrays of LSF point measurements to correct for the inherent error gradients than to map the entire environment with LSF point measurements of sufficient spatial density to produce results of comparable confidence. In other words, multiple-input, experimentally-based enhancement procedures provide the most experimentally efficient means of obtaining imaging data of specified confidence in environments with gradients in the electronic quenching rate coefficient.

The number of secondary measurements required for confident implementation of an experimentally-based PLIF enhancement procedure can be significantly reduced via use of existing knowledge concerning the test environment. Such knowledge generally comes from previous studies of environments related to the test environment. This approach can be used to identify image regions over which error gradients are negligible, and hence, image regions over which a single-input enhancement procedure is applicable. Moreover, this information can identify image regions likely to exhibit error gradients, and regions over which error gradients are nominally uniform. For example, the AIDF study indicated

that the PLIF image exhibits (1) a nominally uniform Q_e -induced error over the equivalence ratio range $0 < \phi \leq 1.4$ and through the flame front, (2) no observable error gradient at the air/combustion interface, (3) strong error gradients at the guard/combustion interface, and (4) a nominally uniform error gradient in the axial direction. These observations now become existing knowledge which are expected to be observed in future investigations of similar AIDFs.

To demonstrate the use of existing knowledge in augmenting the application of experimentally-based PLIF enhancement procedures, a minimal-input, experimentally-based enhancement procedure was implemented assuming the AIDF observations discussed above to be existing knowledge. Since the AIDF should be radially symmetric, only the range $-14 \text{ mm} \leq r \leq 0 \text{ mm}$ is considered. Based on "existing knowledge", it is known that an approximately constant error exists throughout the range of combustion, and an error gradient, which is uniform over the range of elevations observed, exists at the guard/combustion interface. Hence, a single-input enhancement procedure is applicable in the body of the AIDF; specifically, each point in the PLIF image, $N_{T,RT,RQ}(y,r)$, in the range $-11 \text{ mm} \leq r \leq 0 \text{ mm}$ is multiplied by $N_{T,RT}(y_s, r_s)/N_{T,RT,RQ}(y_s, r_s)$, where $(y_s, r_s) = (7, -11)$. To correct for the error gradient at the guard/combustion interface, a multiple-input enhancement procedure is applied in this region; specifically, each point in the PLIF image, $N_{T,RT,RQ}(y,r)$, in the range $-14 \text{ mm} \leq r \leq -12 \text{ mm}$ is multiplied by $N_{T,RT}(7,r)/N_{T,RT,RQ}(7,r)$. Hence, this minimal-input, experimentally-based PLIF enhancement procedure uses a total of only four secondary LSF point measurements.

The binned-PLIF measurements resulting from application of this minimal-input, experimentally-based enhancement procedure are tabulated in Table H.5 of Appendix H. The normalized difference between the 150 PLIF measurements enhanced via the minimal-input procedure and the corresponding LSF measurements was calculated as described in Section 7.3, and the resulting normalized difference curves are shown in Fig. 7.7. Moreover, the average absolute value of the normalized difference for the uncorrected and various enhanced PLIF measurements over various radial ranges is tabulated in Table 7.2. From Fig. 7.7, it is clear that the minimal-input enhancement procedure is effective in correcting for both the uniform error and error gradients in the PLIF image. In fact, only

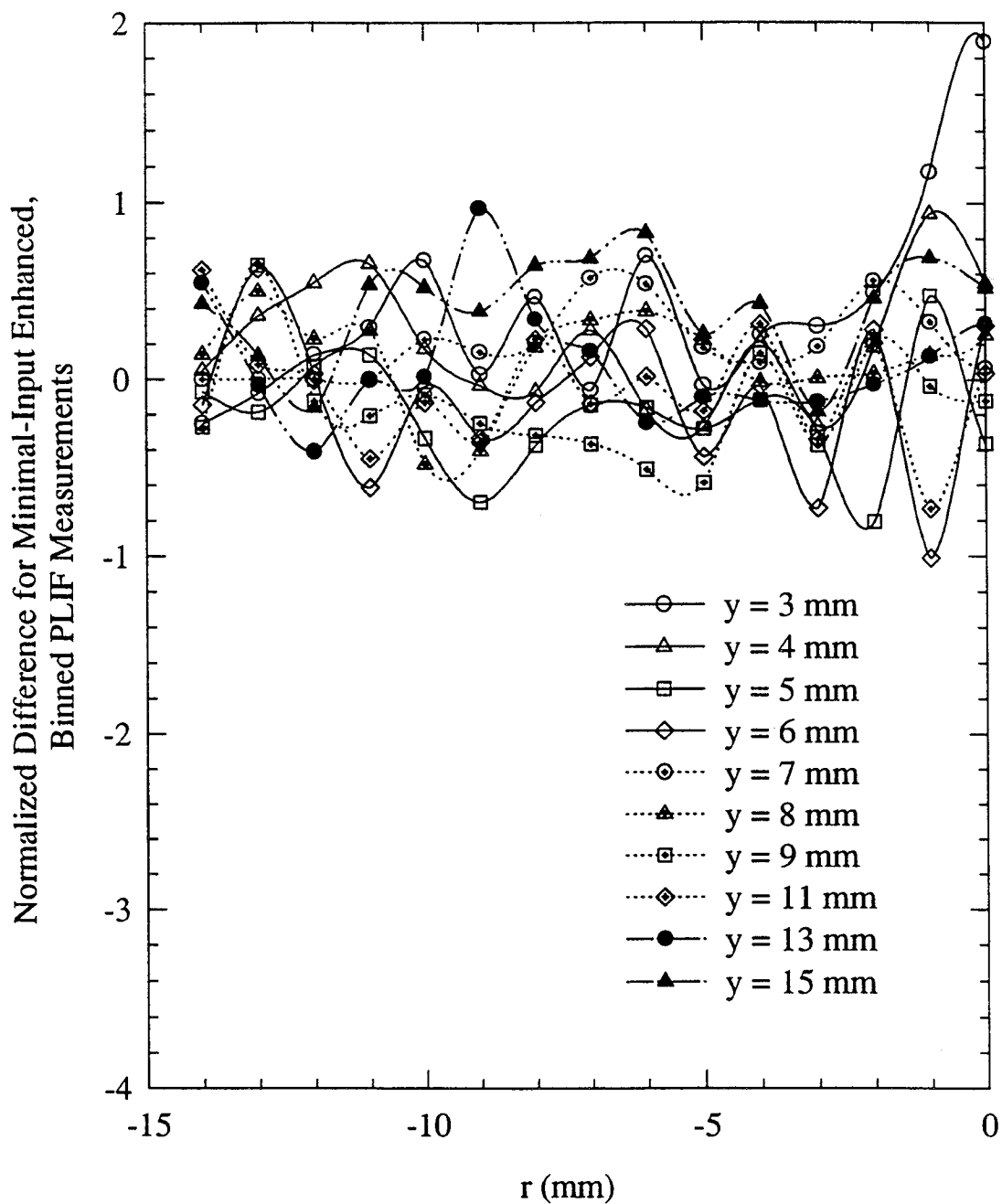


Figure 7.7 Difference in the binned PLIF measurements using the minimal-input, experimentally-based enhancement scheme and the LSF data, normalized by the absolute uncertainty in the corresponding LSF data. The normalized difference is defined as $(N_{T,RT} - N_{T,RT,RQ}) / \delta N_{T,RT}$, where $N_{T,RT}$ and $N_{T,RT,RQ}$ are the LSF and PLIF relative [NO] measurements, respectively, and $\delta N_{T,RT}$ is the absolute uncertainty in the LSF measurements.

Table 7.2 Average absolute values of the normalized difference in the binned PLIF and LSF measurements over various radial ranges in the imaged environment. Average absolute values are given for the uncorrected, single-input enhanced, and multiple-input and minimal-input enhanced PLIF data discussed in Sections 7.3, 7.4.1, 7.4.2 and 7.4.3, respectively. The normalized difference is defined as $(N_{T,RT} - N_{T,RT,RQ})/\delta N_{T,RT}$, where $N_{T,RT}$ and $N_{T,RT,RQ}$ are the LSF and PLIF relative [NO] measurements, respectively, and $\delta N_{T,RT}$ is the absolute uncertainty in the LSF measurements.

	0 mm to -14 mm	0 mm to -11 mm	-11 mm to -14
Uncorrected	0.67	0.63	0.76
Single-input Enhancement	0.57	0.36	1.14
Multiple-input Enhancement	0.36	0.39	0.25
Minimal-input Enhancement	0.31	0.33	0.25

2% of the PLIF measurements enhanced via the minimal-input procedure are outside the $\delta N_{T,RT}$ range of the LSF measurements. From Table 7.2, it is clear that the minimal-input procedure provides ~54% enhancement in the PLIF measurements, and that it is just as effective as the multiple-input procedure described in Section 7.4.2 which used 29 secondary LSF measurements. Notice that in the range $-11 \text{ mm} \leq r \leq 0 \text{ mm}$, the only difference between the minimal-input and the single-input enhancement procedures is the selection of the scaling point, (y_s, r_s) . In fact, the enhancement in the average absolute normalized difference in this range for the minimal-input scheme, 0.33, as compared to that for the single-input scheme, 0.36, is fortuitous; the only difference in these results arise from the uncertainty in the LSF measurements. Similarly, in the range $-14 \text{ mm} \leq r \leq 0 \text{ mm}$, the enhanced PLIF measurements resulting from the minimal-input and multiple-input procedures are equivalent to within the uncertainty of the LSF measurements (and hence to within the uncertainty of the enhanced PLIF measurements as discussed in the previous sections), despite the apparent enhancement for the minimal-input procedure indicated in Table 7.2. As discussed in the previous sections and supported by Fig. 7.7, the uncertainty in the PLIF measurements enhanced by the minimal-input, experimentally-based procedure is limited by that of the LSF measurements. Hence, the number of secondary LSF measurements required to confidently implement an experimentally-based PLIF enhancement procedure, may be minimized by using existing knowledge to tailor the enhancement procedure to the specific test environment. Moreover, the minimal-input enhancement procedure produces PLIF images that are just as quantitative as more extensive multiple-input enhancement procedures, but through the use of much fewer secondary LSF measurements.

7.4.4 PLIF Enhancement Conclusions

We have proposed and evaluated experimentally-based correction schemes for enhancing the quantitative nature of PLIF. These enhancement schemes are based on providing secondary inputs to the PLIF image from LSF point measurements. The single-input enhancement procedure uses a single LSF point measurement to enhance PLIF images of [NO] in environments with negligible gradients in the electronic quenching rate

coefficient. Alternatively, the multiple-input enhancement procedure corrects errors in PLIF images of [NO] due to Q_e gradients. Often it is known a priori that the Q_e gradients in a particular environment are negligible. In such instances, the single-input PLIF enhancement scheme is appropriate and the location at which to make the single secondary LSF point measurement may be selected at convenience. Multiple-input enhancement procedures require more secondary inputs to characterize and correct PLIF images for errors due to Q_e gradients. However, the number of secondary LSF inputs required for a specific test environment may be minimized by incorporating all existing knowledge of that environment into the design of the experimentally-based enhancement procedure. Nevertheless, the single-input and multiple-input, experimentally-based enhancement schemes provide the most experimentally efficient means of obtaining concentration images with a specified uncertainty in general combustion environments. Moreover, experimentally-based enhancement schemes are the only strategies currently applicable to PLIF studies of those species (e.g., radicals) for which insufficient data are available to implement numerically-based enhancement procedures. Finally, we have demonstrated that such experimentally-based enhancement procedures are capable of providing PLIF [NO] images that are nominally as quantitative as a single LSF point measurement.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The quantitative nature of PLIF measurements of [NO] has been experimentally assessed in an atmospheric-pressure inverse diffusion flame. Experimental assessment was based on comparison to a separate array of point LSF measurements of [NO]. In addition, experimentally-based correction procedures, for enhancing the quantitative nature of PLIF images of [NO], have been proposed and evaluated. These experimentally-based procedures correct PLIF images of [NO] for errors due to variations in the electronic quenching rate coefficient, and are based on providing the PLIF image with one or more secondary inputs from separate LSF point measurements of [NO]. Such experimentally-based PLIF enhancement procedures should be more broadly applicable, compared to numerically-based correction procedures, due to the fewer resources necessary for their implementation. Moreover, it was determined that application of the experimentally-based PLIF enhancement procedures produces images of [NO] which are nominally as quantitative as a single LSF point measurement. The result of this work is a more broadly applicable and quantitative PLIF diagnostic.

To generally assess NO formation by IDFs, a chemiluminescent-based study was performed of NO formation in a staged-air combustor. The staged-air combustor creates IDFs when secondary air is injected into the post-flame zone of a primary fuel-rich region. This parametric study investigated the influence of secondary air injection parameters on NO formation in the process of driving fuel-rich combustion to overall fuel lean via air injection. In the transition from fuel-rich to fuel-lean combustion, we observed a strong relationship between the NO emission index and the degree of mixing between the

secondary air and primary combustion products. In this transition region, the degree of mixing was strongly influenced by the secondary air injection parameters. However, at the most fuel-lean stoichiometry, the NO emission index was found to be independent of these injection parameters. This indicates that at this most fuel-lean stoichiometry, the NO is predominantly formed in the IDF-tip regions.

In the process of developing the theory for the PLIF and LSF measurements, a novel formulation of the overlap fraction was developed. The overlap fraction is used in fluorescence theory to account for the spectrally distributed interaction between laser radiation and molecular transitions. The overlap fraction is defined as the spectral integral of the product of the spectral distribution functions of the laser and the absorption transition. The unique form of the overlap fraction results from use of laser temporal and spectral distribution functions that are normalized to their FWHM rather than unity as in the previous literature. This form of normalizing the laser distribution functions was dictated by modeling the laser spectral irradiance so that it can be determined from physically measurable parameters. Use of such laser distribution functions produces a dimensionless overlap fraction, which in turn simplifies the fluorescence theory. However, the more profound result is that such modeling produces an overlap fraction which has a very clear and practical interpretation; in comparison, the traditional overlap fraction has a vague physical meaning. Specifically, the new overlap fraction represents the ratio of the total photon absorption rate in the actual broadened system to that which would exist in the limit of a monochromatic laser interacting resonantly with a monochromatic absorption line. Since calculation of the total photon absorption rate in the monochromatic limit is relatively straightforward, the novel overlap fraction provides a means of relating this unrealistic but simple calculation to actual excitation processes.

A detailed study was performed to identify optimum excitation and detection schemes which minimize the influence of interferences on fluorescence-based measurements when using NB- and BB-detection. This study specifically addressed the interference potential from the Schumann-Runge system of O_2 , which has both distinct and many-lined spectral features throughout the spectral region used in both excitation and detection for fluorescence-based measurements of NO. However, the study and analysis

also included potential interferences from Rayleigh scattering as well as O_2 , N_2 , and H_2O Raman scattering. Uncooled fuel-lean flames were used for this study, as such flames maximize the potential for producing O_2 interferences. Excitation and detection scans in nitrogen- and argon-diluted flames were used to identify potential interferences.

For NB-detection experiments, the optimum excitation/detection scheme was determined to be $Q_2(26.5)$ excitation followed by detection over a 2 to 3-nm range spectrally centered on the $\gamma(0,1)$ band of NO. Figure-of-merit assessment parameters were developed to assess the effectiveness of candidate BB-filtering schemes on interference elimination. These assessment parameters were determined from numerical integration of the experimentally-obtained detection scans in nitrogen- and argon-diluted flames. This analysis demonstrated that BB filter selection requires a compromise between interference rejection and measurement SNR. Based on such a compromise, the generally optimal excitation/detection scheme for BB detection measurements of NO, at both 1.0 and 6.1 atm, is excitation via the $Q_2(26.5)$ rovibronic transition and detection filtering using a two M248V-mirror system and sufficient UG5 CG filter to provide the required Rayleigh scattering rejection. An alternate filtering scheme for both 1.0- and 6.1-atm experiments is a 250-W-2S wide-bandwidth interference filter with sufficient UG5 cofilting for low ST. Although this alternate filtering scheme results in lower NO-attributable signal, it provides comparable interference rejection and is much easier to implement compared to the optimum filtering scheme discussed above. In addition to identifying optimal excitation and detection schemes for NB and BB detection experiments, this work established a methodology for quantitatively evaluating candidate BB filtering and excitation schemes.

To perform the experimental assessment of the quantitative nature of PLIF, a separate PLIF/LSF diagnostics facility was developed. This facility provides the ability to make simultaneous or separate point and planar fluorescence-based measurements in atmospheric flame environments. The facility incorporates a broad-band, detection-based overlap reference system which is used to monitor and optimize the overlap fraction between the laser radiation and the NO absorption transition. The extensive rotameter-based gas control system is capable of delivering up to ten different gases to support a

variety of test burners. Two PCs are used to coordinate and store point and imaging measurements; a Sparc station connected to one PC via Ethernet is used for image reduction and evaluation.

To eliminate difficulties not associated with assessing the quantitative nature of PLIF, a unique axial inverse-diffusion-flame burner was designed and fabricated. The AIDF burner isolates a single axial IDF centered within an annular fuel-rich premixed combustion zone. The AIDF burner also incorporates an argon guard flow to isolate the AIDF from room air. This burner produces very stable and safe flames, and is useful for investigations of IDFs, normal diffusion flames and partially-premixed diffusion flames.

To increase the energy in the UV laser pulse, the optimum operating parameters for two research-grade dyes were developed. These dyes are pyromethene 580 and pyromethene 597. The oscillator and amplifier concentrations which produce the maximum conversion efficiency, as well as the spectral tuning curves for use of these two dyes were determined for a commercial Nd:YAG-pumped dye-laser system. These new dyes provide higher conversion efficiencies and broader tuning curves compared to Rhodamine 590 and 610. Moreover, they provide better conversion efficiency (and hence greater UV energy output) at the wavelengths necessary for NO excitation in the $\gamma(0,0)$ band.

The quantitative nature of PLIF images of [NO] in the AIDF burner was assessed relative to 290 LSF measurements of [NO] taken throughout the imaged environment. To make the comparison between the two measurements, the PLIF image was sampled at locations and areas corresponding to the 290 LSF measurements. These results demonstrate that the PLIF and LSF measurements indicate the same general [NO] trends throughout the AIDF, including enhanced NO formation at the IDF tip. Moreover, 84% of the binned PLIF measurements were within the uncertainty of the LSF measurements. By calculating the normalized difference between the two data sets, it was determined that the PLIF measurements nominally underpredict the [NO] by $\sim 0.64\delta N_{T,RT}$ over the region undergoing combustion, where $\delta N_{T,RT}$ is the absolute uncertainty in the LSF measurements of [NO]. This indicates that the electronic quenching rate coefficient is nominally uniform over the equivalence-ratio range studied with the AIDF and through the

AIDF front. In contrast, the PLIF measurements nominally overpredict the [NO] in the argon guard due to strong gradients in the electronic quenching rate coefficient at the argon-guard/combustion interface.

Two experimentally-based correction procedures for enhancing the quantitative nature of PLIF were proposed and evaluated. The single-input enhancement scheme uses a single secondary LSF point measurement, and is most applicable in environments with negligible gradients in the electronic quenching rate coefficient. It is often known a priori that variations in the electronic quenching rate coefficient of a test environment are negligible. In such instances, the single-input enhancement scheme is the method of choice. For such environments, the optimum location at which to make the single secondary LSF measurement may be chosen at convenience. The multiple-input enhancement schemes use multiple secondary LSF point measurements to correct for the errors in a PLIF image due to gradients in the electronic quenching rate coefficient. Multiple-input enhancement schemes require sufficient secondary LSF measurements to resolve the error gradients and to determine the range in the image over which such gradients are nominally constant. In situations where sufficient knowledge of a test environment exist, this knowledge can be used to develop a minimal-input enhancement procedure which is tailored to that specific environment. Such a minimal-input enhancement scheme minimizes the number of secondary LSF inputs via selective application of the single- and multiple-input enhancement procedures in specific regions of the image.

The single-input, experimentally-based enhancement procedure was implemented using the binned PLIF data, and its effectiveness was evaluated over the range in the image where the gradients in the electronic quenching rate coefficient were negligible. In this range, the single-input enhancement scheme provided an enhancement of approximately 50% in the quantitative nature of the PLIF measurements relative to the uncorrected PLIF results. Moreover, the data indicates that, in this range, the single-input enhanced PLIF image is as quantitative as a single LSF point measurement with greater than 95% confidence. This profound enhancement in the quantitative nature of the PLIF image was achieved via use of a single LSF point measurement.

The multiple-input, experimentally-based enhancement procedure was implemented using the binned PLIF data and a single elevation to characterize the error gradients at the argon-guard/combustion interface at the negative radial locations and for all remaining elevations. This form of application of the multiple-input enhancement scheme is applicable to fields with spatially constant error gradients. Over this range of the image, the multiple-input enhancement scheme provided an enhancement of approximately 50% in the quantitative nature of the PLIF measurements relative to the uncorrected results. Moreover, the data indicates that, in environments with gradients in the electronic quenching rate coefficient, the multiple-input enhancement procedure can produce PLIF concentration images that are just as quantitative as a single LSF point measurement with greater than 95% confidence. Although this enhancement scheme required more secondary LSF inputs compared to the single-input enhancement scheme, it produced the same enhancement but over a range in the image which included gradients in the electronic quenching rate coefficient.

A minimal-input procedure was implemented using the binned PLIF data to demonstrate the utility of existing knowledge in designing experimentally-based enhancement procedures. The minimal-input procedure used a multiple-input scheme in the region of the error gradients and a single-input scheme within the combustion region. This minimal-input procedure was just as effective in enhancing the quantitative nature of the PLIF image as compared to the multiple-input, but required ~73% fewer secondary inputs.

The proposed experimentally-based procedures for enhancing the quantitative nature of PLIF images combine the strengths of the PLIF and LSF measurement techniques to produce spatially resolved measurements of high accuracy. Specifically, the PLIF measurements are used to provide the requisite spatial resolution, and the LSF measurements are used to calibrate and correct the PLIF image for errors arising from the effects of the electronic quenching rate coefficient. Combining the strengths of the two measurements, via the experimentally-based correction procedures, provides the most experimentally efficient means of obtaining spatially resolved concentration measurements within a specified uncertainty. Through use of either the single-input or multiple-input

enhancement schemes, respectively, this experimental efficiency is achievable in general environments with constant and/or varying electronic quenching rate coefficients. These experimental enhancement procedures also produce enhanced PLIF [NO] images that are nominally as quantitative as a single LSF point measurement. Moreover, these experimental enhancement procedures can be applied to other radical species for which no experimental data are available with which to implement numerically-based PLIF enhancement procedures.

8.2 Recommendations

There are several recommendations which would improve the reliability and SNR of both the LSF and PLIF experiments. Both measurements would be enhanced by an improved ORS incorporating an etalon and a linear photodiode array. This would provide more reliable tuning and monitoring of the overlap fraction throughout the experiments compared to the current BB-detection system. Moreover, such a system could be used to monitor and determine both the spectral bandwidth and lineshape of the UV laser radiation. Recommendations specific to the LSF and PLIF measurements are discussed in the following sections.

8.2.1 LSF Recommendations

For the LSF measurements of [NO] we make the following recommendations.

1. The collection optics should be modified to produce a magnification greater than unity. This would allow LSF measurements of higher spatial resolution compared to the current 1-mm limit.
2. The monochromator PMT housing should be modified so that the monochromator exit slit remains the limiting aperture for detection bandwidths greater than ~ 2 nm. This could be implemented by incorporating a different lens in the PMT housing and/or moving the PMT

closer to the monochromator exit slit. This modification would produce greater measurement SNR.

8.2.2 PLIF Recommendations

For the PLIF measurements of [NO] we make the following recommendations.

1. The sheet forming optics should be modified to obtain a more uniform laser sheet and higher transmissions. This may be possible by replacing the two cylindrical lens and slit system with a single, long-focal-length cylindrical lens. The focal length of this single cylindrical lens should be specified to minimize divergence of the laser sheet over the range of the image. By reducing laser-sheet nonuniformities, this modification would allow the use of higher laser fluence values within the linear-fluorescence range. This in turn would increase the SNR of the PLIF measurements.
2. A linear photodiode array should be incorporated in the excitation-optics system. Such a system would provide an active monitor of the shot-to-shot and image-to-image fluctuations in the laser sheet about the nominal bulk laser sheet nonuniformity. This information would allow implementation of a more accurate laser-sheet nonuniformity correction.
3. The M248V/UG5 filter system identified as optimum in Chapter 6 should be incorporated into the collection optics. This optimum filtering scheme provides much greater probe signal transmission compared to that of the F250W/UG5 system used for the current PLIF measurements. This improvement would increase the SNR of the PLIF measurements.
4. Replacing the PLIF collection optics with a faster (i.e., lower $f/\#$) lens should be considered. This could be achieved by use of a cassegrainian

lens. This improvement would make single shot PLIF images more feasible by increasing the measurement SNR.

5. The influence of cooling the ICCD below the current -20°C temperature should be investigated. Because of the long on-chip integration times used for the current PLIF measurements, a majority of the signal dynamic range was taken up by dark noise. Further cooling of the CCD would decrease the dark noise, and hence, increase the measurement SNR. However, this will require a lower temperature water bath (20°C water bath temperature was used for the current PLIF experiments), and ultimately may require methanol coolant.
6. A more detailed study of optimal on-chip integration times should be performed. This would result in a quantitative relationship for the compromise between the integrated NO-fluorescence and dark-noise signal levels.
7. On-chip binning of the PLIF images should be implemented. In on-chip binning, signals from pixel areas are binned together prior to the readout and amplification process. As a result of this binning process, the spatial resolution of the binned image is reduced proportional to the number of pixels that are binned together. However, on-chip binning reduces the readout noise compared to binning via post-processing. This in turn would increase the SNR of the PLIF measurements.
8. An uncertainty analysis based on the individual images should be performed. This would indicate the specific contribution from each measured signal (e.g., dark and readout noise, laser-induced interferences) to the overall measurement uncertainty.

LIST OF REFERENCES

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- Airco (1993). *Special Gases and Equipment, Airco Gases*, Murray Hill, NJ.
- Albritton, D. L., Schmeltekoph, A. L., and Zare, R. N. (1972). "Diatomic intensity factors," tabulated in Krupenie (1972).
- Alden, M, Edner, H., Holmstedt, G., Svanberg, S. and Hogberg, T. (1982). "Single-pulse laser-induced OH fluorescence in an atmospheric flame, spatially resolved with an diode array detector," *Appl. Opt.* **21**, 1236-1240.
- Alden, M, Grafstrom, P, Lundberg, H. and Svanberg, S. (1983). "Spatially resolved temperature measurements in a flame using laser-excited two-line atomic fluorescence and diode-array detection," *Opt. Lett.* **8**, 241-243.
- Alden, M. and Svanberg, S. (1984). "Laser-induced fluorescence and coherent anti-stokes raman scattering (CARS) techniques in combustion diagnostics," *Laser Institute of America 47-Laser Diagnostics and Photochemistry*, ICALEO, 134-143.
- Allen, M., Davis, S. and Konohue, K. (1990). "Planar measurements of instantaneous species and temperature distribution in reacting flows: a novel approach to ground testing instrumentation," AIAA 26th Joint Propulsion Conf., AIAA-90-2383.
- Allen, M.G., Parker, T.E., Reinecke, W.G., Legner, H.H., Foutter, R.R., Rawlings, W.T. and Davis, S.J. (1993). "Fluorescence imaging of OH and NO in a model supersonic combustor," *AIAA J.* **31**, 505-512.
- Allen, M. G. (1994). Physical Sciences Inc., Andover, MA, personal communication.
- Allen, M. G., McManus, K. R., and Sonnenfroh, D. M. (1995). "PLIF imaging in spray flame combustors at elevated pressure," AIAA 33rd Aerospace Sciences Meeting and Exhibit., AIAA-95-0172.

- Andresen, P., Bath, A., Gröger, W., Lülff, H. W., Meijer, G., and ter Meulen, J. J. (1988). "Laser-induced fluorescence with tunable excimer lasers as a possible method for instantaneous temperature field measurements at high pressures: checks with an atmospheric flame," *Appl. Opt.* **27**, 365-378.
- Arnold, A., Ketterle, W., Becker, H. and Wolfrum, J. (1990). "Simultaneous single-shot imaging of OH and O₂ using a two-wavelength excimer laser," *Appl. Phys. B* **51**, 99-102.
- Babcock and Wilcox (1978). *Steam / Its Generation and Use*, 39th edition, The Babcock and Wilcox Company, New York, NY.
- Barlow, R.S. and Collignon, A. (1991). "Linear LIF measurements of OH in nonpremixed methane-air flames: when are quenching corrections unnecessary," AIAA 29th Aerospace Sciences Meeting, AIAA-91-0179.
- Battles, B.E., Seitzman, J.M. and Hanson, R.K. (1994). "Quantitative planar laser-induced fluorescence imaging of radical species in high pressure flames," AIAA 23rd Aerospace Sciences Meeting, AIAA-94-0229.
- Bevington, P.R. and Robinson, D.K. (1992). *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill Inc., New York, NY.
- Born, M., and Wolf, E. (1980). *Principles of Optics*, sixth edition, Pergamon Press, Elmsford, NY.
- Boyer, J.H., Haag, A.M., Sathyamoorthi, G., Soong, M.-L., and Thangaraj, K. (1993). "Pyrromethene-BF₂ complexes as laser dyes: 2," *Heteroatom Chem.* **4**, 39-49.
- Boyer, J.H., Haag, A., Soong, M.-L., Thangaraj, K., and Pavlopoulos, T.G. (1991). "Laser action from 2,6,8-trisubstituted-1,3,5,7-tetramethyl-pyrromethene-BF₂ complexes: part 2," *Appl. Opt.* **30**, 3788-3789.
- Carter, C. D., King, G. B., and Laurendeau, N. M. (1989). "A combustion facility for high-pressure flame studies by spectroscopic methods," *Rev. Sci. Instrum.* **60**, 2606-2609.
- Carter, C. D., King, G. B., and Laurendeau, N. M. (1991). "Quenching-corrected saturated fluorescence measurements of the hydroxyl radical in laminar high-pressure C₂H₆/O₂/N₂ flames," *Combust. Sci. and Tech.* **78**, 247-264.
- Carter, C. D., King, G. B., and Laurendeau, N. M. (1992). "Saturated fluorescence measurements of the hydroxyl radical in laminar high-pressure C₂H₆/O₂/N₂ flames," *Appl. Opt.* **31**, 1511-1522.

- Carter, C. D., and Barlow, R. S. (1994). "Simultaneous measurements of NO, OH, and the major species in turbulent flames," *Opt. Lett.* **19**, 299-301.
- Carter, C. D. (1994). Systems Research Laboratories, Inc., Dayton, OH, personal communication.
- Cheng, T.S., Wehrmeyer, J.A. and Pitz, R.W. (1992). "Simultaneous temperature and multispecies measurements in a lifted hydrogen diffusion flame," *Combust. and Flame* **91**, 323-345.
- Clausing, E.M. (1991). Stability characteristics of inverse diffusion flames in methane-air cross flows, M.S. Thesis, Purdue University.
- Clyne, M.A.A., Thrush, B.A. and Wayne, R.P. (1964). "Kinetics of the chemiluminescent reaction between nitric oxide and ozone," *Trans. Faraday Soc.* **60**, 359-370.
- Correa, S.M. (1992). "A review of NO_x formation under gas-turbine combustion conditions," *Combust. Sci. and Tech.* **87**, 329-362.
- Creek, D. M., and Nicholls, R. W. (1975). "A comprehensive re-analysis of the O₂ ($B^3\Sigma_u^- - X^3\Sigma_g^-$) Schumann-Runge band system," *Proc. R. Soc. Lond. A.* **341**, 517-536.
- Csorba, I. P. (1985). *Image Tubes*, Howard W. Sams & Co., Inc.
- CVI (1994). *Optics and Coatings*, CVI Laser Corporation, Albuquerque, NM.
- Daily, J.W. (1977). "Use of rate equations to describe laser excitation in flames," *Appl. Opt.* **16**, 2322-2327.
- Deézsi, I. (1958). "A recent rotational analysis of the γ bands of the NO molecule," *Acta. Phys. Acad. Sci. Hung.* **9**, 125-150.
- Demtroder, W. (1988). *Laser Spectroscopy, Basic Concepts and Instrumentation*, Springer-Verlag, New York, NY.
- Drake, M.C. and Pitz, R.W. (1985). "Comparison of turbulent diffusion flame measurements of OH by planar fluorescence and saturated fluorescence," *Exp. Fluids* **3**, 283-292.
- Drake, M.C., Correa, S.M., Pitz, R.W., Shyy, W. and Fenimore, C.P. (1987). "Superequilibrium and thermal nitric oxide formation in turbulent diffusion flames," *Combust. and Flame* **69**, 347-365.

- Drake, M.C., Ratcliffe, J.W., Roberts, W.L. and Driscoll, J.F. (1991). "OH fluorescence images of the quenching of a premixed flame during and interaction with a vortex," General Motors Research Laboratories Publication GMR-7539.
- Drake, M.C. and Ratcliffe, J.W. (1993). "High temperature quenching cross sections for nitric oxide laser-induced fluorescence measurements," *J. Chem. Phys.* **98**, 3850-3865.
- Dyer, M.J. and Crosley, D.R. (1982). "Two-dimensional imaging of OH laser-induced fluorescence in a flame," *Optics Letters* **7**, 382-384.
- Eberhardt, E.H. (1979). "Gain model for microchannel plates," *Appl. Opt.* **18**, 1418-1423.
- Eckbreth, A.C. (1988). *Laser Diagnostics for Combustion Temperature and Species*, Abacus Press, Cambridge, MA.
- Enright, M. (1994). Spectra-Physics Lasers - OEM, Mountain View, Calif., personal communication.
- Escoda, M.C. and Long, M.B. (1982). "Rayleigh scattering measurements of the gas concentration field in turbulent jets," *AIAA J.* **21**, 81-84.
- Freeman, C.F. (1973). "Image intensifier tubes," *Proc. SPIE* **42**, San Diego, CA, Aug. 27-29, 3-13.
- Garg, A. (1994). "Specify better low-NO_x burners for furnaces", *Chem. Eng. Prog.* **90**, 46-49.
- Goldsmith, J. E. M., and Anderson, R. J. M. (1986). "Laser-induced fluorescence spectroscopy and imaging of molecular oxygen in flames," *Opt. Lett.* **11**, 67-69.
- Goodman, J.W. (1968). *Introduction to Fourier Optics*, McGraw-Hill Publishing Co., New York, NY.
- Guggenheimer, S.C., Boyer, J.H., Thangaraj, K., Shah, M., Soong, M.-L., and Pavlopoulos, T.G. (1993). "Efficient laser action from two cw laser-pumped pyromethene-BF₂ complexes," *Appl. Opt.* **32**, 3942-3943.
- Greathouse, C. (1991). Varo Inc., Garland, TX, personal communication.
- Gross, K.P., McKenzie, R.L. and Logan, P. (1987). "Measurements of temperature, density, pressure, and their fluctuations in supersonic turbulence using laser-induced fluorescence," *Exp. Fluids* **5**, 372-380.

- Hamamatsu (1991). Photodiodes Catalog, Hamamatsu Corp., Bridgewater, NJ.
- Hamamatsu (1994). Photomultiplier Tubes Catalog, Hamamatsu Corp., Bridgewater, NJ.
- Hanson, R.K. (1986). "Combustion diagnostics: planar imaging techniques," *Twenty-first Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1677-1691.
- Hanson, R.K., Seitzman, J.M. and Paul, P.H. (1990). "Planar laser-fluorescence imaging of combustion gases," *Appl. Phys. B* **50**, 441-454.
- Harris, J. M., Lytle, F. E., and McCain, T. C. (1976). "Squirrel-cage photomultiplier base design for measurements of nanosecond fluorescence decays," *Anal. Chem.* **48**, 2095-2098.
- Hartfield, R.J. Jr., Hollo, S.D. and McDaniel, J.C. (1991). "Planar temperature measurement in compressible flows using laser-induced iodine fluorescence," *Opt. Lett.* **16**, 106-108.
- Hartley, D.L. (1974). "Raman gas mixing measurements and Ramanography," in *Laser Raman Gas Diagnostics*, 311, M. Lapp and C.M. Penney eds., Plenum, New York, NY.
- Hermes, R.E., Allik, T.H., Chandra, S. and Hutchinson, J.A. (1993). "High-efficiency pyrromethene doped solid-state dye lasers," *Appl. Phys. Lett.* **63**, 877-879.
- Hermes, R.E. (1994). "Lasing performance of pyrromethene-BF₂ laser dyes in a solid polymer host," *Proc. Soc. Photo-Opt. Instrum. Eng.* **2115**, 178-183.
- Hertz, H.M. and Alden, M. (1987). "Calibration of imaging laser-induced fluorescence measurements in highly absorbing flames," *Appl. Phys. B* **42**, 97-102.
- Hertz, H.M., Alden, M. and Svanberg, S. (1988). "Correction of imaging errors in spatially resolved laser scattering experiments in flames," *Appl. Phys. B* **45**, 33-36.
- Herzberg, G. (1989). *Molecular Spectra and Molecular Structure Vol. I -Spectra of Diatomic Molecules*, Robert E. Krieger Pub. Co., Malabar, FL (Originally published by Van Norstrand Reinhold Co., 1950).
- Hiller, B., Cohen, L.M. and Hanson, R.K. (1986). "Simultaneous measurements of velocity and pressure fields in subsonic and supersonic flows through image-intensified detection of laser-induced fluorescence," AIAA 24th Aerospace Sciences Meeting, AIAA-86-0161.

- Hiller, B. and Hanson, R.K. (1988). "Simultaneous planar measurements of velocity and pressure fields in gas flows using laser-induced fluorescence," *Appl. Opt.* **27**, 33-48.
- ISA (1994). *Guide for Spectroscopy*, Instruments S.A. Co., Edison, NJ.
- Kandebo, S.W. (1989). "HSCT propulsion studies focus on reducing emissions, noise," *Aviation Week & Space Tech.*, July 10, 34-36.
- Krupenie, P. H. (1972). "The spectrum of molecular oxygen," *J. Phys. Chem. Ref. Data*, **1**, 423-534.
- Kychakoff, G., Howe, R.D., Hanson, R.K. and McDaniel, J.C. (1982). "Quantitative visualization of combustion species in a plane," *Appl. Opt.* **21**, 3225-3227.
- Kychakoff, G., Howe, R.D. and Hanson, R.K. (1983). "Use of planar laser-induced fluorescence for the study of combustion flowfields," AIAA 19th Joint Propulsion Conf., AIAA-83-1361.
- Kychakoff, G., Knapp, K., Howe, R.D. and Hanson, R.K. (1984a). "Flow visualization in combustion gases using nitric oxide fluorescence," *AIAA J.* **22**, 153-154.
- Kychakoff, G., Howe, R.D. and Hanson, R.K. (1984b). "Quantitative flow visualization techniques for measurements in combustion gases," *Appl. Opt.* **23**, 704-712.
- Laurendeau, N.M. (1988). "Temperature measurements by light-scattering methods," *Prog. Energy Combust. Sci.* **14**, 147-170.
- Laurendeau, N.M. and Goldsmith, J.E.M. (1989). "Comparison of hydroxyl concentration profiles using five laser-induced fluorescence methods in a lean subatmospheric-pressure $H_2/O_2/Ar$ flame," *Combust. Sci. and Tech.* **63**, 139-152.
- Lee, M. P., and Hanson, R. K. (1986). "Calculations of O_2 absorption and fluorescence at elevated temperatures for a broadband argon-fluoride laser source at 193 nm," *JQSRT* **36**, 425-440.
- Lee, M. P., McMillin, B. K. and Hanson, R. K. (1993). "Temperature measurements in gases by use of planar laser-induced fluorescence imaging of NO," *Appl. Opt.* **32**, 5379-5396.
- Long, M.B., Webber, B.F. and Chang, R.K. (1979). "Instantaneous two-dimensional concentration measurements in a flow by Mie scattering," *Appl. Phys. Lett.* **34**, 22-24.

- Lucht, R.P., Sweeney, D.W. and Laurendeau, N.M. (1985). "Laser-saturated fluorescence measurements of OH in atmospheric pressure $\text{CH}_4/\text{O}_2/\text{N}_2$ flames under sooting and non-sooting conditions," *Combust. Sci. and Tech.* **42**, 259-281.
- Matheson (1993). *Matheson Gases & Equipment*, Secaucus, NJ.
- Matthews, R.D., Sawyer, R.F. and Schefer, R.W. (1977). "Interferences in chemiluminescent measurement of NO and NO_2 emissions from combustion systems," *Environ. Sci. Tech.* **11**, 1092-1096.
- McMillin, B.K., Seitzman, J.M. and Hanson, R.K. (1994). "Comparison of NO and OH planar fluorescence temperature measurements in scramjet model flowfields," *AIAA J.* **32**, 1945-1952.
- Measures, R.M. (1968). "Selective excitation spectroscopy and some possible applications," *J. Appl. Phys.* **39**, 5232-5245.
- Miles, R.B. (1975). "Resonant Doppler velocimetry," *Phys. Fluids* **18**, 751-752.
- Miles, R.B., Udd, E. and Zimmerman, M. (1978). "Quantitative flow visualization in sodium vapor seeded hypersonic helium," *Appl. Phys. Lett.* **32**, 317-319.
- Milonni, P.W. and Eberly, J.H. (1988). *Lasers*, John Wiley & Sons, New York, NY.
- Nir, I. (1991). Personal communication, Princeton Instruments Inc..
- O'Neil, M.P. (1993). "Synchronously pumped visible laser dye with twice the efficiency of Rhodamine 6G," *Opt. Lett.* **18**, 37-38.
- Ozisik, M.N. (1980). *Heat Conduction*, John Wiley & Sons, New York, NY.
- Partridge, Jr., W.P., Laurendeau, N.M., Johnson, C.C., and Steppel, R.N. (1994). "Performance of Pyrromethene 580 and 597 in a commercial Nd:YAG-pumped dye-laser system," *Opt. Lett.* **19**, 1630-1632.
- Partridge, W. P., Jr., and Laurendeau, N. M. (1995a). "Formulation of a dimensionless overlap fraction to account for spectrally distributed interactions in fluorescence studies," *Appl. Opt.* **34**, 2645-2647.
- Partridge, W. P., Jr., and Laurendeau, N. M. (1995b). "Nitric oxide formation by inverse diffusion flames in staged-air burners," *Fuel* **74**, 1424-1430.

- Paul, P.H., Lee, M.P. and Hanson, R.K. (1989). "Molecular velocity imaging of supersonic flows using pulsed planar laser-induced fluorescence of NO," *Opt. Lett.* **14**, 417-419.
- Paul, P.H., van Cruyningen, I., Hanson, R.K. and Kychakoff, G. (1990). "High resolution digital flowfield imaging of jets," *Exp. Fluids* **9**, 241-251.
- Paul, P.H. and Hanson, R.K. (1990). "Application of planar laser-induced fluorescence imaging diagnostics to reacting flows," AIAA 26th Joint Propulsion Conf., AIAA-90-1844.
- Paul, P.H. (1991). "The application of intensified array detectors to quantitative planar laser-induced fluorescence imaging," AIAA 27th Joint Propulsion Conf., AIAA-91-2315.
- Paul, P.H., Gray, J.A., Durant, Jr., J.L. and Thoman, Jr., J.W. (1993). "A Model for temperature-dependent collisional quenching of NO $A^2\Sigma^+$," *Appl. Phys. B* **57**, 249-259.
- Paul, P.H., Gray, J.A., Durant, Jr., J.L. and Thoman, Jr., J.W. (1994). "Collisional quenching corrections for laser-induced fluorescence measurements of NO $A^2\Sigma^+$," *AIAA J.* **32**, 1670-1675.
- Paul, P.H. and Dee, J.E. (1994). "Imaging of reaction zones in hydrocarbon-air flames by use of planar laser-induced fluorescence of CH," *Opt. Lett.* **19**, 998-1000.
- Piper, L.G. and Cowles, L.M. (1986). "Einstein coefficients and transition moment variation for the NO($A^2\Sigma^+ - X^2\Pi$) transition," *J. Chem. Phys.* **85**, 2419-2422.
- Reisel, J.R. (1991). Laser-saturated fluorescence measurements of nitric oxide in atmospheric-pressure flames, M.S. thesis, School of Mechanical Engineering, Purdue University, West Lafayette, IN.
- Reisel, J.R., Carter, C.D. and Laurendeau, M.N. (1992). "Einstein coefficients for rotational lines of the (0,0) band of the NO $A^2\Sigma^+ - X^2\Pi$ system," *J. Quant. Spectrosc. Radiat. Transfer* **47**, 43-54.
- Reisel, J.R., Carter, C.D., Laurendeau, N.M. and Drake, M.C. (1993). "Laser-saturated fluorescence measurements of nitric oxide in laminar, flat, $C_2H_6/O_2/N_2$ flames at atmospheric pressure," *Combust. Sci. and Tech.* **91**, 271-295.
- Reisel, J.R. (1993). Personal communication.

- Reisel, J.R. and Laurendeau, N.M. (1994). "Laser-induced fluorescence measurements and modeling of nitric oxide formation in high-pressure flames," *Combust. Sci. and Tech.* **98**, 137-160.
- Reisel, J.R. (1994). Laser-induced fluorescence measurements and modeling of nitric oxide in high-pressure premixed flames, Ph.D. thesis, School of Mechanical Engineering, Purdue University, West Lafayette, IN.
- Reisel, J. R., Partridge, W. P., Jr., and Laurendeau, N. M. (1995). "Transportability of a laser-induced fluorescence calibration for NO at high pressure," *JQSRT* **53**, 165-178.
- Ruggieri, D.J. (1972). "Microchannel plate imaging detectors," *IEEE Trans. Nucl. Sci.* **19**, 74-84.
- Salmon, J.T. and Laurendeau, N.M. (1987). "Absolute concentration measurements of atomic hydrogen in subatmospheric premixed $H_2/O_2/N_2$ flat flames with photoionization controlled-loss spectroscopy," *Appl. Opt.* **26**, 2881-2891.
- Schafer, M., Ketterle, W. and Wolfrum, J. (1991). "Saturated 2D-LIF of OH and 2D determination of effective collisional lifetimes in atmospheric pressure flames," *Appl. Phys. B* **52**, 341-346.
- Schott (1991). *Optical Glass Filters, 5th ed.*, Schott Glass Technologies Inc., Duryea, PA.
- Seitzman, J.M., Kychakoff, G. and Hanson, R.K. (1985). "Instantaneous temperature field measurements using planar laser-induced fluorescence," *Opt. Lett.* **10**, 439-441.
- Seitzman, J.M., van Cruyningen, I. and Hanson, R.K. (1990). "Recent developments in laser diagnostics at the Stanford high temperature gasdynamics laboratory," ICALEO '90, 28-38.
- Seitzman, J. M. (1991). Quantitative applications of fluorescence imaging in combustion, Ph.D. dissertation, Department of Mechanical Engineering, Stanford University, Palo Alto, CA.
- Seitzman, J.M. and Hanson, R.K. (1993). "Comparison of excitation techniques for quantitative fluorescence imaging of reacting flows," *AIAA J.* **31**, 513-519.
- Simpson, R.W. (1979). "Noise in large-aperture self-scanned diode arrays," *Rev. Sci. Instrum.* **50**, 730-732.

- Smith, C.E., Talpallikar, M.V. and Holdeman, J.D. (1991). "A CFD study of jet mixing in reduced flow areas for lower combustion emissions," AIAA 27th Joint Propulsion Conf., AIAA-91-2460.
- Smith, W.J. (1990). *Modern Optical Engineering: The Design of Optical Systems Second edi.*, McGraw-Hill Inc., New York, NY.
- Spectra-Physics (1989). Tuning curves for R-590 and R-610 were taken with permission from the PDL-3 manual, Spectra-Physics Lasers, Inc., Mountain View, CA.
- Spectra-Physics (1991). Quanta-Ray GCR-3 and GCR-4, Pulsed Nd:YAG Laser Instruction Manual, Spectra-Physics Lasers, Inc., Mountain View, CA.
- Spectra-Physics (1992). Quanta-Ray series laser system brochure.
- Stanford Research Systems (1993). Fast Gated Integrators and Boxcar Averagers, Stanford Research Systems, Sunnyvale, CA.
- Stepowski, D. and Garo, A. (1985). "Local absolute OH concentration measurement in a diffusion flame by laser induced fluorescence," *Appl. Opt.* **24**, 2478-2480.
- Taylor, J.R. (1982). *An Introduction to Error Analysis, The Study of Uncertainties in Physical Measurements*, University Science Books, Mill Valley, CA.
- Tidona, R.J., Nizami, A.A. and Cernansky, N.P. (1988). "Reducing interference effects in the chemiluminescent measurement of nitric oxides from combustion systems," *JAPCA* **38**, 806-811.
- Torr, M.R. (1985). "Persistence of phosphor glow in microchannel plate image intensifiers," *Appl. Opt.* **24**, 793-795.
- Turns, S.R. and Myhr, F.H. (1991). "Oxides of nitrogen emissions from turbulent jet flames: part I - fuel effects and flame radiation," *Combust. and Flame* **87**, 319-335.
- van Cruyningen, I., Lozano, A. and Hanson, R.K. (1990). "Quantitative imaging of concentration by planar laser-induced fluorescence," *Exp. Fluids* **10**, 41-49.
- Versluis, M., Boogaartx, M., Klein-Douwel, R., Thus, B., de Jongh, W., Braam, A., ter Meulen, J.J., Meerts, W.L. and Meijer, G. (1992). "Laser-induced fluorescence imaging in a 100 kW natural gas flame," *Appl. Phys. B* **55**, 164-170.

- Vranos, A., Liscinsky, D.S., True, B. and Holdeman, J.D. (1991). "Experimental study of cross-stream mixing in a cylindrical duct," AIAA 27th Joint Propulsion Conf., AIAA-91-2459.
- Weast, R.C., ed. (1984). *CRC Handbook of Chemistry and Physics*, 65th edition, CRC Press Inc., Boca Raton, FL.
- Webber, B.F., Long, M.B. and Chang, R.K. (1979). "Two-dimensional average concentration measurements in a jet flow by Raman scattering," *Appl. Phys. Lett.* **35**, 119-121.
- Wiza, J.L. (1979). "Microchannel plate detectors," *Nuclear Instru. and Methods* **162**, 587-601.
- Wood, R.W. (1988). *Physical Optics*, third edition, Optical Society of America, Washington, DC.
- Wysong, I. J., Jeffries, J. B., and Crosley, D. R. (1989). "Laser-induced fluorescence of O($3p^3P$), O₂, and NO near 226 nm: photolytic interferences and simultaneous excitation in flames," *Opt. Lett.* **14**, 767-769.
- Zabieliski, M.F., Seery, D.J. and Dodge, L.G. (1984). "Influence of mass transport and quenching on nitric oxide chemiluminescent analysis," *Environ. Sci. Tech.* **18**, 88-92.

APPENDICES

Appendix A - Chemiluminescent Exhaust Measurements Results

The concentration data resulting from chemiluminescent probe sampling measurements in the staged air combustor exhaust is presented in this appendix for the five combustor configurations. All combustor configurations use two oxidizer jets; the 70° impingement angle configuration is investigated with 2.16 mm and 4.57 mm I.D. jet tubes (1/8 and 1/4 in. O.D., respectively) while the 45° configuration is investigated with 2.16 mm, 4.57 mm and 7.75 mm I.D. jet tubes (1/8, 1/4 and 3.8 in. O.D., respectively). The tabular data presented here are provided in graphical form in Chapter 2.

Table A.1

Chemiluminescence measurement data sheet for operation of the staged air combustor with two 1/8 in O.D oxidizer jets at a 70° impingement angle. DILCORR represents the volumetric flow ratio defined in Eq. (2.1). The subscript d indicates species concentration values in ppm indicated by the analyzer display. T_r is the exhaust temperature measured at the rake, and M_i is the calculated molecular weight of the exhaust gases. Dilution corrected species concentration in ppm is indicated by NO, NO₂ and NO_x. EINO and EINO_x represent the NO and NO_x emission indices, respectively, and the absolute uncertainty in the emission index is indicated by δ EINO and δ EINO_x.

Jet Parameters		
Number	Diameter	Angle
2	0.125	70

V:JET		Equivalence			V:TOTAL V:DILU			DILCORR.			NO _d NO _{2d} NO _{xd}			T _r (C)
[603]	[604]	Ratio												
0	NA	1.55			B126	S84.5		11.2245			5.29	-0.083	5.2	645.00
B18.5	NA	1.41			B126	S84.5		11.2245			5.36	-0.052	5.31	687.00
B45.5	NA	1.27			B126	S84.5		11.2245			5.78	-0.043	5.74	658.00
B84.5	NA	1.13			B126	S84.5		11.2245			5.6	0.005	5.6	702.00
NA	S20	1.00			B124.5	S84.5		12.5786			6.8	0.156	6.96	801.00
NA	S30	0.87			B123.5	S83.5		12.0656			6.02	0.245	6.26	736.00
NA	S44	0.74			B124	S83.5		11.5189			4.79	0.549	5.34	675.00
NA	S64	0.61			B124	S83.5		11.5189			1.459	2.7	4.16	604.00
NA	S89	0.50			B124.5	S83.5		11.1293			0.628	2.89	3.52	533.00

Equivalence		Emission Index :			Uncertainty:	
Ratio	M _i	NO	NO ₂	NO _x	δ EINO	δ EINO _x
1.55	25.22	59.38	-0.93	58.37	0.13	0.13
1.41	25.88	60.16	-0.58	59.60	0.14	0.14
1.27	26.59	64.88	-0.48	64.43	0.15	0.15
1.13	27.36	62.86	0.06	62.86	0.16	0.16
1.00	28.12	85.53	1.96	87.55	0.18	0.18
0.87	28.21	72.63	2.96	75.53	0.20	0.20
0.74	28.3	55.18	6.32	61.51	0.24	0.24
0.61	28.39	16.81	31.10	47.92	0.28	0.28
0.50	28.47	6.99	32.16	39.18	0.34	0.34

Table A.2

Chemiluminescence measurement data sheet for operation of the staged air combustor with two 1/4 in O.D oxidizer jets at a 70° impingement angle. DILCORR represents the volumetric flow ratio defined in Eq. (2.1). The subscript d indicates species concentration values in ppm indicated by the analyzer display. T_r is the exhaust temperature measured at the rake, and M_i is the calculated molecular weight of the exhaust gases. Dilution corrected species concentration in ppm is indicated by NO , NO_2 and NO_x . $EINO$ and $EINO_x$ represent the NO and NO_x emission indices, respectively, and the absolute uncertainty in the emission index is indicated by $\delta EINO$ and $\delta EINO_x$.

Jet Parameters		
Number	Diameter	Angle
2	0.25	70

V:JET	Equivalence		V:TOTAL				DILCORR.		NO _d	NO _{2d}	NO _{3d}	T _r (C)
	[603]	[604]	Ratio	V	DILU	V	DILU	DILCORR.				
0	NA	NA	1.55	B124	S83.5	B124	S83.5	11.5189	4.83	-0.08	4.75	645.00
B18.5	NA	NA	1.41	B123	S83.5	B123	S83.5	12.6122	4.74	-0.047	4.69	692.00
B45.5	NA	NA	1.27	B121	S81.5	B121	S81.5	11.958	4.96	-0.018	4.94	752.00
B84.5	NA	NA	1.13	B121	S81.5	B121	S81.5	11.958	3.15	0.003	3.15	832.00
NA	S20	S20	1.00	B121	S81.5	B121	S81.5	11.958	6.11	0.176	6.29	884.00
NA	S30	S30	0.87	B121	S81.5	B121	S81.5	11.958	6.11	0.172	6.28	877.00
NA	S44	S44	0.74	B121	S81.5	B121	S81.5	11.958	5.29	0.155	5.45	781.00
NA	S64	S64	0.61	B121	S81.5	B121	S81.5	11.958	3.29	1.118	4.41	672.00
NA	S89	S89	0.50	B121	S81.5	B121	S81.5	11.958	1.084	2.5	3.59	597.00

Equivalence		Emission Index :			Uncertainty:			
Ratio	M _i	NO	NO ₂	NO _x	EINO	EINO _x	δEINO	δEINO _x
1.55	25.22	55.64	-0.92	54.71	1.22	1.22	0.13	0.13
1.41	25.88	59.78	-0.59	59.15	1.38	1.39	0.14	0.14
1.27	26.59	59.31	-0.22	59.07	1.47	1.49	0.15	0.15
1.13	27.36	37.67	0.04	37.67	1.04	1.06	0.16	0.16
1.00	28.12	73.06	2.10	75.22	2.12	2.21	0.18	0.18
0.87	28.21	73.06	2.06	75.10	2.41	2.51	0.20	0.20
0.74	28.3	63.26	1.85	65.17	2.45	2.55	0.24	0.24
0.61	28.39	39.34	13.37	52.73	1.88	2.51	0.28	0.28
0.50	28.47	12.96	29.90	42.93	0.86	2.51	0.34	0.34

Table A.3

Chemiluminescence measurement data sheet for operation of the staged air combustor with two 1/8 in O.D oxidizer jets at a 45° impingement angle. DILCORR represents the volumetric flow ratio defined in Eq. (2.1). The subscript d indicates species concentration values in ppm indicated by the analyzer display. T_r is the exhaust temperature measured at the rake, and M_i is the calculated molecular weight of the exhaust gases. Dilution corrected species concentration in ppm is indicated by NO, NO₂ and NO_x. EINO and EINO_x represent the NO and NO_x emission indices, respectively, and the absolute uncertainty in the emission index is indicated by δ EINO and δ EINO_x.

Jet Parameters		
Number	Diameter	Angle
2	0.125	45

V-JET [603]	Equivalence		V:TOTAL	V:DILU	DILCORR	NO _d	NO _{2d}	NO _{xd}	T _r (C)
	[604]	Ratio							
0	NA	1.55	B124	S83.5	11.5189	5.07	-0.086	4.99	644.00
B18.5	NA	1.41	B124	S83.5	11.5189	5.39	-0.082	5.31	635.00
B45.5	NA	1.27	B124	S83.5	11.5189	5.89	-0.064	5.82	615.00
B84.5	NA	1.13	B123	S83.5	12.6122	6.14	0.008	6.15	647.00
NA	S20	1.00	B120	S83.5	17.4612	6.65	0.199	6.85	809.00
NA	S30	0.87	B124	S83.5	11.5189	7.28	0.279	7.56	748.00
NA	S44	0.74	B124	S83.5	11.5189	5.68	0.572	6.25	688.00
NA	S64	0.61	B124	S83.5	11.5189	2.39	2.58	4.97	620.00
NA	S89	0.50	B124	S83.5	11.5189	0.692	3.47	4.16	552.00

Equivalence Ratio	M _i	Emission Index :				Uncertainty:	
		NO	NO ₂	NO _x	EINO	EINO _x	δ EINO δ EINO _x
1.55	25.22	58.40	-0.99	57.48	1.22	1.22	0.13
1.41	25.88	62.09	-0.94	61.17	1.37	1.37	0.14
1.27	26.59	67.85	-0.74	67.04	1.61	1.61	0.15
1.13	27.36	77.44	0.10	77.57	1.99	2.01	0.16
1.00	28.12	116.12	3.47	119.61	3.25	3.37	0.18
0.87	28.21	83.86	3.21	87.08	2.67	2.80	0.20
0.74	28.3	65.43	6.59	71.99	2.42	2.70	0.24
0.61	28.39	27.53	29.72	57.25	1.23	2.59	0.28
0.50	28.47	7.97	39.97	47.92	0.44	2.63	0.34

Table A.4

Chemiluminescence measurement data sheet for operation of the staged air combustor with two 1/4 in O.D oxidizer jets at a 45° impingement angle. DILCORR represents the volumetric flow ratio defined in Eq. (2.1). The subscript d indicates species concentration values in ppm indicated by the analyzer display. T_r is the exhaust temperature measured at the rake, and M_i is the calculated molecular weight of the exhaust gases. Dilution corrected species concentration in ppm is indicated by NO , NO_2 and NO_x . EINO and EINO_x represent the NO and NO_x emission indices, respectively, and the absolute uncertainty in the emission index is indicated by δEINO and δEINO_x .

Jet Parameters		
Number	Diameter	Angle
2	0.25	45

V-JET	[603]	[604]	Equivalence Ratio	V-TOTAL	V:DILU	DILCORR	NO_d	NO_{2d}	NO_{xd}	T_r (C)
0	NA	NA	1.55	B124	S83.5	11.5189	5.36	-0.072	5.29	636.00
B18.5	NA	NA	1.41	B124	S83.5	11.5189	5.38	-0.05	5.33	678.00
B45.5	NA	NA	1.27	B123	S83.5	12.6122	6.22	-0.029	6.2	717.00
B84.5	NA	NA	1.13	B124	S83.5	11.5189	5.95	-0.021	5.93	724.00
NA	S20	S20	1.00	B124	S83.5	11.5189	6.3	0.099	6.39	798.00
NA	S30	S30	0.87	B123	S83.5	12.6122	6.48	0.382	6.86	860.00
NA	S44	S44	0.74	B123	S83.5	12.6122	5.79	0.32	6.11	796.00
NA	S64	S64	0.61	B124	S83.5	11.5189	4.57	0.593	5.16	702.00
NA	S89	S89	0.50	B123	S83.5	12.6122	1.886	2.31	4.2	632.00

Equivalence Ratio		M_i	NO	NO_2	NO_x	Emission Index :		Uncertainty:	
						EINO	EINO _x	δEINO	δEINO_x
1.55	25.22	61.74	-0.83	60.93	1.22	1.22	1.22	0.13	0.13
1.41	25.88	61.97	-0.58	61.40	1.30	1.30	1.30	0.14	0.14
1.27	26.59	78.45	-0.37	78.20	1.78	1.78	1.79	0.15	0.15
1.13	27.36	68.54	-0.24	68.31	1.67	1.67	1.69	0.16	0.16
1.00	28.12	72.57	1.14	73.61	1.94	1.94	1.99	0.18	0.18
0.87	28.21	81.73	4.82	86.52	2.50	2.50	2.67	0.20	0.20
0.74	28.3	73.02	4.04	77.06	2.58	2.58	2.76	0.24	0.24
0.61	28.39	52.64	6.83	59.44	2.19	2.19	2.53	0.28	0.28
0.50	28.47	23.79	29.13	52.97	1.11	1.11	2.71	0.34	0.34

Table A.5

Chemiluminescence measurement data sheet for operation of the staged air combustor with two 3/8 in O.D oxidizer jets at a 45° impingement angle. DILCORR represents the volumetric flow ratio defined in Eq. (2.1). The subscript d indicates species concentration values in ppm indicated by the analyzer display. T_r is the exhaust temperature measured at the rake, and M_i is the calculated molecular weight of the exhaust gases. Dilution corrected species concentration in ppm is indicated by NO, NO₂ and NO_x. EINO and EINO_x represent the NO and NO_x emission indices, respectively, and the absolute uncertainty in the emission index is indicated by δ EINO and δ EINO_x.

Jet Parameters		
Number	Diameter	Angle
2	0.375	45

V:JET	Equivalence Ratio	V:TOTAL	V:DILU	DILCORR	NO _d	NO _{2d}	NO _{xd}	T _r (C)
0	1.55	B124	S83.5	11.5189	5.26	-0.078	5.18	629.00
B18.5	1.41	B123	S83.5	12.6122	5.22	-0.039	5.18	663.00
B45.5	1.27	B123	S83.5	12.6122	5.51	-0.019	5.49	721.00
B84.5	1.13	B121	S81.5	11.958	3.87	0.005	3.87	823.00
NA	1.00	B121	S81.5	11.958	7.45	0.584	8.03	913.00
NA	0.87	B121	S81.5	11.958	6.62	0.342	6.97	818.00
NA	0.74	B121	S81.5	11.958	6.09	0.379	6.47	816.00
NA	0.61	B121	S81.5	11.958	5.02	0.531	5.55	724.00
NA	0.50	B121	S81.5	11.958	3.76	0.741	4.5	696.00

Equivalence Ratio		Emission Index :			Uncertainty:	
Ratio	M _i	NO	NO ₂	NO _x	δ EINO	δ EINO _x
1.55	25.22	60.59	-0.90	59.67	1.22	0.13
1.41	25.88	65.84	-0.49	65.33	1.41	0.14
1.27	26.59	69.49	-0.24	69.24	1.59	0.15
1.13	27.36	46.28	0.06	46.28	1.13	0.16
1.00	28.12	89.09	6.98	96.02	2.43	0.18
0.87	28.21	79.16	4.09	83.35	2.45	0.20
0.74	28.3	72.82	4.53	77.37	2.62	0.24
0.61	28.39	60.03	6.35	66.37	2.57	0.28
0.50	28.47	44.96	8.86	53.81	2.30	0.34

Appendix B - Program for Evaluating Excitation and Filtering Schemes for Broad-band Detection PLIF Measurements

Programs were written to evaluate the requisite assessment parameters for selection of excitation/detection schemes for PLIF measurements using broad-band detection as described in Chapter 6. The program used for analysis of filter 2 (see Table 6.2) is provided below as a typical example of these programs.

FILTER 2

APPLICATION OF UG5 with **two** M248V (i.e., dichroic mirror).

Because M248V does not have sufficient blue cutoff, must use a single M248V filter in conjunction with a number of UG5 CG filters.

A: Q2(25.5) and B: Q2(26.5)

Associate:

A:\filters\ug5.dta with UG5FILTER

A:\filters\N248V.dta with M248V

A:\monodial.dat with LAMDATA

Associate:

A:\nd104av.dat with ONEADATA

A:\ad104av.dat with ONEAINTER

A:\nd602av.dat with SIXADATA

A:\ad601av.dat with SIXAINTER

Associate:

A:\nd102av.dat with ONEBDATA

A:\ad103av.dat with ONEBINTER

A:\nd601av.dat with SIXBDATA

A:\ad602av.dat with SIXBINTER

Q₂(25.5) excitation at 1 atm. :

SS := READPRN(ONEADATA) II := READPRN(ONEAINTER) LL := READPRN(LAMDATA)

imax := rows(SS) - 1 i := 0..imax

S1A := SS^{<0>} I1A := II^{<0>} LAM := LL^{<0>}

SM1A := S1A₅₀₁ IM1A := I1A₅₀₁ SCALE1A := $\frac{SM1A}{IM1A}$

SM1A = 0.0696 IM1A = 0.4057 SCALE1A = 0.1716

Q₂(25.5) excitation at 6 atm. :

SS := READPRN(SIXADATA) II := READPRN(SIXAINTER)

S6A := SS^{<0>} I6A := II^{<0>} SM6A := S6A₄₉₈ IM6A := I6A₄₉₈ SCALE6A := $\frac{SM6A}{IM6A}$

SM6A = 1.0137 IM6A = 1.7867 SCALE6A = 0.5673

Q₂(26.5) excitation at 1 atm. :

SS := READPRN(ONEBDATA) II := READPRN(ONEBINTER)

S1B := SS^{<0>} I1B := II^{<0>} SM1B := S1B₂₅₈ IM1B := I1B₂₅₈ SCALE1B := $\frac{SM1B}{IM1B}$
 SM1B = 0.3850 IM1B = 0.8967 SCALE1B = 0.4293

Q₂(26.5) excitation at 6 atm. :

SS := READPRN(SIXBDATA) II := READPRN(SIXBINTER)

S6B := SS^{<0>} I6B := II^{<0>} SM6B := S6B₂₅₈ IM6B := I6B₂₅₇ SCALE6B := $\frac{SM6B}{IM6B}$
 SM6B = 3.1669 IM6B = 6.2346 SCALE6B = 0.5080

Determine the average spectral step size. Necessary for the integration.

$$dL\lambda M := \frac{1}{imax} \cdot \left[\sum_{i=1}^{imax} (L\lambda M_i - L\lambda M_{i-1}) \right] \quad dL\lambda M = 0.0336$$

Set up range not to integrate over to kick out the N₂ Raman.

N2RAL := 156 N2RAU := 179

N2RBL := 152 N2RBU := 175

Read in spectral transmission data for a 1 mm thickness of UG5

DF1 := READPRN(UG5FILTER)

SF1 := DF1^{<0>} TF1 := DF1^{<1>}

TF1PUMP := $\frac{TF1_2 + TF1_3}{2}$ Transmission at the pump wavelength (about 225 nm)

Read in spectral transmission data for M248V excimer laser mirror

DF2 := READPRN(M248V)

SF2 := DF2^{<0>} TF2 := DF2^{<1>}

TF2PUMP := $TF2_6 + \frac{TF2_7 - TF2_6}{4}$ Transmission at the pump wavelength (about 225 nm)

Interpolate intermediate values via use of a cubic (c) spline.

vscF1 := cspline(SF1, TF1)

vscF2 := cspline(SF2, TF2)

TF1c_i := interp(vscF1, SF1, TF1, LAM_i)

TF2c_i := interp(vscF2, SF2, TF2, LAM_i)

Determine the effective transmission resulting from combining the two filters:

$n=0$: unfiltered, $n=1$: M248V only, $n>1$: M248V with $n-1$ mm of UG5.

$n := 0..10$ $mn := 2..10$

Unfiltered : $n=0$ $Teff_{0,i} := 1$ $TeffPUMP_0 := 1$

M248V Filtering only : $n=1$ $Teff_{1,i} := (TF2c_i)^2$ $TeffPUMP_1 := TF2PUMP^2$

M248V Filtering with $n-1$ mm of UG5 $n>1$ $Teff_{mn,i} := [(TF1c_i)^{mn-1}] \cdot (TF2c_i)^2$ $TeffPUMP_{mn} := TF1PUMP^{mn-1} \cdot TF2PUMP^2$

Apply the filter to the spectrum.

$S1AF_{n,i} := S1A_i \cdot Teff_{n,i}$ $S1BF_{n,i} := S1B_i \cdot Teff_{n,i}$ $I1AF_{n,i} := I1A_i \cdot Teff_{n,i}$ $I1BF_{n,i} := I1B_i \cdot Teff_{n,i}$

$S6AF_{n,i} := S6A_i \cdot Teff_{n,i}$ $S6BF_{n,i} := S6B_i \cdot Teff_{n,i}$ $I6AF_{n,i} := I6A_i \cdot Teff_{n,i}$ $I6BF_{n,i} := I6B_i \cdot Teff_{n,i}$

Integration for Q2(25.5) at 1 atm.:

$$AT1AS_n := \sum_{i=0}^{imax-1} \frac{S1AF_{n,i} + S1AF_{n,i+1}}{2} \cdot dLAM$$

$$AT1ASR_n := \sum_{i=0}^{N2RAL-1} \frac{S1AF_{n,i} + S1AF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RAU}^{imax-1} \frac{S1AF_{n,i} + S1AF_{n,i+1}}{2} \cdot dLAM$$

$$AT1AI_n := \sum_{i=0}^{N2RAL-1} \frac{I1AF_{n,i} + I1AF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RAU}^{imax-1} \frac{I1AF_{n,i} + I1AF_{n,i+1}}{2} \cdot dLAM$$

$$AT1ANO_n := AT1ASR_n - AT1AI_n \cdot SCALE1A$$

Integration for Q2(25.5) at 6 atm.:

$$AT6AS_n := \sum_{i=0}^{imax-1} \frac{S6AF_{n,i} + S6AF_{n,i+1}}{2} \cdot dLAM$$

$$AT6ASR_n := \sum_{i=0}^{N2RAL-1} \frac{S6AF_{n,i} + S6AF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RAU}^{imax-1} \frac{S6AF_{n,i} + S6AF_{n,i+1}}{2} \cdot dLAM$$

$$AT6AI_n := \sum_{i=0}^{N2RAL-1} \frac{I6AF_{n,i} + I6AF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RAU}^{imax-1} \frac{I6AF_{n,i} + I6AF_{n,i+1}}{2} \cdot dLAM$$

$$AT6ANO_n := AT6ASR_n - AT6AI_n \cdot SCALE6A$$

Integration for Q2(26.5) at 1 atm.:

$$AT1BS_n := \sum_{i=0}^{imax-1} \frac{S1BF_{n,i} + S1BF_{n,i+1}}{2} \cdot dLAM$$

$$AT1BSR_n := \sum_{i=0}^{N2RBL-1} \frac{S1BF_{n,i} + S1BF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RBU}^{imax-1} \frac{S1BF_{n,i} + S1BF_{n,i+1}}{2} \cdot dLAM$$

$$AT1BI_n := \sum_{i=0}^{N2RBL-1} \frac{I1BF_{n,i} + I1BF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RBU}^{imax-1} \frac{I1BF_{n,i} + I1BF_{n,i+1}}{2} \cdot dLAM$$

$$AT1BNO_n := AT1BSR_n - AT1BI_n \cdot SCALE1B$$

Integration for Q2(26.5) at 6 atm.:

$$AT6BS_n := \sum_{i=0}^{imax-1} \frac{S6BF_{n,i} + S6BF_{n,i+1}}{2} \cdot dLAM$$

$$AT6BSR_n := \sum_{i=0}^{N2RBL-1} \frac{S6BF_{n,i} + S6BF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RBU}^{imax-1} \frac{S6BF_{n,i} + S6BF_{n,i+1}}{2} \cdot dLAM$$

$$AT6BI_n := \sum_{i=0}^{N2RBL-1} \frac{I6BF_{n,i} + I6BF_{n,i+1}}{2} \cdot dLAM + \sum_{i=N2RBU}^{imax-1} \frac{I6BF_{n,i} + I6BF_{n,i+1}}{2} \cdot dLAM$$

$$AT6BNO_n := AT6BSR_n - AT6BI_n \cdot SCALE6B$$

DEFINE THE VALUE : V :

$$V1A_n := \frac{AT1ANO_n \cdot AT1AS_0 - AT1ANO_0}{AT1ANO_0 \cdot AT1AS_n - AT1ANO_n}$$

$$V6A_n := \frac{AT6ANO_n \cdot AT6AS_0 - AT6ANO_0}{AT6ANO_0 \cdot AT6AS_n - AT6ANO_n}$$

$$V1B_n := \frac{AT1BNO_n \cdot AT1BS_0 - AT1BNO_0}{AT1BNO_0 \cdot AT1BS_n - AT1BNO_n}$$

$$V6B_n := \frac{AT6BNO_n \cdot AT6BS_0 - AT6BNO_0}{AT6BNO_0 \cdot AT6BS_n - AT6BNO_n}$$

DEFINE THE PROBED SPECIES SIGNAL TRANSMISSION : PST :

$$PST1A_n := \frac{AT1ANO_n}{AT1ANO_0}$$

$$PST6A_n := \frac{AT6ANO_n}{AT6ANO_0}$$

$$PST1B_n := \frac{AT1BNO_n}{AT1BNO_0}$$

$$PST6B_n := \frac{AT6BNO_n}{AT6BNO_0}$$

Appendix C - Experimental Determination of Saturated and Linear Fluorescence Regimes

A saturation curve was experimentally generated to determine the laser energy constraints for the PLIF and LSF experiments. The saturation curve indicates the variation in the degree of saturation with increasing laser irradiance. The degree of saturation (DOS) was defined as the bracketed term in Eq. (4.22), as plotted in Fig. 4.2. The linear fluorescence regime may be identified from this saturation curve, and used to define the upper limit on the allowable irradiance for the PLIF experiments. Moreover, the saturation irradiance (Eq. (4.21a)) may be determined from the appropriate minimum-error fit to the saturation curve data. This saturation irradiance may then be used to define the lower limit on the allowable irradiance for the LSF experiments. Experimental determination and analysis of the saturation curve as well as determination of the limits on laser irradiance for the PLIF and LSF experiments are described in the following sections.

C.1 Experimental Generation of the Saturation Curve

The experimental apparatus used to determine the saturation curve is portrayed in Fig. 5.4. The Rochon prism (RP) was used to provide twelve levels of laser attenuation ranging from 1 to 0.0013. At the maximum transmission position of the RP (i.e., 185° from Fig. 5.5), the laser energy in the probe volume was ~ 0.25 mJ/pulse. Based on a measured beam diameter of $214\text{ }\mu\text{m}$, this corresponded to a laser fluence of $\sim 6.84\text{ mJ/mm}^2\text{-pulse}$. The $Q_2(26.5)$ line was used for NO excitation in the 78-ppm doped calibration flame, as described in Appendix E. The monochromator entrance slit was set to $50\text{ }\mu\text{m}$ wide by 2 mm tall, and the signal was integrated over an $\sim 2.7\text{-nm}$ region centered on the $\gamma(0,1)$ band of NO. At each level of attenuation, the horizontal transverse position of SL3 in Fig. 5.4 was adjusted to center the image of the monochromator entrance slit on the focused laser beam. At each level of attenuation, the NO fluorescence signal was averaged over 800 shots.

Figure C.1 shows the variation in NO fluorescence signal with laser power for the twelve levels of attenuation. Both the NO fluorescence signal and laser fluence were normalized by their respective data values at the maximum RP transmission. Figure C.1

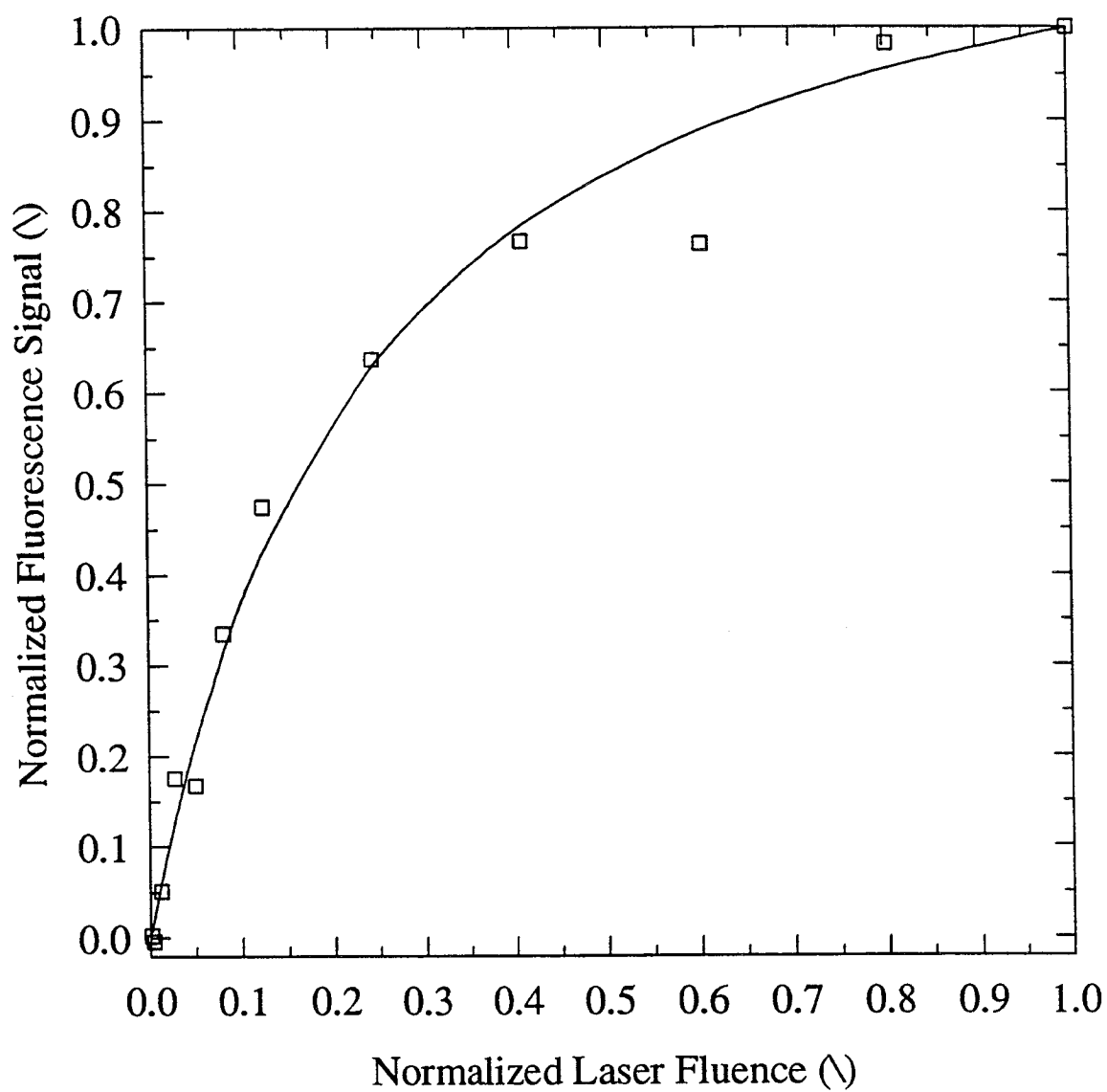


Figure C.1 NO saturation curve data and minimum-error fit. From the fit to the data the saturation fluence was determined to be $\sim 1.64 \text{ mJ/mm}^2\text{-pulse}$.

demonstrates both the strengths and limitations of the RP attenuator; appropriately spaced data was preselected via the RP calibration curve of Fig. 5.5. However, the finite beam steering resulting from rotation of the RP required the image of the monochromator entrance slit to be reset for each level of attenuation. The scatter in the data of Fig. C.1 is due to the precision of making this adjustment. Nevertheless, the data display the expected trends based on Eq. (4.22) and Fig. 4.2.

The saturation irradiance was determined by fitting an equation describing the normalized degree of saturation (NDOS) to the experimental saturation data. The equation for the NDOS was developed from the bracketed term in Eq. (4.22) by normalizing all irradiance values by the maximum irradiance (i.e., at the minimum attenuation RP position) and subsequently normalizing the DOS by the maximum DOS value. Using this method, it may be shown that

$$NDOS = \frac{(1 + \tilde{I}_v^{sat}) \tilde{I}_v^o}{(\tilde{I}_v^o + \tilde{I}_v^{sat})}, \quad (C.1)$$

where $\tilde{I}_v^o = I_v^o / I_v^o|_{\max}$ and $\tilde{I}_v^{sat} = I_v^{sat} / I_v^o|_{\max}$. Hence, the curve in Fig. C.1 represents the variation in NDOS with $\tilde{I}_v^o$, with the value of the normalized saturation irradiance, $\tilde{I}_v^{sat}$, determined from minimizing the error of the fit of Eq. (C.1) to the data of Fig. C.1. Based on multiple experimental data sets, normalized values of the saturation irradiance ranging from 0.21 to 0.24 were determined from the minimum-error (i.e., least-squares) fit. Using Eq. (4.2) and noting that the spectral and temporal FWHMs are constant for a given laser system, relationships for the normalized laser energy and fluence may be developed, as described previously for the laser irradiance. Using such relationships and a normalized saturation irradiance of 0.24, the saturation fluence, F_{sat} , is found to be $\sim 1.64 \text{ mJ/mm}^2\text{-pulse}$. This value may be used to determine the laser energy required for the LSF experiments.

It was determined from the saturation curve that the fluorescence was in the linear fluorescence regime for levels of attenuation below ~ 0.027 (i.e., normalized fluence of

0.027 in Fig. C.1). Hence, the laser fluence must be less than approximately $F_{\text{lin,max}} \approx 0.185 \text{ mJ/mm}^2\cdot\text{pulse}$ to remain in the linear fluorescence regime. This corresponds to $I_v^\circ / I_v^{\text{sat}} = F_{\text{lin,max}} / F_{\text{sat}} \approx 0.11$, which is consistent with the curves in Fig. 4.3. This maximum laser fluence value may be used to determine the limitations on laser energy for the PLIF experiments.

C.2 Laser Energy Specifications for PLIF Experiments

For the PLIF experiments, the laser radiation was formed into an $\sim 400 \mu\text{m}$ thick (w) by $\sim 14.73 \text{ mm}$ tall (h) sheet. Hence, for a perfectly uniform laser sheet, the required laser energy in the probe volume used for the PLIF experiments must be less than $E_{\text{PLIF,max}} = w \cdot h \cdot F_{\text{lin,max}} \approx 1.09 \text{ mJ/pulse}$. Accounting for the 7.1% transmission of the sheet forming optics (Chapter 5), this corresponds to laser energies less than 15.35 mJ/pulse out of the FA of Fig. 5.7.

It was determined that the laser sheet was not uniform but rather displayed structure in the transverse (i.e., vertical) dimension. Based on a 99% confidence interval (3σ), the laser-sheet fluctuations were observed to be $\sim 67\%$ of the average sheet value. If transverse profiles of the laser sheet are observed by the imaging system, the per-pixel signal is a measure of the local value of $w \cdot F$. Hence, to insure that the highest $w \cdot F$ locations in the sheet remain in the linear fluorescence regime, $\overline{w \cdot F} < w \cdot F_{\text{lin,max}} / 1.67$. This indicates that for the PLIF experiments, the average laser fluence must be less than $F_{\text{PLIF,max}} = F_{\text{lin,max}} / 1.67 \approx 0.111 \text{ mJ/mm}^2\cdot\text{pulse}$ and the average laser energy must be less than $E_{\text{PLIF,max}} = w \cdot h \cdot F_{\text{lin,max}} / 1.67 \approx 0.65 \text{ mJ/pulse}$. Accounting for the 7.1% transmission of the sheet forming optics, this corresponds to laser energies less than $\sim 9.2 \text{ mJ/pulse}$ out of the FA of Fig. 5.7.

C.3 Laser Energy Specifications for LSF Experiments

As discussed in Section 4.5.3, the DOS is greater than 90% for normalized laser spectral irradiance values greater than ten times the saturation irradiance. This is the criterion that was used for determining minimum laser energy specifications for the LSF experiments. Based on this criterion, the laser fluence for the LSF experiments must be

greater than $F_{\text{LSF,min}} = 10 \cdot F_{\text{sat}} \approx 16.4 \text{ mJ/mm}^2 \cdot \text{pulse}$ (i.e., a normalized fluence of 2.4 in Fig. C.1). From multiple measurements, the beam diameter used for the LSF experiments was determined to be 180 to 213 μm . Based on the upper limit of this range, the laser energy in the probe volume for the LSF measurements of [NO] must be greater than $E_{\text{LSF,min}} \approx 0.58 \text{ mJ/pulse}$. Accounting for the 16% transmission of the LSF optics, this corresponds to laser energies greater than $\sim 3.65 \text{ mJ/pulse}$ out of the FA of Fig. 5.4. Hence, based on the conclusions of Sections C.2 and C.3, the PLIF and LSF experiments require laser energy levels out of the FA in the range $\sim 3.65 \text{ mJ/pulse}$ to $\sim 9.2 \text{ mJ/pulse}$.

Appendix D - Data Reduction Procedures

A total of seven experimental runs were performed, including two for LSF, which were referred to as runs A and B, and five for PLIF, which were referred to as runs C, D, E, F and G. In Chapter 7, run B is used for LSF and run C is used for PLIF. Some amount of post processing was required to correct the signals from both the LSF and PLIF experiments. These corrected signal levels were then calibrated to provide [NO] in number density (cm^{-3}) or parts per million (ppm) as described in Appendix E. Possible corrections include non-NO-attributable background such as flame luminescence, dark and readout noise, and various interferences, image-to-image fluctuations in the average laser irradiance, laser-sheet nonuniformities, and spatial variations in the ICCD gain and pixel responsivity. The techniques implemented to make the necessary corrections for the LSF and PLIF experiments are discussed in this appendix.

D.1 LSF Data Reduction

The LSF data were collected, as described in Chapter 5, using a 500-ps gate temporally centered on the fluorescence signal. This allowed integration of only the saturated portion of the fluorescence signal, with rejection of partially saturated and linear fluorescence in the wings of the pulse. Hence, the integrated LSF signal can be described using Eq. (4.27) as

$$C_D^{LSF} = \eta G R \frac{\Omega}{4\pi} V_C f_B(T) N_T \frac{A_{N,F}}{\gamma} t_G = K^{LSF} f_B(T) N_T, \quad (\text{D.1})$$

where K^{LSF} represents a group of variables that is constant for a given experimental setup and procedure (i.e., optical alignment, excitation and detection scheme), and is determined from calibration (Appendix E). Equation (D.1) may be inverted to calculate the NO number density (cm^{-3}), N_T , from the measured NO-fluorescence signal, i.e.,

$$N_T = \frac{1}{K^{LSF} f_B(T)} C_D^{LSF}. \quad (\text{D.2})$$

From Eq. (D.2) it is clear that the LSF measurements are independent of laser irradiance. Hence, no correction is required to account for shot-to-shot fluctuations in the laser power. However, the recorded LSF signal must be corrected to produce C_D^{LSF} (V), which is the integrated signal due only to NO fluorescence.

The LSF measurements were corrected for flame luminescence, PMT dark noise and any amplifier noise. All of these effects were integrated into a single background measurement. This background was measured using the normal data acquisition procedures for the LSF measurements but with the laser blocked. The background was found not to vary spatially throughout the IDF. Background measurements were taken for each elevation at the beginning and end of each radial scan. The value of the background was determined as the average of these two measurements. The NO-attributable signal, C_D^{LSF} , was then determined as the difference between the total integrated signal and the elevation-specific average background for the same number of laser shots.

The LSF measurements were not corrected for laser-induced interferences. As discussed in Chapter 6, NB point measurements of [NO] using optimum excitation and detection schemes are relatively free of secondary-species interferences. Moreover, determination of the calibration factor (as described in Appendix E) is independent of the existence of any laser-induced interferences. However, there is the potential for data corruption when such a calibration factor is applied to the measured LSF signal if the interference contribution is significant. Reisel et al. (1993a) have provided a method that accounts for the signal contribution due to laser induced interferences; the method uses a factor (x) which is equal to the ratio of the NO-attributable signal with the laser tuned off and on line. Using the notation of Reisel et al. (1993a), it may be shown that the exact expression for the NO-attributable signal, S_{NO} , is $S_{NO} = (S - B) / (1 - x)$, where S is the total on-line signal and B is the off-line signal. Reisel et al. (1993a) used an approximation to the exact solution (i.e., $S_{NO} = (1 + x)S - B$), which applies in the limit that the laser-induced interferences are much less than the NO-attributable fluorescence signal.

Experiments were performed to assess the magnitude of the laser-induced interferences. This involved making radial LSF scans of [NO] through the IDF as well as

calibration scans with the laser tuned on and off the $Q_2(26.5)$ line of NO. Using this data, the interference signal contribution was investigated by using the exact expression for S_{NO} and the procedures described by Reisel et al. (1993a). For this data, there was an insignificant difference in the results using the exact and approximate expressions described above. The calculated value of the interference signal was approximately one-fifteenth of the detection limit. Moreover, the uncertainty in the calculated value of the interference signal was approximately 4000% based on a 95% confidence interval. This gross uncertainty in the fluorescence correction is due to the fact that it is determined from the difference in two numbers whose difference is much less than either's uncertainty. Moreover, parameters smaller than the detection limit obviously cannot be determined with any substantial accuracy. The small calculated value of the laser-induced interference demonstrates the relative insensitivity of NB detection schemes to interferences. Moreover, the contribution of the laser-induced interference signal to the total LSF signal was found to be insignificant throughout the IDF. Specifically, the interference signal contributed $\sim 0.02\%$ systematic uncertainty to the final measurements, which had a nominal uncertainty of $\sim 20\%$. Accounting for this small factor would complicate the LSF measurements in the spatially varying IDF without significantly enhancing their accuracy. Hence, for the present experiments, the data were not corrected for interferences. However, the interference contribution to LSF measurements should always be investigated for any specific experiment.

D.2 PLIF Data Reduction

Reduction of the PLIF images requires extensive post-processing due to their dependence on a greater number of experimental parameters as compared to the LSF measurements. If the signal integrated by the ICCD was due only to NO fluorescence, then the relationship between the digital pixel signal, C_D^{LF} (counts), and the NO number density, N_T (cm^{-3}), would be described by Eq. (4.24). It is clear from this equation that the integrated PLIF signal is a linear function of laser irradiance, and hence, the measurements must be corrected for image-to-image fluctuations in average laser power. However, reduction of the PLIF images is further complicated by spatial variations in

sheet irradiance, dark and readout noise, intensifier gain, pixel responsivity, background, and laser-induced interferences. Moreover, as discussed in Chapter 6, the PLIF measurements are much more susceptible to interferences as compared to the LSF measurements.

To account for the vast array of signal dependencies in the PLIF images, several images were taken under different experimental conditions. Table D.1 presents an experiment data sheet which describes the experimental conditions corresponding to the sixteen images that were taken for a given run. Images 1 through 4 were taken in the IDF flame by using the optimum filtering scheme determined in Chapter 6; these images correspond to (IM1) the dark and readout noise, (IM2) the background which includes IM1 and flame luminosity, (IM3) the laser-induced background which includes IM2 and interferences, and (IM4) the total image which includes NO fluorescence, IM1, IM2, and IM3. The interdependencies of these images is discussed in detail below. Images 5 through 11 correspond to the calibration procedure, which is discussed in Appendix E. Images 12 through 16 were taken with ambient-temperature nitrogen flowing through the AIDF burner, and were used to correct for spatial variations in laser-sheet irradiance, pixel responsivity, and intensifier gain. It is important to notice that the dark noise image is constant only for a given integration time ($IM1 \neq IM16$). Since the effective per-pixel gain (G) and responsivity (R) are a function of the ICCD, G and R are spatially similar for all images of Table D.1. Moreover, the background image is constant for a given integration time and flame environment, while the laser-induced background is constant for a given integration time, flame environment, and laser irradiance. Hence, the signal contribution from a given phenomenon in a total image may be represented by the specific image attributable to that phenomenon alone. For example, the dark and readout noise image of IM1 is equivalent to the dark and readout noise contribution to images IM2, IM3, and IM4. This also applies for the relationship of image IM2 with IM3 and IM4, and image IM3 with IM4 provided that one accounts for variations in the laser fluence. Using this fact and images IM2, IM3, IM4, IM14, and IM15, the NO number density may be distilled from the total image of IM4.

Table D.1 Experiment data sheet.

Number	name	f/#	t _{exp} (s)	Filter	Laser	Flame	D _R (ppm)	Q ₂ (26.5)	L-Cap	FILE
1	dnr1	4.5	180.05	*	\	IDF	\	\	ON	IM .dta
2	bkg	4.5	180.05	*	OFF	IDF	\	\	OFF	IM .dta
3	lib	4.5	180.05	*	ON	IDF	\	OFF	OFF	IM .dta
4	ima	4.5	180.05	*	ON	IDF	\	ON	OFF	IM .dta
5	cal00	4.5	180.05	*	ON	CAL	0	ON	OFF	IM .dta
6	cal20	4.5	180.05	*	ON	CAL	20	ON	OFF	IM .dta
7	cal40	4.5	180.05	*	ON	CAL	40	ON	OFF	IM .dta
8	cal60	4.5	180.05	*	ON	CAL	60	ON	OFF	IM .dta
9	cal78	4.5	180.05	*	ON	CAL	78	ON	OFF	IM .dta
10	calbkg	4.5	180.05	*	OFF	CAL	0	\	OFF	IM .dta
11	callib	4.5	180.05	*	ON	CAL	0	OFF	OFF	IM .dta
12	snu1	4.5	180.05	*	ON	OFF	\	\ON\	OFF	IM .dta
13	snu1bkg	4.5	180.05	*	OFF	OFF	\	\	OFF	IM .dta
14	snu2	4.5	20.05	NONE	ON	OFF	\	\ON\	OFF	IM 2 .dta
15	snu2bkg	4.5	20.05	NONE	OFF	OFF	\	\	OFF	IM 2 .dta
16	dnr2	4.5	20.05	NONE	\	\	\	\	ON	IM 2 .dta

* : F250W + 6 mm UG5

The PLIF data reduction procedure is simplified if the signals are modeled using effective fluorescence and interference coefficients and the normalized spectral fluence of the laser, $F^v = I_v^0 \cdot \Delta t_L$ ($\text{J}/\text{cm}^2 \cdot \text{cm}^{-1}$). This change in notation facilitates system modeling; moreover, the results can be expanded to full notation for the final results. An effective fluorescence coefficient for a linear fluorescence process, Υ^v ($\text{cm}^2 \cdot \text{cm}^{-1}/\text{J}$), may be defined as

$$\Upsilon^v = \frac{\Omega}{4\pi} V_C f_B(T) N_T \Gamma_{luL} B_{lu} \Phi^{LIN}. \quad (\text{D.3})$$

Using this notation, Eq. (4.24) collapses to

$$C_D^{LIN} = \eta G R \Upsilon^v F^v. \quad (\text{D.4})$$

It is clear from Eq. (D.4) that the product $\eta \Upsilon^v F^v$ is the number of LIF photons arriving at the ICCD photocathode. Similarly, an effective interference coefficient, Υ_I^v ($\text{cm}^2 \cdot \text{cm}^{-1}/\text{J}$), may be defined to account for the signal arising from all laser-induced interferences such as Rayleigh scattering, Raman scattering, and secondary-species fluorescence. A background variable B (photons) can also be defined to account for the environment-specific effective emission including flame luminosity.

Using the notation defined above, the signal contribution to the images IM1, IM2, IM3, IM4, IM14, and IM15 may be modeled as described by Eqs. (D.5a) through (D.5f); a spatial dependance is understood to exist for all variables but is not explicitly indicated. The model assumes that the laser-induced interferences scale linearly with laser fluence.

$$IM1 = dnr1 \quad (\text{D.5a})$$

$$IM2 = bkg = dnr1 + \eta_2 G R B_2 \quad (\text{D.5b})$$

$$IM3 = lib = dnr1 + \eta_2 G R (B_2 + F_3^v \Upsilon_{I,3}^v) \quad (\text{D.5c})$$

$$IM4 = ima = dnr1 + \eta_2 G R (B_2 + F_4^\vee [\Upsilon_{l,3}^\vee + \Upsilon^\vee]) \quad (D.5d)$$

$$IM14 = snu2 = dnr2 + \eta_{14} G R (B_{14} + F_{14}^\vee \Upsilon_{l,14}^\vee) \quad (D.5e)$$

$$IM15 = snu2bkg = dnr2 + \eta_{14} G R B_{14} \quad (D.5f)$$

In Eqs. (D.5a) through (D.5f), the image names (e.g., ima, lib,...) correspond to those used in the image analysis programs of Section D.3. Subscripts are added to η , B , $F^\vee$, and $\Upsilon^\vee$ to indicate image-specific values of the specific parameter. Moreover, the following relationships have been employed : $\eta_2 = \eta_3 = \eta_4$, $\eta_{14} = \eta_{15}$, $B_2 = B_3 = B_4$, $B_{14} = B_{15}$, and $\Upsilon_{l,3}^\vee = \Upsilon_{l,4}^\vee$. For example, the filtering scheme used for IM2, IM3, and IM4 is different from that used for IM14 and IM15; hence, η_2 appears in Eqs. (D.5b) through (D.5d) while η_{14} appears in Eqs. (D.5e) and (D.5f).

The NO number density may be determined via $\Upsilon^\vee$ by manipulating Eqs. (D.5a) through (D.5f) and using the relationships

$$\frac{F_j^\vee}{F_k^\vee} = \frac{I_{vj}^\circ}{I_{vk}^\circ} = \frac{P_{Lj}}{P_{Lk}}, \quad (D.6)$$

for two images j and k . All variables in Eq. (D.6) are understood to be averaged over the integration time of the image. Using Eqs. (D.5b), (D.5c), (D.5d) and (D.6), the intermediate image $Ni1$ (counts) may be defined as

$$Ni1 = \eta_2 G R F_4^\vee \Upsilon^\vee = IM4 - \left[1 - \frac{P_{L,4}}{P_{L,3}} \right] IM2 - \frac{P_{L,4}}{P_{L,3}} IM3. \quad (D.7)$$

Due to the algebra in Eq. (D.7), the pixel values of image $Ni1$ may be fractional counts although those of IM2, IM3, and IM4 are clearly integral. Using Eqs. (D.5e), (D.5f) and (D.7) it may be shown that

$$Ni1 = \frac{P_{L,4}}{P_{L,14}} \frac{TR LSD}{\Upsilon_{L,14}^v} \Upsilon^v, \quad (D.8)$$

where definitions have been invoked for the transmission ratio, $TR=\eta_2/\eta_{14}$, and the laser-sheet distribution, $LSD=IM14-IM15$ (counts). Image Ni1 is calculated from Eq. (D.7) and then Eq. (D.8) is inverted to determine the effective fluorescence coefficient

$$\Upsilon^v = \frac{P_{L,14}}{P_{L,4}} \frac{\Upsilon_{L,14}^v}{TR LSD} Ni1 = \frac{\Upsilon_{L,14}^v}{TR} Ni2, \quad (D.9)$$

where a second intermediate image Ni2 (counts) has been defined. The pixel value of image Ni2 may again be in fractional counts. All of the intermediate images defined above (Ni1, Ni2, and LSD) are used in the PLIF image analysis program. The NO number density in the plane of the laser sheet may now be determined using Eqs. (D.3) and (D.9) as

$$N_T = \frac{\Upsilon_{L,14}^v}{TR K^{LF} \Phi^{LN} f_B(T)} Ni2, \quad (D.10)$$

where K^{LF} ($\text{cm}^3 \cdot \text{cm}^2 \cdot \text{cm}^{-1} / \text{J}$) has been defined as

$$K^{LF} = \frac{\Omega}{4\pi} V_C \Gamma_{lu,L} B_{lu}. \quad (D.11)$$

It is clear from the inclusion of F^v in Eq. (D.4) and the definition of Ni2 in Eq. (D.9) that the NO number density defined by Eq. (D.10) is properly normalized for image-to-image laser-irradiance fluctuations. The five-parameter term multiplying Ni2 in Eq. (D.10) is determined by the calibration procedure. The parameters TR , K^{LF} , and $\Upsilon_{L,14}^v$ are spatially constant parameters for a given experimental setup and procedure. Recall that $\Upsilon_{L,14}^v$ is the effective interference coefficient from a room-temperature nitrogen flow. Errors in the

PLIF images of [NO] will occur via Φ^{LIN} and $f_B(T)$ in Eq. (D.10). The linear fluorescence yield, Φ^{LIN} , will vary with the electronic quenching rate coefficient while the Boltzmann fraction, $f_B(T)$, will vary in a known manner with temperature.

A numerical high-pass filter was applied to portions of the data to eliminate division-by-zero incursions during the image analysis procedure. The numerical high-pass filter passed pixels unchanged if their value was greater than a specified offset; pixels with a value less than or equal to the specified offset were reassigned to the value of the offset. This was necessary because the PLIF image analysis procedure, defined by Eqs. (D.7) through (D.9), requires division of images by other images to determine the image Ni2. Zero pixel values could occur due to dead pixels, or to intermediate pixel values resulting from image differencing. The numerical filter was applied directly to Ni1 and LSD with a specified offset of unity. This eliminated any division-by-zero incursions with minimum biasing of the data.

D.3 PLIF Image Analysis Program

The PLIF images were analyzed using run-specific programs which contained hard inputs of the appropriate image file names, image-specific average laser irradiance file names, output filenames, and the value of the run-specific calibration factor. The program for analyzing Run C of the PLIF measurements of [NO] in an AIDF, IMACORR4c, is provided below as an example. Only the run-specific filenames and values discussed above were different for the other PLIF runs (i.e., runs D, E, F, and G). The program operated directly on the scrambled images acquired by the PC-based Princeton Instruments imaging system operating with CSMA-software; this program was run using the UNIX-based command language version of the Visual Numerics PV-WAVE software. Conversion of the image files from DOS to UNIX format is provided in the body of the program. The program IMACORR4c was used in conjunction with IMACALc to determine the calibration factor, and BIN6c was used to selectively bin and grab the image data for comparison of the PLIF measurements to the LSF measurements.

.*****

```

;IMACORR4c
;program to correct the PLIF images of NO
;
;program operates on the data files from run C and using the calibration
;factor found in imacalc
;
; the program operates on scrambled '____.spe' files from the
; Princeton Instruments ST-130 imaging system.
;
; 5-15-95 wpp jr.
; 5-16-95, 6-25-95
;
;FIELD NOTATION:
;   ima:  total image
;   bkg:  scattering background
;   lib:  laser-induced background
;   snu2:  sheet nonuniformity 2 (different filters)
;   snu2bkg:  background for snu2
;
;POWER NOTATION:
;   P:  average laser power (ALP)
;
;   P3:  ALP for lib
;   P4:  ALP for ima
;   P14: ALP for snu2
;
;SUFFIX NOTATION:
;   a: averaged
;   m: masked
;   s: after background subtraction
;   n: after normalization
;   F: directly operated on by high-pass filter
;   f: indirectly operated on by high-pass filter
;   d: after subtraction of baseline primary combustion field
;
;*****
;
;set plot to X windows
;
set_plot,'X'

;
; If an io error is encountered then execution should resume at the label "end_of_file".
; We need to do this because when the file is read in we may reach the end too soon,

```

```

; causing an error but we still want to execute.
;
on_ioerror,end_of_file

;
;READ IN THE SCRAMBLED *.spe P.I. IMAGE FILES
;
openr,1,'/home/hemingway/a/partridg/images/c4.spe' ;ima
openr,3,'/home/hemingway/a/partridg/images/c2.spe' ;bkg
openr,4,'/home/hemingway/a/partridg/images/c3.spe' ;lib
openr,7,'/home/hemingway/a/partridg/images/c14.spe' ;snu2
openr,8,'/home/hemingway/a/partridg/images/c15.spe' ;snu2bkg

;
;READ IN THE AVERAGE LASER POWER VALUES
;
P=fltarr(16)
status=dc_read_free('/home/hemingway/a/partridg/datfiles/laserpc.dat', $
    P,/col,get_columns=[2])
P3=P(2)
P4=P(3)
P14=P(13)

;
;HARD INPUT THE CALIBRATION FACTOR FROM PROGRAM IMACAL
;
TCAL=105.8859

;
;DECLARE IMAGE ARRAYS
;Images are 578 x 384 pixels of 16 bits each.
;
ima=intarr(384,578)
bkg=intarr(384,578)
lib=intarr(384,578)
snu2=intarr(384,578)
snu2bkg=intarr(384,578)

;
;DECLARE HEADER ARRAYS
;declare an array for discarded header info P.I. uses 4100 longwords of header info.
;
hdr1=lonarr(1025)
hdr3=lonarr(1025)

```

```

hdr4=lonarr(1025)
hdr7=lonarr(1025)
hdr8=lonarr(1025)

;
; READ IN HEADER INFORMATION
;
readu,1,hdr1
readu,3,hdr3
readu,4,hdr4
readu,7,hdr7
readu,8,hdr8

;
; READ IN IMAGE DATA AND STORE IN variable name
;
readu,1,ima
readu,3,bkg
readu,4,lib
readu,7,snu2
readu,8,snu2bkg

end_of_file:

;
;DOS TO UNIX CONVERSION
;Must swap bytes when data is moved from a little-endian machine such as an IBM PC
;to a big-endian machine such as a Sun. The bytes are swapped by twos, since each
;pixel contains two bytes (16 bits) of data.
;
byteorder,ima,sswap=1
byteorder,bkg,sswap=1
byteorder,lib,sswap=1
byteorder,snu2,sswap=1
byteorder,snu2bkg,sswap=1

;
;TRANPOSE IMAGE AND THEN ROTATE 270 DEGREES
;
ima=rotate(ima,6)
bkg=rotate(bkg,6)
lib=rotate(lib,6)
snu2=rotate(snu2,6)
snu2bkg=rotate(snu2bkg,6)

```

```

;
;SET PARAMETERS FOR MASKING THE IMAGES
;
mxs=29           ;beginning mask x value
mxe=577          ;ending mask x pixel value
mys=13           ;beginning mask y pixel value
mye=255          ;ending mask y pixel value
xsz=mxe-mxs+1    ;size of masked image in x direction
ysz=mye-mys+1    ;size of masked image in y direction

;
;SETUP OFFSET FOR HIGH-PASS FILTER
; set all pixels with value less than or equal to the OFFSET to the OFFSET to eliminate
; the problem with division by zero.
;
OFFSET=1

;
;CALCULATE Ni1:
;
Ni1=ima-(1-(P4/P3))*bkg-(P4/P3)*lib
;
;APPLY THE HIGH-PASS FILTER
;af=(a GT OFFSET)*a + (a LE OFFSET)*OFFSET
;      (a GT OFFSET) =1 if aij>OFFSET
;      (a GT OFFSET) =0 if aij<=OFFSET
;
;      (a LE OFFSET) =1 if aij<=OFFSET
;      (a LE OFFSET) =0 if aij>OFFSET
;
Ni1F=(Ni1 GT OFFSET)*Ni1 + (Ni1 LE OFFSET)*OFFSET

;
;SHEET NONUNIFORMITY CORRECTION
;
LSD=snu2-snu2bkg ;Laser sheet distribution I
;
;APPLY THE HIGH-PASS FILTER
;
LSDF=(LSD GT OFFSET)*LSD + (LSD LE OFFSET)*OFFSET
;
;COMPLETE CALCULATION
;
Ni2f=P14*Ni1F/(P4*LSDF)

```

```

;
;APPLY THE CALIBRATION FACTOR
;
Nf=TCAL*Ni2f

;
;APPLY MASK TO THE IMAGES
;goto,skip0    ;skip masking the images
;
Ni2fm=Ni2f(mx:mxs,mys:mye) ;masked image Ni2f
Nfm=Nf(mx:mxs,mys:mye)    ;masked image Nf
skip0:

;
;APPLY MASK TO THE PRIMARY IMAGES
;goto,skip4    ;skip masking the images
;
imam=ima(mx:mxs,mys:mye)      ;masked image ima
bkgm=bkg(mx:mxs,mys:mye)      ;masked image bkg
libm=lib(mx:mxs,mys:mye)      ;masked image lib
sn2m=snu2(mx:mxs,mys:mye)     ;masked image snu2
sn2bm=snu2bkg(mx:mxs,mys:mye) ;masked image snu2bkg
ni1fm=Ni1F(mx:mxs,mys:mye)    ;masked image Ni1F
lsdfm=LSDF(mx:mxs,mys:mye)    ;masked image LSDF
skip4:

;
;Scale the image by three and prepare for presentation with a colorbar
;
Nfms=fltarr(xsz+75,ysz)
Nfms(*,*)=125
Nfms(75:xsz+74,*)=3*Nfm(0:xsz-1,*)

;
;Get the color table
;
get_myct,'idfcOLOR4'

;
;Set up array for colorbar
;
a=strarr(250)
a(210)=70
a(150)=50

```

```

a(90)=30
a(30)=10
a(0)=0

;
;DISPLAY THE FINAL IMAGES
;goto,skip1    ;skip making images
;
;make the image widow xszXysz Sun-pixels big window,xsize=xsz+75,ysize=ysz
tv,Nfms
colorbar2,n_colors=250,legend=a,font=5,offset=-0.6, $
        color=250,pos=[0.006,0.1,0.08,0.9]
skip1:

;
;REBIN THE IMAGE FILES
;rebinning performs a bilinear interpolation to create less dense matrices.
;goto,skip2    ;skip rebinning and making surface plots
;
Ni2fmr2=rebin(Ni2fm,xsz/9,ysz/9)
Nfmr2=rebin(Nfm,xsz/9,ysz/9)

;
;DISPLAY IMAGE SURFACE PLOT
;
window,2,xsize=578,ysize=384
surface,Nfmr2,skirt=0,ax=50,az=10 ;surface of corrected image
skip2:

;
;*****
;MAKE SOME POSTSCRIPT FILES
;goto,skip3    ;skip making postscript files
;
set_plot,'ps'
device,/inches,yoffset=1, xsize=7,ysize=7, $
        /bold,font_size=24,$
        filename='/home/hemingway/a/partridg/psfiles/cNfmr.ps'
surface,Nfmr2, $
        skirt=0,ax=50,az=10, $
        ztitle='[NO] ppm', title='Run C, Nfmr2', $
        subtitle='Bin 9 pixels, Resolution=0.5 mm'
device,/close

```

```

device,/landscape,/color,/inches, $
      xoffset=2.5,ysize=10,bits_per_pixel=8, $
      filename='/home/hemingway/a/partridg/psfiles/cNfms.ps'
tv,Nfms
colorbar2,n_colors=250,legend=a, $
      font=4,offset=-0.9, $
      color=248,pos=[0.006,0.01,0.06,0.36]
device,/close

set_plot,'X'
skip3:

;
;*****
;CLOSE FILES
;
close,1
close,3
close,4
close,7
close,8
end

```


Appendix E - NO Calibration Procedures

Equations were developed in Appendix D for LSF and PLIF measurements which express the NO concentration in terms of the measured fluorescence signal, C_D , and a proportionality or calibration factor (CF). The CF is determined through calibration techniques. Once the experiment-specific CF is determined, a quantitative value of [NO] may be calculated. This appendix describes the calibration procedures used for the LSF and PLIF measurements in Sections E.1 and E.2, respectively. Moreover, an alternate calibration technique which is particularly applicable to PLIF measurements is described in Section E.3. The PLIF image calibration program used for image analysis is provided in Section E.4.

The calibration method used for the LSF and PLIF experiments is referred to as the standard addition technique, and involved doping different levels of NO into a stable premixed fuel-lean flame. The NO fluorescence signal was measured in the post-flame zone at each doping level and was correlated with the NO-doping level to provide the CF. This standard addition technique is only applicable for stable species which may be stored for future doping (such as an NO in an N_2 standard gas mixture), and cannot be used for short lived radical species such as OH. The calibration was performed in a fuel-lean ($\phi=0.80$) flame so that the doped NO would not be destroyed by the premixed flame front (Reisel et al., 1993a). Moreover, the doping was performed such that the NO/ N_2 mixture would exactly replace a fraction of the N_2 in the undoped flame. This allowed the doping procedure to be thermodynamically nonintrusive, since the adiabatic flame temperature of the undoped flame was maintained in all of the doped flames. Two of the primary limitations of this calibration technique are the accuracy of the standard NO in N_2 gas mixture used for NO doping, and the reliability of the rotameter system used for gas metering to the AIDF burner. These limitations are addressed in the uncertainty analysis of Appendix F.

E.1 LSF Calibration Procedure

The CF for the LSF measurements was determined using the standard addition technique in a $\phi=0.80$ premixed $C_2H_6/O_2/N_2/NO$ flame with a dilution ratio of 3.76, at $y=4$ mm and $r=8$ mm (y and r are defined in Fig. 5.17), while using the same experimental configuration and data acquisition procedures as described in Chapter 5. The spatial location at which the calibration was performed was determined to be in the post-flame zone by comparing the CF measured at $y=4, 6$, and 9 mm above the AIDF-burner surface. Table E.1 provides the volumetric flow rates for the five levels of NO doping used in the calibration procedure. In Table E.1, D_R and D_P refer to the doped level in the reactants and products, respectively. D_R was set by the rotameter system using the relationship

$$\dot{V}_R = \frac{\dot{V}_{NO/N_2}}{\dot{V}_T} = \frac{D_R}{C_B}, \quad (E.1)$$

where $\dot{V}_R$ is a volumetric flow ratio, $\dot{V}_{NO/N_2}$ and $\dot{V}_T$ are the standard NO gas and total volumetric flow rates, respectively, and C_B is the NO concentration of the standard gas (313 ppm NO in N_2). D_P is the value of D_R corrected for the increase in the total number of moles in the products relative to that in the reactants. This correction was based on a completely reacted calibration flame for which the ratio of the total number of moles in the products to that in the reactants is $n_P/n_R=1.02$.

Equation (D.2) expresses the NO number density in terms of the measured LSF signal and a proportionality factor. Species concentration in number density ($N_{T,ND}$) is related to that in parts per million ($N_{T,ppm}$) via the ideal gas law, i.e.,

$$N_{T,ND} = \frac{P}{R_u T} \frac{N_A}{10^6} \frac{N_{T,ppm}}{10^6}, \quad (E.2)$$

where P is the absolute pressure, T is the absolute temperature, R_u is the universal gas constant, and N_A is Avogadro's number. Using Eqs. (D.2) and (E.2), one can show that

Table E.1 Volumetric flow rates of the various AIDF-burner gases for the calibration flame at the five levels of NO doping. The parameters D_R and D_P refer to the levels of NO doping relative to the reactants and products of the calibration flame, respectively.

Doping Level (ppm)		Volumetric Flow Rates (SLPM)				
D_R	D_P	C_2H_6	O_2	N_2	NO/N_2	Total
0	0	0.18	0.80	3.01	0.00	4.0
20	19.6	0.18	0.80	2.76	0.26	4.0
40	39.1	0.18	0.80	2.50	0.51	4.0
60	58.7	0.18	0.80	2.25	0.77	4.0
78	76.3	0.18	0.80	2.02	1.00	4.0

$$N_{T,ppm} = \frac{R_u T 10^6}{P N_A} \frac{1}{K^{LSF} f_B(T)} C_D^{LSF} = CF^{LSF} C_D^{LSF}, \quad (E.3)$$

where the calibration factor for the LSF experiments, CF^{LSF} (ppm/V), has been defined. Since the doping procedure is thermodynamically nonintrusive, CF^{LSF} is constant for the five flames used in the calibration procedure. If CF^{LSF} were known, then the [NO] in the calibration flame in ppm could be recovered using Eq. (E.3). Moreover, if the temperature and pressure of the calibration environment were known, this result could be used with Eq. (E.2) to determine the NO number density.

From Eq. (E.3), it is clear that CF^{LSF} is the slope of the fit to the $N_{T,ppm}(D_p)$ vs. $C_D^{LSF}(D_p)$ data. However, $N_{T,ppm}(D_p)$ is unknown since it is the sum of the unknown naturally occurring [NO] in the undoped calibration flame, $N_{T,ppm}(D_p=0)$, and D_p . Nevertheless, since the doping is thermodynamically nonintrusive, $N_{T,ppm}(D_p=0)$ is a constant, and therefore provides only a constant zero offset for the $N_{T,ppm}(D_p)$ vs. $C_D^{LSF}(D_p)$ data. Thus, the slopes of the fits to the $N_{T,ppm}(D_p)$ vs. $C_D^{LSF}(D_p)$ and the D_p vs. $C_D^{LSF}(D_p)$ data are equivalent. Consequently, CF^{LSF} may be experimentally determined as the slope of the fit to the D_p vs. $C_D^{LSF}(D_p)$ data. This demonstrates how the existence of a constant offset signal (e.g., fluorescence or laser-induced interferences) does not influence the determination of the CF as discussed in Section D.1.

To determine CF^{LSF} , the LSF signal attributable to NO was measured in each of the five calibration flames. Figure E.1 shows the D_p vs. $C_D^{LSF}(D_p)$ data and the corresponding least-squares fit to the data. CF^{LSF} was determined to be -344.3 ppm/V from the least-squares fit which had a correlation coefficient of 0.991. Other calibration runs produced less data scatter and hence, higher correlation coefficients. However, the data in Fig. E.1 represents the calibration corresponding to the results presented in Chapter 7. The fact that the calibration curve is linear indicates that either a negligible amount of the doped NO is destroyed in the flame front, or that the destruction rate is a linear function of [NO] which is unlikely (Reisel, 1991). Although CF^{LSF} has been determined, its utility is limited since it applies only to the calibration environment. This is

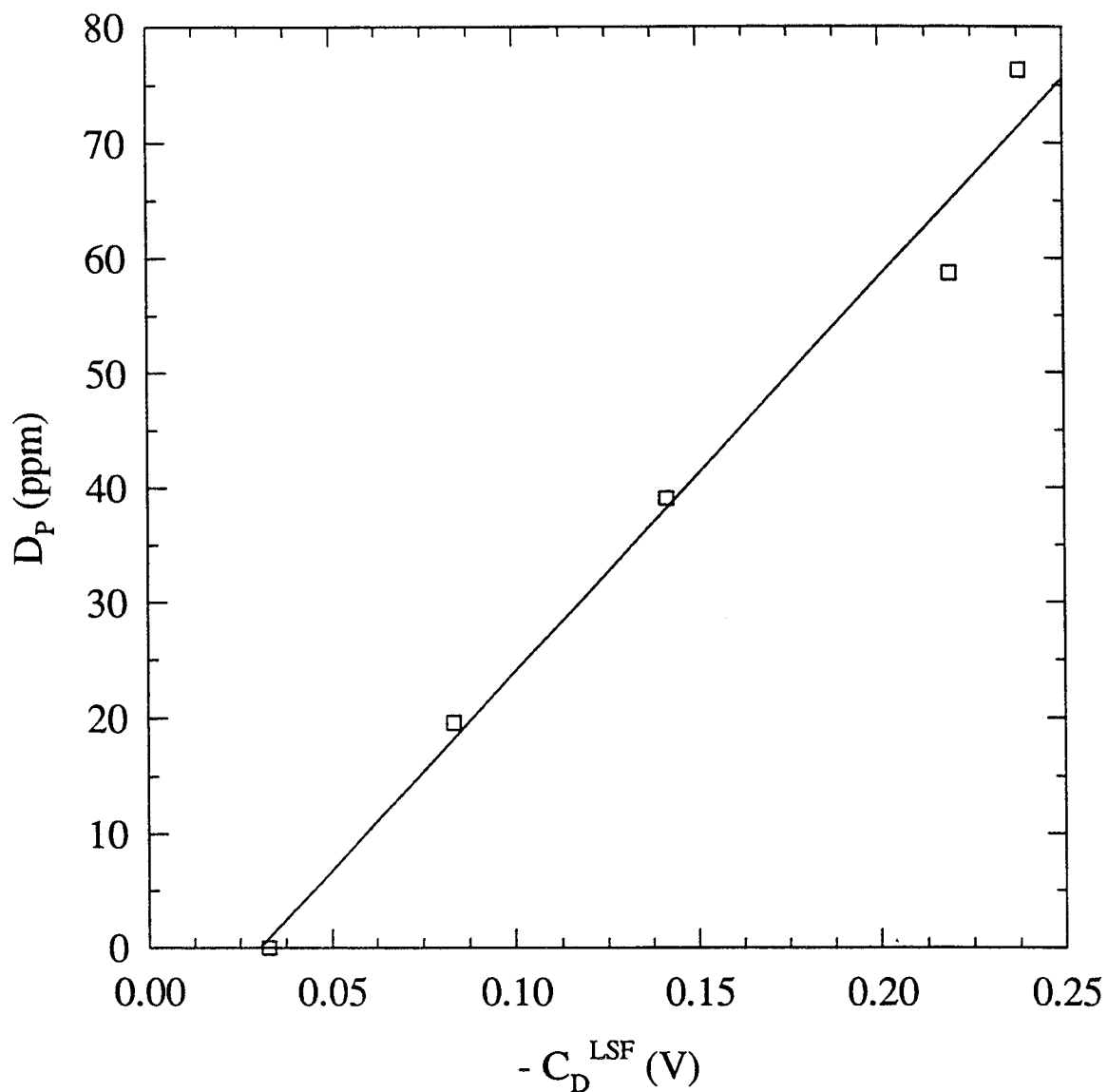


Figure E.1 Calibration curve for the LSF measurements. Calibration was performed in a $\phi=0.8$ premixed $C_2H_6/O_2/N_2/NO$ flame with a dilution ratio of 3.76, at $y=4$ mm and $r=8$ mm. $C_D^{LSF}(D_P)$ are the values of the LSF signal for five levels of NO doping relative to the products ($D_P = 0, 19.6, 39.1, 58.7$, and 76.3 ppm). A least-squares fit to the data provided $CF^{LSF} = -344.3$ ppm/V, and a correlation coefficient of 0.991.

because it is a function of both the temperature and pressure of the calibration environment both directly and through the Boltzmann fraction. Hence, one must take great care in transporting a calibration factor to experimental environments that differ from the calibration environment (Reisel et al., 1995).

To use the calibration factor in LSF studies of the IDF, a relationship must be established between the LSF signal levels in the calibration flame and the IDF. This can be accomplished by using Eq. (D.2) to generate

$$\frac{N_{TND,IDF}}{N_{TND,C}} = \frac{K_C^{LSF} f_{B,C}(T_C)}{K_{IDF}^{LSF} f_{B,IDF}(T_{IDF})} \frac{C_{D,IDF}^{LSF}}{C_{D,C}^{LSF}}, \quad (E.4)$$

where the subscripts C and IDF have been added to indicate parameter values in the calibration and IDF environments, respectively, and the subscript ND indicates a concentration in terms of number density. Canceling terms in Eq. (E.4) that are the same in the calibration and IDF environments, and using Eqs. (E.2) and (E.3), provides

$$N_{TND,IDF} = \left[\frac{P_C N_A}{R_u T_C 10^6} \right] \left[\frac{f_{B,C}(T_C)}{f_{B,IDF}(T_{IDF})} \right] CF^{LSF} C_{D,IDF}^{LSF}. \quad (E.5)$$

The first bracketed term ($\text{cm}^{-3}/\text{ppm}$) in Eq. (E.5) is a function of the calibration environment and effectively cancels a similar term which was integrated into the definition of CF^{LSF} (ppm/V), as evident from Eq. (E.3). The second bracketed term in Eq. (E.5) corrects the calculation for any variation in the Boltzmann fraction between the calibration and IDF environments due to temperature differences. As discussed in Chapter 6, variation in this term throughout the IDF may be minimized by proper selection of the excitation scheme.

Although Eq. (E.5) provides the ultimate reduction of the LSF data, it requires additional measurements of the temperature at the calibration point and throughout the IDF. However, these imposed requirements are actually unnecessary for this study. It will be shown in Section E.2 that the PLIF measurements depend on the two bracketed

terms in Eq. (E.5) in the same manner as do the LSF measurements. Since the same calibration flame and IDF were investigated in the LSF and PLIF experiments, these two bracketed terms provide the same multiplicative correction to the two fluorescence measurements. As the goal of this investigation is to assess the quantitative nature of PLIF imaging of [NO] via comparison to separate LSF measurements, such multiplicative corrections cancel in the comparison. Thus, they were not made for the current PLIF and LSF measurements.

The local NO concentration in ppm relative to the calibration flame temperature, $N_{T,RT}$ (relative ppm), may be calculated as

$$N_{T,RT} = CF^{LSF} C_D^{LSF}, \quad (E.6)$$

where the subscript RT has been added to indicate that the measured [NO] is relative in terms of temperature. With separate temperature and pressure measurements, this [NO] could be put on an absolute basis using Eqs. (E.5) and (E.6) to provide

$$N_{TND} = \left[\frac{P_C N_A}{R_u T_C 10^6} \right] \left[\frac{f_{B,C}(T_C)}{f_B(T)} \right] N_{T,RT}. \quad (E.7)$$

The final LSF measurements of NO in Chapter 7 were calculated using Eq. (E.6).

E.2 PLIF Calibration Procedure

The calibration factor for the PLIF measurements, CF^{PLIF} , was determined via the standard addition technique and the same calibration flames used for the LSF experiments, as described in Table E.1. Using this calibration flame with the appropriate doping level, images IM5 through IM11 were taken under the conditions described in Table D.1. The calibration images may be modeled as described by Eqs. (E.8a) through (E.8c), i.e.,

$$IM10 = calbkg = dnr1 + \eta_2 G R B_{10} \quad (E.8a)$$

$$IM11 = callib = dnr1 + \eta_2 G R (B_{10} + F_{11}^v \Upsilon_{l,11}^v) \quad (E.8b)$$

$$IM5 = cal00 = dnr1 + \eta_2 G R (B_{10} + F_5^v [\Upsilon_{l,11}^v + \Upsilon_5^v]) \quad (E.8c)$$

The spatial dependance in the above equations is understood to exist for all variables but is not explicitly indicated. Although Eq. (E.8c) is written for the undoped calibration flame, it also describes the images of the doped calibration flames, IM6 through IM9. In Eqs. (E.8), the following relationships hold : $\eta_2 = \eta_5 \dots \eta_{11}$, $B_{10} = B_5 \dots B_9 = B_{11}$, and $\Upsilon_{l,11}^v = \Upsilon_{l,5}^v \dots \Upsilon_{l,9}^v$. The background and laser-induced interferences in the calibration flame are different from those in the IDF or in the ambient-temperature nitrogen flow. However, the dark and readout noise is the same for the IDF and calibration images since they employed the same integration time. Images IM1, IM14, and IM15 are also pertinent to the calibration procedure, and are described by Eqs. (D.5a), (D.5e), and (D.5f), respectively.

The above images were processed as described in Appendix D (Section D.2) to produce five corrected images equivalent to the Ni2 distribution for the five calibration flames. However, the previous images Ni1 and Ni2 are referred to here as Ci1 and Ci2, respectively, to emphasize that these images pertain to the calibration procedure.

Calculation of Ci2 follows the development of Eqs. (D.7) and (D.9), i.e.,

$$Ci2_k = \frac{P_{L,14}}{P_{L,k}} \frac{Ci1_k}{LSD} = \frac{P_{L,14}}{P_{L,k}} \frac{1}{LSD} \left\{ IMk - \left[1 - \frac{P_{L,k}}{P_{L,11}} \right] IM10 - \frac{P_{L,k}}{P_{L,11}} IM11 \right\}, \quad (E.9)$$

where $k=5, 6, 7, 8$, and 9 for $D_R = 0, 20, 40, 60$, and 78 ppm, respectively, based on Table D.1. Using Eqs. (D.10), (E.2) and (E.9), one can show that

$$N_{Tppm,k} = \frac{R_u T 10^6}{P N_A} \frac{\Upsilon_{l,14}^v}{TR K^{LF} \Phi^{LN} f_B(T)} Ci2_k = CF^{PLIF} Ci2_k, \quad (E.10)$$

where CF^{PLIF} (ppm/counts) is the calibration factor for the PLIF experiments. As with CF^{LSF} , since the doping procedure is thermodynamically nonintrusive, CF^{PLIF} is a constant for the five calibration flames. Moreover, since the image analysis which produces $Ci2$ corrects for spatial variations in R , G , and F^v , CF^{PLIF} is independent of spatial location. Hence, a single value of CF^{PLIF} applies to each pixel of the image; more importantly, CF^{PLIF} may be determined at any convenient position within the image.

From Eq. (E.10), it is clear that CF^{PLIF} is the slope of the linear fit to the $N_{T,ppm}(D_p)$ vs. $Ci2(D_p)$ data. As discussed in Section E.1, CF^{PLIF} may be equivalently determined as the slope of the D_p vs. $Ci2(D_p)$ data. Since a single CF^{PLIF} applies throughout the image, it was determined based on the average value, $Ci2_{BIN}(D_p)$, of an 18-pixel-by-18-pixel region (~ 1.06 mm square) centered at $(y, r) = (4 \text{ mm}, 8 \text{ mm})$. In other words, the calibration factor was experimentally determined from the slope of the least-squares fit to the D_p vs. $Ci2_{BIN}(D_p)$ data. The resulting fit had a correlation coefficient of 0.991, and indicated that $CF^{PLIF} = 103.6$ ppm/counts for Run C of the PLIF measurements of [NO].

Using Eq. (D.10), the necessary relationship between the PLIF signal in the calibration flame and that in the IDF may be determined to be

$$\frac{N_{TND,IDF}}{N_{TND,C}} = \left[\frac{\Upsilon_{I,14}^v}{TR K^{LIF}} \right]_{IDF} \left[\frac{TR K^{LIF}}{\Upsilon_{I,14}^v} \right]_C \frac{\Phi_C^{LIN}}{\Phi_{IDF}^{LIN}} \frac{f_{B,C}(T_C)}{f_{B,IDF}(T_{IDF})} \frac{Ni2}{Ci2}, \quad (E.11)$$

where subscripts have been added to indicate values in the calibration flame and the IDF. Canceling terms in Eq. (E.11) that are the same in the calibration and IDF environments, and using Eqs. (E.2) and (E.10) produces

$$N_{TND,IDF} = \left[\frac{P_C N_A}{R_u T_C 10^6} \right] \left[\frac{f_{B,C}(T_C)}{f_{B,IDF}(T_{IDF})} \right] \left[\frac{\Phi_C^{LIN}}{\Phi_{IDF}^{LIN}} \right] CF^{PLIF} Ni2. \quad (E.12)$$

The first two bracketed terms in Eq. (E.12) are the same as encountered in Eq. (E.5) for the LSF measurements. Hence, both the LSF and PLIF measurements have equivalent

dependance on these two terms. The third bracketed term in Eq. (E.11) is a ratio of the fluorescence yields, and accounts for the local variation in the electronic quenching rate coefficient relative to the calibration flame. The electronic quenching rate coefficient may be modeled using $\sum N_i \sigma_i v_i$, where N_i (cm^{-3}) and σ_i (cm^2) are the number density and collisional cross-section, respectively, of the i^{th} collision partner and v_i (cm/s) is the relative velocity between the probe molecule and the i^{th} collision partner (Eckbreth, 1988). Thus, the electronic quenching rate coefficient depends on temperature through the number density via the ideal gas law and also through the relative velocity via the Maxwell-Boltzmann velocity distribution. Equation (E.12) demonstrates the basis for selection of an excitation line whose temperature-induced variation in Boltzmann fraction approximately cancels that due to quenching, as discussed in Chapter 3. However, such a selection was not used for the PLIF experiments of this investigation.

As with the LSF measurements, the PLIF measured [NO] in the IDF in ppm relative to the calibration flame temperature and quenching environment, $N_{T,RT,RQ}$ (relative ppm), may be calculated as

$$N_{T,RT,RQ} = CF^{PLIF} Ni2 , \quad (\text{E.13})$$

where the subscripts RT and RQ have been added to indicate the relative value with respect to both temperature and quenching environment. With separate measurements of temperature, pressure and electronic quenching rate coefficient, this relative [NO] could be put on an absolute basis by using Eqs. (E.12) and (E.13) to provide

$$N_{TND} = \left[\frac{P_C N_A}{R_u T_C 10^6} \right] \left[\frac{f_{B,C}(T_C)}{f_B(T)} \right] \left[\frac{\Phi_C^{LIN}}{\Phi^{LIN}} \right] N_{T,RT,RQ} . \quad (\text{E.14})$$

The final PLIF measurements of NO concentration in Chapter 7 were calculated using Eq. (E.13). Based on Eqs. (E.7) and (E.14), it is clear that the LSF and PLIF results in terms of $N_{T,RT}$ and $N_{T,RT,RQ}$, respectively, will differ only through local variations in the electronic quenching rate coefficient relative to the calibration flame.

E.3 Alternate Calibration Procedure

The combined absorption/fluorescence technique uses spatially resolved fluorescence measurements to derive the spatial variation in the number density of the probed species, which may then be put on an absolute basis using absorption measurements. Because this method is based on Beer's law, the absorption measurement may not be made under saturated conditions where nonlinear absorption may be significant (Demtroder, 1988). Although this method has been used for point measurements (Lucht et al., 1985; Stepowski and Garo, 1985), it is particularly suited to imaging (1D or 2D) experiments where the spatial variation in the fluorescence signal along the laser (absorption integration) path is inherently resolved. This technique could be used alone or in conjunction with the standard addition method of Section 5.2. The technique has been used in OH imaging experiments (1D: Hertz and Alden, 1987; 2D: Dyer and Crosley, 1982). Hertz and Alden (1987) give a very thorough description of this calibration technique and present a method that accounts for attenuation of the laser spectral irradiance along the integration path.

To assess the feasibility of the combined absorption/fluorescence calibration technique for quantitative [NO] measurements across an IDF-front, absorption calculations were made, with either concentration or absorption as the independent variable. Typical values for the expected experimental and spectroscopic variables were used ($\Delta\nu_L=0.15\text{ cm}^{-1}$, $\Gamma_{uL}=0.26$, $T=1800\text{ K}$, $P=1\text{ atm}$, $f_B=0.01$; $Q_{22}(26.5)$: $B_u=310.859\text{ cm}^2\text{cm}^{-1}/\text{J}$, $\nu=44330.19\text{ cm}^{-1}$). The first calculation involved determining the flat concentration field over a 2.5 cm integration path required to give 10% absorption of the laser irradiance. These values were chosen because 2.5 cm is a typical laboratory burner dimension and 10% absorption should be resolvable using photodiode monitoring of the laser irradiance before and after the absorbing environment. For 10% absorption, the required flat field concentration was calculated to be approximately 2150 ppm. This value is orders of magnitude greater than typical laboratory data (e.g., chemiluminescent measurements for the JQC indicated a maximum NO concentration of approximately 110 ppm). Moreover, since the immediate interest is to investigate an IDF-front, the NO field will not be flat. A second calculation indicated that given a 10 ppm flat [NO] field over a

2.5 cm integration path, the resulting absorption would be approximately 0.05%. Based on these two calculations, it appears that a combined absorption/fluorescence calibration technique would not be feasible for [NO] measurements. However, because of its applicability to imaging work, the technique should always be considered for probing other molecules of interest.

E.4 PLIF NO Calibration Program

Calibration of the PLIF images was performed using run-specific programs which contained hard inputs of the appropriate image filenames, image-specific file names for the average laser irradiance, and output file names. The program used for determining the calibration factor for Run C of the PLIF measurements of [NO] in an AIDF, IMACALc, is provided below. Moreover, the subroutine, LIN_FITWPP.PRO, which performs the actual least-squares linear fit to the calibration data follows the program IMACALc. The calibration factor determined by this program was used in the image analysis program IMACORR4c contained in Appendix D. The calibration factor was determined from the slope of the least-squares-fit to the average value of the corrected Ci2 data in an 18-pixel square region (1.06-mm square) centered at (y, r) = (4 mm, 8 mm).

```

;*****
;IMACALc
;Program to determine the calibration factor for the PLIF images. This calibration factor
;is used to analyze the PLIF images in program IMACORR4c
;
;The program operates on scrambled '____.spe' files from the Princeton Instruments
;ST-130 imaging system.
;
; 5-8-95 wpp jr.
; 5-9-95,
;
;FIELD NOTATION:
;   cal00:      total image of calibration flame (D=0)
;   cal20:      total image of calibration flame (D=20)
;   cal40:      total image of calibration flame (D=40)
;   cal60:      total image of calibration flame (D=60)
;   cal78:      total image of calibration flame (D=78)

```

```

;      calbkg:      scattering background in cal. flame
;      callib:      laser-induced bkg in cal. flame (D=0)
;      snu2:        sheet nonuniformity 2 (different filters)
;      snu2bkg:     background for snu2
;
;POWER NOTATION:
;      P:  average laser power
;
;      P5:  ALP for cal00
;      P6:  ALP for cal20
;      P7:  ALP for cal40
;      P8:  ALP for cal60
;      P9:  ALP for cal78
;      P11: ALP for callib
;      P14: ALP for snu2
;
;SUFFIX NOTATION:
;      a: averaged
;      m: masked
;      s: after background subtraction
;      n: after normalization
;      F: directly operated on by high-pass filter
;      f: indirectly operated on by high-pass filter
;      d: after subtraction of baseline primary combustion field
;
;*****
;
;set plot to X windows
;
set_plot,'X'
;
; If an io error is encountered then execution should resume at the label "end_of_file".
; We need to do this because when the file is read in we may reach the end too soon,
; causing an error but we still want to execute.
;
on_ioerror,end_of_file
;
;READ IN THE SCRAMBLED *.spe P.I. IMAGE FILES
;
openr,7,'/home/hemingway/a/partridg/images/c14.spe' ;snu2
openr,8,'/home/hemingway/a/partridg/images/c15.spe' ;snu2bkg
openr,10,'/home/hemingway/a/partridg/images/c5.spe' ;cal00
openr,11,'/home/hemingway/a/partridg/images/c6.spe' ;cal20
openr,12,'/home/hemingway/a/partridg/images/c7.spe' ;cal40

```

```

openr,13,'/home/hemingway/a/partridg/images/c8.spe'      ;cal60
openr,14,'/home/hemingway/a/partridg/images/c9.spe'      ;cal78
openr,15,'/home/hemingway/a/partridg/images/c10.spe'     ;calbkg
openr,16,'/home/hemingway/a/partridg/images/c11.spe'     ;callib
;
;READ IN THE AVERAGE LASER POWER VALUES
;
P=fltarr(16)
status=dc_read_free('/home/hemingway/a/partridg/datfiles/laserpc.dat', $
    P,/col,get_columns=[2])
P5=P(4)
P6=P(5)
P7=P(6)
P8=P(7)
P9=P(8)
P11=P(10)
P14=P(13)
;
;DECLARE IMAGE ARRAYS
; Images are 578 x 384 pixels of 16 bits each.
;
snu2=intarr(384,578)
snu2bkg=intarr(384,578)
cal00=intarr(384,578)
cal20=intarr(384,578)
cal40=intarr(384,578)
cal60=intarr(384,578)
cal78=intarr(384,578)
calbkg=intarr(384,578)
callib=intarr(384,578)
;
;DECLARE HEADER ARRAYS
; declare an array for discarded header info P.I. uses 4100 longwords of header info.
;
hdr7=lonarr(1025)
hdr8=lonarr(1025)
hdr10=lonarr(1025)
hdr11=lonarr(1025)
hdr12=lonarr(1025)
hdr13=lonarr(1025)
hdr14=lonarr(1025)
hdr15=lonarr(1025)
hdr16=lonarr(1025)
;

```

```

; READ IN HEADER INFORMATION
;
readu,7,hdr7
readu,8,hdr8
readu,10,hdr10
readu,11,hdr11
readu,12,hdr12
readu,13,hdr13
readu,14,hdr14
readu,15,hdr15
readu,16,hdr16
;
; READ IN IMAGE DATA AND STORE IN variable name
;
readu,7,snu2
readu,8,snu2bkg
readu,10,cal00
readu,11,cal20
readu,12,cal40
readu,13,cal60
readu,14,cal78
readu,15,calbkg
readu,16,callib
end_of_file:
;
;DOS TO UNIX CONVERSION
;Must swap bytes when data is moved from a little-endian machine such as an IBM PC
;to a big-endian machine such as a Sun. The bytes are swapped by twos, since each
;pixel contains two bytes (16 bits) of data.
;
byteorder,snu2,sswap=1
byteorder,snu2bkg,sswap=1
byteorder,cal00,sswap=1
byteorder,cal20,sswap=1
byteorder,cal40,sswap=1
byteorder,cal60,sswap=1
byteorder,cal78,sswap=1
byteorder,calbkg,sswap=1
byteorder,callib,sswap=1
;
;TRANSPOSE IMAGE AND THEN ROTATE 270 DEGREES
;
snu2=rotate(snu2,6)
snu2bkg=rotate(snu2bkg,6)

```

```

cal00=rotate(cal00,6)
cal20=rotate(cal20,6)
cal40=rotate(cal40,6)
cal60=rotate(cal60,6)
cal78=rotate(cal78,6)
calbkg=rotate(calbkg,6)
callib=rotate(callib,6)
;
;SET PARAMETERS FOR MASKING THE IMAGES
;
mxs=29           ;beginning mask x value
mxe=577          ;ending mask x pixel value
mys=13           ;beginning mask y pixel value
mye=255          ;ending mask y pixel value
xsz=mxe-mxs+1    ;size of masked image in x direction
ysz=mye-mys+1    ;size of masked image in y direction
;
;SETUP OFFSET FOR HIGH-PASS FILTER
;set all pixels with value less than or equal to the OFFSET to the OFFSET to eliminate
;the problem with division by zero.
;
OFFSET=1
;
;CALCULATE Ci1:
;
Ci100=cal00-(1-(P5/P11))*calbkg-(P5/P11)*callib
Ci120=cal20-(1-(P6/P11))*calbkg-(P6/P11)*callib
Ci140=cal40-(1-(P7/P11))*calbkg-(P7/P11)*callib
Ci160=cal60-(1-(P8/P11))*calbkg-(P8/P11)*callib
Ci178=cal78-(1-(P9/P11))*calbkg-(P9/P11)*callib
;
;APPLY THE HIGH-PASS FILTER
;af=(a GT OFFSET)*a + (a LE OFFSET)*OFFSET
;      (a GT OFFSET) =1 if aij>OFFSET
;      (a GT OFFSET) =0 if aij<=OFFSET
;
;      (a LE OFFSET) =1 if aij<=OFFSET
;      (a LE OFFSET) =0 if aij>OFFSET
;
Ci100F=(Ci100 GT OFFSET)*Ci100 + (Ci100 LE OFFSET)*OFFSET
Ci120F=(Ci120 GT OFFSET)*Ci120 + (Ci120 LE OFFSET)*OFFSET
Ci140F=(Ci140 GT OFFSET)*Ci140 + (Ci140 LE OFFSET)*OFFSET
Ci160F=(Ci160 GT OFFSET)*Ci160 + (Ci160 LE OFFSET)*OFFSET
Ci178F=(Ci178 GT OFFSET)*Ci178 + (Ci178 LE OFFSET)*OFFSET

```



```

;
;SHEET NONUNIFORMITY CORRECTION
;
LSD=snu2-snu2bkg          ;Laser sheet distribution I
;
;APPLY THE HIGH-PASS FILTER
;
LSDF=(LSD GT OFFSET)*LSD + (LSD LE OFFSET)*OFFSET
;
;COMPLETE CALCULATION (i.e., calculate Ci2)
;
Ci200f=P14*Ci100F/(P5*LSDF)
Ci220f=P14*Ci120F/(P6*LSDF)
Ci240f=P14*Ci140F/(P7*LSDF)
Ci260f=P14*Ci160F/(P8*LSDF)
Ci278f=P14*Ci178F/(P9*LSDF)
;
;APPLY MASK TO THE IMAGES
;goto,skip0      ;skip masking the images
;
Ci200fm=Ci200f(mx:mxs,my:mys)      ;masked image Ci200f
Ci220fm=Ci220f(mx:mxs,my:mys)      ;masked image Ci220f
Ci240fm=Ci240f(mx:mxs,my:mys)      ;masked image Ci240f
Ci260fm=Ci260f(mx:mxs,my:mys)      ;masked image Ci260f
Ci278fm=Ci278f(mx:mxs,my:mys)      ;masked image Ci278f
skip0:
;
;DETERMINE THE AVERAGE VALUE OF THE IMAGES
;IN THE CALIBRATION REGION
;1 : 0.5mm x 0.5mm (9 pixel square) region
;2 : 1.0555mm x 1.0555mm (18 pixel square) region
;p : +z region
;n : -z region
;
AP2=fltarr(5)
AP2(0)=AVG(Ci200fm(409:427,22:40))
AP2(1)=AVG(Ci220fm(409:427,22:40))
AP2(2)=AVG(Ci240fm(409:427,22:40))
AP2(3)=AVG(Ci260fm(409:427,22:40))
AP2(4)=AVG(Ci278fm(409:427,22:40))
;
;SETUP TO DO THE REGRESSION
;
y=[0.0,19.6,39.1,58.7,76.3]

```

```

;
;DO THE REGRESSION
;
TCALP2=LIN_FITWPP(AP2,y,yfp2,sigyp2,sigyxp2,rp2)
;
;DISPLAY THE FINAL IMAGES
;goto,skip1    ;skip making images
;
;make the image widow xszXysz Sun-pixels big
window,xsize=xsz,ysize=ysz    ;masked image
tvsc1,Ci278fm
skip1:
;
;REBIN THE IMAGE FILES
;rebinning performs a bilinear interpolation to create less dense matrices.
;goto,skip2    ;skip rebinning and making surface plots
;
Ci278fmr2=rebin(Ci278fm,xsz/9,ysz/9)
;
;DISPLAY IMAGE SURFACE PLOT
;
window,2,xsize=578,ysize=384
surface,Ci278fmr2,skirt=0,ax=60,az=40    ;surface of corrected image
skip2:
;
.*****
;WRITE THE CALIBRATION DATA TO A FILE
;goto,skip3    ;skip writing cal. data
;
status=dc_write_free('/home/hemingway/a/partridg/datout/ctcalp2.dat', $
    AP2,y,TCALP2,yfp2,sigyp2,sigyxp2,rp2,/col)
skip3:
;
.*****
;CLOSE FILES
;
close,7
close,8
close,10
close,11
close,12
close,13
close,14
close,15

```

```
close,16
end
```

```
*****
;
;
;SUBROUTINES:
;
;*****
;LIN_FITWPP.PRO
;is a modification of POLY_FIT.PRO to give the correlation coeff. Of the fit.
;modified by w.p.partridge,jr. 5-9-95
;code follows methods described by J.P.Holman in Experimental Methods for
;Engineers p.87.
;
FUNCTION LIN_FITWPP,X,Y,YFIT,SIGMA Y,SIGMA YX,R
;
;NAME:
;    LIN_FITWPP
;
;PURPOSE:
;    Least square polynomial fit with optional error estimates.
;    Old version, uses matrix inversion. Newer version is SVDFIT
;    which uses SVD and is more flexible but slower.
;
;CALLING SEQUENCE:
;    COEFF = POLY_FIT(X,Y [,YFIT,SIGMA Y,SIGMA YX,R] )
;
;INPUTS:
;    X = independent variable vector.
;    Y = dependent variable vector, should be same length as x.
;    NDEGREE = degree of polynomial to fit (1 for linear fit)
;
;OUTPUTS:
;    Function result= Coefficient vector, length NDEGREE+1.
;OPTIONAL PARAMETERS:
;    YFIT = Vector of calculated Y's. Has error + or - YBAND.
;    SIGMAy = Standard deviation in Y units.
;    SIGMAyx = Standard deviation in Y units.
;    R = Correlation coefficients.
;
ON_ERROR,2                ;return to caller if error
XX = X*1.                 ;be sure x is floating or double
N = N_ELEMENTS(X)         ;size
IF N NE N_ELEMENTS(Y) THEN $
```

```

        message,'X and Y must have same # of elements'
;
;SET SO THAT WILL ONLY MAKE A LINEAR FIT
;
NDEGREE = 1

;
M = NDEGREE + 1          ;# of elements in coeff vec.
;
A = DBLARR(M,M)          ;coeff matrix
B = DBLARR(M)            ;will contain sum y * x^j
Z = DBLARR(N)+1.
;
A(0,0) = N
B(0) = TOTAL(Y)
;
FOR P = 1,2*NDEGREE DO BEGIN ;POWER LOOP.
    Z=Z*XX                ;z is now x^p
    IF P LT M THEN B(P) = TOTAL(Y*Z)    ;b is sum y*x^j
    SUM = TOTAL(Z)
    FOR J = 0 > (P-NDEGREE), NDEGREE < P DO A(J,P-J) = SUM
END                        ;end of p loop.
;
A = INVERT(A)             ;INVERT MATRIX.
;
;IF A IS MULTIPLIED BY SIGMAy2, IT IS THE
;CORRELATION MATRIX.
;
C = float(b) # a          ;Get coefficients
;
;*****
IF (N_PARAMS(0) LE 2) THEN RETURN,C          ;exit if no fit predictions.
    YFIT = FLTARR(N)+C(0)                    ;init yfit
    FOR K = 1,NDEGREE DO YFIT = YFIT + C(K)*(XX^K)    ;form yfit.
;
;*****
IF (N_PARAMS(0) LE 3) THEN RETURN,C          ;exit if no error estimates.
    YM=TOTAL(Y)/N                            ;compute mean value of y
    SIGMAY = TOTAL((Y-YM) ^ 2) / (N-1)        ;compute sigmay
    SIGMAY = SQRT(SIGMAY)
;
;*****
    SIGMAYX = TOTAL((YFIT-Y) ^ 2) / (N-M)      ;compute sigmayx
    SIGMAYX = SQRT(SIGMAYX)

```

```
;
;*****
R=1-(SIGMAYX^2)/(SIGMAY^2)
R=SQRT(R)

RETURN,C
END
```

Appendix F - Uncertainty Analysis

Both the LSF and PLIF measurements have uncertainties which must be quantified in order to assess the quantitative nature of the resulting [NO] measurements. All fluorescence measurements have an uncertainty associated with their repeatability. This precision varies with local [NO] and, hence, will be a function of location within the IDF. Moreover, it is this precision which dictates the detection limit of the LSF and PLIF measurements. The process of converting the measured fluorescence signal to [NO], via application of the CF, introduces an additional uncertainty due to that of the CF. In fact, the CF has both accuracy and precision components to its uncertainty. The precision of the CF reflects the repeatability of the CF. This is influenced by experiment-to-experiment variations in the calibration flame as well as the measurement precision. The accuracy of the CF is influenced by that of the standard NO gas and the gas metering system, as well as a systematic uncertainty due to the finite destruction of doped NO in the calibration flame. The accuracy of the metering system is related to fluctuations in the rotameter settings about the optimal settings throughout a given calibration process. These individual uncertainties may be combined via the method of propagation of errors to determine the cumulative uncertainty in the final [NO] measurement (Taylor, 1982).

This appendix evaluates the uncertainty in the LSF and PLIF measurements of NO concentration. Common uncertainty contributions due to the accuracy of the calibration factor are evaluated in Section F.1. The cumulative uncertainties in the LSF and PLIF measurements of [NO] are then determined in Sections F.2 and F.3, respectively. All uncertainties are based on a 95% confidence interval.

F.1 Common Measurement Uncertainties

The contribution of the accuracy of the calibration procedure to the final measurement uncertainty is common to both the LSF and PLIF experiments. The doped [NO] in the calibration flame may be expressed using Eq. (E.1) as

$$D_P = \frac{n_R}{n_P} D_R L = \frac{n_R}{n_P} \frac{\dot{V}_{NO/N_2}}{\dot{V}_T} C_B L = \frac{n_R}{n_P} \dot{V}_R C_B L, \quad (F.1)$$

where L represents a constant fraction of NO that is destroyed in the calibration flame. In Eq. (F.1), the total molar ratio (n_R/n_P) is assumed to be known exactly based on a completely reacted calibration flame. The accuracy of $\dot{V}_R$ is dictated by that of the C_2H_6 , O_2 , N_2 , and NO/N_2 rotameter settings, and the accuracy of C_B is dictated by the manufacturer's calibration. The individual accuracies of $\dot{V}_R$, C_B , and L are developed below and then propagated through a least-squares-fitting routine to determine the cumulative accuracy of the CF.

From Eq. (F.1), it is clear that the relative uncertainty in $\dot{V}_R$, $\epsilon \dot{V}_R$, is equal to the quadrature sum of the relative uncertainties in $\dot{V}_{NO/N_2}$ and $\dot{V}_T$, i.e.,

$$\epsilon \dot{V}_R = \left[\left(\epsilon \dot{V}_{NO/N_2} \right)^2 + \left(\epsilon \dot{V}_T \right)^2 \right]^{0.5}. \quad (F.2)$$

However, in order to implement Eq. (F.2), the relative uncertainty in the total volumetric flow rate must be determined. Since the total volumetric flow rate is simply the sum of those of the individual gases, its absolute uncertainty, $\delta \dot{V}_T$, is equal to the quadrature sum of the absolute uncertainties of the component gases, i.e.,

$$\delta \dot{V}_T = \left[\left(\delta \dot{V}_{C_2H_6} \right)^2 + \left(\delta \dot{V}_{O_2} \right)^2 + \left(\delta \dot{V}_{N_2} \right)^2 + \left(\delta \dot{V}_{NO/N_2} \right)^2 \right]^{0.5}. \quad (F.3)$$

Hence, with the absolute accuracy of the individual volumetric flow rates known, $\delta \dot{V}_T$ may be calculated from Eq. (F.3); the relative uncertainty in the total flow rate may then be determined using the relationship $\epsilon \dot{V}_T = \delta \dot{V}_T / \dot{V}_T$, so that $\epsilon \dot{V}_R$ may be calculated using Eq. (F.2) and $\epsilon \dot{V}_{NO/N_2} = \delta \dot{V}_{NO/N_2} / \dot{V}_{NO/N_2}$.

Fluctuations in the volumetric flow rates of the component gases about the desired rotameter settings clearly affected the accuracy of the NO doping. It was observed that the fluctuations were no greater than one scale reading for all gases and calibration flames. Hence, for each gas and calibration flame, the absolute uncertainty in the volumetric flow

rate of a specific gas was calculated based on twice the standard deviation of the mean of three volumetric flow rates : the corresponding optimal rotameter setting, the upper and lower fluctuation limits (i.e., the optimal rotameter setting ± 1 rotameter scale reading). The resulting absolute uncertainties in the component gases are tabulated in Table F.1 as a function of the calibration flame. Table F.1 also contains the calibration-specific results for $\delta \dot{V}_T$, as calculated from Eq. (F.3), and $\epsilon \dot{V}_R$, as calculated from Eq. (F.2). These results demonstrate that the relative uncertainty in the volume flow rate ratio is a function of the NO doping level or the calibration flame.

Based on Eq. (F.1), the relative uncertainty in D_p , ϵD_p , may be determined by the quadrature sum of that in $\dot{V}_R$, C_B , and L , i.e.,

$$\epsilon D_p = \left[(\epsilon \dot{V}_R)^2 + (\epsilon C_B)^2 + (\epsilon L)^2 \right]^{0.5} . \quad (F.4)$$

The relative uncertainty in C_B was taken to be 4% based on manufacturer's specifications (Airco, 1993), and that due to L was taken to be 5% based on previous modeling (Reisel, 1994). Table F.2 contains the component and cumulative relative uncertainties for each doping level as calculated via Eq. (F.4) from the data in Table F.1. In Table F.2, D_p^* is equal to D_p with a constant offset of 0.1 ppm, and is required for the least-squares-fitting routine as described below. Moreover, Table F.2 provides the absolute uncertainty in terms of both D_p and D_p^* .

The uncertainties in the accuracy of D_p may be propagated through a least-squares-fitting routine (Bevington and Robinson, 1992) to determine their influence on the uncertainty in the accuracy of the calibration factor. Recall from Section E.1 that determination of the calibration factor is not influenced by a constant offset. Hence, CF^{LSF} and CF^{PLIF} are not influenced by using D_p^* rather than D_p . Moreover, the absolute uncertainties δD_p^* and δD_p are equivalent to one decimal place. However, the error propagation routine requires some finite but small value at the lowest doping condition. This is the basis for using D_p^* in place of D_p for evaluating the accuracy of the calibration factor.

Table F.1 Uncertainties in the determination of $\dot{V}_R$.

D_p	Absolute Uncertainties, δV_i (SLPM)					Relative Uncertainties, ϵX		
(ppm)	C_2H_6	O_2	N_2	NO/N_2	T	V_{NO/N_2}	V_T	VR
0	0.0039	0.0081	0.0546	0.0000	0.0554	0.0000	0.0138	0.0138
19.6	0.0039	0.0081	0.0549	0.0087	0.0563	0.0341	0.0141	0.0369
39.1	0.0039	0.0081	0.0553	0.0184	0.0590	0.0361	0.0147	0.0390
58.7	0.0039	0.0081	0.0558	0.0192	0.0597	0.0251	0.0149	0.0292
76.3	0.0039	0.0081	0.0565	0.0136	0.0588	0.0136	0.0147	0.0201

Table F.2 Accuracies in the determination of D_p and D_p^* .

D_p	D_p^*	ϵX				δX (ppm)	
(ppm)	(ppm)	VR	C_B	L	D_p	D_p	D_p^*
0	0.1	0.0138	0.0400	0.0500	0.0655	0.0000	0.0066
19.6	19.7	0.0369	0.0400	0.0500	0.0739	1.4485	1.4559
39.1	39.2	0.0390	0.0400	0.0500	0.0750	2.9314	2.9389
58.7	58.8	0.0292	0.0400	0.0500	0.0704	4.1314	4.1385
76.3	76.4	0.0201	0.0400	0.0500	0.0671	5.1196	5.1263

The results for a given LSF and PLIF experiment (Run B for LSF; Run C for PLIF) are tabulated in Table F.3, along with the results of the accuracy propagation for the calibration factor. These calibration factor accuracies were determined by using equations which describe the error in the least-squares fitting procedure (Bevington and Robinson, 1992), i.e.,

$$\delta CF = \left[\frac{1}{\Delta} \sum \frac{1}{\delta D_{Pj}^{*2}} \right], \quad (F.5)$$

and

$$\Delta = \left(\sum \frac{1}{\delta D_{Pj}^{*2}} \right) \left(\sum \frac{C_j^2}{\delta D_{Pj}^{*2}} \right) + \left(\sum \frac{C_j}{\delta D_{Pj}^{*2}} \right)^2, \quad (F.6)$$

where C represents C_D^{LSF} and C_{i2} for the LSF and PLIF measurements, respectively, and j indexes the values of C with the corresponding values of D_p^* (i.e., 0.1, 19.7, 39.2, 58.8, and 76.4). The calibration factors are in units of ppm/V for the LSF experiments and ppm/counts for the PLIF experiments as discussed in Sections E.1 and E.2, respectively. Table F.3 indicates that the cumulative accuracy contribution to the uncertainty in the calibration factor is approximately 3.7% and 3.9% for these specific LSF and PLIF experiments (i.e., Run B for LSF, and Run C for PLIF), respectively. The average value of this uncertainty for all of the LSF and PLIF runs was approximately 3.6% and 3.8%, respectively.

F.2 LSF Measurement Uncertainty

As discussed in Section D.1, C_D^{LSF} was determined as the difference in the measured signal and an elevation-specific background; this background was determined as the average of two background measurements taken at a given elevation. Hence, the absolute uncertainty in C_D^{LSF} may be determined as

Table F.3 Accuracies in the determination of the LSF and PLIF calibration factors.

D_p (ppm)	D_p^* (ppm)	δD_p^* (ppm)	C_D^{LSF} (V)	Ci2 (counts)
0	0.1	0.0066	-0.0329	0.0887
19.6	19.7	1.4559	-0.0834	0.2488
39.1	39.2	2.9389	-0.1414	0.4244
58.7	58.8	4.1385	-0.2189	0.5833
76.3	76.4	5.1263	-0.2380	0.8370

CF :	-344.31	103.56
ϵCF (%) :	3.69	3.92

$$\delta C_D^{LSF} = \left[\left(\delta C_D^{LSF} \right)_{UNC}^2 + \left(\delta C_D^{LSF} \right)_{BKG}^2 \right]^{0.5}, \quad (F.7)$$

where

$$\left(\delta C_D^{LSF} \right)_{BKG} = \frac{1}{2} \left[\left(\delta C_D^{LSF} \right)_{BKG1}^2 + \left(\delta C_D^{LSF} \right)_{BKG2}^2 \right]^{0.5}, \quad (F.8)$$

and the subscripts UNC, BKG, BKG1 and BKG2 have been added to indicate the uncorrected, averaged background, initial background, and final background measurements, respectively. All LSF measurements were determined as the average of 400 signal events. Hence, the uncertainty in each LSF measurement was taken as twice the standard deviation of the mean of the corresponding 400 single-shot measurements. Based on this measurement uncertainty alone (i.e., not accounting for the uncertainty in the CF) and for the LSF calibration at $D_p=0$, the natural [NO] was calculated to be 11.3 ppm for Run B, with an absolute uncertainty of 1.6 ppm which corresponds to a signal-to-noise ratio (SNR) of 7.3. The other D_p calibration flames were observed to have larger SNRs (i.e., $SNR \approx 12$ to 18). These values of the SNR provide an indication of the contribution of the precision of the individual LSF measurements to the final measurement uncertainty at this specific [NO] of ~11.3 ppm.

To determine the precision of the calibration factor for the LSF measurements, the LSF calibration procedure described in Section E.1 was repeated eight times. These multiple calibrations were performed using each of two standard NO mixtures (i.e., $C_B=313$ ppm NO in N_2 from Airco, and $C_B=392$ ppm NO in N_2 from Matheson). The precision of the CF^{LSF} was determined as twice the sample standard deviation of the individual CF^{LSF} values. Using the two extreme CF^{LSF} values to determine the worst case precision, the precision of the CF^{LSF} was determined to be approximately 20%. This was combined with the uncertainty contributed by the accuracy of the CF^{LSF} via quadrature summation (Taylor, 1982), i.e.,

$$\epsilon_{CF}^{LSF} = \left[(\epsilon_{CF}^{LSF})_{PRE}^2 + (\epsilon_{CF}^{LSF})_{ACC}^2 \right]^{0.5}, \quad (F.9)$$

where the subscripts PRE and ACC have been added to indicate the uncertainty contributions due to precision and accuracy, respectively. Hence, the 3.7% accuracy calculated in Section F.1, when combined with the 20% precision, provides a cumulative uncertainty in the LSF calibration factor of 20.3%.

Based on Eq. (E.6), the cumulative uncertainty in the LSF measurement of relative [NO] is

$$\epsilon_{N_{T,RT}} = \left[(\epsilon_{CF}^{LSF})^2 + (\epsilon_{C_D}^{LSF})^2 \right]^{0.5}. \quad (F.10)$$

Using Eqs. (F.7), (F.8), and (F.10) with $\epsilon_{CF}^{LSF}=20.3\%$, the uncertainty in the 310 LSF measurements of $N_{T,RT}$ in the AIDF can be calculated. The resulting relative and absolute uncertainties are plotted versus $N_{T,RT}$ in Fig. F.1. From the relative uncertainty plot of Fig. F.1, it is apparent that the majority of the data points produce signal levels of 20 to 60 relative ppm with a relative uncertainty of $\sim 22\%$. This corresponds to a SNR of ~ 4.5 . The increasing relative uncertainty with decreasing measured [NO] in Fig. F.1 is characteristic of a measurement approaching its detection limit. The LSF detection limit was determined from the $\delta N_{T,RT}$ vs. $N_{T,RT}$ data of Fig. F.1. The least-squares fit to this data was calculated to be $\delta N_{T,RT}=0.206(N_{T,RT})+0.464$. Since the detection limit is defined as the point where the SNR=1, it may be identified on Fig. F.1 as the point where $\delta N_{T,RT}=N_{T,RT}$ (i.e., where the SNR=1 curve crosses the best-fit curve). From this definition, it is clear that the relative uncertainty is 100% at the detection limit. Using the absolute uncertainty data of Fig. F.1, the detection limit of the LSF measurements was determined to be $N_{T,RT}\approx 0.6$ ppm. This value is in good agreement with values previously reported in the literature for LSF measurements of [NO] at atmospheric pressure (Reisel et al., 1993).

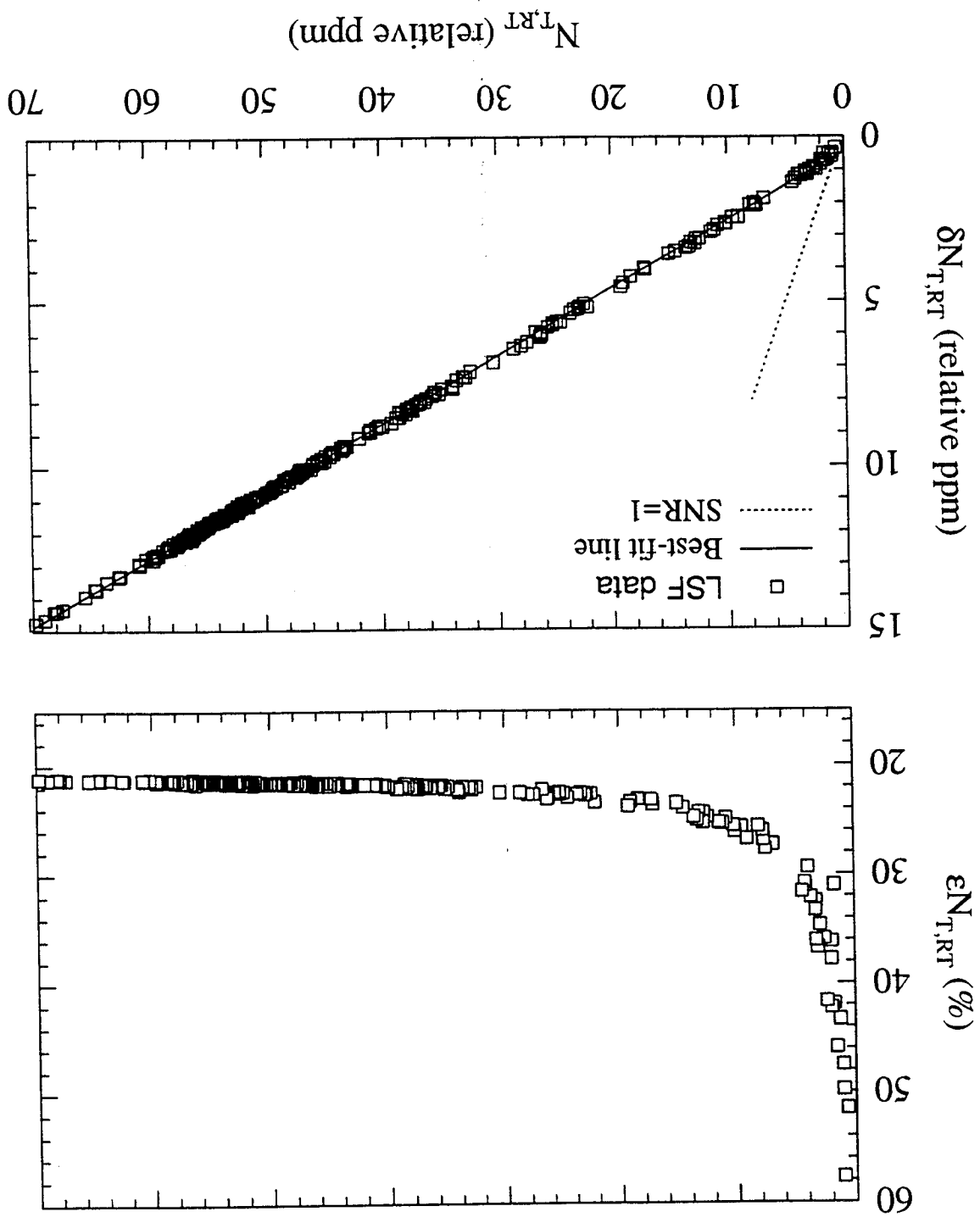


Figure F.1 Uncertainty in the $N_{T,RT}$ LSF measurements of [NO] in the AIDF.

F.3 PLIF Measurement Uncertainty

Evaluation of the uncertainty in the PLIF measurements was complicated by the use of on-chip integration. Recall that on-chip integration consists of integrating multiple PLIF events between CCD readouts. This method was used to enhance the measurement SNR by reducing the readout noise. In fact, integration of 1800 images on chip (as indicated by $t_{\text{exp}}=180.05$ s in Table D.1), reduces the readout noise by a factor of 1/1800 as compared to reading out the images separately and then summing via post processing. Unfortunately, as a result of this on-chip integration, information concerning the shot-to-shot fluctuations in the individual PLIF images is lost. Hence, the precision of the PLIF measurements could not be determined from the standard deviation of the mean of the individual signals as with the LSF measurements.

The precision of the PLIF measurements was based on comparing the results of five PLIF runs (labeled Runs C, D, E, F, and G) on a point-by-point basis. The local precision of any given PLIF measurement was then specified as twice the sample standard deviation of the measured variable Ni2 or Ci2 for the five runs. The standard deviation of the mean was not the appropriate parameter to use here since the results of a single run were ultimately used and not the average of the five runs. Clearly, an analysis based on the uncertainty in the component images would provide more detailed information. Such measurements of the uncertainty in the fundamental images could be propagated through the image analysis routine described in Appendix D to arrive at the uncertainty of the final Ni2 or Ci2 variable. Moreover, such an analysis scheme would indicate the sensitivity of the final measurement to the uncertainty in the individual images. Nevertheless, basing the PLIF measurement precision on the final Ni2 or Ci2 variable provided a realistic and reliable estimate of this component of the measurement uncertainty.

CF^{PLIF} was determined for each of the five PLIF calibrations (corresponding to Runs C, D, E, F, and G) as described in Appendix E. Using the method described above, the precision of CF^{PLIF} , $(\epsilon CF^{\text{PLIF}})_{\text{PRE}}$, was determined to be approximately 20%. This was combined with the 3.9% accuracy of the calibration factor, $(\epsilon CF^{\text{PLIF}})_{\text{ACC}}$, using Eq. (F.9) to provide a cumulative uncertainty in the PLIF calibration factor of approximately 20.4%.

The precision of the PLIF measurements was based on the calculated Ni2 values for the five PLIF runs, as defined in Eq. (D.9). The PLIF image data was binned at 29 radial locations ($-14 \text{ mm} < r < 14 \text{ mm}$) and 10 elevations, as described in Appendix G using the program BIN6. The location and area of the binning approximately corresponded to the location and projected slit area used for the LSF measurements. The binning procedure produced 1450 point measurements for the five PLIF runs. These results were then compared to determining the average and sample standard deviation on a point-by-point basis for the Ni2 parameter. This produced 290 point values of average Ni2 and absolute uncertainty in Ni2, spanning the range of PLIF signals throughout the AIDF. The relative and absolute uncertainties in these Ni2 points are plotted in Fig. F.2 and are labeled ϵNi2 and δNi2 , respectively. There is clearly more scatter in the PLIF data as compared to the LSF data of Fig. F.1. From the relative uncertainty plot in Fig. F.2, it is apparent that the majority of the data points produce a signal level of approximately 0.2 to 0.54 counts and have a relative uncertainty of approximately 18%. This corresponds to a SNR of approximately 5.6. The detection limit for the PLIF measurements was determined from the δNi2 vs. Ni2 data of Fig. F.2. The least-squares fit to this data is shown and was calculated to be $\delta\text{Ni2} = 0.1588 * \text{Ni2} + 0.0112$. The detection limit for the PLIF measurements was determined to be $\text{Ni2} \approx 0.0133$ counts, based on calculation of the point where the best fit line crosses the SNR=1 line. This value corresponds to $N_{\text{T,RT,RQ}}$ values from ~ 1.4 ppm to ~ 1.7 ppm depending on which CF^{PLIF} was used. This was found to be in good agreement with separate estimates of the detection limit based on the PLIF calibrations.

Based on Eq. (E.13), the cumulative uncertainty in the PLIF measurements of relative [NO] is

$$\epsilon N_{\text{T,RT,RQ}} = \left[(\epsilon \text{CF}^{\text{PLIF}})^2 + (\epsilon \text{Ni2})^2 \right]^{0.5}. \quad (\text{F.11})$$

The least-squares fit to the δNi2 vs. Ni2 data of Fig. F.2 was used to characterize the absolute uncertainty in Ni2 for any given PLIF experiment. Hence, δNi2 was calculated for each binned point in the image, and used to determine the relative uncertainty via

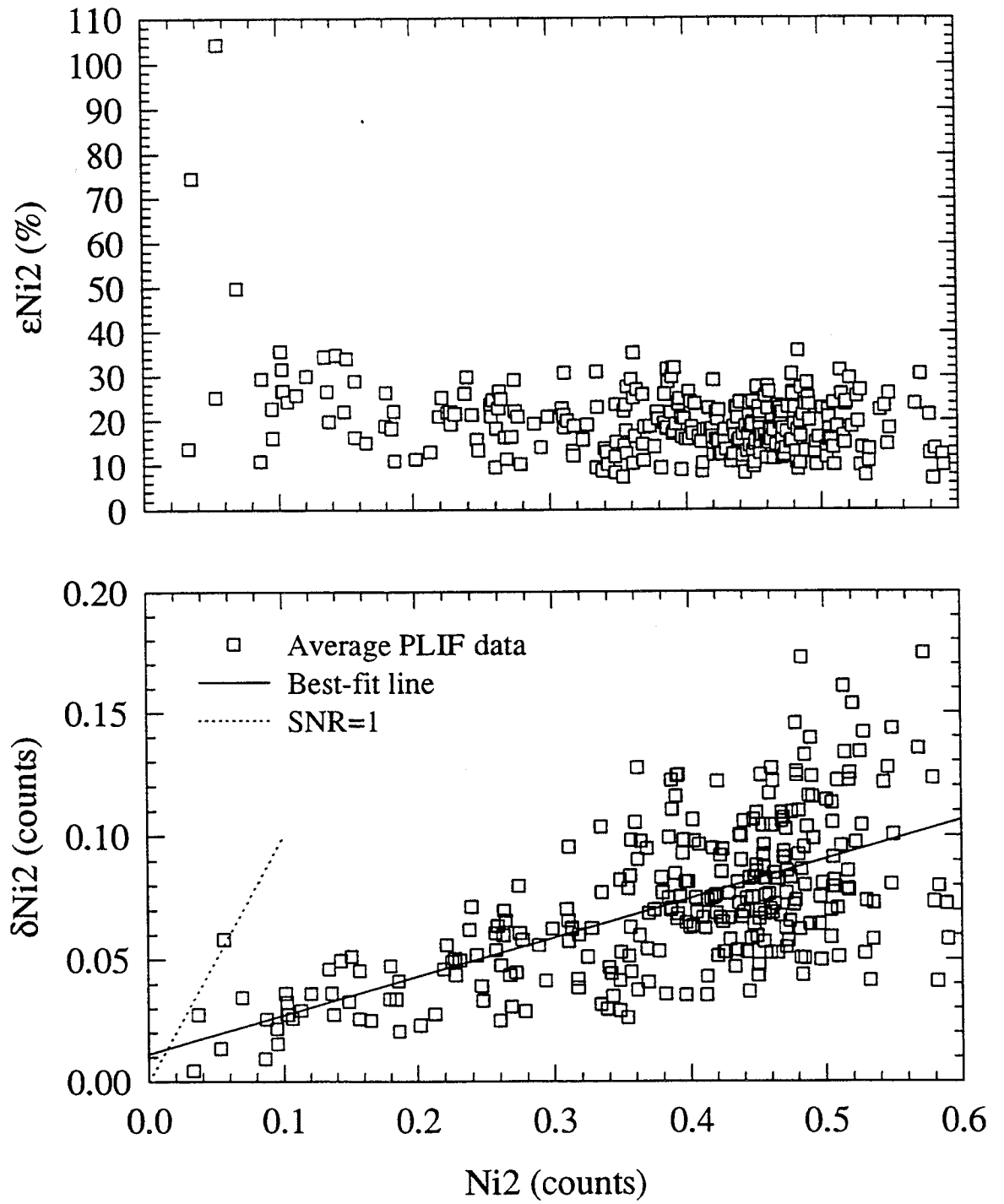


Figure F.2 Uncertainty in the measurement of $Ni2$ for the PLIF measurements of $[NO]$ in the AIDF.

$\epsilon_{\text{Ni2}} = \delta\text{Ni2}/\text{Ni2}$. This value was subsequently used with $\epsilon_{\text{CF}}^{\text{PLIF}}=20.4\%$ and Eq. (F.11) to determine the uncertainty in the 290 binned PLIF measurements of $N_{\text{T,RT,RQ}}$ in the AIDF. The resulting relative and absolute uncertainties for PLIF Run C are plotted versus $N_{\text{T,RT,RQ}}$ in Fig. F.3. The smoothness of the data in Fig. F.3, compared to Fig. F.2, is due to the use of a least-squares fit to characterize the uncertainty in Ni2 as a function of signal level. Figure F.3 indicates that the majority of the 290 binned PLIF measurements correspond to 25 to 55 relative ppm with a relative uncertainty of $\sim 28\%$. This result corresponds to a SNR of ~ 3.6 , which reflects a further degradation of the SNR due to application of the CF. This degradation of the SNR is due to the uncertainty in the CF.

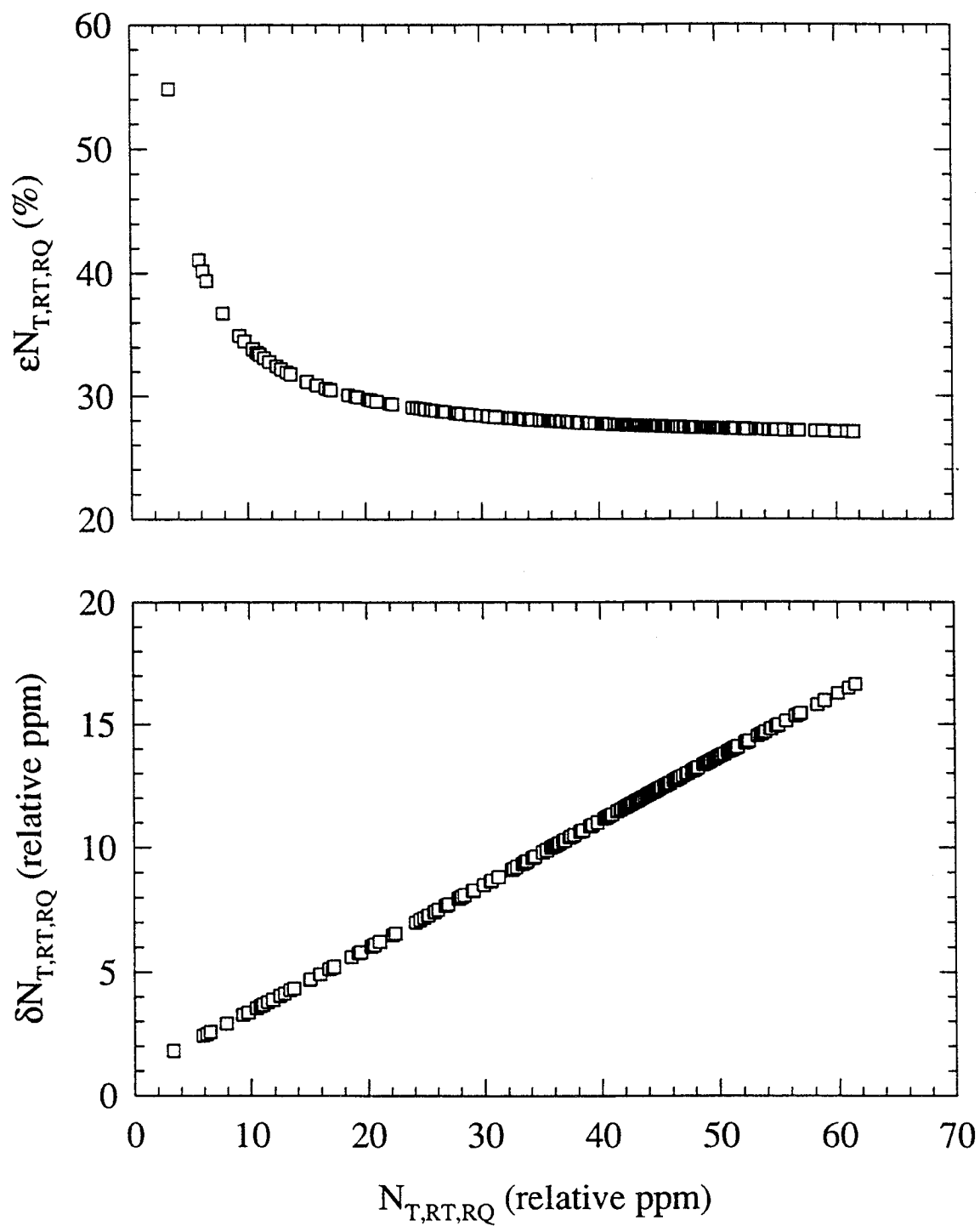


Figure F.3 Uncertainty in the $N_{T,RT,RQ}$ PLIF measurements of [NO] in the AIDF.

Appendix G - Image Binning Program

To compare the PLIF images to the LSF measurements, the PLIF images were sampled at locations corresponding to those of the LSF measurements. Moreover, the PLIF images at these sample locations were binned over a 1 pixel by 19 pixels (i.e., 56 μm by 1.06 mm) region which approximately corresponded to the projected slit area used for the LSF measurements (i.e., 68 μm by 1.0 mm). The program BIN6c was used to perform these operations for PLIF Run C, using data generated in the image analysis program IMACORR4c.

```

;*****
;BIN6c
;Program to bin the PLIF image at selected elevations so that it may be compared to
;the LSF array data.
;
;Program operates on the parameters produced by the program IMACOR4_
;So, run IMACOR4_ first via ".rnew imacor4_" and then run this program
;to generate the appropriate data files via ".run bin1".
;
;Program also provides space specific sampling of the output from the
;primary images. This may be used in the uncertainty analysis of the
;PLIF measurement.
;
;This program works only if the masking parameters used in IMACOR4_
;are as follows:
;mxs=29      ;beginning mask x value
;mxe=577     ;ending mask x pixel value
;mys=13      ;beginning mask y pixel value
;mye=255     ;ending mask y pixel value
;
; 6-10-95 wpp jr.
; 6-24-95, 6-31-95
;
;*****
;
;LOCATION OF Z-PIXELS
;
;z=[14,13,12,11,10,9,8,7,6,5,4,3,2,1,0,-1,-2,-3, $
    -4,-5,-6,-7,-8,-9,-10,-11,-12,-13,-14] ;z locations in mm

```

```

zelements=N_Elements(z)
dz=18           ;density of binned data in z direction (18 pixels = 1 mm)
zpix=274+z*dz   ;corresponding z locations in pixels
bin=19          ;number of pixels binned at each z location
pnbin=(bin-1)/2 ;positive/negative binning range
zstart=zpix-pnbin
zend=zpix+pnbin
;
;LOCATION OF Y-PIXELS
;
y=[3,4,5,6,7,8,9,11,13,15] ;y locations in mm
yelements=N_Elements(y)
dy=18           ;density of binned data in y direction
                    ;18 pixels = 1 mm
ypix=13+(y-3)*dy ;corresponding y location in mm
;
;*****
;CREATE INTERMEDIATE ARRAY OF THE DATA TO BE BINNED:
;First and second indices are the z and y locations, respectively, in the final binned
;array. The third index is the individual data to be binned for each y,z location.
;
;DECLARE ARRAYS TO HOLD INTERMEDIATE DATA
;Note that the original images taken with the PI CSMA software (e.g., ima, bkg,
;lib,...) are integer arrays so they are declared as intarr. However, the processed
;arrays (e.g., Nfmi ...) are not necessarily integer value so are declared as floating
;point arrays or fltarr.
;
Nfmi=fltarr(zelements,yelements,bin)
;
;The following are the supplemental data for the uncertainty analysis. Nomenclature
;is in program imacor4c.
;
imami=intarr(zelements,yelements,bin)
bkgmi=intarr(zelements,yelements,bin)
libmi=intarr(zelements,yelements,bin)
sn2mi=intarr(zelements,yelements,bin)
sn2bmi=intarr(zelements,yelements,bin)
Ni1Fmi=fltarr(zelements,yelements,bin)
LSDFmi=fltarr(zelements,yelements,bin)
Ni2fmi=fltarr(zelements,yelements,bin)

for I=0,yelements-1 do begin ;each elevation
    ypos=ypix(i)
    for j=0,zelements-1 do begin ;each radial location

```

```

        for k=0, bin-1 do begin           ;each bin element
            zpos=zstart(j)+k
            Nfmi(j,i,k)=Nfm(zpos,ypos)
            imami(j,i,k)=imam(zpos,ypos)
            bkgmi(j,i,k)=bkgm(zpos,ypos)
            libmi(j,i,k)=libm(zpos,ypos)
            sn2mi(j,i,k)=sn2m(zpos,ypos)
            sn2bmi(j,i,k)=sn2bm(zpos,ypos)
            Ni1Fmi(j,i,k)=Ni1Fm(zpos,ypos)
            LSDFmi(j,i,k)=LSDFm(zpos,ypos)
            Ni2fmi(j,i,k)=Ni2fm(zpos,ypos)
        endfor
    endfor
endfor
;
;*****
;DECLARE ARRAYS TO HOLD THE BINNED DATA
;
Nfmb=fltarr(zelements,yelements)
;
;The following are the supplemental data for the uncertainty analysis. Nomenclature
;is in program imacor4c.
;
imamb=fltarr(zelements,yelements)
bkgmb=fltarr(zelements,yelements)
libmb=fltarr(zelements,yelements)
sn2mb=fltarr(zelements,yelements)
sn2bmb=fltarr(zelements,yelements)
Ni1Fmb=fltarr(zelements,yelements)
LSDFmb=fltarr(zelements,yelements)
Ni2fmb=fltarr(zelements,yelements)
;
;NOW BIN THE DATA
;First index is the radial location (i.e., z) and the second index is the elevation (i.e., y).
;
for i=0,yelements-1 do begin           ;each elevation
    for j=0, zelements-1 do begin ;each radial location
        vec1=Nfmi(j,i,*)
        Nfmb(j,i)=AVG(vec1)
        vec2=imami(j,i,*)
        imamb(j,i)=AVG(vec2)
        vec3=bkgmi(j,i,*)
        bkgmb(j,i)=AVG(vec3)
        vec4=libmi(j,i,*)

```

```

        libmb(j,i)=AVG(vec4)
        vec5=sn2mi(j,i,*)
        sn2mb(j,i)=AVG(vec5)
        vec6=sn2bmi(j,i,*)
        sn2bmb(j,i)=AVG(vec6)
        vec7=Ni1Fmi(j,i,*)
        Ni1Fmb(j,i)=AVG(vec7)
        vec8=LSDFmi(j,i,*)
        LSDFmb(j,i)=AVG(vec8)
        vec9=Ni2fmi(j,i,*)
        Ni2fmb(j,i)=AVG(vec9)
    endfor
endfor
;
;*****
; WRITE THE BINNED DATA TO A DATA FILE
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/cnfmmb.dat', $
    Nfmb(*,0), Nfmb(*,1), Nfmb(*,2), Nfmb(*,3), Nfmb(*,4), Nfmb(*,5), $
    Nfmb(*,6), Nfmb(*,7), Nfmb(*,8), Nfmb(*,9), /col)
;
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/cimamb.dat', $
    imamb(*,0), imamb(*,1), imamb(*,2), imamb(*,3), imamb(*,4), $
    imamb(*,5), imamb(*,6), imamb(*,7), imamb(*,8), imamb(*,9), /col)
;
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/cbkgmb.dat', $
    bkgmb(*,0), bkgmb(*,1), bkgmb(*,2), bkgmb(*,3), bkgmb(*,4), $
    bkgmb(*,5), bkgmb(*,6), bkgmb(*,7), bkgmb(*,8), bkgmb(*,9), /col)
;
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/clibmb.dat', $
    libmb(*,0), libmb(*,1), libmb(*,2), libmb(*,3), libmb(*,4), $
    libmb(*,5), libmb(*,6), libmb(*,7), libmb(*,8), libmb(*,9), /col)
;
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/csn2mb.dat', $
    sn2mb(*,0), sn2mb(*,1), sn2mb(*,2), sn2mb(*,3), sn2mb(*,4), $
    sn2mb(*,5), sn2mb(*,6), sn2mb(*,7), sn2mb(*,8), sn2mb(*,9), /col)
;
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/csn2bmb.dat', $
    sn2bmb(*,0), sn2bmb(*,1), sn2bmb(*,2), sn2bmb(*,3), sn2bmb(*,4), $
    sn2bmb(*,5), sn2bmb(*,6), sn2bmb(*,7), sn2bmb(*,8), sn2bmb(*,9), /col)
;
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/cni1fmb.dat', $
    Ni1Fmb(*,0), Ni1Fmb(*,1), Ni1Fmb(*,2), Ni1Fmb(*,3), Ni1Fmb(*,4), $
    Ni1Fmb(*,5), Ni1Fmb(*,6), Ni1Fmb(*,7), Ni1Fmb(*,8), Ni1Fmb(*,9), /col)
;

```

```
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/clsdfmb.dat', $
    LSDFmb(*,0), LSDFmb(*,1), LSDFmb(*,2), LSDFmb(*,3), LSDFmb(*,4), $
    LSDFmb(*,5), LSDFmb(*,6), LSDFmb(*,7), LSDFmb(*,8), LSDFmb(*,9), $
    /col)
;
status=dc_write_free('/home/hemingway/a/partridg/datout/bin/cni2fmb.dat', $
    Ni2fmb(*,0), Ni2fmb(*,1), Ni2fmb(*,2), Ni2fmb(*,3), Ni2fmb(*,4), $
    Ni2fmb(*,5), Ni2fmb(*,6), Ni2fmb(*,7), Ni2fmb(*,8), Ni2fmb(*,9), /col)
;
end
```


Appendix H - Fluorescence Measurements Data

The [NO] data resulting from the various measurements and experimentally-based enhancement procedures is presented in this appendix. The 290 LSF measurements of [NO] and their associated absolute uncertainties discussed in Section 7.1 are tabulated in Tables H.1a and H.1b. The 290 binned-PLIF measurements of [NO] and their associated absolute uncertainties discussed in Section 7.3 are tabulated in Tables H.2a and H.2b. The [NO] measurements resulting from application of the single-input, multiple-input and minimal-input experimentally-based PLIF enhancement procedures discussed in Sections 7.4.1, 7.4.2 and 7.4.3, respectively, are tabulated in Tables H.3, H.4 and H.5.

Table H.1a Values and uncertainties for the LSF point measurements of [NO] in the AIDF, at $y = 3, 4, 5, 6$ and 7 mm above the AIDF burner surface, discussed in Section 7.1. The spatial location of the measurements is indicated by the parameters y (mm) and r (mm) as defined in Figure 5.17. $N_{T,RT}$ represents the measured [NO] in relative ppm calculated using Eq. (E.6) and $\delta N_{T,RT}$ represents the corresponding absolute uncertainty in the $N_{T,RT}$ measurement as calculated in Section F.2.

r (mm)	LSF RUN B $y=3$ mm $N_{T,RT}$ (ppm)	LSF RUN B $y=3$ mm $\delta N_{T,RT}$ (ppm)	LSF RUN B $y=4$ mm $N_{T,RT}$ (ppm)	LSF RUN B $y=4$ mm $\delta N_{T,RT}$ (ppm)	LSF RUN B $y=5$ mm $N_{T,RT}$ (ppm)	LSF RUN B $y=5$ mm $\delta N_{T,RT}$ (ppm)	LSF RUN B $y=6$ mm $N_{T,RT}$ (ppm)	LSF RUN B $y=6$ mm $\delta N_{T,RT}$ (ppm)	LSF RUN B $y=7$ mm $N_{T,RT}$ (ppm)	LSF RUN B $y=7$ mm $\delta N_{T,RT}$ (ppm)
14.0	3.9	1.1	4.1	1.3	6.9	1.9	7.7	2.0	9.5	2.4
13.0	17.2	4.0	19.0	4.4	22.1	5.2	23.3	5.3	24.9	5.6
12.0	34.9	7.6	35.7	7.8	37.9	8.3	37.9	8.2	38.6	8.5
11.0	46.4	10.0	45.5	9.8	48.0	10.4	46.0	9.9	50.8	10.9
10.0	53.9	11.5	53.5	11.5	51.0	11.0	53.7	11.5	52.1	11.2
9.0	54.2	11.6	57.4	12.3	55.7	12.0	56.7	12.2	55.8	11.9
8.0	57.4	12.3	56.8	12.2	57.1	12.2	57.4	12.2	57.5	12.3
7.0	56.2	12.1	54.5	11.6	58.1	12.5	52.3	11.2	51.8	11.1
6.0	52.3	11.2	52.5	11.2	51.5	11.1	52.2	11.3	53.7	11.5
5.0	50.7	10.9	48.2	10.4	51.9	11.1	48.6	10.5	50.9	10.9
4.0	47.1	10.2	43.3	9.4	47.2	10.2	46.8	10.1	49.4	10.7
3.0	41.0	8.9	36.3	7.9	40.2	8.8	43.5	9.4	50.3	10.9
2.0	32.4	7.1	34.1	7.6	37.6	8.3	43.0	9.4	44.2	9.5
1.0	15.1	3.5	23.0	5.2	30.4	6.8	36.4	8.0	41.1	8.9
0.0	7.6	2.1	12.7	3.1	25.2	5.7	37.0	8.1	38.5	8.3
-1.0	18.4	4.3	24.5	5.6	35.2	7.8	35.5	7.7	43.1	9.4
-2.0	33.1	7.3	32.9	7.3	36.8	8.1	43.3	9.4	46.7	10.0
-3.0	40.5	8.8	36.7	8.0	45.2	9.7	44.1	9.6	46.9	10.1
-4.0	45.9	9.9	43.2	9.3	47.7	10.2	46.5	10.1	48.5	10.5
-5.0	50.5	10.9	47.3	10.2	51.3	11.0	49.4	10.7	52.0	11.1
-6.0	56.3	12.1	49.6	10.7	54.3	11.6	56.1	12.1	53.3	11.4
-7.0	54.9	11.8	52.3	11.2	55.7	11.9	56.7	12.2	56.3	12.1
-8.0	55.4	11.8	53.7	11.6	56.6	12.1	55.6	11.9	56.6	12.1
-9.0	53.5	11.5	51.4	11.2	52.8	11.4	55.5	11.9	54.1	11.6
-10.0	53.4	11.5	52.3	11.2	50.0	10.8	51.9	11.1	49.3	10.6
-11.0	45.6	9.8	45.2	9.9	47.2	10.2	43.5	9.5	46.1	10.1
-12.0	34.0	7.6	37.4	8.3	38.3	8.4	37.7	8.3	33.6	7.4
-13.0	17.1	4.0	19.2	4.6	22.4	5.1	23.7	5.4	22.8	5.2
-14.0	4.1	1.3	7.5	2.1	9.1	2.4	8.1	2.1	10.2	2.6

Table H.1b Values and uncertainties for the LSF point measurements of [NO] in the AIDF, at $y = 8, 9, 11, 13$ and 15 mm above the AIDF burner surface, discussed in Section 7.1. The spatial location of the measurements is indicated by the parameters y (mm) and r (mm) as defined in Figure 5.17. $N_{T,RT}$ represents the measured [NO] in relative ppm calculated using Eq. (E.6) and $\delta N_{T,RT}$ represents the corresponding absolute uncertainty in the $N_{T,RT}$ measurement as calculated in Section F.2.

r (mm)	LSF RUN B $y=8$ mm	LSF RUN B $y=8$ mm	LSF RUN B $y=9$ mm	LSF RUN B $y=9$ mm	LSF RUN B $y=11$ mm	LSF RUN B $y=11$ mm	LSF RUN B $y=13$ mm	LSF RUN B $y=13$ mm	LSF RUN B $y=15$ mm	LSF RUN B $y=15$ mm
	$N_{T,RT}$ (ppm)	$\delta N_{T,RT}$ (ppm)	$N_{T,RT}$ (ppm)	$\delta N_{T,RT}$ (ppm)	$N_{T,RT}$ (ppm)	$\delta N_{T,RT}$ (ppm)	$N_{T,RT}$ (ppm)	$\delta N_{T,RT}$ (ppm)	$N_{T,RT}$ (ppm)	$\delta N_{T,RT}$ (ppm)
14.0	10.8	2.7	10.1	2.6	13.2	3.2	13.6	3.4	14.5	3.5
13.0	25.7	5.8	28.0	6.3	27.5	6.2	28.6	6.4	23.3	5.3
12.0	39.2	8.7	38.8	8.5	43.5	9.5	37.1	8.1	41.9	9.1
11.0	47.9	10.3	49.9	10.7	47.1	10.2	46.8	10.1	46.9	10.1
10.0	54.4	11.6	52.0	11.1	55.2	11.8	52.2	11.2	35.6	11.9
9.0	57.5	12.4	56.7	12.1	54.7	11.6	54.0	11.6	54.1	11.5
8.0	56.1	12.1	56.6	12.1	59.5	12.7	53.5	11.4	55.7	11.9
7.0	55.2	11.8	57.9	12.3	59.6	12.8	58.5	12.5	51.9	11.1
6.0	55.8	12.0	52.8	11.3	58.2	12.4	50.8	10.9	58.7	12.5
5.0	53.6	11.6	51.9	11.2	59.5	12.7	54.4	11.7	59.3	12.6
4.0	53.6	11.5	52.8	11.4	60.2	12.8	53.8	11.5	60.8	13.0
3.0	51.5	11.2	54.5	11.7	54.8	11.7	59.6	12.7	62.4	13.3
2.0	48.0	10.3	57.0	12.1	62.5	13.3	58.4	12.4	65.5	13.9
1.0	48.4	10.4	51.8	11.2	62.5	13.3	63.6	13.5	67.5	14.3
0.0	47.0	10.0	51.3	11.0	64.5	13.7	69.0	14.7	69.8	14.8
-1.0	47.4	10.3	52.3	11.1	59.7	12.7	68.0	14.4	68.2	14.4
-2.0	52.3	11.3	54.0	11.5	60.8	12.9	59.2	12.7	64.6	13.7
-3.0	50.7	10.9	53.5	11.5	54.5	11.7	56.5	12.0	59.4	12.7
-4.0	51.7	11.1	52.8	11.3	55.3	11.9	54.7	11.6	58.3	12.4
-5.0	52.0	11.2	51.2	11.0	51.6	11.1	50.5	10.9	56.7	12.1
-6.0	51.5	11.0	55.0	11.7	56.5	12.1	52.6	11.3	56.3	12.0
-7.0	54.5	11.7	54.8	11.7	56.6	12.1	53.2	11.5	56.3	12.2
-8.0	57.4	12.2	54.4	11.7	56.4	12.1	54.2	11.6	55.5	11.9
-9.0	56.7	12.1	52.6	11.3	55.0	11.8	56.7	12.2	53.7	11.5
-10.0	49.1	10.5	55.8	12.0	51.5	11.1	52.9	11.3	49.1	10.6
-11.0	47.1	10.1	44.9	9.7	44.5	9.7	44.4	9.6	44.9	9.8
-12.0	37.5	8.2	41.0	8.9	40.0	8.8	38.0	8.4	35.6	7.8
-13.0	26.3	6.1	26.7	5.9	26.2	6.0	26.2	6.0	25.2	5.7
-14.0	11.1	2.8	12.8	3.2	13.3	3.3	12.4	3.1	11.4	2.9

Table H.2a Values and uncertainties for the 290 binned PLIF measurements of [NO] in the AIDF, at $y = 3, 4, 5, 6$ and 7 mm above the AIDF burner surface, discussed in Section 7.3. The spatial location of the 290 binned PLIF measurements is indicated by the parameters y (mm) and r (mm) as defined in Figure 5.17. Image sampling was performed using the program of Appendix G. $N_{T,RT,RQ}$ represents the measured [NO] in relative ppm calculated using Eq. (E.12) and $\delta N_{T,RT,RQ}$ represents the corresponding absolute uncertainty in the $N_{T,RT,RQ}$ measurement as calculated in Section F.3.

r (mm)	PLIF RUN C $y=3$ mm $N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=3$ mm $\delta N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=4$ mm $N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=4$ mm $\delta N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=5$ mm $N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=5$ mm $\delta N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=6$ mm $N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=6$ mm $\delta N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=7$ mm $N_{T,RT,RQ}$ (ppm)	PLIF RUN C $y=7$ mm $\delta N_{T,RT,RQ}$ (ppm)
14.0	5.9	2.4	11.0	3.7	6.2	2.5	9.3	3.3	7.9	2.9
13.0	17.1	5.2	21.0	6.2	22.1	6.5	24.8	7.2	18.6	5.6
12.0	27.9	8.0	26.1	7.5	33.6	9.5	36.4	10.2	33.5	9.4
11.0	33.2	9.3	37.5	10.4	36.3	10.1	40.4	11.2	42.9	11.8
10.0	43.5	12.0	47.0	12.9	42.6	11.8	49.1	13.4	40.7	11.3
9.0	44.5	12.3	47.4	13.0	48.2	13.2	46.3	12.7	44.1	12.1
8.0	49.1	13.4	42.3	11.7	48.3	13.2	49.3	13.5	48.2	13.2
7.0	49.2	13.5	49.8	13.6	49.7	13.6	50.4	13.8	43.5	12.0
6.0	49.3	13.5	45.6	12.5	48.2	13.2	50.0	13.7	43.4	12.0
5.0	43.9	12.1	42.1	11.6	42.8	11.8	44.3	12.2	43.4	12.0
4.0	38.4	10.7	37.3	10.4	43.2	11.9	42.2	11.7	42.6	11.8
3.0	31.2	8.8	32.8	9.2	36.9	10.3	44.3	12.2	41.4	11.5
2.0	25.7	7.4	29.1	8.3	33.6	9.4	36.8	10.3	36.9	10.3
1.0	12.9	4.1	20.6	6.1	26.7	7.7	32.3	9.1	33.7	9.5
0.0	3.3	1.8	9.7	3.4	24.1	7.0	30.5	8.6	33.5	9.4
-1.0	11.8	3.9	17.0	5.2	27.8	7.9	38.2	10.6	35.4	9.9
-2.0	26.0	7.5	27.8	8.0	38.3	10.6	35.9	10.0	36.2	10.1
-3.0	33.4	9.4	34.3	9.6	42.5	11.7	45.1	12.4	39.7	11.0
-4.0	38.3	10.7	36.4	10.2	43.2	11.9	41.4	11.5	42.0	11.6
-5.0	44.9	12.4	44.2	12.2	48.0	13.1	47.7	13.1	44.1	12.2
-6.0	42.2	11.7	45.4	12.5	49.6	13.6	46.5	12.8	41.6	11.5
-7.0	49.1	13.4	43.4	12.0	50.7	13.9	48.7	13.3	43.5	12.0
-8.0	44.1	12.1	48.1	13.2	53.9	14.7	50.4	13.8	47.8	13.1
-9.0	47.0	12.9	45.7	12.6	53.6	14.6	52.5	14.3	46.2	12.7
-10.0	40.3	11.2	44.5	12.3	47.3	13.0	46.2	12.7	41.4	11.5
-11.0	37.7	10.5	34.2	9.6	40.5	11.2	43.5	12.0	40.7	11.3
-12.0	30.0	8.5	29.9	8.5	34.3	9.6	34.1	9.6	30.6	8.7
-13.0	19.2	5.7	19.4	5.8	25.8	7.4	22.3	6.6	25.1	7.3
-14.0	6.5	2.6	10.9	3.7	13.6	4.3	12.4	4.0	15.1	4.7

Table H.2b Values and uncertainties for the 290 binned PLIF measurements of [NO] in the AIDF, at $y = 8, 9, 11, 13$ and 15 mm above the AIDF burner surface, discussed in Section 7.3. The spatial location of the 290 binned PLIF measurements is indicated by the parameters y (mm) and r (mm) as defined in Figure 5.17. Image sampling was performed using the program of Appendix G. $N_{T,RT,RQ}$ represents the measured [NO] in relative ppm calculated using Eq. (E.12) and $\delta N_{T,RT,RQ}$ represents the corresponding absolute uncertainty in the $N_{T,RT,RQ}$ measurement as calculated in Section F.3.

r (mm)	PLIF RUN C $y=8$ mm	PLIF RUN C $y=8$ mm	PLIF RUN C $y=9$ mm	PLIF RUN C $y=9$ mm	PLIF RUN C $y=11$ mm	PLIF RUN C $y=11$ mm	PLIF RUN C $y=13$ mm	PLIF RUN C $y=13$ mm	PLIF RUN C $y=15$ mm	PLIF RUN C $y=15$ mm
	$N_{T,RT,RQ}$ (ppm)	$\delta N_{T,RT,RQ}$ (ppm)	$N_{T,RT,RQ}$ (ppm)	$\delta N_{T,RT,RQ}$ (ppm)	$N_{T,RT,RQ}$ (ppm)	$\delta N_{T,RT,RQ}$ (ppm)	$N_{T,RT,RQ}$ (ppm)	$\delta N_{T,RT,RQ}$ (ppm)	$N_{T,RT,RQ}$ (ppm)	$\delta N_{T,RT,RQ}$ (ppm)
14.0	10.4	3.5	13.3	4.3	12.4	4.0	11.4	3.8	10.8	3.6
13.0	26.7	7.7	28.1	8.0	24.5	7.1	24.1	7.0	20.5	6.1
12.0	32.8	9.2	39.2	10.9	36.4	10.2	33.4	9.4	31.2	8.8
11.0	36.7	10.2	42.5	11.7	40.2	11.1	39.0	10.8	36.0	10.1
10.0	40.7	11.3	50.4	13.8	44.7	12.3	41.4	11.4	35.7	10.0
9.0	43.9	12.1	51.0	13.9	45.0	12.4	45.4	12.5	43.5	12.0
8.0	47.9	13.1	60.0	16.3	49.9	13.7	45.4	12.5	42.0	11.6
7.0	44.9	12.3	53.6	14.6	48.9	13.4	46.2	12.7	43.6	12.0
6.0	44.1	12.1	48.3	13.2	50.8	13.9	44.1	12.1	47.2	13.0
5.0	45.9	12.6	45.7	12.6	55.0	15.0	43.1	11.9	53.5	14.6
4.0	47.4	13.0	46.7	12.8	53.8	14.7	47.8	13.1	47.0	12.9
3.0	47.3	13.0	50.7	13.9	48.9	13.4	50.1	13.7	52.3	14.3
2.0	44.6	12.3	54.9	14.9	53.3	14.5	61.5	16.6	52.3	14.3
1.0	36.3	10.1	47.7	13.1	58.9	16.0	56.9	15.5	55.7	15.1
0.0	39.2	10.9	46.4	12.7	56.5	15.3	56.7	15.4	54.8	14.9
-1.0	40.6	11.2	46.5	12.8	60.9	16.5	58.3	15.8	51.4	14.0
-2.0	45.9	12.6	45.4	12.5	51.3	14.0	52.5	14.3	51.5	14.0
-3.0	44.6	12.3	51.0	13.9	51.6	14.1	51.2	14.0	54.4	14.8
-4.0	45.8	12.6	45.1	12.4	45.5	12.5	49.5	13.6	46.7	12.8
-5.0	43.7	12.0	50.9	13.9	47.3	13.0	45.6	12.5	47.3	13.0
-6.0	41.7	11.5	53.9	14.7	49.7	13.6	48.9	13.4	41.0	11.3
-7.0	44.6	12.3	52.2	14.2	51.4	14.0	45.4	12.5	42.3	11.7
-8.0	48.7	13.3	51.2	14.0	47.3	13.0	44.4	12.2	42.2	11.7
-9.0	54.3	14.8	49.0	13.4	52.2	14.2	39.7	11.0	43.5	12.0
-10.0	47.8	13.1	50.2	13.7	46.7	12.8	46.5	12.8	38.4	10.7
-11.0	39.1	10.9	41.3	11.4	43.1	11.9	39.3	10.9	35.0	9.8
-12.0	32.5	9.2	38.3	10.7	36.4	10.2	37.7	10.5	33.5	9.4
-13.0	25.7	7.4	25.2	7.3	28.3	8.1	29.1	8.3	26.9	7.7
-14.0	15.9	4.9	20.2	6.0	16.7	5.1	15.9	4.9	15.0	4.7

Table H.3 Values for the 290 single-input enhanced binned PLIF measurements of [NO] in the AIDF, discussed in Section 7.4.1. The tabulated data represents the result of applying the single-input enhancement scheme to the binned PLIF data of Table H.2. Specifically, each binned PLIF measurement of Table H.2 was multiplied by $N_{T,RT}(y_s, r_s)/N_{T,RT,RQ}(y_s, r_s)$, where (y_s, r_s) is the location where the secondary LSF measurement was made. The conveniently chosen location, (y_s, r_s) , for the single secondary LSF measurement was (7,7).

r (mm)	PLIF RUN C y=3 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y = 4 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y = 5 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y = 6 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y = 7 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y = 8 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y = 9 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y =11 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y =13 mm N _{T,RT,RQ} (ppm*)	PLIF RUN C y =15 mm N _{T,RT,RQ} (ppm*)
14.0	7.0	13.1	7.4	11.1	9.4	12.4	15.8	14.8	13.5	12.8
13.0	20.3	25.0	26.3	29.5	22.1	31.7	33.4	29.1	28.6	24.3
12.0	33.2	31.0	40.0	43.2	39.8	39.0	46.6	43.3	39.7	37.1
11.0	39.5	44.5	43.2	48.1	51.1	43.7	50.6	47.8	46.4	42.9
10.0	51.8	55.9	50.7	58.4	48.4	48.5	60.0	53.2	49.2	42.5
9.0	53.0	56.4	57.3	55.0	52.4	52.2	60.7	53.5	54.0	51.8
8.0	58.4	50.3	57.4	58.6	57.3	57.0	71.4	59.4	54.0	50.0
7.0	58.5	59.2	59.1	59.9	51.8	53.4	63.8	58.1	55.0	51.8
6.0	58.7	54.2	57.3	59.5	51.6	52.4	57.4	60.5	52.4	56.2
5.0	52.2	50.1	50.9	52.7	51.6	54.6	54.4	65.5	51.2	63.6
4.0	45.7	44.4	51.4	50.2	50.6	56.3	55.5	64.0	56.8	55.9
3.0	37.1	39.0	43.9	52.7	49.3	56.3	60.3	58.2	59.6	62.3
2.0	30.5	34.6	39.9	43.7	43.9	53.1	65.3	63.4	73.2	62.2
1.0	15.3	24.5	31.8	38.4	40.1	43.2	56.8	70.1	67.7	66.2
0.0	3.9	11.6	28.7	36.3	39.9	46.6	55.2	67.2	67.5	65.2
-1.0	14.1	20.2	33.0	45.4	42.1	48.3	55.4	72.5	69.3	61.2
-2.0	31.0	33.1	45.5	42.7	43.1	54.5	54.0	61.0	62.5	61.2
-3.0	39.7	40.8	50.5	53.7	47.2	53.1	60.7	61.3	60.9	64.7
-4.0	45.6	43.3	51.3	49.2	49.9	54.4	53.7	54.1	58.9	55.6
-5.0	53.4	52.5	57.1	56.7	52.5	52.0	60.6	56.3	54.2	56.2
-6.0	50.2	54.0	59.0	55.3	49.5	49.6	64.1	59.1	58.2	48.7
-7.0	58.4	51.6	60.3	57.9	51.8	53.1	62.1	61.1	53.9	50.3
-8.0	52.4	57.2	64.1	60.0	56.8	57.9	61.0	56.3	52.8	50.2
-9.0	55.9	54.4	63.8	62.4	55.0	64.6	58.2	62.1	47.2	51.7
-10.0	48.0	52.9	56.3	54.9	49.2	56.9	59.7	55.6	55.3	45.7
-11.0	44.8	40.7	48.1	51.7	48.4	46.5	49.2	51.3	46.7	41.6
-12.0	35.7	35.6	40.8	40.6	36.4	38.6	45.6	43.4	44.9	39.9
-13.0	22.8	23.1	30.6	26.6	29.9	30.5	30.0	33.7	34.6	32.0
-14.0	7.8	13.0	16.2	14.8	17.9	18.9	24.1	19.8	18.9	17.9

Table H.4 Values for the 290 multiple-input enhanced binned PLIF measurements of [NO] in the AIDF, discussed in Section 7.4.2. The tabulated data represents the result of applying the multiple-input enhancement scheme to the binned PLIF data of Table H.2. Specifically, each binned PLIF measurement of Table H.2 was multiplied by $N_{T,RT}(7,r)/N_{T,RT,RQ}(7,r)$, i.e., a radial-location-specific correction was applied to the binned PLIF measurements. The binned PLIF and LSF data at an elevation of 7 mm above the AIDF-burner surface were used to characterize the error gradient in the image at all elevations.

r (mm)	PLIF RUN C y=3 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y = 4 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y = 5 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y = 6 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y = 7 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y = 8 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y = 9 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y =11 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y =13 mm N _{T,RT,RQ} (ppm**)	PLIF RUN C y =15 mm N _{T,RT,RQ} (ppm**)
14.0	7.1	13.3	7.5	11.2	9.5	12.6	16.0	15.0	13.7	13.0
13.0	22.9	28.1	29.6	33.2	24.9	35.7	37.6	32.7	32.2	27.4
12.0	32.2	30.0	38.7	41.9	38.6	37.7	45.1	42.0	38.4	35.9
11.0	39.3	44.3	42.9	47.8	50.8	43.4	50.3	47.5	46.1	42.6
10.0	55.7	60.1	54.6	62.9	52.1	52.2	64.6	57.3	53.0	45.7
9.0	56.4	60.0	61.0	58.6	55.8	55.6	64.6	56.9	57.4	55.1
8.0	58.5	50.5	57.6	58.8	57.5	57.1	71.6	59.6	54.1	50.1
7.0	58.5	59.2	59.1	59.9	51.8	53.4	63.8	58.1	55.0	51.8
6.0	61.0	56.4	59.6	61.9	53.7	54.5	59.7	62.9	54.5	58.5
5.0	51.5	49.4	50.2	52.0	50.9	53.8	53.7	64.5	50.5	62.7
4.0	44.6	43.3	50.2	49.0	49.4	55.0	54.2	62.5	55.5	54.6
3.0	37.8	39.8	44.8	53.7	50.3	57.4	61.6	59.4	60.8	63.5
2.0	30.8	34.9	40.3	44.1	44.2	53.5	65.9	63.9	73.8	62.7
1.0	15.7	25.1	32.6	39.5	41.1	44.3	58.3	71.9	69.5	68.0
0.0	3.8	11.2	27.7	35.1	38.5	45.1	53.4	65.0	65.2	63.0
-1.0	14.4	20.7	33.9	46.6	43.1	49.5	56.8	74.3	71.1	62.7
-2.0	33.5	35.9	49.3	46.2	46.7	59.1	58.4	66.1	67.6	66.3
-3.0	39.4	40.5	50.1	53.3	46.9	52.7	60.3	60.9	60.4	64.3
-4.0	44.3	42.1	49.9	47.9	48.5	52.9	52.2	52.7	57.3	54.1
-5.0	52.9	52.0	56.5	56.2	52.0	51.5	60.0	55.7	53.7	55.7
-6.0	54.0	58.2	63.5	59.5	53.3	53.4	69.0	63.7	62.6	52.5
-7.0	63.5	56.1	65.6	63.0	56.3	57.7	67.5	66.5	58.7	54.7
-8.0	52.2	57.0	63.9	59.8	56.6	57.7	60.7	56.1	52.6	50.0
-9.0	55.0	53.6	62.8	61.5	54.1	63.6	57.4	61.2	46.5	51.0
-10.0	48.0	53.0	56.3	55.0	49.3	56.9	59.8	55.6	55.4	45.7
-11.0	42.7	38.7	45.8	49.3	46.1	44.3	46.8	48.8	44.5	39.7
-12.0	32.9	32.9	37.7	37.5	33.6	35.7	42.1	40.0	41.4	36.8
-13.0	17.4	17.6	23.4	20.3	22.8	23.3	22.9	25.7	26.4	24.4
-14.0	4.4	7.4	9.2	8.4	10.2	10.7	13.7	11.3	10.7	10.2

Table H.5 Values for the 150 minimal-input enhanced binned PLIF measurements of [NO] in the AIDF, discussed in Section 7.4.3. The tabulated data represents the result of applying the multiple-input enhancement scheme to the binned PLIF data of Table H.2. Only half of the image is evaluated. In the range $-11 \text{ mm} \leq r \leq 0 \text{ mm}$, a single-input procedure is used by multiplying each point in the PLIF image by $N_{T,RT}(7,-11)/N_{T,RT,RQ}(7,-11)$. In the range $-14 \text{ mm} \leq r \leq -12 \text{ mm}$, a multiple-input procedure is used by multiplying each point in the PLIF image by $N_{T,RT}(7,r)/N_{T,RT,RQ}(7,r)$, i.e., a radial-location-specific correction was applied. By augmenting the experimentally-based enhancement procedure design with knowledge of the test environment, the number of secondary LSF measurements required by this minimal-input procedure is reduced to four. Nevertheless, the minimal-input procedure produces PLIF measurements nominally as quantitative as a single LSF measurement.

r (mm)	PLIF RUN C $y=3 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=4 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=5 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=6 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=7 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=8 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=9 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=11 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=13 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})	PLIF RUN C $y=15 \text{ mm}$ $N_{T,RT,RQ}$ (ppm ^{***})
0.0	3.8	11.0	27.3	34.6	38.0	44.4	52.6	64.0	64.3	62.1
-1.0	13.4	19.2	31.5	43.3	40.1	46.0	52.7	69.0	66.0	58.2
-2.0	29.5	31.5	43.4	40.7	41.0	52.0	51.4	58.1	59.5	58.3
-3.0	37.8	38.9	48.1	51.1	45.0	50.6	57.8	58.4	58.0	61.7
-4.0	43.4	41.3	48.9	46.9	47.5	51.8	51.1	51.6	56.1	52.9
-5.0	50.9	50.0	54.4	54.0	50.0	49.5	57.7	53.6	51.7	53.6
-6.0	47.8	51.4	56.2	52.7	47.1	47.3	61.0	56.3	55.4	46.4
-7.0	55.6	49.2	57.5	55.2	49.3	50.6	59.1	58.2	51.4	47.9
-8.0	49.9	54.4	61.1	57.2	54.1	55.2	58.1	53.6	50.3	47.8
-9.0	53.2	51.8	60.8	59.5	52.4	61.6	55.5	59.2	44.9	49.3
-10.0	45.7	50.4	53.6	52.3	46.9	54.2	56.9	53.0	52.7	43.6
-11.0	42.7	38.7	45.8	49.3	46.1	44.3	46.8	48.8	44.5	39.7
-12.0	32.9	32.9	37.7	37.5	33.6	35.7	42.1	40.0	41.4	36.8
-13.0	17.4	17.6	23.4	20.3	22.8	23.3	22.9	25.7	26.4	24.4
-14.0	4.4	7.4	9.2	8.4	10.2	10.7	13.7	11.3	10.7	10.2

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