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DEVELOPMENT OF A TRANS-ROTATIONAL TEMPERATURE DIAGNOSTIC FOR VIBRATIONALLY-EXCITED CARBON MONOXIDE USING SINGLE-PHOTON LASER-INDUCED FLUORESCENCE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for

the Degree Doctor of Philosophy in the Graduate

School of The Ohio State University

By

Robert John Leiweke, M.S.

* * * * *

The Ohio State University 2004

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ABSTRACT

A new trans-rotational temperature diagnostic with ± 50 K accuracy has been developed for use in nonequilibrium, low temperature, monatomic gases seeded with carbon monoxide (CO). The scheme utilizes single-photon laser induced fluorescence (LIF) of CO under vibrationally-excited conditions in which single-photon transitions from the CO $X^{1}\Sigma^{+}$ ground electronic state to upper electronic $A^{1}\Pi$ or $D'^{1}\Sigma^{+}$ states become accessible to a tunable, narrowband ArF excimer laser at 193 nm. Two vibrationally excited environments in which the chemistry is well understood were used as a testbed; an optically-pumped 3% CO/Ar plasma at 100 torr and a 4% CO/He d.c. glow discharge at 8 torr. The LIF saturation limit was experimentally investigated and diagnostic advantages of either regime discussed. For the optically-pumped CO/Ar plasma, a spatially-averaged LIF temperature of 536 ± 103 K (2σ) was obtained from rotationally resolved $X^{1}\Sigma^{+}(v''=20) \rightarrow D'^{1}\Sigma^{+}(v'=2)$ LIF excitation spectra. Temperature measurements pumping the $X^{1}\Sigma^{+}(v''=7) \rightarrow A^{1}\Pi(v'=1) 4^{th}$ Positive (528±51 K) were also found to compare well with line-of-sight Fourier Transform-InfraRed (FT-IR) emission measurements (536 \pm 10 K). Spatially averaged FT-IR spectroscopy of the CO 1st overtone was used to verify that an adequate vibrational population ($\sim 0.1\%$) existed within the positive column of the CO/He d.c. glow discharge. The A-X (7,1) transition was pumped and subsequent (8,1) emission at 200.8 nm collected. The resulting rotational spectral peaks were assigned and a subset used to determine a spatially averaged rotational temperature of 432 ± 44 K on the discharge centerline. This was found to be in good agreement with FT-IR spectroscopy measurements (395 ± 10 K).

As a prelude to Planar-LIF (PLIF) temperature measurements, vibrationallyresolved emission from laser excitation of various rotational lines within the A-X and D'-X bands were used to investigate spectral interferences. This information was used to determine that a simple aqueous organic filter (urea) in the A-X case, or commercial glass filter (UG-11) in the D'-X case, are adequate for rejecting elastically-scattered radiation and extraneous ro-vibrational bands during PLIF imaging.

Single-shot and accumulated PLIF images were obtained for the 3% CO/Ar optically pumped plasma. Using a Two-Line ratio method, A-X band Q-branch images were used to spatially resolve the trans-rotational temperature. While the single-shot precision, determined from four trials, was $\approx \pm 200$ K (2 σ), the accuracy was $\approx \pm 100$ K. The accuracy of PLIF results implied a systematic error which may be attributed to the ICCD camera having a slightly nonlinear response at the 50% gain setting.

Dedicated to my Parents

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Research Publications

- 1. Spanjers, G.G., Malak, J.B., Leiweke, R.J., and Spores, R.A., "Effect of Propellant Temperature on Efficiency in the Pulsed Plasma Thruster", *AIAA Journal of Propulsion and Power*, **14**, No. 4, 545-553 (1998).
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FIELDS OF STUDY

Major Field: Mechanical and Aerospace Engineering Minor Field: Lasers, Plasmadynamics, and Optical Diagnostics

TABLE OF CONTENTS

Page

At De Ac Vi Lis	ii edication
Ch	napters:
1.	Introduction1
	1.1 Laser-induced fluorescence diagnostic potential.11.2 Literature survey of CO LIF diagnostics.51.3 Single-photon LIF using the CO 4 th Positive bands.71.4 Schemes for vibrational excitation.81.5 Survey of chapters.11
2.	Determination of rotational-translational temperature by laser-induced fluorescence
	2.1Laser Induced Fluorescence.132.2The steady state two-level LIF model.142.3Linear, non-linear, and saturated LIF regimes.212.3.1The linear regime.212.3.2The non-linear regime.252.3.3The saturated regime.252.4Carbon monoxide singlet-singlet rovibronic transitions.272.5Rotational temperature extraction from LIF spectra.352.5.1Two-line method.352.5.1.1Two-line method; Linear regime.382.5.1.2Two-line method; Saturated regime.41
	2.5.1.2 Two-line method; Saturated regime
	normalization

	2.5.2.2 Boltzmann Plot; Saturated regime with degeneracy	
	normalization	46
3.	LIF using an injection-locked argon fluoride laser	49
	3.1 Diagnostic strategy using a tunable, narrowband source	50
	3.2 Details of the injection-locked argon fluoride excimer laser	54
	3.3 The argon fluoride laser "locking efficiency	56
	3.4 Wavelength calibration of laser tuning range using ambient O_2 LIF	63
4.	Spacially averaged single-photon LIF temperature measurements using	
	the A-X and D'-X bands	64
	4.1 Model environments for CO LIF under extreme and mild vibrational nonequilibrium	. 64
	4.2 Nonequilbrium plasma characterization by FT-IR vibrational emisson	67
	4.2.1 Plasma creation and optical access	67
	4.2.1.1 Optically pumped plasma	67
	4.2.1.2 D.C. Normal glow discharge plasma	70
	4.2.2 FT-IR spectroscopy diagnostic setup	74
	4.2.3 FT-IR experimental results	75
	4.2.3.1 Optically pumped plasma vibrational level populations	75
	4.2.3.2 D.C. glow discharge vibrational level populations	77
	4.2.4 Rotational temperature using CO fundamental emission	80
	4.2.4.1 Optically pumped plasma	80
	4.2.4.2 D.C. glow discharge plasma	82
	4.3 D'-X band LIF rotational temperature measurements in highly	
	vibrationally-excited CO	83
	4.3.1 Vibrational state resolved LIF emission	83
	4.3.2 LIF excitation and collection	91
	4.3.3 D'-X band rotational LIF temperature results	97
	4.4 A-X band LIF rotational temperature measurements in highly	21
	and mildly vibrationally-excited CO	101
	4.4.1 Vibrational state resolved LIF emission	101
	4.4.2 LIF excitation and collection	107
	4 4 3 A-X band rotational LIF temperature results	115
	4 4 3 1 Highly vibrationally excited CO	115
	4.4.3.2 Mildly vibrationally excited CO	119
5.	Planar LIF imaging and temperature measurements using the	
	CO A-X and D'-X bands	122
	5.1 Planar laser-induced fluorescence	122
	5.1.1 PLIF excitation and collection	126
	5.1.2 A-X and D'-X band PLIF for the optically pumped plasma	129
	5.1.3 Nonequilibrium plasma conditions; "Case A" and "Case B"	132

5.2 A-X band imaging and temperature measurements	136
5.2.1 Spectral interferences and the imaging filter	136
5.2.1.1 Rayleigh scattering interference	137
5.2.1.2 Passive emission due to Swan and A-X bands	145
5.2.1.3 CO Resonance-Enhanced Multi-Photon Dissociation	145
5.2.1.4 D'-X band interference	149
5.2.2 A-X band imaging results	150
5.2.3 Temperature measurement strategy and sensitivity	163
5.2.4 A-X band PLIF temperature results	166
5.3 D'-X band PLIF imaging	180
5.3.1 Spectral interferences and filtering	180
5.3.2 D'-X band imaging results	183
6. Conclusions and future work	193
List of References	198
Appendices	211
A. Tables of numerical values from literature	211
B. LIF saturation and absorption calculations for CO-argon	
optically-pumped plasma conditions	215
C. The FORTRAN 77 synthetic LIF spectra code	
"MoleLIF" (version 6.0)	225
C.1 Sample input file 'input.dat'	225
C.2 Sample excerpt from file 'einstein.dat'	225
C.3 Main input and subroutines	226
D. FORTRAN 77 code for computing ro-vibronic transition lines for	
the A-X and D'-X bands	237
D.1 Molecular constant data input files for X, A, and D' states	260
D.1.1 Input data file for ground electronic state	260
D.1.2 Input data file for D'-state	261
D.1.3 Input data file for A-state	261
D.2 Sample code output for the D'-X band absorption lines within	
the argon-fluoride laser tuning range	262
D.3 Sample code output for the A-X 4^{th} Positive band absorption	
Lines within the argon-fluoride laser tuning range	264

LIST OF TABLES

Table	Pag	<u>ge</u>
4.1 Two-line data, ratios, and temperatures obtained using an ArF beam focused into a sheet. Data obtained on 11/16/01		99
4.2 Two-line data, ratios, and temperatures obtained using an ArF beam focused into a sheet. Data obtained on 11/16/01		99
4.3 Two-line data, ratios, and temperatures obtained using an <i>unfocused</i> ArF beam. Data obtained on 4/25/03	•••	100
4.4 Q(J")÷P(J") ratios obtained from 15 separate A-X LIF excitation scans with ArF laser intensitites spanning 5 orders of magnitude. Also shown is theoretical ratios for J"=10 and 17		112
5.1 Estimated CO laser beam diameters within imaging region	••••	135
5.2 Summary of A-X band Q(10) PLIF; S/N and 1σ noise in "counts"	••	157
5.3 Average axial centerline A-X PLIF temperature measurements (September 7, 2003)		168
5.4 Average axial centerline A-X PLIF temperature measurements (September 23, 2003)	•••	168
5.5 Average axial centerline A-X PLIF temperature measurements (October 4, 2003)		169
5.6 Summary of D'-X P(15) PLIF; S/N and 1σ noise in "counts"	•••	185
A.1 ¹² C ¹⁶ O molecular constants for $X^1\Sigma^+$, $A^1\Pi$, and $D'^1\Sigma^+$ electronic states		211

A.2 Absolute vibronic Einstein $A_{v'v''}$ transition probabilities (units of 10^{+7} s^{-1}) and effective lifetimes τ_{eff} (ns) for the ${}^{12}\text{C}{}^{16}\text{O}$ A-X bands as measured by electron impact excitation and emission specroscopy	212
A.3 ¹² C ¹⁶ O effective quenching and vibrational relaxation cross- sections at 300 K	213
A.4 Lorentian collision broadening parameters for ${}^{12}C^{16}O$ used in this work	214

LIST OF FIGURES

<u>Figure</u> <u>P</u>	age
1.1 CO Potential energy diagram illustrating the vibronic states and transitions discussed in this chapter	6
2.1 Conceptual energy-level diagram illustrating the important processes involved in LIF	15
2.2 Nondimensional Fluoresence Signal vs. Nondimensional Irradiance showing the linear, non-linear, and saturated LIF regimes	23
2.3 CO Potential energy diagram illustrating the vibronic states and transitions discussed in this chapter	28
2.4 Energy level and transition diagram for the CO $X^1\Sigma^+$ - $A^1\Pi$ band. The $X^1\Sigma^+$ - $D'^1\Sigma^+$ is similar (refer to text)	29
2.5. Example of Boltzmann plot method. (a) Proper choice of normalization function $f(J'')$ has been used and the locus of points for each branch falling on the same line with slope $\bar{a}=-B_{v''}/kT_{avg}$. (b) An improperly chosen normalization function is used in which the branches <i>may</i> be offset.	. 45
3.1 Two-Line Method Signal Ratio S _{m:n} vs. Rotational Temperature: Demonstration of measurement sensitivity for various transition pairs	53
3.2 Schematic diagram of Lambda Physik COMPex 150 in injection- locked tuning mode. Note that the amplifier resonator is unstable with a 3:1 telescope configuration	. 55
3.3 Lambda Physik COMPex 150T emission spectra of injection-locked ArF output for different wavelengths	57
3.4 Side-view illustration of the optics and monochrometer/PMT setup used to measure the COMPex 150T ArF locking efficiency	58

3.5	Front-view illustration of the monochrometer entrance port and beam alignment	60
3.6	Experimental ArF laser locking efficiency and average beam energy measurements	61
4.1	Experimental and theoretical steady-state vibrational distribution functions at different CO partial pressures	65
4.2	Photograph of the liquid nitrogen cooled CO laser used to optically-pump CO in test cell (not shown)	66
4.3	Top view of apparatus for creating the optically pumped plasma	68
4.4	Photographs of the optically-pumped CO plasma as viewed through a side viewport	69
4.5	Side view of flow cell illustrating the electrode geometry and electrical connections used in generating the d.c. normal glow discharge	70
4.6	Current-Voltage (I-V) characteristic for the cases of pure helium and 3.6% CO/He mixture at 8.3 torr	71
4.7	Photographs of pure helium d.c. glow discharge at 8.0 torr, 25 mA	73
4.8	Photographs of 0.3 torr CO added to the pure helium discharge shown in Figure 4.7 with the current still maintained at 25mA	73
4.9	Top view of experimental configuration for FT-IR spontaneous emission measurements	75
4.10	CO 1 st overtone FT-IR spectra (16 cm ⁻¹ resolution) of the 3 torr, 100 torr argon optically-pumped plasma as a function of added helium	76
4.1	1 CO 1 st overtone spectrum at 8 cm ⁻¹ resolution of the 3.6% CO/He d.c. glow discharge at 8.3 torr	78
4.12	2 Vibrational Distribution Function derived from Figure 4.11 CO 1^{st} overtone spectrum. Solid line is a best-fit at $T_{vib} = 2500$ K to the Treanor distribution function.	79
4.13	3 CO fundamental spectrum obtained by FT-IR spectroscopy and used to extract a line-of-sight average temperture of an (unfocused) optically pumped plasma.	81

4.14	Boltzmann plot and temperatures obtained from FT-IR fundamental spectra (see Figure 4.13) of the 3% CO/Ar optically pumped plasma with (i) no added helium and (ii) 42 torr helium added (refer to Figure 4.10). Also, the extend of "cold" CO self-absorption modeled using the HITRAN 2000 database is shown	82
4.15	Top view of the experimental setup for LIF measurements of either the glow discharge or optically pumped plasma. The inset shows the relation between LIF collection volume and plasma	84
4.16	Side-view illustration of the OMA and monochromator collection systems used for vibrational state resolved LIF measurements of the optically pumped plasma. Spacial dimensions shown are for entendue-matching conditions	86
4.17	Potential energy (Morse) diagram for carbon monoxide illustrating the relevant vibronic manifolds and LIF schemes	88
4.18	Vibrational state resolved D'-X band LIF using the OMA described in the text	89
4.19	Photograph showing the vertical mount and optical collection through the top viewport using the H-10 monochromator	91
4.20	 (a) Experimental LIF excitation scan due to X(v"=20)→D'(v'=2) absorption. (b) Synthetic spectrum generated using MoleLIF 	93
4.21	Experimental $X(v''=20) \rightarrow D'(v'=2)$ LIF excitation scans in an optically pumped plasma as a function of added helium	94
4.22] e	Experimental X(v"=20) \rightarrow D'(v'=2) P(15) LIF as a function of incident excimer beam energy.	95
4.23	Boltzmann plot of $X(v''=20) \rightarrow D'(v'=2)$ LIF along with least-squares fit of data and extracted rotational temperatures	98
4.24	Vibrationally resolved LIF spectrum generated using the narrowband ArF laser to pump the $X^1\Sigma^+(v''=7) \rightarrow A^1\Pi(v'=1) Q(10)$ rotational line. When tuned off resonance, the signal decreased by $\approx 70 \times$ (see lower trace near bottom of plot).	102
4.25	This high-resolution (0.05 nm spectral bandwidth), deep-UV spectrum of molecular oxygen shows total optical transmission between 175 – 200 nm, illustrating the strong influence of the Schumann-Runge bands in this spectral region.	104

4.26	5 Vibrationally resolved LIF spectrum generated using the narrowband ArF laser to pump a rotational line within the $X^1\Sigma^+(v''=12) \rightarrow$	
	$A^{1}\Pi(v'=8)$ absorption band	106
4.27	Bandpass characterization of the H-10 monochromator	108
4.28	 B (a) Experimental LIF excitation scan due to X(v"=7)→A(v'=1) absorption. (b) Synthetic spectrum generated using MoleLIF. 	111
4.29	Plot of both experimental and theoretical $Q(J'')$ ÷ $P(J'')$ ratios given in Table 4.4 as a function of ArF laser intensity	114
4.30	A-X LIF excitation spectra (a) unsaturated, linear regime(b) partially saturated regime	116
4.31	Boltzmann plot using "line-strength normalization of peak intensities given in Figure 4.30	117
4.32	2 Boltzmann plot of same data shown in Figure 4.30 except the partially saturated case has been "degeneracy" normalized. The P-Q branch offset nearly vanishes since the proper normalization is used	118
4.33	Excitation scans taken under mildly vibrationally excited conditions created by a CO/He d.c. normal glow discharge. (a) Saturated LIF experimental spectrum (b) MoleLIF Synthetic spectra	121
5.1	Typical geometry for planar LIF imaging of illuminated flowfield	123
5.2	Side-view illustration of the ICCD camera used for PLIF imaging and the entendue-matched LIF monochromator collection systems	127
5.3	Top view of the experimental setup for PLIF imaging of either the glow discharge or optically pumped plasma	128
5.4	<u>Left</u> : photograph of the ArF attenuation mirror, ASE mask, sheet-forming lens, and energy meter. <u>Right</u> : CaF ₂ window attenuation stack placed between the mask and ArF mirror	131
5.5	Top view of apparatus for creating the <u>Case B</u> environment	133
5.6	Geometry of <u>Case B</u> focusing and image coordinate system	135
5.7	A-X Q(10) vibrational state resolved LIF, ArF laser line, and urea filter transmission curve.	137

5.8	Single-shot ArF laser scattering images acquired in ambient room air without and with urea filter	139
5.9 I v	mage of C ₂ Swan and A-X band passive emission due to highly ribrationally excited CO without ArF laser excitatio	144
5.10	CO REMPD excitation scan using ArF laser intensity $\approx 60 \text{ MW/cm}^2$	145
5.11	Overlay of A-X band LIF and CO REMPD excitation scans to show potential interferences near Q(10) transition	147
5.12	Overlay of A-X band LIF and CO REMPD excitation scans to show potential interferences near Q(17) transition	148
5.13	Overlay of A-X band LIF and D'-X band LIF excitation scans to show potential interferences near Q(10) transition	149
5.14	Overlay of A-X band LIF and D'-X band LIF excitation scans to show potential interferences near Q(17) transition	150
5.15	A-X Q(10) LIF using spectral monitor to find on and off-resonance conditions. Note the boxcar time constant = 10 shots	151
5.16	Single-Shot A-X Q(10) PLIF; Case A "No Focus" plasma, f/4.5 aperture	153
5.17	Single Shot A-X Q(10) PLIF; Case B "Loose" Focus Plasma, f/4.5 aperture	154
5.18	18 Shot A-X Q(10) PLIF; <u>Case A</u> "No Focus" plasma, f/4.5 aperture	155
5.19	18 Shot A-X Q(10) PLIF; <u>Case B</u> "Loose" Focus Plasma, 18, f/11 aperture	156
5.20	Single Shot Histogram; A-X Q(10) PLIF Case A plasma, f/4.5 aperture	159
5.21	Single Shot A-X Q(10) PLIF; Case A "Tight" Focus Plasma, f/4.5 aperture.	161
5.22	3 Shot A-X Q(10) PLIF; <u>Case C</u> "Tight" Focus Plasma, f/5.6 Aperture	162
5.23	A-X band LIF excitation scan using spectral monitor; On & Off resonance	164
5.24	A-X band PLIF temperature measurements; Case A, High UV	171
5.25	A-X band PLIF temperature measurements; Case A, High UV	172
5.26	A-X band PLIF temperature measurements; Case A, High UV	173
5.27	A-X band PLIF temperature measurements; Case A, Low UV	174

5.28 A-X band PLIF temperature measurements; <u>Case B, Low UV</u> 175
5.29 <u>Case A LowUV</u> ; Boltzmann plot and Q-branch temperature 178
5.30 D'-X Vibrational state resolved LIF using a broadband ArF laser sheet with intensity ≈30 MW/cm ²
5.31 D'-X vibrational state resolved LIF with and without UG-11 imaging filter. Also, transmission for 2 mm thick UG-11 filter
5.32 D'-X P(15) LIF using spectral monitor to find on and off-resonance conditions. Note the boxcar time constant = 10 shots
5.33 Single Shot D'-X P(15) PLIF; <u>Case A</u> "No Focus" Plasma, f/4.5 aperture 186
5.34 Single Shot D'-X P(15) PLIF Case B "Loose Focus" Plasma, f/4.5 aperture187
5.35 35-Shot D'-X P(15) PLIF; <u>Case A</u> "No Focus" Plasma, f/4.5 aperture188
5.36 11-Shot D'-X P(15) PLIF; <u>Case B</u> "Loose Focus" Plasma, f/5.6 aperture 189
5.37 Gray scale histogram for <u>Case B</u> "Loose" Focus Plasma, P(15) Image 191
5.38 Gray scale histogram for <u>Case A</u> Plasma, P(15) imaging 191

CHAPTER 1

INTRODUCTION

1.1 LASER-INDUCED FLUORESCENCE DIAGNOSTIC POTENTIAL

Nonequilibrium, low translational temperature molecular plasmas form the basis of a wide variety of engineering systems used for materials processing [1], molecular gas lasers [2,3], pollution control [4], pre-ignition radical production for combustion rate enhancement [5], and radio-frequency (RF) sustained supersonic flows [6]. Such systems, by definition, are characterized by disequilibrium between internal degrees of freedom, particularly between the rotational/translational modes, vibrational mode, and electronic states. Since the partitioning of energy in such systems is dominated by kinetics of energy transfer and/or chemical reaction, accurate knowledge of rotational/translational temperature is extremely important. This is particularly true in systems in which substantial rotational/translational temperature gradients exists, either transiently or in the steady state.

Recently, much effort has been devoted to the study of shock wave propagation (M ~ 1.5 - 4.5) within weakly ionized (n_e/n ~ $10^{-8} - 10^{-6}$), nonequilibrium plasmas [7-13]. These steady-state, low translational temperature (≤ 1000 K) plasmas were typically

sustained by a d.c. normal glow discharge using various gases (air, CO₂, N₂, Ar, He) at modest pressure (3 - 100 torr). It has been inferred from line-of-sight optoacoustic measurements that, as the shock wave traverses the plasma region, it tends to (i) accelerate, (ii) weaken, and (iii) disperse and split [7-13]. Debate regarding the underlying mechanism for these observations has centered upon (i) a spatially nonuniform temperature distribution within the quiescent plasma due to joule heating, (ii) curvature of the shock front due to viscous shear stress at the wall, and (iii) electrostatic space-charge layers with large localized Joule heating near the shock front. Recent experimental and modeling efforts intended to separate thermal and charge-species mechanisms have been performed. For example, line-of-sight temperature measurements were performed [12] at various radial and axial locations within a steady, uniform, argon d.c. glow discharge at 30 torr by seeding the gas flow (100 ccm) with 3.3% CO and using spontaneous emission spectroscopy to rotationally-resolve the C₂ Swan bands. The results in this study indicated that the axial temperature variations were ~10 K while the radial gradient between the discharge centerline and the cell wall was ~600 K [12]. While these measurements were insightful, it is important to note that they did not spatially or temporally resolve thermal variations during the time interval in which the shock wave was propagating through the plasma. This thesis has been motivated by the need to acquire non-intrusive, spatially and temporally resolved temperature measurements in the vicinity of a propagating shock wave within a low density, low temperature, weakly ionized nonequilibrium plasma.

Numerous non-intrusive optical diagnostic techniques are available for flow visualization, temperature, and species concentration measurements [14-18]. For

example, time-resolved step-scan Fourier-Transform Infra-Red (FT-IR) spectroscopy [19] is relatively simple and has been used to study the kinetics of vibrational-vibrational energy transfer processes within low temperature, optically pumped CO plasmas (to be described below) [20]. While the time-resolution of this instrument can be on the order of nanoseconds, the step-scan technique requires a repetitively pulsed experiment and is hence not suitable for a single-pulse experiment such as a shock tunnel [20]. Furthermore, the technique provides only spatially-averaged information.

Filtered Rayleigh Scattering (FRS) has been used [21] to spatially resolve the temperature variations within a steady d.c. normal glow discharge consisting of either pure argon or a 1% N₂/Ar mixture at 50 torr. However, the signals are weak in this low density plasma and the technique suffers from stray scattering such that even single-point measurements required long integration times (~20 minutes) and a very specialized, high power injection seeded ti:sapphire laser. The extension of this technique to low density flows, especially helium, would present a significant challenge.

Spontaneous Raman scattering has been used in conjunction with a KrF excimer laser [16,22] and butyl acetate filter to perform temporally and spatially resolved point measurements of temperature within a lifted hydrogen jet diffusion flame at atmospheric pressure [22]. However, the signal levels are expected to be ~1000× lower than that of FRS in a low density plasma [14,16].

Laser Induced Fluorescence (LIF) has been proven to be a versatile and powerful tool, for nonintrusive measurement of both temperature and state selective species concentration, and has been demonstrated in a variety of harsh environments, such as flames and plasmas [14-16]. LIF is a relatively simple diagnostic which has the advantage that signal actually *increases* as the flow density decreases, due, as will be discussed in Chapter 2, to decreased collisional quenching. Time-resolving capability (~10 ns) is routinely obtained using an excitation source such as a pulsed excimer laser [16]. This type of laser has the additional advantage of high spectral brightness which is necessary for performing single-shot, spatially resolved imaging of selected species within the flow field [16]. Planar LIF imaging (PLIF) is an extension of LIF used to assess the spatial variation of flow properties [14-16]. For example, a narrowband (~0.5 cm⁻¹) ArF excimer laser has been used to perform single-shot PLIF imaging of a normal shock propagating through a mixture of 5% NO/Ar initially at 25 torr and 295 K using the NO $X^2\Pi(0,1)\rightarrow D^2\Sigma^+ R_2(28.5)$ absorption transition [23]. The spatial variation in fluorescence signal in the images reflected the evolving population of the NO ground electronic state $X^2\Pi(v''=1)$ vibrational level behind the propagating normal shock.

In this thesis we have developed a translational/rotational temperature measurement diagnostic, similar to that of Reference [23], for use within low temperature/density, steady state, monatomic plasmas (e.g., Ar or He) seeded with small amounts (~3 %) of carbon monoxide. As will be shown in Chapter 5, these proof-of-concept measurements indicate that this diagnostic has the potential for temporally resolved temperature measurements. In addition, this diagnostic may find broad applicability within thermally equilibrated environments at modest pressure (≤ 1 atm) and high temperature (~2000 K) so long as the LIF signal is not compromised by collisional quenching, particulate scattering, and interfering spectral emissions [14-16]. At higher pressures (>> 1 atm), other techniques such as spontaneous Raman scattering become more attractive than LIF due to increased signal levels [14,16].

1.2 LITERATURE SURVEY OF CO LIF DIAGNOSTICS

Carbon monoxide (CO) is particularly attractive as a thermometric tracer due to factors such as ease of seeding, relative chemical inertness and thermal stability. It also has a significant presence in many combustion system reaction products. A simplified potential diagram for CO, illustrating the states most relevant to the present discussion, is shown in Figure 1.1. Note that the ground electronic state, $X^1\Sigma^+$, is characterized by a deep potential well with a dissociation energy [24] of ~11 eV (89,460 cm⁻¹). Forty-two vibrational levels have been observed to date [20].

To date, most reported CO LIF diagnostic schemes for use in combustion have centered on the two-photon absorption Hopfield-Birge $X^{1}\Sigma^{+}\rightarrow B^{1}\Sigma^{+}$ system [25] using a tunable dye laser excitation source in the vicinity of 230 nm, followed by $B^{1}\Sigma^{+}\rightarrow A^{1}\Pi$ emission (Ångström system [25]) in the range 450-750 nm [26-29]. As shown in Figure 1.1, however, excitation from the ground electronic state (X) requires *two photons*, which introduces significant diagnostic complexity and results in relatively weak signals [14]. Nonetheless, planar imaging employing this scheme has been reported in one paper, but required use of a cylindrical multi-pass cell [27]. A second technique, two photon $X^{1}\Sigma^{+}$ - $A^{1}\Pi$ 4th Positive band [30,31] absorption (290 nm), has been reported [32-34] in atmospheric pressure flames, but the observed signals are also, typically, rather weak which can not generally be used in plasmas. Alternatively, spontaneous $B^{1}\Sigma^{+}\rightarrow X^{1}\Sigma^{+}$ fluorescence in the VUV (120 nm) has been observed by populating the $B^{1}\Sigma^{+}$ after laserassisted intermolecular collisional energy transfer [35], but this technique is not very general. Finally, planar imaging by excitation of a rotational line in the CO 1st overtone



Figure 1.1 CO potential energy diagram illustrating the vibronic states and transitions discussed in this chapter.

 $(2 \leftarrow 0)$ band near 2.35 µm with fundamental band emission collected (using appropriate filters) at 4.7 µm has been used as a flow visualization tool [36].

1.3 SINGLE-PHOTON LIF USING THE CO 4th POSITIVE BANDS

This thesis focuses on the development and application of *single-photon* LIF and PLIF temperature measurements in low density, vibrationally-excited nonequilibrium plasmas. It is evident from Figure 1.1 that when CO is highly vibrationally excited, several single photon allowed transitions become energetically accessible, particularly at the ArF excimer laser wavelength of 193 nm (51,800 cm⁻¹). For levels of approximately seven (or higher), single-photon absorption to the A¹ Π state becomes accessible [30,31,37], and for levels of approximately twenty (or higher), absorption to the D^{,1} Σ^+ becomes accessible [38-45]. As will be discussed in Chapters 2 and 4, all of these excitation possibilities (both single and two photon) are readily distinguishable by simple spectroscopic selection rules.

In Chapter 4, we describe temperature measurements in *highly* vibrationally excited environments (v≤42) using single photon LIF of carbon monoxide [46,47]. This scheme employs a diagnostic strategy that takes advantage of a strong single-photon allowed absorption between the v"=20 level of the $X^1\Sigma^+$ ground electronic state and the v'=2 level of the D' $^1\Sigma^+$ excited electronic state [46]. This scheme was found to have significant temperature measurement potential (±50 K or better) in systems exhibiting extreme vibrational disequilibrium. As mentioned above, however, many important engineering systems such as glow discharge plasmas and flames are characterized by more modest levels of vibrational excitation.

A second LIF temperature diagnostic, based on the *single photon* allowed CO $X^{1}\Sigma^{+}(v''=7) \rightarrow A^{1}\Pi(v'=1)$ (4th Positive) transition has also been developed, for use in *mildly nonequilibrium* (v ≤ 8) plasmas and possibly combustion flows [47-49].

1.4 SCHEMES FOR VIBRATIONAL EXCITATION

Recently, it has been established that the CO laser [50,51] can be used to initiate and sustain electron production in mixtures of CO and a variety of noble gas and diatomic buffers using a process (described below) referred to as "optical pumping" [20,52-60]. Molecular species within these relatively cool (T < 2000 K), weakly ionized plasmas typically exhibit only modest ($v \le 8$) levels of vibrational excitation. Note that these conditions may sometimes be characteristic of flames and combustion systems [61] in complete thermal equilibrium if the temperature is sufficiently high.

The single-photon CO LIF diagnostic takes advantage of the fact that the vibrational distribution function (VDF) of the ground electronic state, $X^{1}\Sigma^{+}$, of CO may attain a non-Boltzmann character for both optically-pumped [20,52-55] and glow discharge [2,3,62-65] CO gas mixtures. Briefly, the process of *optical pumping* consists of two mechanisms, (i) "triggering" within a test cell by the direct excitation of the CO (seed gas) vibrational levels v<10 via resonance absorption of mid-IR (\approx 4.8 µm) laser radiation and (ii) collisional V-V exchange processes [53,66]. The triggering radiation is

produced by a continuous wave (cw), liquid nitrogen cooled CO laser [50,51] with output on the lowest 10 fundamental vibrational lines in a single photon stepwise process

$$CO(v-1) + hv \rightarrow CO(v)$$
 (1.1)

Cryogenically cooling the laser allows emission on low vibrational transitions of CO, down to $2\rightarrow 1$ (and, in some cases, $1\rightarrow 0$), which are essential for initiating the second process; anharmonic collisional V-V up-pumping [53,66]:

$$CO(v) + CO(w) \Leftrightarrow CO(v-1) + CO(w+1), \tag{1.2}$$

where v and w are vibrational quantum numbers such that w>v. The up-pumping is driven by the anharmonicity of the intramolecular potential, which results in the process described by Equation (1.2) being exothermic in the forward direction. Detailed balance [53,64,67,68] then requires that the forward rate of Equation (1.2) to exceed the reverse rate:

$$\frac{k_{f}}{k_{b}} \propto e^{\frac{\Delta E}{kT}} > 1 \quad , \tag{1.3}$$

where $\Delta E \equiv (E_v - E_{v-1}) - (E_{w+1} - E_w) > 0$ is the so-called "resonance defect", so that the molecule with the larger initial quantum number, w, are preferentially excited by the forward V-V energy transfer process. This mechanism can produce an overpopulation of

high vibrational levels on condition that any vibration-translation (V-T) energy transfer rates (either with CO itself or admixture species) are slow compared to the V-V energy transfer rate. In the case of CO seeded (3%) gas mixtures not containing fast V-T relaxants (*e.g.*, He) [66,67] and V-V relaxants (*e.g.*, H₂O, O₂, N₂) [66,67] optical pumping is known to produced significant CO vibrational populations (0.1% up to v=30) at low translational temperatures (T<700 K depending on CO concentration) [18]. In atmospheric *dry* air with modest CO laser intensity (~10 W/cm²), V-V energy transfer from CO has been shown to mildly vibrationally excite O₂ and N₂ (v≤13, again depending on species concentrations) [55]. Electron production in optically-pumped CO/Ar mixtures [56] proceeds via associative ionization:

$$AB(v) + AB(w) \rightarrow AB_2^+ + e^-$$

$$E_v + E_w > E_{ion}$$
(1.4)

where AB is any diatomic molecule, E_j is vibrational energy within level j, and E_{ion} is the ionization potential of the diatomic AB. Estimated [56] steady-state electron densities sustained by a 10 W CO laser in optically-pumped CO/Ar/He mixtures with vibrational level populations $n_{co}(v\sim30)\approx10^{15}$ cm⁻³ are $n_e\sim10^{10}-10^{11}$ cm⁻³.

In the d.c. glow discharge environment, energy flows into the lower vibrational states ($v\leq8$, especially v=1) via direct electron-vibration (e-V) excitation [69-71] with subsequent excitation to even higher levels by means of Equation (1.2) V-V quanta exchange [53,66]. Although associative ionization does occur within a normal glow discharge for diatomic/noble gas mixtures (along with electron impact ionization in the

positive column), the primary means of net electron generation at low diatomic concentrations is secondary emission at the cathode with subsequent acceleration through the large potential gradient within the cathode sheath [1,3,64,67,71]. While mean electron energies and densities are on the order of 2-3 eV and 10^{10} cm⁻³, respectively, translational temperatures remain low (T≤700 K). As in the optically-pumped environment at these moderate temperatures, the forward rate of CO "up-pumping" exceeds the backward rate in Equation (1.3) for vibrational levels less than ≈30 to the extent that the net rate compensates for the depopulating mechanisms of fast V-T and V-V relaxation on light atomic species (*eg.* helium) [67] and dissociation products (*eg.* CO₂, C₂, C₂O, O) [20,52,57,60,62,63] that tend to truncate the VDF. Even with translational temperatures greater than 500 K (5% CO/helium mixtures), significant X(v″=7) populations (0.4%) have been routinely observed [62].

1.5 SURVEY OF CHAPTERS

This thesis contains 6 chapters. In Chapter 2 we describe the fundamental LIF processes and develop a theoretical framework for extracting the trans-rotational temperature from experimentally obtained LIF signals.

In Chapter 3, we discuss the general diagnostic strategy using a tunable, narrowband ArF excimer laser to perform single-photon A-X and D'-X band LIF. This discussion involves the suitable choice of absorption transitions which provide optimum signal levels along with maximum temperature measurement sensitivity.

In Chapter 4, we first discuss the characterization of both highly and mildly vibrationally excited model plasma environments using FT-IR emission spectroscopy. Next, we use vibrational state resolved LIF of the optically pumped plasma to explore filtering schemes (aqueous urea and UG-11) necessary to suppress stray light scattering of the fundamental ArF laser radiation as well as extraneous band emissions. Later in the chapter, we present spatially and temporally averaged temperature measurements of these steady state environments using this diagnostic for both the A-X and D'-X bands and then compare the results to those obtained by FT-IR spectroscopy.

In Chapter 5, we present both single-shot and time averaged, spatially resolved, A-X band PLIF imaging and temperature measurements within a steady state, optically pumped plasma exhibiting extreme vibrational disequilibrium. We also present temporally resolved PLIF images of this plasma using the D'-X band.

Chapter 6 concludes by discussing future directions and applications of the diagnostic technique developed in this thesis.

CHAPTER 2

DETERMINATION OF ROTATIONAL-TRANSLATIONAL TEMPERATURE BY LASER-INDUCED FLUORESCENCE

2.1 LASER-INDUCED FLUORESCENCE

Spectroscopic diagnostics such as Laser-Induced Fluorescence (LIF) use electromagnetic quanta (photons) to probe discrete energy state populations through the processes of scattering, absorption, and emission [14]. By this method, we acquire statistical information regarding the population distribution that, in turn, can be used to quantify certain macroscopic properties of the gas. In particular, if the state population is in *thermodynamic equilibrium* at a unique temperature T (K), then the fraction of particles in the ith energy state obeys the Boltzmann distribution [68]

$$\beta(T) \equiv \frac{n_i}{n^o} = \frac{g_i}{Z(T)} e^{-\frac{E_i}{kT}}$$
, (2.1)

where n_i is the population number density (molecules/cm³) of the ith state, n^o is the total number density, E_i is the ith level energy (J or cm⁻¹), g_i the level statistical

degeneracy, Z(T) the partition function, and k is Boltzmann's constant (J/K or cm⁻¹/K). Note that $\beta(T)$ is typically referred to as the "*Boltzmann fraction*". If the population cannot be described by Equation 2.1, then the distribution is called *nonequilibrium* in which a single parameter describing "temperature" cannot be uniquely defined [65,68]. Depending upon energy transfer timescales, it is possible to consider some energy modes (translation, vibration, *etc.*) as if they were in thermal equilibrium while the population of other modes must be considered strictly nonequilibrium. For the present work we will consider the CO molecule translation and rotational modes to be in mutual thermal equilibrium at temperature T, while the vibrational mode is nonequilibrium with a predetermined distribution function, f_v . In this case, the population fraction then becomes $f_{v,l} = f_v \beta(T)$.

2.2 THE STEADY STATE THREE-LEVEL LIF MODEL

Atomic or molecular fluorescence is defined as the *spontaneous emission* of a photon from a higher energy state to a lower state of the same total electronic spin multiplicity [72]. The excited state can be populated by numerous means (*e.g.*, inelastic collisions) [1-3,60-67,73] while many pathways also exist for radiative and nonradiative relaxation. Laser-Induced Fluorescence (LIF) refers to the use of coherent polarized laser radiation to populate, via resonant *stimulated absorption*, an upper energy level that exhibits quantum mechanically allowed fluorescence channels [14].

Figure 2.1 is a conceptual energy-level diagram illustrating common LIF processes. Each arrow represents a process occuring at a rate proportional to the

population of the level from which it points. Single-photon *resonant absorption* at wavelength λ_{12} (or frequency v_{12}) is denoted by the arrow in Figure 2.1 from level (1) to level (2) and occurs at the rate $n_1 \cdot W_{12}$ (molecules/s-cm³), where n_1 is the level (1) population number density during laser excitation and W_{12} (s⁻¹) is the *rate coefficient* for



Figure 2.1 Conceptual energy-level diagram illustrating the important processes involved in LIF.

stimulated absorption [14]. Fluorescence is indicated by wavy arrows from level (2) to (1), (3), ..., (i), each occuring in parallel at the rate $n_2 \cdot A_{2i}$ with wavelengths λ_{2i} , where n_2 is the level (2) number density during laser excitation and the A_{2i} (s⁻¹) are the Einstein transition probabilities for spontaneous emission (*i.e.*, "A-coefficients"). Note that the total fluorescence rate is $n_2 \cdot A_2^{\text{eff}}$, where we define [14,15]

$$\mathbf{A}_{2}^{\mathrm{eff}} \equiv \sum_{i} \mathbf{A}_{2i} = \frac{1}{\tau_{2}^{\mathrm{eff}}}$$
(2.2)

such that τ_2^{eff} is the e-fold decay "lifetime" (s) of level (2). Transitions from levels (3)...(i) \rightarrow (1), depicted as dashed arrows in Figure 2.1, are assumed to have either infinite rates or at least very fast in comparison to n_1W_{12} and n_2A_{2i} . This implies that our model is a classic "three-level" system in which the fine structure populations of all levels are assumed to be either *frozen*, with no transfer to adjacent levels, or *completely relaxed* [14]. This latter case is valid when very rapid rotational energy transfer [14,67,74-81] is known to establish a Boltzmann distribution within the manifold of rotational states [14].

The laser radiation field itself induces a depopulation of the excited state occuring at a rate $n_2 \cdot W_{21}$ and wavelength $\lambda_{21} = \lambda_{12}$, where W_{21} is the rate coefficient for *stimulated emission* [14,15] in Figure 2.1. Elaborated upon below in detail, an important condition called "*saturation*" occurs when the rate $n_2 \cdot W_{21} \sim n_1 \cdot W_{12}$ [14]. Finally, Figure 2.1 shows two commonly encountered energy exit channels that "drain" population from level (2); (i) fast molecular predissociation (rate coefficient P) and (ii) nonradiative collisional energy transfer ("*quenching*") to another particle (rate coefficient Q) [14,15].

Using the energy level notation in Figure 2.1, it is useful to define the fraction of isotropically fluorescing photons that pass through a bandpass filter and impinge upon the detector photocathode:

$$\varphi \equiv \frac{A_{21}\eta_{21} + A_{23}\eta_{23} + \dots etc}{A_2^{\text{eff}}} \cdot \frac{\Omega}{4\pi} \equiv \frac{\overline{A}_2^{\text{coll}}}{A_2^{\text{eff}}} \cdot \frac{\Omega}{4\pi} \quad , \qquad (2.3)$$

where \bar{A}_2^{coll} is the sum of "weighted" A-coefficients, $\eta(\lambda)$ is the wavelength dependent transmission function, and $\Omega/4\pi$ is the *solid angle collection efficiency* [14,15] representing the fraction of solid angle Ω (steradians) subtended between the LIF probe volume V (cm³) and collection lens. Implicit within the definition of Equation 2.3 is the assumption there is no vibration-vibration (V-V) population transfer within the finestructure of level (2). Note that this is consistent with the frozen level model discussed above. With this understanding, Equation 2.3 can be simplified if it is assumed that the transmission function has equal weight for each emission band wavelength;

$$\overline{A}_{2}^{\text{coll}} \simeq A_{2}^{\text{coll}} \eta_{\text{bp}} \quad , \tag{2.4}$$

where A_2^{coll} (s⁻¹) is the sum of the appropriate A-coefficients and η_{bp} is the bandpass transmission. The rate at which these selected photons impinge upon the detector is

$$\dot{N}_{p} = n_{2} A_{2}^{\text{eff}} \phi V \simeq n_{2} A_{2}^{\text{coll}} \frac{\Omega}{4\pi} V \eta_{bp} \qquad , \qquad (2.5)$$

while the rate at which photoelectrons (i.e., signal, "S") are generated is

$$S = n_2 A_2^{\text{coll}} V \frac{\Omega}{4\pi} \eta_{bp} \eta_{qe} \quad , \qquad (2.6)$$

where η_{qe} is the photocathode quantum efficiency.
To express n_2 in terms of key experimental parameters, we first define a population constraint such that the total number density of resonant absorbers in level (1) *prior* to laser excitation is [14]

$$\mathbf{n}_1^{\circ} \equiv \mathbf{n}_1 + \mathbf{n}_2 \qquad . \tag{2.7}$$

Note that the Boltzmann fraction for the level 1 population according to Equation 2.7 is

$$\beta(T) = \frac{n_1^{\circ}}{n^{\circ}} \quad . \tag{2.8}$$

From Figure 2.1, the rate equation governing level (2) can be written [14]

$$\frac{dn_2}{dt} = n_1 W_{12} - n_2 \left[W_{21} + A_2^{\text{eff}} + Q + P \right] \quad .$$
(2.9)

Assuming steady-state conditions by setting $dn_2/dt \equiv 0$, Equations 2.7 and 2.9 are solved for n_2 and rearranged in the following form [14]:

$$n_{2} = n_{1}^{o} \cdot \left[\frac{\frac{W_{12}}{W_{12} + W_{21}}}{1 + \frac{A_{2}^{eff} + Q + P}{W_{12} + W_{21}}} \right] .$$
(2.10)

The rate coefficients W_{12} and W_{21} can be expressed in terms of the incident laser intensity per unit frequency bandwidth, or *spectral irradiance* I_v (W/cm²-GHz) and the Einstein transition probabilities for stimulated absorption and emission, B_{12} and B_{21} (cm³/W-s³) [14,15]:

$$W_{12} = \frac{B_{12}I_v}{c}, \qquad W_{21} = \frac{B_{21}I_v}{c}$$
 (2.11a,b)

where c is the vacuum speed of light (cm/s). Note that these Einstein "B-coefficients" are related by [14,15]

$$g_2 B_{21} = g_1 B_{12} \tag{2.12}$$

where g_1 and g_2 are degeneracies of levels (1) and (2). A second independent relation between spontaneous and stimulated emission is [14,15]

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h}{\lambda_{21}^3} \qquad . \tag{2.13}$$

Equations 2.11a,b substituted into Equation 2.10 yields

$$n_{2} = n_{1}^{o} \cdot \frac{B_{12}}{\left[B_{12} + B_{21}\right] \left[1 + \frac{I_{v}^{sat}}{I_{v}}\right]}$$
(2.14)

where the saturation spectral irradiance (W/cm²-GHz) is defined as [14]

$$I_{\nu}^{\text{sat}} = \frac{A_{2}^{\text{eff}} + Q + P}{\frac{1}{c} \cdot \left[B_{12} + B_{21} \right]} \qquad (2.15)$$

Using Equation 2.12, Equation 2.15 can be written in the alternative form

$$I_{v}^{\text{sat}} = \frac{A_{2}^{\text{eff}} + Q + P}{\frac{B_{12}}{c} \cdot \left[1 + \frac{g_{1}}{g_{2}}\right]} \quad .$$
(2.16)

Combining Equations 2.6, 2.8, 2.12, and 2.14, the steady-state LIF signal (photoelectrons/s) can be written as

$$S = n^{\circ}\beta(T)B_{12} \cdot \left[\frac{A_{2}^{\text{coll}}}{B_{12} + B_{21}}\right] \cdot \Phi\left(\frac{I_{v}}{I_{v}^{\text{sat}}}\right) \eta V , \qquad (2.17)$$
$$= n^{\circ}\beta(T) \cdot \frac{A_{2}^{\text{coll}}}{\left[1 + \frac{g_{1}}{g_{2}}\right]} \cdot \Phi\left(\frac{I_{v}}{I_{v}^{\text{sat}}}\right) \eta V$$

where we have lumped the efficiencies into $\eta \equiv (\Omega/4\pi) \cdot \eta_{qe} \cdot \eta_{bp}$ and defined a nondimensional fluorescence rate as

$$\Phi\left(\frac{I_{v}}{I_{v}^{\text{sat}}}\right) \equiv \frac{1}{1 + \frac{I_{v}^{\text{sat}}}{I_{v}}} \qquad (2.18)$$

2.3 LINEAR, NON-LINEAR, AND SATURATED LIF REGIMES

Two important limits of Equation 2.17 are known as the *linear* and *saturation* regimes [14]. In this section we derive simpler limiting forms of Equation 2.17 that will be used to analyze experimental data.

2.3.1 THE LINEAR LIF REGIME

The *linear regime* can be illustrated by first multiplying the numerator and denomenator of Equation 2.18 by I_v/I_v^{sat} and then expanding as a geometric series:

$$\Phi = \frac{\mathbf{I}_{v}}{\mathbf{I}_{v}^{\text{sat}}} - \left[\frac{\mathbf{I}_{v}}{\mathbf{I}_{v}^{\text{sat}}}\right]^{2} + O\left(\left[\frac{\mathbf{I}_{v}}{\mathbf{I}_{v}^{\text{sat}}}\right]^{3}\right) , \quad \mathbf{I}_{v} < \mathbf{I}_{v}^{\text{sat}} .$$
(2.19)

Note from Equation 2.19 that if $I_v \ll I_v^{sat}$, then the first-order linear term dominates and, as shown in Figure 2.2 the response is approximately linear up to $I_v/I_v^{sat} \approx 0.10$. In this limit Equation 2.17 becomes [14]

$$S^{\text{lin}} = n^{\circ}\beta(T) \cdot \frac{\mathbf{B}_{12}\mathbf{I}_{\nu}}{c} \cdot \mathbf{Y}_{2}\eta \mathbf{V}$$
(2.20)

where the *fluorescence quantum yield* (or, "Stern-Vollmer coefficient") is defined as [14,15]

$$Y_{2} \equiv \frac{A_{2}^{\text{coll}}}{A_{2}^{\text{eff}} + Q + P} \,. \tag{2.21}$$

Physically, the linear regime corresponds to an ideal case where the rate of stimulated emission is negligable compared to absorption; $n_2W_{21} \ll n_1W_{12}$. Using Equations 2.11a,b and 2.12 we find that [14]

$$\frac{W_{21}}{W_{12}} = \frac{g_1}{g_2} \sim O(1) \tag{2.22}$$

so that $n_2W_{21} \ll n_1W_{12}$ implies

$$\mathbf{n}_2 \ll \mathbf{n}_1 \tag{2.23}$$

within the linear LIF regime.

One of the most challenging aspects of using LIF for absolute concentration and temperature measurements can be the evaluation of the quench rate, Q, which in general depends on the energy levels probed and the spatial distribution of gas composition and



Figure 2.2 Nondimensional Fluoresence Signal vs. Nondimensional Irradiance showing the linear, non-linear, and saturated LIF regimes.

temperature [14]. Several methods are outlined in the literature dealing with this issue: (i) performing time-resolved LIF to measure quenching and energy transfer rates directly, (ii) semi-empirical quenching estimates, and (iii) work within the saturated LIF regime [14]. Simple quenching estimates based on available cross-section data are typically calculated using [14,68]

$$Q = \sum_{i} n_i \sigma_i v_i \qquad , \qquad (2.24)$$

where n_i is the number density of the deactivating species, σ_i the cross-section (cm²) for deactivation, and v_i the relative velocity (cm/s) of species i and the deactivated species. The relative velocity is [14,68]

$$v_i = \sqrt{\frac{8kT}{\pi\mu_i}} \quad , \tag{2.25}$$

where the reduced mass is $\mu_i \equiv m_i M/(m_i+M)$, and m_i , M are the molecular weights (kg/kmol) of the deactivating species and deactivated species, respectively. When applying Equation 2.24, it must be kept in mind that (i) tabulted σ_i data are typically valid for a limited temperature range, (ii) σ_i can often be energy level dependent, and (iii) σ_i for dipolar diatomic rotational energy transfer can actually exceed that computed using a *gas kinetic* (hard-sphere) approximation [14] (this is borne in the literature for CO-CO

vibrational quenching cross-sections for the $A^1\Pi$ [82-84] shown in Table A.1, Appendix A).

2.3.2 THE NON-LINEAR LIF REGIME (PARTIAL SATURATION)

The regime defined approximately between $0.10 \le I_v/I_v^{sat} \le 10$ will be referred to here as the *non-linear*, or *partially saturated* LIF regime. As shown in Figure 2.2 it is characterized by a slow asymptotic rolloff in $\Phi(I_v/I_v^{sat})$ due to a non-negligable stimulated emission rate, n_2W_{21} . Two LIF cases are denoted in Figure 2.2 in which I_v^{sat} for a one absorption line (Case B; $I_v/I_v^{sat,B} = 0.4$) is taken to be half that of another (Case A; $I_v/I_v^{sat,A} = 0.2$) while the spectral irradiance I_v is the same. As a consequence, the nondimensional LIF signal for Case B exhibits greater deviation from linearity compared to that of Case A. This situation will be encountered in later chapters when we perform LIF using two separate rotational branch transitions (P & Q) having differing I_v^{sat} . In Section 2.5 below we will show that, unless $\Phi(I_v/I_v^{sat})$ is known for each branch transition, the temperature measurement calculations should be performed using each branch seperately.

2.3.3 THE SATURATED LIF REGIME

The *saturated* regime is obtained by observing the limit $\Phi \rightarrow 1$ as $I_v^{sat}/I_v \rightarrow 0$ in Equation 2.18 so that Equation 2.17 becomes [14]:

$$S^{\text{sat}} = n^{\circ}\beta(T)B_{12} \cdot \left[\frac{A_2^{\text{coll}}}{B_{12} + B_{21}}\right] \cdot \eta V$$

$$= n^{\circ}\beta(T) \cdot \frac{A_2^{\text{coll}}}{\left[1 + \frac{g_1}{g_2}\right]} \cdot \eta V$$
(2.26)

From Equations 2.12 and 2.14, we note that the saturation condition implies

$$\mathbf{n}_2 = \left(\frac{\mathbf{g}_2}{\mathbf{g}_1}\right) \cdot \mathbf{n}_1 \sim \mathbf{n}_1 \qquad . \tag{2.27}$$

For practical purposes, "saturation" will be defined here as $I_v/I_v^{sat} \ge 10$ (see Figure 2.2). This regime has a number of advantages; first, the LIF emission rate is now *independent* of incident irradiance and quenching rate, Q [14]. An important consequence of this is that as $\Phi \rightarrow 1$, the detected signal is directly proportional to the unknown Boltzmann fraction, lending quenching corrections unnecessary. Second, the LIF signal is maximized, providing the highest species detection sensitivity [14]. Third, the signal becomes insensitive to random fluctuations in spectral irradiance. This point has been illustrated in Figure 2.2 for the two cases (C) and (D); $I_v/I_v^{sat,C} = 2$ and $I_v/I_v^{sat,D} = 4$. However, it must be noted that several problems are associated with using the saturated regime. For example, high intensities have the potential to be *intrusive* with such effects as laser-induced photochemistry or even electrical breakdown within the gas [14]. All of these points will be encountered in later chapters regarding the experimental data.

2.4 CARBON MONOXIDE SINGLET-SINGLET ROVIBRONIC TRANSITIONS

The three-level model as shown in Figure 2.1 is insufficient to describe the details of rotational LIF for the specific case of CO $A^{1}\Pi - X^{1}\Sigma^{+}$ (4th Positive) [24,30,31,37] and $D'^{1}\Sigma^{+} - X^{1}\Sigma^{+}$ [38-45] bands. We now expound upon Equation 2.17 in terms of the rovibrational manifold of levels within each electronic state as well as the rules associated with transitions. It should be re-emphasized that this three-level model assumes no V-V population transfer in the upper electronic state subsequent to laser excitation.

Figure 2.3 is a CO potential energy diagram in which single-photon absorption has been highlighted for the X–A and D', while two-photon absorption is shown for the X–B. The singlet nature of these electronic states allows us to use a *symmetric top* model in which the total rotational quantum number is [15,25,72,76]

$$\mathbf{J} = \Lambda, \ \Lambda + 1, \ \Lambda + 2, \ \dots \qquad , \tag{2.28}$$

where Λ is the quantum number for the internuclear component of electron angular momentum (for a Σ -state, Λ =0 while for Π -states, Λ =1).



Figure 2.3 CO potential energy diagram illustrating the vibronic states and transitions discussed in this chapter.



Figure 2.4 Energy level and transition diagram for the CO $X^1\Sigma^+$ - $A^1\Pi$ band. The $X^1\Sigma^+$ - $D'^1\Sigma^+$ is similar (refer to text).

Figure 2.4 is a conceptual energy diagram similar to Figures 2.1 and 2.3 except that some levels within the rovibrational manifold of the ground $(X^1\Sigma^+)$ and upper electronic states $(A^1\Pi \text{ or } D'^1\Sigma^+)$ have been distinguished. We now change notation to be consistent with spectroscopic literature; a double-prime (") will now denote the ground electronic state $(X^1\Sigma^+)$ while single-prime (') denotes the upper $(A^1\Pi \text{ or } D'^1\Sigma^+)$. Note that the upper electronic state in Figure 2.4 represents the $A^1\Pi$ where the first rotational level must begin with quantum number J=1. However, the only change necessary to represent the $D'^1\Sigma^+$ case is the allowance for J=0 [25]. Identification of A–X bands in LIF spectra is straightforward because it is easily distinguished from either the two-photon X→B (see Figure 2.3) or the single photon $X\rightarrow D'$ based on simple selection rules [14,25]. Since the single-photon X→A is ${}^{1}\Sigma{}^{-1}\Pi$, we expect to observe, within the *linear* LIF regime, P, Q, and R branches with the emission intensity of the Q branch being approximately double that of the P and R. The spectroscopic selection rules for rotational transitions within the A–X bands are [25,72]

$$\Delta \mathbf{J} = \begin{cases} -1 \; ; \; \text{ P-branch} \\ 0 \; ; \; \text{ Q-branch} \\ +1 \; ; \; \text{ R-branch} \end{cases}$$
(2.29)

where $\Delta J \equiv J'-J''$. Figure 2.4 illustrates the P(3) absorption line $X(v'',J''=3) \rightarrow A^1\Pi(v',J'=2)$ with subsequent fluorescence to all possible lower states X(v'',J'') consistent with these selection rules. In the case of single-photon $X \rightarrow D'$, the transition is ${}^{1}\Sigma - {}^{1}\Sigma$ so we expect a simple set of P/R branches in contrast to the two-photon $X^{1}\Sigma \rightarrow B^{1}\Sigma$ which is dominated by an unresolved Q branch [27]. For the X–D' bands the spectroscopic selection rules for rotational transitions are [25,72]

$$\Delta \mathbf{J} = \begin{cases} -1 \; ; \; \text{ P-branch} \\ +1 \; ; \; \text{ R-branch} \end{cases}$$
(2.30)

In addition to these selection rules, each transition has an inherent probability, or "strength", of occuring based upon the square magnitude of the electric dipole transition-

moment vector, $|\mathbf{R}|^2$ (debye²) [25,72]. Under the Born-Oppenheimer approximation, the nuclear and electronic motions are considered to be decoupled so that the total wavefunction can be separated into a product of vibrational, electronic, and rotational parts [25,72,88]. The transition-moment vector \mathbf{R} can then be separated into a product of functions that represent the transition strength for each mode. For heteronuclear diatomic molecules, the Einstein B-coefficient for rovibronic stimulated absorption is [25,88]

$$\mathbf{B}_{\mathbf{v}''\mathbf{J}',\mathbf{v}'\mathbf{J}'}^{abs} = \frac{\lambda_{\mathbf{v}'\mathbf{J}',\mathbf{v}'\mathbf{J}''}^{3}}{8\pi\hbar} \mathbf{A}_{\mathbf{v}'\mathbf{v}''} \left[\frac{2 - \delta_{0\Lambda'}}{2 - \delta_{0\Lambda'} \delta_{0\Lambda''}} \right] \hat{\mathbf{s}}_{\mathbf{J}'\mathbf{J}''}$$
(2.31)

where $\lambda_{v'J',v''J''}$ is the transition wavelength, $A_{v'v''}$ are vibronic transition Einstein Acoefficients, and $\delta_{0\Lambda''}$ and $\delta_{0\Lambda'}$ are the Kroneker deltas defined as [88]

$$\delta_{0\Lambda} \equiv \begin{cases} 1 & \text{if } \Lambda = 0 \\ 0 & \text{otherwise} \end{cases}$$
(2.32)

For all electronics states involved here,

$$\left[\frac{2-\delta_{0\Lambda'}}{2-\delta_{0\Lambda'}\delta_{0\Lambda''}}\right] = 1 \qquad (2.33)$$

and hence this expression will not be explicitly included in further equations. The $\hat{s}_{J'J''}$ term in Equation 2.31 is called the *normalized* Hönl-London rotational "line-strength" factor defined as [25,27,89]

$$\hat{s}_{J'J''} \equiv \frac{S_{J'J''}}{2J''+1}$$
 , (2.34)

where $S_{J'J''}$ is the "Hönl-London factor" typically quoted in literature. For each branch of the $X^{1}\Sigma^{+}-A^{1}\Pi$, these $S_{J'J''}$ factors are [25,72,89]

$$S_{J'J''} = \begin{cases} \frac{1}{2}(J''-1) &= \frac{1}{2}J' & ; P-branch\\ \frac{1}{2}(2J''+1) &= \frac{1}{2}(2J'+1); Q-branch\\ \frac{1}{2}(J''+2) &= \frac{1}{2}(J'+1); R-branch \end{cases}$$
(2.35)

while for the $X^1\Sigma^+$ – $D'^1\Sigma^+$ they are [25,89]

$$S_{J'J''} = \begin{cases} J'' = J' + 1 ; & P-branch \\ J'' + 1 = J' ; & R-branch \end{cases}$$
(2.36)

It is important to note the so-called rotational sum rule [25]: *the sums of the line strengths of all the transitions from or to a given rotational level are proportional to to statistical weight of that level.* A consequence of this rule is [25]

$$\sum_{\Delta J=-1}^{1} \hat{s}_{J'J''} = 1 . \qquad (2.37)$$

Note that Equation 2.37 can be easily verified by simply adding each term together in Equation 2.35 (or 2.36) and dividing by 2J''+1 (or 2J'+1) when $\hat{s}_{J'J''}$ is expressed in terms of lower levels (or upper levels). From Equations 2.13 and 2.31, the rovibronic Einstein A-coefficient is [88]

$$A_{v'J',v''J''} = A_{v'v''} \frac{S_{J'J''}}{2J'+1} \qquad (2.38)$$

Numerical values of $A_{v'v''}$ obtained from literature [31] for the A-X band and used in this work are listed in Table A.2 of Appendix A. Assuming that level (2) is frozen with respect to v', (*i.e.*, *no V-V population transfer* within the upper vibronic manifold) but is in equilibrium with respect to J' [14,74-81], and using Equation 2.38, the J-independent effective Einstein A-coefficient (see Equation 2.2) is

$$A_{v'}^{eff} = \sum_{v''=0}^{v'_{max}} \sum_{\Delta J=-1}^{+1} A_{v'J',v'J'} = \left(\sum_{v''=0}^{v'_{max}} A_{v'v''}\right) \cdot \left(\sum_{\Delta J=-1}^{+1} \frac{S_{J'J''}}{2J'+1}\right) \quad ,$$
(2.39)

where v' is the upper vibronic level directly pumped by resonant laser absorption and v''_{max} is the total number of vibrational levels in the ground electronic state (for CO, forty-two levels have been observed to date [20]). To see that Equation 2.39 is

independent of J, we substitute Equation 2.37 with $S_{J'J''}$ expressed in terms of J' into Equation 2.39, finding

$$\mathbf{A}_{\mathbf{v}'}^{\text{eff}} = \sum_{\mathbf{v}''=0}^{\mathbf{v}''_{\text{max}}} \mathbf{A}_{\mathbf{v}'\mathbf{v}''} \quad .$$
(2.40)

Literature values [31] for the effective lifetimes are given in Table A.2 in Appendix A. By a similar argument, the total spontaneous emission rate for "collected" LIF from vibronic band transitions, also independent of J, is

$$A_{v'}^{coll} \simeq \sum_{v''} A_{v'v''}$$
 , (2.41)

where now the summation is over *only* those LIF vibronic bands transmitted through the bandpass filter. The total statistical weight (valid only for $J \ge S + \Lambda$ in ${}^{1}\Sigma$, ${}^{1}\Pi$, ${}^{1}\Delta$, etc., and ${}^{2}\Sigma$ -states in *heteronuclear* diatomic molecules) is [88]

$$g = (2 - \delta_{0\Lambda})(2S + 1)(2J + 1) = \begin{cases} 2J + 1 & ; X^{1}\Sigma^{+} \text{ and } D'^{1}\Sigma^{+} \\ 2(2J + 1) & ; A^{1}\Pi \end{cases}$$
(2.42)

where the S is the total electron spin quantum number (for the present singlet states, S=0). In Equation 2.42, the prefactor $2-\delta_{01}=2$ for the A¹ Π accounts for degenerate Λ -doublet states of e/f parity at each rotational level, J [76,88].

2.5 ROTATIONAL TEMPERATURE EXTRACTION FROM LIF SPECTRA

The diagnostic strategy is to probe the thermalized rotational population distribution function of a single vibrational level within the ground electronic state via resonant absorption resulting in the fluorescence signal given by Equation 2.17 [14-16]. Here we discuss the extraction of rotational temperature from experimental spectra using either the *"Two-Line"* or *"Boltzmann plot"* method for both the linear and saturated LIF regimes [14,15].

2.5.1 THE TWO-LINE METHOD

The simplest procedure is known as the *Two-Line method* [14-16,93] in which a narrowband laser is tuned to two resonance absorption lines originating from levels $X(v'',J_m''=m)$ and $X(v'',J_n''=n)$ where $n\neq m$. From Equations 2.1 and 2.17, the ratio of the resulting two signals S_m and S_n are

$$\frac{S_{\rm m}}{S_{\rm n}} \equiv S_{\rm m:n} = \frac{g_{\rm m}''}{g_{\rm n}''} \cdot \frac{\left[1 + g_{\rm m}''/g_{\rm n}'\right]}{\left[1 + g_{\rm m}''/g_{\rm m}'\right]} \cdot \frac{\Phi_{\rm m}}{\Phi_{\rm n}} \cdot e^{-\frac{(E_{\rm m} - E_{\rm n})}{kT}} , \qquad (2.43)$$

where E_m and E_n are the rovibrational energies in the ground electronic state. Letting

$$D_{m:n} \equiv \frac{g_m''}{g_n''} \cdot \frac{[1 + g_n''/g_n']}{[1 + g_m''/g_m']} \cdot \frac{\Phi_m}{\Phi_n} \qquad (2.44)$$

the two-line rotational temperature is

$$T = \frac{E_{v',J''=n} - E_{v'',J''=m}}{k \ln \left[\frac{S_{m:n}}{D_{m:n}}\right]} , \qquad (2.45)$$

where [15,25]

$$E_{v'',J''} = G_{v''} + F_{v',J''}$$
(2.46a)

and the usual Dunham expansions term values for a non-rigid rotator are [15,25]

$$G_{v''} = T_e + \omega_e (v'' + \frac{1}{2}) - \omega_e x_e (v'' + \frac{1}{2})^2 + \omega_e y_e (v'' + \frac{1}{2})^3 + \dots$$
(2.46b)

$$F_{v'',J''} \simeq B_{v'}J''(J''+1) - D_{v'}J''^2(J''+1)^2$$
(2.46c)

$$\mathbf{B}_{\mathbf{v}} = \mathbf{B}_{\mathbf{e}} - \alpha_1 (\mathbf{v}'' + \frac{1}{2}) + \alpha_2 (\mathbf{v}'' + \frac{1}{2})^2 + \cdots$$
(2.46d)

$$D_{v''} \simeq D_e + \beta_1 (v'' + \frac{1}{2})$$
 . (2.46e)

Table A.3 (Appendix A) shows literature values for the molecular constants used in this work for the X [94], A [30], and D' [41] states, respectively. It should be noted that centrifugal distortion coefficients in Equation 2.46e are not available in literature for the D' state, so they have been computed using [25]

$$D_e = \frac{4B_e^3}{\omega_e^2}$$
(2.47a)

and

$$\beta_{1} = D_{e} \left[\frac{8\omega_{e} x_{e}}{\omega_{e}} - \frac{5\alpha_{1}}{B_{e}} - \frac{\alpha_{1}^{2} \omega_{e}}{24B_{e}^{3}} \right] \quad .$$
(2.47b)

Taking the differential of T in Equation 2.45 with respect to $ln(S_{m:n}/D_{m:n})$ for fixed energies, we see that [14,16]

$$\frac{\mathrm{dT}}{\mathrm{T}} = \frac{\mathrm{kT}}{\mathrm{E}_{\mathrm{n}} - \mathrm{E}_{\mathrm{m}}} \cdot \mathrm{d} \ln \left[\frac{S_{\mathrm{m:n}}}{\mathrm{D}_{\mathrm{m:n}}} \right] \quad , \qquad (2.48)$$

which implies that the relative temperature measurement error will be reduced when one judiciously chooses the largest energy level separation possible. Assuming purely random errors in measuring S_m and S_n , the first-order variance of the Two-Line temperature measurement is [95]

$$\sigma_{\rm T}^2 \approx \left(\frac{\partial {\rm T}}{\partial S_m}\right)^2 \cdot \sigma_{\rm m}^2 + \left(\frac{\partial {\rm T}}{\partial S_n}\right)^2 \cdot \sigma_{\rm n}^2 \qquad , \qquad (2.49)$$

where σ_m^2 and σ_n^2 are the variances of S_m and S_n , respectively. Also, assuming that $\sigma_m^2 = \sigma_n^2$, then the relative temperature standard deviation is [95]

$$\frac{\sigma_{\rm T}}{T_{\rm avg}} \approx \frac{\sqrt{2}kT_{\rm avg}}{E_{\rm n} - E_{\rm m}} \quad . \tag{2.50}$$

We will use Equation 2.50 in Chapters 4 and 5 to estimate Two-Line ratio temperature measurement confidence intervals.

Also note in Equation 2.43 that we have distinguished the nondimensional fluorescence functions $\Phi(I_v/I_v^{sat})$ for both transitions m and n since it has been shown in Section 2.3 that they are not necessarily equal when $I_v/I_v^{sat} \leq 10$. Furthermore, since $I_v^{sat} \propto Q \propto \sigma_i \sqrt{T}$, there is an implicit temperature dependence within the Φ -ratios of Equation 2.43 that needs to be assessed. For data analysis of LIF spectra obtained within either the linear or saturated regimes, we used limiting expressions of Equation 2.43 that are not only more convenient but also provide physical insight into the effect of key parameters.

2.5.1.1 TWO-LINE METHOD; LINEAR REGIME

In the linear LIF regime where $I_v \ll I_v^{sat}$, Equation 2.43 reduces to

$$S_{m:n}^{lin} = \frac{g_m'' B_{m2} I_{m,v} Y_m}{g_n' B_{n2} I_{n,v} Y_n} e^{-\frac{(E_m - E_n)}{kT}} , \qquad (2.51)$$

where we have allowed for the excitation laser to have different spectral irradiances at the wavelengths corresponding to resonant absorption. Combining Equations 2.31-2.34 and 2.42 into Equation 2.51, we find that for both A–X and D'–X bands

$$S_{m:n}^{lin} \simeq \frac{S_{J'J''=m}I_{m,\nu}Y_m}{S_{J'J''=n}I_{n,\nu}Y_n} e^{-\frac{(E_m - E_n)}{kT}}$$
(2.52)

where $S_{J'J''}$ are the Hönl-London factors given by either Equations 2.35 or 2.36. Substituting the Equation 2.35 Hönl-London factors into Equation 2.52, the two-line ratios corresponding to P, Q, and R-branches in the **A–X band** are

$$S_{P(m:n)}^{lin} \simeq \frac{(J_m''-1)}{(J_n''-1)} \cdot \frac{I_{m,\nu}Y_m}{I_{n,\nu}Y_n} \cdot e^{-\frac{(E_m-E_n)}{kT}} ; P-branch$$
(2.53a)

$$S_{Q(m:n)}^{lin} \simeq \frac{(2J_m''+1)}{(2J_n''+1)} \cdot \frac{I_{m,v}Y_m}{I_{n,v}Y_n} \cdot e^{\frac{-(E_m-E_n)}{kT}} ; \text{ Q-branch}$$
(2.53b)

$$S_{R(m:n)}^{lin} \simeq \frac{(J_m''+2)}{(J_n''+2)} \cdot \frac{I_{m,v}Y_m}{I_{n,v}Y_n} \cdot e^{-\frac{(E_m-E_n)}{kT}}$$
; R-branch . (2.53c)

Substition of Equation 2.36 into Equation 2.52 for the P and R-branches of the D'-X band gives

$$S_{P(m:n)}^{lin} \simeq \frac{J_m''}{J_n''} \cdot \frac{I_{m,v} Y_m}{I_{n,v} Y_n} \cdot e^{-\frac{(E_m - E_n)}{kT}} ; P-branch \qquad (2.54a)$$

$$S_{R(m:n)}^{lin} \simeq \frac{(J_m''+1)}{(J_n''+1)} \cdot \frac{I_{m,v}Y_m}{I_{n,v}Y_n} \cdot e^{-\frac{(E_m-E_n)}{kT}} ; \text{ R-branch} . \qquad (2.54b)$$

Since the quench rate may be dependent upon upper rotational level, the quantum yield ratio

$$\frac{Y_{m}}{Y_{n}} = \frac{A_{v'}^{eff} + Q_{J'_{m}}}{A_{v'}^{eff} + Q_{J'_{m}}} = \frac{1 + \tau_{v'}^{eff} Q_{J'_{m}}}{1 + \tau_{v'}^{eff} Q_{J'_{m}}}$$
(2.55)

must be evaluated on a case-by-case basis. Note in Equation 2.55 that if (i) both pumplevels J_m and J_n satisfy $\tau_v^{\text{eff}} \cdot Q_{J'} \ll 1$ (i.e., the radiative decay rate >> collisional quenching rate) or (ii) $Q_{J'=m} \approx Q_{J'=n}$, then we can assume that $Y_m/Y_n \approx 1$. Numerical estimates shown in Appendix B for $\tau_v^{\text{eff}} \cdot Q$ have been performed using Equations 2.24, 2.25, $\tau_{v=1}^{\text{eff}} \approx 7.78$ ns [31] from Table A.2 of Appendix A, and A¹ Π effective quenching cross-sections [82-85] in Table A.1 of Appendix A. Note that the CO-CO quenching cross-sections in Table A.1 were obtained by pumping the X-A (0,0) Q(14) & Q(24) lines [84], (0,9) Q(22) [85], and (0,14) P(10) & R(14) [86] rovibronic bands with rotationallyresolving fluorescence collection. An average value $\sigma_{CO-CO} = 100$ Å² for the A(v'=1) has been used in all following quenching calculations. The A(v'=1) CO-Ar ($\sigma_{CO-Ar} \approx 25$ Å²) [85] and CO-He ($\sigma_{CO-He} \approx 3$ Å²) [85] values were obtained by exciting the X-A (0,0-7) bands using synchrotron radiation while the fluorescence was only vibrationallyresolved, implying that these are band-integrated values. Under typical experimental conditions for a 3% CO/Ar optically-pumped plasma at 100 torr and T=500 K, we find that Q $\approx 10^8$ s⁻¹ implying that $\tau_{v'}^{\text{eff}} \cdot \mathbf{Q} \approx O(1)$. For typical 3% CO/He glow discharge plasmas in this work (8 torr, T=400 K) we find $\mathbf{Q} \approx 10^7 \text{ s}^{-1}$, which implies $\tau_{v'}^{\text{eff}} \cdot \mathbf{Q} \ll O(1)$. With the absence of rotational-state specific quenching information, we have assumed $\mathbf{Y}_m/\mathbf{Y}_n = 1$ for all experimental data analysis in later chapters.

2.5.1.2 TWO-LINE METHOD; SATURATED REGIME

In the saturated regime where $I_v >> I_v^{sat}$, Equation 2.43 becomes

$$S_{\text{m:n}}^{\text{sat}} = \frac{g_{\text{m}}''}{g_{\text{n}}''} \cdot \left[\frac{1 + g_{\text{m}}''/g_{\text{n}}'}{1 + g_{\text{m}}''/g_{\text{m}}'} \right] \cdot e^{\frac{(E_{\text{m}} - E_{\text{n}})}{kT}} .$$
(2.56)

Using Equation 2.42 and $\Delta J \equiv J' - J''$, the saturated regime signal ratio for each branch in the **A**-**X** band is

$$S_{P(m:n)}^{sat} \simeq \frac{(2J_m''+1)(2J_m''-1)(6J_n''-1)}{(2J_n''+1)(2J_n''-1)(6J_m''-1)} \cdot e^{\frac{(E_m-E_n)}{kT}}; \text{ P-branch}$$
(2.57a)

$$S_{Q(m:n)}^{sat} \simeq \frac{(2J_m''+1)}{(2J_n''+1)} \cdot e^{-\frac{(E_m-E_n)}{kT}}$$
; Q-branch (2.57b)

$$S_{R(m:n)}^{sat} \simeq \frac{(2J_m''+1)(2J_m''+3)(6J_n''+7)}{(2J_n''+1)(2J_n''+3)(6J_m''+7)} \cdot e^{-\frac{(E_m-E_n)}{kT}}; \text{ R-branch} \quad . \quad (2.57c)$$

Note in Equation 2.57b that the prefactor term $(2J''_m+1)/(2J''_n+1)$ is identical to that in Equation 2.53b for the linear regime Q-branch. This coincidence will be exploited in Chapter 5 involving PLIF temperature extraction. The **D'**–**X band** saturated regime signal ratio for the P and R-branches are

$$S_{P(m:n)}^{sat} = \frac{(2J_m''+1)}{(2J_n''+1)} \cdot \frac{(4J_n''+1)}{(4J_m''+1)} \cdot \frac{J_m}{J_n} \cdot e^{-\frac{(E_m - E_n)}{kT}} ; P-branch$$
(2.58a)

$$S_{R(m:n)}^{sat} = \frac{(2J_m''+1)(J_m''+1)(4J_n''+3)}{(2J_n''+1)(J_n''+1)(4J_m''+3)} \cdot e^{-\frac{(E_m-E_n)}{kT}} ; \text{ R-branch . } (2.58b)$$

2.5.2 THE BOLTZMANN PLOT METHOD

The Boltzmann plot method for computing temperature employs a set of LIF excitation spectra covering a wide range of J" values [14-16]. Using Equation 2.1, 2.8, 2.31, and 2.42, we can express each spectral peak signal given by Equation 2.17

$$S = n^{\circ}\beta(T) \cdot \frac{A_{2}^{\text{coll}}}{\left[1 + \frac{g''}{g'}\right]} \cdot \Phi\left(\frac{I_{v}}{I_{v}^{\text{sat}}}\right) \eta V$$
(2.17)

in the generalized form

$$S = \mathbf{A} \cdot f(\mathbf{J}'') \cdot \mathbf{e}^{\frac{\mathbf{E}_{\mathbf{v},\mathbf{J}'}}{\mathbf{K}\mathbf{T}}} , \qquad (2.59)$$

where A is a factor assumed to be independent of the pumped ground state rotational level J" and f(J'') is a "normalization" function to be determined. Let the normalized signal be defined as

$$\rho(J'',T) \equiv \frac{S}{f(J')}$$
(2.60)

Substituting Equations 2.59 and 2.46a-e into Equation 2.60 and taking the natural logarithm of of both sides yields [14-16]

$$\ln(\rho) \approx -\frac{B_{v''}}{kT} \cdot J''(J''+1) + b, \qquad (2.61)$$

where b is the ordinate crossing at J"=0 and we have ignored the higher-order centrifugal distortion term $D_{v''}$ given in Equation 2.46c. The advantage of using Equation 2.61 is that it is *linear* with slope $a \equiv -B_{v''}/kT$

$$\mathbf{y}(\mathbf{x}) = \mathbf{a} \cdot \mathbf{x} + \mathbf{b} \quad , \tag{2.62}$$

where we have defined $x \equiv J''(J''+1)$. Thus, if we use Equations 2.60 and 2.61 to analyze a set of experimental LIF resonance peaks, we expect the points to form a straight line as

shown in Figure 2.5a. In practice, we used a linear Least-Squares fit [95] to obtain the mean slope, \bar{a} , from which the mean temperature is

$$T_{avg} = \frac{-B_{v''}}{k\overline{a}} = \frac{B_{v''}}{k|\overline{a}|} \quad .$$
(2.63)

Questions now remain with regard to the proper form of the normalization function f(J''), and how each branch (P, Q, and R) behaves within the linear and saturated LIF regimes for the A-X and D'-X bands.

2.5.2.1 BOLTZMANN PLOT; LINEAR REGIME WITH LINE-STRENGTH NORMALIZATION

From Equations 2.1, 2.20, 2.31, and 2.34 we find that the linear regime signal is

$$S^{\text{lin}} = \frac{n^{\circ} \lambda^{3} A_{v'v'} I_{v} Y_{J'} \eta V}{8\pi hc \cdot Z(T)} \cdot S_{J'J''} \cdot e^{-\frac{E_{v',J''}}{kT}}$$
(2.64)

and has the form of Equation 2.59 if we assume that $Y_{J''}$ and I_{ν} are independent of J''. If we now choose the normalization function to be equivalent to the respective branch Hönl-London factors

$$f(J') \equiv S_{J'J''}$$
, (2.65)

$$\frac{\rho_Q^{\rm lin}}{\rho_P^{\rm lin}} = 1 \qquad (2.66)$$



Figure 2.5. Example of Boltzmann plot method. (a) Proper choice of normalization function *f*(J") has been used and the locus of points for each branch falling on the same line with slope ā=-B_{v"}/kT_{avg}. (b) An improperly chosen normalization function is used in which the branches *may* be offset. Also, nonlinear behavior can occur at low J". For high J", however, the average slopes are practically equal, ā_{,Q} ≅ ā_{,P}, such that T_{avg,Q} ≅ T_{avg,P} (refer to text).

for all J". Re-arranging and taking the natural logarithm of Equation 2.66 gives

$$\ln(\rho_{\rm O}^{\rm lin}) = \ln(\rho_{\rm P}^{\rm lin}) \tag{2.67}$$

which implies that both P and Q-branches will be co-located on the same line in a Boltzmann plot as shown in Figure 2.5a. Note that this result is valid for both the A-X and D'-X bands within the linear LIF regime.

2.5.2.2 BOLTZMANN PLOT; SATURATED REGIME WITH DEGENERACY NORMALIZATION

Combining Equation 2.1 with Equation 2.26, the saturated LIF signal is

$$S^{\text{sat}} = \frac{n^{\circ} A_2^{\text{coll}} \eta V}{Z(T)} \cdot \frac{g''}{\left[1 + \frac{g''}{g'}\right]} \cdot e^{-\frac{E_{vT''}}{kT}}$$
(2.68)

where g''=2J''+1 and g' is given by Equation 2.42 for either the A or D' electronic state. Equation 2.68 will have the form of Equation 2.59 if we now define a "*degeneracy normalization*" function as

$$f(J'') = \frac{2J''+1}{\left[1 + \frac{(2J''+1)}{g'}\right]} \quad .$$
(2.69)

Substituting Equation 2.42 and $J' = J'' + \Delta J$ into Equation 2.69 for each branch of the **A-X band**, we find, in the saturated limit (I >> I^{sat})

$$f_{\rm P}(J') \equiv \frac{2(2J''+1)(2J''-1)}{(6J''-1)}$$
; P-branch (2.70a)

$$f_{\rm Q}(J'') \equiv \frac{2}{3} \cdot (2J''+1);$$
 Q-branch (2.70b)

$$f_{\rm R}(J') \equiv \frac{2(2J''+1)(2J''+3)}{(6J''+7)}$$
; R-branch. (2.70c)

It is instructive to demonstrate the consequences of improperly using only the ground state rotational degneracy (*i.e.*, $f(J'') \equiv 2J''+1$) to normalize the LIF signal. For example, normalizing Equation 2.68 using 2J''+1 results in

$$\rho_{P(J')}^{\text{sat}} \propto \frac{2(2J''-1)}{(6J''-1)} \cdot e^{-\frac{E_{v',J''}}{kT}};$$
P-branch (2.71)

Taking the natural logarithm of both sides of Equation 2.71, we find that

$$\ln\left[\rho_{P(J')}^{\text{sat}}\right] \simeq -\frac{B_{v''}}{kT} J''(J''+1) + b' \cdot \ln\left[\frac{2(2J''-1)}{(6J''-1)}\right] , \qquad (2.72)$$

where b' is a constant. As shown in Figure 2.5b, a number of potential problems may result from Equation 2.72; first, the term $\ln[2(2J''-1)/(6J''-1)]$ is not quite constant for low J''. This contradicts the assumption that the ordinate crossing in Equation 2.61 is independent of J'' and implies that the locus of P-branch points on a Boltzmann plot for low J'' will be slightly nonlinear, as shown in Figure 2.5b. Furthermore, the locus of

points representing the other branches may not coincide with the P-branch, resulting in an "offset" as shown in Figure 2.5b. For these reasons, we will always normalize the A-X band signals using Equations 2.70a-c in the saturated regime. We note that this offset may also develop as a result of incomplete saturation if the $\Phi(I_v/I_v^{sat})$ for each rotational branch are not accurately known (see Section 2.3.2 nonlinear LIF regime).

Using Equation 2.69, the **D'-X band** degeneracy normalization functions in the saturated limit (I >> I^{sat}) are

$$f_{\rm P}(J'') \equiv \frac{J''(2J''+1)}{4J''+1}$$
; P-branch (2.73a)

$$f_{\rm R}(J') \equiv \frac{(J''+1)(2J''+1)}{4J''+3}$$
; R-branch. (2.73b)

CHAPTER 3

LIF USING AN INJECTION-LOCKED ARGON FLUORIDE EXCIMER LASER

In this chapter, we first discuss the general strategy employed to perform singlephoton A-X (and D'-X) band LIF/PLIF. The LIF/PLIF diagnostic strategy was designed for maximum signal-to-noise (S/N) and measurement sensitivity by considering a confluence of issues; (i) the separation and strength of A-X band rovibonic absorption transitions, (ii) the desire to collect Stokes-shifted emissions having wavelengths that lie outside the vacuum ultraviolet (VUV), (iii) using the lowest possible ground-state vibrational level (*i.e.*, having a large population of absorbers), (iv) using a rotational level(s) having a largest population of absorbers at the anticipated temperature (v) availability of a narrowband, tunable laser source with output wavelengths coincident with the desired transitions, and (vi) filtering schemes for rejecting extraneous bands and scattered laser radiation. Complete experimental details for each diagnostic technique will be given in Chapters 4 and 5. The ArF laser source is central to each and will be described here.

3.1 DIAGNOSTIC STRATEGY USING A TUNABLE, NARROWBAND SOURCE

As discussed in Chapter 2, the rotational LIF technique probes the ground state rotational population distribution within a single vibrational level through resonant absorption and emission collection. To achieve high signal-to-noise (S/N), it is best to choose a vibrational level having the largest possible population (e.g., v"=0 or 1), especially in low vibrationally-excited environments. For single-photon A-X band LIF, we see from Table A.2 in Appendix A that many vibronic bands in the range $X(v'' \le 4) - A(v' \le 7)$ have very favorable transition strengths (or, Franck-Condon probablities) [30,31]. However, the wavelengths of these bands [24] lie deep within the vacuum ultraviolet (VUV) which is defined roughly as $\lambda \le 190$ nm ($\approx 53,000$ cm⁻¹) where radiation propagating through the ambient laboratory air is strongly absorbed by O_2 Schumann-Runge bands [96]. The use of a VUV source or collection of VUV LIF emission in this region requires careful purging of ambient O₂ from all optical paths which compounds the experimental difficulty. From the Deslandres Table 4 in Reference [24], we find that our choices for single-photon A-X transitions with energies lower than the VUV cutoff are limited to about $X(v'' \ge 6)$. From Table A.2, note that the lowest ground vibrational state above v''=6 with a reasonably strong transition probability outside the VUV is the X(v''=7) \rightarrow A(v'=1) with A_{1,7} \approx 1.7×10⁶ s⁻¹. Using the molecular constants in Table A.3 (Appendix A) along with Equations 2.46a-c in Chapter 2, we find that the transition wavelength is ≈ 193.12 nm (51,781 cm⁻¹). It is well known [37,54-56,62-65] that under nonequilibrium conditions within an optically-pumped CO/Ar

plasma or CO/He glow discharge that the vibrational population of the CO X(v''=7) can be significant (~0.1%) to the extent that this scheme is made practically possible.

This wavelength (193 nm) is coincident with the output of a tunable, injectionlocked argon-fluoride (ArF) excimer laser [16,97-101]. This type of laser has become increasingly popular as a combustion diagnostic tool due to it's high spectral brightness and flexibility in allowing simultaneous measurements of flow properties using a combination of methods [16]. The bandwidth of a typical injection-locked ArF laser is ≈ 0.5 cm⁻¹ (15 GHz) with tunability over a ≈ 1 nm range (192.8–193.8 nm) [16,99-101]. For two rotational absorption lines in the ground vibronic state separated by one quanta (i.e., J_m=J_n-1) and using Equation 2.46c, we find that the energy separation is

$$\Delta E \approx B_{v''} \left[J_m'' (J_m'' + 1) - J_n'' (J_n'' + 1) \right]$$

= $2B_{v'} J_n''$ (3.1)

The rotational population of CO at T=500 K has a maximum at [72]

$$J_{max}'' = \sqrt{\frac{kT}{2B_{v''}}} - \frac{1}{2}$$
(3.2)

so that with $B_7 \approx 1.8 \text{ cm}^{-1}$ for X(v"=7) from Table A.3 we find that $J''_{\text{max}} \approx 10$, corresponding to an energy separation of $\Delta E \approx 36 \text{ cm}^{-1} \approx 0.13 \text{ nm}$ (1 THz). This indicates that there should be numerous resonance absorption features within the ArF tuning range. Using the Lorentzian collision broadening parameters in Appendix A,

Table A.4, calculations of a Voigt profile linewidth [102] have been performed in Appendix B that show the lines are predominately Doppler broadened $\approx 0.2 \text{ cm}^{-1} \approx 1 \text{ pm}$ (6 GHz) FWHM bandwidth. Note that this value is 2.5× smaller than the typical ArF injection-locked bandwidth (FWHM), an indication that an excitation scan across the line should approximately represent the laser linewidth. This result is important because (i) when the laser is fixed upon a resonance peak, we expect the signal (hence, measurement uncertainty) to be less sensitive to wavelength shot-to-shot "jitter" as compared to when the laser bandwidth is much smaller than the Doppler-broadened line and (ii) for I_v >> I_v ^{sat}, potentially most or all of the Doppler-broadened absorption line will be saturated [14].

Using the Two-Line ratio expression given in Chapter 2, Equation 2.43, the molecular term energy expressions in Equations 2.46a-e, and the CO ground electronic state molecular constants listed in Table A.3, Appendix A, we have assessed the potential measurement sensitivity for particular choices of Q-branch signal ratios, $S_{m:n}$, as a function of rotational temperature, T. Figure 3.1 shows the results of this analysis in which we have chosen to plot the $S_{11:10}$, $S_{17:10}$, $S_{22:10}$, and $S_{22:6}$ Q-branch ratios in the range 200 K to 1000 K. From Equation 2.50 (Chapter 2) we see that the relative measurement uncertainty, σ_T/T_{avg} , is inversely proportional to the ground elecronic state energy separation (E_n - E_m) between the two absorption resonances. Hence, it is not surprising that the $S_{11:10} \equiv Q(11)/Q(10)$ curve in Figure 3.1 indicates temperature measurement uncertainties of at least 100% when the signal ratio uncertainty is specified as 10% for the range 400 K – 700 K. On the other hand, the Q(17)/Q(10) curve implies that the measurement uncertainties will be only $\approx 10\%$ - 15%, corresponding to $\approx \pm 30$ K and ± 80 K at 400 K and 700 K, respectively. Two additional cases are shown in Figure



Figure 3.1 Two-Line Method Signal Ratio $S_{m:n}$ vs. Rotational Temperature: Demonstration of measurement sensitivity for various transition pairs.

3.1 which have a larger energy separation. Note that the slope (*i.e.*, dS_{m:n}/dT \Leftrightarrow "sensitivity") of the Q(22)/Q(10) pair in the 400 K-700 K range is nearly equal to that of Q(17)/Q(10). The largest practical separation for this diagnostic is the Q(22)/Q(6) pair indicated by the arrow in Figure 3.1. At 400 K, this pair has a sensitivity equivalent to the Q(17)/Q(10) and Q(22)/Q(10) pairs, and is only slightly better than either pair at 700 K (±25 K). Note that at 300 K, this particular ratio is actually *less* sensitive than the Q(17)/Q(10) pair. Since the Q(22) population is relatively low in the 300 K – 700 K range and the ArF laser locking efficiency falls off quickly with increasing wavelength, we would expect the uncertainty in measuring the Q(22)/Q(6) signal ratio to be larger
than 10%, and as such the relative temperature measurement uncertainty to be larger than indicated in Figure 3.1. From this analysis, we conclude that our choice to use Q(10)/Q(17) pair for Two-Line temperature measurements is reasonable from the standpoint of sensitivity.

3.2 DETAILS OF THE INJECTION-LOCKED ARGON FLUORIDE LASER

All LIF measurements were performed by wavelength scanning the narrowband output of an injection-locked ArF excimer laser (Lambda Physik COMPex 150T) in standard oscillator/amplifier configuration, shown in Figure 3.2 [103-105]. The oscillator generates low energy (< 1 mJ/pulse), narrowband, horizontally-polarized radiation using multiple prisms (P1,P2,P3) and a stepper-motor controlled grating (G) in a Littrow arrangement. The pulsed 17 ns output is directed through a 1 mm hole in the amplifier high reflector (HR), shown in Figure 3.2. The amplifier Cassegrain resonator optics form an unstable cavity [105,106] intended to reduce beam divergence (< 2 mrad). With an optimal time delay between the firing of the two laser discharge tubes, the injected lowpower seed is amplified during multiple round-trips through the coupled oscillator/amplifier so that the two resonators "lock" [103-105], generating a high-energy, narrowband, horizontally polarized ($\approx 20:1$) beam with high spectral irradiance. It must be noted, however, that the unstable resonator optics lead to a spectrally broadband background radiation due to unpolarized *amplified spontaneous emission* (ASE) [103,104,107] and a slightly spatially inhomogeneous beam profile (due to the



- Figure 3.2 Schematic diagram of Lambda Physik COMPex 150T injectionlocked tuning mode. Note that the amplifier resonator is unstable with a 3:1 telescope configuration.
- \leftrightarrow (20:1) Polarization in plane of page (horizontal).
- G Externally controlled grating for wavelength selection.

P1,P2,P3 – Prisms for dispersing excimer radiation.

- A1 1 mm diameter aperture for wavelength selection.
- A2 Variable diameter iris for regecting oscillator ASE.
- OC1 Oscillator output coupler.
- M1,M2 Turning mirrors.
- HR Amplifier high reflector, 1 mm diameter pinhole aperture (+3075 mm radius of curvature).
- OC2 Amplifier output coupler (UVFS uncoated miniscus lens, -300 mm radius of curvature).

"Cassegrain hole"). Furthermore, the fraction of broadband radiation is a function of the (i) narrowband frequency (*i.e.*, tuning), (ii) discharge timing delay ("tdiff"), (iii) temperature and age of laser gases, and (iv) age of the discharge switch thyratrons. It is noted that shot-to-shot variablility can be greatly reduced by carefully aligning all laser optics, using an empirically determined optimal time separation between firing of the oscillator and amplifier discharges, termed "tdiff", and also by properly adjusting both thyratron's cathode heater and reservoir voltages.

3.3 THE ARGON FLUORIDE LASER 'LOCKING' EFFICIENCY

As discussed above, the fraction of laser power channeled into the tunable narrowband output component varies widely over the ~1 nm ArF broadband gain profile, with the maximum occuring at the center wavelength ~193.35 nm. This is illustrated in Figure 3.3 as a series of spectra acquired by Lambda Physik using a low resolution monochromator for different tuning wavelengths within the ArF gain profile [108]. The (unpolarized) broadband spectrum of the free-running amplifier (*i.e.*, without seeding) is shown at the bottom of Figure 3.3. The dips in this broadband spectrum are caused by the Schumann-Runge absorption bands of O₂ present in the beam path between laser and spectrometer [108]. From top-to-bottom in this figure, as the oscillator grating turns, the narrowband radiation wavelength is tuned towards the middle of the ArF gain curve from far left to right. As the grating angle is tuned toward the middle of the gain curve, the oscillator's narrowband seed energy increases so that the amplifier's broadband ASE, in



Figure 3.3 Lambda Physik COMPex 150T emission spectra of injection-locked ArF output for different wavelengths [108]. Note that the bottom spectrum is of the free-running amplifier enhanced by 1.5×.

competition with stimulated emission induced by the seed, is increasingly "pulled" toward the narrowband wavelength. In the process, note that the area (*i.e.*, spectrally integrated energy) under the amplifier's narrowband portion increases while it's total broadband component decreases. The portion of narrowband energy in the amplifier output is a strong function of injected seed pulse energy.

Since the rotational LIF technique depends upon exciting only *one* absorption line at a time, any LIF due to the broadband component will constitute a potential source of "background interference" manifest as a voltage offset in the LIF collection signal. While this background/offset can be subtracted, we must also know the fraction of energy



Figure 3.4 Side-view illustration of the optics and monochromator/PMT setup used to measure the COMPex 150T ArF locking efficiency.

within the narrowband at the absorption resonance wavelength in order to properly compare multiple peaks. This can be understood by referring to Chapter 2 where it was shown that the linear regime LIF signal is directly proportional to the incident spectral irradiance (*e.g.*, see Equation 2.20). Additionally, if one desires to work within the saturated regime there needs to be some assurance that $I_v >> I_v^{sat}$ for *all* peak measurements. Thus, we see that not only the measurement of total pulse energy is important, but the fraction of the total energy partitioned into the narrowband radiation needs to be properly accounted for in order to analyze the experimental data.

This fraction of narrowband radiation is called the "locking efficiency" and is defined for a particular wavelength as the ratio of the narrowband energy to the total emitted energy. We have simultaneously measured the LIF excitation spectra, total excimer pulse energy at the LIF test cell, and the locking efficiency in a manner similar to that described in Reference [109]. In our work, however, this locking measurement was achieved by monitoring a small portion of the unpolarized amplifier broadband radiation using a medium resolution monochromator (JobinYvon HR320, 30 cm, 2400 g/mm UV blaze) set to a bandpass of ~0.1 nm and a Hamamatsu 1P28 photomultiplier tube (PMT). Figure 3.4 shows a side-view illustration of the experimental setup in which the horizontally polarized excimer output is turned 45° upward using ArF mirror #1, and turned once more out of the page plane towards the LIF test cell. A small fraction (< 3%) of the beam is transmitted through ArF mirror #1 shown in Figure 3.4 and impinges upon a 1 mm pinhole aperture in front of the monochromator slit. Figure 3.5 is a front view of the monochromator entrance port detailing the alignment of the excimer beam and

pinhole aperture. Best results were obtained when the beam "edge" just overlaps the pinhole.

The monochromator grating (2^{nd} order) was set to a spectral region near the edge of the laser gain (~195.1 nm) in order to avoid stray narrowband radiation. When the oscillator seed beam was blocked, the resulting broadband emission signal, V_b, provided



Figure 3.5 Front-view illustration of the monochromator entrance port and beam alignment. A 1 mm pinhole apeture covers the the slit, allowing only a small portion of the intense excimer radiation to enter the monochromator.

an "unlocked" reference condition. When the oscillator was unblocked and the laser tuned into locking, this signal $V(\lambda)$ decreased. The locking efficiency was then computed over the tuning range using

% Lock =
$$100 \cdot \left[1 - \frac{V(\lambda)}{V_b} \right]$$
, (3.3)

where λ is the excimer wavelength in nm. This locking signal from the PMT was fed into a 300 MHz, 5X preamplifier (Stanford Research Systems SR240) before being processed by a gated "boxcar" integrator (SRS SR250) with a time-constant of 100 shots (6.7 s at 15 Hz trigger rate). Figure 3.6 shows a typical locking efficiency measurement



Figure 3.6 Experimental ArF laser locking efficiency and average beam energy measurements.

obtained using this method. In this figure, we see that the locking efficiency between \approx 193.1 nm - 193.6 nm is \approx 55%, and falls off rapidly outside this range. This result is in good agreement with locking efficiency measurements performed using a similar ArF laser in Reference [108]. Figure 3.6 also shows a simultaneous measurement of average excimer pulse energy, $E_L(\lambda)$, performed using a pyroelectric power meter (Scientech Vector S310 Meter and AC50UV Detector) placed in front of the \approx 2 m long beam pipe. Note that the beam energy measured at \approx 192.8 nm is \approx 40 mJ/pulse. This energy corresponds to the output of the free-running amplifier without injecting the oscillator beam. As the oscillator is tuned toward the center of the gain profile, note that the beam output energy is due to the extraction of gain from the amplifier due to the injected oscillator seed beam. This can also be realized by comparing the energy curve of Figure 3.6 with the gain profile of the free-running amplifier as shown in the bottom spectrum in Figure 3.3.

As discussed in Chapter 2, linear regime LIF peak intensities must be "corrected" for this wavelength dependent beam energy. The portion of energy within the narrowband of the ArF laser beam is computed from

$$E_{L}^{nar}(\lambda) = \frac{\% Lock(\lambda)}{100} \cdot E_{L}(\lambda) \quad , \qquad (3.4)$$

where %Lock(λ) and E_L(λ) are the locking effiency and average beam energy experimentally measured at excitation wavelength λ . In the next section, we describe the procedure for determining the absolute excitation wavelength, λ .

3.4 WAVELENGTH CALIBRATION OF LASER TUNING RANGE USING AMBIENT O_2 LIF

In a separate experiment, we calibrated the excimer's narrowband spectral line position using rotationally-resolved, ambient O₂ Schumann-Runge LIF originating from $X^{3}\Sigma_{g}(v''=0) \rightarrow B^{3}\Sigma_{u}(v'=4)$ resonant absorption [96,110]. As the laser was slowly tuned across its' gain profile while collecting $B(v'=4) \rightarrow X(v''=7)$ emission near 240 nm, the grating stepper-motor position was recorded at each P/R-branch maxima. The tabulated X \rightarrow B line positions [96] were assigned to these peaks and then correlated to the laser grating positions by a least-squares fit (5300 ± 200 nm/step). This implies that the uncertainty in spectral line positions, relative to the (0,4) Schumann-Runge band assignments, is less than \approx 4%.

CHAPTER 4

SPATIALLY AVERAGED SINGLE-PHOTON LIF TEMPERATURE MEASUREMENTS USING THE A-X AND D'-X BANDS

4.1 MODEL ENVIRONMENTS FOR CO LIF UNDER EXTREME AND MILD VIBRATIONAL NONEQUILIBRIUM

As discussed in Chapters 1-3, two types of single-photon LIF techniques are available to vibrationally-excited CO within the tuning range of an argon-fluoride (ArF) excimer laser. Proof-of-concept exploration using LIF was deemed a critical first step in verifying that both X-A and X-D' transitions can be reliably used as a temperature measurement tool. This is especially critical for spatially-resolved planar-laser induced fluorescence (PLIF) imaging where the pump laser radiation is formed into a wide "sheet" such that the intensity is low compared to a symmetrically focused spot. To demonstrate the potential of this new LIF technique we have used two vibrational excitation schemes discussed in Chapter 1; (i) *optical pumping* of a 100 torr, 3% CO/Ar mixture to produce high vibrational excitation such that both the D'-X and A-X transitions may be explored and compared and (ii) a modest pressure (8 torr) 4% CO/He *d.c. glow discharge* with mild vibrational excitation allowing only the A-X band to be accessable. These model environments have been chosen because they are both wellcharacterized [20,52-59,62-66,69,70,111], exhibit relative chemical simplicity and, by adjusting the total volumetric flow rate, input power, admixture species and concentrations [20,52-59], we can "tailor" the extent of the CO vibrational level populations. This last point is important since most engineering systems of interest for this LIF diagnostic exhibit only modest levels of vibrational excitation [1-6].



Figure 4.1 Experimental and theoretical steady-state vibrational distribution functions at different CO partial pressures. Reproduced from [20].

Figure 4.1 [20] shows steady-state, nonequilibrium, ground electronic state vibrational distribution functions (VDFs) of an 0.5-3.5% CO/argon mixture at 100 torr which has been optically pumped using a CO laser [20,50-56,59], as described in Chapter 1. It is interesting, although not central to the discussion, that the VDF can be varied by varying the CO partial pressure. Note in this figure that the nonequilibrium vibrational populations of X(v''=7) and X(v''=20) are $\approx 0.5\%$ and $\approx 0.05-0.2\%$, respectively, at translational temperatures of $\approx 400-730$ K. It is also important to note that these measurements represent spatial averages since they were obtained using line-of-sight FT-



Figure 4.2 Photograph of the liquid nitrogen cooled CO laser [50,51] used to optically-pump CO in test cell (not shown).

IR emission spectroscopy of the CO 1st overtone [19,20,112]. This issue notwithstanding, we initiated proof-of-concept exploration of $X(v''=7)\rightarrow A(v'=1)$ and $X(v''=20)\rightarrow D'(v'=2)$ band LIF using optical-pumping because of (i) the relative ease at which these highly excited populations can be produced at high pressure and low transrotational temperature and (ii) access to a cryogenically-cooled CO laser at The Ohio State University Nonequilibrium Thermodynamics Laboratory [91]. A photograph of the CO laser [50,51] in operation is shown in Figure 4.2. As a first step towards demonstration of the potential for LIF temperature measurements, we need to define and characterize a baseline nonequilibrium plasma environment. This process is described in the next section.

4.2 NONEQUILIBRIUM PLASMA CHARACTERIZATION BY FT-IR VIBRATIONAL EMISSION

4.2.1 PLASMA CREATION AND OPTICAL ACCESS

4.2.1.1 OPTICALLY PUMPED PLASMA

Figure 4.3 shows the arrangement used for all optical pumping experiments in this chapter [47]. A cylindrical Pyrex glass cell, 78 cm long \times 5.7 cm diameter, is used to contain a slowly flowing (~1 cm/s) gas mixture of carbon monoxide, argon, and helium. A gas manifold delivers mixtures of research-grade (99%) argon, helium, and high purity (99.9%) CO, with composition and total pressure controlled by flow meters and a



Figure 4.3 Top view of apparatus for creating the optically pumped plasma.

vacuum pump choke valve. The total pressure, typically ~100 torr, is monitored with a Baratron pressure gauge. Four perpendicular 5.1 cm long × 5.1 cm diameter glass arms provide optical access to the region of interest. Two of these arms are oriented with their axes in the plane of Figure 4.3, while the other two are directed vertically out of the page. The cell ends and arms are equipped with flanges for mounting either 1" dia. calcium fluoride (CaF₂) or UV-grade fused silica windows (UVFS) to provide spectral transmittance in either the infrared or UV, as appropriate. An optically-pumped plasma is formed by directing an unfocused, continuous wave (cw), Gaussian mode (TEM₀₀) CO laser beam into the gas cell, as shown in Figure 4.3 (for clarity, the beam stop has not been illustrated). Note that in some cases we have used a 1" dia., 250 mm (f/10) planoconvex CaF₂ lens (outside the cell) to focus the CO laser beam ($\lambda \approx 4.6 \ \mu$ m) within the imaging region. The inset of Figure 4.3 illustrates the relative size and position of the finger-like plasma, concentric with the axis of the CO laser pump beam, as viewed through the top window. The total CO laser power is typically ~10-12 W. The unfocused beam diameter within the imaging region has been estimated [113] to be ≈ 6.6 mm, corresponding to an average IR pump-beam intensity of ~30 W/cm². When the CaF₂ lens is placed 40 cm from the imaging region, the beam diameter was ≈ 4 mm [114], with a resulting intensity ~90 W/cm². The tendency of carbonacous deposits to form on the CO laser entrance window (due to the CO + CO \rightarrow CO₂ + C reaction [52,54,57]) was eliminated by use of an argon purge illustrated in Figure 4.3. Variation of the purge flow rate also allowed for fine axial-position control of the optically-pumped gas region. By using the characteristic C₂ Swan-band [25,57,61] "blue glow" as a visual aid prior to helium addition, the plasma was centered within the window ports as shown by the photographs in Figure 4.4



Figure 4.4 Photographs of the optically-pumped CO plasma as viewed through a side viewport [47]. Laser beam propogation and gas flow is from left to right. Left: unfocused CO laser beam, <u>Right</u>: focused beam. Note the argon purge volume on the left side of each photograph.

4.2.1.2 D.C. NORMAL GLOW DISCHARGE PLASMA

The flow cell and gas handling system used for the D.C. glow discharge plasma is the same as described for the optically pumped plasma, except that the argon purge was removed and electrodes were inserted into the Pyrex[™] tube using ChemThread[™] fittings as shown in Figure 4.5 [48]. Note that Figure 4.5 illustrates the geometry of the



Figure 4.5 Side view of flow cell illustrating the electrode geometry and electrical connections used in generating the d.c. normal glow discharge [48].

electrodes as well as the external power system. Both ring shaped, 306 stainless-steel electrodes are 1 mm thick and 3 cm in (outer) diameter. The anode is 1.3 cm long and the cathode is 5.0 cm long. These electrodes are spaced 19.5 cm apart, concentric with



Figure 4.6 Current-Voltage (I-V) characteristic for the cases of pure helium and 3.6% CO/He mixture at 8.3 torr [48].

the flow cell. The asymmetry of the electrode placement with respect to the viewports insured optical access to the glow discharge positive column. The gas mixture concentration was 3.6% CO/He at a total pressure of 8.3 torr.

A 600 W d.c. power supply (Glassman High Voltage # EW10R60) was connected in series with a nominal 100 k Ω ballast resistor (measured to be 99.7 k Ω when hot) and the discharge plasma. The power supply was operated in positive-polarity, currentcontrolled mode. Typical power supply voltages (3.1 kV, 77 W for pure helium, 3.6 kV, 90 W for the CO/He mixture) and interelectrode voltages (500 V pure helium and 900 V CO/helium) were measured using a 1000× (reducing) high-voltage probe (Fluke 80k-40) and a hand-held multimeter (BK Precision 389A). Figure 4.6 displays the resulting current-voltage (I-V) characteristic for both the pure helium discharge and the CO/He mixture taken on three different days. Note that while the addition of only \approx 4% CO nearly doubles the interelectrode voltage, it is still possible to maintain a stable, normal glow [1,3,64] over the range of current supplied. For all experiments in this paper, the current was maintained at 25mA, corresponding to the minimum observed in the CO/He I-V curve in Figure 4.6. Under this condition, the lumped resistance across the electrodes were \approx 20 k Ω (pure He) and \approx 40 k Ω (CO/He). It should be noted that while there is slight variability of the I-V characteristic for the CO/He mixture (possibly due to electrode carbonization), these results illustrate reasonable repeatability of the gas flow and discharge conditions.

Using the measured electrode voltage drop, we can make a rough estimate of the positive column reduced electric field [1,3,64]

$$\frac{E}{n} \approx \frac{kT(V_p - V_{cf})}{pd} \quad , \tag{4.1}$$

where p is the total gas pressure, d, the interelectrode spacing, k, Boltzmann's constant, T, the gas translational temperature, V_p is the measured electrode drop for the CO/He mixture ($V_p \approx 900$ V), and V_{cf} is the cathode fall voltage. Assuming T ≈ 500 K and $V_{cf} \approx$ 450 V [64], p=8 torr, and d=20 cm, we get E/n $\approx 1.5 \times 10^{-16}$ V-cm². It is well known [62-64,69,70] that the REF required to maximize electron kinetic energy transfer to diatomic vibrational modes is about 3×10^{-16} V-cm².



Figure 4.7 Photographs of pure helium d.c. glow discharge at 8.0 torr, 25 mA. Left: Overall photo of cell; flow is from left-to-right. <u>Right</u>: Photo from side viewport.



Figure 4.8 Photographs of 0.3 torr CO added to the pure helium discharge shown in Figure 4.7 with the current still maintained at 25 mA. Left: Overall photo of cell; note the complete formation of cathode sheath. Right: Photo taken from side viewport; note the diffuse C_2 Swan band emission within the central axial field of view.

Figure 4.7 shows a picture of the pure helium d.c. glow discharge at 8.0 torr. Figure 4.8 is a photograph taken of the d.c. glow discharge after adding 0.3 torr of CO (3.6% CO/He mixture). It is noteworthy to mention the left photo in Figure 4.8 showing that the cathode is completely enveloped in a stationary sheath which is another indication that the discharge resides within the normal d.c. glow regime [1,64]. In the right photograph of Figure 4.8 we also see that the C_2 Swan band emission within the positive column is diffusely distributed along the cell axis within the field of view.

4.2.2 FT-IR SPECTROSCOPY DIAGNOSTIC SETUP

A Fourier Transform-InfraRed (FT-IR) spectrometer [19] (BioRad FTS-175C) incorporating a cryogenically cooled indium antimonide (InSb) detector was used with moderate resolution (16 cm⁻¹) to resolve the vibrational transitions of the CO 1st overtone emission spectrum from v'=1 to 40 as well as at higher resolution (0.25 cm⁻¹) to resolve rotational transitions of the fundamental v=1 \rightarrow 0 band. As shown in Figure 4.9, the optical path was aligned to image the plasma spontaneous emission directly through the side window using a 4 cm off-axis paraboloidal concave gold mirror. For all infrared measurements, a short-pass filter (Infrared Optical Products, Inc. #W03187) with a cutoff at ~4.9 µm (2040 cm⁻¹) with a bandwidth of ~3.1 µm (5500 cm⁻¹) was used to attenuate the fundamental emission so as not to saturate the InSb detector. The total instrumental response was determined using a blackbody calibration source at 700 K. For FT-IR measurements of the optically pumped plasma, the intermediate optical path containing "cold" CO (~290 K) between the plasma and cell port was reduced to 2.5 cm by using a

recessed-flange fitted with a flush CaF_2 window. This helped to mitigate the effects of CO self-absorption along the optical path.



Figure 4.9 Top view of experimental configuration for FT-IR spontaneous emission measurements.

4.2.3 FT-IR EXPERIMENTAL RESULTS

4.2.3.1 OPTICALLY PUMPED PLASMA VIBRATIONAL LEVEL POPULATIONS

Using the FT-IR setup shown in Figure 4.9 and described in Section 4.2.2, Figure 4.10 shows results of vibrationally resolved (16 cm⁻¹) CO first overtone spontaneous emission spectra, obtained, in the optically pumped plasma as a function of added helium

[47]. The uppermost curve, corresponding to the case of 3% CO in argon at 100 torr (no helium) and 11.6 watts CO laser pump power (unfocused), is labeled with the upper vibrational levels of the $\Delta v=2$ emission transition. The effect of helium quenching of the



Figure 4.10 CO 1st overtone FT-IR spectra (16 cm⁻¹ resolution) of the 3 torr, 100 torr argon optically-pumped plasma as a function of added helium. Top trace is 0 torr helium, while others are, from top to bottom, 7.5 torr, 17.5 torr, 26.5 torr, 34 torr, and 42 torr, respectively.

CO vibrational distribution function (VDF) is readily observed [66,67]. A qualitative indication of the high vibrational level populations in this optically-pumped plasma can be ascertained by noting that intensities of the v=40 transition (at ~2400 cm⁻¹) in the upper most spectrum is of the same order of magnitude as the low levels v=2-10. The five lower spectra (top-to-bottom order) in Figure 4.10 illustrate the results of adding 7.5 torr (7%), 17.5 torr (14.5%), 26.5 torr (20%), 34.0 torr (25%), and finally 42.0 torr (29%) of helium, respectively. As more helium is added, the signal from levels v≥15 diminishes rapidly, an indication of preferential V-T relaxation of the higher levels [66,67]. At the 42 torr (29%) helium concentration, the v"=20 population has been completely quenched, leaving levels v ≤ 15 significantly populated. As will become clearer in the following sections of this chapter, we will use the results of Figure 4.10 to create plasmas with what we term "high" vibrational disequilibrium and "mild" vibrational disequilibrium. Separate LIF diagnostic strategies, described completely in Sections 4.3 and 4.4, will be used to obtain LIF trans-rotational temperature measurements in each case.

4.2.3.2 D.C. GLOW DISCHARGE VIBRATIONAL LEVEL POPULATIONS

In order to characterized the population of the CO $X^{1}\Sigma^{+}(v''=7)$ level in preparation to performing A-X band LIF in a mildly vibrationally excited environment, we again used FT-IR spectroscopy to resolve (8 cm⁻¹) the CO first overtone spontaneous emission eminating from within the positive column of the CO/He d.c. glow discharge. A typical result for the conditions stated in Section 4.2.1.2 is shown in Figure 4.11 [48]. Note in



Figure 4.11 CO 1st overtone spectrum at 8 cm⁻¹ resolution of the 3.6% CO/He d.c. glow discharge at 8.3 torr.

this figure that the signal from the $v''=7\rightarrow 5$ is roughly the same magnitude as lower level transitions, an encouraging indication that the v''=7 is populated. To quantify the fractional vibrational populations, we have used the technique of Reference [115] to iteratively extract the normalized VDF from this 1st overtone spectra. These results are shown in the Boltzmann plot of Figure 4.12. In this figure, the resulting vibrational level population fractions are overlayed with a best-fit Treanor distribution at $T_{rot} \equiv 400$ K and $T_{vib} \equiv 2500$ K. The rotational temperature was prescribed based on FT-IR CO fundamental band emission spectroscopy measurements which will be described below in Section 4.2.4.2. It should be noted that the v''=0 and 1 populations are derived from this

best-fit Treanor curve. Agreement with the Treanor distribution [53] is good, and we see that under the conditions stated in Section 4.2.1.2 the v''=7 is well populated at ~0.1%.



Figure 4.12 Vibrational Distribution Function derived from Figure 4.11 CO 1st overtone spectrum. Solid line is a best-fit at $T_{vib} = 2500$ K to the Treanor distribution function [53]. Note that $T_{rot} \equiv 400$ K was chosen based upon experimental rotationally resolved (0.25 cm⁻¹) FT-IR CO fundamental spectra as discussed in Section 4.2.4.2.

4.2.4 ROTATIONAL TEMPERATURE USING CO FUNDAMENTAL EMISSION

4.2.4.1 OPTICALLY PUMPED PLASMA

In order to provide a comparison for the LIF temperature measurements within highly vibrationally excited plasma, to be described in Sections 4.3.3 and 4.4.3, we also obtained *rotationally* resolved (0.25 cm⁻¹) R-branch FT-IR emission spectra of the CO fundamental, $v=1\rightarrow 0$ band as a function of added helium under optically pumped conditions [47]. These measurements were performed with 100 torr argon, 3 torr CO, and up to 42 torr of helium with 11.4 W laser power. A typical result is shown in Figure 4.13 for the case of 42 torr helium which corresponds to the lowest spectrum in Figure 4.10. As can be seen in Figure 4.13, thirty-four well resolved, high S/N transitions ranging between R(2)-R(5) and R(10)-R(34), can be distinguished. Also shown in Figure 4.13 is the combined FT-IR instrument and shortpass filter response used to correct the peak values. To attain the line-of-sight averaged temperature, background subtracted and instrument-response corrected peak intensities were then mapped onto a Boltzmann plot, as described in Chapter 2 (in this case the appropriate normalization is by the rotational degeneracy of the upper vibrational level). As can be seen in the Boltzmann plot of Figure 4.14, it is clear that a linear region exists from R(19) to R(34). The region from R(2) to R(18) shows a pronounced non-linearity due to CO selfabsorption [112]. In order to confirm that the plasma is optically thin in the spectral region used for the least-squares temperature estimate, we used the HITRAN 2000



Figure 4.13 CO fundamental spectrum obtained by FT-IR spectroscopy (0.25 cm⁻¹ resolution) and used to extract a line-of-sight average temperature of an (unfocused) optically pumped plasma. Gas mixture for the spectra shown in figure is 100/42/3 torr Ar/He/CO for which a least-squares fit indicates a rotational temperature of 393 ± 10 K.

database [116] to model the self absorption caused by the ≈ 2 cm path length of cold CO located between the plasma and the cell window. Figure 4.14 shows the results (dashed curve) of these calculations overlayed on the Boltzmann plot. This result indicates that lines J'~19 to 34 coincide with a spectral region of negligable self-absorption (1% or less), indicating that we may use these points to extract the gas temperature. For 0 torr added helium (upper curve in Figure 4.10, a least-squares regression of these points results in a rotational temperature of 536 ± 10 K. For the case of 42 torr helium shown in Figure 4.13, the corresponding temperature was estimated to be 393 ± 10 K.



Figure 4.14 Boltzmann plot and temperatures obtained from FT-IR fundamental spectra (see Figure 4.13) of the 3% CO/Ar optically pumped plasma with (i) no added helium and (ii) 42 torr helium added (refer to Figure 4.10). Also, the extend of "cold" CO self-absorption modeled using the HITRAN 2000 database [116] is shown.

4.2.4.2 D.C. GLOW DISCHARGE PLASMA

We repeated the rotationally-resolved FT-IR measurements (described in Section 4.2.4.1) for the CO/He d.c. glow discharge and again used the HITRAN 2000 database [112,116] to model self-absorption at 290 K. The results are similar to those shown in

Figure 4.14 and are not repeated here. The least-squares slope indicated a line-of-site averaged CO rotational temperature of 395 ± 10 K within the CO/He d.c. glow discharge positive column. It should be mentioned that we based the rotational temperature of the best-fit Treanor distribution [53] (Figure 4.12) using this experimentally-derived value.

Having fully characterized the VDF's and trans-rotational temperatures of a set of optically pumped plasmas created with known and reproducible conditions, we now proceed to the development and demonstration of CO single-photon LIF.

4.3 D'-X BAND LIF ROTATIONAL TEMPERATURE MEASUREMENTS IN HIGHLY VIBRATIONALLY-EXCITED CO

4.3.1 VIBRATIONAL STATE RESOLVED LIF EMISSION

Before performing LIF temperature measurements it is essential to obtain resolved fluorescence emission spectra in order to verify that the detected signal originated with the CO and to identify the emission transitions that will be used, ultimately, for the LIF temperature measurements. For these measurements, we employed narrowband laser excitation and vibrational state resolved detection of an unfocused optically pumped plasma.

The tunable excimer laser used for LIF excitation has been described in Chapter 3, along with the method of the wavelength range calibration and locking efficiency. The experimental arrangement for the flow cell, excimer laser, and data acquisition systems



Figure 4.15 Top view of the experimental setup for LIF measurements of either the glow discharge or optically pumped plasma. The inset shows the relation between LIF collection volume and plasma.

are shown in Figure 4.15. Note the ArF mirror (1-3% transmission) used to attenuate the excimer laser beam in some experiments. Also, For clarity purposes, the CO laser has not been illustrated in Figure 4.15 and we refer the reader to Figure 4.3. Figure 4.16 shows a side-view illustration of the flow cell and optical paths for which fluorescence was collected using two separate systems. In Figure 4.16, we see that the top viewport provided access for an Optical Multichannel Analyzer (OMA) used for resolving the vibrational band emission. This OMA consisted of a 30 cm, f/4.0 aperture, single-grating spectrometer (Acton Research SpectraPro -300i), a nitrogen gas purged ICCD camera (Princeton Instruments ICCD-512-EFT-6/RB-E with 1.5× fiber optic taper and 512×512 15 µm CCD pixels), a camera coolant circulator (PI CC-100), a 12 bit, 1 MHz camera controller (PI ST-138), a high voltage pulser (PI PG-200), and data acquisition/postprocessing software (WinSpec/32 version 2.5.15.5). Note that the ICCD camera had $\sim 10\%$ overall quantum efficiency in the UV. Automated wavelength calibration of the OMA was performed using an Hg-Ar "pen" lamp (Oriel lamp 6035 and power supply 6060) [117] and the WinSpec/32 software. Emission was collected (f/12) using a single 38.1 mm diameter, 75 mm biconvex UVFS lens (≈ 68 mm focal length at $\lambda = 200$ nm) resulting in an $\approx 3 \times$ magnification of the plasma at the image plane. We note that the optical configuration in Figure 4.16 was chosen to approximately match the entendue of the collection lens and OMA spectrometer [118]. The inset in Figure 4.15 displays the subsequent collocation of the area imaged by the ≈ 0.5 mm OMA spectrometer slit (3) mm²), the plasma region, and the unfocused excimer laser beam (≈ 2 cm wide $\times 0.7$ cm thick). The resulting imaging volume from which the LIF signal was obtained was ~ 21 mm^3 .

Also shown in Figure 4.16, the bottom viewport was used to provide optical access for acquiring LIF excitation spectra using a small, low resolution monochromator (Jobin-Yvon H-10, 10 cm, f/3.5, 1200 g/mm UV blaze) [118]. Using a 1" dia., 100 mm



Figure 4.16 Side-view illustration of the OMA and monochromator collection systems used for vibrational state resolved LIF measurements of the optically pumped plasma. Spacial dimensions shown are for entenduematching conditions.

(\approx 85.5 mm focal length at λ =200 nm) UVFS biconvex lens with the geometry shown in Figure 4.16, the collection is at f/8 and magnification \approx 2.5×. Front and back slits were chosen to be 0.5 mm (bandpass of \approx 4 nm, FWHM) and the monochromator was set to

 $\lambda \approx 270$ nm. The imaging volume illustrated in Figure 4.15 was ~ 28 mm³. A photomultiplier tube (PMT) housing, mounted to the monochromator, contained a 350U (S-5) PMT (Hamamatsu R212) with ~20% quantum efficiency at 270 nm. Signals from the PMT were fed into a 300 MHz, 5× preamplifier (Stanford Research Systems SR240) before being processed by an SR250 gated "boxcar" integrator [14,119]. Using an SR245 computer interface, the boxcar averaged data was plotted and stored on a PC computer. As shown in Figure 4.15, synchronization of the laser, boxcar gates, and OMA gate was accomplished using multichannel pulse delay generator (Stanford Research Systems DG-535). The gate signal from each instrument was used to trigger a multichannel oscilloscope while the laser delay was adjusted on the DG-535 pulse delay generator. Synchronization was confirmed, using the oscilloscope traces as a guide, by maximizing the boxcar and OMA LIF signals.

Using the computer code given in Appendix D along with the molecular constants for the CO X [94] states and D' [41] (see Appendix D.1.1 and D.1.2), we searched for all possible rovibronic absorption transitions within the tuning range of the ArF laser. Sample output from the code as shown in Appendix D.2 indicates that two vibronic absorption bands, $X(v''=20)\rightarrow D'(v'=2)$ at 192.53 nm and $X(v''=21)\rightarrow D'(v'=5)$ at 193.13 nm, are energetically possible. To this author's knowledge, published data for the D'-X band Einstein A-coefficients does not exist and so the strength of these transitions were assessed from the following semi-classical Franck-Condon argument. Figure 4.17 shows a potential energy diagram for CO in which the vibronic manifolds were computed using the molecular constants of References [41], [94], along with a Morse potential approximation [25,72]. In this figure, we find that the $X(v''=20)\rightarrow D'(v'=2)$ is "more



Figure 4.17 Potential energy (Morse) diagram for carbon monoxide illustrating the relevant vibronic manifolds and LIF schemes.

vertical" than the $X(v''=21) \rightarrow D'(v'=5)$ transition to either D' classical turning point. Thus, we expected the $X(v''=20) \rightarrow D'(v'=2)$ absorption transition to be stronger.

Figure 4.18 shows the resulting vibrational state resolved LIF emission spectra when the ArF laser is tuned to a peak consistent with the CO P(15) $X(v''=20) \rightarrow D'(v'=2)$ at \approx 193.217 nm (see Appendix D.2). We note that this spectrum is a composite of 18



Figure 4.18 Vibrational state resolved D'-X band LIF using the OMA described in the text. Here, narrowband ArF radiation pumps the $X(v''=20) \rightarrow D'(v'=2) P(15)$ absorption line with subsequent spontaneous emission D'(v'=2) $\rightarrow X(v)$. (*) D'(v'=0) $\rightarrow X(v'')$; v''=21-27, (#) D'(v'=1) $\rightarrow X(v'')$; v''=25-27
separate spectra in which a 240 nm blaze grating (2400 g/mm) was used [120]. The excimer beam in this case was not focused into a sheet, so that the average pulse energy and incident intensity is estimated to be ≤ 1 mJ/pulse and ≤ 40 kW/cm², respectively.

Using the line position code given in Appendix D, the primary spectral peak wavelengths in Figure 4.18 were unambiguously assigned to $D'(v'=2) \rightarrow X(v'')$ spontaneous emission. When the ArF laser was tuned off resonance, the resulting signal decreased by at least two orders of magnitude. This observation implies that the ArF laser locking efficiency is high, giving us confidence that the observed emission is primarily due to pumping the $X(y''=20) \rightarrow D'(y'=2) P(15)$ rotational line. It is interesting to note the minimum in peak intensities in the progression from $D'(v'=2) \rightarrow X(v''=22)$ at $\lambda \approx 205$ nm to D'(v'=2) \rightarrow X(v''=30) at $\lambda \approx 270$ nm. This spectral trend is in opposition to the specified diffraction grating efficiencies for \perp and \parallel polarization as well as the aluminum substrate reflectance curve [120], but is consistent with a Franck-Condon "parabola" in emission as described on page 197 of Reference [25]; there are two intensity maxima to be expected in a v"-progression (v'=constant), one at small v and a second at large v". This observation is also consistent with the following semi-classical argument using Figure 4.17. In this figure, a vertical line drawn from the left D'(v=2)turning point intersects the X(v'') manifold at v'' ≈ 10 with wavelength at $\lambda \approx 143.7$ nm, while a vertical line from the right D'(v'=2) turning point intersects the ground state potential surface at v" \approx 35, corresponding to $\lambda \approx$ 332.2 nm. We then expect a minimum intensity transition to lie at the average of the two wavelength limits (*i.e.*, $\lambda_{\min} \approx \frac{1}{2}$ [143.7

nm + 332.2 nm] \approx 238 nm). Observe in Figure 4.17 that indeed a minimum intensity occurs at $\lambda \approx 235.0$ nm, corresponding to the D'(v'=2) \rightarrow X(v''=26) transition.

4.3.2 LIF EXCITATION AND COLLECTION

LIF excitation spectra of an unfocused optically-pumped plasma (see Figure 4.4, left photo) were acquired by wavelength scanning the injection-locked ArF excimer laser



Figure 4.19 Photograph showing the vertical mount and optical collection through the top viewport using the H-10 monochromator. We note that this configuration is the same for either the d.c. glow discharge (shown in photo) or the optically pumped plasma.

and collecting subsequent LIF from one particular vibronic band using the small H-10 monochromator described in Section 4.3.1. The experimental setup is similar to that shown in Figure 4.15 except the OMA was removed and the H-10 monochromator mounted above the top viewport window to increase collection efficiency. Figure 4.19 is a photograph of a typical arrangement. Emission was collected (f/8) and focused onto the 0.5 mm front slit using a single 1" dia., 100 mm biconvex UVFS lens with a 39 cm object/image distance (2.5:1 magnification). The back slit was chosen to be 0.5 mm, giving a FWHM bandpass of ~4 nm. This bandpass was adequate for rejection of Rayleigh scattering, extraneous ro-vibrational bands, and possible photochemically induced emission. While not the primary objective of this work, we mention that the ArF laser radiation is known to photochemically dissociate CO X(v"=0) molecules, subsequently forming excited-state atomic carbon $({}^{1}P_{1}^{0})$, and emitting to the ground state ¹S_o at 247.9 nm [121-123]. The mechanism is known as Resonantly Enhanced Multi-Photon Dissociation of CO (REMPD) and proceeds (in absorption) through the weak, spin forbidden transition $X^{1}\Sigma^{+}(v''=0) \rightarrow a^{3}\Pi(v'=2)$ [121-123]. It is important to note that the vibrational state resolved LIF emission spectrum shown in Figure 4.18 does not exhibit this feature because the ArF pump beam intensity was attenuated below the REMPD threshold. This potential source of interference will be elaborated upon in Chapter 5 regarding PLIF imaging and temperature measurement.

Figure 4.20 shows the resulting LIF excitation spectra taken with the monochromator grating adjusted to capture fluorescence from the (2,32) vibrational band at 294 nm (see Figure 4.18) while tuning the ArF laser through its gain profile at a rate of 1 step/s at a pulse repetition rate of 10 Hz. The average pulse energy of the unfocused



Figure 4.20 (a) <u>Lower</u>; Experimental LIF excitation scan due to $X(v''=20) \rightarrow D'(v'=2)$ absorption. (b) <u>Upper</u>; Synthetic spectrum generated using MoleLIF.

UV beam at the cell window was estimated to be $\approx 60 \text{ mJ/pulse}$ (intensity $\approx 2.5 \text{ MW/cm}^2$). Note that the locking efficiency was measured to be 50% or better in the central portion of the gain profile (refer to Chapter 3 for details on locking efficiency measurements). Figure 4.20b shows a synthetic spectrum (T_{rot}=500 K) generated using the MoleLIF code



Figure 4.21 Experimental X(v"=20)→D'(v'=2) LIF excitation scans in an optically pumped plasma as a function of added helium. Top most trace is a synthetic spectrum generated using the MoleLIF code.

(Appendix C) assuming that laser absorption occurs within the $X(v''=20)\rightarrow D'(v'=2)$ band. As shown in the figure, the experimental LIF spectrum displays a simple set of paired rotational lines consistent with the R/P branches of a ${}^{1}\Sigma{}^{-1}\Sigma$ transition, correlating well with the synthetic spectrum. Note that the anomalously low intensity of the P(14), R(17) pair is presumably due to overlap with an O₂ Schumann-Runge absorption which



Figure 4.22 Experimental $X(v''=20) \rightarrow D'(v'=2) P(15)$ LIF as a function of incident excimer beam energy. Solid line is a cubic polynomial fit of the data points.

reduces the injected seed power, and hence locking efficiency of the ArF laser. Nonetheless, as can be seen, the line positions are in excellent agreement with the predictions and so we have assigned the peaks to P/R branches within the $X(v''=20) \rightarrow D'(v'=2)$ absorption band. A complete listing of these theoretical line positions are given in Appendix D.2.

Another experiment, intended to provide further evidence that the LIF originates from $X\rightarrow D'$ absorption was performed in which the same concentrations of helium as used in the FT-IR quenching experiments (Figure 4.10) were added to the CO/Ar mixture. As shown in Figure 4.21, the resulting LIF signal decreases rapidly with increasing helium concentration. Note within Figure 4.10 that with 34 torr of added helium, the CO 1st overtone $v''=20\rightarrow18$ spontaneous emission signal has dropped by nearly a factor of 10, while the $v''=7\rightarrow5$ is only ~4. These FT-IR 1st overtone emission results are consistent with the LIF in Figure 4.21, implying that the X(v''=20) level population does indeed absorb the ArF laser radiation. From this data, along with the vibrational state resolved LIF spectra in Figure 4.18 and excellent agreement with the rotational assignments, we eliminate the possibility that the observed LIF in Figure 4.20a originates from the 4th Positive band system. We conclude that the observed LIF signal is due to single photon allowed X(v''=20) \rightarrow D'(v'=2) absorption.

Recall from Chapter 2 that the LIF regime in which temperature measurements are acquired will determine which normalization factor to use in the data analysis. In order to assess the $X(v''=20) \rightarrow D'(v'=2)$ LIF signal response to incident laser power, we performed an experiment in which the unfocused narrowband ArF laser was scanned slowly three times across the strong P(15) absorption line (refer to Figure 4.20a) for various incident laser energies. Beam energy attenuated was accomplished using an ArF mirror and various CaF₂ windows in succession [14]. The results of this experiment are presented in Figure 4.22 along with a cubic polynomial regression best-fit. The results imply that the $X(v''=20) \rightarrow D'(v'=2) P(15)$ absorption saturates at $\approx 60-70 \text{ mJ/pulse}$ (unfocused) laser energy ($\approx 2-3 \text{ MW/cm}^2$).

4.3.3 D'-X BAND ROTATIONAL LIF TEMPERATURE RESULTS

For temperature measurements, it is optimal to utilize absorption lines falling within a region of high ArF laser locking efficiency, while avoiding those which overlap the strong ambient O_2 Schumann-Runge absorption bands. In Figure 4.20a, we find that the P(15), R(18), P(17), and R(20) absorption lines appear to be reasonable choices for our measurements. Based on the results shown in Figure 4.22, we have assumed the D'-X LIF to be saturated since the incident excimer beam intensity was at least 2.5 MW/cm² for all temperature measurements. Both the "Two-Line" and "Boltzmann plot" methods are used to estimate the temperature as discussed in Chapter 2.5. The Two-Line measurements used background subtracted peaks obtained from slow excitation scans (1 steps/s) over the entire gain profile, while the Boltzmann plot data were obtained by slowly (0.5 step/s) tuning the laser across only the P(15), R(18), P(17), and R(20) six to seven times. Figure 4.23 displays the resulting Boltzmann plot with temperature results obtained using a least-square fit [95]. In the figure, the upper set of data was obtained by focusing the excimer laser beam into a $\approx 300 \,\mu\text{m}$ thick $\times 2 \,\text{cm}$ wide sheet [75] using a 40 mm × 25.5 mm, 500 mm focal length (454 mm at 193 nm) cylindrical plano-convex



Figure 4.23 Boltzmann plot of $X(v''=20) \rightarrow D'(v'=2)$ LIF along with least-squares fit of data and extracted rotational temperatures.

UVFS lens (CVI Laser Corp. RCX-40.0-25.4-254.3-UV). The average temperature from a least-squares fit, is 608 ± 130 K (2σ) where the standard deviation is $\sigma \approx 130$ K. Recall that the corresponding FT-IR measurement in Section 4.2.4.1 gave 536 ± 10 K (1σ). A repeated measurement using an *unfocused* ArF beam (FWHM profile \approx 7 mm thick × 2.0 cm wide [101]), shown as the lower set of data in Figure 4.23, gave 536 ± 103 K (2σ). We also mention a measurement [47] (not shown) using the excimer sheet which gave 442 ± 95 K (2σ) while the associated FT-IR result was 454 ± 14 K (1σ).

Peak	Value (a.u.)	Ratio S _{m:n}	D _{m:n}	$ \Delta E $ (cm ⁻¹)	Branch T (K) ± 2σ	$\begin{array}{c} T_{avg}\left(K\right)\\ \pm 2\sigma\end{array}$
P(15)	12.9	1 1727	0.88406	103.588	531 ± 100	508 ± 86
P(17)	11.0	1.1727				
R(18)	9.5	1 2014	0.90358	122.318	486 ± 72	
R(20)	7.3	1.3014				

Table 4.1 Two-line data, ratios, and temperatures obtained using a ArF beam focused into a sheet. Data obtained on 11/16/01. FT-IR result gave 536 ± 10 K. "Accuracy" $\approx \pm 50$ K.

Peak	Value (a.u.)	Ratio S _{m:n}	D _{m:n}	$ \Delta E $ (cm ⁻¹)	Branch T (K) ± 2σ	$\begin{array}{c} T_{avg}\left(K\right)\\ \pm 2\sigma\end{array}$
P(15)	12.7	1.1651	0.88406	103.588	544 ± 104	460 ± 74
P(17)	10.9					
R(18)	10.7	1 4459	0.90358	122.318	377 ± 43	
R(20)	7.4	1.4439				

Table 4.2 Two-line data, ratios, and temperatures obtained using a ArF beam
focused into a sheet. Data obtained on 11/16/01. FT-IR result gave
 536 ± 10 K. "Accuracy" $\approx \pm 50$ K.

Peak	Value (a.u.)	Ratio S _{m:n}	D _{m:n}	$ \Delta E $ (cm ⁻¹)	Branch T (K) ± 2σ	$\begin{array}{c} T_{avg}\left(K\right)\\ \pm 2\sigma\end{array}$
P(15)	9.2	1 1795	0.88406	103.588	520 ±95	
P(17)	7.8	1.1775				547 ±98
R(18)	7.5	1 2205	0.90358	122.318	575 ± 101	
R(20)	6.1	1.2295				

Table 4.3 Two-line data, ratios, and temperatures obtained using an *unfocused* ArF beam. Data obtained on 4/25/03. "Accuracy" $\approx \pm 50$ K.

Temperature measurements obtained using the Two-Line method are shown in Table 4.1 and 4.2 below using the focused UV "sheet" as well at Table 4.3 using an unfocused ArF beam. Referring to the notation in Chapter 2, Section 2.5.1, the tables display background subtracted peak values in arbitrary units, the ratio $S_{m:n}$, the (saturated) exponential prefactor $D_{m:n}$, the energy separation of the two lines, the resulting "branch temperature", and the average of the two branches. These Two-Line temperature measurements are in good agreement with the FT-IR and D'-X band LIF results. The 2σ confidence intervals, computed using Equation 2.50 in Chapter 2, Section 2.51, indicate a precision of ±100 K and "accuracy" of ± 50 K.

4.4. A-X BAND LIF ROTATIONAL TEMPERATURE MEASUREMENTS IN HIGHLY AND MILDLY VIBRATIONALLY EXCITED CO

4.4.1 VIBRATIONAL STATE RESOLVED LIF EMISSION

In a manner similar to that performed for the D'-X band, we repeated the vibrational state resolved LIF emission measurements for the A-X bands using highly vibrationally excited CO created within an unfocused optically pumped plasma (see Figure 4.3 and Figure 4.4, left photo). The same apparatus, described in Section 4.3.1 and Figures 4.15, 4.16, were used. The only changes are with respect to the LIF excitation scan monochromator; (i) we now used a UV optimized PMT (Hamamatsu 250S R166UH) having ~30% quantum efficiency at 200 nm, (ii) the front and back slits were 1.0 mm and 0.1 mm, respectively, giving a bandpass of ~8 nm (FWHM) (iii) the center wavelength was set to $\lambda \approx 201$ nm. It is important to note that the OMA gate was set to 100 ns.

The computer code and data given in Appendix D, D.1.1, and D.1.3 was used to search for all energetically possible vibronic absorption bands accessible to the ArF laser at 193 nm. Two bands, reasonable from a semiclassical Franck-Condon argument, were found; the $X^{1}\Sigma^{+}(v''=7)\rightarrow A^{1}\Pi(v'=1)$ and $X^{1}\Sigma^{+}(v''=12)\rightarrow A^{1}\Pi(v'=8)$. The $X(7)\rightarrow A(1)$ vibrational wavelength is computed to be 193.11 nm while the $X(12)\rightarrow A(8)$ was 193.62 nm. Appendix D.3 shows a sample output of expected $X(7)\rightarrow A(1)$ rotational P, Q, and R branch absorption line positions.

Figure 4.24 shows the resulting vibrational state resolved LIF emission spectra when the narrowband ArF laser was tuned to the X(7) \rightarrow A(1) Q(10) line at (calculated) 193.20 nm. We note that similar specta were obtained pumping the X(7) \rightarrow A(1) Q(17) and P(12) lines at 193.36 nm and 193.38 nm, respectively. In this case, the incident excimer beam was unfocused and attenuated (\approx 1 mJ/pulse \Rightarrow I \approx 42 kW/cm²) by using an



Figure 4.24 Vibrationally resolved LIF spectrum generated using the narrowband ArF laser to pump the $X^1\Sigma^+(v''=7) \rightarrow A^1\Pi(v'=1) Q(10)$ rotational line. When tuned off resonance, the signal decreased by $\approx 70 \times$ (see lower trace near bottom of plot).

ArF turning mirror as shown in Figure 4.15. We note that the spectrum in Figure 4.24 is a composite of 8 separate spectra acquired using a 2400 g/mm grating blazed at 240 nm [120]. When the laser was tuned off resonance, the signal decreased by \approx 70×, an indication that the broadband ArF radiation component is relatively small and hence the locking efficiency is high. In highly vibrationally excited CO plasmas, it is known [60] that electron-mediated electronic state population transfer from high-lying X¹ Σ (v≥39) to A¹ Π (v<5) leads to spontaneous 4th Positive emission. The strength of this emission, for our conditions, was assessed by obtaining vibrationally resolved spontaneous emission spectra of the blue glow (*i.e.*, *without* ArF laser excitation) using the *same* optical collection as that of the LIF spectrum of Figure 4.24. Our results indicate that the spontaneous 4th Positive emission due to electron-mediated E-V transfer was ≈5 orders of magnitude less than that due to the LIF shown in Figure 4.24 since the total exposure time of the OMA required an increase from 2µs to 200 ms in order to achieve a total pixel count of ≈700,000.

With the aid of the line position code (Appendix D), nearly all the emission bands within Figure 4.24 have been assigned. The important assignments have been label in the figure. Note that the A \rightarrow X emission lines labeled (1,6), (1,8), (1,9), and (1,10) are present, consistent with our hypothesis that we were directly pumping a rotational line within the X(7) \rightarrow A(1) band. That this hypothesis is reasonable can also be argued from the standpoint of the Einstein A-coefficients given in Appendix A, Table A.2. In this table, we see that the strength of the A(v'=1) \rightarrow X(v") spontaneous emission decreases monotonically by two orders of magnitude as v" increases from 4 to 8. While the (1,6) appears to have the same intensity as the (1,8) in Figure 4.24, we note that it lies within the VUV and is more strongly attenuated by the ambient O_2 present within the 72 cm optical path between the flow cell and ICCD photocathode surface (42 cm from cell window to the slit plus 30 cm within the OMA spectrometer). The influence of the Schumann-Runge absorption at the edge of the VUV is illustrated in Figure 4.25 which displays an experimentally obtained transmission spectra taken from Reference [124]. In this figure, we find that there are sharp variations in transmission in the \approx 180–195 nm range that, without purging or vacating the optical path, must be considered when



Figure 4.25 This high-resolution (0.05 nm spectral bandwidth), deep-UV spectrum of molecular oxygen shows total optical transmission between 175 – 200 nm, illustrating the strong influence of the Schumann-Runge bands in this spectral region. Note that the fine structure is due to the rotational P/R branch triplet absorption. Taken from Reference [124].

analyzing the 4th Positive band emission intensities. Furthermore, we note that the OMA grating efficiency has a sharp cutoff below 200 nm [120]. Thus, with the exception of the (1,9) at 202.68 nm, the (1,6), (1,8) and (1,10) emission intensities labeled in Figure 4.24 follow the trend given by the Einstein coefficients in Table A.2. Note that the data in Table A.2 implies that the (1,8) emission intensity at 200.70 nm should be half that of the (1,9) at 208.81 nm. Since both these transitions lie outside the VUV they may be directly compared (see Figure 4.25). However, in contradiction to this expectation, we actually find the (1,8) is actually about *twice* the (1,9) as shown in Figure 4.24. The reason for this is not clear, but perhaps indicates an error in the Einstein-A coefficients given in Appendix A, Table A.2.

The emission spectrum within Figure 4.24 exhibits additional features worth noting. In that spectrum we have been able to unambiguously assign transitions originating from the lower A(v'=0) as well as those *higher* than the directly pumped A(v'=1) level. Specifically, we note the (0,5-9) as well as the (2,v''), (3, v'') bands. Not shown in this figure are numerous peaks of low intensitiy that correlate well with levels $4 \le v' \le 9$. The fact that we observe vibrational population transfer on a timescale ≤ 100 ns (OMA gate) suggests that the frozen vibrational level assumption, used in deriving the LIF model developed in Chapter 2, is not strictly valid under the present conditions.

Figure 4.26 shows a vibrational state resolved emission spectrum obtained by exciting a rotational line within the $X(12) \rightarrow A(8)$ band. Again, we have been able to use the line position code to attribute the most intense emission to (8, v"=13-21) as well as the (7, v"=11-20), (9,v"=13-21), and (10,v"=19,20) progressions.



Figure 4.26 Vibrationally resolved LIF spectrum generated using the narrowband ArF laser to pump a rotational line within the $X^{1}\Sigma^{+}(v''=12) \rightarrow A^{1}\Pi(v'=8)$ absorption band.

Using the vibrational state resolved emission shown in Figure 4.24 along with the transition probabilities in Table A.2, the strongest emission (due to to $X(v'=7) \rightarrow A(v'=1)$) laser excitation) is the A(v'=1) \rightarrow X(v''=6) at 186 nm. Concerns of systematic errors due to VUV O₂ Schumann-Runge band absorption of CO A-X rotational emission lines, however, prompted us to collect the slightly weaker $A(v'=1) \rightarrow X(v''=8)$ at 200.8 nm. We note that this transition was sufficiently strong to obtain high S/N data. Since this $A(1) \rightarrow X(8)$ band is also relatively close to the ArF 193 nm excitation line, we wished to verify that stray light and Rayleigh scattering levels would be adequately rejected by the H-10 monochrometer. We characterized this monochromator using Rayleigh scattering of broadband ArF laser radiation within ambient room air. The monochromator grating was tuned by hand in steps of ≈ 0.1 nm with the boxcar averaged PMT signal recorded at each step. The results, shifted to coincide with the A(1) \rightarrow X(8) emission line at 200.8 nm, are shown in Figure 4.27 for a fixed back slit of 0.1 mm and various front slit apertures. From these results we find the 1.0 mm front/0.1 mm back slit combination gives an ≈ 8 nm FWHM bandpass but may transmit a small fraction of the Rayleigh scattered component. Furthermore, when the center wavelength is set to pass $A(1) \rightarrow X(8)$ emission line at 200.8 nm, a possible source of interference, under extreme vibrational excitation, will arise from the coincidentally overlapping $D'(v'=2) \rightarrow X(v''=21)$ emission at 199 nm (see Figure 4.18).



Figure 4.27 Bandpass characterization of the H-10 monochromator. Back slit fixed at 0.1 mm, front slit varied.

We repeated the LIF excitation spectrum scans for the A-X band using the experimental setup previously described in Section 4.3.2 and shown in Figure 4.20a. Figure 4.28a shows an experimentally obtained 4th Positive excitation spectrum obtained for an optically pumped plasma created by a *focused* CO laser beam (see Figure 4.4, right photo). In this case, the incident ArF laser beam was focused into a sheet as described in Section 4.3.3. Since the maximum incident laser energy was measured to be \approx 46 mJ/pulse, we estimate the beam intensity to be \approx 45 MW/cm². The LIF emission volume

was ~3 mm³. Note that the locking efficiency was $\approx 60\%$ or better except in spectral regions where ambient O₂ absorption diminishes the oscillator/amplifier radiation.

Using the line position code in Appendix D, we were able to identify nearly all the spectral peaks intensities (for clarity, we have not displayed all assignments in Figure 4.28a). Assignments within the range 193.1 nm – 193.2 nm were, however, complicated by the spectral overlap of conjected features and extraneous lines due, presumably, to the coincidental D'(v'=2) \rightarrow X(v"=21) emission as mentioned above. Four peak intensities, relevant to Planar LIF imaging in Chapter 5, have been highlighted in Figure 4.28a; Q(10), P(10), Q(17), and P(17).

Figure 4.28b shows a synthetic saturated LIF spectrum generated using the MoleLIF code (Appendix C), and molecular constants in Appendix A, Table A.3. It is important to note that the excimer intensity and locking efficiency in the synthetic spectrum was assumed to be constant. The temperature of the synthetic spectrum was chosen to be $T_{rot}=750$ K based on a heuristic comparison of peak ratios in the 193.2 – 193.7 nm range. While this temperature is reasonable (see Figure 4.1 for the case of a focused CO laser beam and 3.5% CO/Ar mixture), a more systematic and accurate method of extracting the rotational temperature will be discussed below in Section 4.4.3. Finally, note the excellent agreement of the bandhead positions, especially the $X(v''=12)\rightarrow A(v'=8)$ absorption band where the excimer locking efficiency is about 50%.

Before making any A-X band LIF excitation scans to extract rotational temperature, it was deemed necessary to determine the incident excimer laser intensities which correspond to the linear and saturated signal regimes. To do this, we performed 15 excitation scans similar to that shown in Figure 4.28(a) (using the same plasma conditions) in which the beam intensity was varied over a range spanning at least five orders of magnitude. Since these spectra were obtained using different PMT voltages (ranging from -400 to -700 VDC) and optical collection efficiencies, a two-line technique was used in which we compared the Q-to-P branch peak intensities originating from the same ground J" rotational level. This Q/P ratio was expected to be a function of only the incident spectral irradiance in the high-J" limit so that an experimentally obtained intensity plot (see Chapter 2.3, Figure 2.2) would expose the linear and saturation regimes.



Figure 4.28 (a) <u>Lower</u>; Experimental LIF excitation scan due to $X(v''=7) \rightarrow A(v'=1)$ absorption. (b) <u>Upper</u>; Synthetic spectrum generated using MoleLIF.

Pulse	Beam	Intensity,	J″=10	J″=10	J″=11	J‴=12	J‴=17	J″=17	Expt.	
Energy, mJ	Area, cm ²	MW/cm ²	Expt.	Thry.	Expt.	Expt.	Expt.	Thry.	Average	
0.001	1.4	4×10 ⁻⁵	2.36	2.330	1.91	1.83	2.37	2.183	2.11	
0.02			8×10 ⁻⁴	(4.67)	2.328	2.07	1.87	3.03	2.181	2.32
		4×10 ⁻²	2.80	2.238	1.72	1.73	2.50	2.100		
0.0			1.78		1.98	1.69	2.39		2.08	
0.9			2.45		2.44	1.66	2.57			
			(3.82)		1.92	1.47	2.33			
0.3	0.06	0.25	2.10	1.889	2.38	1.88	1.08	1.786	1.86	
0.5		0.5	2.12	1.685	0.96			1.603	1.54	
0.6		06	2.56	1.626	1.60	1.22		1.550	1.61	
		0.0	1.84	1.020	1.05	1.41		1.550	1.01	
1]	0.8	1.89	1.469	1.90	1.78	1.88	1.409	1.86
90	1.4	4	1.24	1.185	1.36	1.24	1.10	1.154		
			(4.29)		1.24	1.36	1.24		1.22	
			1.13		1.05	1.05	1.27			
46	0.06	45	1.06	1.049	0.97	0.88	1.88	1.033	1.20	

Table 4.4 Q(J'')÷P(J'') ratios obtained from 15 separate A-X LIF excitation scans with ArF laser intensities spanning 5 orders of magnitude. Also shown is theoretical ratios for J''=10 and 17.

Only excitation lines lying within regions of high locking efficiency and low Schumann-Runge absorption were used in this saturation study; Q(10)÷P(10), Q(11)÷P(11), Q(12)÷P(12), and Q(17)÷P(17) (refer to Figure 4.28a and Appendix D.3 for line positions). Excimer beam attenuation was performed using a combination of ArF turning mirrrors and CaF₂/UVFS windows. Table 4.4 shows experimental results for J''=10, 11, 12 and 17 transitions as well as theoretical ratios for J''=10 and 17, as computed using the MathCad[™] program listed in Appendix B. It is important to note that the theoretical Q/P ratios were obtained using the Einstein A-coefficients listed in Appendix Table A.2, $A^{1}\Pi(v'=1)$ CO/CO and CO/Ar quenching cross-section data listed in Appendix Table A.1, and by assuming an excimer narrowband linewidth of 0.5 cm⁻¹ Previously, in Chapter 3, we have demonstrated that this is a (15 GHz FWHM). reasonable approximation to the excimer narrowband linewidth in the region of high locking efficiency. We note that the results of this calculation (Appendix B) indicate $I^{sat,P} \approx 1 \text{ MW/cm}^2$ and $I^{sat,Q} \approx 0.5 \text{ MW/cm}^2$ at 500 K for a 3% CO/Ar mixture with the vibrational population fraction assumed to be $f_{v=7} \approx 0.5\%$.

As detailed in Chapter 2, for large J" we expect that the Q/P ratios will approach two in the unsaturated limit and unity in the saturated limit. To aid in interpreting this data we have, for a given intensity, averaged the ratios across the columns and placed the result in the column lableled "Expt. Average". Figure 4.29 shows a plot of the experimentally obtained ratios along with the averages. We note that the data within the parentheses of column "J" = 10 Expt" has not been plotted in Figure 4.29 since they are believed to be "outlying" points [95]. Figure 4.29 also displays the theoretically obtained values listed in Table 4.4. In Figure 4.29 we find that the experimental averages are in excellent agreement with the theoretical expectations for both J'' = 10 and 17. These results lend confidence that we can determine the LIF regime from the estimated incident laser intensity and hence, the proper normalization.



Figure 4.29 Plot of both experimental and theoretical Q(J'')÷P(J'') ratios given in Table 4.4 as a function of ArF laser intensity.

4.4.3 A-X BAND ROTATIONAL LIF TEMPERATURE RESULTS

4.4.3.1 HIGHLY VIBRATIONALLY EXCITED CO

Figure 4.30 shows the results of two LIF excitation scans at 1 step/s taken within an optically-pumped plasma created by an unfocused CO laser beam. Figure 4.30a corresponds to an incident excimer beam intensity $I \approx 0.04 \text{ MW/cm}^2$ while that of Figure 4.30b is \approx 4 MW/cm². Using the results shown in Figure 4.29, we find the spectrum of Figure 4.30a corresponds to unsaturated, linear LIF while that of Figure 4.30b is partially saturated. To demonstrate the consequences of using the proper normalization function to extract rotational temperature, we have employed the Boltzmann plot method as detailed in Chapter 2.5.2 to analyze both excitation scans in Figure 4.30. Under the assumption that the LIF regime is linear, we used the appropriate Hönl-London factors for the P and Q branches to normalize the peak intensities shown in Figure 4.30a, with the resulting Boltzmann plot shown as the uppermost set of points (\blacksquare) in Figure 4.31. In this case, note that both P/Q branch peak intensities fall close to the least-squares fit line that results in a 2σ rotational temperature of 528 ± 51 K. This case contrasts that of the partially saturated peak intensities shown in Figure 4.30b, which have been *improperly* "line- strength" normalized and plotted as the lower two data sets in Figure 4.31. Note the offset between the P (\blacktriangle) and Q (\bullet) branches. As discussed in Chapter 2.5.2, this is expected because the P branch saturation intensity is about half that of the Q-branch, and has not been properly accounted for by the normalization. Also, note in Figure 4.31 that



Figure 4.30 A-X LIF excitation spectra (a) unsaturated, linear regime, (b) partially saturated regime.



Figure 4.31 Boltzmann plot using "line-strength normalization of peak intensities given in Figure 4.30. Top data set taken under the linear LIF regime has been properly normalized. The lower two sets show an offset in the P-Q branches due to improper normalization. ▲=P-branch, ●=Q-branch, ■= combined Q and P-branch data.



Figure 4.32 Boltzmann plot of same data shown in Figure 4.30 except the partially saturated case has been "degeneracy" normalized. The P-Q branch offset nearly vanishes since the proper normalization is used. ▲=P-branch, ●=Q-branch, ■= combined Q and P-branch data.

the temperatures have been extracted separately for each branch; $T_P = 525 \pm 25$ K and $T_Q = 448 \pm 25$ K, giving an overall average of T = 486 ± 25 K. Recall from Section 4.2.4.1 that the FT-IR rotational temperature of a similar optically pumped plasma gave T = 536 ± 10 K.

When the peak signals of the saturated LIF excitation scan shown in Figure 4.30b are properly analyzed using "degeneracy" normalization (Chapter 2.5.2.2, Equations 2.70a,b), we find that the P-Q branch separation nearly vanishes as shown in the lower data set of Figure 4.32. We attribute the small offset between the four higher J-values to

partial saturation. In this figure, we see that a single least-squares fit can now be made resulting in a rotational temperature $T = 503 \pm 50$ K For comparison, the linear regime LIF Boltzmann plot has been reproduced from Figure 4.31 and shown as the upper data set in Figure 4.32.

4.4.3.2 MILDLY VIBRATIONALLY EXCITED CO

Using the CO/He d.c. normal glow discharge under mildly vibrationally excited conditions as described in Sections 4.2.1.2 and 4.2.3.2, along with the apparatus setup shown in Figures 4.15 and 4.19, we performed spatially averaged LIF temperature measurements using the Boltzmann plot method. Figure 4.33a shows a typical LIF excitation scan obtained at a slow scan rate (1 step/s) using a beam energy measured to be ≈ 60 mJ/pulse in the center portion of the ArF gain profile. The excimer beam was focused into a sheet, resulting in an intensity of ≈ 60 MW/cm². We performed calculations similar to those shown in Appendix B using the CO/He $A^{1}\Pi(v'=1)$ quenching cross-section data shown in Appendix A, Table A.1, finding that the saturation intensities of the rotational branches are similar in magnitude to those of the CO/Ar optically pumped plasma. Thus, we expect that the absorption features shown in Figure 4.33a are well within the saturated LIF regime. For comparison, Figure 4.33b shows a synthetic spectrum generated using the MoleLIF code assuming that T_{rot}=300 K. Using the degeneracy normalized peak intensities of the spectrum shown in Figure 4.33a, we obtained a least-squares rotational temperature of 306 ± 32 K [49]. We note that FT-IR temperature measurements were not obtained for comparison using this particular d.c.

glow discharge experiment. However, FT-IR measurements *were* performed 12 months prior under similar conditions, giving 395 ± 10 K. The associated A-X band excitation spectra were similar to that shown in Figure 4.33a, and the resulting least-squares temperature was 432 ± 44 (2σ) K, implying an accuracy of ± 50 K obtained using the Boltzmann plot method.



Figure 4.33 Excitation scans taken under mildly vibrationally excited conditions created by a CO/He d.c. normal glow discharge. (a) Lower; Saturated LIF experimental spectrum (b) Upper; MoleLIF Synthetic spectra.

CHAPTER 5

PLANAR LIF IMAGING AND TEMPERATURE MEASUREMENTS USING THE CO A-X AND D'-X BANDS

5.1 PLANAR LASER INDUCED FLUORESCENCE

In Chapter 4 we used single-photon CO $X(v''=20)\rightarrow D'(v'=2)$ and $X(v''=7)\rightarrow A(v'=1)$ LIF to perform *spatially averaged* temperature measurements within both extreme and mildly vibrationally-excited CO plasmas. The background subtracted LIF transition peaks had sufficient S/N to provide ±50 K (2 σ) accuracy. In this chapter, we present *spatially resolved* temperature measurements within model plasma environments (see Chapter 4) using Planar LIF (PLIF) imaging.

The primary goal of PLIF imaging was to demonstrate single laser "shot" temperature measurements within a vibrationally-excited CO plasma. In general, this capability is important because it can provide spatially resolved measurements of temperature and species concentration within time-varying flowfields [14-17,23,26,27,29,125-128]. We have addressed the following three important issues bearing upon the outcome of our proof-of-concept measurements; (i) as compared to the LIF measurements in Chapter 4, the smaller PLIF measurement volume associated with

image formation onto a CCD array results in a reduction of the signal per pixel, (ii) replacement of the monochromator requires a suitable imaging filter to reject interfering radiation, and (iii) sufficient temperature measurement sensitivity must be maintained by choosing sufficiently rotational transitions having a large energy separation (see Chapter 2, Section 5.2.1, Equations 2.48 and 2.50) while also resulting in high signal-to-noise ratio (S/N) PLIF images.

To perform PLIF imaging, the laser beam is formed into a thin "sheet", directed into the flow region of interest [14-17]. A synchronized camera, usually oriented perpendicular to the plane of the sheet, is used to record the subsequent LIF eminating from within the small "slice" volume during the laser excitation time period. Figure 5.1 illustrates the typical geometry in which the camera lens optics are represented by an



Figure 5.1 Typical geometry for planar LIF imaging of illuminated flowfield.

equivalent lens aperture and principal points separated by distance ΔP [129]. Also shown in the figure is the object-to-lens distance s₁, the lens-to-image (on photocathode) distance s₂, the ICCD camera photocathode, and the CCD chip pixel array.

Due to the extended size of the laser beam necessary for planar imaging, the signal available from each volume element $\Delta L \times \Delta W \times t_{sheet}$ in most PLIF experiments is low relative to the signal available in ordinary pointwise LIF [15,16]. Recall in Chapter 4, Sections 4.3.3 and 4.4.2 that we acquired LIF temperature measurements using a laser sheet of dimension W≈20 mm wide × t_{sheet} ≈0.03 mm thick with average beam intensities of ≈34 MW/cm² (D'-X) and ≈4 MW/cm² (A-X), respectively. Although the S/N was adequate, it is not clear from these experiments whether single-shot imaging is possible since the data was boxcar averaged at a 10 Hz laser repetition rate. In addition, the total signal resulted from photons emitted from a relatively large collection volume (V_{coll} ≈ 20 mm³) and accumulated on a relatively large cross-sectional area photomultiplier tube (PMT).

Using the geometry and nomenclature given in Figure 5.1 along with Equation 2.20 in Chapter 2, we find the photoelectron generation rate (*i.e.*, "signal") per pixel for the *linear LIF regime* under a given object-to-CCD image magnification $m \equiv 1.5 \cdot L_{pix}/\Delta L$ = $|-s_2/s_1|$ and f-number (denoted here simply as f/# or f) is [14]

$$\Delta S_{\text{pix}}^{\text{lin}} = n^{\circ} \beta(T) f_{v''} \cdot \frac{3B_{12}E_{L}}{32c\Delta v_{\text{laser}}} \cdot \frac{\Delta L_{\text{pix}}m}{f^{2} \left[1+m\right]^{2}} \cdot Y_{2}\eta \quad ,$$
(5.1)

where n° is the total population number density, $\beta(T)$ is the temperature dependent rotational Boltzmann fraction, $f_{v''}$ is the vibrational level population fraction, B_{12} the absorption Einstein coefficient, Δv_{laser} is the laser narrowband component linewidth (FWHM), E_L the average energy within the magnified pixel element $\Delta L \times \Delta W$ (see Figure 5.1), L_{pix} the pixel length, Y_2 is the fluorescence quantum yield, and η is the combined detector quantum efficiency and bandpass transmission. In the *saturated LIF regime* we find from Equation 2.26 in Chapter 2

$$\Delta S_{pix}^{sat} = n^{\circ} \beta(T) f_{v''} \cdot \frac{A_2^{coll}}{\left[1 + \frac{g_1}{g_2}\right]} \cdot \frac{9A_{pix} t_{sheet}}{64f^2 \left[1 + m\right]^2} \cdot \eta \qquad , \qquad (5.2)$$

where A_2^{coll} is the sum of Einstein A-coefficients corresponding to collection band photons, g_1 , g_2 are the lower and upper state degeneracies, respectively, $A_{pix}=L_{pix}\cdot W_{pix}$ is the pixel area, and t_{sheet} is the laser sheet thickness. Equations 5.1 and 5.2 both include the 1.5:1 fiber optic taper ratio from the ICCD camera Micro-Channel Plate (MCP) phosphor screen to the CCD chip. Note that for a fixed magnification, both expressions depend inversely upon the *square* of the f/#, so that it becomes important to pay careful attention to collection efficiency. More important, however, is the linear dependence of the average beam energy E_L within the magnified pixel element $\Delta L \times \Delta W$ in Equation 5.1 and illustrated in Figure 5.1. In typical PLIF imaging applications, the laser energy is generally not large enough to produce saturation in which the signal becomes independent of E_L and Y_2 , as shown by Equation 5.2 [14]. Consequently, the
measurements obtained using linear regime PLIF need to be corrected for any spatial variations in fluorescence quantum yield and laser sheet energy [14,17,130]. However, to avoid complicating issues involving correction factors, we have attempted to explore proof-of-concept PLIF imaging and temperature measurements as close to the saturated regime as possible. While the unintentional imaging of non-saturated fluorescence induced by sub-threshold spatial and temporal intensity variations is certainly an important consideration [14], we have placed it secondary to the issue of spectral interferences and choice of imaging filters. These filtering schemes will be discussed below in Sections 5.2.1 and 5.3.1 for the A-X and D'-X bands, respectively.

5.1.1 PLIF EXCITATION AND COLLECTION

The experimental setup for the PLIF imaging, shown in Figures 5.2 and 5.3, closely follows that previously described in Chapter 4, Section 4.3.1. Figure 5.2 shows a side-view illustration of the optical collection arrangement relative to the flow cell geometry. Figure 5.3 is a top view of the experimental arrangement for the flow cell, ArF laser, and data acquisition systems. Synchronization of the ArF laser, ICCD camera, and boxcar averaging system again utilitized a multichannel delayed pulse generator.

Notice in both figures that we have replaced the Optical Multichannel Analyzer (OMA) with a vertically mounted ICCD camera fitted with a 105 mm UV-Nikkor lens (spectral range of 190 nm to 1300 nm) with apertures f/4.5, f/5.6, f/8, f/11, f/16, f/22, and f/32 and magnification range $0.0155 \le m \le 0.5050$ [129]. The distance between principal points, ΔP , is 9 mm as shown in Figure 5.1 [129]. As described in Chapter 4, Section

4.3.1 and shown in Figure 5.2, the LIF resonance peaks were monitored with the small H-10 monochromator as the ArF laser wavelength was tuned.

The ICCD camera (Princeton Instruments ICCD-512-EFT-6/RB-E), which was part of the previous OMA system, consisted of a Gen II UV-NIR Enhanced (180-800 nm) intensified photocathode 1.5:1 fiber-optically coupled to a 512×512 CCD array with pixel size $L_{pix} = W_{pix} = 15 \ \mu m$ (see Figure 5.1) [131]. The photocathode Quantum Efficiency (QE) was 13 % in the 150-300 nm range for a 5 ns exposure. The camera gating had an



Figure 5.2 Side-view illustration of the ICCD camera used for PLIF imaging and the entendue-matched LIF monochromator collection systems.



Figure 5.3 Top view of the experimental setup for PLIF imaging of either the glow discharge or optically pumped plasma.

on/off ratio of 5×10^6 :1 with a sensitivity of 1-35 "counts" per photoelectron, depending on the variable gain setting, which ranged from 0 to 1000 (arbitrary units). Using the 12 bit A/D converter, the image dynamic range was $2^{12} = 4096$ "counts". Nonuniformity of pixel response was quoted as 12%. The CCD readout noise was 1-1.5 counts/pixelsecond) in Gate mode. Detection of extremely weak signals is typically limited by the dark current of the intensifier's photocathode, refered to as the Equivalent Brightness Intensity (EBI). The EBI for this camera is quoted as being < 5 counts/pixel-seconds, which represents < 0.1% of the 12-bit A/D dynamic range. The camera controller (PI ST-138) regulates the temperature of the CCD array via a Peltier effect thermoelectric cooler in order to reduce this "dark current" noise response. For all measurements in this chapter, the camera temperature was set to -34 °C, which required that the camera housing be continuously flushed with dry nitrogen gas so that condensation did not form on the CCD or photocathode. All statistical analyses of image S/N within this chapter are based on the assumption of photon-noise limited ICCD camera operation [14,132].

5.1.2 A-X AND D'-X BAND PLIF FOR THE OPTICALLY PUMPED PLASMA

Recall from Chapter 4, Section 4.4.2 (also Figure 4.29) that the P and Q-branch saturation intensities for a 3% CO/Ar mixture at 100 torr and 500 K were estimated to be $\approx 1 \text{ MW/cm}^2$ and $\approx 0.5 \text{ MW/cm}^2$, respectively. As mentioned above, we desired to work within the fully saturated regime (I/I^{sat} ≥ 10) to avoid complicating issues of local energy variations. However, high intensities have the potential to induce photochemical processes [14] that may lead to further quenching and/or spectral interferences (*e.g.*, CO

REMPD [121-123] as discussed in Sections 5.2.1 and 5.3.1). A set of calibrated neutral density filters was not available, so we chose to attenuate the \approx 65-80 mJ/pulse ArF beam with a 45° ArF turning mirror (\approx 1-3% transmission) as discussed in Chapter 4, Sections 4.3 and 4.4. This is illustrated in Figures 5.3 and 5.4 (left photograph). Note in Figure 5.4 that we also used a 2.3 cm × 1.0 cm aperture to mask some of the low energy, broadband amplified spontaneous emission (ASE) [107] at the beam edges.

The laser sheet, 2 cm × \approx 300 µm (FWHM), was formed using a single 500 mm UVFS cylindrical planoconvex lens (F \approx 454 mm at 193 nm). We have estimated the resulting laser intensity, called the "<u>HighUV</u>" case, to be \approx 0.7 - 2.2 MW/cm² so that for the A-X P(10) and Q(10) transitions, I/I_P^{sat} \approx 0.7 - 2.2 and I/I_Q^{sat} \approx 1.5 - 4.5, respectively. Unfortunately, both of these intensity ratios lie within the *non-linear LIF regime* with the Q-branch being closer to saturation than the P-branch (see Chapter 2, Figure 2.2 and Chapter 4, Section 4.4.2 and Figure 4.29). For this reason we have used only the Q-branch for A-X PLIF imaging. Saturation studies of the D'-X band P(15) transition in Chapter 4, Section 4.3.2 (Figure 4.22) indicated that I_P^{sat} \approx 2 MW/cm² so that the resulting PLIF is probably only partially-saturated.

We performed an additional set of experiments in which a set of seven CaF₂ windows (\approx 37% total transmission) were introduced after the ArF mirror. The intent was to characterize the influence of possible photochemically-induced emissions (to be discussed below) that have a potential to interfere with the desired fluorescence. This attenuation stack/ArF mirror combination is shown in the right photograph of Figure 5.4. The resulting sheet intensity, referred to as the "LowUV" case, was \approx 260 – 800 kW/cm².



Figure 5.4 <u>Left</u>: photograph of the ArF attenuation mirror, ASE mask, sheet-forming lens, and energy meter. <u>Right</u>: CaF_2 window attenuation stack placed between the mask and ArF mirror.

The camera image was brought into focus on a paper Modulation Transfer Function (MTF) test pattern placed horizontally within the cell and bisecting the axis (see Reference [139]). The ArF laser sheet height was then adjusted to match the plane of the MTF pattern by observing the visible fluorescence on the paper's edge. Since the imaging depth of field was $\approx 4 \times$ greater than the laser sheet thickness at lens aperture f/4.5, the alignment was not particularly difficult. Once the sheet was established within the object plane of focus, the alignment could not be disturbed. The CO laser beam height was adjusted, using the C₂ Swan "blue glow" as a visual guide, to be coincident with the ArF laser sheet. The demagnification for all optically-pumped plasma images was chosen to be m=0.5 (in practice, we confirmed that m≈0.49 using test images) using a 2 cm extension ring so that the axial extent of the plasma PLIF image filled the entire width of the CCD chip (512×512 pixels, ΔL_{pix} =15 µm, L_{CCD} =W_{CDD}=7.68 mm). As shown in Figure 5.2, the lens-object distance was s₁=31.5 cm, leading to a 23.6 mm × 23.6 mm field of view, a resolution of ≈200 µm (5 pixels), ≈1 mm depth of field at lens aperture f/4.5, ≈3 pixel diameter "circle of least confusion", and an optical collection efficiency $\Omega/4\pi \approx 0.06\%$ (f/13.5) (see Appendix E) [133]. The collection volume for a single pixel was ≈6×10⁴ mm³ (note that this is ≈10⁴× smaller than that of the LIF).

Two different imaging filters were used to mitigate spectral interference, depending upon the LIF bands being explored. For A-X band PLIF we used an aqueous urea filter [134] while for the D'-X PLIF imaging we used a SchottTM UG-11 filter glass [135]. The sources of spectral interference and the transmission characteristics of these filters will be discussed further in Sections 5.2.1 and 5.3.1.1 for A-X and D'-X band PLIF, respectively.

5.1.3 NONEQUILIBRIUM PLASMA CONDITIONS; "CASE A" AND "CASE B"

To explore the diagnostic potential of A-X and D'-X band PLIF imaging, we have created two optically pumped plasma environments, both consisting of CO/Ar mixtures but exhibiting significant differences in trans-rotational temperatures. The first environment, <u>Case A</u>, consisted of 3% CO/Ar at 103 torr *without focusing* the CO laser beam and was the identical to the conditions in Chapter 4 where spatially averaged measurements were obtained along the plasma centerline. Those measured trans-rotational temperatures ranged between 460 K - 608 K (\pm 100 K, 2 σ) using the D'-X and 503 K - 528 K (\pm 50 K, 2 σ) using the A-X band.



Figure 5.5 Top view of apparatus for creating the <u>Case B</u> environment.

The second environment, <u>Case B</u>, consisted of 8% CO/Ar at 108 torr along with *focusing* the CO laser beam using a 1" diameter, 250 mm CaF₂ lens as shown in Figure 5.5. This case was motivated by the results shown in Chapter 4, Figure 4.1 in which the CO VDF, and consequently, the translational temperature were shown to be dependent upon the CO partial pressure [20]. We note that the results in that figure were obtained for a focused CO laser beam.

While the visible extent of the "blue glow" (Figure 4.4) is qualitatively useful, we have made quantitative estimates of focused CO laser beam diameters (FWHM) within the imaging region for later comparison with the PLIF images. Figure 5.6 is a top view illustration of the imaging viewport, CCD chip field of view (m = 0.5), laser sheet, optically pumped plasma, and the diverging CO laser beam due to the focusing optic. The unfocused Gaussian beam diameter (FWHM), d_{laser}, has been estimated [113] to be ≈ 6.6 mm. Using Figure 5.6 and the principles of geometric optics [114], the beam diameter within the imaging field of view using a lens with focal length F placed a distance L >> F is

$$\frac{\mathrm{d}}{\mathrm{d}_{\mathrm{laser}}} = 1 - \frac{\mathrm{L}}{\mathrm{F}} \qquad (5.3)$$

Table 5.1 displays the results of Equation 5.3 for three focusing cases using F=250 mm and m = 0.5.



Figure 5.6 Geometry of <u>Case B</u> focusing and image coordinate system.

CO Laser Focusin g Case	L (cm)	Left Edge d(mm) # pixels wide	Image Center d (mm) # pixels wide	<u>Right Edge</u> d (mm) # pixels wide
Unfocus		6.6	6.6	6.6
ed		140	140	140
"Loose"	40.0	4.5 42	4.0 30	3.4 20
"Tight" 30.5		2.0	1.4	1.0
		42	30	20

Table 5.1 Estimated CO laser beam diameters within imaging region.

5.2 A-X BAND PLIF IMAGING AND TEMPERATURE MEASUREMENTS

In this section we present CO A-X band PLIF imaging and temperature measurements for both <u>Case A</u> and <u>Case B</u> optically pumped plasmas (Section 5.1.2). Using the Two-Line method (Chapter 2, Section 2.5.1), we extract a two-dimensional temperature field from the PLIF images using only the Q-branch, and compared the result with spatially averaged LIF temperatures obtained simultaneously along the plasma centerline.

5.2.1 SPECTRAL INTERFERENCES AND THE IMAGING FILTER

A number of potential spectral interference sources must be considered for A-X band PLIF imaging. These are (i) scattering of the ArF laser radiation (193 nm) by the gas (Rayleigh) as well the experimental apparatus [14,15,136], (ii) "passive" C₂ Swan band ("blue glow") emission in the 400-650 nm range [52,57,58] and 4th Positive band emission (180-250 nm) due to E-V transfer under the present extreme vibrational nonequilibrium condition [60], (iii) spectral overlaps between the X(7,J") \rightarrow A(1,J') absorption transitions and CO Resonance-Enhanced Multi-Photon Dissociation (REMPD) free carbon emission [121-123], and (iv) spectral overlaps between the X(7,J") \rightarrow A(1,J') and X(20,J") \rightarrow D'(2,J') absorption. Each of these items are addressed in the following sections.

5.2.1.1 RAYLEIGH SCATTERING INTERFERENCE

In Chapter 4, Section 4.4.1 we presented a vibrational state resolved $A(v'=1)\rightarrow X(v'')$ LIF spectrum (Figure 4.24) produced by tuning an *unfocused* narrowband ArF laser (≈ 1 mJ/pulse, 42 kW/cm²) to the X(7) \rightarrow A(1) Q(10) transition at 193.20 nm. This result is reproduced below in Figure 5.7 where we have assigned the



Figure 5.7 A-X Q(10) vibrational state resolved LIF, ArF laser line, and urea filter transmission curve.

transitions above the signal peaks. Notice in this figure that the (1,6), (3,8), and (0,6)emissions are at shorter wavelengths than the ArF laser line at 193.5 nm. In Chapter 4, Section 4.4.1 we mentioned that these transitions lie within the vacuum UV (VUV) and as such, chose to collect LIF only from those transitions that are Stokes-shifted to longer wavelengths, such as the (1,8) at 200.8 nm. To achieve high S/N, it is imperative to reject scattered ArF laser radiation and to collect as much of the Stokes-shifted ($\lambda \ge 195$ nm) A-X band emission as possible. Note from Figure 5.7 that to achieve this goal, we require an imaging filter with a very sharp cut-on at ≈ 195 nm. An aqueous urea filter has been reported in the literature [134] as having been used to reject such ArF laser scattering. Depending upon the urea molar concentration (moles/liter \equiv M), the sharp cut-on wavelength was shown to vary between 200 nm - 206 nm [134]. A 2" diameter \times 1 cm path UVFS dye cell (NSG Precision Cells, Inc., T-35, 16.6 ml capacity) was filled with a 0.01 M concentration of laboratory grade urea and distilled water and, by placement in front of the OMA spectrometer, used to filter the A-X Q(10) LIF of the <u>Case A</u> optically pumped plasma prior to dispersion. From the resulting filtered vibrational state resolved spectrum, the peak intensities from each band were extracted. By defining the unfiltered spectrum peak transmission as 100%, we then computed the urea filter transmission by comparison. Additional spectra were obtained under the same optical and plasma conditions using diluted solutions as shown in Figure 5.7. Note in this figure that at 193 nm where the transmission has been *interpolated*, the 0.01 M and 0.005 M solutions are predicted to have $\approx 0\%$ transmission while the 0.0025 M solution is $\approx 3\%$. On the other hand, the two former solutions exhibit greater attenuation ($T \approx 35\%$ and 20%)







(c) Urea Filter, Lower Mirror Covered

Figure 5.8 Single-shot ArF laser scattering images acquired in ambient room air without and with urea filter.

Uncovered

of the desired Stokes-shifted A-X LIF, especially the (1,8) at 200.8 nm, than the latter $(T\approx50\%)$. Since the transmission estimates at 193 nm are approximate, we chose to use the 0.005 M urea solution.

In order to assess the rejection quality of this filter, we acquired planar Rayleigh scattering images with the flow cell open to the ambient room air (see Section 5.2.1). In order to avoid O₂ LIF due to the strong Schumann-Runge bands [96,110,127], the ArF laser was tuned to the middle of the gain profile (≈193.355 nm) where absorption is minimal. Figure 5.8a shows the resulting single-shot inverse gray-scale image without the 0.005 M urea solution, while Figure 5.8b is that acquired with the filter. Figure 5.8d is an axial slice plot at r=0 (see Figure 5.6 for coordinate system) showing that the beam energy is asymmetrically shaped with the maximum at $z \approx 9$ mm upstream. In this author's opinion, this asymmetry is due to a slight misalignment of the injected oscillator beam within the amplifier cavity. Using heat-sensitive paper placed in the beam path (prior to sheet formation), the seed beam profile could be identified by a circular diffraction pattern residing within the main rectangular profile. The center of this pattern was slightly displaced in a direction consistent with the maximum shown in Figure 5.12d. Comparison of Figure 5.12a with Figure 5.12b suggests that the filter indeed rejects Rayleigh scattered radiation, with the exception of the small circular feature at the upper right in Figure 5.12b. The origin of the remaining light was determined by placing a piece of paper over the bottom viewport turning mirror and



Continued

Figure 5.8 (d) <u>Upper</u>: Axial slice, Rayleigh Scatter with and without urea filter. (e) <u>Lower</u>: Axial slice, Magnified scale, Rayleigh scatter with urea filter and lower mirror (i) not covered and (ii) lower mirror covered.

acquiring an additional image, shown in Figure 5.12c. Figures 5.21d,e show an axial slice along r=0 that indicates the scattered light has been essentially suppressed when the bottom mirror is covered. However, since this mirror was necessary for spectral monitoring, it was not covered for the following experiments.

5.2.1.2 PASSIVE EMISSION DUE TO SWAN AND A-X BANDS

In Chapter 4, Section 4.4.1 we used the OMA to estimate the relative intensity of C₂ Swan and 4th Positive band emission in the *absence* of ArF laser excitation as compared to LIF under the same optical conditions. We found that these "passive" emissions induced by extreme vibrational nonequilibrium were ≈5 orders of magnitude less than the LIF emission. Here, we have repeated this experiment to ascertain the extent of spectral interference using the Case A optically pumped plasma. Figure 5.9a shows a typical inverse gray scale image of the optically pumped plasma obtained at f/4.5 lens aperture and 50% gain for 4 s at 10 Hz repetition rate without ArF laser excitation. Using a 150 ns gate, the total exposure time is 6 µs. The CO laser beam and gas flow propogation are from right-to-left in the image (see Figures 5.5 and 5.6 for reference). In Figure 5.9a, the faint, dark, horizontal region across the lower half of the image is the signal obtained from all "passive" emission from the optically pumped plasma. Using the radial-axial coordinate system defined in Figure 5.6, we have taken radial slice plots across the image axial midsection (+12 mm upstream, pixel 256) with and without optical pumping, shown in Figure 5.9b. In this figure, the lower scale is calibrated in radial distance (mm) across the cell diameter while the upper axis is the corresponding pixel number. In Figure 5.9b, we find that when the CO laser is blocked so that no optical pumping can occur, a radial slice of the resulting "dark-currrent" noise is nearly constant at ≈ 60 "counts" (out of a possible 4096 counts). Superimposed upon Figure 5.9b is a radial slice plot through Figure 5.9a at the same axial midsection which shows the presence of a low S/N emission between -2 mm $\leq r \leq 6$ mm. For reference, we also

indicate the estimated diameter (FWHM) of the unfocused CO laser beam as given in Table 5.1. Based on these results, we conclude that interference due to this passive emission is negligable for single-shot imaging (150 ns gate). Furthermore, it is considered negligable for the multiple-shot images in which the ICCD was exposed for no more than 35 shots ($\approx 6 \mu s$) at f/4.5 aperture.



(a) Image



Figure 5.9 Image of C₂ Swan and A-X band passive emission due to highly vibrationally excited CO without ArF laser excitation.

5.2.1.3 CO RESONANCE-ENHANCED MULTIPHOTON DISSOCIATION

In Chapter 4, Section 4.3.2 we mentioned the coincidental overlap of CO Resonance-Enhanced Multi-Photon Dissociation (REMPD) within the tuning range of the ArF laser. This two-photon REMPD process is thought to proceed through weak, spin forbidden rotational transitions of the $X^1\Sigma^+(v''=0)\rightarrow a^3\Pi(v'=2)$ to an (as yet) unknown dissociative state of suspected triplet character [122,123]. Dissociation results



Figure 5.10 CO REMPD excitation scan using ArF laser intensity $\approx 60 \text{ MW/cm}^2$

in ${}^{1}P_{0}{}^{}\rightarrow{}^{1}S_{0}{}^{}$ free-carbon atom emission at 247.8 nm (the remaining unbound oxygen atom is in the ground state) [121-123]. Notice in Figure 5.7 that the 0.005 M urea filter will *not* reject REMPD free-carbon emiission. In this work, we have used two strategies to avoid this interference; (i) employ an ArF laser intensity below the CO REMPD threshold and (ii) choose A-X band PLIF resonances not coinciding (spectrally) with any CO REMPD absorption transitions.

Figure 5.10 is an LIF excitation scan of the <u>Case A</u> plasma which reveals the weak resonant rotational structure associated with $X^{1}\Sigma^{+}(v''=0)\rightarrow a^{3}\Pi(v'=2)$ absorption. It is very important to note that the ArF laser sheet intensity used in this LIF scan was ~60 MW/cm². The LIF was collected using the small H-10 monochromator (see Figure 5.2) set at $\lambda \approx 248$ nm with ≈ 2 nm FWHM bandpass. We note that this experimental spectrum closely resembles the synthetic model spectrum computed by the authors of Reference [121]. If the ArF laser has high locking efficiency, then it is possible to avoid interference altogether by judiciously choosing a rotational transition within the $X(v''=7)\rightarrow A(v'=1)$ band that does not overlap a REMPD absorption line. Within Figure 5.10, we see that there are numerous resonances within the range 193.2 nm – 193.25 nm and 193.355 nm – 193.405 nm that coincide with these A-X band.

Figure 5.11 shows an A-X band LIF excitation scan overlaid onto the CO REMPD spectrum of Figure 5.10. Again, we note that the CO REMPD was obtained with an unattenuated ArF laser *sheet* having I \approx 60 MW/cm², whereas the A-X band LIF spectrum in Figure 5.11 was obtained with the \approx 2.2 MW/cm² <u>HighUV</u> intensity. Notice in Figure 5.11 that there is a slight overlap between the Q(10) and one of the CO REMPD transitions. In this figure, we estimate that the relative positional uncertainty between the

A-X LIF and REMPD features is $\approx \pm 0.003$ nm. If the ArF laser intensity is above the REMPD threshold when performing PLIF imaging using the urea filter, the extent of the overlap interference will depend upon (i) the ArF laser locking efficiency and (ii) the (predominantly) Doppler-broadened linewidths. Figure 5.12 shows that the A-X Q(17) transition has little chance for interference from CO REMPD when the ArF laser locking efficiency is high.



Figure 5.11 Overlay of A-X band LIF and CO REMPD excitation scans to show potential interferences near Q(10) transition.

Using the OMA system described in Chapter 4, we performed vibrational state resolved LIF spectra by pumping the $X(7) \rightarrow A(1) Q(10)$ absorption resonance using a *focused* ArF laser sheet of <u>HighUV</u> intensity. The resulting spectra was similar to that shown in Figure 5.7; *no REMPD emission at 247.8 nm was detected under the <u>Case A</u> <i>plasma condition*.



Figure 5.12 Overlay of A-X band LIF and CO REMPD excitation scans to show potential interferences near Q(17) transition.

Figure 5.13 is an X(7) \rightarrow A(1) LIF excitation (solid line, collecting (1,8) emission at ≈ 201 nm) overlaid with an X(20) \rightarrow D'(2) LIF excitation scan (dashed line, collecting (2,30) emission at ≈ 272 nm). It is evident from this figure that there is no Q(10) interference by the D'-X bands. Figure 5.14 is a similar plot showing the absense of potential D'-X band interference with the Q(17) line.



Figure 5.13 Overlay of A-X band LIF and D'-X band LIF excitation scans to show potential interferences near Q(10) transition.



Figure 5.14 Overlay of A-X band LIF and D'-X band LIF excitation scans to show potential interferences near Q(17) transition.

5.2.2 A-X BAND IMAGING RESULTS

The PLIF images in this section correspond to the Q(10) absorption line at \approx 193.20 nm. The ArF laser was slowly tuned to this transition while monitoring the boxcar averaged LIF signal, shown as the encircled region within Figure 5.15. After this "on resonance" signal was maximized, the camera intensifier was triggered synchronously (150 ns gate) with the ArF laser at a 10 Hz repetition rate while the CCD

array was exposed for a specified period of time. For example, a single-shot image was acquired by setting the CCD exposure time to 0.10 s. Multiple-shot images were



Figure 5.15 A-X Q(10) LIF using spectral monitor to find on and off-resonance conditions. Note the boxcar time constant = 10 shots.

acquired by increasing the CCD exposure time while gating the intensifier at the laser repetition rate. This process was then repeated for the "off resonance" condition, shown in Figure 5.15, by tuning the laser off-resonance (increasing wavelength) to minimize the LIF spectral monitor signal. Note in Figure 5.15 that the ArF laser energy was nearly constant at \approx 56 mJ/pulse during this \approx 6 minute time period and that the background subtracted S/N \approx 30 using a 10-shot (1.0 s) boxcar averaging time constant.

Figures 5.16 and 5.17 display typical *single-shot* imaging results for <u>Case A</u> and <u>Case B</u> optically pumped plasmas, respectively. Note that the lens aperture was f/4.5 in both cases. In both Figure 5.16a and 5.17a, the "net signal" was obtained by subtracting the off-resonance image from the on-resonance image using the WinSpec/32 post-processing software. Figures 5.16c,d and 5.17c,d are radial and axial slice plots of the on-resonance, off-resonance, and net signal taken at image locations z = 12 mm and r = 1.5 mm, respectively, with the corresponding pixel numbers placed along the top abscissa (the coordinate axis orientation was defined in Figure 5.6. The vertical dashed lines in all radial slice plots (c) demarcate the CO laser beam diameter (FWHM) according to the estimates given in Table 5.1, Section 5.1.2. It is important to note that they have been overlayed such that their centerlines coincide with the radial signal maximum.

Figure 5.16c shows a radial slice plot of the on-resonance, *single-shot*, <u>Case A</u> image. The maximum gray scale value of is $\approx 500 \pm 56 (1\sigma)$ counts with a S/N ≈ 9 at r \approx +1.5 mm, z = 12 mm. The radial signal decreases symmetrically from this maximum with increasing radius and approaches the off-resonance background of $\approx 50 \pm 7 (1\sigma)$ counts for r \leq -6 mm and r \geq +9 mm. The radial off-resonance background has a similar gray scale distribution but with a maximum of $\approx 57\pm 19 (1\sigma)$ counts and S/N ≈ 3 . These values along with a summary of all results are summarized in Table 5.2. The spatially averaged on and off-resonance gray scale values in the vicinities of r = -12 mm and +12 mm are nearly identical and have been attributed to the "dark current" background noise. We note that the on/off resonance data, as summarized in Table 5.2, was obtained by subtracting the average "dark current" obtained from the vicinity of r=-12 mm (*i.e.*, pixel 0). The *net* radial signal has a maximum of $\approx 413 \pm 59$ counts (1 σ) with S/N ≈ 7 , and a



Figure 5.16 Single-Shot A-X Q(10) PLIF; Case A "No Focus" plasma, f/4.5 Aperture.

153



Figure 5.17 Single Shot A-X Q(10) PLIF; Case B "Loose" Focus Plasma, , f/4.5 Aperture.



Figure 5.18 18 Shot A-X Q(10) PLIF; Case A "No Focus" plasma, f/4.5 Aperture.

155



Figure 5.19 18 Shot A-X Q(10) PLIF; Case B "Loose" Focus Plasma, 18, f/11 Aperture.

	Figure #	f/#	# Shots	<u>On</u> <u>Resonance</u> S/N (Noise)	Off Resonance S/N (Noise)	<u>Net</u> <u>Image</u> S/N (Noise)		
<u>Case A</u>	5.16	4.5	1	9 (56)	3 (19)	7 (59)		
(no focus)	5.18	4.5	18	17 (202)	10 (58)	14 (181)		
<u>Case B</u> ("loose" focus)	5.17	4.5	1	18 (166)	12 (71)	13 (166)		
	5.19	11	18	19 (168)	12 (78)	13 (178)		
<u>Case A</u> ("tight" focus)	5.21	4.5	1	15 (221)	11 (73)	11 (198)		
	5.22	5.6	3	16 (188)	13 (67)	10 (243)		

Table 5.2 Summary of A-X Q(10) PLIF; S/N is in bold and 1σ noise is in parenthesis.

radial profile FWHM of ≈ 8 mm. We attribute the net radial signal profile to the distribution of CO X(v"=7,J"=10) population fraction. To understand this, first note that the CO laser FWHM was estimated to be ≈ 7 mm in Table 5.1. Furthermore, we have estimated (Appendix B) the absorption of the ArF laser beam through a 1 cm path length of plasma was $\leq 1\%$, assuming a typical X(v"=7) vibrational population fraction of $\approx 0.7\%$ and a rotational temperature of 500 K. From this, it is reasonable to expect the laser energy, E_L, to be nearly constant across the plasma radius and, by Equation 5.1, the

signal is directly proportionally to the relative ground state population fraction, $f_{v'',J''}$ and the quantum yield, Y₂. Using Equations 2.24 and 2.25 in Chapter 2, Section 2.3.1 and the quenching cross-sections in Table A.1, Appendix A, we estimated that Y₂ can vary by ≈25% for rotational temperatures between 300 K - 500 K in a 3% CO/Ar mixture. However, the distribution of absorbers along the z-axis is more difficult to interpret. In Figure 5.16d, the axial gray scale slice plot exhibits a broad distribution from z=0 mm to z=24 mm with a maximum at $z \approx 11$ mm. Note that this profile is qualitatively similar to that obtained from Rayleigh scattering, Figure 5.8d. Hence, the strong variations in the ArF laser beam profile, coupled with the nonlinear PLIF regime, makes it difficult to determine the distribution of absorber population fraction. This situation could be aleviated by homognizing the ArF laser profile using phase-randomizing optics [101].

The single-shot, on-resonance Case B image shown in Figure 5.17c, has a maximum of $\approx 2988 \pm 166 (1\sigma)$ counts with S/N ≈ 18 . The off-resonance background is \approx 850 ± 71 counts. The *net* signal maximum is found to be \approx 2158 ± 166 counts (S/N \approx 13) while the radial profile FWHM is ≈ 6 mm narrower than that of Case A. While this net signal maximum is 5× greater than that of <u>Case A</u>, Table 5.2 shows that the 1σ standard deviation "noise" increased by $\approx 2.8 \times$ so that the overall S/N increase is only $\approx 2 \times$.

In general, multiple-shot accumuation images of Figures 5.18 and 5.19 show similar spatial distribution of gray scale values as the single-shot, except for increased S/N. However, the data within Table 5.2 reveals an important trend regarding the dependency of S/N on the number of accumulated shots, M. It is well known that under low-light level conditions, high-performance ICCD camera systems become photon-noise limited at short (< 1ms) exposure times such that the photon count obeys Poisson 158

statistics, varying as \sqrt{M} [14,119,132]. The signal is expected to accumulate linearly with M so that the S/N~ \sqrt{M} [14,119,132]. Observe in Table 5.2 for <u>Case A</u> that the onresonance image S/N for M=18 is only 2× larger than the single-shot, rather than $\sqrt{18}\approx4\times$ which would result in S/N ≈30 . This expectation is consistent with that obtained using the simultaneous spectral monitoring LIF shown in Figure 5.15. In that figure, using a boxcar averaging time-constant of M=10 shots, we find a net S/N ≈30 . Note in Table 5.2,



Figure 5.20 **Single Shot** Histogram; A-X Q(10) PLIF <u>Case A</u> plasma, f/4.5 aperture.

however, that the PLIF imaging noise *did* increased by $\approx 4\times$. Thus, if the on-resonance image signal were to be increased by M=18, the gray value would have been \approx 9000, exceeding the 12-bit dynamic range. Figures 5.20 shows a gray-scale histogram obtained from the brightest PLIF regions in Figure 5.16 [-6 mm $\leq r \leq +9$ mm; 0 mm $\leq z \leq 24$ mm]. The abcissa represents the 12-bit dynamic range while the ordinate is the number of occurances of each count. It is obvious from Figure 5.20 that gray scale overflow did not occur since the values do not exceed 1024 counts. However, it is possible that at the 50% ICCD gain setting used, the camera response became nonlinear (i.e., saturated). This may explain why the signal did not increase \sqrt{M} . If so, then this is encouraging since it implies that high S/N is possible with lower gain and less shot accumulations.

Figures 5.21 and 5.22 are special cases of the <u>Case A</u> plasma environment created using a "tight" CO laser beam focusing condition as shown in Table 5.1, Section 5.12. The CO laser FWHM was predicted to be 1.0 mm wide at the image right edge, 1.4 mm in the middle, and 2.0 mm at the left edge, resulting in a divergence angle of $\approx 2.4^{\circ}$. From the image in either figure, the divergence angle was measured using a protracter and found to be $\approx 2.5^{\circ}$. Radial slice plots taken at z=12 mm upstream, shown in Figures 5.21c and 5.22c, are again demarcated with the predicted CO laser beam width (FWHM). It is interesting to note the striations in the PLIF intensity oriented parallel to the in radial direction within the PLIF images of Figures 5.21a and 5.22a. The axial slice plots indicate that the striations vary in intensity up to $\approx 20\%$ within the range 2 mm $\leq z \leq 12$ mm. Striations of this type were also observed in previous D'-X and A-X band PLIF images discussed above, but since they vary by $\leq 5\%$, they are not easily distinguishable



Figure 5.21 Single Shot A-X Q(10) PLIF; Case A "Tight" Focus Plasma, f/4.5 Aperture.


Figure 5.22 **3 Shot** A-X Q(10) PLIF; <u>Case C</u> "Tight" Focus Plasma, f/5.6 Aperture.

from the photon-shot noise in the axial slice plots. However, as we will show in the next section discussing PLIF temperature measurements, these striations can lead to systematic errors in these measurements. While the source of these striations are not completely understood, this has lead us to believe that the striations are due to spatially coherent diffraction patterns within either the oscillator seed beam itself or possibly a misalignment of the telescopic optics arrangement.

5.2.3 TEMPERATURE MEASUREMENT STRATEGY AND SENSITIVITY

In this section, we present two-dimensional PLIF temperature field "maps" extracted using the so-called *Two-Line method* (Chapter 2, Section 2.5.1) for both the <u>Case A</u> and <u>Case B</u> conditions (Section 5.1.1). For all PLIF temperature measurements, we have chosen to use the Q(10) and Q(17) absorption transitions that (i) are well separated by \approx 352.308 cm⁻¹ and provide adequate measurement sensitivity, (ii) lie within a spectral region of the ArF laser tuning range for which the average incident intensities and locking efficiencies are similar, (iii) do not exhibit significant overlapping absorption resonances with CO REMPD or the D'-X band as discussed in Section 5.2.1, and (iv) have Two-Line ratio normalization functions which are (presumably) valid for the nonlinear PLIF regime.

Recall from Section 5.2.1.3, Figure 5.11, that we noted some uncertainty in the relative spectral positions between the Q(10) and a CO REMPD resonance which is a source of potential interference if the ArF laser intensity is above the multiphoton threshold. Also recall that the vibrational state resolved LIF spectra using the <u>HighUV</u>

ArF laser intensity under <u>Case A</u> plasma conditions did *not* indicate any REMPD interference with the Q(10) resonance. As a precaution, however, we have also employed an additional <u>LowUV</u> (I $\approx 260 - 800 \text{ kW/cm}^2$) laser intensity for PLIF temperature measurements, as discussed in Section 5.1.2.

Both of the <u>HighUV</u> and <u>LowUV</u> intensities lie just below the Q-branch saturation threshold within the *nonlinear* PLIF regime. Expressions that connect the rotational temperature to the two-line signal ratios (Chapter 2, Section 2.5.1) were



Figure 5.23 A-X band LIF excitation scan using spectral monitor; On & Off resonance.

derived only for the linear and saturated limits, and hence, it is not clear whether the normalization factor should be expressed in terms of the Hönl-London line strengths (see Equation 2.52 for linear) or the population degeneracies (see Equation 2.56 for saturated). Note, however, in Chapter 2, Sections 2.5.1.1 and 2.5.1.2, that both Q-branch pre-exponential factors are $(2J_m"+1)/(2J_n"+1)$ for both the linear (Equation 2.53b) and saturated (Equation 2.57b) LIF limiting regimes. We have exploited this coincidence by presuming the proper nonlinear regime normalizaton function is also given by $(2J_m"+1)/(2J_n"+1)$.

As shown in Chapter 2, Section 2.5.1.1, Equation 2.55, the ratio of quantum fluorescence yields, Y_m/Y_n , is a potential source of a systematic error, especially when performing a Two-Line temperature measurement within the linear LIF regime. We have assumed in all PLIF temperature analysis that $Y_m/Y_n \equiv 1$. This assumption was based on the LIF excitation scans in Chapter 4 in which we did not observe any clear bias in the Q(10) and Q(17) peak intensities.

Systematic errors related to the performance of the CO laser and the elapsed time between on-resonance PLIF imaging should be mentioned. Regarding the CO laser, three significant observations were noted during these PLIF experiments; (i) the inability to trigger the up-pumping mechanism without the aid of a focusing lens, (ii) sometimes the blue glow would "split" into two "lobes", indicating spatially non-Gaussian beam (presumed to be the TEM(1,0) mode [114]) and (iii) occasional unsteady behavior of the blue glow and LIF signal. All three of these phenomena can be associated with contaminated Brewster windows [137,138] that degrade the intensity of lasing on low lying CO laser vibrational level transitions (*i.e.*, $1\rightarrow 0$, $2\rightarrow 1$, *etc.*).

Figure 5.24 is the boxcar averaged LIF signal obtained by the spectral monitor showing the Q(10) and Q(17) on and off-resonance time history for the <u>Case A</u> opticallypumped plasma using LowUV ArF laser intensity. Note that the ArF laser average energy is also plotted in the figure. At t=0 minutes, the CO laser was filled with liquid nitrogen and the optically pumped plasma was initialized. Seven minutes were required to tune (≈ 2 Hz) the ArF laser across the A-X band LIF features to find the Q(10) absorption resonance, indicated by the circle. After acquiring both multiple-shot and single-shot Q(10) PLIF images, the ArF laser was then tuned (increasing wavelength) off resonance and the imaging repeated. The CO laser was then refilled with liquid nitrogen at t=20 minutes and the entire procedure, as shown in Figure 5.24, was again repeated for the Q(17) feature. Note that ≈ 15 minutes elapsed between Q(10) and Q(17) PLIF imaging. This fairly long time period between the acquisition of the on-resonance PLIF images is significant because it is not possible to ascertain the extent to which the CO laser beam quality and, consequently, the plasma conditions changed. Unsteady behavior was observed during some experiments in which the on-resonance LIF signal would exhibit large fluctuation. At the same time, the blue glow would exhibit both intensity and spatial fluctuations. The author acquired and accepted PLIF images only when the LIF monitor signal and blue glow remained stable for *both* on-resonance conditions.

5.2.4 A-X BAND PLIF TEMPERATURE RESULTS

Four single-shot images were acquired under <u>Case A</u> and <u>Case B</u> conditions for each Q(10) and Q(17) transition, both on and off-resonance. Each off-resonance image, chosen at random, was subtracted from a corresponding on-resonance image also chosen at random, resulting in a *net* signal image. Next, a Q(17) net image, chosen at random, was divided by a Q(10) image, also chosen at random. Using the degeneracy ratio ($D_{17\cdot10}$ = 5/3), the temperature field was then extracted using Equation 2.45 in Chapter 2, Section 2.51. We note that the process of dividing the two images resulted in a large "noise" outside of the plasma regions where the photon counts were near the dark-current baseline. This noise was smoothed by constructing a digital imaging filter [139] for use with the WinSpec/32 software, details of which are described in Reference [139]. It is important to note, however, that this digital filter was designed to only reject spatial features having spatial wavenumbers greater exceeded the experimentally determined Modulation Transfer Function cutoff wavenumber, ≈ 52 cm⁻¹. We have confirmed that this filter does not affect the temperatures within the bright PLIF regions, but does succeed in reducing random, numerically-induced "noise" within regions where the image photon count (gray scale value) was at the dark-current baseline. For cosmetics, we then "clipped" the temperature field values below 200 K and above 800 K (in some cases, 1200 K). It is very important to understand that this procedure did not alter any temperature results within the PLIF regions.

After computing the set of four temperature fields, we extracted an average temperature from a 2.31 mm (z) × 13.85 mm (r) region along the plasma centerline having spatial coordinates [4.61 mm $\leq z \leq 18.46$ mm , -1.85 mm $\leq r \leq .+0.46$ mm]. For example, Table 5.4 shows four, single-shot (and 25 shot), average centerline temperatures along with 1 σ uncertainties. Note that these uncertainties represent the extent of spatial

Optically Pumped Plasma Condition	Intensity	<u>40-Shot PLIF</u> Trial Average (1σ) Average (2σ)
Case A	High UV	363 ± 14 364 ± 12 389 ± 13 352 ± 12 367 ± 25

Table 5.3 Average axial centerline A-X PLIF temperature measurements (September 7, 2003).

Optically Pumped Plasma Condition	Intensity	$\frac{\text{Single-Shot}}{\text{PLIF}}$ Trial Average (1σ) Average (2 σ)	<u>25-Shot PLIF</u> Trial Average (1σ) Average (2σ)
Case A	High UV	456 ± 54 408 ± 41 468 ± 68^{a} 522 ± 88 463 ± 74	$374 \pm 16 418 \pm 23 405 \pm 21^{a}424 \pm 18405 \pm 35$

Table 5.4 Average axial centerline A-X band PLIF temperature measurements (September 23, 2003).

Optically Pumped Plasma Condition	Intensity	$\frac{\text{Single-Shot PLIF}}{\text{Trial Average}}$ $\frac{(1\sigma)}{\text{Average }(2\sigma)}$	$\frac{\text{Multi-Shot}}{\text{PLIF}}$ Trial Average (1 σ) Average (2 σ)	<u>Spectral</u> <u>Monitor</u> <u>LIF</u> Two-Line	Spectral Monitor LIF Excitation Scan Boltzman n Plot
Case A	<u>High</u> <u>UV</u>	$140 \pm 30 \\ 421 \pm 36 \\ 222 \pm 19 \\ 461 \pm 86 \\ \\ 311 \pm 246 \\ \hline 391 \pm 103^{a} \\ 329 \pm 22 \\ 239 \pm 14 \\ 461 \pm 121 \\ \\ 355 \pm 150 \\ \hline $	25 Shots 370 ± 16 349 ± 17 344 ± 15 394 ± 19 $$ 364 ± 36 15 Shots 335 ± 17 349 ± 15^{a} 315 ± 13 326 ± 14 $$ 331 ± 23	375 ± 15 375 ± 15	• 481 ± 17
	Low UV	$206 \pm 29 \\ 315 \pm 19 \\ 367 \pm 27^{b} \\ 546 \pm 299 \\ \\ 358 \pm 225 \\ \hline$	26 Shots 394 ± 24 356 ± 12 401 ± 23 369 ± 14^{b}	395 ± 15	453 ± 14

Table 5.5 continued

Optically Pumped Plasma Condition	Intensity	Single- Shot PLIF Trial Average (1σ) Average (2σ)	$\frac{\text{Multi-Shot}}{\text{PLIF}}$ Trial Average (1σ) Average (2 σ)	<u>Spectral</u> <u>Monitor</u> <u>LIF</u> Two-Line	Spectral Monitor LIF Excitation Scan Boltzman n Plot
Case B	High UV	$589 \pm 39 \\ 351 \pm 50 \\ 681 \pm 66 \\ 500 \pm 25^{\circ} \\ \\ 530 \pm 223$	13 Shots 532 ± 38 496 ± 41 455 ± 31 $472 \pm 31^{\circ}$ 489 ± 53	713 ± 50	701 ± 27
	Low UV	$539 \pm 34 \\ 491 \pm 37^{d} \\ 327 \pm 20 \\ 500 \pm 29 \\ \\ 464 \pm 149$	10 Shots 545 ± 38^{d} 533 ± 49 624 ± 54 659 ± 60	604 ± 50	687 ± 43



Figure 5.24 A-X band PLIF temperature measurements; <u>Case A, High UV</u> (see Table 5.4).



Figure 5.25 A-X band PLIF temperature measurements; Case A, High UV (see Table 5.5).



Figure 5.26 A-X band PLIF temperature measurements; <u>Case A, Low UV</u> (see Table 5.5)



Figure 5.27 A-X band PLIF temperature measurements; <u>Case B,HighUV</u> (see Table 5.5)



Figure 5.29 A-X band PLIF temperature measurements; <u>Case B, Low UV</u> (see Table 5.5)

variations in temperature for each particular trial. Below each list of trial results, we present the average temperature and the 2σ confidence interval. For example, in Table 5.4, the average (of four) single-shot temperature for the <u>Case A</u> plasma using the <u>HighUV</u> intensity was 463 ± 74 K. Highlighted trial values indicate that the corresponding temperature field has been selected for presentation as one of the Figures 5.25 to 5.29. For example, in Table 5.4 note that the single-shot trial having a centerline temperature of 468 ± 68 K (third from top) is closest to the mean. The corresponding PLIF temperature field is shown in Figure 5.25b along with radial and axial slice plots (dashed line).

In general, the Case A plasma slice plots shown within Figures 5.25 to 5.27 indicate agreement between single-shot and multiple-shot temperature good For example, Figure 5.27c,d (Table 5.5) indicate that the 26-shot measurements. accumulation temperature field had an average centerline temperature of 369 ± 33 K while the single-shot had 367 ± 225 K. Note the degradation of the temperature field outside of the estimated CO laser diameter FWHM ($-4 \text{ mm} \le \text{r} \le +3 \text{ mm}$) in a region where the Q(10) and Q(17) image had only dark-current gray scale values. In Figure 5.25c, the slice plot shows that the temperature is largest in the center and decreases symetrically with increasing radius to 300 K at r \approx -6 mm and r \approx +5 mm, where the noise then overtakes the temperature field. Figure 5.26 shows a similar radial profile (taken on a different day) having a systematic offset such that the temperature at the plasma edge is \approx 50 K below room temperature. Any effort to interpret the physical meaning of these radial temperature profiles must be met with caution because in some cases the curvature was *opposite* to those shown in Figures 5.25c and 5.26c. These systematic errors may be 176

related to changes in CO laser performance during the elapsed time between Q(10) and Q(17) PLIF images or to a nonlinear ICCD camera response at the 50% gain setting. This implies that the uncertainty of the PLIF temperature measurements near the plasma edges is probably much greater than that of quoted in Tables 5.3 - 5.4, which are valid along the plasma centerline. It is interesting to note that spontaneous vibrational Raman scattering temperature measurements [140], performed for a tightly focused optically pumped plasma, resulted in a uniform radial temperature distribution within the vicinity of the CO laser beam.

As expected, the <u>Case B</u> plasma, PLIF temperature measurements imply that the trans-rotational temperatures are higher than <u>Case A</u>. Figures 5.28a,b and 5.29a,b show temperatures ranging between 464 ± 149 K to 530 ± 223 K for single-shot and 489 ± 53 K to 590 ± 98 K for multiple-shots (see Table 5.5). Note that the confidence intervals at these elevated temperatures are greater than those exhibited for <u>Case A</u>, which is consistent with the anticipated loss in measurement sensitivity as discussed in Section 5.2.2 and shown in Figure 5.23.

Along with the PLIF results summarize in Tables 5.3, 5.4, and 5.5, we also list the corresponding LIF Two-Line and Boltzmann plot least-squares temperatures. The LIF Two-Line measurements were made from plots similar to that shown in Figure 5.24 acquired simultaneously with the PLIF images, while the least-squares temperatures were obtained from a Boltzmann plot of absorption resonance peak signals extracted from slow (1 Hz) LIF excitation scans made on the same day and plasma conditions as the PLIF images. An example of the Boltzmann plot is shown in Figure 5.30 for the <u>Case A</u>

plasma using the <u>LowUV</u> ArF laser intensity. As shown in Figure 5.30, we have performed both a linear and saturated LIF regime analysis on the excitation scan peak



Figure 5.29 Case A LowUV; Boltzmann plot and Q-branch temperature.

intensities (see Chapter 2, Equations 2.65 and 2.70a,b). We note that the linear regime analysis included locking efficiency corrections as described in Chapter 3. Although we have also plotted the P-branch in Figure 5.30, it must be emphasized that the temperature analysis is performed *only* for the Q-branch. Note that in Figure 5.30 the P-branch data lie closest to the Q-branch when the regime is assumed to be linear. This trend was also

observed for the <u>HighUV</u> intensity in both <u>Case A</u> and <u>Case B</u> plasmas and tends to support our assumption that the PLIF is not fully saturated.

Comparing the <u>Case A</u> plasma PLIF centerline temperatures in Table 5.5 with the Two-Line and least-squares LIF, we see reasonable agreement. We note however, that both single and multiple shot temperatures (~350 K) are, on average, slightly lower than the Two-Line (~380 K) and least squares results (~467 K). The <u>Case B</u> single-shot (~497 K) and multiple-shot (~539 K) are also lower, on average, than the two-line (~658 K) and least-squares measurements (~694 K). This implies that the PLIF temperature measurements are systematically biased towards lower temperatures. It may be possible that the Q(10) absorption transition has some interference with CO REMPD, especially for <u>Case B</u> (Section 5.2.1, Figure 5.11). This is plausable for three reasons; (i) <u>Case B</u> has nearly $3 \times$ higher CO partial pressure than <u>Case A</u> which increases optical density (ii) the elevated temperatures within the <u>Case B</u> plasma have increased Doppler broadened linewidths which lead to more overlap, and (iii) the observed bias towards lower temperatures is consistent with the hypothesis that the net Q(10) signal is larger due to a REMPD overlap.

On the other hand, it is possible that this systematic error in temperature could be related to the quantum fluoresecence yield ratio, Y_{17}/Y_{10} , which we have assumed to be unity. Note from Chapter 2, Equations 2.16, 2.21, and 2.43-2.45 that the nonlinear LIF regime signal ratio is a function of Y_{17}/Y_{10} . In this case, the bias towards lower temperature would indicate a higher quenching of the Q(17) absorption resonance LIF signal. However, this hypothesis is contrary to the observed results obtained by the LIF spectral monitor. In Table 5.4, we see that the spatially averaged centerline temperature

using both the Boltzmann plot least-squares and *simultaneous* Two-Line method show good agreement.

5.3 D'-X BAND PLIF IMAGING

In Chapter 4, we demonstrated that the A-X band LIF temperature diagnostic requires only relatively mild vibrational excitation to achieve ± 50 K accuracy. However, under extreme vibrational nonequilibrium, the higher vibrational levels are significantly populated and so the D'-X band diagnostic becomes available for temperature measurements. In this section we will demonstrate the capability to perform D'-X band PLIF imaging that, in principle, exhibits sufficient S/N for two-dimensional temperature measurements. Single-shot and time integrated D'-X PLIF imaging using only the <u>HighUV</u> (0.7 MW/cm² - 2.2 MW/cm²) laser sheet intensity (Section 5.1.1.1) is presented here for both <u>Case A</u> and <u>Case B</u> optically pumped plasma conditions (see Section 5.1.2).

5.3.1 SPECTRAL INTERFERENCES AND FILTERING

In Chapter 4, Section 4.3.1 we presented a vibrational state resolved $D'(v'=2) \rightarrow X(v'')$ emission spectrum (Figure 4.18) produced by tuning a narrowband ($\approx 0.5 \text{ cm}^{-1}$ FWHM) ArF laser, with relatively low intensity ($\leq 40 \text{ kW/cm}^2$), to the P(15) $X(v''=20) \rightarrow D'(v=2)$ transition at 193.217 nm. Most of this Stokes-shifted emission occurred in the 240 nm to 330 nm range for which numerous commercial spectral filter options exist [135,141].

Figure 5.31 shows a low resolution (\approx 5 nm), vibrational state resolved D'-X LIF emission spectrum using the OMA for <u>Case A</u> conditions. The ArF laser was operated in broadband mode with \approx 30 mJ/pulse. The beam was *unattentuated and focused* into a sheet so that the intensity was \approx 30 MW/cm² [46]. In this figure, we clearly see the strong REMPD emission at 247.8 nm.



Figure 5.30 D'-X Vibrational state resolved LIF using a broadband ArF laser sheet with intensity ≈30 MW/cm² [46]

One particularly attractive filter for D'-X PLIF imaging is UG-11 SchottTM glass [135] because it is inexpensive and easy to use. Depending upon thickness, it has an 80%-95% transmission from \approx 240 nm to 350 nm (FWHM) and 25% from \approx 680 nm to 750 nm. Figure 5.32 shows a vibrational state resolved D'(v'=2) \rightarrow X(v") LIF emission spectrum with and without a 2" square, 2 mm thick UG-11 filter placed directly in front of the OMA front slit. In that figure, the filter curve for a 2 mm thick glass was obtained by computing the square of the transmission for 1 mm thick filter glass [135]. It is clear from Figure 5.32 that the UG-11 filter adequately attenuates all LIF emission below \approx 260 nm. Using the OMA as well as the ICCD camera imaging system, we also verified that this filter rejected all scattered ArF laser radiation at 193 nm (not shown).



Figure 5.31 D'-X vibrational state resolved LIF with and without UG-11 imaging filter. Also, transmission for 2 mm thick UG-11 filter.

5.3.2 D'-X BAND IMAGING RESULTS

The image acquisition methodology in which an on and off-resonance image(s) are acquired is the same as discussed in Section 5.2.2. For example, Figure 5.33 is a boxcar averaged LIF time history showing the on and off-resonance signals acquired by the spectral monitor system simultaneously with the <u>Case A PLIF</u> images shown below in Figures 5.34 and 5.36. The boxcar averaging time constant was 10-shots (1 s) in this



Figure 5.32 D'-X P(15) LIF using spectral monitor to find on and off-resonance conditions. Note the boxcar time constant = 10 shots.

figure, which resulted in a background subtracted S/N \approx 35. In general, the D'-X band PLIF signal levels are $\approx \frac{1}{2}$ of those obtained in Section 5.2.2, due presumable to (i) transmission characteristics between the urea and UG-11 filters, (ii) vibrational level population fractions, and (iii) rovibronic Einstein B-coefficients (absorption).

For convenience, a summary of the results are presented in Table 5.6 giving the S/N and the accompanying 1σ standard deviation "noise" (in parentheses) obtained from a small areal strip along the brightest part of the image. The images and slice plots corresponding to each of these cases are presented in Figures 5.34 to 5.37 below.

In general, these results indicate that the background subtracted D'-X PLIF images have adequate S/N to perform quantitative temperature measurements using the CO X(v"=20) population. It is interesting to note, however, two trends revealed within Table 5.6; (i) as with the A-X band PLIF case, the D'-X PLIF multiple-shot image S/N does not increase as $\sim \sqrt{M}$, where M is the number of accumulated shots, and (ii) when compared to the respective on-resonance gray scale values, the D'-X PLIF image off-resonance values are much lower than in the A-X PLIF images (see Section 5.2.2).

The deviation of multiple-shot S/N from the expected behavior is unclear, but, as shown in the gray-scale histograms of Figures 5.38 and 5.39 below, the 12-bit dynamic range was not exceeded in either the <u>Case A</u> or <u>Case B</u> plasma images.

	Figure #	f/#	# Shots, M	<u>On</u> <u>Resonance</u> S/N (Noise)	Off Resonance S/N (Noise)	<u>Net</u> <u>Image</u> S/N (Noise)
<u>Case A</u> (no focus)	5.14	4.5	1	7 (33)	2 (7)	7 (32)
	5.18	4.5	35	18 (180)	5 (24)	16 (202)
<u>Case B</u> ("loose" focus)	5.15	4.5	1	14 (87)	3 (14)	13 (87)
	5.19	5.6	11	19 (171)	6 (28)	18 (175)

Table 5.6 Summary of D'-X P(15) PLIF; S/N is in bold and 1σ noise in parenthesis.



Figure 5.33 Single Shot D'-X P(15) PLIF; Case A "No Focus" Plasma, f/4.5 Aperture.

186



Figure 5.34 Single Shot D'-X P(15) PLIF Case B "Loose Focus" Plasma, f/4.5 Aperture.



Figure 5.35 **35-Shot** D'-X P(15) PLIF; Case A "No Focus" Plasma, f/4.5 Aperture.

188



Figure 5.36 **11-Shot** D'-X P(15) PLIF; <u>Case B</u> "Loose Focus" Plasma, f/5.6 Aperture.

Regarding the background, one could argue that the relative off-resonance backgrounds were lower for the D'-X P(15) images, as compared to the A-X Q(10) images, simply because the ArF laser locking efficiency was higher. While certainly possible, this is unlikely since (i) the images were acquired only hours apart on the same day, using the same CO laser sustained plasma conditions, and without interruption of the ArF laser 10 Hz operation (*i.e.*, the *only* difference was the imaging filter, (ii) both transitions have similar wavelengths and lie within a spectral region for which the ArF laser locking efficiency does not change rapidly; the A-X Q(10) lies at 193.20 nm while the D'-X P(15) is at 193.22 nm, (iii) comparing Figures 5.15 and 5.33 we see that the ArF laser energy (and locking), are similar (see Chapter 3 for details). The most likely explanation is that the broadband ArF laser component excites more nearby resonant absorption transitions of the A-X Q(10) than for the D'-X P(15). This can be understood by considering two points; (i) the UG-11 filter blocks all Stoke-shifted A-X band PLIF but transmits much of the D'-X band (see Figure 5.32), and (ii) the difference in the respective transition state densities near the absorption line being excited by the narrowband component. Note that the free-running ArF laser amplifier has a natural bandwidth of $\approx 150 \text{ cm}^{-1}$ (FWHM) [98,99,104,107,108]. Using Equations 2.46c,d from Chapter 2, Section 2.5.1, we find that the rotational energy separation $\Delta k_{I'}$ (cm⁻¹) between two rotronic levels in the high-J limit is

$$\Delta k_{J''} \sim 2J''(B_e'' - B_e') , \qquad (5.4)$$



Figure 5.37 Gray scale histogram for <u>Case B</u> "Loose" Focus Plasma, P(15) Image.



Figure 5.38 Gray scale hisogram for <u>Case A</u> Plasma, P(15) imaging.

where the B_e values for the X, A, and D' states are given in Table A.3 of Appendix A.

Using these values, we find for the A-X band Q(10) at 193.20 nm, $\Delta F \sim 6 \text{ cm}^{-1}$ while for the D'-X P(15) at 193.22 nm, $\Delta F \sim 28 \text{ cm}^{-1}$. Thus, the density of absorbing rotational transitions near the D'-X P(15) line is $\approx 5 \times less$ than those near the A-X Q(10) line. Unless the ArF laser locking efficiency is 100%, the broadband component will inadvertantly excite more extraneous transitions in the A-X band case than with the D'-X, leading to the A-X band LIF having a greater on-to-off resonance signal ratio.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

This thesis has detailed the proof-of-concept development of a *single-photon*, LIF/PLIF trans-rotational temperature diagnostic employing the CO A-X (4th Positive) band for use in mildly vibrationally excited, low temperature (\approx 300 K – 800 K), high pressure molecular plasmas. For plasma conditions exhibiting extreme vibrational nonequilibrium at low trans-rotational temperatures, the CO D'-X band may also be used.

A pulsed, injection-locked, ArF excimer laser has been employed to produce narrowband (0.5 cm⁻¹) radiation having a tuning range coincident with rotational absorption transitions within the CO $X^{1}\Sigma^{+}(v''=7)\rightarrow A^{1}\Pi(v'=1), X^{1}\Sigma^{+}(v''=12)\rightarrow A^{1}\Pi(v'=8),$ and $X^{1}\Sigma^{+}(v''=20)\rightarrow D'^{1}\Sigma^{+}(v'=2)$ vibronic bands. We have simplified a method found in literature [109] used to quantify the fraction of narrowband ArF laser radiation output (*i.e.*, "locking efficiency") as a function of tuning wavelength. Our method employed a monochromator to monitor a portion of the amplified spontaneous emission (ASE) as the ArF laser was continuously (in time) tuned across it's gain profile, rather than scanning the *monochromator* at numerous fixed laser wavelengths [109]. The resulting locking efficiency, measured *simultaneously* with LIF spectrum and total beam energy, was used to correct the spectral peak intensities within the linear regime. LIF temperature measurements were performed using a 10 cm monochromator with \approx 8 nm bandwidth (FWHM) which collected Stokes-shifted fluorescence corresponding to A-X (1,8) emission at (pumping X(7)) and A-X (8,13) emission (pumping X(12)) at \approx 201 nm. For the D'-X band, the monochromator was set to \approx 273 nm to collect the (2,32) emission. Proof-of-concept saturated LIF temperature measurements were we performed using the A(1)-X(7) band within a well characterized model environment, tailored to exhibit mild vibrational nonequilibrium (d.c. normal glow discharge with the X¹Σ⁺(v"=7) level \approx 0.1% populated) and low trans-rotational temperature (\approx 400 K). The results indicate ±50 K measurement accuracy at 400 K. This accuracy was maintained for both linear and saturated A-X and D'-X band LIF regimes when applied to optically pumped plasma environments exhibiting extreme vibrational nonequilibrium (3% CO/Ar mixture at 103 torr having X(v"=7) \approx 0.5% and X(v"=20) \approx 0.1% populated) with trans-rotational temperature of \approx 500 K.

By attenuating the ArF laser intensity over a range spanning 5 orders of magnitude, we found that the A-X Q(10) and Q(17) absorption transitions saturated at ≈ 0.5 MW/cm² within the 3% CO/Ar mixture at 103 torr at ≈ 500 K, consistent with simple predictions that neglected rotational relaxation. Under similar conditions, we found that the D'-X P(15) absorption transition saturated at ≈ 1 MW/cm².

Using vibrational state resolved LIF, we identified all Stokes-shifted emission subsequent to exciting the $X(v''=7) \rightarrow A(v'=1) Q(10)$ and Q(17) transitions within a 3% CO/Ar optically pumped plasma. We observed emission originating not only from the

directly pumped $A^{1}\Pi(v'=1)$ level, but also a substantial fraction emitted from $A^{1}\Pi(v'=2,3)$ and higher. This was also observed to occur for emission subsequent to $X^{1}\Sigma^{+}(v''=12) \rightarrow A^{1}\Pi(v'=8)$ pumping, but *not* for $X^{1}\Sigma^{+}(v''=20) \rightarrow D'^{1}\Sigma^{+}(v'=2)$. Though not central to the development of this diagnostic, this result is interesting from the standpoint of the relatively short OMA gate (150 ns) used.

A 2" diameter × 1 cm wide UVFS dye cell containing a 0.005 molar urea solution (aqueous) [82] was found to reject all Rayleigh scattered ArF laser radiation while transmitting \approx 35% of the Stoke-shifted (1,8) emission band at 200.8 nm. A commercial UG-11 glass filter was found adequate for both Rayleigh scattered light as well as CO REMPD emission when exciting the D'-X P(15) transition.

For optically pumped 3% CO/Ar (unfocused CO laser beam) and 9% CO/Ar (focused) mixtures exhibiting extreme vibrational nonequilibrium, we have demonstrated *single-shot* A-X Q(10) and D'-X P(15) PLIF image S/N~10. For an ICCD camera operating within the shot-noise limited regime, the S/N was expected to increase as $\sim\sqrt{M}$, where M is the number of accumulated images. This behavior was not observed for either the A-X Q(10) or the D'-X P(15) PLIF imaging cases studied, which may indicate problems with the laser/ICCD camera synchronization. While the PLIF regime was nonlinear, the fractional absorption of the ArF laser sheet across the plasma diameter was estimated to be $\leq 1\%$. In this case, the resulting PLIF radial profiles (assuming uniform fluorescence quantum yields) using using the $X^1\Sigma^+(v''=7)\rightarrow A^1\Pi(v'=1)$ Q(10), $X^1\Sigma^+(v''=12)\rightarrow A^1\Pi(v'=8)$ R(8), and $X^1\Sigma^+(v''=20)\rightarrow D'^1\Sigma^+(v'=2)$ P(15) absorption bands are indicative of the radial distribution of the respective ground state populations. It was

not possible to extract information regarding the axial population distribution because (i) the ArF laser sheet intensity profile was highly nonuniform, and (ii) the average beam intensity was below the saturation threshold. Single-shot PLIF temperature field measurements using the $X^1\Sigma^+(v''=7) \rightarrow A^1\Pi(v'=1) Q(10)$ and Q(17) transitions indicate $\pm 100 \text{ K} - 200 \text{ K}$ precision within both 3% and 9% CO/Ar optically pumped plasmas. Increased precision ($\approx \pm 25 \text{ K} - 50 \text{ K}$) could be achieved with multiple shot (10 to 25) accumulations. For the 9% CO/Ar optically pumped (focused) plasma, PLIF measurements confirmed the expected rise in temperature. However, the results indicate that there is a systematic error up to 40% under these conditions. Interference between the A-X Q(10) and a weak CO REMPD absorption transition may be the cause of this systematic error.

In the future we recommend (i) that the urea filter molar concentration be optimized to increase the transmission of A-X (1,8) emission at 201 nm while suppressing Rayleigh scattered laser radiation at 193 nm, (ii) performing single-shot PLIF imaging and temperature measurements using this optimized urea filter for the mildly vibrationally excited, 3.6% CO/He d.c. normal glow discharge at 8 torr, (iii) using a homogenized ArF laser beam intensity profile (iv) understanding the extent to which CO REMPD intereferes with A-X band PLIF for each environment under consideration, (v) attenuating the ArF beam just below the CO REMPD threshold but insuring that the entire profile is above the A-X band saturation threshold.

Regarding the operation of the ArF laser source, it may be of interest to explore A-X band LIF using only the narrowband output ArF oscillator ($\leq 1 \text{ mJ/pulse}$) to perform linear regime temperature measurements without the complicating issue of the amplifier's broadband interference. Operation of this laser in "single-pass" mode (*i.e.*, without Cassegrain telescope optics in the amplifier), while reducing the beam energy and increasing the divergence, would provide a spatially-homogeneous beam profile with suppressed broadband ASE [134,142]. Furthermore, it may be possible to implement a simultaneous two-wavelength operation of the narrowband ArF laser, as reported in literature using the KrF laser [143]. This would allow two-line PLIF measurements to be made without the uncertainty of changing plasma characteristics. We also note that two-line PLIF combustion temperature measurements (OH P₁(8) and Q₁(11)) have been reported using "fast wavelength switching" of the Lambda Physik COMPex 150T ArF laser [144]. The ability to perform simultaneous two-line PLIF measurements would be especially useful in unsteady nonequilibrium environments such as a low temperature molecular plasma shock tube.
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CO Collision Partner	A ¹ П Vibrational level v'	Effective Quenching Cross-Section σ (Å ²)	$\begin{array}{c} A^{1}\Pi(v'=1) \ \text{Effective} \\ \text{Vibrational Relaxation} \\ \text{Cross-Section} \\ \sigma\left(\mathring{A}^{2}\right) \end{array}$	Referenc e
CO	0	60^{a}		[82]
CO	9	130 ^b		[83]
CO	14	208 ^c		[84]
Ar	0	3.3 ^e	$11.4^{\rm f}$	[86]
Ar	1	25.6	12.4 ^f	[87]
Ar	1	25 ^d		[85]
Ar	9	3.8 ^b		[83]
Не	0	0.035 ^e	$0.37^{\rm f}$	[86]
Не	1	1.09	0.45^{f}	[87]
He	1	2.7^{d}		[85]
Не	9	0.51 ^b		[83]
Не	14	< 0.016 ^c		[84]

APPENDIX A

Table A.1 ¹²C¹⁶O *effective* quenching and vibrational relaxation cross sections at 300K.

^a Obtained from rotationally-resolved LIF using tunable vuv laser to pump the X-A (0,0) Q(14) and Q(24) lines.

- ^b Pumped the X-A (0,9) Q(22) using atomic O emission line at 130.6 nm.
- ^c Pumped the X-A (0,14) P(10) and R(14) using atomic H emission Lyman-α line at 121.6 nm.
- ^d Used synchrotron radiation to excite X-A (0,0-7) bands.
- ^e Authors state that A(v'=1) quenching is "nearly the same" as this value given. Note that later work of same authors and others indicates these values are probably too low by at least an order of magnitude.

^f Note that vibrational relaxation cross-section is for $A(v'=1 \rightarrow v'=0)$.

$\mathbf{v}'' {\rightarrow}$	0	1	2	3	4	5	6	<mark>7</mark>	8	9	10	11	$A^{eff}_{v'}$	$\tau^{\rm eff}_{\rm v'}$
$v' \downarrow 0$	2.29	4.65	4.00	2.34	0.88	0.20 184.16	(0.04) 191.25	(0.01) 198.80	(0.00) 206.85	(0.00) 215.47	(0.00) 224.71	(0.00) 234.63	14.41	6.94
1	<mark>5.18</mark>	<mark>2.25</mark>	<mark>(0.03)</mark>	<mark>1.09</mark>	<mark>1.86</mark>	<mark>1.52</mark>	<mark>0.59</mark> 185.98	0.17 193.11	<mark>(0.05)</mark> 200.70	<mark>(0.10)</mark> 208.81	<mark>(0.02)</mark> 217.47	(0.00) 226.75	<mark>12.86</mark>	<mark>7.78</mark>
2	6.20	0.13	1.60	1.57	(0.04)	0.67	0.78	0.79 187.86	0.32 195.04	0.11 202.68	(0.19) 210.84	(0.00) 219.55	12.40	8.06
3	5.58	0.67	2.01	(0.00)	1.37	0.92	(0.00)	0.51	0.70 189.81	0.43 197.05	(0.50) 204.74	(0.05) 212.94	12.74	7.85
4	4.04	3.18	0.60	1.25	0.75	0.15	1.00	0.32	(0.04) 184.98	0.46 191.84	0.44 199.12	(0.28) 206.88	12.51	7.99
5	2.52	4.58	0.06	1.83	(0.01)	1.35	0.19	0.41	0.66	(0.07) 187.02	0.11 193.94	0.35 201.28	12.14	8.24
6	1.45	4.44	1.49	0.69	0.92	0.57	0.65	0.84	(0.00)	0.44	(0.31) 189.14	(0.00) 196.12	11.80	8.47
7	0.77	3.70	2.98	(0.00)	1.48	(0.04)	1.15	(0.00)	0.74	(0.21)	(0.11)	0.43 191.34	11.61	8.61

Table A.2 Absolute vibronic Einstein $A_{v'v''}$ transitions probabilities (units of 10^{+7} s⁻¹) and effective lifetimes τ^{eff} (ns) for the ${}^{12}C^{16}O$ A-X bands as measured by electron impact excitation and emission spectroscopy; reproduced from Table 2 in Reference [31]. Authors of Reference [31] generated the values in parentheses from a model. Values of (0.00) correspond to transition probabilities of less than 10^{+5} s⁻¹. Transition wavelengths (nm) lying outside the vacuum UV are given below the probabilities. Note these wavelengths were computed using the molecular constants in Table A.3.

212

	$\mathrm{X}^{1}\Sigma^{+}$	$A^1\Pi$	${\mathsf D'}^1\Sigma^+$
Reference	[94]	[30]	[41]
Te	0.0	65079.09165	89438.4
ω _e	2169.81358	1518.24	651.4
ω _e x _e	13.28831	19.4	20.4
$\omega_e y_e$	1.0511×10^{-2}	7.6584×10^{-1}	
$\omega_e z_e$	5.74×10 ⁻⁵	-1.4117×10 ⁻¹	
$\omega_e a_e$	9.83×10 ⁻⁷	1.434×10^{-2}	
$\omega_e b_e$	-3.16×10 ⁻⁸	-8.051×10 ⁻⁴	
$\omega_e c_e$	_	2.36×10 ⁻⁵	
$\omega_e d_e$	_	-2.9×10^{-7}	
Be	1.93128087	1.6115	9.805×10 ⁻¹
α_1	1.750441×10^{-2}	2.3251×10 ⁻²	2.656×10 ⁻²
α_2	5.487×10 ⁻⁷	1.5911×10 ⁻³	
α_3	2.54×10 ⁻⁸	-5.716×10 ⁻⁴	
α_4		8.2417×10 ⁻⁵	
α_5		-5.9413×10 ⁻⁶	
α_6	_	2.1149×10 ⁻⁷	
α_7	_	-2.991×10 ⁻⁹	
D _e	6.1214×10 ⁻⁶	7.29×10 ⁻⁶	8.886×10 ⁻⁶
β_1	-1.153×10 ⁻⁹	1.05×10^{-7}	8.423×10 ⁻⁷
β_2	1.8×10^{-10}		

Table A.3 ¹²C¹⁶O molecular constants for $X^1\Sigma^+$, $A^1\Pi$, and $D'^1\Sigma^+$ electronic states. Notation and usage follows traditional Dunham expansion coefficients for energy term values. All units are in cm⁻¹.

γ (HWHM)	Temperature	Γ (HWHM)	Exponent, n
(cm^{-1})	(K)	$(\text{cm}^{-1}/\text{atm})$	
CO–CO ^a	296.8	0.087	0.73
CO–Ar ^b	301.5	0.14	0.75
CO–He ^c	301.5	0.046	0.73

Table A.4	Lorentian	collision	broadening	parameters	for ¹	$^{2}C^{16}C$) used	in this	work

- ^a Γ and n obtained from IR rotationally resolved spectra of CO X¹ Σ^+ , Reference [90].
- ^b Γ obtained from rotationally-resolved narrowband VUV laser absorption spectra for numerous CO A¹Π($v''=0 \rightarrow v'$) bands, Reference [91]. ^c CO X¹Σ⁺ from Reference [92].

APPENDIX B

LIF SATURATION AND ABSORPTION CALCULATIONS FOR CO-ARGON OPTICALLY-PUMPED PLASMA CONDITIONS

Input code for MathCad 7.0 (Mathsoft Engineering & Education, Inc.)

<u>*Pump* X(v"=7) to A(v=1)</u>

 $k_{B} := 1.38065810^{-23} \cdot \frac{joule}{K}$ $k := 0.695038759 \frac{cm^{-1}}{K}$

Define Vibrational Level Transition Quantum Numbers:

 $v_{low} := 7 v_{up} := 1$

Optically-Pumped Plasma Gas Properties:

$$m_{co} := 28 \cdot amu \qquad m_{ar} := 39.948 amu \qquad \mu_{coar} := \frac{m_{co} \cdot m_{ar}}{m_{co} + m_{ar}}$$

$$\mu_{coar} = 16.462^{\circ} amu \qquad x_{co} := 3.0\% \qquad x_{ar} := 1 - x_{co}$$

$$x_{ar} = 97^{\circ} \% \qquad p := 103 \cdot torr \qquad T := 500 \cdot K$$

$$n := \frac{p}{k_{B} \cdot T} \qquad n_{co} := x_{co} \cdot n \qquad n_{ar} := x_{ar} \cdot n$$

$$L := 1.0 \cdot cm \qquad \theta_{vib} := 3120 \cdot K \qquad \theta_{rot} := 2.78 \cdot K$$

 $n_{\rm co} = 5.968 10^{16} \, {\rm cm}^{-3}$

 $n_{ar} = 1.93 \cdot 10^{18} \circ cm^{-3}$

Einstein A and Lifetime of A(v'=1) (from Beegle, et al.)

$$A_{1,0} := 5.18 \cdot 10^7 \cdot \frac{1}{\text{sec}} \quad A_{1,1} := 2.25 \cdot 10^7 \cdot \frac{1}{\text{sec}} \quad A_{1,2} := 3 \cdot 10^5 \cdot \frac{1}{\text{sec}}$$

$$A_{1,3} := 1.09 \cdot 10^7 \cdot \frac{1}{\text{sec}} \quad A_{1,4} := 1.86 \cdot 10^7 \cdot \frac{1}{\text{sec}} \quad A_{1,5} := 1.52 \cdot 10^7 \cdot \frac{1}{\text{sec}}$$

$$A_{1,6} := 5.9 \cdot 10^6 \cdot \frac{1}{\text{sec}} \quad A_{1,7} := 1.7 \cdot 10^6 \cdot \frac{1}{\text{sec}} \quad A_{1,8} := 5.0 \cdot 10^5 \cdot \frac{1}{\text{sec}}$$

$$A_{1,9} := 1.0 \cdot 10^6 \cdot \frac{1}{\text{sec}} \quad A_{1,10} := 2.0 \cdot 10^5 \cdot \frac{1}{\text{sec}}$$

Asum 1:=
$$A_{1,0} + A_{1,1} + A_{1,2} + A_{1,3} + A_{1,4} + A_{1,5}$$

Asum 2:= $A_{1,6} + A_{1,7} + A_{1,8} + A_{1,9} + A_{1,10}$
Asum := Asum 1 + Asum 2
Asum = $1.28610^8 \cdot \sec^{-1} \tau_{eff} \coloneqq \frac{1}{Asum}$

 $\tau_{\rm eff} = 7.776$ msec

Molecular Constants, X-State (from Huber & Herzberg):

$$T_{e1} := 0.0 \cdot cm^{-1}$$

$$\omega_{e1} := 2169.81358 cm^{-1}$$

$$B_{e1} := 1.93128087 cm^{-1}$$

$$D_{e1} := 6.1214 \cdot 10^{-6} \cdot cm^{-1}$$

$$\omega_{e1} := 13.2883 \cdot cm^{-1}$$

$$\alpha_{11} := 1.750441 \cdot 10^{-2} \cdot cm^{-1}$$

$$\beta_{11} := -1.153 \cdot 10^{-9} \cdot cm^{-1}$$

$$\omega_{e1} := 1.0511 \cdot 10^{-2} \cdot cm^{-1}$$

$$\alpha_{12} := 5.487 \cdot 10^{-7} \cdot cm^{-1}$$

$$\beta_{12} := 1.8 \cdot 10^{-10} \cdot cm^{-1}$$

 $\omega z_{e1} := 5.74 \cdot 10^{-5} \cdot cm^{-1}$ $\alpha_{13} := 2.54 \cdot 10^{-8} \cdot \text{cm}^{-1}$ $\omega_{e1} := 9.83 \cdot 10^{-7} \cdot \text{cm}^{-1}$ $\omega b_{e1} := -3.16 \cdot 10^{-8} \cdot cm^{-1}$

<u>Molecular Constants, $A^{1}\Pi$ -State (from Tilford & Simmons):</u>

B_{e2} := 1.6115 cm⁻¹
T_{e2} := 65079.09165 cm⁻¹

$$ω_{e2}$$
 := 1518.24 cm⁻¹
 $ω_{e2}$:= 19.4 cm⁻¹
 $ω_{e2}$:= 19.4 cm⁻¹
 $ω_{e2}$:= 1.4117.10⁻¹ cm⁻¹
 $ω_{e2}$:= 1.434.10⁻² cm⁻¹
 $ω_{e2}$:= 2.36.10⁻⁵ cm⁻¹
 $ω_{e2}$:= 2.36.10⁻⁵ cm⁻¹
 $ω_{e2}$:= 2.36.10⁻⁵ cm⁻¹
 $ω_{e2}$:= 2.3251.10⁻² cm⁻¹
 $ω_{21}$:= 2.3251.10⁻² cm⁻¹
 $α_{21}$:= 2.3251.10⁻² cm⁻¹
 $α_{23}$:= -5.716.10⁻⁴ cm⁻¹
 $α_{23}$:= -5.716.10⁻⁴ cm⁻¹
 $α_{25}$:= -5.9413.10⁻⁶ cm⁻¹
 $α_{26}$:= 2.1149.10⁻⁷ cm⁻¹
 $α_{27}$:= -2.991.10⁻⁹ cm⁻¹
 D_{e2} := 7.29.10⁻⁶ cm⁻¹
 $β_{21}$:= 1.05.10⁻⁷ cm⁻¹

 $\frac{\text{Term Values:}}{m_{\text{low}} := v_{\text{low}} + \frac{1}{2}} \quad m_{\text{up}} := v_{\text{up}} + \frac{1}{2}$ $G_{low} := \omega_{e1} \cdot m_{low} - \omega x_{e1} \cdot m_{low}^{2} + \omega y_{e1} \cdot m_{low}^{3} + \omega z_{e1} \cdot m_{low}^{4} + \omega a_{e1} \cdot m_{low}^{5} + \omega b_{e1} \cdot m_{low}^{6}$ $B_{low} := B_{e1} - \alpha_{11} \cdot m_{low} + \alpha_{12} \cdot m_{low}^{2} + \alpha_{13} \cdot m_{low}^{3}$ $D_{low} := D_{e1} + \beta_{11} \cdot m_{low} + \beta_{12} \cdot m_{low}^{2}$

$$G1_{up} := T_{e2} + \omega_{e2} \cdot m_{up} - \omega x_{e2} \cdot m_{up}^{2} + \omega y_{e2} \cdot m_{up}^{3} + \omega z_{e2} \cdot m_{up}^{4}$$

$$G2_{up} := \omega a_{e2} \cdot m_{up}^{5} + \omega b_{e2} \cdot m_{up}^{6} + \omega c_{e2} \cdot m_{up}^{7} + \omega d_{e2} \cdot m_{up}^{8}$$

$$G_{up} := G1_{up} + G2_{up}$$

$$B1_{up} := B_{e2} - \alpha_{21} \cdot m_{up} + \alpha_{22} \cdot m_{up}^{2} + \alpha_{23} \cdot m_{up}^{3} + \alpha_{24} \cdot m_{up}^{4}$$

$$B2_{up} := \alpha_{25} \cdot m_{up}^{5} + \alpha_{26} \cdot m_{up}^{6} + \alpha_{27} \cdot m_{up}^{7}$$

$$B_{up} := B1_{up} + B2_{up}$$

$$D_{up} := D_{e2} + \beta_{21} \cdot m_{up}$$

Compute Rotational Levels and Energies for P and Q-branches:

$$J := 2...30$$
 $JP_J := J - 1$ $JQ_J := J$

$$g_{\text{low}_{J}} \coloneqq 2 \cdot J + 1$$

$$g_{\text{Pup}_{J}} \coloneqq 2 \cdot (2 \cdot J P_{J} + 1) \quad g_{\text{Qup}_{J}} \coloneqq 2 \cdot (2 \cdot J Q_{J} + 1)$$

$$Flow_{J} := B_{low} \cdot J \cdot (J+1) - D_{low} \cdot J^{2} \cdot (J+1)^{2}$$

$$FupP_{J} := B_{up} \cdot JP_{J} \cdot (JP_{J} + 1) - D_{up} \cdot (JP_{J})^{2} \cdot (JP_{J} + 1)^{2}$$

$$FupQ_{J} := B_{up} \cdot JQ_{J} \cdot (JQ_{J} + 1) - D_{up} \cdot (JQ_{J})^{2} \cdot (JQ_{J} + 1)^{2}$$

Compute Ground State Total Population Fraction:

$$Q_{\text{rot}} := \frac{T}{\theta_{\text{rot}}}$$

$$f_{rot_J} := \frac{(2 \cdot J + 1)}{Q_{rot}} \cdot e^{-\frac{Flow_J}{k \cdot T}}$$

 $\frac{f_{tot_{J}} := f_{NEQvib} \cdot f_{rot_{J}}}{n_{coX7_{J}} := n_{co} \cdot f_{tot_{J}}}$

 $Q_{rot} = 179.856$

$$f_{\text{NEQvib}} = 0.1.\%$$

 $f_{\text{rot}_{10}} = 6.606\%$

$$f_{tot_{10}} = 6.606 \cdot 10^{-3} \cdot \%$$

 $h_{coX7_{10}} = 3.942 \cdot 10^{12} \cdot \frac{1}{cm^3}$

Compute Transition Wavelengths:

$$\Delta G := G_{up} - G_{low} \quad \lambda_v := \frac{1}{\Delta G}$$

$$\Delta FP_J := FupP_J - Flow_J \quad \Delta FQ_J := FupQ_J - Flow_J$$

$$\Delta EP_J := \Delta G + \Delta FP_J \quad \Delta EQ_J := \Delta G + \Delta FQ_J$$

$$\lambda P_J := \frac{1}{\Delta EP_J} \quad \lambda Q_J := \frac{1}{\Delta EQ_J}$$

$$\lambda Q_{10} = 193.20075 nm$$

$$\omega_{P_J} := \frac{c}{\lambda P_J} \quad \omega_{Q_J} := \frac{c}{\lambda Q_J}$$

$$\lambda P_{10} = 193.31856 nm$$

Compute Normalized Honl-London Rotational Line Strengths:

$$S_{P_J} := \frac{J-1}{2 \cdot (2 \cdot J + 1)}$$
 $S_{Q_J} := \frac{1}{2}$

Natural Broadening (FWHM)

$$\Delta \omega_n := \frac{A_{v_{up}, v_{low}}}{2 \cdot \pi}$$

 $\Delta \omega_{\rm n} = 270.563$ kHz

Collision Broadening (FWHM)

$$\Delta \omega_{\text{coco}} := 0.087 \frac{\text{cm}^{-1}}{\text{atm}} \cdot \mathbf{p} \cdot \mathbf{x}_{\text{co}} \cdot \mathbf{c} \cdot \left(\frac{\text{T}}{296.8\text{K}}\right)^{0.73}$$
$$\Delta \omega_{\text{coar}} := 0.14 \frac{\text{cm}^{-1}}{\text{atm}} \cdot \mathbf{p} \cdot \mathbf{x}_{\text{ar}} \cdot \mathbf{c} \cdot \left(\frac{\text{T}}{301.5\text{K}}\right)^{0.75}$$

 $\Delta \omega_{\rm c} := 2 \cdot \left(\Delta \omega_{\rm coco} + \Delta \omega_{\rm coar} \right)$

 $\Delta \omega_{\rm coco} = 15.51$ % MHz

 $\Delta \omega_{\text{coar}} = 806.315$ MHz

 $\Delta \omega_{\rm c} = 1.644$ GHz

Total Lorentzian Collision+Natural Broadening (FWHM)

$$\Delta \omega_{L} := \Delta \omega_{n} + \Delta \omega_{c}$$

$$\Delta \omega_{L} = 1.644 \text{GHz}$$
Doppler Broadening (FWHM) at Nominal Wavelength
$$\omega_{v} := \frac{c}{\lambda_{v}}$$

$$\omega_{v} = 1552.445 \text{THz}$$

$$\Delta \omega_{d} := \frac{2 \cdot \omega_{v}}{c} \cdot \sqrt{\frac{2 \cdot \ln(2) \cdot k_{B} \cdot T}{m_{co}}}$$

$$\Delta \omega_{d} = 4.699 \text{GHz}$$

$$\Delta \omega_{d} = 4.699 \text{GHz}$$

$$\Delta \omega_{u} = 0.5346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.5346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.5346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.5346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.5346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.5346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.6346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.6346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.6346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.6346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.6346 \Delta \omega_{L} + \sqrt{0.2166 \Delta \omega_{L}^{2} + \Delta \omega_{d}^{2}}$$

$$\Delta \omega_{v} := 0.6396 \text{Hz}$$

$$\Delta \omega_{v} := 0.636 \text{Hz}$$

$$\Delta \omega_{v} := 0.6396 \text{Hz}$$

$$\Delta \omega_{v} := 0.636 \text{Hz}$$

$$\Delta \omega_{v} := 0.636 \text{Hz}$$

$$\Delta \omega_{v} := 0.636 \text{Hz}$$

$$\Delta \omega_{v} := 0.6$$

 $\operatorname{gnrm}_{\mathbf{V}_{i}} := \operatorname{g}_{1_{i}} + \operatorname{g}_{2_{i}} + \operatorname{g}_{3_{i}} \cdot \left(\operatorname{g}_{4_{i}} - \operatorname{g}_{5_{i}}\right)$

$$g_{V_i} = g_{max} gnrm_{V_i}$$

$$\frac{1}{g_{\text{max}}} = 6.769$$
 GHz

Compute Single-Photon Integrated Absorption Cross-Section for P & Q Branches:

$$B_{Pabs_{J}} := A_{v_{up}, v_{low}} \cdot S_{P_{J}} \cdot \frac{(\lambda P_{J})^{2} \cdot \lambda_{v}}{8 \cdot \pi \cdot h}$$
$$B_{Qabs_{J}} := A_{v_{up}, v_{low}} \cdot S_{Q_{J}} \cdot \frac{(\lambda Q_{J})^{2} \cdot \lambda_{v}}{8 \cdot \pi \cdot h}$$

$$B_{\text{Pabs}_{10}} = 1.579 \cdot 10^{23} \cdot \frac{\text{cm}^3}{\text{watt} \cdot \text{sec}^3}$$
$$B_{\text{Qabs}_{10}} = 3.679 \cdot 10^{23} \cdot \frac{\text{cm}^3}{\text{watt} \cdot \text{sec}^3}$$

$$A_{v_{up},v_{low}} = 1.7 \cdot 10^6 \cdot \frac{1}{\text{sec}}$$

A
$$P_{10} = 4.013 \cdot 10^5 \cdot \frac{1}{\text{sec}}$$

$$A_{Q_{10}} = 8.488 \, 10^5 \, \frac{1}{\text{sec}}$$

$$\sigma_{\text{Pabs}_{10}} = 7.994 \text{-} \text{Ang}^2$$

$$\sigma_{\text{Qabs}_{10}} = 18.642 \text{-} \text{Ang}^2$$

$$A_{P_{J}} := \left(\frac{\lambda_{v}}{\lambda P_{J}}\right)^{3} \cdot A_{v_{up},v_{low}} \cdot \frac{S_{P_{J}} \cdot (2 \cdot J + 1)}{2 \cdot J P_{J} + 1}$$

$$A_{Q_{J}} := \left(\frac{\lambda_{v}}{\lambda Q_{J}}\right)^{3} \cdot A_{v_{up}, v_{low}} \cdot \frac{S_{Q_{J}} \cdot (2 \cdot J + 1)}{2 \cdot J Q_{J} + 1}$$

$$\sigma_{\text{Pabs}_{J}} := \frac{B_{\text{Pabs}_{J}} \cdot h \cdot \omega_{P_{J}}}{c} \cdot g_{\text{max}}$$
$$\sigma_{\text{Qabs}_{J}} := \frac{B_{\text{Qabs}_{J}} \cdot h \cdot \omega_{Q_{J}}}{c} \cdot g_{\text{max}}$$

 $\alpha_{P_{10}} = 3.152 \cdot 10^{-3} \cdot \frac{1}{cm}$ $\alpha_{Q_{10}} = 7.349 \cdot 10^{-3} \cdot \frac{1}{cm}$

$$OD_{P_{J}} := n_{coX7_{J}} \cdot \sigma_{Pabs_{J}} \cdot L$$
$$OD_{Q_{J}} := n_{coX7_{J}} \cdot \sigma_{Qabs_{J}} \cdot L$$

$$OD_{P_{10}} = 3.15210^{-3}$$

 $OD_{Q_{10}} = 7.34910^{-3}$

 $TransP_{J} := e^{-OD} P_{J} TransQ_{J} := e^{-OD} Q_{J}$ $AbsP_{J} := 1 - TransP_{J} AbsQ_{J} := 1 - TransQ_{J}$

Excimer Laser Sheet Properties (193nm):

width := 2.1 cm thick := 300 µm area := width thick η_{lock} := 100% Δt := 17 nsec f_{laser} := 10 Hz E_L := 1.0 mJ $\Delta \omega_L$:= 16 GHz ω_0 := 193.35 nm

$$I_{L} := \frac{E_{L} \cdot \eta_{lock}}{\operatorname{area} \cdot \Delta t} \qquad I_{L\nu} := \frac{I_{L}}{\Delta \omega_{L}}$$

 $I_{L} = 0.934 \cdot \frac{MW}{cm^{2}}$ $I_{Lv} = 0.058 \cdot \frac{MW}{cm^{2} \cdot GHz}$

$$B_{Pse} := B_{Pabs_{10}} \cdot \frac{g_{low_{10}}}{g_{Pup_{10}}} \qquad B_{Qse} := B_{Qabs_{10}} \cdot \frac{g_{low_{10}}}{g_{Qup_{10}}}$$
$$W_{Pabs} := \frac{B_{Pabs_{10}} \cdot IL}{c \cdot \Delta \omega_L} \qquad W_{Qabs} := \frac{B_{Qabs_{10}} \cdot IL}{c \cdot \Delta \omega_L}$$



W Pse :=
$$\frac{B_{Pse} \cdot I_L}{c \cdot \Delta \omega_L}$$
 W Qse := $\frac{B_{Qse} \cdot I_L}{c \cdot \Delta \omega_L}$

W Pse = $1.69810^8 \cdot \frac{1}{\text{sec}}$ W Qse = $3.58 \cdot 10^8 \cdot \frac{1}{\text{sec}}$

Ndot $_{\text{XAP}} := -W_{\text{Pabs}} \cdot n_{\text{coX7}}_{10}$ Ndot $_{\text{XAQ}} := -W_{\text{Qabs}} \cdot n_{\text{coX7}}_{10}$

Ndot
$$_{\text{XAP}} = -1.21 \cdot 10^{21} \cdot \frac{1}{\text{cm}^3 \cdot \text{sec}}$$

Ndot $_{\text{XAQ}} = -2.823 \cdot 10^{21} \cdot \frac{1}{\text{cm}^3 \cdot \text{sec}}$

CO 4th Positive A(v=1) Effective Quench Rates with Argon and CO

 $\sigma_{AXcoar} := 25 \cdot Ang^{2} \qquad \sigma_{AXcoco} := 100 \cdot Ang^{2}$ $v_{coar} := \sqrt{\frac{8 \cdot k_{B} \cdot T}{\pi \cdot \mu_{coar}}} \quad v_{coco} := \sqrt{\frac{16 \cdot k_{B} \cdot T}{\pi \cdot m_{co}}}$ $v_{coar} = 802^{\circ} \frac{m}{sec} \qquad v_{coco} = 869.58^{\circ} \frac{m}{sec}$ $Q_{AXcoar} := \sigma_{AXcoar} \cdot n_{ar} \cdot v_{coar} \qquad Q_{AXcoco} := \sigma_{AXcoco} \cdot n_{co} \cdot v_{coco}$ $Q_{AXcoar} := Q_{AXcoar} + Q_{AXcoco}$ $Q_{AXcoar} = 3.869 \cdot 10^{8} \cdot \frac{1}{sec}$ $Q_{tot} = 4.387 \cdot 10^{8} \cdot \frac{1}{sec}$

Compute Saturation Intensity:

$$I_{Psat} := \frac{Asum + Q_{tot}}{\frac{B_{Pabs}_{10}}{c \cdot \Delta \omega_{L}} \cdot \left(1 + \frac{g_{low_{10}}}{g_{Pup_{10}}}\right)}$$

$$I_{Qsat} := \frac{Asum + Q_{tot}}{\frac{B_{Qabs}_{10}}{c \cdot \Delta \omega_{L}} \cdot \left(1 + \frac{g_{low_{10}}}{g_{Qup_{10}}}\right)}$$

$$I_{Qsat} = 0.493 \frac{MW}{cm^{2}}$$

$$SatRatioP := \frac{I_{L}}{I_{Psat}}$$

$$SatRatioQ := \frac{I_{L}}{I_{Qsat}}$$

$$SatRatioQ = 1.894$$

APPENDIX C

THE FORTRAN 77 SYNTHETIC LIF SPECTRA CODE 'MOLELIF' (VERSION 6.0)

C.1 SAMPLE INPUT FILE 'INPUT.DAT'

1.3e-3, 2.0e-4, 29.0, 1.0e4 70.0, 17.0, 16.0, 0.063 550.0, 4000.0, 104.0, 3.0 28.0, 40.0, 0.087, 0.14 1.0e-14, 2.5e-15 hetero 0.0, 15.0, 0.0, 10.0

Collection Volume (cm^3), Collection Eff., Quantum Eff. (%), PM Gain Pulse Energy (mJ), Pulse Time (ns), Laser Linewidth (GHz), Laser Beam Area (cm^2) Ttrans (K), Tvib (K), Total Pressure (Torr), LIF Species Mole Fraction (%) LIF Species Wt. (amu), Buffer Wt. (amu), Self-Broad Coef (cm-1/atm), Buff-Broad Coef Self-Quenching x-section (cm^2), Buffer Quenching x-section (cm^2) Specify "hetero" or "homo"-nuclear LIF species First Grd, Last Grd, First Exc, Last Exc

C.2 SAMPLE EXERPT FROM FILE 'EINSTEINA.DAT'

22	34		
1	0	5.18e+000	1509.81715
1	1	2.25e+000	1560.30790
1	2	3.00e+000	1613.60272
1	3	1.09e+000	1669.93009
1	4	1.86e+000	1729.54377
1	5	1.52e+000	1792.72631
1	б	5.90e+000	1859.79329
1	7	1.70e+006	1931.09827
1	8	5.00e+005	2007.03867
1	9	1.00e+000	2088.06277
1	10	2.00e+000	2174.67811
1	11	1.00e+000	2267.46160

C.3 MAIN INPUT AND SUBROUTINES

```
program MoleLIF
*
         MoleLIF: Version 6.0
* Original O2 LIF code provided by Professor Walter Lempert
* The Ohio State University
* Department of Mechanical Engineering,
 Nonequilibrium Thermodynamics Laboratories (NETLab) &
     Department of Chemistry
* Last modified on December 1, 2003 by
 Robert John Leiweke, M.S.
     Candidate for Ph.D.
 Graduate Research Associate
implicit doubleprecision (a-h,o-z)
     logical LIF, absorb
     character*6 nukespec
     integer vgdMAX, vexMAX, Omega, halfpnts
     dimension PopFrac(0:200), array(50000)
     double precision LineWidth, LS, kBoltz, kBoltzGas, lifmass
     double precision melec, muvac
     common/const1/Te(2),we(2),wexe(2),weye(2),weze(2)
     common/const2/Be(2),alphae(2),gammae(2),De(2),betae(2),
    &
          beta2(2), gamma2(2), gamma3(2), gamma4(2),
          gamma5(2), gamma6(2)
    &
     common/const3/weae(2), webe(2), wece(2), wede(2),
              deltae(2), delta2(2)
    &
     common/const4/Gvv(0:55,2), Bvv(0:55,2), Dvv(0:55,2), Hvv(0:55,2)
     common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm
     common/fizcon2/melec, muvac, epvac, pascal
     common/prims/zero, half, one, two, three, four, five, eight
     common/split/wfreq(9,0:200), HLFactor(9,0:200)
     common/spinstat/spindegn(2), LS, odd, even, Gratio
     common/enrgy/Energy(2,0:200), freq(5,0:200), wave(5,0:200)
     common/emissn/PLIF(0:200), QLIF(0:200), RLIF(0:200)
     common/absrbn/Pabs(0:200), Qabs(0:200), Rabs(0:200)
     common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass,
     buffmass,
    &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff
     common/elecquant/Lambda(2), Omega(2)
```

```
common/rotquant/firstJP(2), firstJQ(2), firstJR(2)
     common/vibquant/vstate(4), vgdMAX, vexMAX
      common/widths/LineWidth(0:200), widthLrz, FWHMlaser, brdSelf,
     &brdBuff
      common/laser/PulseTime, AreaLaser, EnrgyLaser
     common/detect/pmGain, CollectVol, CollectEff, QuantEff
     common/spec1/fstwave, fnlwave, waveinc, nspec
     common/spec2/SumSpec(25000)
     common/einA/Acoef(0:55,0:55), vbandhead(0:55,0:55), AvEff(0:55),
     &
                                            Acoll(0:55), tauvEff(0:55)
     common/einB/B12P(0:200), B12Q(0:200), B12R(0:200), fosc12
*
     Enter/open file for storage of screen I/O [for printing]
     open(unit = 60, file = "screen.out")
     zero = 0.0d0
     half = 5.0d-1
     one = 1.0d0
     two = 2.0d0
     three = 3.0d0
      four = 4.0d0
      five = 5.0d0
     eight = 8.0d0
*
     Note that from E=h*nu (joules) and nu=c*freq (Hz), we get
*
     E=h*c*freq,
*
     where h*c is a conversion factor between wavenumber and joules:
*
                     h*c = joules*cm = J/cm-1
     Define fundamental constants. Note that the vacuum speed of
     light, c
*
     is defined here in units of cm/sec and Boltzmann's constant,
*
     kBoltz,
     is expressed in terms of wavenumber, i.e., kBoltz == k/hc so that
     it has units of cm-1/K. kBoltzGas is the usual gas-kinetically
*
     defined
     value in terms of J/K. Atomic mass unit (amu) as well as the
     electron rest mass (melec) are expressed in kg. Planck's
*
     constant
     is in joule-sec, "pascal" is 1 atm in newtons/m^2, and the
      fundamental
*
     charge (qelec) in Coulombs.
     Be CAREFUL! The permeability and permittivity of vacuum values
     are in MKS units, but this code uses centimeters in most spectral
*
     situations (like wavenumber cm-1). Thus, muvac (permeability) in
*
     MKS units is newtons/ampere^2 and epvac (permittivity) MKS units
*
     are farads/meter = coulomb^2/(newton*meter). Whenever you use
*
     these constants in this code, make damn sure that meters are
     converted to centimeters!
     pi = 3.14159265358979d0
     h = 6.626075540d - 34
     c = 2.99792458d10
```

```
227
```

```
qelec = 1.6021773349d-19
     melec = 9.1093897d-31
     kBoltz = 6.95038759d-1
     kBoltzGas = 1.380658d-23
     amu = 1.6605402d-27
     atm = 760.0d0
     pascal = 1.01325d5
     muvac = four*pi*1.0d-7
     epvac = one/(muvac*c**2)
     LIF = .true.
     absorb = .false.
     loop = 0
*
     Begin program calls.
     call Header
     write(6,*)'Begin Step 1'
     read(5,*)istep
     if(istep.eq.9)goto 1000
     call GetInput(loop,nukespec)
     call TermValues(nukespec)
     call Header
     write(6,*)'Proceed to Step 2'
     read(5,*)istep
     if(istep.eq.9)goto 1000
     call StepSize
     call Header
     write(6,*)'Now, do Step 3'
     read(5,*)istep
     if(istep.eq.9)goto 1000
     write(6,*)'
                   1
     write(6,*)'------'
     write(6,100)
80
100
     format(' Enter # Rotational States to Calculate ')
     write(6,*)'
                     1
     BvApprx = Bvv(0,1)
     JrotApprx = INT(DSQRT(one + four*kBoltz*Trot/BvApprx) + 1)
     write(6,105)Trot, JrotApprx
     format(1x,'Note: For Trot =',F7.1, ' K, Max Jrot =',I3)
105
     write(6,*)'-----'
     read(5,*,err=80)nrot
     vgdfst = vstate(1)
     vexcfst = vstate(2)
     nvgd = INT(vstate(3) - vstate(1) + 1.0d-2)
     nvexc = INT(vstate(4) - vstate(2) + 1.0d-2)
     do j = 0, nvexc
```

```
vstate(2) = vexcfst + j
     do i = 0, nvgd
   vstate(1) = vgdfst + i
   call Ouanta(nrot)
   call Splittings(nrot)
   call HonlLondon(nrot)
   call Einstein(nrot)
   call PopStats(PopFrac,Q,Qratio,nrot,nukespec)
   call LIFsignal(PopFrac,Q,Qratio,nrot)
   call LineShape(nrot,ndat,halfpnts,PopFrac,array)
   call SpectraSum(ndat,halfpnts,array,LIF,absorb)
      enddo
    enddo
   close(unit = 60)
    call SpectraOut
1000 stop
    end
subroutine Header
implicit doubleprecision (a-h,o-z)
   write(6,*)'
              1
   write(6,*)'
                     MoleLIF Version 6.0'
   write(6,200)
   .
   write(6,*)'
200
  format(' Program Steps',10x,'Description',//,
   % 3x, 'Step 1 ..... Display Input Paramaters',/,
   % 3x,'Step 2 ..... Compute Excitation Stepsize',/,
   % 3x,'Step 3 ..... Perform Spectral Calculations',/,
   % 3x,'
                                       ',/,
   % 3x, 'Type 9 ..... Terminate Program',/)
   return
    end
subroutine GetInput(loop,nukespec)
implicit doubleprecision (a-h,o-z)
    character*50 mess
    character*6 nukespec
   dimension mess(18), var(18)
    integer Omega, vgdMAX, vexMAX, vexc, vgd
```

```
double precision LineWidth, lifmass, LS
      logical expon
     common/prims/zero, half, one, two, three, four, five, eight
      common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass,
     buffmass,
     &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff
      common/vibquant/vstate(4), vgdMAX, vexMAX
      common/widths/LineWidth(0:200), widthLrz, FWHMlaser, brdSelf,
     &brdBuff
      common/laser/PulseTime, AreaLaser, EnrgyLaser
     common/detect/pmGain, CollectVol, CollectEff, QuantEff
     common/einA/Acoef(0:55,0:55), vbandhead(0:55,0:55), AvEff(0:55),
                                            Acoll(0:55), tauvEff(0:55)
    &
     common/einB/B12P(0:200), B12Q(0:200), B12R(0:200), fosc12
*
     Read in all the Einstein A-coefficients from a data file.
     open(unit = 40, file = 'einsteinA.dat')
     read(40,*)vexMAX, vgdMAX
     do vexc = 0, vexMax
         do vgd = 0, vgdMax
          read(40,*)dummy, dummy, Acoef(vexc,vgd), vbandhead(vexc,vgd)
         enddo
      enddo
     close(unit = 40)
*
     Now we define the character messages for the user-friendly
     interface. Note that "nvar" is the number of these nice
     messages.
     nvar = 18
     mess(1)='LIF collection volume (cm^3) = '
     mess(2)='LIF collection efficiency = '
     mess(3)='Detector quantum efficiency = '
     mess(4)='Photomultiplier Gain = '
     mess(5) = 'Laser beam area (cm^2) = '
     mess(6)='Laser beam energy (mJ/pulse) = '
     mess(7)='Pulse duration (ns) = '
     mess(8)='Laser Beam Spectral FWHM (GHz) = '
     mess(9)='Total gas pressure (Torr) = '
     mess(10)='LIF species mole fraction (%)= '
     mess(11)='LIF Species Mol. Wt. (amu) ='
     mess(12)='Buffer Gas Mol. Wt. (amu) ='
     mess(13)='Trans-Rotational temperature (K) = '
     mess(14)='Vibrational temperature (K) = '
     mess(15)='First gd state vibrational quantum number = '
     mess(16)='Last gd state vibrational quantum number = '
     mess(17)='First exc state vibrational quantum number = '
     mess(18)='Last exc state vibrational quantum number = '
```

```
230
```

Now we read in the simulation conditions from a data file.

```
if(loop.eq.0)then
         open(unit = 40, file = "input.dat")
         read(40,*)CollectVol, CollectEff, QuantEff, pmGain
         read(40,*)EnrgyLaser, PulseTime, FWHMlaser, AreaLaser
         read(40,*)Trot, Tvib, press, xspec
         read(40,*)lifmass, buffmass, brdSelf, brdBuff
         read(40,*)xLIFSelf, xLIFBuff
         read(40,*)nukespec
         read(40,*)vstate(1), vstate(3), vstate(2), vstate(4)
         close(unit = 40)
         loop = loop + 1
         xbuff = 1.0d2 - xspec
      else
      endif
*
      Assign the variable names.
      var(1) = CollectVol
      var(2) = CollectEff
      var(3) = OuantEff
      var(4) = pmGain
      var(5) = AreaLaser
      var(6) = EnrgyLaser
      var(7) = PulseTime
      var(8) = FWHMlaser
      var(9) = press
      var(10) = xspec
      var(11) = lifmass
      var(12) = buffmass
      var(13) = Trot
      var(14) = Tvib
      var(15) = vstate(1)
      var(16) = vstate(3)
      var(17) = vstate(2)
      var(18) = vstate(4)
100
      continue
      write(6,*)'
      write(6,*)'
      do i = 1, nvar
         value = var(i)
         call DetFormat(value,expon)
         if(.not.expon)write(6,300)i, mess(i), var(i)
         if(expon)write(6,310)i, mess(i), var(i)
      enddo
300
      format(I4,4x,A50,F10.4)
310
      format(I4,4x,A50,E10.4)
      write(6,*)'
      write(6,*)'
      write(6,400)
```

```
format(' Enter Parameter # to Change:',/,' (Entering 0 EXITS)',$)
400
     write(6,*)'
     write(6,*)'
     read(5,*)change
     nchange = INT(change + 1.0d-2)
     if(nchange.eq.0)then
       go to 1000
     else
        write(6,500)var(nchange)
500
        format(' Old Value = ',E10.4,/,' Enter NEW: ',$)
        read(5,*)var(nchange)
        goto 100
     endif
1000 continue
*
     Write parameters to screen.out file.
     write(60,*)'
     write(60,*)'
                         Input Parameters'
     write(60,*)'
     do i = 1, nvar
        call DetFormat(var(i),expon)
        if(.not.expon)write(60,300)i, mess(i), var(i)
        if(expon)write(60,310)i, mess(i), var(i)
     enddo
                               ٢
     write(60,*)'
     write(60,*)'
     CollectVol = var(1)
     CollectEff = var(2)
     QuantEff = var(3)
     pmGain = var(4)
     AreaLaser = var(5)
     EnrgyLaser = var(6)
     PulseTime = var(7)*1.0d-9
     FWHMlaser = var(8)
     press = var(9)
     xspec = var(10)
     lifmass = var(11)
     buffmass = var(12)
     Trot = var(13)
     Tvib = var(14)
     vstate(1) = var(15)
     vstate(3) = var(16)
     vstate(2) = var(17)
     vstate(4) = var(18)
     return
     end
*
```

```
subroutine DetFormat(value,expon)
                                ******
    implicit doubleprecision (a-h,o-z)
    common/prims/zero, half, one, two, three, four, five, eight
    logical expon
    max = 4
    if(value.ne.zero)then
       exponent = DLOG10(value)
       expon = .false.
       if(exponent.gt.max)expon = .true.
       if(exponent.lt.-2)expon = .true.
    else
       expon = .false.
    endif
    return
    end
subroutine TermValues(nukespec)
implicit doubleprecision (a-h,o-z)
    character*6 nukespec
    integer Omega, v, vexc, vgd, vgdMAX, vexMAX
    double precision LS, lifmass
    dimension delLam(2)
    common/spinstat/spindegn(2), LS, odd, even, Gratio
    common/rotquant/firstJP(2), firstJQ(2), firstJR(2)
    common/elecquant/Lambda(2), Omega(2)
    common/vibquant/vstate(4), vgdMAX, vexMAX
    common/const1/Te(2),we(2),wexe(2),weye(2),weze(2)
    common/const2/Be(2),alphae(2),gammae(2),De(2),betae(2),
    Ŷ
         beta2(2), gamma2(2), gamma3(2), gamma4(2),
    ÷
         gamma5(2), gamma6(2)
    common/const3/weae(2), webe(2), wece(2), wede(2),
    %
              deltae(2), delta2(2)
    common/const4/Gvv(0:55,2), Bvv(0:55,2), Dvv(0:55,2), Hvv(0:55,2)
    common/prims/zero, half, one, two, three, four, five, eight
    common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass,
    buffmass,
    &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff
    common/einA/Acoef(0:55,0:55), vbandhead(0:55,0:55), AvEff(0:55),
                                     Acoll(0:55), tauvEff(0:55)
    &
*
    Define the total Spin, S, of both upper and lower electronic
    states and the Multiplicity Mplet = (2*S + 1)
```
```
Spin = 0.0d0
     Mplet = INT(two*Spin + one)
     Define molecular constants for the ground electronic state,
     denoted by index 1. Data taken from Reference [6].
     data Lambda(1), Omega(1)/0, 0/
     data Te(1), we(1), wexe(1)/0.0d0, 2169.81358d0, 13.28831d0/
     data weye(1), weze(1), weae(1), webe(1)/1.0511d-2, 5.74d-5,
     2
                   9.83d-7, -3.16d-8/
     data wece(1), wede(1)/0.0d0, 0.0d0/
     data Be(1), alphae(1), gammae(1), gamma2(1)/1.93128087d0,
     ò
              1.750441d-2, 5.487d-7,2.54d-8/
     data gamma3(1), gamma4(1), gamma5(1), gamma6(1)/0.0d0, 0.0d0,
                    0.0d0, 0.0d0/
     data De(1), betae(1), beta2(1)/6.1214d-6, -1.153e-9, 1.8d-10/
     data deltae(1), delta2(1)/5.83d-12, -1.73d-13/
     Define molecular constants for the excited electronic state,
     denoted as 2. Values taken from Tilford & Simmons.
     data Lambda(2), Omega(2)/1, 0/
     data firstJP(2), firstJQ(2), firstJR(2)/1.0d0, 1.0d0, 1.0d0/
     data Te(2), we(2), wexe(2)/65079.09165d0, 1518.24d0, 19.4d0/
     data weye(2), weze(2), weae(2), webe(2)/7.6584d-1,-1.4117d-1,
                   1.434d-2,-8.051d-4/
     data wece(2), wede(2)/2.36d-5, -2.9d-7/
     data Be(2),alphae(2),gammae(2),gamma2(2)/1.6115d0, 2.3251d-2,
     %
                1.5911d-3, -5.716d-4/
     data gamma3(2), gamma4(2), gamma5(2), gamma6(2)/8.2417d-5,
              -5.9413d-6, 2.1149d-7, -2.991d-9/
     Ŷ
     data De(2), betae(2), beta2(2)/7.29d-6, 1.05d-7, 0.0d0/
     data deltae(2), delta2(2)/0.0d0, 0.0d0/
     Due to nuclear spin statistics, homo-nuclear molecules require
*
     that even = zero but for hetero-nuclear, even = one.
     odd = one
     if(nukespec.eq.'hetero')then
        even = one
     elseif(nukespec.eq.'homo')then
        even = zero
     else
     endif
     Now compute each electronic state's spin statistical weight
     spindegn = (2 - delLam)*(2*S + 1).
     do ne = 1, 2
        if(Lambda(ne).eq.0)then
          delLam(ne) = one
        else
          delLam(ne) = zero
```

```
endif
         spindegn(ne) = (two - delLam(ne))*DFLOAT(Mplet)
      enddo
     Gratio = (two - delLam(2))/(two - delLam(1)*delLam(2))
*
     Here we define the first allowed quantum level for the ground
*
      electronic state to be firstJ(2)-Jmin" == deltaJ such that
     Jmin" == firstJ(1) = firstJ(2) - deltaJ.
      firstJP(1) = firstJP(2) + one
      firstJQ(1) = firstJQ(2)
      firstJR(1) = firstJR(2) - one
      Specify the LS energy due to split electronic states,
      if necessary.
     LS = zero
*
     Define the LIF Species' characteristic temperatures of
     vibration and rotation.
     ThetaVib = 3070.0d0
      ThetaRot = 2.78d0
*
     Compute molecular term-values for each electronic state.
*
     Here, the maximum number of vibrational states for the
*
      excited electronic state is taken to be the same as the
*
     ground electronic state. This is usually not true, and
*
      non-physical energies must be expected if the vibrational
*
      level is beyond the accuracy limit of the molecular
      constants. This means that you must know the limitations
     of the system under study.
     do ne = 1, 2
        do v = 0, vqdMAX
          vm = DFLOAT(v) + half
     vm2 = vm**2
     vm3 = vm**3
     vm4 = vm**4
     vm5 = vm**5
     vm6 = vm**6
     vm7 = vm**7
     vm8 = vm**8
     Gvv(v,ne) = Te(ne) + we(ne)*vm - wexe(ne)*vm2
                    + weye(ne)*vm3 + weze(ne)*vm4 + weae(ne)*vm5
    &
    &
              + webe(ne)*vm6 + wece(ne)*vm7 + wede(ne)*vm8
     Bvv(v,ne) = Be(ne) - alphae(ne)*vm + gammae(ne)*vm2
              + gamma2(ne)*vm3 + gamma3(ne)*vm4
    &
              + gamma4(ne)*vm5 + gamma5(ne)*vm6 +
    &
                        gamma6(ne)*vm7
    &
     Dvv(v,ne) = De(ne) + betae(ne)*vm + beta2(ne)*vm2
     Hvv(v,ne) = deltae(ne) + delta2(ne)*vm
         enddo
      enddo
```

```
*
    For each excited vibrational level, we sum over
*
     all ground vibrational levels to compute the effective Einstein
*
     coefficient. The inverse of this value is the effective
     spontaneous decay lifetime for that particular excited
    vibrational state. Later, in subroutine Einstein, we will use
     this to compute the overall rovibronic effective rate. Note here
* that we protect from divide-by-zero when we invert AvEff(vexc),
* with an arbitrarily (and ridiculous) large value.
     write(60,*)'Effective Spontaneous Emission & Lifetimes'
    write(60,*)'
                        1
    write(60,*)' Note: "unknown" ==> AvEff < 10^4 /sec'</pre>
    write(60,*)'
    write(60,*)'vexc
                      AvEff (10^7/sec) Lifetime (ns)'
    write(60,*)'
    do vexc = 0, vexMax
       Sum = zero
       do vgd = 0, vgdMAX
         Sum = Sum + Acoef(vexc,vgd)
  enddo
       AvEff(vexc) = Sum*Gratio
       if(AvEff(vexc).gt.1.0d4)then
         tauvEff(vexc) = one/AvEff(vexc)
         write(60,801)vexc, AvEff(vexc)/1.0d7, tauvEff(vexc)*1.0d9
       else
         write(60,800)vexc
       endif
     enddo
800
     format(1x,I2,10x,'unknown',8x,'unknown')
801
    format(1x, I2, 10x, F6.2, 8x, F7.2)
    return
     end
subroutine StepSize
implicit doubleprecision (a-h,o-z)
    double precision kBoltz, kBoltzGas, LineWidth
     common/spec1/fstwave, fnlwave, waveinc, nspec
     common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm
     common/prims/zero, half, one, two, three, four, five, eight
     common/widths/LineWidth(0:200), widthLrz, FWHMlaser, brdSelf,
    &brdBuff
    do i = 1, 5
       write(6,*)'
     enddo
    write(6,*)'
```

```
236
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```
write(6,*)'Specify Excitation Scan Wavelength Range'
    write(6,*)'-----'
80
    write(6,100)
    write(6,*)'-----'
100
    format(' Enter Starting Absorption Wavelength (nm):')
    read(5,*)fstwave
    write(6,*)'------'
    write(6,200)
    write(6,*)'-----'
200
    format(' Enter Ending Absorption Wavelength (nm): ')
    read(5,*)fnlwave
    write(6,*)'------'
    write(6,300)
    write(6,*)'-----'
300
    format(' Enter Number of Points < 25,000')</pre>
    read(5,*)nspec
    waveinc = (fnlwave - fstwave)/(nspec - 1)
    waveavg = (fnlwave + fstwave)/two
    freqinc = c*waveinc*1.0d-3/waveavg**2
    nfreqpnts = INT(FWHMlaser/freqinc)
    if(nspec.gt.25000)then
      write(6,320)
320
      format(' Max # of points exceeded - TRY AGAIN! ')
      goto 80
    endif
    write(6,*)'
              '
    write(6,*)'-----'
    write(6,340)waveinc*1.0d3
    write(6,*)'-----'
    write(6,400)waveavg, freqinc
    write(6,*)'-----'
    write(6,500)FWHMlaser, nfreqpnts
    write(6,*)'------'
            '
    write(6,*)'
    write(6,*)'
               1
340
    format(' Wavelength Increment =', F6.3, ' pm')
    format(' Increment at ',F5.1,' nm =',F7.4,' GHz')
400
    format(' Points within the',F5.1,' GHz Laser Source = ',I3)
500
    return
    end
subroutine Quanta(nrot)
*
*
      First, this subroutine calculates ground and excited state
*
    energies for each value of Jlow for the current (vexc,vqd)
    absorption bands in the main loop. Calculation is based upon the
```

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237
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*
     expansion defined in introduction to Huber and Herzberg. The O
*
     and S-branches correspond to two-photon transitions and may not
*
     be important for most LIF applications.
        Next, we calculate the O,P,Q,R, and S Branch absorption
*
     frequencies in cm-1 units.
*
     Note that absorption wavelengths are computed in Angstrom.
*
                       Branch Name = 0 P Q R S
*
             Delta J = Jup - Jlow = -2 - 1 \ 0 \ 1 \ 2
*
                      Branch Index = 1 \ 2 \ 3 \ 4 \ 5
*
*
     Note that this branch index notation is not the same as that of
*
     subroutines Splittings, HonlLondon, and LineShape.
implicit doubleprecision (a-h,o-z)
     integer vib, deltaJ, branch, vgdMAX, vexMAX
     double precision kBoltz, kBoltzGas, lifmass
     common/enrgy/Energy(2,0:200), freq(5,0:200), wave(5,0:200)
     common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass,
     buffmass,
     &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff
     common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm
     common/const1/Te(2),we(2),wexe(2),weye(2),weze(2)
     common/const4/Gvv(0:55,2), Bvv(0:55,2), Dvv(0:55,2), Hvv(0:55,2)
     common/vibquant/vstate(4), vgdMAX, vexMAX
     common/prims/zero, half, one, two, three, four, five, eight
*
     First, compute the ro-vibrational energies for each electronic
*
     state. We compute up to Jlow = nrot+2 to avoid negative
     transition energies when computing freq(branch>3,nrot)
     do ne = 1, 2
        vib = INT(vstate(ne) + 1.0d-2)
        Gv = Gvv(vib, ne)
        Bv = Bvv(vib, ne)
        Dv = Dvv(vib, ne)
        Hv = Hvv(vib, ne)
        do J = 0, nrot+2
     aJ = DFLOAT(J^*(J + 1))
     aJ2 = aJ^{**2}
     aJ3 = aJ**3
     FvJ = Bv*aJ - Dv*aJ2 + Hv*aJ3
     Energy(ne,J) = Gv + FvJ
        enddo
     enddo
```

*

Now compute the O,P,Q,R,S-branch absorption energies in

```
*
     wavenumber
     and wavelengths in Angstrom.
     deltaJ = -2
     do branch = 1, 5
       do Jlow = 0, nrot
         Jup = Jlow + deltaJ
         dEnrgy = Energy(2,Jup) - Energy(1,Jlow)
         freq(branch,Jlow) = dEnrgy
         wave(branch,Jlow) = 1.0d8/freg(branch,Jlow)
       enddo
       deltaJ = deltaJ + 1
     enddo
     return
     end
subroutine Splittings(nrot)
*
*
      This subroutine computes wavelengths due to energy
*
      transitions split into additional wavelengths due to spin-orbit
*
       interactions. Up to M = 2S+1 = 3 multiplicity is modeled here.
      Triplet-splitting is maintained for convenient user changes in
*
      the the multiplicity (for example, from 1Sig-1Pi to 2Sig-2Pi).
*
*
         In the case of singlet energy levels, no splittings occur.
       Thus, the values for f1, f2, and f3 are set to zero. Note that
*
       the special case of 1Sig-1Sig (LamUp=0 & LamLow=0 ==> dLam=0)
*
       electronic transitions do not allow a Q-branch, so these should
*
       be set to zero in that situation.
*
    The basis for these calculations are Hunds' (b). Note
*
       that either Hunds' (a) or (b) lead to the same description for
       Sigma-Pi transitions. For more details on this topic, see
      Herzberg pg. 245.
implicit doubleprecision (a-h,o-z)
     integer branch, findex
     dimension f1(0:200,3), f2(0:200,3), f3(0:200,3)
     common/split/wfreq(9,0:200), HLfactor(9,0:200)
     common/prims/zero, half, one, two, three, four, five, eight
*
     First, we calculate and store the Energy level splittings in cm-1
     as a function of J for ground and excited states. Note that
     branch = 1, 2, 3 are the P, Q, R-Branches, respectively.
     do branch = 1, 3
       do Jlow = 0, nrot+2
      fl(Jlow,branch) = zero
          f2(Jlow, branch) = zero
```

```
239
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f3(Jlow, branch) = zero
        enddo
     enddo
*
     Now Calculate P/Q/R branch transition frequency splittings
*
     wfreq(findex,J). P-splittings are in array locations
*
     findex = (1,2,3), Q in (4,5,6) and R in (7,8,9). Each branch may
     have up to three splittings depending upon the multiplicity.
*
     For multiplicity = 1 (singlets), all wfreq values are zero
*
     (no splits). If you want the multiplicity = 2, then you
*
     must change the wfreq functional to have doublet values such that
*
     branches with findex = (1,4,7) and (2,5,8) are non-zero.
                                                          For
*
     triplets, we make the wfreq functional non-zero for all findex.
*
     The following index table should help as a guide to making the
*
     appropriate changes:
*
                                 P Q R
*
*
     Doublet or Triplet => findex = 1, 4, 7
*
     Doublet or Triplet => findex = 2, 5, 8
               Triplet => findex = 3, 6, 9
     do Jlow = 0, nrot+2
        do branch = 1, 3
    findex = 3*(branch - 1) + branch
    wfreq(findex,Jlow) = zero*f1(Jlow,branch)
    wfreq(findex,Jlow) = zero*f2(Jlow,branch)
    wfreq(findex,Jlow) = zero*f3(Jlow,branch)
        enddo
     enddo
     return
     end
subroutine HonlLondon(nrot)
  *
*
*
    The "Honl-London" factor is the ro-electronic transition
*
      strength S(J^{"}). This subroutine computes the normalized
*
      Honl-London factor:
*
              HLfactor(findex,J") = Sn(J") = S(J")/(2J" + 1)
*
       where J" is the lower rotronic state energy level.
implicit doubleprecision (a-h,o-z)
     common/split/wfreq(9,0:200), HLfactor(9,0:200)
     common/prims/zero, half, one, two, three, four, five, eight
     Note that P-splittings are in wfreq array indices 1, 2, 3;
*
     R-splittings in 4, 5, 6; Q-splittings in 7, 8, 9. Currently,
*
     these Honl-London factors are for Siq+ <-> Pi transitions.
     See Hertzberg page 207. It is important to note that the
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240
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*
     following indexing table for HLfactor(findex,J) is consistent
*
     with that of subroutine Splittings:
*
*
                                 P Q R
                                 _____
*
     Multiplicity = 1 \Rightarrow findex = 1, 4, 7
*
     Multiplicity = 2 =>
                          findex = 2, 5, 8
*
     Multiplicity = 3 =>
                          findex = 3, 6, 9
*
*
     For multiplicity = 1 (singlet), only HLfactor([1,4,7],J) are
*
     non-zero. If multiplicity = 2 (doublet), then the set (2,5,8)
*
     are included. For multiplicity = 3 (triplet), all normalized
*
     Honl-London functions are to be used.
     do Jlow = 0, nrot+2
*
     For the case of no splittings (Multiplicity = 1); These functions
     should be non-zero (unless there is no Q-branch).
   HLfactor(1,Jlow) = half*(Jlow - one)/(two*Jlow + one)
      HLfactor(4, Jlow) = half
   HLfactor(7,Jlow) = half*(Jlow + two)/(two*Jlow + one)
     For Doublets (Multiplicity = 2), this, along with (1,4,7) should
     be used.
        HLfactor(2, Jlow) = zero
        HLfactor(5, Jlow) = zero
        HLfactor(8,Jlow) = zero
     For Triplets (Multiplicity = 3), this should be included along
     with the other two sets (1,4,7) and (2,5,8).
        HLfactor(3, Jlow) = zero
        HLfactor(6, Jlow) = zero
    HLfactor(9,Jlow) = zero
     enddo
     return
     end
subroutine Einstein(nrot)
*
*
     First, we calculate the "oscillator strength" f12, which is the
*
     dimensionless ratio (0 < f12 < 1) of the actual absorption to
*
     that of a hypothetical model in which absorption is attributed
     to the dissipating term of a classical electromagnetic dipole
*
     oscillator. This ratio is useful for calculating the density
*
     of the ideal oscillators required to produce the same absorption
*
     effect as the actual ground-state absorbers. The emission
*
     strength can be computed from the reciprocity relationship
*
                   q1*f12 = q2*f21
```

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241
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*
*
     where g is the state degeneracy g(J,S) = (2J+1)*(2S+1).
*
     Note that we divide the grouping of physical constants by 100
     in order to account for the conversion of meters to centimeters
     as well as frequency in Hertz to wavenumbers. This calculation
*
     is performed for a P(10) absorption line such that
*
     g^2/g^1 = (2J'+1)/(2J''+1) = 19/21 = 0.904762.
     Also, note that we eliminate non-physical, negative values
*
     of Einstein B-coefficients by using the first allowed ground
     electronic state rotational level as a criterion.
implicit doubleprecision (a-h,o-z)
     integer vgd, vexc, vgdMAX, vexMAX
     double precision kBoltz, kBoltzGas, melec, muvac, LS
     common/vibquant/vstate(4), vgdMAX, vexMAX
     common/rotquant/firstJP(2), firstJQ(2), firstJR(2)
     common/spinstat/spindegn(2), LS, odd, even, Gratio
     common/const4/Gvv(0:55,2), Bvv(0:55,2), Dvv(0:55,2), Hvv(0:55,2)
     common/enrgy/Energy(2,0:200), freq(5,0:200), wave(5,0:200)
     common/einA/Acoef(0:55,0:55), vbandhead(0:55,0:55), AvEff(0:55),
    &
                                         Acoll(0:55), tauvEff(0:55)
     common/einB/B12P(0:200), B12Q(0:200), B12R(0:200), fosc12
     common/prims/zero, half, one, two, three, four, five, eight
     common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm
     common/fizcon2/melec, muvac, epvac, pascal
     common/split/wfreq(9,0:200), HLfactor(9,0:200)
*
     Compute the appropriate (absorption) Einstein B-coefficients for
*
     the current vibronic absorption bands. The loop index here
     is Jlow = J".
     vgd = INT(vstate(1) + 1.0d-2)
     vexc = INT(vstate(2) + 1.0d-2)
     EinsteinA = Acoef(vexc,vgd)
     x1 = melec*epvac*c/(two*pi*1.0d2*gelec**2)
     fosc12 = x1*(19.0d0/21.0d0)*HLfactor(1,10)*EinsteinA/
    &
                                                     freq(2,10)**2
     cnst = vbandhead(vexc,vgd)*Gratio*1.0d-24/(eight*pi*h)
     do Jlow = 0, nrot+2
        B12P(Jlow) = cnst*(wave(2,Jlow)**2)*EinsteinA*HLfactor(1,Jlow)
        B12Q(Jlow) = cnst*(wave(3, Jlow)*2)*EinsteinA*HLfactor(4, Jlow)
        B12R(Jlow) = cnst*(wave(4,Jlow)**2)*EinsteinA*HLfactor(7,Jlow)
     enddo
     return
     end
subroutine PopStats(PopFrac,Q,Qratio,nrot,nukespec)
```

```
* * *
*
   This subroutine calculates the total ro-vibrational partition
     function, Q, for the LIF species molecule. It is assumed that
     the ground state of the transition is also the electronic ground
     state (Te=0). LS split electronic states are included in the
*
     calculation, if appropriate, as are the spin statistics.
     We loop over both vibrational and rotational levels (of even/odd
     J to incorporate appropriate spin-statistical effects) in order
*
 to compute the total two-temperature, coupled ro-vibrational
* Partition Function and ro-vib population. For homogeneous
* diatomics, every other rotational line is missing, but for
* heterogeneous diatomics, we need them all (see subroutine
* TermValues where (even=1, odd=1)for heterogeneous, and (even=0,
*
 odd=1) for homonuclear diatomic molecules.
     This even-odd spin-statistical accounting is easily recognized as
     the so-called rotational "symmetry number" when the rotational
     partition function is approximated by a continuous integration
     from J=0 to J=infinity:
          Qrot(Trot) = Trot/(symnum*ThetaRot)
     where symnum=1 for any hetero-nuclear diatomic (CO, NO, etc.) and
*
     symnum=2 for any homo-nuclear (O2, N2, etc.) diatomic molecule].
*
*
  Note that rotational and translational temperatures are NOT
     assumed to be equilibrated. This means that we must compute the
*
     coupled ro-vibrational Partition Function using separate
*
     temperatures. We then compare this result with the approximate
     decoupled Partition Function:
*
                  Q(Trot,Tvib) =~ Qrot(Trot)*Qvib(Tvib)
 implicit doubleprecision (a-h,o-z)
     character*6 nukespec
     integer vib, vgd, vgdMAX, vexMAX, Omega
     double precision LS, LSengy, kTvib, kBoltz, kBoltzGas, lifmass
     dimension PopFrac(0:200)
     common/emissn/PLIF(0:200), QLIF(0:200), RLIF(0:200)
     common/spinstat/spindegn(2), LS, odd, even, Gratio
     common/const4/Gvv(0:55,2), Bvv(0:55,2), Dvv(0:55,2), Hvv(0:55,2)
     common/elecquant/Lambda(2), Omega(2)
     common/vibquant/vstate(4), vgdMAX, vexMAX
     common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass,
     buffmass,
    &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff
     common/prims/zero, half, one, two, three, four, five, eight
     common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm
```

```
243
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```
*
     Note that Boltzmann's constant is defined in terms of wavenumber,
*
      i.e., units of k/hc are cm-1/K, NOT J/K. Thus, kTvib gets
      converted to units of wavenumber (cm-1).
      if(nukespec.eq.'hetero')then
         symnum = one
      elseif(nukespec.eq.'homo')then
         symnum = two
      endif
     kTvib = kBoltz*Tvib
     Qvib = one/(two*DSINH(ThetaVib/(two*Tvib)))
     Qrot = Trot/(symnum*ThetaRot)
     Qaprx = Qvib*Qrot
      if(INT(LS).eq.0)nLSstates = 1
      if(INT(LS).ne.0)nLSstates = 2
     Note that we jump out of the following loop over rotational
* states if the magnitude of the Boltzmann fraction exponent is
* "large" (chosen here to be 20.0). This helps to avoid
* accumulation of errors in the sum and avoids floating point
* overflows.
     Qsum = zero
     do i = 1, nLSstates
        LSengy = LS*(i - 1)
   do vib = 0, vgdMAX
     Gv = Gvv(vib, 1)
     Bv = Bvv(vib,1)
     Dv = Dvv(vib, 1)
     Hv = Hvv(vib, 1)
     Evib = Gv + LSengy
           do Jlow = 0, 200
       aJ = DFLOAT(Jlow*(Jlow + 1))
       aJ2 = aJ^{**2}
       aJ3 = aJ**3
       gJ = two*Jlow + one
       FvJ = Bv*aJ - Dv*aJ2 + Hv*aJ3
             exponent = (Evib + Tvib*FvJ/Trot)/kTvib
             if(exponent.gt.20.0d0)goto 300
       Qsum = Qsum + even*spindegn(1)*gJ*DEXP(-exponent)
300
             continue
           enddo
   enddo
      enddo
     Next, we compare the combined ro-vibrational Partition
     Function with the approximate ro-vibrationally decoupled case:
     Q = Qsum*Qvib
     Qratio = Q/Qaprx
     Last, calculate ground electronic state populations for
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244
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```
each ro-vibrational state beginning at J=0, for the current
     vibronic transition.
     vgd = INT(vstate(1) + 1.0d-2)
     Gv = Gvv(vgd, 1)
     Bv = Bvv(vgd, 1)
     Dv = Dvv(vgd, 1)
     Hv = Hvv(vqd, 1)
     Evib = Gv + LSengy
     do Jlow = 0, nrot + 2
        gJ = two*Jlow + one
        aJ = Jlow^*(Jlow + one)
        aJ2 = aJ^{**2}
        aJ3 = aJ**3
        FvJ = Bv*aJ - Dv*aJ2 + Hv*aJ3
        exponent = (Evib + Tvib*FvJ/Trot)/kTvib
        PopFrac(Jlow) = even*spindegn(1)*gJ*DEXP(-exponent)/Q
     enddo
     return
     end
subroutine LIFsignal(PopFrac,Q,Qratio,nrot)
*
*
        This subroutine computes the total (integrated) number of
*
     photons collected by the detector for each rotational branch,
*
     seperately.
        First, the Lorentzian (Natural + Collision) and Gaussian
     (Doppler) linewidths are used to compute the Voigt linewidth,
*
     FWHM in GHz. Then, the rates for quenching and pre-dissociation
*
     (if necessary) are computed. Using this, the ro-vibrational
     population fractions, and Einstein-B coefficients we compute
*
     stimulated emission rates, Fluorescence Quantum Yields, and
*
     number of photons emitted during the excitation time.
*
        The number of photons detected are based upon the collection
*
     efficiency and detector quantum efficiency.
       ******
     implicit doubleprecision (a-h,o-z)
     double precision LineWidth, kBoltz, kBoltzGas, lifmass, melec
     double precision muvac, Intensity, IsatP, IsatQ, IsatR, LS
     double precision IratioP, IratioQ, IratioR
     integer vgd, vexc, vgdMAX, vexMAX
     dimension PopFrac(0:200)
     common/vibquant/vstate(4), vgdMAX, vexMAX
     common/rotquant/firstJP(2), firstJQ(2), firstJR(2)
     common/enrgy/Energy(2,0:200), freg(5,0:200), wave(5,0:200)
     common/emissn/PLIF(0:200), QLIF(0:200), RLIF(0:200)
```

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245
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```
common/absrbn/Pabs(0:200), Qabs(0:200), Rabs(0:200)
     common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass,
     buffmass,
     &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff
      common/widths/LineWidth(0:200), widthLrz, FWHMlaser, brdSelf,
    &brdBuff
     common/laser/PulseTime, AreaLaser, EnrgyLaser
     common/detect/pmGain, CollectVol, CollectEff, QuantEff
     common/einA/Acoef(0:55,0:55), vbandhead(0:55,0:55), AvEff(0:55),
    &
                                            Acoll(0:55), tauvEff(0:55)
     common/einB/B12P(0:200), B12Q(0:200), B12R(0:200), fosc12
     common/prims/zero, half, one, two, three, four, five, eight
     common/fizcon1/pi, c, h, kBoltz, gelec, amu, kBoltzGas, atm
     common/spinstat/spindegn(2), LS, odd, even, Gratio
     vgd = INT(vstate(1) + 1.0d-2)
     vexc = INT(vstate(2) + 1.0d-2)
     Acoll(vexc) = AvEff(vexc)
     call LineWidths(nrot)
     call LossRate(Qrate, PreRate, densLIF, densBuff)
*
     Compute the incident laser power (W), intensity (W/cm^2), and
*
     the excitation volume (cm<sup>3</sup>). Resistance of coax signal cable
     is specified in Ohms.
     PowerLaser = 1.0d-3*EnrgyLaser/PulseTime
     Intensity = PowerLaser/AreaLaser
     pmCurnt = QuantEff*pmGain*gelec/PulseTime
     Resistance = 50.0d0
     do Jlow = 0, nrot+2
         if(Jlow.ge.firstJP(1))then
          JupP = Jlow - 1
         else
          goto 400
         endif
         if(Jlow.ge.firstJQ(1))then
          JupQ = Jlow
         else
           goto 400
         endif
         if(Jlow.ge.firstJR(1))then
           JupR = Jlow + 1
         else
           goto 400
         endif
     Compute the number density of ground electronic-state absorbers
     within rotational state Jlow (#/cm^3).
         if(PopFrac(Jlow).eq.0)goto 400
         AbsrbDens = PopFrac(Jlow)*densLIF
```

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246
```

Compute the Stimulated Absorption Rate (1/sec) for each branch, for the current main-loop absorption band (vgd,vexc). W12P = B12P(Jlow)*Intensity/(c*FWHMlaser*1.0d9) W12Q = B12Q(Jlow)*Intensity/(c*FWHMlaser*1.0d9) W12R = B12R(Jlow)*Intensity/(c*FWHMlaser*1.0d9) Compute roelectronic degeneracy ratio g1/g2 and 1/(1+[g1/g2])for each branch. spinratio = spindegn(1)/spindegn(2) rotratioP = (two*Jlow + one)/(two*Jlow - one) rotratioQ = one rotratioR = (two*Jlow + one)/(two*Jlow + three) g1g2P = spinratio*rotratioP g1g2Q = spinratio*rotratioQ glg2R = spinratio*rotratioR gfacP = one/(one + g1g2P)gfacQ = one/(one + g1g2Q)gfacR = one/(one + g1g2R)* Compute the Stimulated Emission B-coefficients [cm^3/(W-sec^3)]. B21P = B12P(Jlow)*q1q2PB210 = B120(Jlow)*q1q20B21R = B12R(Jlow)*g1g2R* Compute the Stimulated Emission Rates (1/sec). W21P = B21P*Intensity/(c*FWHMlaser*1.0d9) W21Q = B21Q*Intensity/(c*FWHMlaser*1.0d9) W21R = B21R*Intensity/(c*FWHMlaser*1.0d9) Compute the saturation intensity ratio Isat/I and the nondimensional fluorescence rate function, PHI. x1 = Aveff(vexc) + Orate + PreRatexP = (B12P(Jlow) + B21P)/(c*FWHMlaser*1.0d9)IsatP = x1/xPIratioP = IsatP/Intensity PHIP = one/(one + IratioP) xQ = (B12Q(Jlow) + B21Q)/(c*FWHMlaser*1.0d9)IsatQ = x1/xQIratioQ = IsatQ/Intensity PHIQ = one/(one + IratioQ) xR = (B12R(Jlow) + B21R)/(c*FWHMlaser*1.0d9)IsatR = x1/xRIratioR = IsatR/Intensity PHIR = one/(one + IratioR)

```
*
     Compute the number of photons per unit volume emitted into 4*pi
*
     steradians during the excitation pulse time. Note that we
     have assumed negligable self-absorption and radiation trapping.
       Pphotons = AbsrbDens*Acoll(vexc)*gfacP*PHIP*PulseTime
       Qphotons = AbsrbDens*Acoll(vexc)*gfacQ*PHIQ*PulseTime
       Rphotons = AbsrbDens*Acoll(vexc)*gfacR*PHIR*PulseTime
     We adhere to the quantum selection rule that the first J-levels
*
     allowed in each state depend on the quantum number
     firstJ = Omega = Lambda + Sigma for Hund's Case (a).
       if(Jlow.lt.INT(firstJP(1)))Pphotons = zero
       if(Jlow.lt.INT(firstJQ(1)))Qphotons = zero
       if(Jlow.lt.INT(firstJR(1)))Rphotons = zero
     Compute the signal (mVolts) for each rotational line of the
* present vibronic transition using the number of photons emitted
* along with experimental setup conditions.
       PLIF(Jlow) = Pphotons*CollectVol*CollectEff*pmCurnt*
    &
                                                 Resistance*1.0d3
       QLIF(Jlow) = Qphotons*CollectVol*CollectEff*pmCurnt*
    &
                                                 Resistance*1.0d3
       RLIF(Jlow) = Rphotons*CollectVol*CollectEff*pmCurnt*
    &
                                                 Resistance*1.0d3
*
     Use Beer's Law to compute the fraction of the input intensity
     transmitted and absorbed within the given path length.
       AbsConst = zero
       transmission = one
       absorption = zero
       Pabs(Jlow) = absorption
       Qabs(Jlow) = absorption
       Rabs(Jlow) = absorption
400
       continue
     enddo
     return
     end
subroutine LineWidths(nrot)
*
*
*
       This subroutine calculates the Lorentzian, Gaussian, and
     Voigt linewidth (FWHM) in GHz. The broadening coefficients and
*
     temperature exponent are experimentally determined.
*
     Note that the excitation laser source is assumed to be spectrally
     Gaussian and independent of tuning (i.e., "locking" efficiency).
```

```
implicit doubleprecision (a-h,o-z)
     double precision LineWidth, kBoltz, lifmass, kBoltzGas
      integer vgdMAX, vexMAX, vgd, vexc
     common/einA/Acoef(0:55,0:55), vbandhead(0:55,0:55), AvEff(0:55),
                                            Acoll(0:55), tauvEff(0:55)
    &
     common/widths/LineWidth(0:200), widthLrz, FWHMlaser, brdSelf,
     &brdBuff
     common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass,
     buffmass,
     &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff
      common/enrgy/Energy(2,0:200), freq(5,0:200), wave(5,0:200)
     common/prims/zero, half, one, two, three, four, five, eight
     common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm
     common/vibquant/vstate(4), vgdMAX, vexMAX
*
     Calculate Natural Broadening (FWHM Lorentzian) in GHz for the
     current vibrational band.
     vgd = INT(vstate(1) + 1.0d-2)
     vexc = INT(vstate(2) + 1.0d-2)
     EinsteinA = Acoef(vexc,vgd)
     widthNat = EinsteinA/(two*pi*1.0d9)
     enrqyk = DSQRT(two*DLOG(two)*kBoltzGas*Trot/lifmass)
     Calculate Collisional ("Pressure") Broadening (FWHM
*
     Lorentzian) in GHz. Trot is in Kelvin, pressure p is in atm,
*
     avgspeed cm/sec. The broading coefficients (brdSelf, brdBuff)
     have units of cm-1/atm.
     dwSelf = brdSelf*(press/atm)*(xspec/1.0d2)*c*
    &
                                               (Trot/296.8d0)**7.5d-1
     dwBuff = brdBuff*(press/atm)*(xbuff/1.0d2)*c*
    &
                                               (Trot/301.5d0)**7.5d-1
     widthCol = (dwSelf + dwBuff)/1.0d9
*
     Calculate the total Lorentzian broadening (FWHM) in GHz.
     widthLrz = widthNat + widthCol
     Calculate Doppler Broadening (FWHM Gaussian) in GHz. The
     total Gaussian width is the sum of the Doppler and (assumed)
     excitation laser linewidth. Then, compute the approximate
     Voigt linewidth (FWHM) in GHz using the "Whiting Formula".
     do J = 0, nrot+2
         widthDop = two*freq(2,J)*enrgyk/1.0d7
         widthGss = DSQRT(widthDop**2 + FWHMlaser**2)
        LineWidth(J) = 5.346d-1*widthLrz +
                             DSQRT(2.166d-1*widthLrz**2 + widthGss**2)
    &
     enddo
```

return

end subroutine LossRate(Orate, PreRate, densLIF, densBuff) * * * This subroutine computes the rate of non-radiative energy transfer from the excited electronic ro-vibrational states to other energy modes. The equations used are based upon * experimentally determined quenching cross-sections for individual vibrational states within the excited electronic state. implicit doubleprecision (a-h,o-z) double precision kBoltz, kBoltzGas, lifmass, melec, muvac common/prims/zero, half, one, two, three, four, five, eight common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm common/fizcon2/melec, muvac, epvac, pascal common/gasprop/xspec, xbuff, press, Trot, Tvib, lifmass, buffmass, &ThetaVib, ThetaRot, xLIFSelf, xLIFBuff * Compute the reduced mass in kg. redmass = buffmass*lifmass*amu/(buffmass + lifmass) * Using the reduced mass, compute the relative velocities of the * colliding particles based upon the mean thermal speeds. Note units are in cm/sec. spdRed = 1.0d2*DSQRT(eight*kBoltzGas*Trot/(pi*redmass)) spdLIF = 1.0d2*DSQRT(two*eight*kBoltzGas*Trot/(pi*amu*lifmass)) * Compute the particle number density of each species, in $\#/cm^3$. densTot = (press/atm)*pascal*1.0d-6/(kBoltzGas*Trot) densLIF = (xspec/1.0d2)*densTot densBuff = (xbuff/1.0d2)*densTot* Compute the quenching rates (per second). QrateLIF = xLIFSelf*densLIF*spdLIF QrateBuff = xLIFBuff*densBuff*spdRed Qrate = QrateLIF + QrateBuff * Compute the Pre-Dissociation Rate (per second), if necessary. PreRate = zero return end

subroutine LineShape(nrot,ndat,halfpnts,pop,array) ***** ***** * * * This subroutine computes the spectral lineshape for each * rotational line of the current vibronic transition. The * "Whiting Formula" is used as an approximation for the Voigt * lineshape. Note that the convolution of each transitions's * contribution to the total lineshapes is not performed here, * but in subroutine SpectraSum. The basic idea here is to compute * the signal dS, (intensity) as a function of frequency (wavelength * in Angstrom) from * * dS/Stot = g(freq)*dfreq * * where Stot is the total integrated signal (PLIF, QLIF, RLIF), * g(freq) the lineshape function in 1/GHz, and dfreq the * frequency increment in GHz. Note that we express the detuning * parameter in wavelengths using the relation * freq(GHz) = c/(10*wave(Ang)).* By taking the derivative of the above expression, the frequency * increment is dfreq = c*dwave/(10*wave^2) * * All resonance wavelengths and integrated fine-structure * components for the P, Q, and R-branches are contained in a single vector called "array". This is a holdover from the old * 02 LIF code in order to accomodate writing one's own plotting routines, and is somewhat reminiscent of a "Pointered Array". * * This vector contains, in consecutive order for P,Q,R-branches, * the wavelengths with index "iwave" and signal integrated over * the fine-structure components with index "isig". * * The scheme for the placement of each branches' data into the * vector "array()" is as follows: * * array(i+iwave) or array(i+isig) * * $i = \{1, 2, 3, \dots, (2*halfpnts + 1)\}$ where iwave = ndat*(branch - 1) * isig = ndat*(branch + 2) * ndat = (2*halfpnts + 1)*(nrot + 1)* Typically, halfpnts 75 so that the total number of points used to resolve the lineshape structure for each peak is * 2*halfpnts + 1 = 151 pnts. This can be changed if necessary, but * remember that the array() has limited space (unless this * dimension is increased). * * In table format, the array positions are: * * Branch Name branch # iwave isiq * _____ _____ _____ 0 to ndat 3*ndat to 4*ndat Ρ 1

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251
```

```
*
                           2
                                  ndat to 2*ndat
                                                  4*ndat to 5*ndat
               Q
*
                                2*ndat to 3*ndat
               R
                           3
                                                  5*ndat to 6*ndat
*
*
     The fine-structure integration indices are consistent with
     subroutines Splittings and HonlLondon:
*
                                                   P Q R
*
                                                    _____
           Doublet or Triplet; fine = 1 => findex = 1, 4, 7
           Doublet or Triplet; fine = 2 => findex = 2, 5, 8
                      Triplet; fine = 3 \Rightarrow findex = 3, 6, 9
implicit doubleprecision (a-h,o-z)
     dimension array(50000), pop(0:200)
     integer branch, halfpnts
     double precision LineWidth, kBoltz, kBoltzGas
     common/enrgy/Energy(2,0:200), freq(5,0:200), wave(5,0:200)
     common/emissn/PLIF(0:200), QLIF(0:200), RLIF(0:200)
     common/widths/LineWidth(0:200), widthLrz, FWHMlaser, brdSelf,
    &brdBuff
     common/split/wfreq(9,0:200), HLfactor(9,0:200)
     common/prims/zero, half, one, two, three, four, five, eight
     common/fizcon1/pi, c, h, kBoltz, qelec, amu, kBoltzGas, atm
     Compute the number of rotational levels with non-zero
*
     populations. If all levels have non-zero population,
*
     then ncount = nrot+1.
*
     Here we define "Mgammas" as the number of Voigt half-widths
*
     away from line-center. Also, "halfpnts" is the number of
*
     points (wavelength steps) within the space of Mgamma. Note
     that halfpnts cannot exceed half of the allotted memory
     of the vector storage space "array".
     ten = 10.0d0
     Mgammas = 15
     narray = 48000
     halfpnts = INT(((narray/(6*nrot)) - 1)/2) - 1
     ncount = 0
     do J = 0, nrot
        if(pop(J).eq.0)goto 30
        ncount = ncount + 1
30
        continue
     enddo
*
     Note that if all levels have non-zero populations, then
*
     we have ndat=2*halfpnts*(nrot+1). Also, this leads to the
*
     maximum values isig = 2*halfpnts*(nrot+1)*(branch+2) and
*
     iwave = 2*halfpnts*(nrot)*(branch-1).
     ndat = (2*halfpnts + 1)*ncount
```

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252
```

```
do branch = 1, 3
         i = 1
         isig = ndat*(branch + 2)
         iwave = ndat*(branch - 1)
         do J = 0, nrot
*
      Skip transitions with zero population in gd state (even J for
     homonuclear diatomics)
           if(pop(J).eq.0)qoto 300
*
     GHzAng is the GHz/Angstrom conversion function at the appropriate
*
      wavelength.
           GHzAng = 1.0d-1*c/wave(1+branch,J)**2
           gamma = half*LineWidth(J)
           if(branch.eq.1)TotSig = PLIF(J)
           if(branch.eq.2)TotSig = QLIF(J)
           if(branch.eq.3)TotSig = RLIF(J)
           dwave = Mgammas*gamma/(GHzAng*halfpnts)
           wavestart = wave(1+branch,J) - Mgammas*gamma/GHzAng
*
     Here is where the signal lineshape for each J-level is computed
*
     as a function of wavelength. At the end we store the wavelength
*
      in nm. The Whiting Formula is used to approximate the Voigt
      lineshape to within 1-2%.
           do ipnt = 0, 2*halfpnts
             waverun = wavestart + ipnt*dwave
             detune = DABS(1.0d-1*c*(one/waverun-one/wave(1+branch,J)))
             wratio = widthLrz/LineWidth(J)
             dratio = detune/LineWidth(J)
             g1 = (one - wratio)*DEXP(-2.772d0*dratio**2)
             q2 = wratio/(one + four*dratio**2)
             g3 = 1.6d-2*(one - wratio)*wratio
             g4 = DEXP(-4.0d-1*dratio**2.25d0)
             g5 = ten/(ten + dratio**2.25d0)
             quadratic = 1.065d0 + 4.47d-1*wratio + 5.8d-2*wratio**2
             gmax = one/(LineWidth(J)*quadratic)
             gNorm = g1 + g2 + g3*(g4 - g5)
             gVoigt = gmax*gNorm
*
     Now compute the signal as a function of wavelength.
             dSignal = TotSig*gVoigt*c*dwave/(ten*waverun**2)
             array(i+isig) = dSignal
       array(i+iwave) = waverun/ten
       i = i + 1
           enddo
300
           continue
         enddo
      enddo
```

```
return
     end
subroutine SpectraSum(ndat, halfpnts, array, LIF, absorb)
implicit doubleprecision (a-h,o-z)
     dimension array(50000)
     logical LIF, absorb
     integer bin, branch, halfpnts, fullpnts
     common/spec1/fstwave, fnlwave, waveinc, nspec
     common/spec2/SumSpec(25000)
     common/prims/zero, half, one, two, three, four, five, eight
     delmax = fnlwave - fstwave
     fullpnts = 2*halfpnts
     Begin the loop on each branch with the appropriate starting
     position within array(i) as "isig" or "iwave". The accumulated
     integer "npnts" is the number of points per branch.
     do branch = 1, 3
        nBrnchPnts = 0
        isig = ndat*(branch + 2)
        do i = 1, ndat
          nBrnchPnts = nBrnchPnts + 1
          iwave = ndat*(branch - 1)
          delta = array(i+iwave) - fstwave
          if(delta.gt.delMax)goto 100
          if(delta.lt.waveinc)goto 100
          bin = INT(delta/waveinc + 5.0d-2)
     For overlapping fluorescence, intensities add. For overlapping
     absorption, transmissions multiply since EXP(a+b) = EXP(a)*EXP(b)
          if(LIF)then
           SumSpec(bin) = SumSpec(bin) + array(i+isig)
          endif
          if(absorb)then
           SumSpec(bin) = one - (one - SumSpec(bin))*
    Ŷ
                                 (one - array(i+isig))
          endif
          if(i.eq.1)LastBin = bin
*
     Since the wavelength spacing of the summed spectrum is generally
     less than the wavelength spacing of the individual high
* resolution spectra, the loop on i will generally skip over
* several points of the summed spectrum, resulting in several zero
* values of SumSpec(bin). This is corrected by interpolation.
* Note: this interpolation is ignored every (2*halfpnt+1) point,
```

```
* due to change in J. Note that 2*halfpnt+1 = 151 in the original
* code, but doesnt have to be necessarily.
         nmissed = bin - LastBin
         if(nBrnchPnts.eq.(fullpnts+2))then
          nmissed = 0
          nBrnchPnts = 1
          LastBin = bin
         endif
         if(nmissed.eq.0)goto 100
         diff = array(i+isig) - array(i+isig-1)
         do k = 1, nmissed-1
           if(LIF)then
            SumSpec(LastBin+k) = SumSpec(LastBin+k) +
    %
                DFLOAT(k/nmissed)*diff + array(i+isig-1)
           endif
           if(absorb)then
            SumSpec(LastBin+k) = one - (one -
    °
                    SumSpec(LastBin+k))*(one - DFLOAT(k/nmissed)*
    %
                    diff)*(one - array(i+isig-1))
           endif
         enddo
         LastBin = bin
100
         continue
       enddo
     enddo
    return
     end
subroutine SpectraOut
implicit doubleprecision (a-h,o-z)
     character*1 ido
     character*20 filnam
     common/prims/zero, half, one, two, three, four, five, eight
     common/spec1/fstwave, fnlwave, waveinc, nspec
     common/spec2/SumSpec(25000)
    write(6,*)'
                 .
    write(6,*)'-----'
80
    write(6,100)
100
     format(' Enter Spectra Output File Name:')
    write(6,*)'["none" will skip output]'
    write(6,*)'-----'
    read(5,300)filnam
    write(6,*)'
     if(filnam.eq.'none')goto 600
```

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255
```

```
open(unit = 40, file = filnam, err = 80)
*
      Find the maximum signal value for normalization, if
*
      desired.
      SignalMax = -one
      do i = 1, nspec
         SignalMax = MAX(SignalMax,SumSpec(i))
      enddo
*
      Prompt User to determine if Normalization is desired. If
*
      not, then just divide the spectra by unity.
      write(6,*)'
                     1
      write(6,500)
      read(5,550)ido
      write(6,*)'
                      1
      if(ido.eq.'n')SignalMax = one
      wave = fstwave
      do i = 1, nspec
         write(40,320)wave, SumSpec(i)/SignalMax
         wave = wave + waveinc
      enddo
      close(unit = 40)
300
      format(A20)
320
      format(1x, F14.7, 1x, E12.5)
500
      format(' Do you want to Normalize the Spectra? ',$)
550
      format(1A1)
600
      continue
      return
      end
```

APPENDIX D

FORTRAN 77 CODE FOR COMPUTING RO-VIBRONIC TRANSITION LINES FOR THE A-X AND D'-X BANDS

```
program lineposit
* This program computes the RoVibronic band line positions,
*
 given the molecular term values Gv, Bv, and Dv based upon the
    molecular constant data.
*
*
*
    Written by: Robert John Leiweke, M.S.
          Candidate for Ph.D.
*
     Graduate Research Associate
*
     The Ohio State University
     Dept. of Mechanical Engineering
*
     NonEquilibrium Thermodynamics Laboratory
* Last Updated: December 1, 2003
*
    implicit doubleprecision (a-h,o-z)
    dimension Gv(0:50,2), Bv(0:50,2), Dv(0:50,2)
***** Open term-value data files for both molecular states. Note that
***** the lower electronic state should have unit=1 and the upper
***** should have unit=2.
    open(unit=1,file="Xterms.dat")
    open(unit=2,file="Aterms.dat")
    open(unit=9,file="AXlines.out")
***** Define Constants. zero = 0.0d0
    half = 5.0d-1
    one = 1.0d0
```

```
two = 2.0d0
     h = 6.626075540d - 34
     c = 2.99792458d8
     xx = 1.98645d-23
     xmin = 192.8d0
     xmax = 193.8d0
***** Read term-value data. Note that the upper state is defined as
****** index = 2 and the lower state is index = 1.
     read(1,*)nvibLow
     read(2,*)nvibUp
     nvib = MIN0(nvibLow,nvibUp)
     do i = 0, nvibLow - 1
  read(1,*)Gv(i,1), Bv(i,1), Dv(i,1)
     enddo
     do i = 0, nvibUp - 1
  read(2,*)Gv(i,2), Bv(i,2), Dv(i,2)
     enddo
     close(unit=1)
     close(unit=2)
***** Begin computation of RoVibRonic transition wavelengths.
     write(9,*)'AlPi -> XlSigma+ RoVibRonic Transitions'
     write(9,*)'
     write(9,800)xmin
     write(9,801)xmax
     write(9,*)'
     write(9,*)'
     do nvUp = 0, nvibUp - 1
  do nvLow = 0, nvibLow - 1
    delEv = Gv(nvUp,2) - Gv(nvLow,1)
    wavelnth = h*c*1.0d9/(delEv*xx)
     if(wavelnth.ge.xmin.and.wavelnth.le.xmax)then
       write(9,*)'-----'
       write(9,*)'vUp vLow wavelength (nm)'
       write(9,*)'-----'
       write(9,950)nvUp, nvLow, wavelnth
       write(9,*)' Branch(Jlow), Jup, Lambda (nm)'
       do Jup = 0, 30
          aJup = Jup*(Jup + 1)
          aJup2 = aJup**2
          FvUp = Bv(nvUp,2)*aJup - Dv(nvUp,2)*aJup2
          do Jlow = Jup-1, Jup+1
                                258
```

```
if(Jlow.lt.0)goto 10
              aJlow = Jlow^{*}(Jlow + 1)
              aJlow2 = aJlow**2
              Fvlow = Bv(nvLow,1)*aJlow-Dv(nvLow,1)*aJlow2
              delEr = delEv + (FvUp - FvLow)
              wavelnth = h*c*1.0d9/(delEr*xx)
              dJ = Jup - Jlow
              if(dJ.lt.zero)then
                 write(9,960)Jlow, Jup, wavelnth
              elseif(dJ.eq.zero)then
                 write(9,961)Jlow, Jup, waveInth
              elseif(dJ.gt.zero)then
                 write(9,962)Jlow, Jup, wavelnth
              else
              endif
10
              continue
           enddo
           write(9,*)'-----'
        enddo
     write(9,*)'
                   '
     else
     endif
        enddo
     enddo
     close(unit=9)
800
     format(1x, 'lamMin =', 1x, F9.5)
     format(1x, 'lamMax =',1x,F9.5)
801
900
     format(2x, I2, 1x, I2)
950
     format(1x, I2, 3x, I2, 1x, F10.2)
960
     format(6x,'P(',I2,')',4x,I2,1x,F12.5)
961
     format(6x,'Q(',I2,')',4x,I2,1x,F12.5)
962
     format(6x, 'R(', I2, ')', 4x, I2, 1x, F12.5)
      stop
```

end

D.1 MOLECULAR CONSTANT DATA INPUT FILES FOR X, A, AND D' STATES.

D.1.1 INPUT DATA FILE FOR GROUND ELECTRONIC X-STATE.

46		
1081.59	1.9225	.61209E-05
3224.86	1.9050	.61201E-05
5341.65	1.8875	.61196E-05
7432 03	1 8700	61196E-05
9196.06	1 9525	61100E-05
11522 01	1 0250	6120EE 05
12535.01	1.0350	.01203E-05
13545.36	1.81/5	.612158-05
15530.77	1.8000	.61229E-05
17490.12	1.7825	.61246E-05
19423.49	1.7651	.61267E-05
21330.96	1.7476	.61292E-05
23212.59	1.7301	.61320E-05
25068.48	1.7126	.61352E-05
26898.71	1.6951	.61387E-05
28703.35	1.6777	.61426E-05
30482.49	1.6602	.61468E-05
32236.22	1.6427	.61514E-05
33964.61	1.6253	.61564E-05
35667.77	1.6078	.61617E-05
37345.76	1.5903	.61674E-05
38998.67	1.5729	.61735E-05
40626 59	1 5554	61799E-05
42229 61	1 5380	61867F-05
43807 79	1 5206	61938F-05
45261 22	1 5031	62013E-05
45301.22	1 4057	62001E 05
40009.99	1.4057	.02091E-05
48394.16	1.4683	.621/38-05
49873.81	1.4509	.62259E-05
51329.00	1.4334	.62348E-05
52759.80	1.4160	.62441E-05
54166.27	1.3986	.62538E-05
55548.46	1.3812	.62638E-05
56906.43	1.3638	.62741E-05
58240.22	1.3465	.62849E-05
59549.86	1.3291	.62960E-05
60835.38	1.3117	.63074E-05
62096.80	1.2943	.63192E-05
63334.14	1.2770	.63314E-05
64547.40	1.2596	.63439E-05
65736 57	1 2423	63568E-05
66901.64	1,2249	.63701E-05
68042 56	1 2076	63837E-05
69159 20	1 1903	63976-05
70251 Q1	1 1720	64120E-05
71201 01	1 1 5 5 7	
/1320.U1	1 1 2 0 4	.0420/8-05
/2363.8⊥	⊥.⊥384	.644⊥7E-05

D.1.2 INPUT DATA FILE FOR D'-STATE.

8

89759.00	.9672	.93071E-05
90369.60	.9407	.10149E-04
90939.40	.9141	.10992E-04
91468.40	.8875	.11834E-04
91956.60	.8610	.12676E-04
92404.00	.8344	.13518E-04
92810.60	.8079	.14361E-04
93176.40	.7813	.15203E-04

D.1.3 INPUT DATA FILE FOR A-STATE.

23		
65833.45	1.6002	.73425E-05
67314.77	1.5786	.74475E-05
68761.11	1.5571	.75525E-05
70173.13	1.5347	.76575E-05
71550.83	1.5115	.77625E-05
72894.03	1.4876	.78675E-05
74202.63	1.4633	.79725E-05
75476.66	1.4389	.80775E-05
76716.27	1.4146	.81825E-05
77921.64	1.3903	.82875E-05
79092.89	1.3659	.83925E-05
80229.97	1.3413	.84975E-05
81332.58	1.3162	.86025E-05
82400.13	1.2904	.87075E-05
83431.68	1.2639	.88125E-05
84425.90	1.2364	.89175E-05
85380.98	1.2078	.90225E-05
86294.43	1.1779	.91275E-05
87162.74	1.1461	.92325E-05
87980.92	1.1110	.93375E-05
88741.56	1.0703	.94425E-05
89433.70	1.0199	.95475E-05
90041.12	.9535	.96525E-05
90540.01	.8616	.97575E-05

D.2 SAMPLE CODE OUTPUT FOR THE D'-X BAND ABSORPTION LINES WITHIN THE ARGON-FLUORIDE LASER TUNING RANGE

D1Sigma+ -> X1Sigma+ RoVibRonic Transitions

lamMin = 192.00000 lamMax = 193.80000

vUp	vLow	waveleng	gth (nm)
2	20	192.53	Lambda (nm)
Bra	nch(Jlc	w), Jup,	
++++	R(11) P(13)	12 12 12	192.76881 193.06113
	R(12)	13	192.82098
	P(14)	13	193.13684
	R(13)	14	192.87813
	P(15)	14	193.21755
	R(14)	15	192.94028
	P(16)	15	193.30330
	R(15)	16	193.00743
	P(17)	16	193.39409
	R(16)	17	193.07961
	P(18)	17	193.48995
	R(17)	18	193.15683
	P(19)	18	193.59090
	R(18) P(20)	19 19 19	193.23912 193.69696
	R(19)	20	193.32649
	P(21)	20	193.80815
	R(20) P(22)	21 21 21	193.41898 193.92451
	R(21)	22	193.51660
	P(23)	22	194.04606

vUp	vLow	waveleng	gth (nm)
5	21	193.13	Lambda (nm)
Brar	nch(Jlo [.]	w), Jup,	
++++-	+++++++	++++++++	
	P(1)	0	193.14578
	R(0)	1	193.12795
	P(2)	1	193.16276
	R(1)	2	193.12710
	P(3)	2	193.18513
	R(2)	3	193.13164
	P(4)	3	193.21289
	R(3)	4	193.14156
	P(5)	4	193.24604
	R(4)	5	193.15688
	P(6)	5	193.28460
	R(5)	6	193.17758
	P(7)	6	193.32856
	R(6) P(8)	7 7 7	193.20370 193.37795
	R(7) P(9)	8 8 8	193.23522 193.43278
	R(8)	9	193.27217
	P(10)	9	193.49305
	R(9)	10	193.31456
	P(11)	10	193.55879
	R(10)	11	193.36240
	P(12)	11	193.63000
	R(11)	12	193.41571
	P(13)	12	193.70672
	R(12)	13	193.47450
	P(14)	13	193.78896

D.3 SAMPLE CODE OUTPUT FOR THE A-X 4th POSITIVE BAND ABSORPTION

LINES WITHIN THE ARGON-FLUORIDE LASER TUNING RANGE

AlPi -> X1Sigma+ RoVibRonic Transitions

lamMin = 192.80000 lamMax = 193.80000

vUp	vLo	SW	waveleng	gth (nm)
 1 Bra ++++	 7 nch +++-	 (Jlo ++++	193.11 w), Jup, ++++++++	Lambda (nm)
	Q(P(0) 1) 	0	193.10960
	R(0)	1	193.09782
	Q(1)	1	193.11125
	P(2)	1	193.13810
	R(1)	2	193.08770
	Q(2)	2	193.11455
	P(3)	2	193.15483
	R (2)	3	193.07924
	Q (3)	3	193.11950
	P (4)	3	193.17322
	R (3)	4	193.07242
	Q (4)	4	193.12611
	P (5)	4	193.19326
	R (4)	5	193.06726
	Q (5)	5	193.13437
	P (6)	5	193.21496
	R(5)	6	193.06376
	Q(6)	6	193.14429
	P(7)	6	193.23831
	R(6)	7	193.06191
	Q(7)	7	193.15586
	P(8)	7	193.26332
	R(Q(P(7) 8) 9)	8 8 8 8	193.06173 193.16908 193.28999
	 R(8)	9	193.06320

9	193.18397
9	193.31832
10	193.06633
10	193.20052
10	193.34832
11 11 11 11	193.07112 193.21873 193.37998
12	193.07758
12	193.23860
12	193.41331
13	193.08570
13	193.26014
13	193.44831
14	193.09550
14	193.28335
14	193.48499
15	193.10697
15	193.30824
15	193.52334
16	193.12011
16	193.33479
16	193.56337
17	193.13493
17	193.36303
17	193.60508
18	193.15143
18	193.39295
18	193.64848
19	193.16962
19	193.42456
19	193.69358
20	193.18950
20	193.45786
20	193.74036
21 21 21 21	193.21107 193.49285 193.78885
	9 9 9 10 10 10 11 11 11 11 11 12 12 12 12 12 12 12 13 13 13 13 13 13 13 13 13 13 13 13 13