TRACER-BASED PLANAR LASER-INDUCED FLUORESCENCE DIAGNOSTICS: QUANTITATIVE PHOTOPHYSICS AND TIME-RESOLVED IMAGING

A DISSERTATION
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Abstract

Two advances to tracer-based planar laser-induced fluorescence (PLIF) diagnostics are presented in this work. The first improvement is the development of a 3-pentanone fluorescence quantum yield (FQY) database and model for a wide range of conditions in support of quantitative PLIF diagnostics. In addition, this work presents a sensitive, time-resolved tracer-based PLIF diagnostic, accomplished by using a continuous-wave (CW) laser with the high-FQY tracer toluene.

Because of its ease of use and desirable photophysical properties, PLIF diagnostics using 3-pentanone as a tracer are common, particularly for internal combustion engine (ICE) diagnostics. Thus, there is a need for 3-pentanone FQY measurements and modeling over a wide range of temperatures, pressures, and excitation wavelengths. For insight into the collisionless process in the FQY model, measurements were made in 3-pentanone vapor at low-pressures across a range of temperatures using a flowing cell. Laser excitation with 248, 266, 277, 308 nm wavelengths were utilized, and Rayleigh scattering of the laser beam was used to calibrate the optical efficiency of the collection optics and detector. This low-pressure data allows calculation of the 3-pentanone fluorescence rate and non-radiative de-excitation rate in the fluorescence model. The vibrational relaxation cascade parameter for 3-pentanone collisions was also determined.

Measurements of 3-pentanone FQY were also made over a range of temperatures and pressures relevant to diagnostic applications, and, in particular, combined high-temperature and high-pressure conditions applicable to internal combustion engines (ICE). These data were collected in a custom-built optical cell capable of simultaneous
high-pressure and high-temperature conditions. The behavior of the FQY in nitrogen for temperatures up to 745 K and in air up to 570 K was examined for pressures from 1 to 25 bar. These data were used to further optimize the parameters in the FQY model representing collisional processes. The large quantity of data with 308 nm excitation allowed optimization of the nitrogen quenching rate, and data in air were used to optimize the oxygen quenching rate. These data were also used to optimize the vibrational relaxation parameters for nitrogen and oxygen. The model with the updated parameters is consistent with the data collected in the current work, as well as with fluorescence measurements made in optical ICEs up to 1100 K and 28 bar.

Another area of tracer-based PLIF diagnostics development is time-resolved imaging. Because PLIF diagnostics are often performed using pulsed lasers, the time resolution of measurements is limited to the pulse rate of laser. Use of a high-powered visible laser with an off-the-shelf cavity frequency doubler is shown to produce a moderate-power CW beam in the ultraviolet wavelength regime. Application of this CW source to excite toluene, a high-FQY tracer, yields a sensitive, time-resolved tracer-based PLIF diagnostic. Fluctuation detection limits for tracer mole fraction were investigated by applying the diagnostic to an atmospheric temperature and pressure nitrogen jet seeded with 4% toluene, and detection limits of better than 1% of the maximum toluene mole fraction were achieved for detection of fluorescence signal at a point, along a line, and over a plane. The diagnostic was also demonstrated on a turbulent jet for line and planar detection and demonstrated the potential for toluene time-resolved PLIF diagnostics with CW lasers.
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Many people in my life have helped me develop as a student, researcher, and person during my time in graduate school. My advisor, Professor Ronald Hanson, has provided invaluable wisdom and perspective. His insight and guidance have been instrumental in the completion of this work. Throughout my years here, I have also made many friends in the Hanson group, and I thank them for their advice and camaraderie. I am also indebted to my many friends in the community, who have provided fulfillment in other areas of my life. Finally, I would like to thank my family for their support and encouragement.

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Table of Contents

Chapter 1 Introduction

1.1 Background and Motivation .............................. 1
1.2 3-pentanone Photophysics for Quantitative Imaging 3
1.3 Time-resolved Imaging Using Toluene PLIF .......... 4
1.4 Thesis Overview .................................................. 5

Chapter 2 3-pentanone Photophysics Overview

2.1 Background on Quantitative 3-pentanone PLIF 7
2.2 Status of Absorption Cross-Section Data and Modeling 8
2.3 Status of FQY Data and Modeling ........................ 10
2.4 3-pentanone Electronic Transition Photophysics .......... 12
2.5 FQY Model Structure ............................................ 17
2.6 Strategy for Photophysics Measurement and Modeling 21

Chapter 3 Low-pressure 3-pentanone Photophysics

3.1 Low-pressure FQY Background .......................... 23
3.2 Low-pressure Photophysics Theory ....................... 24
3.3 Absorption Cross-section Measurement Methodology 25
3.4 FQY Measurement Using Rayleigh Scattering .......... 26
3.5 Experimental Setup .................................................................................................................. 29
   3.5.1 Optical Cell Design ............................................................................................................ 29
   3.5.2 Laser and Collection Optics Setup .................................................................................... 32
   3.5.3 Experimental Setup Spectral Characterization ................................................................. 34
3.6 Measurement Results .................................................................................................................. 37
   3.6.1 Absorption Cross-Section ............................................................................................... 37
   3.6.2 Fluorescence Spectrum ..................................................................................................... 39
   3.6.3 Absolute FQY ..................................................................................................................... 41
3.7 Model Development .................................................................................................................. 47
   3.7.1 Determination of Fluorescence Rate $k_f$ ........................................................................ 47
   3.7.2 Determination of Non-radiative Rate $k_{nr}$ ..................................................................... 51
   3.7.3 3-pentanone Self-collision Vibrational Relaxation ......................................................... 53
   3.7.4 Model Performance .......................................................................................................... 53
3.8 Low-pressure Photophysics Conclusions ............................................................................... 56

Chapter 4 Measurements and Modeling of 3-pentanone FQY at Extended $T$ & $p$ ........................... 59
4.1 Extended $T$ & $p$ Photophysics Background .......................................................................... 59
4.2 Experimental Setup .................................................................................................................. 61
   4.2.1 High $T$ & $p$ Optical Cell Design .................................................................................... 61
   4.2.2 Laser and Collection Optics Setup .................................................................................... 64
   4.2.3 Experimental Setup Spectral Characterization ................................................................. 65
4.3 Fluorescence Measurement Results ......................................................................................... 66
   4.3.1 Fluorescence Spectrum ..................................................................................................... 67
   4.3.2 FQY Measurements .......................................................................................................... 69
4.4 Model Development .................................................................................................................. 75
   4.4.1 Collisional Quenching and Vibrational Relaxation Background ................................... 75
   4.4.2 Sensitivity Analysis and Optimization Strategy ............................................................... 79
   4.4.3 Optimization of Model Parameters .................................................................................. 82
Appendix A  3-pentanone Model Parameters......................................................... 137

Appendix B  Rayleigh-calibrated FQY Data ......................................................... 139

Appendix C  3-pentanone Extended T & p FQY Data............................................ 145

Appendix D  Uncertainty Analysis......................................................................... 157
  D.1  Absorption Cross-Section.............................................................................. 157
  D.2  Absolute FQY Measurements....................................................................... 159

Appendix E  3-pentanone FQY Model Sample MATLAB Script ......................... 163

Bibliography ............................................................................................................. 167
List of Tables

Table 3.1 Published values of acetone FQY near 312 nm [16, 72-74].................................47
Table 3.2 Fluorescence rate determined in the current work as well as by previous work [31, 40]..................................................................................................................51
Table 3.3 Non-radiative rate expression determined from FQY measurements in the current work. $E$ is in units of cm$^{-1}$. The expression from the Koch model is shown for comparison [31]. .................................................................51
Table 3.4 Vibrational relaxation cascade parameters for 3-pentanone determined from FQY measurements in the current work. $T$ is in units of K. The expression from the Koch model is shown for comparison [31]. ..................53
Table 3.5 Summary of updated model parameters from the current work. $E$ is in units of cm$^{-1}$ and $T$ is in units of K.................................................................54
Table 4.1 Summary of vibrational relaxation energy loss per collision between hydrocarbons and bath gases from previous studies [78-83]...........................77
Table 4.2 Nitrogen quenching rate determined from absolute FQY measurements. $E$ is in units of cm$^{-1}$ and $T$ is in units of K. The expression from Koch is shown for comparison [31].................................................................84
Table 4.3 $q_{O_2}$ determined from absolute FQY measurements. $E$ is in units of cm$^{-1}$. The expression from Koch is shown for comparison [31].................................86
Table 4.4 Vibrational relaxation cascade parameters for 3-pentanone collisions with nitrogen and oxygen determined from FQY measurements in the
current work. The expressions from the Koch model are shown for comparison [31].

Table 4.5 Summary of updated 3-pentanone FQY model parameters for use over a wide range of pressures and temperatures in nitrogen and air. $E$ is in units of cm$^{-1}$, $n_{N_2}$ is in cm$^{-3}$, and $T$ is in units of K.

Table 5.1 Absorption cross-section measurements at 295 K. Work from [96] is shown for comparison.

Table A.1 Lennard-Jones collision parameters used to calculate the collision frequency. Values for 3-pentanone are from [47], and values for nitrogen and oxygen are from [66].

Table A.2 3-pentanone vibrational frequencies used to calculate the thermal vibrational energy. These values are from [47]. 3-pentanone

Table B.1 Absorption cross-section for 3-pentanone.

Table B.2 FQY of 3-pentanone vapor calibrated using Rayleigh scattering.

Table B.3 3-pentanone FQY in nitrogen calibrated using Rayleigh scattering.

Table B.4 3-pentanone FQY in air calibrated using Rayleigh scattering.

Table C.1 3-pentanone FQY in nitrogen.

Table C.2 3-pentanone FQY in air.

Table D.1 Uncertainty analysis for 3-pentanone absorption cross-section.

Table D.2 Uncertainty analysis for toluene absorption cross-section.

Table D.3 Uncertainty analysis for Rayleigh-scattering calibrated FQY measurements with 3-pentanone.

Table D.4 Uncertainty analysis for Rayleigh-scattering calibrated FQY measurements with toluene.

Table D.5 Uncertainty analysis for fluorescence calibrated FQY measurements with 3-pentanone.
List of Figures

Figure 1.1 Generic PLIF diagnostic setup. .................................................................2

Figure 1.2 Process for extracting quantitative measurements from raw fluorescence signal images. The chart illustrates the importance of photophysical databases and models in this process .................................................................2

Figure 2.1 3-pentanone molecular structure. .............................................................7

Figure 2.2 Absorption spectrum for 3-pentanone at various temperatures calculated using the model in [38]. The absorption spectrum shifts to the red and increases in magnitude with temperature ...................................................9

Figure 2.3 Temperature and pressure ranges for which 3-pentanone FQY data is available from previous work [19, 29-31]. Comparison to ICE compression curve shows previous work is inadequate for engine diagnostics .................................................................11

Figure 2.4 Jablonski diagram of 3-pentanone ground and excited electronic states. The figure also shows collisional and collisionless interactions between the electronic states .................................................................13

Figure 2.5 Condensed transition structure used in the photophysics model. The diagram also shows rates and parameters representing various collisional and collisionless processes .................................................................18

Figure 2.6 Sensitivity of 3-pentanone FQY to non-radiative rate $k_{nr}$ at initial vibrational energy $E_1$ for a) 248 nm excitation and b) 308 nm excitation for a range of temperatures and nitrogen pressures calculated with the
Koch model [31]. The partial pressure of 3-pentanone is 20 mbar. The FQY is most sensitive to $k_{nr}$ with no added nitrogen.................................20

Figure 3.1 Schematic of cell seeding system and pressure and temperature measurement sensors. .................................................................................................................29

Figure 3.2 Optical diagnostic setup for the measurement of fluorescence and absorption........................................................................................................................................32

Figure 3.3 Measurements of deuterium lamp and tungsten lamp spectrum for 340 and 440 nm center wavelengths. The spectra show that grating rotation has little effect on measured signal. ..............................................................................................................................35

Figure 3.4 RSR of collection optics, spectrograph, and ICCD measured using deuterium and tungsten calibration lamps. .................................................................................................................36

Figure 3.5 Sample plot of absorbance with number density used to calculate absorption cross-section. This figure shows data for 531 K, 10 to 30 mbar of 3-pentanone, and 308 nm excitation.................................................................................................................................37

Figure 3.6 Measured 3-pentanone absorption cross-section as a function of temperature for 248, 266, 277, and 308 nm. The data are consistent with previous data and a Gaussian fit of the absorption spectrum [38, 39]. Error bars represent 4% uncertainty.................................................................................................................38

Figure 3.7 Sample fluorescence image taken by the ICCD camera, corrected for background. The fluorescence spectrum corrected for RSR is also shown. To determine the total fluorescence signal, the spectrum is integrated from 327 to 563 nm. This image and spectrum is for 30 mbar of 3-pentanone at 298 K with 308 nm excitation.................................................................................................................................39

Figure 3.8 3-pentanone fluorescence spectra at 298 K and 1.3 bar nitrogen show slight narrowing of spectrum with increased excitation wavelength. The current work shows good agreement with previous work [28].................................................40

Figure 3.9 Variation of 3-pentanone fluorescence spectrum for neat vapor and in a nitrogen bath gas for two temperatures. Results are shown for a) 248 and b) 308 nm excitation. .................................................................................................................................40
Figure 3.10 Sample Rayleigh scattering image taken by the ICCD camera, corrected for background. The resulting spectrum from the summation of the central 100 rows and corrected for RSR is also shown. To determine total Rayleigh signal, the spectrum is integrated +/- 14 nm from the peak. This image and spectrum is for 248 nm excitation and 1.5 bar of nitrogen. 

Figure 3.11 Sample plot of Rayleigh signal with nitrogen number density. The slope of the curve used to normalize the signal and calculate FQY. This figure shows data for 295 K and 248 nm excitation.

Figure 3.12 Absolute FQY measurements in 3-pentanone vapor for a) 248 b) 266 c) 277 and d) 308 nm excitation at several temperatures. Error bars represent 6% uncertainty.

Figure 3.13 Absolute FQY variation for 248, 266, and 308 nm excitation in nitrogen or air at 1.3 bar total pressure. Current measurements are made with 3-pentanone partial pressure of 20 mbar. The current work follows similar trends as previous work [28]. Error bars represent 6% uncertainty.

Figure 3.14 Comparison of absolute FQY measurements made at room temperature (295 K). Current work and measurements from [16] made at 20 mbar of 3-pentanone; measurements from [40] made at 13 mbar. Error bars represent uncertainties from their respective studies.

Figure 3.15 Variation of absolute FQY for 3-pentanone vapor for pressures around 10 mbar with initial vibrational energy $E_1$. Previous measurements are shown for comparison [16]. Error bars correspond to 6% uncertainty in FQY measurements.

Figure 3.16 $k_{nr}$ as a function of vibrational energy $E_1$ calculated from $\tau_f$ data [40, 57]. The indicated data point is ignored because the lifetime measured in the study was similar to the time resolution. Error bars represent uncertainties in their respective studies.

Figure 3.17 Fluorescence rate $k_f$ as a function of vibrational energy calculated from FQY measurements and lifetime data from [40, 57]. Comparison is
made to previous calculations of \( k_f \) [31]. Error bars are for the 17% combined uncertainty in the FQY measurements and lifetime data.

Figure 3.18 \( k_{nr} \) as a function of vibrational energy calculated from constant \( k_f \) and FQY measurements. The current work shows good agreement with previous work [40, 57]. Fits to expressions from the current work and previous work are also shown [31].

Figure 3.19 Comparison of absolute FQY data for 10 to 30 mbar of 3-pentanone and a) 248 b) 266 c) 277 and d) 308 nm excitation to current and previous models [31]. Error bars are equivalent to 8%.

Figure 4.1 Photograph of fully assembled optical cell and tubing used to connect to gas feed lines.

Figure 4.2 a) Exploded and b) cutaway views of the viewport for the optical cell. The cutaway view excludes the gland nut.

Figure 4.3 Schematic of cell seeding system and pressure and temperature measurement sensors.

Figure 4.4 Optical diagnostic setup for the measurement of fluorescence and absorption.

Figure 4.5 RSR of collection optics, spectrograph, and ICCD measured using deuterium and tungsten calibration lamps.

Figure 4.6 Sample fluorescence image taken by the ICCD camera, corrected for background. The fluorescence spectrum, taken from the central 100 rows and corrected for RSR, is also shown. To determine the total fluorescence signal, the spectrum is integrated from 318 to 563 nm. This image and spectrum is for 20 mbar of 3-pentanone in 9 bar of nitrogen at 298 K with 248 nm excitation.

Figure 4.7 Variation of 3-pentanone fluorescence spectrum with temperature for 1.3 bar and 25 bar of nitrogen. Spectra are shown for a) 248 and b) 308 nm excitation. For both wavelengths, the fluorescence spectrum widens and shifts to the blue with increasing temperature.
Figure 4.8 Comparison of 3-pentanone fluorescence spectra in nitrogen and air for several temperatures and excitation wavelengths shows that the addition of oxygen has little effect.

Figure 4.9 Relative $S_{LIF}^*$ with temperature in air and nitrogen at 1.3 bar total pressure. Results are shown for the four excitation wavelengths used in this study and show good agreement to measurements from section 3.6. Error bars correspond to 7% uncertainty.

Figure 4.10 Relative $S_{LIF}^*$ with temperature in nitrogen at 1-1.3 bar total pressure. Generally, the current work agrees well with previous work [19, 27-30, 41]. Error bars indicate 7% uncertainty.

Figure 4.11 Variation of absolute FQY with pressure in nitrogen at various temperatures for a) 248 nm b) 266 nm c) 277 nm and d) 308 nm excitation. The data is compared to previous work [30, 31]. Error bars indicate 7% uncertainty.

Figure 4.12 Variation of absolute FQY with pressure in air at various temperatures for a) 248 nm b) 266 nm c) 277 nm and d) 308 nm excitation. The data is compared to previous work [19, 27, 29-31]. Error bars indicate 7% uncertainty.

Figure 4.13 Sensitivity of 3-pentanone FQY to relaxation parameter $\alpha$ for a) 248 nm excitation and b) 308 nm excitation for a range of temperatures and nitrogen pressures. The partial pressure of 3-pentanone is 20 mbar. The sensitivity for 248 nm excitation is significantly higher than for 308 nm excitation.

Figure 4.14 Sensitivity of 3-pentanone FQY to oxygen quenching rate $k_{O2}$ for a) 248 nm excitation and b) 308 nm excitation for a range of temperatures and nitrogen pressures. The partial pressure of 3-pentanone is 20 mbar.

Figure 4.15 3-pentanone absolute FQY for pure vapor and in nitrogen at various pressures as a function of initial vibrational energy $E_1$. Comparison with engine FQY data at high pressures shows little pressure dependence for 308 nm excitation [44]. Quenching is apparent from 7000 to 12500 cm$^{-1}$.
Addition of an energy-dependent nitrogen quenching rate $k_{N2}$ improves model performance. .........................................................................................................................83

Figure 4.16 Variation of $qO_2$ with vibrational energy. Comparison to previous work is shown [31]...........................................................................................................................................85

Figure 4.17 3-pentanone FQY in nitrogen at about 745 K indicates that $\alpha$ has vibrational energy dependence. The solid lines are for the model including vibrational energy dependence for $\alpha$; the dashed lines are temperature dependence only........................................87

Figure 4.18 Comparison of 3-pentanone FQY measurements in nitrogen for a) 248 b) 266 c) 277 and d) 308 nm excitation to FQY models from current work and [31]. The model from the current work shows good agreement with the cell measurements. Error bars equivalent to 10%........................................90

Figure 4.19 Comparison of 3-pentanone FQY measurements in air for a) 248 b) 266 c) 277 and d) 308 nm excitation to FQY model from current work and [31]. The model from the current work shows good agreement with the cell measurements. Error bars equivalent to 10%...........................................91

Figure 4.20 Comparison of 3-pentanone FQY measurements from other workers in air to FQY models show the current model has improved performance over the Koch model at higher temperatures for 248 nm excitation [19, 29, 31]. Error bars equivalent to 10%........................................................92

Figure 4.21 Comparison of 3-pentanone FQY measurements from other workers in oxygen to FQY models show good agreement [19, 31]. Error bars equivalent to 10%.................................................................92

Figure 4.22 Comparison of 3-pentanone $S_{LIF}$ in air for 248 nm excitation from optical ICE [42] to FQY model from current work and [31] show good agreement except for lower pressures, where toluene fluorescence signal interference may be occurring. Error bars equivalent to 15%...........................................93

Figure 4.23 Comparison of 3-pentanone $S_{LIF}$ for 277 and 308 excitation from an optical ICE [47] to values predicted by the FQY models show the current
model improves the predictive performance over the Koch model [31]. The bath gas is a) nitrogen and b) air. Error bars equivalent to 10%.

Figure 4.24 Comparison of 3-pentanone $S_{LIF}^*$ for 277 and 308 excitation from an optical ICE [44] to values predicted by the FQY model from the current work show excellent agreement up to 28 bar and 1100 K. The bath gas is a) nitrogen and b) air. Comparison to the previous model is also shown [31]. Error bars equivalent to 10%.

Figure 5.1 Schematic of optical cell and static gas feed system.

Figure 5.2 Schematic of laser and fluorescence collection optics.

Figure 5.3 RSR of the collection optics, spectrograph, and ICCD camera measured using argon arc calibration lamp.

Figure 5.4 Sample fluorescence image and resulting spectrum determined from the central 250 row and corrected for RSR. Total signal is determined by integrating the spectrum from 269 to 340 nm. This image is for 20 mbar of pure toluene at 295 K and for 248 nm excitation.

Figure 5.5 Fluorescence spectrum normalized for the peak value at several toluene and nitrogen partial pressure. Results are shown for a) 248 and b) 266 nm excitation. The results are compared to previous work [92].

Figure 5.6 Absolute FQY for 248 and 266 nm excitation for pure toluene at 295 K. The error bars indicate the 8% uncertainty in the current work. Comparison is shown to previous measurements [37].

Figure 5.7 FQY with added nitrogen pressure for various excitation and wavelengths and toluene partial pressures. The error bars indicate the 8% uncertainty. The current work is consistent with previous work [99].

Figure 5.8 Setup for measurement of fluctuation detection limits with single-point LIF and line LIF imaging.

Figure 5.9 Variation of fluctuation detection limit with laser power for a jet seeded with 4% toluene in N₂ at 1 atm for single-point measurement of a 1 mm³ region. The detector has a bandwidth of 8.5 kHz.
Figure 5.10 Sample line LIF image of jet used in detection limit measurements. Image was taken with 351 mW of laser power and 104 μs exposure time, and corrected for background and spatial variations in detector response. Data from the central region of the jet is used in analysis.

Figure 5.11 Line LIF imaging detection limits for each pixel as a function of laser power. Detection limits shown in a) for 4, 14, 54 and 104 μs exposure times (250, 71.4, 18.5 and 9.6 kHz frame rates) where each pixel images a region 0.04 x 0.2 x 0.4 mm; in b) the exposure time is 54 μs and detection limits are shown for two spatial resolutions, 0.04 x 0.2 x 0.4 mm/pixel and 0.3 x 0.2 x 0.4 mm/pixel.

Figure 5.12 Signal time-histories at different radial distances from the centerline of a turbulent jet, Re = 9800, 8 mm (4.7 D) downstream of jet exit. Images were taken with a laser power of 400 mW, a detector exposure time of 54 μs, and pixel resolution of 0.04 x 0.2 x 0.4 mm.

Figure 5.13 Time-averaged radial line image for a turbulent jet 8 mm (4.7 D) and 16 mm (9.5 D) downstream of the jet exit, Re = 9800. The average is taken across 196 single-shot images. The mean profile is fit with a Gaussian. Each line image is 1 x 125 pixels in size with a pixel resolution of 0.04 x 0.2 x 0.4 mm. Images were taken with 400 mW of laser power and a 54 μs exposure time (18.5 kHz frame rate) in a room-temperature, isobaric nitrogen seeded with 4% mole fraction of toluene.

Figure 5.14 RMS variation of signal 8 and 16.2 mm downstream the jet exit of a turbulent jet, Re = 9800, plotted against the radial coordinate r.

Figure 5.15 Setup for measurement of PLIF fluctuation detection limits.

Figure 5.16 Sample single-shot image used to calculate detection limits, corrected for background, laser sheet energy profile, and absorption of the laser sheet by toluene. This image is taken with a 100 μs exposure time and 235 mW of laser energy.

Figure 5.17 PLIF imaging detection limits for each pixel as a function of laser power. Detection limits shown in a) for 1, 10, 50 and 100 μs exposure
times, where each pixel images a region 0.05 x 0.05 x 0.4 mm; in b) the exposure time is 100 μs and detection limits are shown for two spatial resolutions, 0.05 x 0.05 x 0.4 mm/pixel and 0.4 x 0.4 x 0.4 mm/pixel.............126

Figure 5.18 2-D PLIF imaging of relative toluene concentration in a turbulent jet (Re = 10700) using PI-MAX camera. 203 mW of laser power was used. Comparison of single-shot image to mean of 50 single-shot images is shown. In a), images are 400 x 150 pixels in size with 0.054 x 0.054 x 0.4 mm/pixel resolution and are taken with 10 μs exposure time. In b), images are 100 x 38 pixels in size with 0.2 x 0.2 x 0.4 mm/pixel resolution and are taken with 1 μs exposure time. .................................................................128

Figure 5.19 Time-resolved 2-D PLIF imaging of relative toluene concentration in a turbulent jet (Re = 10700) using PI-MAX2 camera. 203 mW of laser power was used. Two sequential images and the difference between them are shown. In a), images are 400 x 150 pixels in size with 0.054 x 0.054 x 0.4 mm/pixel resolution and are taken with 50 μs exposure time (18.9 kHz frame rate). In b), images are 100 x 38 pixels in size with 0.2 x 0.2 x 0.4 mm/pixel resolution and are taken with 10 μs exposure time (76.9 kHz frame rate). ...........................................................................................................129
Chapter 1  Introduction

1.1 Background and Motivation

Tracer-based planar laser induced fluorescence (PLIF) imaging has emerged as a powerful diagnostic for measurements of flow field parameters and has significant utility in many fundamental combustion and fluid physics studies. PLIF imaging is a species-specific and non-invasive optical diagnostic that provides both spatial and temporal resolution of flow field parameters determined from the fluorescence signal of a component species, here assumed to be a tracer species. Many different forms of the diagnostic have been utilized to make measurements in a wide range of applications and have successfully measured flow field parameters such as temperature [1-6], pressure [3, 4, 7], velocity [7], and species concentration [8-11]. These applications have utilized a variety of tracers, such as NO [5], I₂ [2], OH [1, 8, 9], CO₂ [4, 12, 13], and large hydrocarbons [14]. The tracer-based PLIF diagnostic has applications in many fields, including chemistry, biology, engineering, medicine, and physics.

A generic PLIF diagnostic is depicted in Figure 1.1. A laser sheet is passed through the flow field of interest that contains the fluorescing tracer species, and the wavelength of the laser sheet is chosen to correspond with a resonant transition of the species. The tracer molecules absorb photons from the laser sheet and release fluorescence photons, which are collected by a camera or other suitable detector. Post-processing of the collected fluorescence images using fluorescence theory and knowledge of the relevant photophysics yields quantitative information on the flow field.
Figure 1.1 Generic PLIF diagnostic setup.

Figure 1.2 Process for extracting quantitative measurements from raw fluorescence signal images. The chart illustrates the importance of photophysical databases and models in this process.
While PLIF is an established diagnostic, work continues to further develop and refine the diagnostic. As the diagnostic is applied to conditions departing from ambient temperature and pressure, there exists a need to further understand the photophysics of fluorescence in those regimes. In addition, the integration of developments in laser technology can extend the capabilities of tracer-based PLIF to different applications. This work examines both aspects of the continuing development of PLIF.

1.2 3-pentanone Photophysics for Quantitative Imaging

The use of ketones as fluorescent tracers in PLIF diagnostics was initiated by previous work that identified acetone as a potential tracer species for PLIF diagnostics because of its desirable properties [15]. Acetone is a readily available solvent that is relatively inexpensive and easy to handle safely. Photophysically, it has a broadband ultraviolet (UV) absorption spectrum that can be accessed by commercially available pulsed lasers and a broadband fluorescence spectrum in the near UV and visible that can be collected using commercially available scientific-grade charge-coupled-device (CCD) cameras. Fundamental photophysics studies have been performed with acetone [16-19], and it has remained a popular tracer for PLIF diagnostics [6, 10, 11, 20-22].

Since the introduction of acetone, 3-pentanone has also been identified as a tracer species possessing the same desirable traits as acetone, and several factors motivate the use of 3-pentanone over acetone. First, 3-pentanone typically has a higher fluorescence quantum yield (FQY) than acetone, improving the signal-to-noise ratio (SNR) of the diagnostic [16]. More importantly, for internal combustion engine (ICE) studies, the PLIF diagnostic is often used to track the dispersal of fuel, usually iso-octane, making it necessary for the tracer to mimic the fuel. While it should be noted that having a similar boiling point does not guarantee that 3-pentanone will track iso-octane in all conditions [23], the similarity of the boiling points of 3-pentanone (375.15 K) and iso-octane (372.35 K) does allow it to track fuel dispersal better than acetone, the boiling point of which is significantly lower (329.25 K) [14]. As a result of these properties, 3-pentanone is a common tracer in ICE studies [14, 24-26].
As with all PLIF diagnostic applications, the accuracy of quantitative measurements in ICE studies utilizing 3-pentanone PLIF depends on knowledge of 3-pentanone photophysics. Figure 1.2 illustrates the process of quantitatively measuring parameters like temperature from raw images. Central to this process are models of FQY and absorption cross-section, as well as the experimental measurements of these quantities on which these models are optimized and validated. For ICE studies, there is a need for photophysics information at combined high-pressure and high-temperature conditions, corresponding to the pre-ignition top-dead-center condition of the engine. Previous studies of 3-pentanone photophysics have either covered limited ranges of temperature and pressure [19, 27, 28], or have studied a single wavelength across a larger pressure and temperature regime [29, 30].

To extend knowledge of 3-pentanone photophysics, measurements of FQY were performed in this work across a wide range of temperature, pressure, and bath gas compositions for several laser excitation wavelengths. Utilizing this data, significant improvements were made to an existing semi-empirical photophysical model for FQY [31], and the model has excellent agreement with measurements of fluorescence signal in ICE studies. Thus, this work extends the range of temperatures and pressures for which 3-pentanone PLIF can confidently yield quantitative measurements of flow field parameters.

1.3 Time-resolved Imaging Using Toluene PLIF

Tracer-based PLIF diagnostics have traditionally utilized pulsed laser systems for their high photon fluence to maximize the generated fluorescence signal. The disadvantage of using a pulsed laser is that the temporal resolution of the diagnostic is limited, in part, by the pulse rate of the laser. Most commercially available pulsed UV lasers have repetition rates between 10-1000 Hz, significantly slower than mixing and combustion phenomena occurring on timescales of microseconds. While some recent studies have employed ultrafast pulsed lasers and acquired time-resolved PLIF images [32-34], the frame rate of the diagnostic is fixed by the pulse rate of the laser system,
which may not be the optimum frame rate for the flow field of interest. Moreover, the complex laser systems involved in some of these studies allow for only a limited number of images to be taken. Thus, pulsed laser sources remain a limitation on the temporal resolution of fluorescence diagnostics.

Use of continuous-wave (CW) excitation would alleviate the temporal resolution limitations imposed by pulsed lasers, but the low output of CW lasers in the UV has limited their use in tracer-based PLIF diagnostics. Some previous fluorescence studies in gaseous flows have been performed using high-powered visible CW lasers, but the diagnostics are limited by the low FQY of the tracer [7, 35, 36]. Developments in frequency-doubling techniques have allowed for the generation of moderate levels of CW UV light using these high-powered visible lasers, allowing access to many of the broadband tracers characterized for gaseous flow [14]. Pairing this CW excitation with toluene, an aromatic tracer with high FQY that absorbs and fluoresces in the UV, allows for the development of a highly sensitive time-resolved tracer-based PLIF diagnostic [16, 37].

This thesis develops a time-resolved toluene fluorescence diagnostic using CW laser excitation. Measurements of toluene photophysics were performed at room temperature to aid quantitative imaging. The sensitivity of the diagnostic was investigated by measuring the detection limits for single-point collection, line imaging, and planar imaging of the fluorescence signal acquired using different detector systems. The diagnostic was applied to a turbulent jet to demonstrate its ability to perform time-resolved imaging and its potential to provide insight into high-speed flows. Portions of this imaging work has been previously published in a peer-reviewed journal [38], with the author of this thesis being the first author of the publication, and the primary faculty advisor for this thesis being the second author of the publication.

1.4 Thesis Overview

The goal of this thesis is to present improvements to quantitative tracer-based PLIF diagnostics. The creation of a database of 3-pentanone FQY measurements and the
optimization of an FQY model for use across a wide range of conditions allows for greater accuracy in quantitative measurements using 3-pentanone as a tracer. This thesis also presents a technique for sensitive, time-resolved measurements of PLIF by combining CW UV lasers with toluene, a high-FQY tracer. Chapter 2 provides background information on the photochemistry behind 3-pentanone fluorescence and the structure of the fluorescence model. Chapter 3 describes measurements of 3-pentanone absolute FQY at low pressures in pure vapor, as well as diluted in nitrogen and air bath gases, and the measurements were used to optimize collisionless rates in the fluorescence model. Chapter 4 describes measurements of 3-pentanone absolute FQY in nitrogen and air across a wide range of temperatures and pressures. These measurements were used to optimize the collisional rates in the FQY model, resulting in a comprehensive model able to predict fluorescence signal at ICE conditions. Chapter 5 presents room-temperature measurements of toluene photophysics and details the development of a high-speed PLIF imaging technique utilizing CW lasers. Finally, Chapter 6 provides conclusions and recommendations for future work.
Chapter 2  3-pentanone Photophysics
Overview

2.1 Background on Quantitative 3-pentanone PLIF

3-pentanone is an aliphatic ketone molecule with the structure shown in Figure 2.1. The absorption and fluorescence features of 3-pentanone occur in the near-UV region of the electromagnetic spectrum. 3-pentanone has a smooth, non-featured absorption spectrum that spans approximately 220 to 350 nm, with peak absorption occurring around 280 nm at 300 K. The fluorescence spectrum spans approximately 320 to 600 nm, with peak fluorescence occurring at around 410 nm.

![3-pentanone molecular structure](image)

Several idealizations allow condensation of the photophysics into a simple equation describing the fluorescence signal. 3-pentanone fluorescence diagnostics often use pulsed laser sources with pulsewidths on the order of tens of nanoseconds for excitation, and the resulting fluorescence is collected over a significantly longer period. This fact, combined with the relatively weak broadband absorption feature, implies that
the ground state population distribution does not significantly change, and the fluorescence signal $S_f$ in number of photons can be described using the weak excitation fluorescence equation:

$$S_f = \frac{E}{\hbar c} n(p, T, X_{3p}) L \sigma(\lambda, T) \phi(\lambda, p, T, X_{3p}, X_M) \frac{\Omega}{4\pi} \eta$$  \hspace{1cm} (2.1)$$

$E$ is the incident laser energy fluence [$J/cm^2$], $\hbar$ is Planck’s constant [$J s$], $c$ is the speed of light in vacuum [cm/s], $\lambda$ is the laser wavelength [nm], $n$ is the number density of fluorescing tracer [cm$^{-3}$], $L$ is the length of the illuminated volume [cm], $\Omega$ is the detector collection angle [ster], and $\eta$ is the detector collection efficiency. The absorption cross-section $\sigma [cm^2]$ and the FQY $\phi$ are photophysical parameters that describe the propensity for a molecular to absorb and emit photons, respectively, when excited by a laser of wavelength $\lambda$. As the equation shows, the dependence of the fluorescence signal on the flow field properties of temperature $T$ [K], pressure $p$ [bar], 3-pentanone mole fraction $X_{3p}$, and mole fraction of other bath gases $X_M$, is defined by the number density and photophysical parameters. Number density, for most PLIF diagnostic applications, can be easily modeled using the ideal gas equation:

$$n = \frac{X_{3p} p}{k_b T}$$  \hspace{1cm} (2.2)$$

where $p$ is the pressure, $X_{3p}$ is the 3-pentanone mole fraction, $k_b$ is the Boltzmann constant, and $T$ is temperature. In this thesis, $n$ is considered in units of cm$^{-3}$. Thus, the ability to utilize 3-pentanone PLIF on a quantitative basis depends primarily on knowledge of the FQY and absorption cross-section based on measurements, and the ability to predict these parameters via a photophysical model.

### 2.2 Status of Absorption Cross-Section Data and Modeling

3-pentanone is a broadband absorber, typical of ketones, so the absorption spectrum is the superposition of many individual features. As a result, the absorption cross-section is unaffected by pressure broadening, but remains a function of temperature and excitation wavelength. The temperature dependence of the 3-pentanone absorption spectrum has been well studied in recent years. The absorption spectrum for 3-pentanone
was studied for temperatures between 300 and 1100 K in a shock tube using a deuterium lamp [39]. Absorption cross-section measurements were also made using laser excitation in a heated optical absorption cell for 248, 266, and 308 nm laser sources at temperatures between 300 and 900 K [28]. Prior to these studies, only room temperature absorption cross-section measurements were available [40]. These studies show that, at room temperature, the peak absorption occurs around 280 nm with a cross-section of about $6 \times 10^{-19}$ cm$^2$, and the peak absorption increases and shifts to the red with increasing temperature.

Figure 2.2 Absorption spectrum for 3-pentanone at various temperatures calculated using the model in [39]. The absorption spectrum shifts to the red and increases in magnitude with temperature.

The study performed in the shock tube also found that the absorption feature of 3-pentanone is well-fit by a Gaussian expression. The absorption cross-section at a given temperature and wavelength can be modeled by

$$\sigma(\lambda, T) = A(T) \exp\left( -\frac{(\lambda - \lambda_c(T))^2}{w(T)} \right)$$  

(2.3)
where $A$ is the amplitude in $[cm^2]$, $\lambda_c$ is the center wavelength $[nm]$, and $w$ is the width of the absorption feature $[nm]$. These parameters are temperature dependent and are expressed by

$$A(T) = 4.77 \times 10^{-20} + 4.87 \times 10^{-23} T$$  \hspace{1cm} (2.4)
$$\lambda(T) = 273.7 + 0.0186T$$ \hspace{1cm} (2.5)
$$w(T) = 25.1 + 0.0101T$$ \hspace{1cm} (2.6)

Figure 2.2 show the absorption cross-section, as calculated using equation (2.3) for temperatures from 300 K to 1100 K, illustrating the increase in the peak magnitude of the absorption feature and a red-shift of the peak with increasing temperature.

The increase in the magnitude of the absorption feature with temperature is the result of better overlap between excited vibrational modes in the ground state singlet with the excited state singlet, resulting in more favorable Frank-Condon factors. Thus, the increase in vibrational energy with higher temperature results in a stronger absorption transition. Moreover, the increased vibrational energy in the ground state at higher temperatures reduces the photon energy necessary to excite the molecule into the excited singlet, resulting in a red-shift of the absorption spectrum.

In this study, absorption cross-section measurements were made as part of the determination of absolute FQY. The current work is consistent with the previous literature and the Gaussian fit of the absorption spectrum.

### 2.3 Status of FQY Data and Modeling

The dependencies of FQY are more complex than for absorption cross-section. In addition to temperature and excitation wavelength dependence, there is also dependence on pressure and gas composition. Thus, FQY measurements and modeling are necessary across a range of excitation wavelengths, pressures, and temperatures for different bath gases in order to quantitatively measure flow field properties using 3-pentanone PLIF diagnostics over a wide range of conditions.
There have been several studies utilizing optical cells to determine the temperature and pressure dependence of 3-pentanone FQY. Early studies examined room-temperature behavior at pressures below the vapor pressure of 3-pentanone over a range of excitation wavelengths [41]. As the utility of 3-pentanone PLIF was realized for ICEs, studies focused on the variation of FQY with temperature and pressure in various bath gases. However, only a limited range of pressures and temperatures was covered, as shown in Figure 2.3. Many of the optical cell studies consider a narrow band of temperature; most studies do not exceed temperatures of 600 K [19, 27, 30, 42]. Studies that consider a wider range of temperatures up to 900 K have either considered only a limited pressure range [28], or a limited number of excitation wavelengths [29]. Fluorescence measurements were also made in ICEs with optical access, but early studies did not exceed 600 K [24, 43, 44]. More recent studies in optical ICEs have explored a wider range of temperatures [25, 45]. However, because ICEs achieve high temperature...
conditions via compression of the intake charge, FQY measurements at high-temperature and low-pressure conditions cannot be measured using this experimental setup. The current state of FQY measurements limits the ability to apply the diagnostic on ICEs with a compression ratio greater than 8.5:1, which is lower than ratios employed in current ICE research. In order to extend 3-pentanone PLIF into a diagnostic that can be applied over a wide range of temperature and pressure conditions, it is necessary to develop a database of absolute FQY values across a broad range of pressures, temperatures, and excitation wavelengths.

Koch introduced the first semi-empirical step-ladder photophysical model predicting 3-pentanone FQY [31]. The multistep decay structure is based on a previous acetone FQY model [17], and similar models have also been used to predict the pressure dependence of fluorescence spectra [46] and photochemical activation [47]. The Koch model was optimized using FQY measurements for temperatures from 300-900 K in nitrogen bath gas at 1 bar of pressure, and for pressures from 1-6 bar in nitrogen, oxygen, and air at 300 K. Only a limited set of high-pressure, high-temperature data was considered [31], and the Koch model has been found to be inadequate at ICE conditions [48]. Updates to the model have been performed subsequently by other FQY studies in optical cells [29, 30] and optical engines [25]. The availability of a database of FQY data at a wide range of conditions relevant to diagnostic applications would be beneficial to model development, but an examination of 3-pentanone photophysical transition shows that measurements at low pressures would allow for greater insight into the model.

2.4 3-pentanone Electronic Transition Photophysics

Development of the photophysical model requires an examination of the electronic structure of 3-pentanone. Absorption and fluorescence in the near-UV originates from the \( (n, \pi^*) \) rovibronic transition that is characteristic of aliphatic ketones. Upon absorption of a photon, an electron is promoted from the bonding orbital \((n)\) to the anti-bonding orbital \((\pi^*)\) of the \(\text{C}=\text{O}\) double bond. The transition is symmetry forbidden, but a non-zero transition dipole moment is produced via vibronic coupling with Rydberg
transitions in the deep-UV, allowing it to occur [49]. However, the \((n, \pi^*)\) transition is an order of magnitude weaker than the allowed \((\pi, \pi^*)\) transition typical of aromatic molecule like toluene [49].

Figure 2.4 Jablonski diagram of 3-pentanone ground and excited electronic states. The figure also shows collisional and collisionless interactions between the electronic states.

Previous investigations into the general photochemistry of the \((n, \pi^*)\) system of aliphatic ketones [50-54] provide a starting point for understanding 3-pentanone fluorescence. The transition is depicted through a Jablonski diagram in Figure 2.4. The unexcited ground state \((S_0)\) and the first excited state \((S_1)\) are singlet electronic states, where the electrons are paired and their spins opposite. Fluorescence in the near-UV originates from \(S_1\). These two singlet states interact with the first excited triplet state \((T_1)\)
[51], which differs from the singlet in that the electrons have identical spins. Finally, for ketones, the $S_2$ transition is derived from the $(n_0, 3s)$ Rydberg transition [55]. As shown in Figure 2.4, the zero-point energy of $S_1$ is 30770 cm$^{-1}$ higher than the zero-point of $S_0$ [41], the $T_1$ zero-point energy is 25800 cm$^{-1}$ higher [49], and the $S_2$ zero-point energy is 51300 cm$^{-1}$ higher [56]. The ionization potential of 3-pentanone is 76040 cm$^{-1}$ [56]. Figure 2.4 also shows the interactions between the ground-state singlet, the excited singlet, and the excited triplet states.

The processes shown in Figure 2.4 define the photophysical mechanism through which fluorescence occurs. In the following equations, $P^0$ represents a 3-pentanone molecule in $S_0$, $P^1$ represents a molecule in $S_1$, and $P^T$ represents a molecule in $T_1$. The 3-pentanone molecule is first excited from the ground state into the excited singlet state via the absorption of a photon with frequency $\nu_{\text{exc}}$ corresponding to a resonant frequency. This process is represented in equation (2.7).

$$P^0 + h\nu_{\text{exc}} \xrightarrow{\text{Absorption}} P^1$$  \hspace{1cm} (2.7)

Following absorption, the molecule can undergo a number of different processes that transfer energy within and out of the excited vibronic energy state $S_1$, as shown in Figure 2.4. These processes can be divided into two categories: collisionless processes that do not require collisions between molecules to occur, and collisional processes that occur as a result of molecular collisions. Collisionless processes considered in this thesis are fluorescence (producing signal), internal conversion (IC), and intersystem crossing (ISC), depicted with the blue arrows in Figure 2.4. As with previous ketone FQY modeling work by Thurber and Koch, in this thesis IC and ISC are will be represented in modeling using a single collisionless non-radiative rate [17, 31]. Collisional processes include vibrational relaxation and collisional quenching, which are depicted with the green arrows in Figure 2.4. Vibrational relaxation only reduces the vibrational energy of the excited molecule, but does not remove the molecule from $S_1$. In collisional quenching, collisions transfer excited molecules out of $S_1$, and previous investigations of oxygen quenching with ketones show that the predominant transfer is to the triplet state $T_1$ [57]. Competition between fluorescence and the other processes that do not involve emission.
give rise to the temperature, pressure, and wavelength dependencies of the FQY, and these processes discussed in further detail in the remainder of this section.

\[ P^1 \xrightarrow{k_f} P^0 + h\nu_f \]  

(2.8)

The molecule can fluoresce by emitting a photon with frequency \( \nu_f \), returning the molecule to its ground state, shown in equation (2.8). Because fluorescence competes with other processes, \( \nu_f \) typically is not equal to the absorption photon frequency \( \nu_{exc} \). For ketones, fluorescence typically occurs at a rate \( k_f \) of \( 10^5 - 10^6 \) s\(^{-1} \) [50].

\[ P^1 \xrightarrow{k_{IC}} P^0 \]  

(2.9)

\[ P^1 \xrightarrow{k_{ISC}} P^T \]  

(2.10)

The collisionless processes of IC and ISC are shown in equations (2.9) and (2.10), respectively. As the equations show, the processes occur without molecular collisions and are the result of intramolecular interactions between the \( S_0 \), \( S_1 \), and \( T_1 \). ISC is generally considered more important than IC in ketones. In ISC, the molecule transitions from the excited singlet (\( S_1 \)) into the triplet state (\( T_1 \)). Generally, this process occurs because of spin-orbit coupling between the two states. For (\( n, \pi^* \)) systems, ISC involves “forbidden” spin orbit mechanisms where an electron must reverse its spin, but the relatively small singlet and triplet zero-point energy difference, along with favorable Franck-Condon factors, allows ISC to occur relatively efficiently. The rate of ISC \( k_{ISC} \) is typically about \( 10^8 \) to \( 10^9 \) s\(^{-1} \) [49], which is significantly higher than the fluorescence rate \( k_f \). Previous work has found that \( k_{ISC} \) increases with increasing vibrational energy in the excited singlet [31, 50, 58].

In IC, the molecule transitions from the excited singlet to an upper vibrational energy level of the ground state singlet. For the (\( n, \pi^* \)) system, the Franck-Condon factors for this transition are not favorable; the IC rate \( k_{IC} \) for an (\( n, \pi^* \)) system molecule where the ground state and excited zero-point energies differ by about 100 kcal/mol (35000 cm\(^{-1} \)) is \( 10^5 \) s\(^{-1} \), several orders of magnitude lower than ISC [49], showing that ISC is the dominant collisionless process for ketones. However, calculations examining the photochemistry as a quasi-diatomic C=O double-bonded molecule indicate that IC becomes a significant process at higher vibrational energies [59]. Nonetheless, due to the dominance of ISC, previous ketone FQY modeling has combined the rates \( k_{IC} \) and \( k_{ISC} \)
into a single collisionless non-radiative process rate $k_{nr}$ [17, 31], and the model presented in this work will use $k_{nr}$ to represent the effects of IC and ISC.

Due to the high rate of ISC compared to fluorescence and IC, the fate of most 3-pentanone molecules excited into $S_1$ is to enter $T_1$, so it is necessary to examine the processes transferring energy from the $T_1$ state. Molecules within $T_1$ may undergo laser-induced photolysis, which has been the subject of previous 3-pentanone photophysical studies [52, 54]. Phosphorescence also originates from the $T_1$ state, in which the molecule emits a photon and returns to the ground state $S_0$. Previous work has found the phosphorescence spectrum is centered around 447 nm with a half-width of about 118 nm and has a lifetime of 18 ms [60]. Phosphorescence signal can potentially contaminate fluorescence measurement, but because the observed fluorescence lifetime is on the order of nanoseconds [41, 58], the phosphorescence signal can be separated from fluorescence signal in measurements using microsecond detector exposure times.

$$P^1(v''') + M \xrightarrow{k_{vb}} P^1(v') + M$$ (2.11)

In addition to the collisionless processes, collisional processes also compete with fluorescence, and hence this thesis includes the effects of vibrational relaxation and collisional quenching. In vibrational relaxation, shown in equation (2.11), collisions between the excited 3-pentanone molecule and bath gas molecules cause the 3-pentanone molecule to transition to a lower vibrational energy level in the excited singlet. The rate of vibrational relaxation, $k_{vib}$, is often modeled as the Lennard-Jones collision frequency due to the effectiveness of collisions in transferring vibrational energy [61]. Vibrational relaxation is significant because as the excited 3-pentanone loses vibrational energy, it is less likely to experience ISC or IC, and thus, is more likely to fluoresce, increasing FQY.

$$P^1 + O_2^T \xrightarrow{k_{o2}} P^S + O_2^S$$ (2.12)
$$P^1 + M \xrightarrow{k_{o2}} P^T + M$$ (2.13)

The other collisional transfer process considered is collisional quenching. Collisional quenching refers to the situation in which molecular collisions between the bath gas molecules and excited molecules reduce the fluorescence signal via transfers of molecules out of $S_1$ without the emission of a photon. Previous investigations of collisional quenching with oxygen collisions showed that interactions between the
excited singlet of the ketone molecule and the ground state triplet of oxygen resulted in transfers from $S_1$ to $T_1$, as shown in equation (2.12) [57]. 3-pentanone collisional quenching with molecules besides oxygen is shown in equation (2.13). As with collisional quenching by oxygen, the predominant transfer due to collisional quenching is considered to be from the $S_1$ to the $T_1$ state, although transitions to $S_0$ have been considered in other excited molecules [57, 62, 63]. For some collider species, the collisional quenching is theorized to occur through the creation of a collision complex that allows for more efficient spin-orbit coupling within the excited molecule [64, 65].

2.5 FQY Model Structure

The transition can be modeled using the master equation, which results in a set of coupled differential equations. Solver routines, such as Multiwell [61], can be used to numerically solve these equations. However, the purpose of this model is to facilitate image processing for PLIF diagnostics, so low computational overhead, ease of integration into existing image processing codes, and ease of adaptation to various applications are important considerations. A simple conceptual model addresses these considerations, and for this reason, previous work has utilized a semi-empirical step-ladder decay model for PLIF image processing using ketone tracers [17, 31, 48].

The step-ladder model numerically represents a condensed version of the $(n, \pi^*)$ transition as shown in Figure 2.5. To simplify the model, only the average vibrational energy of the population distribution is considered. Upon absorption of a photon, the molecule enters the excited singlet with vibrational energy $E_1$, given by

$$E_1 = \frac{10^7}{\lambda} + E_{\text{thermal}} - E_{0-0}$$

where $\lambda$ is the wavelength of the photon [nm] and $E_{0-0}$ is the zero-point energy difference between the excited and ground singlet states [cm$^{-1}$]. $E_{\text{thermal}}$ is the thermal vibrational energy [cm$^{-1}$] calculated by summing the contributions of the 42 vibrational modes of 3-pentanone at the local temperature, which is feasible on the assumption that the modes of the molecule are harmonic oscillators. The frequencies of the modes are tabulated in
Appendix A. $E_1$, and all other vibrational energies $E_n$ mentioned in this model are referenced to the zero-point energy of the excited singlet.

Figure 2.5 Condensed transition structure used in the photophysics model. The diagram also shows rates and parameters representing various collisional and collisionless processes.

The model calculates the overall FQY by summing the contribution to FQY from each of $n$ vibrational levels with energy $E_n$ weighted by the probability the molecule relaxes to $E_n$ from $E_1$. The summation ends at vibrational energy level $N$, where $E_N$ equals $E_{\text{thermal}}$. This calculation can be represented via the following equation:

$$\phi = \phi_0 + \sum_{n=2}^{N-1} \phi_n \prod_{j=1}^{n-1} P_j + \phi_N \prod_{j=1}^{N-1} P_j$$  \hspace{1cm} (2.15)$$

For $\phi_N$, the molecule is at vibrational energy $E_{\text{thermal}}$ and $k_{\text{vib}}$ is set to zero because the molecule can no longer relax. The contribution to FQY from a given vibrational level $n$ with energy $E_n$ is given by
The probability the molecule at vibrational level \( n \) relaxes to level \( n+1 \) is given by

\[
\phi_n = \frac{k_f}{k_f + k_{\text{vib}} + k_{\text{nr}}(E_n) + k_{O_2}(E_n) + k_{N_2}(E_n)} \tag{2.16}
\]

From equations (2.16) and (2.17), the FQY depends on the rates of fluorescence and other processes previously described. The collisionless processes of fluorescence, ISC, and IC are represented via two rates. Fluorescence is represented by the fluorescence rate \( k_f \) [s\(^{-1}\)], which has been treated as a constant with vibrational energy in previous work [31, 50]. As mentioned in section 2.4, the collisionless non-radiative processes, IC and ISC, are summed into a collisionless non-radiative rate \( k_{\text{nr}} \) [s\(^{-1}\)], as shown below.

\[
k_{\text{nr}} = k_{\text{ISC}} + k_{\text{IC}} \tag{2.18}
\]

The collisional processes of vibrational relaxation and collisional quenching are also represented via rate parameters. The Koch model considers a vibrational relaxation rate \( k_{\text{vib}} \) [s\(^{-1}\)] and an oxygen quenching rate \( k_{O_2} \) [s\(^{-1}\)]. The current work also considers collisional quenching from nitrogen, previously believed not to occur, which is represented by the rate \( k_{N_2} \) [s\(^{-1}\)].

Previous work has shown that the \( k_{\text{vib}} \) can be calculated as the sum of the collision rate between 3-pentanone and all other species present [61], represented by

\[
k_{\text{vib}} = \sum_{m=1}^{M} Z_{\text{coll},m} n_m \tag{2.19}
\]

where \( Z_{\text{coll},m} \) is the collision frequency factor [cm\(^3\)s\(^{-1}\)] between 3-pentanone and species \( m \). \( Z_{\text{coll},m} \) is calculated using Lennard-Jones collision theory using approximations from [66] and molecule properties from [67]. Appendix A tabulates parameters used to calculate the collision frequency.

Due to the high density of vibrational states in 3-pentanone, the decline of vibrational energy during relaxation can be represented as an exponential decline. In the model, if the molecule undergoes vibrational relaxation, it relaxes to a vibrational energy given by
\[ E_{n+1} = E_n - \Delta E_{\text{coll}} = E_n - \alpha(E_n - E_{\text{thermal}}) \]  \hfill (2.20)

where \( \alpha \) is the vibration relaxation cascade parameter [cm\(^{-1}\)]. Previous work has determined that \( \alpha \) has temperature dependence, and the current work also considers the vibrational energy dependence of \( \alpha \) [31]. When multiple species are present, \( \alpha \) is weighted by the relative collision rate of that species:

\[
\alpha = \frac{1}{k_{\text{vib}}} \sum_{m=1}^{M} \alpha_m Z_{\text{coll},m} n_m
\]  \hfill (2.21)

where \( \alpha_m \) is the cascade parameter for species \( m \).

From this model structure, several parameters from the fluorescence model can be optimized using FQY data: the fluorescence rate \( k_f \), non-radiative rate \( k_{nr} \), the vibrational relaxation cascade parameter \( \alpha \), oxygen quenching rate \( k_{O2} \), and nitrogen quenching rate \( k_{N2} \). Previous work has primarily used data at pressures of 1 bar or greater to optimize these parameters [29-31, 48].

Figure 2.6 Sensitivity of 3-pentanone FQY to non-radiative rate \( k_{nr} \) at initial vibrational energy \( E_1 \) for a) 248 nm excitation and b) 308 nm excitation for a range of temperatures and nitrogen pressures calculated with the Koch model [31]. The partial pressure of 3-pentanone is 20 mbar. The FQY is most sensitive to \( k_{nr} \) with no added nitrogen.
However, a sensitivity analysis reveals that the collisionless non-radiative rate $k_{nr}$ is most sensitive to low-pressure FQY data. The sensitivity of the FQY to $k_{nr}$ is calculated by

$$s = \frac{k_{nr}(E_i)}{\phi(T, p, \lambda)} \left| \frac{\partial \phi(T, p, \lambda)}{\partial k_{nr}(E_i)} \right|$$  (2.22)

The FQY is calculated using the Koch model, and the derivative is approximated using a central difference method.

Figure 2.6 shows the calculated sensitivity of the FQY to $k_{nr}$ for excitation wavelengths of 248 and 308 nm for 20 mbar of 3-pentanone in nitrogen. The FQY is most sensitive to $k_{nr}$ with no added nitrogen for both excitation wavelengths, and the sensitivity drops by a factor of 5-10 with the addition of nitrogen. At low pressures, the FQY is dominated by $k_{nr}$ because it is unaffected by collisions, but as nitrogen is added, collisional processes begin affecting the FQY. Based on this sensitivity analysis, in the current work, low-pressure data over a wide range of temperatures was obtained in addition to data over a wide range of temperatures and pressures relevant to diagnostic applications to effectively optimize the FQY model.

### 2.6 Strategy for Photophysics Measurement and Modeling

In order to turn 3-pentanone tracer PLIF into a versatile diagnostic, it is necessary to have a database of FQY measurements, as well as an FQY model valid across a wide range of temperature and pressures. The current work approaches this problem in two ways. Measurements of absolute FQY are made at pressures below the vapor pressure of 3-pentanone to obtain rate information on collisionless processes, benefitting the model development. Moreover, this study develops a database of absolute FQY values across a wide range of pressures, temperatures, and excitation wavelengths that are relevant to the application of 3-pentanone PLIF as a quantitative diagnostic to flow fields and combustion systems. These are used to optimize an FQY model that is suitable for high-pressure and high-temperature applications.
Chapter 3  Low-pressure 3-pentanone Photophysics

This chapter details 3-pentanone photophysics studies performed at low pressures. An optical cell facility was used to study the absorption cross-section, fluorescence spectrum, and absolute FQY across a range of temperatures. The results are used to determine collisionless rates in the FQY model.

3.1 Low-pressure FQY Background

Measurements and modeling of the FQY across a wide range of conditions are necessary for quantitative PLIF imaging. As discussed previously, there has been experimental work measuring the FQY across a limited range of pressures, temperatures, and excitation wavelengths [16, 19, 28-30, 41] and the proposal of a step-ladder model [31]. Several parameters in the model represent various processes between the ground and excited electronic states. Collisionless processes that do not depend on collisions between molecules are represented by the fluorescence rate $k_f$ and the non-radiative rate $k_{nr}$. Collisional processes that result from collisions are represented by the oxygen quenching rate $k_{O_2}$, nitrogen quenching rate $k_{N_2}$, and vibrational relaxation cascade parameters $\alpha$ for each collision partner. Previous studies have utilized various databases of FQY data to optimize the rates of this model structure [29-31].

These previous studies have primarily used FQY data at pressure conditions in excess of 1 bar, where both non-radiative deactivation and vibrational relaxation have
significant effect on the FQY. However, at these pressures, collisional and collisionless effects are both significant, and insight into any particular process is difficult. The solution to separating these effects is highlighted in the sensitivity analysis from section 2.5: at low pressures the FQY is dominated by the collisionless processes. Moreover, because vibrational relaxation becomes less active at low pressures, the assumption that the molecule remains at its initial vibrational energy level $E_1$ becomes valid. Thus, to investigate collisionless rates and their dependence on upper-state vibrational energy, it is useful to examine 3-pentanone photophysics at low pressures. Unfortunately, the availability of FQY data at these conditions is limited. Koch made measurements at room temperature and low pressure in a static optical cell, and used this data to optimize $k_f$ and $k_{nr}$ [31]. Additional room-temperature, low-pressure studies are also available [41].

This work looks to provide a comprehensive set of low-pressure 3-pentanone FQY data over temperatures from 300 K to 690 K, and for excitation wavelengths of 248, 266, 277, and 308 nm. The measurements will be used to further knowledge of the fluorescence rate $k_f$ and the non-radiative rate $k_{nr}$ at higher vibrational energies. In addition, the vibrational relaxation cascade parameter for 3-pentanone collisions, $\alpha_{3p}$, is determined using FQY variation with 3-pentanone pressure, and a model for predicting FQY for pure 3-pentanone is presented.

3.2 Low-pressure Photophysics Theory

At low pressures, the vibrational relaxation rate $k_{vib}$ and collisional quenching rates $k_{O2}$ and $k_{N2}$ in the FQY model are small compared to the non-radiative rate $k_{nr}$. Previous work has also shown the fluorescence rate $k_f$ is small compared to the $k_{nr}$ [31, 41]. In this work, as with previous fluorescence models for ketones, $k_f$ is treated as a constant independent of vibrational energy [17, 31]. The FQY model from section 2.5 then simplifies to
Because vibrational relaxation is considered insignificant at low-pressures, there is no cascade of vibrational energy, and $k_{nr}$ only needs to be considered at the initial energy $E_1$, which is calculated from the excitation wavelength and temperature using

$$E_1 = \frac{10^7}{\lambda} + E_{\text{thermal}} - E_{0-0}$$

In this expression, $\lambda$ is the wavelength of the photon in nm, $E_{0-0}$ is the zero-point energy difference between the excited and ground singlet states, and $E_{\text{thermal}}$ is the thermal vibrational energy in $S_1$, summed from the 42 vibrational modes of 3-pentanone tabulated in Appendix A at the local temperature.

### 3.3 Absorption Cross-section Measurement Methodology

The absorption cross-section was determined using the Beer-Lambert equation:

$$\frac{I}{I_0} = \exp(-n\sigma L)$$

where $I_0$ is the incident beam intensity, $I$ is the transmitted beam intensity, $n$ is the 3-pentanone number density, $L$ is the path length, and $\sigma$ is the absorption cross-section.

In this study, variations in incident beam energy were monitored by splitting a fraction of the beam energy with a beam splitter and sending it to a fast photodiode. The beam energy after passing through the cell is also measured using a fast photodiode. The optical setup is further discussed in section 3.5.2. The transmission can be determined by comparing the ratio of the two photodiode measurements with and without 3-pentanone in the cell:

$$\frac{I}{I_0} = \left(\frac{I_2}{I_1}\right)\left(\frac{I_{1,0}}{I_{2,0}}\right)$$

where $I_2$ is the transmitted beam energy measurement, $I_1$ is the split beam measurement, and the ‘0’ subscript denotes a measurement with no 3-pentanone in the cell. The absorption cross-section can then be determined by
3.4 FQY Measurement Using Rayleigh Scattering

The fluorescence signal is described by the linear fluorescence equation

\[
S_f = \frac{E\lambda}{h c} n L \sigma(\lambda, T) \eta_{LIF} \phi(\lambda, p, T, X_{5p}, X_M) \Omega \frac{\Omega}{4\pi} \eta_{LIF}
\]  

(3.6)

where \( E \) is the incident laser energy fluence, \( h \) is Planck’s constant, \( c \) is the speed of light in vacuum, \( \lambda \) is the laser wavelength, \( n \) is the number density of fluorescing tracer, \( L \) is the length of the illuminated volume, \( \Omega \) is the detector collection angle, and \( \eta_{LIF} \) is the collection efficiency. However, to calculate FQY from collected fluorescence signal level requires knowledge of the collection angle and efficiencies, both of which are difficult to quantify accurately. As a result, absolute FQY measurements are often determined via calibration of the signal to other known radiative processes to account for these parameters. This thesis will use Rayleigh scattering as the primary reference source, but due to limitations of the experimental setup at higher temperatures, room-temperature 3-pentanone FQY is also used as a reference. These limitations are discussed in section 3.5.

When using a well-characterized fluorescent species as a reference, the FQY can be calculated using

\[
\phi = \frac{S_{LIF}}{S_{LIF,0}} \frac{n_o \sigma_o}{n \sigma} \phi_0
\]

(3.7)

where \( S_{LIF} \) is the fluorescence signal, \( \sigma \) is the absorption cross-section, and \( n \) is the tracer number density. The ‘0’ subscript refers to the quantity measured for the reference species. Hansen and Lee used this method for calibrating 3-pentanone FQY using acetone at 296 K and 313 nm excitation as a reference [41]. This method of calibration for measurements of FQY is used in the current work over a limited range of temperatures where the Rayleigh scattering method fails due to experimental setup limitations.

Absolute FQY measurements can also be calibrated to Rayleigh scattering, and 3-pentanone measurements have previously been made in this laboratory using nitrogen Rayleigh scattering as the reference emission [16]. This technique was adapted from
previous work calibrating fluorescence saturation concentration measurements to Rayleigh scattering [68]. The current work primarily utilizes Rayleigh scattering of nitrogen to reference measurements of 3-pentanone FQY.

Nitrogen is chosen as the scatterer because a significant amount of theory and literature is available to describe the Rayleigh scattering from diatomic molecules [69]. The Rayleigh signal collected orthogonal to the plane defined by the polarization vector and the propagation vector of the laser beam can be described by the following equation:

\[ S_{Ray} = \frac{E_{Ray} \lambda}{hc} n_{Ray} L \left( \frac{\partial \sigma}{\partial \Omega} \right) \Omega \eta_{Ray} \]  

where \( E \) is the incident laser energy fluence, \( h \) is Planck’s constant, \( c \) is the speed of light in vacuum, \( \lambda \) is the laser wavelength, \( n_{Ray} \) is the number density of the scatterer, \( L \) is the length of the illuminated volume, \( \left( \frac{\partial \sigma}{\partial \Omega} \right) \) is the differential Rayleigh cross-section [cm²/ster], \( \Omega \) is the detector collection angle, and \( \eta_{Ray} \) is the collection efficiency. Normalizing the fluorescence signal to Rayleigh signal and solving for the FQY results in the expression

\[ \phi = 4\pi \frac{S_{LIF}}{E_{LIF} \eta_{LIF}} \frac{E_{Ray} n_{Ray} \eta_{Ray} \left( \frac{\partial \sigma}{\partial \Omega} \right) 1}{S_{Ray}} \]  

Equation (3.9) assumes that the collected signal and collection efficiencies are independent variables. However, because 3-pentanone is a broadband emitter and the collection efficiency varies significantly over the fluorescence spectrum, it is necessary to integrate the spectrum normalized for the spectral responsivity \( R(\lambda) \) instead of simply normalizing for collection efficiency. Fortunately, because both the fluorescence and Rayleigh signal will be normalized, the relative spectral responsivity (RSR) can be used instead of absolute responsivity. The RSR is defined as

\[ RSR = \frac{R(\lambda)}{R(\lambda_{ref})} \]  

where \( \lambda_{ref} \) is a reference wavelength. The FQY can then be calculated by

\[ \phi = 4\pi \frac{E_{Ray} n_{Ray}}{E_{LIF} n_{LIF}} \left( \frac{\partial \sigma}{\partial \Omega} \right) \frac{1}{\sigma} \int_{\lambda_{LIF}}^{\lambda_{Ray}} \frac{S_{LIF}(\lambda)}{R_{LIF}(\lambda)} d\lambda \int_{\lambda_{Ray}}^{\lambda_{Ray}} \frac{RSR(\lambda)}{S_{Ray}(\lambda)} d\lambda \]  

Most parameters in equation (3.11) are determined from measurements. However, the differential Rayleigh cross-section is determined using literature values. Miles
provides a review of Rayleigh scattering theory [69], which states that the differential cross-section for diatomic molecules is determined by

\[
\left( \frac{\partial \sigma}{\partial \Omega} \right) = \frac{4\pi}{\lambda^2} \frac{3 + 7F_K}{10} \left( \frac{r-1}{n} \right)^2
\]  

(3.12)

where \( \lambda \) is the laser wavelength in nm, \( F_K \) is the King factor, and \( (r-1) \) is the simple index of refraction at the laser wavelength.

The equation is based on electric dipole theory for a simple atomic spherical scatterer, such as argon; the King factor is an anisotropic factor for polyatomic molecules. For this study, the King factor for nitrogen is given by [70]:

\[
F_K = 1.034 + \frac{317}{\lambda^2}
\]  

(3.13)

The ratio of the refractive index \( (r-1) \) with number density \( n \) is proportional to the polarizability of the species. Because polarizability is an intrinsic property of the species, in accordance with the Lorentz-Lorenz equation, the ratio of the refractive index with the number density \( n \) is a constant for a given species, and can be determined using measurements made for a particular number density of the scatterer. This work utilizes an expression based on a fit to experimental measurements of the refractive index of nitrogen in the UV [71]:

\[
r - 1 = \frac{1.966}{22086 - \left( \frac{1000}{\lambda} \right)^2} + \frac{0.02745}{133.86 - \left( \frac{1000}{\lambda} \right)^2}
\]  

(3.14)

These refractive index measurements were made at 273 K and 1.013 bar, so the number density \( n \) is \( 2.686 \times 10^{19} \) cm\(^{-3} \). For equations (3.13) and (3.14), the unit of wavelength \( \lambda \) is nm.

The use of Rayleigh scattering as a reference for absolute FQY measurement requires consideration of polarization for both the laser beam and collected signals. Rayleigh scattering depends on the laser beam polarization, and equation (3.11) only applies to a vertically polarized laser beam. Moreover, the polarization of the fluorescence and Rayleigh signals must also be considered. Because fluorescence is not instantaneous, the movement of molecules will randomize the dipole direction, effectively depolarizing the fluorescence signal. However, Rayleigh scattering for
diatomics like nitrogen is largely, but not completely, polarized. Thus, to obtain an accurate count of total fluorescence or Rayleigh photons, the detector setup must be polarization insensitive. These considerations influence the design of the optical cell system and collection optics described in the following section.

3.5 Experimental Setup

3.5.1 Optical Cell Design

![Figure 3.1 Schematic of cell seeding system and pressure and temperature measurement sensors.](image)

The overall experimental setup is shown in Figure 3.1. The optical cell body is a MDC Vacuum “cube” fitting with a high-vacuum copper flange seal. The body accepts 2.75 in (69.85 mm) diameter MDC Vacuum viewports. The windows along the axis of the collection optics are MDC Vacuum UV-grade sapphire viewports with a window thickness of 0.080 in (2.032 mm) and a viewing diameter of 0.94 in (23.876 mm). For measurements taken between 300 and 560 K, the laser beam passed through MDC Vacuum UV grade fused silica viewports with a window thickness of 0.125 in (3.175 mm) and a viewing diameter of 2.312 in (58.7248 mm); the laser beam path length...
between these windows is 88.3 mm. These viewports are limited to temperatures of 560 K because the brazing holding the window to the flange melts at around that temperature. For temperatures higher than 560 K, the fused silica viewports were replaced with sapphire viewports due to the higher melting point (720 K) of the brazing. The beam path length between the sapphire ports is 73.8 mm. The viewports are not rated by the manufacturer for pressures greater than 1 bar, but they were used up to 2 bar in this experiment.

Fused silica windows were used for most of the measurements because they are amorphous, ensuring low birefringence and maintenance of a laser beam polarization. The beam polarization was confirmed to remain vertical after passing through the fused silica windows by placing a Rochon polarizer downstream of the cell to pass the horizontal polarization and verifying the beam is completely filtered. However, above temperatures of 570 K, Rayleigh scattering can no longer be used as a reference emission due to the use of sapphire viewports, which are crystalline and birefringent. To measure the FQY at these temperatures above 570 K, the fluorescence signal was scaled according to equation (3.7), with fluorescence from 3-pentanone at 296 K in nitrogen with a total pressure of 1.3 bar used as the reference.

Gas was introduced into the cell via a flowing system shown in Figure 3.1, which was chosen over static systems used in other low-pressure measurements [16, 41]. In static systems, the tracer number density can decrease with time due to adsorption onto the cell walls, but a flowing system maintains constant tracer composition. Moreover, although 3-pentanone pyrolysis has been determined to be insignificant below 700 deg C [72], the flowing system decreases the time the gases spend at elevated temperatures, further reducing the risk of pyrolysis effects on the fluorescence signal. Finally, measurements by Koch show that 3-pentanone begins to photolyze after about 1000 laser pulses with less than 1 mJ of energy [31]; flowing the tracer allows the detector to accumulate the fluorescence from a large number of pulses without concern for photolysis, improving the SNR of the measurement.

The system was able to introduce both 3-pentanone mixed with nitrogen or air, as well as pure vapor, into the optical cell. The 3-pentanone in this experiment was from
Alfa Aesar and of 99.9% purity, and the liquid was degassed under vacuum before use. Compressed gases were filled by Praxair; 99.995% grade nitrogen gas was used in these experiments, and air was simulated using mixtures of 21% oxygen and 79% nitrogen. For 3-pentanone and nitrogen/air mixtures, the system introduced nitrogen/air using a Teledyne Hastings HFC-D-303 mass flow controller. The 3-pentanone was introduced into the gas flow using an Eldex Optos 2LMP liquid metering pump. The pump drew liquid 3-pentanone from a sealed glass flask and injected the liquid into a modified 0.25 in (6.35 mm) Swagelok “T” junction using a 0.0625 in (1.5875 mm) tube. The tube is positioned such that the 3-pentanone immediately contacted the interior surface of the fitting after exiting the tube, as shown in Figure 3.1. Because the junction was heated to about 150 deg C, the 3-pentanone vaporized on contact and was entrained by the bath gas flow. Downstream of this junction, a heated mixing chamber filled with stainless steel mesh baffling ensured complete mixing of the 3-pentanone with the bath gas. The mass flow controller provided 2.5 SLPM of nitrogen or air, and the pump provided 0.185 mL/min of 3-pentanone liquid. The residence time of the gas in the optical cell was about 0.2 s. The stream passed through the cell and exhausted into ambient air.

The system was also able to provide a stream of pure 3-pentanone vapor. A 3-way valve directed the exhaust to a mechanical pump instead of ambient air, which drew vapor from the flask of liquid 3-pentanone and through the optical cell. A Brooks 5850 mass flow controller was used to regulate the flow of the 3-pentanone vapor, and the flow rate was kept constant at 23 SCCM throughout the study.

The gas stream was fed into the top of the optical cell, vented out of the bottom of the cell and exhausted to atmosphere. The pressure in the cell can be changed using the needle valve at the exhaust, or by varying the flow rate from the mass flow controllers. The pressures of 3-pentanone and nitrogen/air mixtures were measured with a Setra 280E 0-50 psia pressure transducer tapped into the exhaust line. 3-pentanone vapor pressures were measured with a MKS 1000 torr Baratron. The Baratron head was directly connected to the optical cell using a 30 cm long tube because the flow of vapor introduces a pressure drop of 0.3 mbar/meter of tubing, a significant error at low
pressures. To avoid composition variation due to gas trapped in the connecting tube, the system was evacuated prior to changing the gas flow composition.

The temperature of the cell was varied using a Mellen Company viewport-equipped furnace. The interior gas temperature and the external cell surface temperature were monitored using K-type thermocouples. To ensure temperature uniformity within the cell, measurements were taken when the cell external and internal temperature agreed within about 5 K. The voltage output from the thermocouples and pressure transducers were collected using a National Instruments PCI-MIO-16XE-50 data acquisition board installed on a Windows PC computer. Measurements of gas flow rate from the gas mass flow controller, the liquid pump flow rate, and the oven temperature were also read by this computer using RS-232 inputs.

3.5.2 Laser and Collection Optics Setup

![Optical diagnostic setup for the measurement of fluorescence and absorption.](image)

Figure 3.2 Optical diagnostic setup for the measurement of fluorescence and absorption.

Figure 3.2 shows layout of the laser excitation and optical signal collection systems. Four different laser excitation wavelengths were employed in this study: 248, 266, 277, and 308 nm. The 248 nm beam was provided by a Coherent CompexPro 102
krypton fluoride excimer laser. The output from the excimer laser was also used to generate the 277 nm beam using a Lambda Physik RS-75 Raman shifter filled with 19 bar of hydrogen gas and equipped with 30 cm focal length cylindrical lens end windows for added conversion efficiency. The 277 nm beam was selected from the output of the Raman cell using a Pellin-Broca prism. The 266 nm beam was provided by a frequency-quadrupled Spectra-Physics QuantaRay GCR-170 Nd:YAG laser, and the 532 nm output of the laser was also used to pump a Lumonics HD-500 pulsed dye laser circulating Rhodamine 640 laser dye. The dye laser was tuned to output a 616 nm laser beam, which was frequency doubled to 308 nm using a BBO crystal.

The laser beams were routed to the optical cell using wavelength-appropriate high-efficiency reflectors and were aligned to pass through the center of the optical cell’s windows. Each beam first passed through an iris set at 10 mm diameter to reduce it to the aperture of the following optics. The beam then passed through an MgF2 Rochon polarizer with a 14.5 mm diameter aperture. The polarizer was aligned to allow the vertical polarization of the lasers to pass undeviated and deflect the horizontal polarization, which is blocked. The polarizer is necessary because the excimer laser beam is not fully polarized and has some horizontal polarization content. The output from the Nd:YAG laser is fully polarized and is unaffected by the polarizer. The vertically polarized beam was passed through a 1000 mm focal length cylindrical lens to collimate the beam in the vertical direction. The beam was then passed through an iris to reduce the beam diameter to 2 mm diameter. For 248 nm and 266 nm beams, the beam energy was about 0.4 mJ/pulse; for 277 and 308 nm beams, the beam energy was about 0.1 mJ/pulse. A mechanical shutter was used to block the beam from the optical cell until measurements were ready to be taken.

To monitor the laser beam energy, about 10% of the beam energy was diverted using a 3° deg fused silica wedge to the beam energy detector. The beam was focused into a custom-made aluminum integrating sphere with an internal diameter of 1 in (25.4 mm) using a 100 mm focal length fused silica lens. A Thorlabs DET10A high-speed photodiode monitored the output from the integrating sphere, and the photodiode signal was sent to a Tektronix TDS620B oscilloscope, corrected for detector dark current, and
integrated to determine laser energy. The laser beam exiting the optical cell was also sent to an identical integrating sphere, photodiode, and oscilloscope setup to monitor output beam energy. The energy measurements were used to normalize the fluorescence signal for laser energy variations and to measure absorption.

Fluorescence signal was collected using a 105 mm Nikkor 4.5 UV lens and imaged onto the 250 μm wide slit of an Acton SP-150 spectrograph. The spectrograph grating is blazed at 300 nm with 300 grooves/mm with a spectral resolution of about 4.0 nm/pixel. The output of the spectrograph was imaged using 512 x 512 pixel intensified charge coupled device (ICCD) Princeton Instruments PI-MAX camera. To increase SNR, the intensifier is set at maximum gain for all measurements and the readout speed is set to the slowest setting of 100 kHz. The gating time of the intensifier was set to 1 μs. Due to the low density of grooves, the grating is polarization insensitive, which is confirmed by manufacturer specifications, as well as previous studies utilizing this spectrograph and grating [16]. The camera and spectrograph combination was controlled by a PC computer using WinSpec32 v. 2.5.16.5, a Princeton Instruments proprietary software package.

3.5.3 Experimental Setup Spectral Characterization

The spectrograph wavelength calibration and the RSR of the optical cell and collection optics characteristics are characterized using calibration lamps. The calibration lamps are placed as indicated in Figure 3.2. For the calibration, only the viewport between the laser beam and the collection optics was installed.

In order to capture the entire 3-pentanone fluorescence and the Rayleigh scattering of the laser beams used in this study, the spectrograph must be used from about 240 nm to 570 nm, requiring the rotation of the grating turret, and the spectral characterization needs to take this into account. Previous work by Koch et. al. used a 14% correction factor in lieu of rotating the grating, but this introduces error due to the shifts in the fluorescence spectrum with pressure [16]. The spectrograph grating was rotated to a center wavelength of 440 nm to measure the fluorescence signal and 340 nm to measure Rayleigh signal. Thus, it is necessary to characterize the detector system for the spectrograph set at 340 and 440 nm center wavelengths.
Calibration of the spectrograph for wavelength was performed with lines from a Newport 6035 Hg(Ar) calibration lamp. The spectrograph, centered at 340 nm, was calibrated using 6 lines from this lamp. At this center wavelength, the spectrograph has a range from 215.3 to 462.5 nm. Centered at 440 nm, 5 lines from the lamp were used; at this center wavelength, the spectrograph has a range from 317.1 to 562.0 nm. Repeated measurements after rotating the grating between these center wavelengths demonstrated that this calibration is repeatable to within 0.1 nm.

![Graph showing measurements of deuterium lamp and tungsten lamp spectrum for 340 and 440 nm center wavelengths.](image)

**Figure 3.3** Measurements of deuterium lamp and tungsten lamp spectrum for 340 and 440 nm center wavelengths. The spectra show that grating rotation has little effect on measured signal.

With the spectrograph calibrated for wavelength, the RSR of the collection optics was determined using two calibration lamps. A Newport 63979 30 W deuterium lamp was used to calibrate the RSR of the system from 220 to 370 nm, and an Optronic Laboratories OL-550 75 W tungsten lamp was used above 350 nm. The lamps were warmed up for at least 30 minutes following manufacturer’s instructions to ensure stable lamp spectral output. The deuterium lamp output was collected by the ICCD over a 100 μs exposure time, and the tungsten lamp output was collected over 50 μs. The measured
spectra were determined by summing 100 rows of pixels in the center of the background-corrected image. Figure 3.3 shows the measured spectrum for both lamps with the spectrograph centered at 340 and 440 nm. The lamp spectra for both lamps measured at the two center wavelengths agree well. Rotation of the spectrograph did not alter the measured lamp spectra, demonstrating that the rotation of the spectrograph grating does not influence the collected signal, and that the system can be characterized by a single RSR curve.

![Graph showing RSR of collection optics, spectrograph, and ICCD measured using deuterium and tungsten calibration lamps.](image)

**Figure 3.4 RSR of collection optics, spectrograph, and ICCD measured using deuterium and tungsten calibration lamps.**

To determine the RSR, the above spectra are normalized to the manufacturer provided spectral photon flux [photons/ster nm mm²] calibration. The RSR is arbitrarily normalized to the value at 350 nm. The calculation can be represented by:

\[
RSR(\lambda) = \frac{S_{\text{spectrum}}(\lambda)}{E_p(\lambda)} \frac{1}{RSR(350 \text{ nm})}
\]

where \( S_{\text{spectrum}} \) is the measured spectrum and \( E_p \) is the calibrated spectral photon flux provided from the manufacturer. The resulting RSR curve, shown in Figure 3.4, peaks at
about 270 nm and falls to about 10% of the peak value at 562 nm. The RSR measured by the two calibration lamps agrees well within the overlapping region of 350 to 370 nm.

3.6 Measurement Results

3.6.1 Absorption Cross-Section

![Sample plot of absorbance with number density used to calculate absorption cross-section. This figure shows data for 531 K, 10 to 30 mbar of 3-pentanone, and 308 nm excitation.](image)

3-pentanone absorption cross-section was determined using equation (3.5), and in this calculation, the absorbance is normalized by the 3-pentanone number density. To determine this quantity, measurements of transmission, averaged over 500 laser pulses, were taken at 3-pentanone pressures from 10 to 30 mbar, and the slope of the absorbance plotted against number density was used to calculate absorption cross-section. Figure 3.5 shows a sample plot of the absorbance versus 3-pentanone number density for 308 nm excitation at 531 K.
Figure 3.6 Measured 3-pentanone absorption cross-section as a function of temperature for 248, 266, 277, and 308 nm. The data are consistent with previous data and a Gaussian fit of the absorption spectrum [39, 40]. Error bars represent 4% uncertainty.

Figure 3.6 shows the absorption cross-section measurements for the 248, 266, 277, and 308 nm laser wavelengths at various temperatures. The estimated uncertainty in these experiments is about +/- 4%, primarily the result from uncertainties in the temperature and beam transmission measurements. An uncertainty analysis is presented in Appendix D. These measurements are compared to laser absorption cross-section measurements made in an optical cell [28], absorption spectra measurements made in a shock tube [39], and room temperature measurements made in a spectrophotometer [40]. Measurements are also compared to a Gaussian fit of the absorption spectrum [39]. There is excellent agreement with previous cell measurements for 248 and 308 nm, but for 266 nm excitation, Koch measured an absorption cross-section about 10% lower, which may be the result of local saturation effects due to the non-uniformity of the laser beam used in his work [31]. However, the current work also shows excellent agreement with shock tube and spectrophotometer data, as well as the Gaussian absorption spectral fit, for all
wavelengths. These values of absorption cross-section, which are tabulated in Appendix B, will be used to determine the FQY according to equation (3.11).

3.6.2 Fluorescence Spectrum

Fluorescence signal was measured by imaging the output from the spectrograph. 500 images were accumulated on the ICCD to improve the SNR, except for measurements at temperatures at 650 K for 277 and 308 nm excitation, where 1000 images were accumulated due to low levels of signal. The acquired image was corrected for background using an image taken with the cell under vacuum. The fluorescence spectrum was calculated from the corrected images by summing the central 100 rows of pixels and correcting for the RSR. A sample background-corrected image and fluorescence spectrum is shown in Figure 3.7.

![Sample fluorescence image and spectrum](image)

Figure 3.7 Sample fluorescence image taken by the ICCD camera, corrected for background. The fluorescence spectrum corrected for RSR is also shown. To determine the total fluorescence signal, the spectrum is integrated from 327 to 563 nm. This image and spectrum is for 30 mbar of 3-pentanone at 298 K with 308 nm excitation.
Figure 3.8 3-pentanone fluorescence spectra at 298 K and 1.3 bar nitrogen show slight narrowing of spectrum with increased excitation wavelength. The current work shows good agreement with previous work [28].

Figure 3.9 Variation of 3-pentanone fluorescence spectrum for neat vapor and in a nitrogen bath gas for two temperatures. Results are shown for a) 248 and b) 308 nm excitation.
Figure 3.8 compares the 3-pentanone fluorescence spectrum for 248 and 308 nm excitation at 298 K and 20 mbar of 3-pentanone in 1.3 bar of nitrogen. At this temperature, the spectrum narrows slightly with increasing excitation wavelength. In addition, the figure shows that the current measurements agree well with previous work [28].

Previous work on ketone photophysics has either found, for acetone, or assumed, for 3-pentanone, that the fluorescence spectrum remained constant with temperature [17, 28]. This work allows the investigation of that assumption for several 3-pentanone and nitrogen compositions, and the results show that this assumption applies in certain situations, but is invalid in others. Figure 3.9 shows fluorescence spectra for several gas compositions and temperatures for 248 and 308 nm excitation. In pure 3-pentanone vapor, the fluorescence spectrum does remain effectively constant with temperature, although a slight blue shift is observed. Moreover, the spectrum is unaffected by increasing 3-pentanone vapor pressure. Thus, for 3-pentanone vapor, the assumption of constant fluorescence spectrum is effectively valid up to 642 K.

However, as Figure 3.9 shows, the addition of a nitrogen bath gas renders this assumption incorrect. At 298 K, nitrogen causes a narrowing of the fluorescence spectrum to the left of the peak, and the magnitude of this shift is larger for 248 nm excitation than for 308 nm excitation. At 642 K, however, there is almost no narrowing with the addition of nitrogen for either 248 or 308 nm excitation. Thus, in nitrogen, the shape of the fluorescence does have dependence on temperature, rendering the assumption of constant spectral shape incorrect in this situation. The variation of the spectrum in nitrogen with temperature and pressure is investigated over a wider range of conditions in Chapter 4.

3.6.3 Absolute FQY

The total signal was determined by integrating the fluorescence spectrum from 329 nm to 562 nm to determine total fluorescence signal. The total signal was further corrected for losses in laser energy due to 3-pentanone absorption and variations in laser
pulse energy using simultaneous measurements of energy from the photodiodes and normalized for the number laser pulses accumulated on the ICCD.

Figure 3.10 Sample Rayleigh scattering image taken by the ICCD camera, corrected for background. The resulting spectrum from the summation of the central 100 rows and corrected for RSR is also shown. To determine total Rayleigh signal, the spectrum is integrated +/- 14 nm from the peak. This image and spectrum is for 248 nm excitation and 1.5 bar of nitrogen.

Rayleigh scattering signal was measured in a similar manner with the spectrograph grating rotated to a center wavelength 340 nm. The Rayleigh signal from the laser beam was collected by accumulating 50 to 100 laser pulses on the ICCD. A sample background-corrected image and spectrum for Rayleigh signal is shown in Figure 3.10. The total Rayleigh signal was determined by correcting the line measurement for the RSR of the system, integrating the line +/- 14.3 mm from the laser wavelength, and normalizing for laser energy. To normalize the Rayleigh signal for scatterer number density, the slope of the signal with nitrogen number density for a pressure range from 0
to 2 bar was calculated, as shown in Figure 3.11 for 295 K and 248 nm excitation. The FQY was calculated using these quantities according to equation (3.11).

![Figure 3.11](image)

**Figure 3.11** Sample plot of Rayleigh signal with nitrogen number density. The slope of the curve used to normalize the signal and calculate FQY. This figure shows data for 295 K and 248 nm excitation.

Figure 3.12 shows the measured absolute FQY for 3-pentanone vapor from about 10 to 30 mbar pressure and 248, 266, 277, and 308 nm excitation for a range of temperatures. The FQY generally decreases with increasing temperature for all four excitation wavelengths, but it remains essentially constant with pressure except at 295 K for 248 and 266 nm excitation, where increased FQY is observed with additional pressure. Moreover, for a given temperature, the 3-pentanone FQY increases with increasing excitation wavelength.

Additional measurements of absolute FQY for 20 mbar of 3-pentanone in air and nitrogen at a total pressure of 1.3 bar over a range of temperatures is shown in Figure 3.13. The FQY is identical in air and nitrogen, consistent with previous measurements at these conditions [28, 29]. The FQY in the bath gases at 1.3 bar total pressure is also higher than for 3-pentanone vapor at the same temperature, although this effect lessens with increasing wavelength and temperature. The uncertainty in the absolute FQY
measurements is primarily due to the uncertainties in the absorption cross-section measurement, the RSR measurement, and the collected signal from the ICCD, resulting in an overall estimated uncertainty of about 6%. A tabulation of this data can be found in Appendix B, and an uncertainty analysis is presented in Appendix D.

Figure 3.12 Absolute FQY measurements in 3-pentanone vapor for a) 248 b) 266 c) 277 and d) 308 nm excitation at several temperatures. Error bars represent 6% uncertainty.
Figure 3.13 Absolute FQY variation for 248, 266, and 308 nm excitation in nitrogen or air at 1.3 bar total pressure. Current measurements are made with 3-pentanone partial pressure of 20 mbar. The current work follows similar trends as previous work [28]. Error bars represent 6% uncertainty.

The current work can be compared to previous measurements of relative FQY [28], scaled to absolute FQY using the room-temperature value measured in this work, shown in Figure 3.13. Generally, the current work is consistent with trends observed in the previous work for all excitation wavelengths. For 308 nm excitation, the current work shows good agreement with Koch and Hanson, but, for 248 and 266 nm excitation, the FQY in the current work is lower by about 10%. One contributing factor is uncertainty in the composition of the cell mixture. Koch and Hanson utilized a bubbler system to seed their optical cell and assumed the vapor was saturated with 3-pentanone to infer tracer number density. The current work, however, meters the 3-pentanone and nitrogen gas mixture resulting in direct knowledge of the composition. Moreover, the difference in 266 nm absorption cross-section discussed in section 3.6.1 contributes to the discrepancy. Nonetheless, both studies show similar trends in FQY with temperature.
Figure 3.14 Comparison of absolute FQY measurements made at room temperature (295 K). Current work and measurements from [16] made at 20 mbar of 3-pentanone; measurements from [41] made at 13 mbar. Error bars represent uncertainties from their respective studies.

Figure 3.14 compares room-temperature 3-pentanone absolute FQY measurements from the current work to previous measurements at low 3-pentanone pressures [16, 41]. The current work is consistent with previous work by Koch et. al. for 248 and 266 nm excitation. For 308 nm excitation, the current work is about 10% lower, but still within the 15% error of the previous work, as shown in the figure. However, the current measurements are approximately 3 times smaller than the FQY measured by Hansen and Lee, and this discrepancy may be due to uncertainty in the absolute FQY of the reference species. Measurements from Hansen and Lee were calibrated to acetone fluorescence at 313 nm excitation, and the acetone FQY was taken from the literature [73]. However, a survey shows that there is poor agreement among different measurements of acetone FQY at this excitation wavelength [16, 74, 75]. These measurements are summarized in Table 3.1. As the table shows, published acetone FQY values cover a large range, and this uncertainty in the reference value may be the root cause of the differences in measured 3-pentanone FQY.
<table>
<thead>
<tr>
<th>Study</th>
<th>FQY x 10^4</th>
<th>Wavelength (nm)</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heicklen and Noyes</td>
<td>2.07</td>
<td>313</td>
<td>103-271 mbar, 313 K</td>
</tr>
<tr>
<td>Halpern and Ware</td>
<td>1.20</td>
<td>313</td>
<td>267 mbar in air, 298 K</td>
</tr>
<tr>
<td>Luckey and Noyes</td>
<td>2.00</td>
<td>313</td>
<td>200 mbar, 323 K</td>
</tr>
<tr>
<td>Koch et. al.</td>
<td>0.71</td>
<td>308</td>
<td>20 mbar, 297 K</td>
</tr>
</tbody>
</table>

Table 3.1 Published values of acetone FQY near 312 nm [16, 73-75].

3.7 Model Development

Low-pressure measurements of FQY are motivated by the need for insight into the collisionless processes of fluorescence and collisionless non-radiative de-excitation. The addition of nitrogen and air, even at pressures of 1.3 bar, can significantly increase the FQY, demonstrating how collisional processes like vibrational relaxation become important even at atmospheric pressure. In this study, the vibrational energy dependence of the fluorescence rate \( k_f \) and non-radiative de-excitation rate \( k_{nr} \) were investigated using the absolute FQY data from section 3.6.3 for 3-pentanone vapor at the lowest available pressures, around 10 mbar. This data is shown in Figure 3.15 as a function of the initial vibrational energy \( E_1 \), calculated using equation (3.2). With updated \( k_f \) and \( k_{nr} \) expressions, the temperature dependence of the vibrational relaxation cascade parameter for 3-pentanone \( \alpha_{3p} \) can also be optimized using absolute FQY data from section 3.6.3 over a range of 3-pentanone vapor pressures.

3.7.1 Determination of Fluorescence Rate \( k_f \)

According to equation (3.1), \( k_f \) can be determined with low-pressure FQY data and knowledge of \( k_{nr} \). Fortunately, \( k_{nr} \) can be determined from the observed fluorescence lifetime \( \tau_f [s] \) at low pressures by

\[
k_{nr}(E_1) = \frac{1}{\tau_f(E_1)} \tag{3.16}
\]
Figure 3.15 Variation of absolute FQY for 3-pentanone vapor for pressures around 10 mbar with initial vibrational energy $E_1$. Previous measurements are shown for comparison [16]. Error bars correspond to 6% uncertainty in FQY measurements.

Hansen and Lee made measurements of $\tau_f$ at room temperature over a range of wavelengths, and Ossler and Alden made measurements of $\tau_f$ at 266 nm excitation over a range of temperatures [41, 58]. Zimmerman repeated measurements at Ossler and Alden’s conditions and claimed to have similar results [76]. Figure 3.16 shows $k_{nr}$ as a function of vibrational energy determined from $\tau_f$. From 1000 to 6000 cm$^{-1}$, $k_{nr}$ remains roughly constant, and at energy levels greater than 11000 cm$^{-1}$, $k_{nr}$ increases rapidly. As indicated in the figure, one data point from Hansen and Lee is ignored because the measured lifetime was 2.1 ns, close to the time resolution of 2.0 ns for the study.

With this knowledge of $k_{nr}$ and with the low-pressure FQY data, $k_f$ can be calculated. Figure 3.17 shows $k_f$ as a function of vibrational energies calculated from the current FQY data, as well as calculated with low-pressure FQY measurements from [16]. The value of $k_{nr}$ at 10500 cm$^{-1}$ was calculated by linear interpolation of the lifetime data from Ossler and Alden. The error bars (17%) on $k_f$ measurements are a combination of
the uncertainty in the $\tau_f$ measurement (15% for both studies) and the uncertainty in the FQY measurements (6.3%). From about 2000 to 13000 cm$^{-1}$, $k_f$ is constant within the indicated error, and the current work agrees with previous measurements at the coincident vibrational energies [16].

![Figure 3.16](image.png)

Figure 3.16 $k_{nr}$ as a function of vibrational energy $E_1$ calculated from $\tau_f$ data [41, 58]. The indicated data point is ignored because the lifetime measured in the study was similar to the time resolution. Error bars represent uncertainties in their respective studies.

The fluorescence rate $k_f$ has previously been considered to be a constant with vibrational energy [50], and previous models of acetone and 3-pentanone FQY made this assumption [17, 31]. The constancy of the fluorescence rate can be examined using the Strickler-Berg equation for radiative lifetime [77], which is analogous to the relationship between the Einstein $A$ and $B$ coefficients for atomic transitions. The Strickler-Berg equation shows that the fluorescence rate is dependent on the cube of the average fluorescence frequency. The results from the thesis have shown that the fluorescence spectrum for pure 3-pentanone vapor remains constant for all excitation wavelengths over a range of temperatures. Thus, the average fluorescence frequency remains constant and $k_f$ should also be a constant. The measurements in the current work confirm the constant
$k_f$ assumption in the vibrational energy range from 2000 to 13000 cm$^{-1}$, and the overall rate was determined by averaging the data points in Figure 3.17 and assumed to be valid across all vibrational energies.

The average is shown in Table 3.2 along with the rate from Koch et. al., which is about 11% higher [31], and the discrepancy is because the current work averages more data points across a wider range of vibrational energies than Koch. The rate determined by Hansen and Lee is significantly higher due to the discrepancy in FQY values previously described. The $k_f$ value from the current work is consistent with previous measurements for several other ketones, including acetone, and aldehydes, including formaldehyde, that range from $10^5 – 10^6$ s$^{-1}$ [50]. Furthermore, a $k_f$ of 1.1 x $10^5$ s$^{-1}$ was estimated using the Strickler-Berg equation [77], which is about a factor of three smaller than the measured value. This discrepancy is because the equation is better suited for strong transitions, but for weak transitions, it can generally predict the order of magnitude of $k_f$. Thus, the measurement of $k_f$ from the current work is consistent with previous work.

![Figure 3.17](image)

Figure 3.17 Fluorescence rate $k_f$ as a function of vibrational energy calculated from FQY measurements and lifetime data from [41, 58]. Comparison is made to previous calculations of $k_f$ [31]. Error bars are for the 17% combined uncertainty in the FQY measurements and lifetime data.
<table>
<thead>
<tr>
<th>Study</th>
<th>Fluorescence rate $k_f \times 10^5 \text{ s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>3.70</td>
</tr>
<tr>
<td>Koch</td>
<td>4.15</td>
</tr>
<tr>
<td>Hansen and Lee</td>
<td>11.00</td>
</tr>
</tbody>
</table>

Table 3.2 Fluorescence rate determined in the current work as well as by previous work [31, 41].

### 3.7.2 Determination of Non-radiative Rate $k_{nr}$

Once the value of $k_f$ has been determined, $k_{nr}$ can be calculated from the FQY data over a range of vibrational energies using equation (3.1). Figure 3.18 shows $k_{nr}$ determined from the FQY data as a function of vibrational energy compared to $k_{nr}$ determined from lifetime data. The current work shows good agreement with the previous work. However, the current work shows a slight dip in $k_{nr}$ at 10500 cm$^{-1}$ compared to Koch’s model and extends knowledge of $k_{nr}$ to 15100 cm$^{-1}$, a higher vibrational energy level than in previous work [41, 58].

<table>
<thead>
<tr>
<th>Study</th>
<th>Non-radiative rate $k_{nr} \text{ (s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>$k_{nr} = 4.00\times10^8 + 1.80\times10^7 \exp\left(\frac{E-1175}{500}\right) + \frac{2.26\times10^{12}}{\pi} \frac{2650}{4(E-10340)^2+2650^2} + \frac{9.44\times10^9}{\sqrt{\pi/2}} \exp\left(-2\left(\frac{E-17800}{5490}\right)^2\right)$</td>
</tr>
<tr>
<td>Koch</td>
<td>$k_{nr} = 3.78\times10^8 + 8.15\times10^6 \exp\left(\frac{E}{2466}\right) + 216 \exp\left(\frac{E}{10220}\right)$</td>
</tr>
</tbody>
</table>

Table 3.3 Non-radiative rate expression determined from FQY measurements in the current work. $E$ is in units of cm$^{-1}$. The expression from the Koch model is shown for comparison [31].

The current work updates the formula fit of $k_{nr}$ as a function of vibrational energy using the measurements of $k_{nr}$. The general strategy of the fit was to sum functions that fit $k_{nr}$ over various ranges of vibrational energy, but are insignificant outside that range. The
The first component of the fit is a constant offset that fits the $k_{nr}$ data between 3000 and 6000 cm$^{-1}$. The second component is an exponential function to account for the slight rise in $k_{nr}$ at energies below 3000 cm$^{-1}$. The rise of $k_{nr}$ at energies above 6000 cm$^{-1}$ to the peak centered at about 10000 cm$^{-1}$ is fit using a Lorentzian centered at 10340 cm$^{-1}$. Finally, the rise of $k_{nr}$ at energies above 11000 cm$^{-1}$ is fit using a Gaussian centered 17800 cm$^{-1}$.

Figure 3.18 $k_{nr}$ as a function of vibrational energy calculated from constant $k_f$ and FQY measurements. The current work shows good agreement with previous work [41, 58]. Fits to expressions from the current work and previous work are also shown [31].

The expression is shown in Table 3.3, as well as the previous fit from [31], and both expressions are plotted in Figure 3.18. The current fit shows good agreement with $k_{nr}$ data across all vibrational energies, while the Koch expression underpredicts $k_{nr}$ above 12700 cm$^{-1}$. This difference is because Koch used FQY data in 1 bar of nitrogen with 248 nm excitation to fit his $k_{nr}$ expression at higher energy levels [31], but as the current work shows, the addition of nitrogen at 1 bar increases the FQY due to vibrational relaxation, resulting in the calculation of a lower $k_{nr}$ value.
3.7.3 3-pentanone Self-collision Vibrational Relaxation

By measuring the FQY as a function of 3-pentanone vapor pressure, insight can be gained into the vibrational relaxation characteristics of tracer to tracer collisions. The vibrational relaxation energy cascade is defined by the cascade parameter $\alpha$, which has a dependence on the identity of the collider and the temperature. Previous work has considered the vibrational relaxation cascade parameter for 3-pentanone collisions, $\alpha_{3p}$, to be a constant with temperature [31]. However, as the measurements show, the FQY remains constant with pressure at higher temperatures, indicating that no vibrational relaxation is occurring. Thus, the current work shows that $\alpha_{3p}$ should decrease with increasing temperature, contrary to what previous work had assumed. Using the model structure described in Chapter 2, a new expression for $\alpha_{3p}$ was optimized using 3-pentanone FQY data from 10 to 30 mbar and updated $k_f$ and $k_{nr}$ expressions from the current work. The fit was performed by determining the appropriate $\alpha_{3p}$ value that produced the best model agreement with FQY data at each temperature and fitting a temperature-dependent exponential expression to the resulting values of $\alpha_{3p}$. The updated $\alpha_{3p}$ expression is shown in Table 3.4.

<table>
<thead>
<tr>
<th>Study</th>
<th>3-pentanone vibrational relaxation cascade parameter (−)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>$\alpha_{3p} = 15.4 \exp\left(-\frac{T}{65.55}\right) + 0.00238$</td>
</tr>
<tr>
<td>Koch</td>
<td>$\alpha_{3p} = 0.15$</td>
</tr>
</tbody>
</table>

Table 3.4 Vibrational relaxation cascade parameters for 3-pentanone determined from FQY measurements in the current work. $T$ is in units of K. The expression from the Koch model is shown for comparison [31].

3.7.4 Model Performance

Table 3.5 summarizes the updated expressions for the 3-pentanone FQY model based on the low-pressure data, and Figure 3.19 shows the performance of the updated
model at vapor pressures of 10 to 30 mbar across a range of temperatures. The results from the Koch model are also shown on the figure for comparison.

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence rate ( k_f ) (s(^{-1}))</td>
<td>( k_f = 3.70 \times 10^5 )</td>
</tr>
<tr>
<td>Non-radiative rate ( k_{nr} ) (s(^{-1}))</td>
<td>[ k_{nr} = 4.00 \times 10^8 + 1.80 \times 10^7 \exp \left( \frac{E - 1175}{500} \right)^2 ] + [ \frac{2.26 \times 10^{12}}{\pi} \frac{2650}{4(E - 10340)^2 + 2650^2} + \frac{9.44 \times 10^9}{\sqrt{\pi/2}} \exp \left( -2 \left( \frac{E - 17800}{5490} \right)^2 \right) ]</td>
</tr>
<tr>
<td>3-pentanone cascade parameter ( \alpha_{3p} ) (( - ))</td>
<td>( \alpha_{3p} = 15.4 \exp \left( - \frac{T}{65.55} \right) + 0.00238 )</td>
</tr>
</tbody>
</table>

Table 3.5 Summary of updated model parameters from the current work. \( E \) is in units of cm\(^{-1}\) and \( T \) is in units of K.

The updated model shows agreement with the low-pressure FQY data within 8% across all conditions. For 248 nm excitation, the model shows excellent agreement with the FQY data across the temperature and pressure range, and significantly improves on the performance of the Koch model. For 266 and 277 nm excitation, the model shows excellent agreement with the data, except at 650 K, where the model differs from the data by up to 8%. These conditions correspond to vibrational energies of about 11000 cm\(^{-1}\), where \( k_{nr} \) begins to rapidly rise with increasing vibrational energy. This rise has been hypothesized to be the result of an increase in IC rate contribution to \( k_{nr} \) [59], but further work clarifying the ISC and IC rates would assist in improving the model agreement at these wavelength and temperature conditions. This performance is an improvement over the performance of the Koch model, which generally performs similarly at lower temperatures, but breaks down at higher temperatures. For 308 nm excitation, both the model in the current work and the Koch model show similar performance and differ from the FQY data by about 5%. This discrepancy could be also be improved by further
measurements characterizing ISC and IC. Thus, the model optimized using low-pressure FQY data in the current work shows significant improvement over the previous model. The MATLAB code used to perform the model calculations is shown in Appendix E.

Figure 3.19 Comparison of absolute FQY data for 10 to 30 mbar of 3-pentanone and a) 248 b) 266 c) 277 and d) 308 nm excitation to current and previous models [31]. Error bars are equivalent to 8%.
3.8 Low-pressure Photophysics Conclusions

Absolute FQY measurements were made for 3-pentanone at temperatures from 295 to 690 K, and at pressures of 10 to 30 mbar, for excitation wavelengths of 248, 266, 277, and 308 nm. In addition, absolute FQY measurements were also made for this temperature range for 20 mbar of 3-pentanone in nitrogen and for 20 mbar of 3-pentanone in air for temperatures from 295 to 485 K at 1.3 bar of total pressure. Fluorescence signals were calibrated for the efficiencies of the collection optics, spectrograph, and ICCD camera using nitrogen Rayleigh scattering. The FQY measurements are in excellent agreement with previous work utilizing a similar calibration method. While there is significant disagreement with previous measurements calibrated using acetone fluorescence, the large variation in published FQY values for acetone introduces significant uncertainty in that previous work.

Measurements of absorption cross-section were also made for excitation wavelengths of 248, 266, 277, and 308 nm from 295 to 690 K. The data are in excellent agreement with previous work, and agree well with previously published Gaussian fit of the absorption spectrum.

The low-pressure data was used to optimize a previously proposed FQY model and allows for insight into the fluorescence rate $k_f$ and the intramolecular non-radiative deactivation rate $k_{nr}$. The data was also used to optimize the vibrational relaxation cascade parameter $\alpha_{3p}$. The updated model shows good agreement with 3-pentanone FQY data for pressures of 10 to 30 mbar and temperatures of 295 to 690 K.

The current work combines ISC and IC rates into a single rate, but future work could investigate these rates separately. Insight into the ISC rate could be derived from an examination of the triplet population via the yield of photolysis products like CO, since photolysis of 3-pentanone has been postulated to occur from the triplet state. Phosphorescence may be another candidate process for monitoring the triplet population. Improved understanding of these processes would be beneficial to improving model performance.
Another area for future work is creating a similar database of low-pressure fluorescence lifetimes over a wide range of temperature and excitation wavelengths. As the current work demonstrates, fluorescence lifetime can provide insight into the non-radiative de-excitation of the first excited singlet. A fluorescence lifetime database coupled with an FQY database at low pressures and a wide range of temperatures and excitation wavelengths would allow for significant insight into the collisionless processes of the excited singlet.
Chapter 4 Measurements and Modeling of 3-pentanone FQY at Extended $T \& p$

This chapter presents measurements of 3-pentanone FQY over a wide range of temperatures and pressures in nitrogen and air bath gases. A custom-built optical cell capable of simultaneous high-pressure and high-temperature conditions was used to collect these data, and the results were used to optimize the 3-pentanone FQY model for applications over a wide range of temperatures and pressures.

4.1 Extended $T \& p$ Photophysics Background

3-pentanone tracer-based PLIF is commonly used as a diagnostic for ICE studies and has been used to spatially measure temperature and fuel distribution at different times in the pre-ignition phase of the engine cycle [14, 24-26]. Obtaining information in this application requires knowledge of the FQY over a wide range of temperature, excitation wavelength, pressure, and composition, including combined high-pressure, high-temperature conditions corresponding to top dead center in an ICE. FQY measurements over a range of temperatures and pressures have been made by previous workers in optical cells, but, with the exception of recent measurements by Braeuer et. al., investigated temperatures have been limited to 600 K [19, 27, 29, 30]. Previous work with optical ICEs are able to achieve simultaneous high-temperature and high-pressure conditions, but the range of temperatures and pressures cannot be easily varied
independently [43, 45, 48]. In order to maximize the utility of 3-pentanone PLIF, there is a need to extend the range of temperatures and excitation wavelengths for which the pressure variation of 3-pentanone FQY is known.

A simple step-ladder kinetic model of FQY has been proposed [31], and the structure of this model was previously described in Chapter 2. The original version of the model was optimized by Koch using measurements of 3-pentanone FQY over a range of temperatures at 1 bar, as well as measurements at room temperature in nitrogen, air, and oxygen [31], and has been found to be inadequate at higher temperatures and pressures [48]. Several subsequent studies have each produced an updated model to fit their individual additional measurements of FQY, but these models are applicable only over a limited range of conditions [29, 30, 48]. This work approaches model optimization by categorizing the model parameters as collisionless or collisional. The collisionless parameters of fluorescence rate $k_f$ and non-radiative rate $k_{nr}$, as well as the vibrational relaxation cascade parameter for 3-pentanone self collisions $\alpha_{3p}$, were optimized using low-pressure FQY data, as described in section 3.7. The collisional parameters of oxygen quenching rate $k_{O2}$, nitrogen quenching rate $k_{N2}$, and vibrational relaxation cascade parameter $\alpha$, however, are not active at low pressures, and optimization of these remaining model parameters requires data over a wider range of pressures and temperatures in bath gases.

This work measured the 3-pentanone FQY across a range of excitation wavelengths, temperatures, and pressures and used these data to optimize the FQY model. Measurements were made in nitrogen for temperatures from 295 to 750 K and for pressures from 1 to 25 bar, corresponding to an ICE compression ratio of about 11:1. Data were also acquired in air from 295 to 580 K and from 1 to 25 bar. Laser excitation wavelengths of 248, 266, 277, and 308 nm were utilized. These data were used to optimize the collisional model parameters describing the vibrational relaxation and collision quenching effects of nitrogen and oxygen. The result of this work is a comprehensive database of FQY measurements and an FQY photophysical model that is applicable to diagnostic applications over a wide range of temperatures and pressures, including ICE conditions.
4.2 Experimental Setup

4.2.1 High $T$ & $p$ Optical Cell Design

![Figure 4.1 Photograph of fully assembled optical cell and tubing used to connect to gas feed lines.](image)

In order to access a wide range of temperature and pressure conditions, it was necessary to use a custom-built optical cell designed to operate at pressures between 1 and 60 bar at temperatures of up to 1000 K. The assembled cell and associated plumbing can be seen in Figure 4.1. To ease the manufacturing effort, the cell utilizes off-the-shelf components, with modifications made as necessary. The cell body is a modified High Pressure Equipment Company 20-24LF16-INC medium-pressure cross fitting. Because the cell was designed to be held at high temperatures as fluorescence data are collected, the cross fitting is made from Inconel 625 for increased strength and creep resistance at high temperature. The four windows are bolted in an orthogonal configuration using the existing ports in the fitting, and four additional ports were machined into the corners of the cell to allow gas flow in and out of the cell. Gas, preheated using a 1-m loop of 0.25 in (6.35 mm) tubing, is fed into the cell via the corner fittings in the foreground of Figure
4.1 and exhausted through the corner fittings in the background. Two ports were machined on the top of the cell to allow for thermocouple mounting.

![Diagram showing the viewport design](image)

**Figure 4.2** a) Exploded and b) cutaway views of the viewport for the optical cell. The cutaway view excludes the gland nut.

The cell viewport design is based on another high-pressure cell design [78], and exploded and cutaway views of the windows are shown in Figure 4.2. High Pressure Equipment Company 20-7LM16-INC plug fittings, made from Inconel 625, were modified to accept windows. In addition to its high-strength and low-creep properties, Inconel possesses a lower thermal expansion coefficient than stainless steel, which facilitates the sealing of the window in the holder since window materials also tend to have low thermal expansion coefficients. The window shape is a conical frustrum tapered such that the gas pressure in the cell will force the window against the holder. A conical copper gasket is sandwiched between the window and the window holder, and the window is secured into the viewport using a custom-machined stainless steel nut with a hexagonal aperture. A copper washer cushions the window from the nut, and Belleville washers are placed between the copper washer and nut to maintain pressure on the window as the Inconel window holder expands with temperature. The assembled viewports are held in the cell body using stainless steel High Pressure Equipment Company 20-2LM16 stainless steel gland nuts. Stainless steel is utilized in these assemblies, along with nickel-based anti-seize, to minimize galling during assembly. The
petroleum base of the anti-seize was baked out of the cell prior to use by holding the cell at 700 K for 8 hours while nitrogen was flowed through the cell.

Figure 4.3 Schematic of cell seeding system and pressure and temperature measurement sensors.

The windows utilized in the cell are custom made from UV-grade sapphire. Sapphire was chosen for its surface hardness and high compressive strength over a wide range of temperatures, allowing the window to be held under high compressive load by the viewport hex nut, as well as the gas pressure in the cell. The crystal axis is aligned with the center axis of the frustum, which is also the optical axis of the window. The window diameter is 0.625 in (15.875 mm) at the base and tapers to 0.5 in (12.7 mm) over a 0.5 in (12.7 mm) thickness. Once installed in the window holder, the viewing diameter 0.5 in (12.7 mm), and the beam path length between the windows is 61.7 mm.

The cell temperature was varied by heating the cell inside a Mellen Company furnace with viewports to allow for optical access to the furnace interior. No windows were used with these viewports. To monitor the gas temperature, a K-type thermocouple was mounted to the top of the cell as shown in Figure 4.1. In addition, the cell’s external surface temperature was also monitored using a second K-type thermocouple. To ensure
temperature uniformity within the cell, fluorescence data were taken only when these two thermocouples read within 5 K of each other or less.

Gas was introduced into the cell via a flowing system shown in Figure 4.3, which is identical to the system described in section 3.5 except for the removal of the MKS Baratron low-pressure transducer and the addition of a Kistler RAT50A 1-100 bar pressure transducer to measure pressure above 3 bar. For this study, the gas stream was composed of 20 mbar of 3-pentanone with excess nitrogen or air at total pressures varying from 1 to 25 bar. To achieve this composition at various pressures, the flow rates of nitrogen and air ranged from 2.5 SLPM at 1 bar to 30 SLPM at 25 bar. The pressure was also adjusted as necessary using the needle valve on the gas exhaust circuit. The pump output was adjusted to achieve the correct 3-pentanone mole fraction, and the liquid flow rate ranged from about 0.1 to 0.2 mL/min of 3-pentanone liquid. With these flow rates, the residence time of the gas in the optical cell was about 0.2 s at 2.5 SLPM and 0.017 s at 30 SLPM.

4.2.2 Laser and Collection Optics Setup

![Laser and Collection Optics Setup](image)

Figure 4.4 Optical diagnostic setup for the measurement of fluorescence and absorption.
The optical setup for this work is shown in Figure 4.4. The optical setup is identical to that in section 3.5, with the exception that an Asahi Spectra Company 325 nm high pass optical filter was placed in front of the collection lens. The spectrograph was centered at 440 nm to collect the fluorescence spectrum.

4.2.3 Experimental Setup Spectral Characterization

Figure 4.5 RSR of collection optics, spectrograph, and ICCD measured using deuterium and tungsten calibration lamps.

In order to correctly measure the shape of the fluorescence spectrum, the spectrograph and ICCD camera need to be calibrated for wavelength. In addition, raw spectral measurements need to be corrected for the relative spectral responsivity (RSR) of the collection optics, spectrograph, and ICCD camera. Calibration lamps, placed as shown in Figure 4.4, were used to calibrate the spectrograph wavelength and determine the RSR of the optical cell and collection optics. For the calibration, only the viewport between the laser beam and the collection optics was installed in the cell body.

The wavelength calibration of the spectrograph was performed with 5 lines from a Newport 6035 Hg(Ar) calibration lamp, and the range of the spectrograph was
determined to be 318.4 to 563.7 nm. The RSR of the collection optics was determined using two calibration lamps. A Newport 63979 30 W deuterium lamp was used to calibrate the RSR of the system from 318 to 370 nm. An Optronic Laboratories OL-550 75 W tungsten lamp was used to calibrate the RSR above 350 nm. The lamps were warmed up for at least 30 minutes following manufacturer’s instructions to ensure the stability of the lamp output. The deuterium lamp output was collected over an exposure time of 800 μs; the tungsten lamp output was collected over 20 μs. The output from the spectrograph was normalized to the manufacturer provided calibration lamp spectrum to determine the RSR, shown in Figure 4.5. The RSR is highest at 319 nm and decreases with increasing wavelength to about 10% of that value at 563 nm.

4.3 Fluorescence Measurement Results

![Sample fluorescence image taken by the ICCD camera, corrected for background. The fluorescence spectrum, taken from the central 100 rows and corrected for RSR, is also shown. To determine the total fluorescence signal, the spectrum is integrated from 318 to 563 nm. This image and spectrum is for 20 mbar of 3-pentanone in 9 bar of nitrogen at 298 K with 248 nm excitation.](image)

Figure 4.6 Sample fluorescence image taken by the ICCD camera, corrected for background. The fluorescence spectrum, taken from the central 100 rows and corrected for RSR, is also shown. To determine the total fluorescence signal, the spectrum is integrated from 318 to 563 nm. This image and spectrum is for 20 mbar of 3-pentanone in 9 bar of nitrogen at 298 K with 248 nm excitation.
In this work, the cell is heated to a set temperature, and the fluorescence signal is measured as total pressure is varied. Fluorescence signal was measured by imaging the spectrograph output using the ICCD camera, which accumulated signal over a minimum of 400 laser pulses to improve the SNR. At higher temperatures, up to 1000 images were accumulated due to low levels of signal. The image was corrected with a background image taken with only bath gas flowing through the cell. The fluorescence spectrum was determined by summing the middle 100 rows of the background corrected image and normalizing for the RSR. Figure 4.6 shows a sample background corrected image and the resulting fluorescence spectrum.

4.3.1 Fluorescence Spectrum

Previous work with acetone has found that the fluorescence spectrum is invariant with temperature [17], and this assumption had been carried over to 3-pentanone [28]. While measurements presented in section 3.6 show this assumption is true for 3-pentanone fluorescence spectrum of pure vapor up to 642 K, in the presence of nitrogen there is variation with temperature. The current work expands the temperature and pressure range for measurements of fluorescence spectra in nitrogen and air. Figure 4.7 shows fluorescence spectra for 248 and 308 nm excitation at 1.3 bar and 25 bar in nitrogen with a 3-pentanone partial pressure of 20 mbar for temperatures between 298 and 745 K. For 308 nm excitation, the peak shifts slightly to the blue, and the spectrum to the left of the peak widens by about 20 nm between 298 and 745 K, while the spectrum remains unchanged to the right of the peak. This blue shift may be the result of fluorescence from higher vibrational energy levels in the upper electronic state. In addition, at a fixed temperature, the addition of nitrogen has no effect on the spectrum, showing that vibrational relaxation has little effect on the upper state population at this excitation wavelength.
Figure 4.7 Variation of 3-pentanone fluorescence spectrum with temperature for 1.3 bar and 25 bar of nitrogen. Spectra are shown for a) 248 and b) 308 nm excitation. For both wavelengths, the fluorescence spectrum widens and shifts to the blue with increasing temperature.

Figure 4.8 Comparison of 3-pentanone fluorescence spectra in nitrogen and air for several temperatures and excitation wavelengths shows that the addition of oxygen has little effect.
For 248 nm excitation, the same blue shift in the peak occurs as for 308 nm excitation. Unlike 308 nm excitation, though, the fluorescence spectrum widens on both sides of the peak. In addition, the curvature of the spectrum to the left of the peak changes with increased temperatures. The change in fluorescence spectrum shape may be due to the rapid increase in non-radiative rate at high vibrational energies. Increasing the nitrogen pressure significantly narrows the fluorescence spectrum and restores the original spectral curvature, illustrating the significant effect of vibrational relaxation. These results show that temperature and nitrogen pressure have an effect on the shape of the fluorescence spectrum, contrary to previous assumptions.

Previous measurements of the fluorescence spectrum found that, at room temperature, the fluorescence spectrum does not vary with the addition of oxygen [28]. Current work also found that this observation held at higher temperatures. Figure 4.8 compares the fluorescence spectrum for several pressure and temperature conditions. At these conditions, the replacement of nitrogen with air has no effect on the fluorescence spectrum, reaffirming that oxygen has little effect on the fluorescence spectrum.

4.3.2 FQY Measurements

To determine the total fluorescence signal, the measured spectrum was integrated across the spectrograph range and corrected for laser energy and absorption of the beam energy as it traverses the cell. The FQY can be determined by calibrating the total signal normalized for tracer number density and the laser energy to the known FQY at a reference condition. At a fixed temperature, the absorption cross-section is a constant, and thus, is not a factor in the calculation. The FQY can then be calculated using

\[
\phi = \frac{S_{\text{LIF}}}{S_{\text{LIF},0}} \frac{E_0 n_0}{En} \phi_0
\]  

Variables denoted with a ‘0’ subscript represent quantities measured at the reference conditions. Because of the availability of absolute FQY measurements for 20 mbar of 3-pentanone in nitrogen up to 690 K and air up to 490 K at 1.3 bar total pressure, as described in section 3.6, the 1.3 bar pressure condition was chosen as the reference. Laser energy-corrected fluorescence signal per molecule \((S_{\text{LIF}}^*)\) measurements were made.
relative to the signal at the reference pressure, and then scaled to absolute FQY using equation (4.1).

For higher temperatures, the reference condition was chosen to be 1.3 bar and 295 K. In this case, it is also necessary to normalize $S_{LIF}^*$ for absorption cross-section. This calculation is expressed by

$$\phi = \frac{S_{LIF}^*(T, p)}{S_{LIF}^*(T, 1.3 \text{ bar})} \frac{S_{LIF}^*(295 \text{ K, 1.3 bar})}{\sigma(T)} \phi_0$$

(4.2)

where $S_{LIF}^*(T, p)$ is the fluorescence signal per molecule at temperature $T$ and pressure $p$, and $\sigma$ is the absorption cross-section. The absorption cross-section was determined using a published expression [39], and measurements were made of $S_{LIF}^*$ variation over a range of temperatures at 1.3 bar pressure.

Figure 4.9 shows relative $S_{LIF}^*$ as a function of temperature for 248, 266, 277, and 308 nm for 20 mbar of 3-pentanone in nitrogen up to 800 K, as well as in air up to 570 K, at a total pressure of 1.3 bar. The data in air is limited in temperature due to
observed reduction in fluorescence signal at temperatures above 600 K, possibly due to the oxidation of 3-pentanone. At 570 K, the fluorescence signal did not vary with air gas flow rate at 1.3 bar, confirming that oxidation was not occurring. $S^*_{LIF}$ determined from absolute FQY measurements in section 3.6 are also plotted in the figure for comparison and show excellent agreement with the current work. Moreover, the results show that, up to 570 K, $S^*_{LIF}$ variation is identical for either gas, consistent with previous work [28].

Figure 4.10 Relative $S^*_{LIF}$ with temperature in nitrogen at 1-1.3 bar total pressure. Generally, the current work agrees well with previous work [19, 27-30, 42]. Error bars indicate 7% uncertainty.

In Figure 4.10, measurements from other work in 1 bar of air or nitrogen are plotted against the nitrogen measurements of the current work for comparison [19, 27-30, 42]. The temperature variation of the current work generally agrees with previous measurements within the measurement error, although at 266 nm, the current data are lower than those of Koch and Hanson by about 20% [28]. Koch and Hanson introduced 3-pentanone into the optical cell by bubbling nitrogen through flasks of 3-pentanone and
inferred the tracer number density by assuming the bath gas was saturated with 3-pentanone [28]. In this work, 3-pentanone and nitrogen are metered, resulting in direct knowledge of the tracer number density and lower uncertainties in tracer number density.

Figure 4.11 Variation of absolute FQY with pressure in nitrogen at various temperatures for a) 248 nm b) 266 nm c) 277 nm and d) 308 nm excitation. The data is compared to previous work [30, 31]. Error bars indicate 7% uncertainty.

Measurements of 3-pentanone FQY were made for 20 mbar of 3-pentanone in nitrogen from 295 K to 750 K for pressures of 1 to 25 bar, and in air from 295 K to 570 K for pressures of 1 to 25 bar, shown in Figure 4.11 and Figure 4.12, respectively. These
measurements are scaled from $S_{LIF}^*$ using equations (4.1) or (4.2) as appropriate. The primary sources of uncertainty are the value of the absolute FQY at the reference condition and the measurement of fluorescence signal normalized for laser energy, resulting in an overall uncertainty of about +/- 7%. These data are tabulated in Appendix C, and an uncertainty analysis is presented in Appendix D.

Figure 4.12 Variation of absolute FQY with pressure in air at various temperatures for a) 248 nm b) 266 nm c) 277 nm and d) 308 nm excitation. The data is compared to previous work [19, 27, 29-31]. Error bars indicate 7% uncertainty.
There are previous measurements of relative FQY variation with pressure across a range of temperatures and pressures for 248, 266, 277 and 308 nm excitation in nitrogen and air to which the current measurements can be compared [19, 27, 29-31]. For comparison purposes, these previous measurements are scaled to absolute FQY using equations (4.1) or (4.2) as appropriate. Figure 4.11 shows a comparison of this work with previous data in a nitrogen bath gas. Measurements of relative FQY variation with pressure up to 6 bar are available for room temperature and 248, 266, and 308 nm excitation, which have excellent agreement with the current work [31]. In addition, data are available at higher temperatures for 266 nm excitation from Modica et. al. and show a significantly larger increase in FQY with pressure than the current work [30]. The discrepancy may be due to the extremely high laser pulse energy (28 mJ) utilized by Modica et. al. This previous work also presents measurements in air that are inconsistent with the current work and other previous work, as the following comparison shows.

Figure 4.12 shows a comparison of the current measurements to previous work in an air bath gas, and generally, the current work is consistent with previous work. The largest inconsistency is seen with Modica et. al. As with the measurements in nitrogen, previous measurements in air for 266 nm excitation show a significantly larger increase in FQY with pressure than the current work [30]. However, the current work agrees well with previous measurements by Fujikawa et. al. for 266 nm excitation and 248 nm excitation, as well as for previous data up to 6 bar at room temperature [31]. At higher temperatures, work by Braeuer et. al. at 423 K is 15% higher than the current data, while measurements at 573 K show good agreement [29]; the source of this discrepancy is not immediately apparent. Finally, measurements by Grossman et. al. using 248 and 277 nm excitation are in good agreement up to 473 K, but show a 10% decrease in signal with pressure at 523 K [19]. This discrepancy may be due to oxidation of 3-pentanone, which may occur at this temperature since the gases were held at elevated temperatures in a static optical cell in the previous work.
4.4 Model Development

In addition to the FQY measurements described in the previous section, quantitative 3-pentanone PLIF diagnostics require the development of an FQY model. From the description of the model in section 2.5, several parameters from the model can be optimized using FQY data: the fluorescence rate $k_f$, non-radiative rate $k_{nr}$, the vibrational relaxation cascade parameter $\alpha$, oxygen quenching rate $k_{O2}$, and nitrogen quenching rate $k_{N2}$.

Section 3.7 describes the optimization of collisionless parameters in the FQY model, namely $k_f$ and $k_{nr}$, using low-pressure FQY data, as well as vibrational relaxation cascade parameter for 3-pentanone $\alpha_{3p}$. However, to extend the model applicability to ICE conditions, it is necessary to account for vibrational relaxation and collisional quenching, which occur when bath gas and 3-pentanone molecules collide. This work considers collisional quenching by both nitrogen and oxygen, represented by the rates $k_{N2}$ and $k_{O2}$, respectively. The vibrational relaxation cascade parameters $\alpha_{N2}$ and $\alpha_{air}$ for nitrogen and air, respectively, are also optimized. The current work provides 3-pentanone FQY data across a wide range of pressure, temperatures, and excitation wavelengths in nitrogen and air, allowing for optimization of parameters in the model related to these processes.

4.4.1 Collisional Quenching and Vibrational Relaxation

Background

Generically, collisional quenching is the deactivation of the 3-pentanone molecule from the excited singlet to another electronic state due to collisions with bath gas molecules. This deactivation does not release a photon, thereby quenching the fluorescence signal. A common mechanism for collisional quenching is collisionally-assisted ISC, where collisions between excited molecules and other species result in the deactivation of the excited molecule into the triplet. The excited singlet molecule and the bath gas molecule collide to form an intermediate collision complex [64, 65]. If the complex has a configuration that facilitates spin-orbit coupling of the excited singlet
molecule, the complex decomposes into the triplet molecule and the bath gas molecule. Collisionally-assisted ISC is a well-documented phenomenon in liquid solutions [62], and previous work has documented this process occurring in the gas phase for aromatics with xenon bath gas [63].

The current work considers collisional quenching of 3-pentanone with nitrogen and oxygen molecules. Previous work has stated that nitrogen quenching is an insignificant effect [31], but this conclusion is based on a limited set of FQY measurements in nitrogen over a limited range of temperatures. The availability of data across a wide range of conditions in the current work allows further investigation of nitrogen quenching.

For ketones and other organic molecules, oxygen quenching is a well-documented effect [57]. Oxygen quenching is effective in ketones because, in addition to collisionally-assisted ISC, oxygen quenching can occur via collisionally-assisted IC and interaction between the electronic levels of the oxygen molecule and the ketone molecule [57]. The quenching rate \( k_{O_2} \) has been previously modeled using a bimolecular collision rate [31], given by

\[
k_{O_2} = q_{O_2}(E)Z_{3p-O_2} n_{O_2}
\]  

(4.3)

where \( q_{O_2} \) is the vibrational energy-dependent quenching efficiency, \( Z_{3p-O_2} \) is the collision frequency calculated using Lennard-Jones formulation, and \( n_{O_2} \) is the oxygen number density. This thesis used FQY data in air to optimize the quenching efficiency.

The other collisional process of interest is vibrational relaxation, in which collisions between excited molecules and other species cause the decay of vibrational energy in the excited molecule towards the thermal energy level. While this process plays important roles in photochemistry and chemical kinetics, work is ongoing to obtain a fundamental understanding of the process [61].

The current work uses FQY data to optimize the vibrational relaxation cascade parameter, which controls relaxation as described in section 2.5. Upon absorption of a photon, the molecule enters an elevated vibrational energy level in the excited singlet described by
\[ E_i = \frac{10^7}{\lambda} + E_{\text{thermal}} - E_{0-0} \]  

where \( \lambda \) is the wavelength of the photon in nm and \( E_{0-0} \) is the zero-point energy difference between the excited and ground singlet states. As excitation wavelength and temperature increase, the molecule will be driven into a higher \( E_1 \). The loss in vibrational energy per collision is determined by \( \alpha \) and given by

\[ \Delta E_{\text{col}} = \alpha \left( E - E_{\text{thermal}} \right) \]  

where \( E \) is the vibrational energy and \( E_{\text{thermal}} \) is the thermal energy level. When multiple species are present, the total \( \alpha \) is an average of \( \alpha_M \) for each species \( M \) weighted by the relative collision rate of that species, as described by equation (2.21). Section 3.7 describes the determination of \( \alpha_{3p} \) for 3-pentanone collisions, and this section will utilize FQY data in nitrogen and air to determine \( \alpha_{N2} \) and \( \alpha_{O2} \).

<table>
<thead>
<tr>
<th>Polyatomic</th>
<th>Collider</th>
<th>( E - E_{th} ) (cm(^{-1}))</th>
<th>( \Delta E ) (cm(^{-1}))</th>
<th>( \alpha )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azulene</td>
<td>( N_2 )</td>
<td>14021</td>
<td>136</td>
<td>0.010</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>( N_2 )</td>
<td>13940</td>
<td>175</td>
<td>0.013</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>( O_2 )</td>
<td>13940</td>
<td>160</td>
<td>0.011</td>
<td>[80]</td>
</tr>
<tr>
<td>Toluene</td>
<td>( N_2 )</td>
<td>21640</td>
<td>130</td>
<td>0.006</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td>( O_2 )</td>
<td>21640</td>
<td>160</td>
<td>0.007</td>
<td>[81]</td>
</tr>
<tr>
<td>Biphenylene</td>
<td>( N_2 )</td>
<td>10000</td>
<td>145</td>
<td>0.015</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>( O_2 )</td>
<td>10000</td>
<td>153</td>
<td>0.015</td>
<td>[82]</td>
</tr>
<tr>
<td>Pyrazine</td>
<td>( N_2 )</td>
<td>24000</td>
<td>60</td>
<td>0.003</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td>( O_2 )</td>
<td>24000</td>
<td>74</td>
<td>0.003</td>
<td>[83]</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>( N_2 )</td>
<td>18000</td>
<td>110</td>
<td>0.006</td>
<td>[84]</td>
</tr>
</tbody>
</table>

Table 4.1 Summary of vibrational relaxation energy loss per collision between hydrocarbons and bath gases from previous studies [79-84].
Previous work allows some insight into the magnitude and dependencies of the vibrational energy loss per collision $\Delta E_{\text{coll}}$ and, thereby, $\alpha$. Investigations into gas phase relaxation has focused primarily on cyclic molecules [61], and, to the author’s knowledge, there has been no work specifically investigating the vibrational relaxation of ketones, though work has been performed for the carbonyl ethyl acetate. $\Delta E_{\text{coll}}$ at around 300 K for these molecules with nitrogen or oxygen bath gas molecules from these studies are summarized in Table 4.1. The previous work shows that, for these hydrocarbons (with the exception of pyrazine), the average vibrational energy loss is around 100-200 cm$^{-1}$ per collision with both nitrogen and oxygen, resulting in $\alpha$ values from 0.006 to 0.014. The small amount of energy transferred compared to collisions between hydrocarbons is due to the limited modes available in the diatomic molecules.

Previous iterations of the 3-pentanone FQY model have utilized temperature-dependent expressions for $\alpha_{N_2}$ and $\alpha_{O_2}$ [29-31, 48], which is supported by previous relaxation studies in nitrogen. While work with toluene has found that there is little temperature dependence [81], previous work with azulene and biphenylene has found that $\alpha$ decreases with increasing temperature [80, 82, 85]. Work with ethyl acetate, an aliphatic carbonyl molecule like 3-pentanone, has also found that the magnitude of energy lost decreases with temperature [84]. This temperature dependence is reproduced in statistical theories, where the widening of the vibrational energy distribution with temperature results in a decrease in collisional efficiency [86]. It has also been shown in trajectory calculations for aromatics that for temperatures below the well-depth of the system, the increased efficiency of vibrational relaxation is due, in part, to contributions from collisions at large impact parameters, which, can still result in interactions and energy transfer at low temperatures [87].

Unlike the previous 3-pentanone fluorescence models, however, this work will also consider vibrational energy dependence of $\alpha$. The availability of FQY data in air and nitrogen will allow for examination of both the temperature and energy dependence of $\alpha_{N_2}$ and $\alpha_{O_2}$. Previous work with toluene has found that the rate of energy loss decreases as the vibrational energy approaches the thermal energy level [88]. Work with azulene and pyrazine have found the opposite; at higher vibrational energies, the energy loss per
collision decreases [80, 83]. Calculations for cyclopropane collision with helium using a statistical-dynamical theory suggest that the amplitude of the step-size distribution is affected by a vibrational-energy dependent fraction of inelastic collisions [89], but further work is necessary for physical insight into the vibrational energy dependence of \( \alpha \) [61].

### 4.4.2 Sensitivity Analysis and Optimization Strategy

The optimization of the model parameters relating to collisional quenching and vibrational relaxation is complicated by the fact that the FQY can be simultaneously affected by these processes. Thus, determination of these parameters involves a strategy, determined by sensitivity analysis, to isolate temperature, pressure, and excitation wavelength regimes where one process dominates the other.

![Figure 4.13 Sensitivity of 3-pentanone FQY to relaxation parameter \( \alpha \) for a) 248 nm excitation and b) 308 nm excitation for a range of temperatures and nitrogen pressures. The partial pressure of 3-pentanone is 20 mbar. The sensitivity for 248 nm excitation is significantly higher than for 308 nm excitation.](image)

The behavior of the 3-pentanone FQY in nitrogen was considered first because only one bath gas molecule is present. As the variation of FQY with pressure may depend on both vibrational relaxation and collisional quenching, a sensitivity analysis of the FQY to \( \alpha_{N_2} \) was performed over a range of pressures, temperatures, and excitation wavelengths.
to determine under what conditions vibrational relaxation is most significant. The sensitivity is given by:

\[ s = \frac{\alpha_{N2}}{\phi} \times \left| \frac{\partial \phi}{\partial \alpha_{N2}} \right| \]  

(4.6)

For this analysis, the FQY and \( \alpha_{N2} \) were calculated using the Koch model [31]. The derivative was approximated using a central difference method. The results of this analysis for 248 and 308 nm excitation are shown in Figure 4.13.

One result from this sensitivity analysis is that the sensitivity of the FQY to \( \alpha_{N2} \) is over an order of magnitude smaller for 308 nm excitation than for 248 nm excitation, showing that vibrational relaxation has almost no effect on the FQY for 308 nm excitation. At this wavelength, the molecule is excited to a vibrational energy only slightly higher than the thermal energy level \( E_{\text{thermal}} \) and is essentially fully relaxed. The sensitivity analysis indicates that an effective way to investigate collisional quenching rate \( k_{N2} \) without interference from vibrational relaxation is to use 308 nm excitation data in nitrogen.

The sensitivity analysis also indicates that the FQY is more sensitive to \( \alpha_{N2} \) at higher temperatures and pressures. For 248 nm excitation, the sensitivity begins to increase around 400 K, corresponding to an \( E_1 \) of 11400 cm\(^{-1}\) per equation (4.4), and the sensitivity is largest at around 800 K and 15 bar. As the molecule relaxes, the likelihood of fluorescing from the vibrational level increases due to variation in \( k_{nr} \), and larger variations result in a greater effect from vibrational relaxation. As shown in section 3.7, \( k_{nr} \) begins increasing rapidly around 11000 cm\(^{-1}\), corresponding to the increase in sensitivity at 400 K. This analysis indicates FQY data at high temperature and short excitation wavelength conditions, corresponding to a higher vibrational energy \( E_1 \), are more sensitive to vibrational relaxation and should be used to optimize \( \alpha_{N2} \).

With the determination of \( k_{N2} \) and \( \alpha_{N2} \), FQY data in air can be used to determine \( \alpha_{O2} \) and \( q_{O2} \). A sensitivity analysis of the FQY in air to \( \alpha_{O2} \) yields similar results as for \( \alpha_{N2} \) described previously. At longer excitation wavelengths, because the molecule is excited into an \( E_1 \) near \( E_{\text{thermal}} \) and is closer to being fully relaxed, the FQY is less sensitive to \( \alpha_{O2} \). The largest effect from vibrational relaxation occurs at high
temperatures and short wavelengths, corresponding to a high $E_1$. Thus, $q_{O2}$ optimization is best performed with long excitation wavelength data, and $\alpha_{O2}$ optimization with high temperature, short excitation wavelength data.

Figure 4.14 Sensitivity of 3-pentanone FQY to oxygen quenching rate $k_{O2}$ for a) 248 nm excitation and b) 308 nm excitation for a range of temperatures and nitrogen pressures. The partial pressure of 3-pentanone is 20 mbar.

A sensitivity analysis was performed for $q_{O2}$ at vibrational energy $E_1$ to determine the pressure and temperature conditions that would be most useful for parameter optimization, and the results of this analysis for 248 and 308 nm excitation are shown in Figure 4.14. The sensitivity is calculated by

\[ s = \frac{q_{O2}(E_1)}{\phi} \times \left| \frac{\partial \phi}{\partial q_{O2}(E_1)} \right| \]

where $q_{O2}(E_1)$ and the FQY are calculated using the Koch model and the derivative is approximated using a central difference method. The FQY is most sensitive to $q_{O2}$ at higher temperatures and shorter excitation wavelengths, corresponding to higher $E_1$. Since $q_{O2}$ increases with increasing vibrational energy, oxygen quenching has a larger effect on the FQY under these conditions. Unfortunately, $\alpha_{O2}$ also has a significant effect at these conditions. However, sensitivity to $q_{O2}$ is also increased at higher pressures because the oxygen quenching rate $k_{O2}$ is proportional to oxygen number density,
resulting in a higher oxygen quenching effect. Based on this result, FQY data in air at higher pressures and shorter wavelengths are useful in the optimization of oxygen quenching.

In summary, the sensitivity analysis provides a plan for optimizing the model parameters related to collisional processes. To minimize the effect of vibrational relaxation, the collision quenching parameters $k_{N_2}$ or $q_{O_2}$ were optimized using long excitation wavelength FQY data in nitrogen and air, respectively. Further $k_{N_2}$ optimization utilized atmospheric pressure data in nitrogen, another condition where vibrational relaxation has a lesser effect, while $q_{O_2}$ optimization also utilized high-pressure data in air as indicated by the sensitivity analysis. Short excitation wavelength FQY data, especially at higher temperatures, is utilized for the optimization of $\alpha_{N_2}$ and $\alpha_{O_2}$.

4.4.3 Optimization of Model Parameters

4.4.3.1 Nitrogen Quenching

Following the optimization strategy, the current work investigates collisional quenching using FQY data in nitrogen with 308 nm excitation over a wide range of temperatures. An examination of FQY data in nitrogen for 308 nm plotted in Figure 4.11 shows that it remains approximately constant with nitrogen pressure for temperatures from 295 to 750 K. A comparison of 1.3 bar FQY measurements with data taken at high pressures and a range of pressures in an optical engine further illustrates the constancy of the FQY with nitrogen pressure [45]. The high-pressure, high-temperature measurements were taken in an ICE, and for the current work were scaled to absolute FQY using equation (4.2). These data are plotted versus $E_1$ in Figure 4.15 and show that, at a given vibrational energy, the FQY is constant with pressure. The optimization of $k_{N_2}$ can utilize 308 nm excitation data in nitrogen at any pressure, with only consideration of $E_1$ being necessary. Moreover, the data confirm that vibrational relaxation has no significant effect on the FQY.
Figure 4.15 3-pentanone absolute FQY for pure vapor and in nitrogen at various pressures as a function of initial vibrational energy $E_1$. Comparison with engine FQY data at high pressures shows little pressure dependence for 308 nm excitation [45]. Quenching is apparent from 7000 to 12500 cm$^{-1}$. Addition of an energy-dependent nitrogen quenching rate $k_{N_2}$ improves model performance.

If vibrational relaxation has little effect on the FQY at 308 nm, and no collision quenching occurs, then one would expect that the FQY for 308 nm excitation in a nitrogen bath gas at a given pressure would be identical to the FQY for pure 3-pentanone at low-pressures, where collisional effects are insignificant. Figure 4.15 also shows a comparison between the 308 nm data in nitrogen and the pure vapor FQY data from 3.6. Up to a vibrational energy of 7000 cm$^{-1}$, the data agree well, confirming that no collision quenching is occurring. However, between 7000 and 12500 cm$^{-1}$, the FQY in nitrogen decreases below the low-pressure data, confirming that introduction of nitrogen has a quenching effect.

Examination of the data in Figure 4.15 allows for the development of an overall rate expression for $k_{N_2}$. It is apparent that $k_{N_2}$ has vibrational energy dependence, but has very little dependence on nitrogen number density due to the constancy of the FQY with
pressure. The vibrational energy dependence is best fit using a double Gaussian function, and a weak pressure dependence is added to maintain the model fit to high pressure FQY data in nitrogen for 308 nm excitation. Additional examination of data at 1.3 bar in nitrogen motivates the inclusion of a temperature-dependent term. The final expression for the quenching rate is shown in the Table 4.2. The Koch model did not have a term for nitrogen collisional quenching (i.e. \( k_{N2} = 0 \)). Figure 4.15 compares the model with and without \( k_{N2} \) nitrogen quenching to FQY data, and the addition of \( k_{N2} \) greatly improves the fit of the model to the data.

<table>
<thead>
<tr>
<th>Study</th>
<th>Nitrogen quenching rate ( k_{N2} ) (s(^{-1}))</th>
</tr>
</thead>
</table>
| Current   | \[
  k_{N2} = 1.789 \left[ \exp \left( -2 \left( \frac{E - 8700}{2379} \right)^2 \right) + 1.1 \exp \left( -2 \left( \frac{E - 11608}{2037} \right)^2 \right) \right] \times \exp \left( \frac{T}{190} \right) T^{0.28} n_{N2}^{0.28}
\] |
| Koch      | \( k_{N2} = 0 \) |

Table 4.2 Nitrogen quenching rate determined from absolute FQY measurements. \( E \) is in units of cm\(^{-1}\) and \( T \) is in units of K. The expression from Koch is shown for comparison [31].

The developed \( k_{N2} \) expression differs significantly from the bimolecular expression for \( k_{O2} \), shown in equation (4.3). However, a bimolecular collision rate expression would predict a steady decrease in FQY with pressure, and because the FQY remains roughly constant with nitrogen pressure, a bimolecular expression is not appropriate for \( k_{N2} \). For oxygen quenching, the bimolecular expression is consistent with quenching via direct interaction between the ground-state triplet of oxygen and the excited singlet of 3-pentanone. Because the expression for \( k_{N2} \) is not bimolecular, nitrogen quenching does not appear to be a direct interaction between nitrogen and 3-pentanone molecules, but may be the combination of collisional ISC and collisional IC. Further work examining the population of the triplet and ground state singlet would be necessary to develop the exact mechanism by which nitrogen quenching occurs. Since
such data are not available, this work uses the overall rate expression to represent nitrogen quenching.

4.4.3.2 Oxygen Quenching

The sensitivity analysis indicated that the oxygen quenching efficiency $q_{O2}$ is best optimized utilizing FQY data with 308 nm excitation in air, as well as data at high air pressures. The optimized expression for $q_{O2}$ from the current work and previous work [31] is shown in Table 4.3, and the expressions are plotted in Figure 4.16. The current work found that the exponential expression used by the Koch model, with some adjustment, allows the model to reproduce the FQY data in air. However, the Koch model predicted a step increase in $q_{O2}$ at 11000 cm$^{-1}$, while the current work continues with the exponential expression. Since the previous work also used FQY data in air to optimize the $q_{O2}$ at high vibrational energies, the sudden increase in efficiency may be the result of the assumption that nitrogen quenching does not occur.

![Figure 4.16 Variation of $q_{O2}$ with vibrational energy. Comparison to previous work is shown [31].](image-url)
Study | Oxygen quenching efficiency $q_{O_2}$ (-)
--- | ---
Current | $q_{O_2} = 0.00190 \exp\left( \frac{E}{20408} \right)$
Koch | $q_{O_2} = \begin{cases} 
0.00230 \exp\left( \frac{E}{20000} \right), & E < 11000 \text{ cm}^{-1} \\
0.25, & E \geq 11000 \text{ cm}^{-1}
\end{cases}$

Table 4.3 $q_{O_2}$ determined from absolute FQY measurements. $E$ is in units of cm$^{-1}$. The expression from Koch is shown for comparison [31].

### 4.4.3.3 Vibrational Relaxation

Per the sensitivity analysis, expressions for $\alpha_{N_2}$ and $\alpha_{O_2}$ were determined by optimization with FQY data in nitrogen and air, respectively, at 248 nm excitation, as well as data at high temperatures and high pressures. Previous work only considered the temperature dependence of $\alpha_{N_2}$ and $\alpha_{O_2}$, but, based on results from the literature, the current work also considers vibrational energy dependence.

To examine the temperature dependence, FQY data in nitrogen and air at shorter wavelengths (248 nm) and lower temperatures up to 450 K, as well as longer wavelengths (266 and 277 nm) and temperatures up to 650 K, were used in the optimization. This data was chosen to examine a wide range of temperature, but avoids $E_1$ greater than about 11000 cm$^{-1}$. At each temperature, optimum values of $\alpha_{N_2}$ and $\alpha_{O_2}$ were determined, and these optimum values were fit using an exponential function.

The vibrational energy dependence was considered next. To illustrate the importance of including energy dependence, Figure 4.17 shows FQY variation with pressure in nitrogen for a temperature of 745 K and various excitation wavelengths. The plot also shows the model with the temperature-dependent exponential function for $\alpha_{N_2}$ and $\alpha_{O_2}$. As the excitation wavelength decreases, the model with only temperature dependence begins to underpredict the increase in FQY with pressure, indicating that at higher vibrational energies, relaxation occurs more efficiently. To account for this effect, an exponential term with a near-unity value at lower vibrational energies, but with increasing effect at higher vibrational energies, was optimized using 248 nm data at higher temperatures and multiplied to the temperature dependent term. Optimized
expressions for these parameters are shown in Table 4.4, along with expressions from previous work [31].

<table>
<thead>
<tr>
<th>Study</th>
<th>N\textsubscript{2} cascade parameter $\alpha_{N_2}$ (-)</th>
<th>O\textsubscript{2} cascade parameter $\alpha_{O_2}$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>$\alpha_{N_2} = \left(0.900 \exp\left(-\frac{T}{82.18}\right) + 0.0035\right) \times \left(0.0027 \exp\left(-\frac{E}{2150}\right) + 0.95\right)$</td>
<td>$\alpha_{O_2} = \left(3.341 \exp\left(-\frac{T}{59.22}\right) + 0.00503\right) \times \left(0.0027 \exp\left(-\frac{E}{2150}\right) + 0.95\right)$</td>
</tr>
<tr>
<td>Koch</td>
<td>$\alpha_{N_2} = 0.05 \left(\frac{T}{300}\right)^{-1.2}$</td>
<td>$\alpha_{O_2} = 0.05 \left(\frac{T}{300}\right)^{-1.2}$</td>
</tr>
</tbody>
</table>

Table 4.4 Vibrational relaxation cascade parameters for 3-pentanone collisions with nitrogen and oxygen determined from FQY measurements in the current work. The expressions from the Koch model are shown for comparison [31].

Figure 4.17 3-pentanone FQY in nitrogen at about 745 K indicates that $\alpha$ has vibrational energy dependence. The solid lines are for the model including vibrational energy dependence for $\alpha$; the dashed lines are temperature dependence only.
4.4.4 Model Performance with Cell Data

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence rate $k_f$ (s$^{-1}$)</td>
<td>$k_f = 3.70 \times 10^3$</td>
</tr>
<tr>
<td>Non-radiative rate $k_{nr}$ (s$^{-1}$)</td>
<td>$k_{nr} = 4.00 \times 10^8 + 1.80 \times 10^7 \exp \left( \frac{E - 1175}{500} \right) + \frac{2.26 \times 10^{12}}{\pi} \frac{2650}{4(E - 10340)^2 + 2650^2} + 9.44 \times 10^{9} \exp \left( -2 \frac{E - 17800}{5490} \right)^2$</td>
</tr>
<tr>
<td>3-pentanone cascade parameter $\alpha_{3p}$</td>
<td>$\alpha_{3p} = 15.4 \exp \left( -\frac{T}{65.55} \right) + 0.00238$</td>
</tr>
<tr>
<td>N$<em>2$ cascade parameter $\alpha</em>{N2}$</td>
<td>$\alpha_{N2} = \left( 0.900 \exp \left( -\frac{T}{82.18} \right) + 0.0035 \right) \left( 0.0027 \exp \left( \frac{E}{2150} \right) + 0.95 \right)$</td>
</tr>
<tr>
<td>O$<em>2$ cascade parameter $\alpha</em>{O2}$</td>
<td>$\alpha_{O2} = \left( 3.341 \exp \left( -\frac{T}{59.22} \right) + 0.00503 \right) \left( 0.0027 \exp \left( \frac{E}{2150} \right) + 0.95 \right)$</td>
</tr>
<tr>
<td>O$<em>2$ quenching efficiency $q</em>{O2}$</td>
<td>$q_{O2} = 0.00190 \exp \left( \frac{E}{20408} \right)$</td>
</tr>
<tr>
<td>N$<em>2$ quenching rate $k</em>{N2}$ (s$^{-1}$)</td>
<td>$k_{N2} = 1.789 T^{-0.28} \exp \left[ -2 \left( \frac{E - 8700}{2379} \right)^2 \right] + 1.1 \exp \left[ -2 \left( \frac{E - 11608}{2037} \right)^2 \right] \times \exp \left( \frac{T}{190} \right) n_{N2}^{0.28}$</td>
</tr>
</tbody>
</table>

Table 4.5 Summary of updated 3-pentanone FQY model parameters for use over a wide range of pressures and temperatures in nitrogen and air. $E$ is in units of cm$^{-1}$, $n_{N2}$ is in cm$^{-3}$, and $T$ is in units of K.

The updated parameters for the FQY model are summarized in Table 4.5, and these parameters are applied to the model structure as described in section 2.5. The non-radiative rate $k_{nr}$, fluorescence rate $k_f$, and vibrational relaxation cascade parameter $\alpha_{3p}$ for 3-pentanone self-collisions are taken from low-pressure work described in section 3.7. A comparison of the model to FQY data over a range of pressures, temperatures, and
excitation wavelengths in air and nitrogen is shown in Figure 4.18 and Figure 4.19, respectively. Figure 4.18 also includes FQY measurements with no added nitrogen (i.e. 3-pentanone vapor) at pressures of 20 mbar from section 3.6. The model provides excellent agreement with the current measurements, and agrees within 10% across the indicated conditions. The model shows the weakest agreement FQY data taken with 248 nm excitation at 540 K in nitrogen, 248 nm excitation at 430 K in air, and 266 nm excitation at 480 K in air. This discrepancy is likely due to the representation of $k_{N2}$ as a complex empirical fit. A further understanding of the nitrogen quenching process would likely yield improved model agreement with the FQY data at these conditions.

This agreement is a significant improvement over the Koch model, which is also plotted in the figures for comparison. In nitrogen, the Koch model significantly overpredicts the increase in FQY with pressure at temperatures above room temperature, which may be the result of the exclusion of nitrogen quenching. In air, the Koch model predicts a greater decrease in FQY with pressure, especially for the 248 and 266 nm excitation, which is likely the result of the step increase of $q_{O2}$. The MATLAB code used to perform the model calculations is shown in Appendix E.

To further evaluate its performance, the model is used to predict the relative variation of the FQY in air at other temperatures, shown in Figure 4.20 [19, 29]. The model shows good agreement with the previous work, except at 692 K, where there is disagreement at pressures greater than 12 bar. This discrepancy may be due to the occurrence of 3-pentanone oxidation, which was shown to be a consideration above 600 K in the current work. The Koch model, also plotted in Figure 4.20, predicts the longer wavelength data accurately, but greatly underpredicts the increase in FQY with pressure for 248 nm excitation, which is again due to the step increase in $q_{O2}$.

Figure 4.21 shows the performance of the model compared to relative FQY measurements performed in pure oxygen at various temperatures [19, 31]. Both the current and Koch models show agreement with the measurements within 10%. However, the agreement at room temperature is better than at 383 K. Because FQY data at high temperatures in oxygen is unavailable, additional measurements are necessary to further verify the model in oxygen.
Figure 4.18 Comparison of 3-pentanone FQY measurements in nitrogen for a) 248 b) 266 c) 277 and d) 308 nm excitation to FQY models from current work and [31]. The model from the current work shows good agreement with the cell measurements. Error bars equivalent to 10%.
Figure 4.19 Comparison of 3-pentanone FQY measurements in air for a) 248 b) 266 c) 277 and d) 308 nm excitation to FQY model from current work and [31]. The model from the current work shows good agreement with the cell measurements. Error bars equivalent to 10%.
Figure 4.20 Comparison of 3-pentanone FQY measurements from other workers in air to FQY models show the current model has improved performance over the Koch model at higher temperatures for 248 nm excitation [19, 29, 31]. Error bars equivalent to 10%.

Figure 4.21 Comparison of 3-pentanone FQY measurements from other workers in oxygen to FQY models show good agreement [19, 31]. Error bars equivalent to 10%.
4.4.5 Model Performance with Optical ICE Data

In addition to optical cell data, additional relative $S_{LIF}^*$ data is available from optical ICE studies for comparison to the FQY model. Optical engines are able to access simultaneous high-pressure and high-temperature conditions beyond those typically accessed using optical cells. Furthermore, this comparison can confirm the applicability of the model to optical ICE diagnostics. To compare the model to optical ICE data, the FQY determined from the model is multiplied with the absorption cross-section calculated using the expression in [39] and normalized to a reference condition to determine relative $S_{LIF}^*$.

![Comparison of 3-pentanone S\textsubscript{LIF}\textsuperscript{*} in air for 248 nm excitation from optical ICE [43] to FQY model from current work and [31] show good agreement except for lower pressures, where toluene fluorescence signal interference may be occurring. Error bars equivalent to 15%.](image)

In Figure 4.22, the performance of the current model is compared to the $S_{LIF}^*$ for 248 nm excitation measured in an optical engine [43], in which a mixture of 3-pentanone, toluene, and iso-octane is injected into air. The engine study covers temperatures from 318 to 605 K and pressures from 0.5 to 7.9 bar. The model in the current work, as well as
the Koch model which is also shown for comparison, predicts $S_LIF^*$ within about 15% of the measured signal. The greatest differences between the models and the measurements occur at lower pressures, where both models underpredict $S_LIF^*$. This difference may be due to toluene fluorescence signal interference, which would be stronger at the lower oxygen number density and temperatures at intake conditions than at top dead center [90].

Figure 4.23 Comparison of 3-pentanone $S_LIF^*$ for 277 and 308 excitation from an optical ICE [48] to values predicted by the FQY models show the current model improves the predictive performance over the Koch model [31]. The bath gas is a) nitrogen and b) air. Error bars equivalent to 10%.

At higher temperatures and pressures, though, the current model performs significantly better than the Koch model. Figure 4.23 shows a comparison of the two models with measurements made in an optical ICE for 277 and 308 nm excitation [48]. A premixed charge of 0.09% 3-pentanone in air or nitrogen was introduced into the cylinder, and fluorescence signal measurements were made over a temperature range from 400 to 810 K and pressures from 1.3 to 16.4 bar. As the figure shows, the current model reproduces the measured $S_LIF^*$ within 10% for all temperatures, even predicting the decrease in signal for 277 nm excitation beginning at 500 K. The Koch model greatly overpredicts the fluorescence signal temperatures beyond 650 K, in contrast with the
current model, thus demonstrating the advances in predicting fluorescence at top dead center conditions from the current work.

Figure 4.24 Comparison of 3-pentanone $S_{LIF}^*$ for 277 and 308 excitation from an optical ICE [45] to values predicted by the FQY model from the current work show excellent agreement up to 28 bar and 1100 K. The bath gas is a) nitrogen and b) air. Comparison to the previous model is also shown [31]. Error bars equivalent to 10%.

Similar measurements for 277 and 308 nm excitation were performed at even higher pressures and temperatures in another engine study using 0.15% 3-pentanone in air or nitrogen [45], shown in Figure 4.24. The pressure and temperature range for these measurements is 560 to 1120 K and 4.5 to 28.1 bar, respectively. The Koch model poorly predicts the $S_{LIF}^*$ variation, especially at temperatures greater than 700 K. The current model improves upon this performance and is able to reproduce the variation of signal within 10% up to 1100 K. At temperatures higher than 1100 K, there is a slight decline in measured fluorescence signal as compared to the model which may be the result of 3-pentanone pyrolysis or oxidation. Nonetheless, the current work extends the model to temperature and pressure conditions significantly beyond the previous work in support of ICE diagnostics.
4.5 Conclusion for 3-pentanone Photophysics over a Range of $T \& p$

FQY measurements were made for 20 mbar of 3-pentanone in nitrogen for temperatures from 298 K to 745 K and pressures of 1 to 25 bar and in air for temperatures from 298 K to 570 K and pressures from 1 to 25 bar. 248, 266, 277, and 308 nm excitation wavelengths were utilized in the current work. Absolute FQY values were determined by scaling to Rayleigh scattering calibrated measurements made at atmospheric pressure described in Chapter 3. The data are consistent with previous measurements from previous work up to 600 K. The current work extends the range of temperature and pressure for which FQY data are available beyond that of previous work, allowing for quantitative PLIF diagnostics for a variety of flow fields including ICEs with compression ratios up to 11:1.

Collisional parameters in the FQY model were optimized using data from the current work according to a strategy developed through sensitivity analysis. In particular, the nitrogen and oxygen quenching rates $k_{N_2}$ and $k_{O_2}$, as well as the vibrational relaxation cascade parameters $\alpha_{N_2}$ and $\alpha_{O_2}$, were updated. The current work shows that nitrogen quenching, previously assumed to be non-existent, does occur for 3-pentanone. Moreover, $\alpha_{N_2}$ and $\alpha_{O_2}$ were found to have vibrational energy dependence in addition to temperature dependence. This new model agrees with measurements from the current work within 10% across all temperature, pressure, and excitation wavelength conditions, as well as relative FQY measurements from previous work in air and oxygen over a range of temperatures. This performance is an improvement over that of the Koch model, especially at combined high-temperature and high-pressure conditions.

The model also shows good agreement with measurements of fluorescence signal in optical ICEs. For 248 nm excitation and temperatures up to around 605 K, the model agrees within 15%, similar to the performance of the Koch model. For engine measurements with 277 and 308 nm excitation up to 1100 K, agreement is within 10%, a significant improvement over the Koch model. These comparisons establish that the new
model is valid for the high-temperature and high-pressure conditions found in ICEs and a significant improvement over previous models.

One area of future work is to extend the temperatures at which FQY measurements in air and oxygen are available. The current work was limited to 570 K in air due to evidence that oxidation was occurring at temperatures above 600 K, even with a residence time of 0.2 s, and no measurements were made in oxygen. To avoid the effects of oxidation, optical ICEs can be used to achieve high-pressure and high-temperature conditions over short times. Measurements of FQY in air or oxygen at higher temperature conditions allow additional insight into the collisional effects of oxygen. One area of interest is whether the double-Gaussian energy dependency observed with nitrogen quenching occurs with oxygen as well. This information could be determined through measurements of FQY in oxygen at pressures around 1 bar with 308 nm excitation, similar to what was performed in this study with nitrogen.

Future work can also examine the nitrogen quenching mechanism, which does not appear to follow the simple bimolecular collision behavior of oxygen quenching. The quenching of the fluorescence signal may be the result of collisional ISC or IC, or some combination thereof. Investigation of the mechanism, then, would benefit from information on the triplet state population. Thus, measurements of yields for processes originating from the triplet state, such as the photolysis or phosphorescence, over a range of temperature and pressure conditions, would aid in the development of a nitrogen quenching mechanism. An improved quenching mechanism would assist in improving the performance of the FQY model.
Chapter 5  Time-resolved Toluene PLIF Diagnostic Development

This chapter describes the development of a novel time-resolved PLIF diagnostic using CW laser excitation and toluene as a tracer. Preliminary photophysical measurements for toluene were made in an optical cell using techniques applied to 3-pentanone. In addition, to determine the sensitivity of this diagnostic and illustrate its potential in the imaging of high-speed flows, the detection limits of the diagnostic were measured, and the diagnostic was applied to turbulent jets.

5.1 Introduction

Tracer-based PLIF imaging has been shown to be an effective diagnostic for measuring parameters like temperature and composition in gaseous flow fields [14]. Simultaneous measurements of temperature and toluene mole fraction have also been demonstrated using a single laser and single camera by utilizing the red-shift of the toluene fluorescence spectrum with temperature [91]. These diagnostics typically use a pulsed laser system to generate high instantaneous UV light intensity to compensate for the low FQY and resulting low signal levels with most tracers. An inherent disadvantage of using a pulsed laser is that the temporal resolution of the LIF diagnostic is typically limited by the pulse rate of the laser. Commercially available excimers, frequency-quadrupled Nd:YAGs, and pumped dye lasers producing UV light typically have repetition rates of 10 to 30 Hz, significantly slower than mixing and combustion
phenomena, which occur on timescales of micro- and milliseconds. As a result, fully time-resolved measurements have not been available in gaseous flows using a tracer-LIF diagnostic.

Some progress has been made recently, however, with ultrafast pulsed lasers. One pioneering study used a cluster of four Nd:YAG-pumped dye lasers, with each dye laser producing a double pulse of 282 nm light, enabling acquisition of 8 sequential OH LIF images at a rate of 8 kHz [33]. More recently, sustained LIF imaging at 12 kHz of biacetyl was demonstrated in an optical ICE study [34], with excitation light provided by a single frequency-tripled ultrafast Nd:YAG laser emitting 355 nm light. In another approach, imaging of 20 sequential images at 100 kHz of NO LIF was demonstrated in a flame; the 226 nm laser excitation was produced using an optical parametric oscillator pumped by a unique burst-mode Nd:YAG laser [32]. While these studies have yielded time-resolved LIF images, the frame rate of the diagnostic is still limited by the maximum pulse rate of the laser system, which may not be the optimum frame rate for the flow field of interest; moreover, the complex laser systems involved in [33] and [32] allowed for only a limited number of images to be taken. Thus, the available laser sources remain a limitation on the temporal resolution of fluorescence diagnostics.

Use of continuous-wave (CW) excitation would alleviate the limitations imposed by ultrafast pulsed lasers. High-power CW lasers are commercially available with visible wavelengths, and past studies have utilized these for tracer-LIF diagnostics in gaseous flows. For example, time-averaged planar velocity measurements have been made using iodine fluorescence, with 1 W of 514.5 nm excitation provided by a CW argon-ion laser [7]. In the UV, wavelength-modulated CW dye lasers outputting 1 mW of 225 nm light and 7 mW of 306 nm light have been used to measure velocity, temperature, and pressure in a variety of NO- and OH-seeded flow fields, respectively [35, 36]. As the NO LIF studies demonstrate, CW UV lasers emit low power levels, resulting in low LIF signals; these studies addressed this problem by taking LIF measurements only at a single point in the flow using efficient light collection [35, 36]. Due to such low laser powers, CW UV lasers have not been commonly used in tracer-based PLIF imaging diagnostics.
The approach of the current work for time-resolved imaging is to combine use of high-efficiency frequency-doubling systems with a high-FQY tracer. Output from a 5.5 W 532 nm diode-pumped-solid-state (DPSS) laser is doubled using a commercially available cavity doubler to generate about 600 mW of 266 nm beam power, significantly higher than the amount of power seen in previous CW LIF studies in the UV. This study also employs toluene as a tracer. The \((\pi, \pi^*)\) electronic transition in toluene vapor has a high FQY as compared to other commonly used tracers like 3-pentanone and biacetyl [16, 37, 92]. The combined use of toluene as a tracer with the increased laser power from the cavity-doubled CW laser yields a highly sensitive, time-resolved fluorescence diagnostic.

5.2 Toluene Photophysics

The weak excitation fluorescence equation describes the LIF signal. For CW excitation, however, the laser energy term is slightly modified:

\[
S_f = \frac{P \lambda}{hc} \frac{Xp}{\lambda T} \sigma(\lambda, T) \phi(\lambda, p, T) \frac{\Omega}{4\pi} \eta
\]

where \(P\) is the incident laser power, \(\lambda\) is the laser wavelength, \(\Delta t\) is the exposure time, \(p\) is the total pressure, \(T\) is the temperature, \(X\) is the mole fraction of fluorescing tracer, \(L\) is the length of the illuminated volume, \(\Omega\) is the detector collection angle, and \(\eta\) is the detector collection efficiency. The FQY, \(\phi\), and absorption cross-section, \(\sigma\), are measured photophysical parameters describing the variation of LIF signal with temperature, pressure, and excitation wavelength, and characterizing these parameters is key to enabling quantitative measurements. Moreover, one of the motivating factors for using toluene in CW LIF imaging is its high fluorescence signal relative to ketones, and knowledge of the absolute FQY is necessary to make this comparison.

The absorption cross-section of toluene has been the subject of previous work. Earlier work examined the absorption spectrum at room temperature [37], and subsequent work characterized the absorption feature at elevated temperatures using shock tubes [93, 94]. In addition, absorption cross-section measurements over a range of temperatures using laser excitation at 248 and 266 nm have been performed in optical cells [93].
Studies of the FQY have been previously performed at room temperature [37]. The quenching of toluene fluorescence in the presence of oxygen has also been a subject of study [95]. Recent measurements have examined the effect of varying oxygen and nitrogen concentrations on toluene FQY over a range of temperatures for 1 bar of pressure and found that the presence of oxygen can decrease the FQY by three orders of magnitude at room temperature [90]. The study also found that the FQY also decreases by several orders of magnitude with increasing temperature in nitrogen at 1 bar [90].

As stated in section 3.4, measuring the FQY of a species requires calibration to an emission source with a known yield. Burton and Noyes utilized benzene fluorescence as their calibration source and referenced their toluene FQY measurement to previous published values of benzene FQY. The Rayleigh calibration technique for FQY measurement used with 3-pentanone has been shown to be an effective method for measuring absolute FQY, and that technique is applied to toluene in this work. In addition, measurements of FQY are made at pressures greater than 1 bar.

5.2.1 Absolute FQY Measurement Methodology

The theory of this methodology is presented in section 3.4, and the equation used to calculate the FQY based on this theory is

\[
\phi = 4\pi \frac{E_{\text{Ray}} n_{\text{Ray}}}{E_{\text{LIF}} n_{\text{LIF}}} \left( \frac{\partial \sigma}{\partial \Omega} \right) \frac{1}{\sigma_{\text{LIF}}} \int R_{\text{R}}(\lambda) d\lambda \int R_{\text{SR}}(\lambda) S_{\text{Ray}}(\lambda) d\lambda
\]

The fluorescence and Rayleigh signals are normalized for laser pulse energy and number density of the tracer and scatterer, respectively. The equation also indicates that knowledge of the differential Rayleigh cross-section, the RSR, and absorption cross-section of toluene are necessary to calculate absolute FQY.

In this study, oxygen was used as the scatterer in these measurements due to the availability of Rayleigh scattering cross-section information. In addition, because toluene fluorescence is heavily quenched by oxygen, the Rayleigh scattering signal is not contaminated with fluorescence signal from toluene. The differential Rayleigh scattering cross-section of oxygen was calculated using equation (3.12), requiring information on
the King correction factor and the index of refraction, which are available from [96]. The
King correction factor for oxygen used in this study is given by

$$F_K = 1.096 + \frac{1385}{\lambda^2} + \frac{1.447 \times 10^8}{\lambda^4}$$  \hspace{1cm} (5.3)

The index of refraction, calibrated to 1.013 bar and 273.15 K, is given by

$$r - 1 = 2.21204 \times 10^{-4} + \frac{2.031876 \times 10^{-3}}{40.9 - \left(\frac{1000}{\lambda}\right)^2}$$ \hspace{1cm} (5.4)

In equations (5.3) and (5.4), \(\lambda\) is in units of nm.

### 5.2.2 Photophysics Experimental Setup

Photophysics measurements were performed in a static optical cell. The cell body is a MDC Vacuum cross that accepts 2.75 in (69.85 mm) diameter MDC Vacuum flanges. With the exception of the fluorescence signal collection window, MDC Vacuum UV grade fused silica viewports with a window thickness of 0.125 in (3.175 mm) and a viewing diameter of 2.312 in (58.7248 mm) are installed. The collection window is a MDC Vacuum UV grade sapphire viewport with a window thickness of 0.080 in (2.032 mm) and a viewing diameter of 0.94 in (23.876 mm). The viewports are limited to 6 bar of pressure.

The cell is fed via a Swagelok fitting mounted in the top flange and the gas mixture in the cell was provided via the static setup shown in Figure 5.1. Because the cell is static, a magnetic stirring bar was placed in the cell to ensure complete mixing of the gas mixture. The pressure in the system was monitored via two pressure transducers. Pressures up to 1.3 bar were monitored using a 1000 torr MKS Baratron. Pressures above 1.3 bar were monitored using a Setra Model 204 250 psi pressure transducer. The surface temperature of the cell was monitored using a K-type thermocouple. Aldrich brand toluene of 99.8% purity was used for this study, and prior to use, the liquid was degassed using the freeze-pump-thaw method. The bath gases used in this study were Praxair 99.998% nitrogen and 99.99% oxygen. Prior to filling, the cell and manifold were heated to around 100 deg C using heating tape and held under vacuum for approximately 30 minutes to remove toluene that may have absorbed onto the walls. To fill the cell, the
vapor from a toluene filled glass flask was fed into the gas manifold and the optical cell. The flow of vapor was controlled with the needle valve. Once the cell was filled to the appropriate toluene pressure, the cell was shut off from the manifold with a valve, and the manifold was emptied via vacuum pump. If bath gas was to be introduced in the optical cell, the bath gas was introduced into the manifold. To minimize the escape of toluene vapor from the cell, the valve to the cell was opened once the bath gas pressure was higher than the toluene pressure inside the cell, and the cell was filled to the desired bath gas pressure. Once the desired mixture is attained, the valve to the cell was again closed, and the manifold emptied. The mixture was allowed to mix for about 5 minutes prior to fluorescence signal collection, but no significant differences in fluorescence signal were observed for mixing times as short as 1 minute.

Figure 5.1 Schematic of optical cell and static gas feed system.

Figure 5.2 shows the setup of the excitation and fluorescence signal collection optics, which is similar to that described in the 3-pentanone measurements. 248 nm excitation was provided by a Coherent CompexPro 102 krypton fluoride excimer laser, and 266 nm excitation was provided by a frequency-quadrupled Spectra-Physics QuantaRay GCR-3 Nd:YAG laser. The beams were passed through an iris set at 10 mm diameter before passing through a magnesium fluoride Rochon polarizer aligned to allow the vertical polarization of the lasers to pass undeviated and deflect the horizontal
polarization. The vertically polarized beam was passed through a 1000 mm focal length cylindrical lens, used to collimate the beam in the vertical plane before entering the cell. The beam was then passed through a 2 mm diameter aperture iris. The resulting output beam was about 2 mm in diameter and had an energy of about 0.4 mJ/pulse. The beam was blocked from entering the cell using a beam block until just before fluorescence measurements were to be made to avoid the buildup of residue on the viewports.

Figure 5.2 Schematic of laser and fluorescence collection optics.

The energy of the laser beam was monitored both before and after the optical cell. The laser beam energy was determined by sending the beam into a custom made aluminum integrating sphere with an internal diameter of 1 in (25.4 mm). Thorlabs DET210 high-speed silicon detectors monitor the integrating sphere ports. The signal from the detectors is sent to a Tektronix TDS3032, and the measured voltage pulse is averaged over 64 laser pulses and integrated to determine laser energy. Laser energy is measured before and after the optical cell using this detector system. Prior to entering the optical cell, about 10% of the beam energy is diverted using a 3 degree wedged fused silica window. This energy measurement is used to normalize the fluorescence signal to laser energy. The laser beam exiting the optical cell is also sent to a laser energy detector; this measurement is used to measure absorption according to equation (3.5).
The fluorescence signal was collected using a 105 mm Nikkor 4.5 UV lens and imaged onto the slit of an Acton SP-150 spectrograph. The spectrograph contains a grating blazed at 300 nm with 300 grooves/mm and has a spectral resolution of about 3.0 nm. The output of the spectrograph is imaged over 64 laser pulses using a 512 x 512 pixel Thompson ICCD in a Princeton Instruments PI-MAX camera. The camera and spectrograph combination is controlled by a PC computer using WinSpec32 v. 2.5.16, a Princeton Instruments proprietary software package.

Figure 5.3 RSR of the collection optics, spectrograph, and ICCD camera measured using argon arc calibration lamp.

In order to calculate the FQY according to equation (3.11), the spectrograph needs to be calibrated to wavelength, and the RSR of the collection optics and detectors need to be measured. The spectrograph, centered at 340 nm, was calibrated using 6 lines from a Newport 6035 Hg(Ar) calibration lamp and was found to have a range from 210.1 to 457.9 nm. The RSR of the optics and detectors was measured using a NIST-calibrated argon arc lamp from 230 to 400 nm, and the result is shown in Figure 5.3.
5.2.3 Photophysics Measurements

Table 5.1 shows the absorption cross-section for 248 and 266 nm excitation at 295 K. The measurements are compared to previous work [97]. The accuracy of this study is calculated to be +/-4%, primarily due to uncertainty in the transmission measurement. An uncertainty analysis is presented in Appendix D. For both excitation wavelengths, the current measurements are about 10-15% higher than results from Koban et. al. The previous study seeded its optical cell by bubbling nitrogen through flasks of toluene and assumed that the gas was saturated with toluene to calculate the composition, which results in uncertainty in the mole fraction of toluene.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Current work (10^{-18} cm^2)</th>
<th>Koban et. al. (10^{-18} cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>248</td>
<td>3.35</td>
<td>2.90</td>
</tr>
<tr>
<td>266</td>
<td>2.06</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Table 5.1 Absorption cross-section measurements at 295 K. Work from [97] is shown for comparison.

The fluorescence spectrum is calculated by summing the central 250 rows of the ICCD image and correcting the resulting spectrum for the RSR. A sample background-corrected image and resulting RSR-corrected fluorescence spectrum is shown in Figure 5.4. The normalized fluorescence spectra at various pressure conditions for 248 nm and 266 nm excitation are shown in Figure 5.5.

Previous work has found that the fluorescence spectrum for 248 nm excitation red-shifts with temperature and oxygen concentration [90, 97], so the effect of toluene and nitrogen pressure on the spectral shape is of interest. As the figure shows, the current work agrees well with previous spectral measurements in nitrogen. The peak of the spectrum remains roughly constant at 280 nm with nitrogen and toluene pressure variation. However, to the right of the peak the spectrum narrows with increasing toluene pressure, or with the addition of 1 bar of nitrogen. The addition of nitrogen also produces an “elbow” feature at about 275 nm. However, once added, additional nitrogen does not have any effect on the spectrum.
Figure 5.4 Sample fluorescence image and resulting spectrum determined from the central 250 row and corrected for RSR. Total signal is determined by integrating the spectrum from 269 to 340 nm. This image is for 20 mbar of pure toluene at 295 K and for 248 nm excitation.

Figure 5.5 Fluorescence spectrum normalized for the peak value at several toluene and nitrogen partial pressure. Results are shown for a) 248 and b) 266 nm excitation. The results are compared to previous work [93].
For 266 nm excitation, the shape of the fluorescence spectrum narrows slightly with increasing toluene pressure, but, for the most part, remains constant for all pressure conditions. This result is consistent with previous work that found the fluorescence spectrum does not vary with oxygen concentration for 266 nm excitation [90].

![Graph showing Absolute FQY for 248 and 266 nm excitation for pure toluene at 295 K. The error bars indicate the 8% uncertainty in the current work. Comparison is shown to previous measurements [37].](image)

The FQY is calculated using equation (3.11) after integrating the fluorescence spectrum from 269.8 nm to 339.8 nm. The range was chosen to avoid Rayleigh scattering from the laser beam. Figure 5.6 shows the data for pure toluene for pressures from 1 to 29 mbar at 295 K. For 266 nm excitation, the FQY remains constant with pressure at around 0.19. However, for 248 nm excitation, the FQY increases from 0.036 at 5.5 mbar to 0.056 at 27.0 mbar, which may be due to effective vibrational relaxation at higher vibrational energies [88]. The uncertainty in the measurement is primarily due to the uncertainty in the argon lamp calibration and absorption cross-section, resulting in an overall uncertainty of +/- 8%. Appendix D presents an uncertainty analysis of the measurement.
Previous measurements from Burton and Noyes are higher than the current work by about 70% [37]. Some of the difference is due to the difference in absorption cross-section in this work. Moreover, Burton and Noyes calibrated their values to the FQY of benzene at 253 nm excitation of 0.18 [98]. However, another measurement at the same condition was 0.234, approximately 30% higher [99], introducing a large uncertainty into the toluene FQY.

In order to examine the effects of nitrogen gas, the absolute FQY was measured for 0 to 5 bar of added nitrogen at 295 K. The results are shown in Figure 5.7. For 248 nm excitation, the addition of nitrogen increases the FQY, similar to 3-pentanone and acetone. However, the partial pressure of toluene also influences the magnitude of the increase. Moreover, for 266 nm excitation, the addition of nitrogen quenches the fluorescence. The current work shows good agreement with previous work for 248 nm excitation [100].

![Figure 5.7 FQY with added nitrogen pressure for various excitation and wavelengths and toluene partial pressures. The error bars indicate the 8% uncertainty. The current work is consistent with previous work [100].](image-url)
The current work, while extending the knowledge of toluene photophysics, also illustrates that the behavior of toluene fluorescence is different from that of ketones. As a result, measurements across a wide range of temperatures, pressures, and toluene partial pressures are necessary for quantitative PLIF diagnostics with toluene, as well as to understand toluene photophysics.

5.3 Diagnostic Sensitivity Background

This study aims to examine the detection limits of time-resolved toluene LIF diagnostics performed using CW laser excitation at 266 nm in N₂ flows. Three separate detection schemes are examined: single-point (0-D) LIF, line imaging (1-D) LIF, and planar imaging (2-D) LIF, or PLIF. In single-point LIF, a laser beam is passed through the flow field and the resulting LIF signal is collected from a single point by a single detector. This detection scheme is the most sensitive because it utilizes the full laser power and captures the LIF signal on an efficient photomultiplier tube (PMT). In the line imaging scheme, the LIF signal from the laser beam is collected by one row of 512 pixels. This detection scheme, while still sensitive, trades some of the sensitivity of the single-point scheme for spatial resolution because the small pixel size of cameras limits the volume of the imaged region. Finally, the PLIF imaging utilizes a 512 x 512 pixel detector, allowing 2-D spatial resolution of flow field features. However, as the energy of the laser beam is spread out to illuminate the imaged plane, the LIF signal along each row of pixels is a fraction of that available in line imaging; the detection scheme yields 2-D measurements, but produces less LIF signal per pixel.

As previously discussed, the FQY of toluene is strongly quenched in the presence of oxygen, and this effect is avoided by studying nitrogen jets seeded with toluene. In addition, detection limits were measured in the potential core of the jets, where no oxygen is present. Since the jets exhaust into the atmosphere at room temperature, they are assumed to be virtually isobaric and isothermal. Thus, the FQY and absorption cross-section of the toluene within the flow field are uniform, and the LIF signal variation is directly proportional to fluctuations in the toluene mole fraction of the jet. This diagnostic
could also be used to measure temperature in an isobaric flow field with a known toluene concentration using knowledge of the variation of FQY and absorption cross-section with temperature [93].

The signal from a fluorescence diagnostic is useful only if it is large enough in magnitude to be distinguished from noise; thus, the noise characteristics of the diagnostic dictate the minimum detectable signal fluctuation. Noise characterizations of imaging techniques often consider both spatial and phase noise. Spatial noise refers to variations in the measured fluorescence signal in space when imaging a flow with uniform tracer mole fraction. Phase noise refers to variations in the fluorescence signal with time when imaging a flow with steady tracer mole fraction. The major difference between the two methods is that phase noise looks only at shot-to-shot variation in signal, while spatial noise incorporates non-uniformities in the field, such as spatial variations in laser sheet intensity, absorption of the laser light by the tracer, and detector non-uniformity, as well as shot to shot variation [101]. Since the purpose of this study is to examine the potential of time-resolved measurements of signal variation, phase noise is used in assessing fluctuation detection limits, though spatial uniformity is also examined after correcting for the previously mentioned effects.

The fluctuation detection limit for this study is defined as the ratio of the phase noise to the mean LIF signal, i.e. the inverse of the SNR, which can be defined as

\[ f = \frac{\sigma_f}{S_f} = \frac{1}{SNR} = \frac{\Delta X_{tol}}{X_{seed}} \]  

Noise \( \sigma_f \) is defined as the root-mean-square (RMS) of signal deviation from the mean signal over multiple time steps. For an isothermal, isobaric, and oxygen-free system, such as the jets used in this work, \( f \) is simply the noise-equivalent fractional variation in mole fraction, so the smallest detectable change in toluene mole fraction \( \Delta X_{tol} \) is the product of the detection limit with the seeding mole fraction of toluene \( X_{seed} \):

\[ \Delta X_{tol} = fX_{seed} \]  

In the case of the shot-noise limit, a fundamental limit of the LIF intensity noise related to the discrete nature of photons, the fluctuation detection limit can be predicted using

112
\[ f = \frac{1}{\sqrt{S_f}} \propto \sqrt[3]{\frac{B}{nVP}} \] (5.7)

where \( S_f \) is given by equation (5.1), \( B \) is the frame rate or bandwidth of the detector, \( n \) is the number density of the tracer, \( V \) is the illuminated volume imaged by the detector, and \( P \) is laser power.

5.4 Single-point LIF

5.4.1 Experimental setup for measurement of fluctuation detection limits

The experimental setup for measuring the fluctuation detection limits of single-point LIF is shown in Figure 5.8. 266 nm light was generated by doubling the output of a Coherent Verdi 5W DPSS 532 nm CW laser with a Spectra-Physics Wavetrain cavity doubler. The 532 nm beam was directed into the Wavetrain using 532 nm high reflectors; a 1 m focal length lens was used to focus the laser beam to achieve mode matching in the Wavetrain cavity. The cavity-doubler output was up to 600 mW with 5.5 W of 532 nm input. The 266 nm beam was directed through the flow field using a series of 266 nm
high-reflector optics. A 1 m focal length lens was inserted into the beam to focus the laser beam at the flow field to a 1/e diameter of 0.4 mm as it passed through the flow field. A 1 mm diameter iris was placed just before the flow field to eliminate stray laser light. Laser power was monitored by a Melles Griot 13PEM001 Laser Power meter positioned downstream of the flow field. Due to losses in the reflectors and the lens, the maximum laser power incident on the flow field was about 450 mW.

The flow field utilized was a jet of tracer-seeded N₂ issuing into air from a 28 cm long, 7 mm inner diameter, round stainless-steel tube. The jet was mounted such that the flow exits downward. Measurements were taken in the potential core of the jet (Re = 1670), where the flow was steady and no oxygen was present. The laser beam was passed approximately 1 mm below the jet exit through the center of the jet for the single-point measurement. Seeding was performed with two Chemglass bubblers in series; the nitrogen was assumed to be saturated with toluene vapor at 293 K, yielding a mole fraction of about 4% toluene.

This jet, as well as others used in this study, was exhausted into a fume hood to prevent accidental respiration, similar to the precautions taken when using acetone- or 3-pentanone-seeded jets. In addition, personnel wore respirators rated for organic vapor filtering to avoid exposure to vapors, as well as safety glasses and gloves when handling the fluid to avoid splashing.

For the single-point detection scheme, the LIF signal was collected by a 50 mm diameter, 100 mm focal length, fused silica lens onto a Hamamatsu 1P21 PMT. The collection solid angle was about 0.08 sr. The cathode quantum efficiency of the PMT at 280 nm is about 20%. A 2 mm wide slit was placed in front of the PMT housing to limit the collection of LIF signal to a collection volume of 1 mm (along laser beam) x 0.4 mm (beam diameter, longitudinal direction) x 0.4 mm (beam diameter, depth) within the center of the flow field. The PMT was powered by a high-voltage power supply operating at 400 V; the PMT current output was monitored using a National Instruments PCI-E data acquisition board sampling at 20 kHz. The -3 dB frequency response bandwidth of the PMT with this acquisition system was measured using a rapidly-switched light-emitting diode and found to be 8.5 kHz.
The laser power incident on the flow field was varied from 60 mW to 430 mW. For each selected value of laser power, 500 sequential samples of the PMT current were collected. Since the laser output from the cavity doubler is affected by vibrations from the surroundings, care was taken to avoid excessive vibration during the data collection. The samples were also corrected for background light. Noise was calculated using the RMS variation from the mean over 20 time steps. The detection limit is calculated according to equation (5.5).

5.4.2 Results and Discussion

![Figure 5.9 Variation of fluctuation detection limit with laser power for a jet seeded with 4% toluene in N\textsubscript{2} at 1 atm for single-point measurement of a 1 mm\textsuperscript{3} region. The detector has a bandwidth of 8.5 kHz.](image)

Figure 5.9 shows the measured detection limit as a function of laser power. At 430 mW of laser power, the single-point LIF diagnostic demonstrated a fluctuation detection limit of only 0.028%. Using equation (5.6), the smallest measurable variation in toluene mole fraction is 11.2 ppm in the jet. The detection limit exhibits an inverse square root dependence on laser power, consistent with the diagnostic being shot-noise limited; other
noise sources from the laser or the jet are negligible. Even at these UV power levels, single-point detection of toluene LIF is clearly capable of high sensitivity for detecting small changes in mole fraction.

Because the diagnostic is shot-noise limited, the shot-noise relations (5.7) can be used to predict diagnostic performance at different conditions of laser power and bandwidth. Figure 5.9 predicts a fluctuation detection limit of only 0.022% if the entire 600 mW is passed into flow field, or a signal-to-noise ratio of about 4600. This detection limit corresponds to 8.8 ppm variation in toluene mole fraction in the jet.

### 5.5 Line LIF imaging

#### 5.5.1 Experimental setup for measurement of fluctuation detection limits

The experimental setup is shown in Figure 5.8. The same laser system and jet setup from the single-point experimental setup was used in this setup; however, a different detection system was employed.

For the line-imaging detection scheme, the LIF signal was collected by a 50 mm diameter, 100 mm focal length lens into a Roper Scientific NTE/CCD 512 x 1024BFT detector with kinetic readout. The lens collection angle is about 0.08 sr. The CCD array is coated to enhance UV responsiveness and has a quantum efficiency of about 10% at 280 nm. The 1024 x 512 CCD array is masked except for the top 5 rows, each 512 pixels long; the LIF signal was focused via the lens onto these rows. The 5 pixels in each column were binned together on chip, effectively providing a single row of 512 “composite” (1 x 5) pixels. Each of these composite pixels imaged a region of the flow field 0.04 mm wide (beam direction) x 0.2 mm (transverse direction) x 0.4 mm (beam diameter, depth). In kinetic readout mode, the unmasked rows are exposed for a set exposure time and then shifted under the mask over 4 μs. Thus, the total exposure time is equal to the user-specified exposure time plus 4 μs. 196 time-sequential line images were collected on the CCD array, taken at a frame rate that is the inverse of the total exposure
time. The output from the CCD array was collected on a PC using Roper Scientific’s proprietary hardware and software.

Measurements of toluene LIF were made for laser powers varying from 70 to 461 mW, and for exposure times (including the 4 μs shift time) varying from 4 to 104 μs. In addition, measurements were taken in which the pixels are further binned into a single row of 64 composite pixels, each imaging a region 0.3 x 0.2 x 0.4 mm in size.

Figure 5.10 Sample line LIF image of jet used in detection limit measurements. Image was taken with 351 mW of laser power and 104 μs exposure time, and corrected for background and spatial variations in detector response. Data from the central region of the jet is used in analysis.

Figure 5.10 shows a single-shot line image of the jet taken 1 mm from the jet exit that was corrected for background light and spatial non-uniformity in detector responsivity. Phase noise was calculated by examining the RMS variation from the mean over time for pixels imaging the potential core of the jet, which is steady, uniform in tracer concentration, and free of oxygen; the noise was then averaged across the 30 pixels imaging the core of the jet. This calculation can be described by the equation
\[
\sigma = \frac{1}{N_p} \sum_{x=1}^{N_x} \sqrt{\frac{1}{N} \sum_{i=1}^{N} (S_{x,i} - \overline{S_x})^2}
\]  

(5.8)

where \( N \) is the number of time steps, \( N_p \) is the number of pixels in the region, \( S_{x,i} \) is the signal at time step \( i \) and pixel \( x \), and \( \overline{S_x} \) is the mean signal at pixel \( x \) over the \( N \) time steps. 20 time steps were used to calculate the noise. The fluctuation detection limit was calculated as described by equation (5.5).

## 5.5.2 Results and Discussion

![Figure 5.11 Line LIF imaging detection limits for each pixel as a function of laser power. Detection limits shown in a) for 4, 14, 54 and 104 μs exposure times (250, 71.4, 18.5 and 9.6 kHz frame rates) where each pixel images a region 0.04 x 0.2 x 0.4 mm; in b) the exposure time is 54 μs and detection limits are shown for two spatial resolutions, 0.04 x 0.2 x 0.4 mm/pixel and 0.3 x 0.2 x 0.4 mm/pixel.](image)

Figure 5.11a shows the fluctuation detection limit as a function of laser power for various exposure times. For these results, each pixel imaged a region 0.04 x 0.2 x 0.4 mm in size. At 461 mW of laser power, the line imaging diagnostic is able to achieve a detection limit of 2.63% for an exposure time of 4 μs (a frame rate of 250 kHz); for an exposure time of 104 μs (frame rate of 9.7 kHz), a detection limit of 0.55% is achieved. Using equation (5.6), these detection limits correspond to the smallest detectable changes
in toluene mole fraction of 0.11% and 0.022%, respectively, for the nitrogen jet used in the study. For each exposure time, the variation of fluctuation detection limit with laser power follows an inverse square root relation. In addition, at each laser power, the variation of detection limit with exposure time also follows an inverse square root relation. Both these observations are consistent with shot-noise limited performance. For the two exposure times mentioned above, the spatial RMS variations of single-pixel signals, relative to the mean signal of the 30 pixel sub-regions, are 2.85% and 0.56%, respectively. The similarity between the spatial variations and the fluctuation limits demonstrates that the spatial detection limits are also shot-noise limited. The slight difference between the spatial variation and fluctuation detection limit can be attributed to the corrections for absorption and spatial variations in detector response. Using the shot-noise relations (5.7), if all 600 mW of laser power exiting the cavity doubler were passed through the flow field, the diagnostic should be able to achieve a 0.46% fluctuation detection limit with an exposure time of 104 μs, corresponding to a toluene mole fraction of 0.018% in the jet used in this work.

Figure 5.11b shows the variation in fluctuation detection limit with laser power for a 54 μs exposure time (frame rate of 18.5 kHz) for two different camera resolutions. When each pixel images a region 0.04 x 0.2 x 0.4 mm in size, a detection limit of 0.73% was achieved with 461 mW of power. When each pixel images a 0.3 x 0.2 x 0.4 mm region, a detection limit of 0.23% is achieved with 440 mW of laser power with 4% seeding of toluene, or a toluene mole fraction variation of 92 ppm. If pixels are further binned so that each pixel images a region 0.9 x 0.2 x 0.4 mm in size, the shot-noise-limit relations predict that a detection limit of 0.13% can be achieved with 440 mW of laser power; with 600 mW, a 0.11% fluctuation detection limit can be achieved. These detection limits correspond to 52 and 44 ppm toluene mole fraction variations, respectively, for the seeded nitrogen jet used in the current work. This example illustrates that very sensitive detection limits are possible while maintaining good spatial resolution.
5.5.3 Line Imaging Applied to Turbulent Jet

To demonstrate the line imaging diagnostic, the 7 mm stainless steel jet in the experimental setup was replaced with a 1.7 mm diameter glass jet pointing upwards. The jet discharges nitrogen seeded with 4% toluene by mole fraction into ambient air at room temperature with a Re of 9800, in the turbulent regime. The laser power was set to 400 mW. Time-resolved line imaging was performed at several downstream locations with a 54 μs exposure time (18.5 kHz frame rate). Images were corrected for background light and spatial non-uniformity in detector responsivity.

Figure 5.12 Signal time-histories at different radial distances from the centerline of a turbulent jet, Re = 9800, 8 mm (4.7 D) downstream of jet exit. Images were taken with a laser power of 400 mW, a detector exposure time of 54 μs, and pixel resolution of 0.04 x 0.2 x 0.4 mm.

Figure 5.12 shows signal time histories taken at three locations along the beam: at the centerline, 0.5 mm radially from the centerline, and 1.0 mm radially from the centerline. The time histories were taken simultaneously at a distance 8 mm (4.7 diameters) downstream of the exit, demonstrating the ability for the line imaging
diagnostic to provide simultaneous temporal and spatial information at an 18.5 kHz frame rate.

In addition to time histories of the centerline concentration, the mass concentration at different spatial locations can be examined and compared to previous work on turbulent jets. The mean concentration field has been determined in prior work to follow

\[ C = \kappa C_0 \frac{D_s}{x - x_0} g \left( \frac{r}{x - x_0} \right) = \kappa \frac{C_0}{\chi} g(\eta) \]  

(5.9)

where \( C_0 \) is the initial concentration, \( g(\eta) \) is approximately Gaussian, and \( \kappa \) a constant between 4 and 6. \( \chi \) and \( \eta \) are non-dimensional coordinates for the downstream distance, \( x \), and the radial coordinate, \( r \), incorporating a virtual origin \( x_0 \) [102]. Figure 5.13 shows the mean of 196 line images of the jet 8 mm (4.7 D) and 16.2 mm (9.5 D) downstream of the jet exit, \( \text{Re} = 9800 \). The average is taken across 196 single-shot images. The mean profile is fit with a Gaussian. Each line image is 1 x 125 pixels in size with a pixel resolution of 0.04 x 0.2 x 0.4 mm. Images were taken with 400 mW of laser power and a 54 μs exposure time (18.5 kHz frame rate) in a room-temperature, isobaric nitrogen seeded with 4% mole fraction of toluene.

Figure 5.13 Time-averaged radial line image for a turbulent jet 8 mm (4.7 D) and 16 mm (9.5 D) downstream of the jet exit, \( \text{Re} = 9800 \). The average is taken across 196 single-shot images. The mean profile is fit with a Gaussian. Each line image is 1 x 125 pixels in size with a pixel resolution of 0.04 x 0.2 x 0.4 mm. Images were taken with 400 mW of laser power and a 54 μs exposure time (18.5 kHz frame rate) in a room-temperature, isobaric nitrogen seeded with 4% mole fraction of toluene.
jet exit. Both signal profiles show good agreement with Gaussian fits, and, as expected, the width of the Gaussian increases with downstream distance. The slight dip in the 16.2 mm profile near the centerline is due to the corrections made for spatial detector responsivity. Since the jet will entrain air, the measured signal profiles would need to be corrected for oxygen quenching in order to directly correlate to the toluene concentration. However, the Gaussian shape of the concentration profile predicted by equation (5.9) will yield Gaussian-shaped LIF signal profiles. Thus, the Gaussian nature of the LIF signal profile is consistent with the theory, and the diagnostic is able to resolve the spatial characteristics of the jet.

Figure 5.14 RMS variation of signal 8 mm and 16.2 mm downstream the jet exit of a turbulent jet, Re = 9800, plotted against the radial coordinate r.

To examine the ability of this diagnostic to resolve temporal variations in the jet, the RMS statistics of the concentration time histories were calculated. Figure 5.14 shows the RMS variation of the signal 8 mm and 16.2 mm downstream of the exit. The RMS variations show the expected twin peak shape, with the peaks off the centerline of the jet [102]. Ideally, these peaks would occur symmetrically about the jet centerline; the asymmetry may be due to a slight tilt of the jet from vertical. Compared to previous
work, these peaks occur nearer to the centerline of the jet [103], which may be due to oxygen quenching of the LIF signal as the jet mixes with air. However, the current time-resolved measurements exhibit the same qualitative behavior as previous work.

5.6 PLIF Imaging

5.6.1 Experimental setup for measurement of fluctuation detection limits

The experimental setup for PLIF imaging is shown in Figure 5.15. The 7 mm diameter jet used in the single-point and line-imaging setup to assess detection limits was used as the flow field of interest. However, optics were changed to produce a laser sheet, and an intensified CCD array was used.

![Figure 5.15 Setup for measurement of PLIF fluctuation detection limits.](image)

600 mW of 266 nm light was produced using the 532 nm laser with the cavity doubler, and the beam was routed using 266 nm high reflectors as before. The beam was expanded in the vertical direction using a -50 mm focal length cylindrical lens and re-collimated in the vertical direction using a 1 m focal length cylindrical lens. The sheet was focused in the horizontal plane using a 400 mm focal length cylindrical lens. The resulting sheet was passed through a 20 mm diameter iris to limit the sheet height and
clip the edges of the sheet to achieve a laser sheet with a near “flat-top” intensity profile. A 1 mm wide slit before the flow field reduced stray laser light. The sheet was 20 mm tall and 0.4 mm thick as it passed through the flow field. A 50 mm diameter, 50 mm focal length spherical lens focused the sheet onto the detector head of the laser energy monitor to measure sheet energy. Because the sheet is clipped by the iris, the maximum power in the sheet is only 270 mW, less than half the output power from the cavity doubler.

The resulting fluorescence was collected using a 105 mm Nikkor 4.5 UV lens and imaged onto the intensified Thomson 512 x 512 frame transfer CCD array of a Princeton Instruments PI-MAX camera. The lens collection angle is about 0.08 sr. The readout from the ICCD array was collected on a PC using Princeton Instruments’ proprietary hardware and software. Each pixel imaged a region in the flow field 0.05 mm (beam direction) x 0.05 mm (transverse direction) x 0.4 mm (sheet thickness, depth). The intensifier was set to the highest gain setting for all images, and the intensifier gating time was used to limit the exposure time, which can be as short as 1 μs. The camera is only capable of several frames per second; however, to evaluate the performance of the diagnostic, multiple images taken using the same exposure time were used to calculate the fluctuation detection statistics.

PLIF images were taken with the laser sheet powers varying from 50 to 270 mW and exposure times varying from 1 to 100 μs. For each laser sheet power and exposure time condition, 20 PLIF images were taken for the calculation of noise. These images were repeated with the ICCD binned 8 by 8 so that each pixel imaged a region 0.4 x 0.4 x 0.4 mm. The images were corrected for background light, the spatial distribution of laser energy, and absorption of the laser light by toluene.

Figure 5.16 shows a single-shot image that is corrected for the laser energy profile, laser sheet absorption, and background light. Noise was calculated by examining a 30 x 30 pixel sub-region imaging the potential core of the jet, as shown in Figure 5.16, which is steady, has uniform toluene concentration and is free of oxygen. The noise in the image is the average of the pixel noise across all the pixels in the sub-region. For each pixel, noise is the RMS variation from the mean over the 20 images taken. This calculation is described by
\[ \sigma = \frac{1}{N_{p,x}N_{p,y}} \sum_{x=1}^{N_{p,x}} \sum_{y=1}^{N_{p,y}} \sqrt{\frac{1}{N} \sum_{i=1}^{N} (S_{x,y,i} - \overline{S_{x,y}})^2} \]  

where \( N \) is the number of images, \( N_{p,0} \) and \( N_{p,y} \) are the number of pixels in the horizontal and vertical directions, \( S_{x,y,i} \) is the signal for image \( i \) and at pixel location \( (x,y) \), and \( \overline{S_{x,y}} \) is the mean signal at pixel location \( (x,y) \) over the \( N \) images.

5.6.2 Results and discussion

The variation of fluctuation detection limit with laser sheet power for several exposure times is shown in Figure 5.17a. Each pixel on the ICCD imaged a region 0.05 x 0.05 x 0.4 mm in the flow field. With a laser sheet power of 271 mW, the diagnostic achieved a detection limit of 20.3% with a 1 μs exposure time. A detection limit of 2.47% was achieved with a 100 μs exposure time and a laser sheet power of 235 mW. For the nitrogen jet used in this study, these detection limits correspond to variations in toluene mole fraction of 0.82% and 0.099%, respectively. As with the single-point and line
imaging results, the fluctuation detection limit results are consistent with the shot-noise limit. For the two previously mentioned exposure times, the spatial RMS variations of single pixel signals, relative to the mean signal in the sub-regions, were found to be 21.0% and 3.91%, respectively. The similarity between the fluctuation detection limits and spatial variations indicates the spatial capabilities of diagnostic are nearly shot-noise limited. The difference between the spatial variations and the detection limits can be attributed to the corrections for laser sheet profile and absorption. With a 100 μs exposure time, the shot-noise-limit relations (5.7) predict a detection limit of 1.36% if all 600 mW of laser power available from the cavity doubler is used in the laser sheet, which, for the jet in the current work, is a toluene mole fraction variation of 0.054%.

Figure 5.17 PLIF imaging detection limits for each pixel as a function of laser power. Detection limits shown in a) for 1, 10, 50 and 100 μs exposure times, where each pixel images a region 0.05 x 0.05 x 0.4 mm; in b) the exposure time is set to 100 μs and detection limits are shown for two spatial resolutions, 0.05 x 0.05 x 0.4 mm/pixel and 0.4 x 0.4 x 0.4 mm/pixel.

The variation of detection limit with laser energy is shown for a pixel resolution of 0.05 x 0.05 x 0.4 mm and 0.4 x 0.4 x 0.4 mm in Figure 5.17b. For both cases, the exposure time is set to 100 μs. The coarser resolution achieved a detection limit of 0.88% with a laser sheet power of 205 mW. A detection limit of 0.55% is predicted for a laser
sheet power of 600 mW using shot-noise-limit relations. For the jet in the current work, these detection limits correspond to toluene mole fraction variations of 0.035% and 0.022%, respectively. This result serves to illustrate the potential of this PLIF diagnostic to monitor small changes in mixture fraction with very good spatial resolution.

5.6.3 PLIF Imaging Applied to Turbulent Jet

To demonstrate the PLIF imaging diagnostic, the 7 mm stainless steel jet in the experimental setup was replaced with a 1.7 mm diameter round jet pointed downward. The jet emitted nitrogen seeded with 4% toluene mole fraction at a Re of 10700. To avoid reduction of LIF signal by oxygen quenching as the jet mixed with the surrounding air, a nitrogen coflow was also used. The coflow consists of a 28 cm long, 27 mm inner diameter copper tube with an Re number of 1600. A 20 mm tall by 0.4 mm thick laser sheet with 203 mW of energy was passed through the jet, just above the exit. Images of the jet and coflow were taken using the PI-MAX camera described previously. In addition, two image sequences were also taken with a Princeton Instruments PI-MAX2 camera. The PI-MAX2 uses an intensified KAI 1024 x 1024 interline-transfer CCD capable of taking two sequential images separated by 3 μs.

Figure 5.18 shows 2-D PLIF images of relative concentration, normalized to the concentration at the jet exit and corrected for background light and the laser sheet’s energy profile. A representative single-shot image and the mean across 50 single-shot images are shown, and the difference between these two images is shown for comparison. Figure 5.18a shows images taken with 10 μs exposure times, an image size of 400 x 150 pixels, and a pixel resolution of 0.05 x 0.05 x 0.4 mm. Figure 5.18b shows images taken with 1 μs exposure time, an image size of 100 x 38 pixels, and a pixel resolution of 0.2 x 0.2 x 0.4 mm. The Taylor scale of the turbulent jet is approximately 0.15 mm at the centerline 17 mm downstream of the exit ($x/D$ of 10) [104], so the two resolutions correspond to three times finer and coarser than the Taylor scale, respectively.
Figure 5.18 2-D PLIF imaging of relative toluene concentration in a turbulent jet ($Re = 10700$) using PI-MAX camera. 203 mW of laser power was used. Comparison of single-shot image to mean of 50 single-shot images is shown. In a), images are $400 \times 150$ pixels in size with $0.054 \times 0.054 \times 0.4$ mm/pixel resolution and are taken with $10 \mu s$ exposure time. In b), images are $100 \times 38$ pixels in size with $0.2 \times 0.2 \times 0.4$ mm/pixel resolution and are taken with $1 \mu s$ exposure time.
Figure 5.19 Time-resolved 2-D PLIF imaging of relative toluene concentration in a turbulent jet (Re = 10700) using PI-MAX2 camera. 203 mW of laser power was used. Two sequential images and the difference between them are shown. In a), images are 400 x 150 pixels in size with 0.054 x 0.054 x 0.4 mm/pixel resolution and are taken with 50 μs exposure time (18.9 kHz frame rate). In b), images are 100 x 38 pixels in size with 0.2 x 0.2 x 0.4 mm/pixel resolution and are taken with 10 μs exposure time (76.9 kHz frame rate).
The mean images show some asymmetry, which is due to vertical tilting of the jet and possibly interaction of the jet with the coflow. Both figures show single-shot images that differ significantly from their respective mean images, showing the utility of time-resolved imaging in capturing the behavior of turbulent phenomena. In addition, the images demonstrate the ability of the diagnostic to be utilized at very short exposure times, with a tradeoff in spatial resolution.

Figure 5.19 shows time-resolved 2-D PLIF images of relative concentration. Two sequential images corrected for background light and laser sheet energy profile are shown, along with the difference between these images for comparison. The images in Figure 5.19a were taken with a 50 μs exposure time (18.7 kHz frame rate, accounting for the 3 μs delay in between images); the image size is 400 x 15 pixels with a pixel resolution of 0.05 x 0.05 x 0.4 mm. The images in Figure 5.19b were taken with a 10 μs exposure time (76.9 kHz frame rate); the image size is 100 x 38 pixels with a pixel resolution of 0.2 x 0.2 x 0.4 mm. These images demonstrate the potential of this diagnostic to provide continuous recording at this spatial resolution once a high-repetition-rate camera is used.

### 5.7 Time-resolved Imaging Conclusions

A novel toluene-tracer LIF diagnostic is reported using CW laser excitation with the goal of providing variable, high-bandwidth or framing rate recording with high spatial resolution. The diagnostic is enabled by the high FQY of toluene flows without oxygen and the use of cavity doubling of a 532 nm DPSS CW laser to achieve high 266 nm laser power. The diagnostic is shown to provide high sensitivity for monitoring mixture fluctuations with frame rates in the kilohertz regime. The LIF signal fluctuation detection limits of this diagnostic were explored by measuring noise in the LIF signal on a nitrogen jet seeded with 4% toluene by mole fraction. For single-point detection of a 1 x 0.4 x 0.4 mm volume using a PMT with 8.5 kHz bandwidth, the diagnostic achieved a detection limit of 0.028% with 430 mW of laser energy incident on the jet. For line imaging using a kinetic readout CCD camera, the diagnostic achieved a detection limit of 0.55% with a
frame rate of 9.7 kHz with 461 mW of laser energy incident with each pixel imaging a 0.04 x 0.2 x 0.4 mm region; with a decrease in resolution to 0.3 x 0.2 x 0.4 mm, the detection limit improved to 0.23% with 440 mW of incident laser energy. Finally, for a PLIF imaging detection scheme using an ICCD camera, the diagnostic achieved a detection limit of 2.47% with 100 μs intensifier gating time, incident laser sheet energy of 235 mW, and a collection region 0.054 x 0.054 x 0.4 mm per pixel. With the resolution decreased to 0.4 x 0.4 x 0.4 mm per pixel, the diagnostic achieved a detection limit of 0.88% with 205 mW of laser sheet energy. For the turbulent jet used in this study (Re ~10000), the Taylor microscale is 0.15 mm, so these spatial resolutions are about a factor of 3 smaller and larger than the microscale, respectively.

Using line imaging, time histories of the fluorescence signal were successfully obtained at a frame rate of 18.5 kHz for a turbulent jet (Re 9800) at several axial locations with 400 mW of laser energy. In addition, PLIF images of spatial concentration variation were successfully obtained for a turbulent jet (Re 10700) seeded with toluene in a nitrogen coflow. For the single-shot intensified camera, images showing jet structure details were obtained for exposure times of 10 and 1 μs. In addition, time-resolved PLIF image pairs were acquired at frame rates of 18.7 and 76.9 kHz.

Several improvements to the diagnostic are envisioned. First, high-speed cameras for the UV will be necessary in order to extend the PLIF diagnostic beyond two-shot sequences. Laser improvements to increase laser power, such as using a higher power pump beam, will aid in improving the fluctuation detection limits. Other techniques, such as multi-passing the laser sheet through the flow field, could also increase the amount of laser power incident on the flow field. In addition, changes to the optics creating and routing the laser sheet to the flow field with the goal of converting the beam to a “flat top” profile and minimizing loss will also benefit the fluctuation detection limits. Conversion of the laser beam to a “flat top” profile will allow the creation of a near flat sheet without the need to use only the center of the laser beam, thereby reducing losses.
Chapter 6  Conclusions and Future Work

This chapter reviews the broader conclusions of this work with regard to tracer-based PLIF diagnostic development. Conclusions and recommendations specific to 3-pentanone photophysics measurements and modeling, as well as time-resolved imaging with toluene, were presented at the end of Chapters 3, 4, and 5.

6.1 Conclusions for 3-pentanone Photophysics

The popularity of 3-pentanone as a fluorescence tracer in ICE diagnostics is due to its physical similarity to iso-octane and its desirable photophysical traits. The key to quantitative flow field measurements in an ICE or other flow fields is data on the behavior of the FQY with temperature, pressure, and composition, especially at combined high-temperature and high-pressure conditions. Previous measurements and modeling of the FQY covered a limited range of conditions, and this work provides a more complete database and modeling of 3-pentanone FQY. In addition to providing this information on 3-pentanone fluorescence, this work also provides a guide to the experimental methods for characterizing photophysics that can be applied to other tracers.

Chapter 3 and Chapter 4 outline experimental methods used to investigate the FQY of 3-pentanone. Measurements were made in a custom-built optical cell across a wide range of pressures and temperatures for ICE applications. However, an examination of the 3-pentanone ($n, \pi^*$) transition motivates additional measurements at low pressures for insight into collisionless rates, which were also acquired in this study. FQY measurements were calibrated to absolute values by using Rayleigh scattering calibration.
In the current work, these experimental methods were used to provide a database of 3-pentanone FQY measurements for both ICE diagnostics and model development. Moreover, this process can be applied to other tracers that absorb and fluoresce in the near UV for photophysical measurements and modeling in support of tracer-based PLIF.

The current work also outlines the methodology used to develop a semi-empirical FQY model from measurements. The key to the development of the model was the identification of pressure and excitation wavelength regimes where the FQY is dominated by certain parameters of the model. Low-pressure measurements are particularly useful in ascertaining the rates of collisionless processes, such as fluorescence and non-radiative de-excitation. Vibrational relaxation can be minimized when the tracer is excited using a laser wavelength that corresponds to the ground and excited state zero-point energy gap, allowing the investigation of collisional quenching by bath gas molecules. This systematic approach allowed for the determination that nitrogen quenching was occurring, contrary to assumptions made in previous work. In addition, the vibrational energy dependence of the relaxation process was also determined. This methodology guided the optimization of a 3-pentanone FQY model that shows good agreement with ICE work up to 1100 K and 28 bar, and future work can use this process as a guide for optimization of models for other tracers.

Future tracer photophysics studies would benefit from the addition of several additional tools. 3-pentanone fluorescence lifetime measurements in previous work significantly aided the determination of fluorescence and non-radiative de-excitation rates. However, unlike FQY data, lifetime data are available only over a limited range of temperatures, pressures, and excitation wavelengths. The installation of a time-correlated single photon counting (TCSPC) measurement system on this experimental setup would allow for the creation of a lifetime database, similar to how the current work created a database of FQY measurements, which can provide further insight into de-excitation and quenching processes. Moreover, measurements of phosphorescence or photolysis products will allow for insight into the triplet state and the ISC process. The addition of these diagnostics will complement the absorption and fluorescence diagnostics presented in this work and aid in understanding the photophysics behind fluorescence tracers.
6.2 Conclusions for Time-resolved Imaging

Time-resolved PLIF imaging is an area of increasing study due to its utility in making measurements of fluctuating flows. This diagnostic could be applied to a wide range of problems, ranging from scientific imaging, such as the measurements of boundary layer development in shock tubes, to more practical applications, such as crank angle-resolved ICE imaging. This work combined developments in frequency doubling, allowing for moderate UV laser power, with the high-FQY tracer toluene to create a highly sensitive, time-resolved imaging. Chapter 5 describes the investigation of CW PLIF detection limits and application of the diagnostic to a turbulent jet. The current work illustrates the potential of CW PLIF diagnostics in time-resolved imaging.

Future work can build on the current work by implementing the diagnostic with high-speed cameras to acquire multiple time-resolved images. Improvements in laser output power would also aid the sensitivity of the diagnostic and can be achieved using a more powerful pump laser or through optical techniques, such as passing the laser sheet through the flow field multiple times. However, the greatest challenge in implementing this CW PLIF diagnostic for quantitative imaging is the scarcity of photophysics data for toluene. Chapter 5 presents absolute FQY measurements of toluene over a range of pressure conditions at room temperature using the Rayleigh scattering calibration technique employed for 3-pentanone. Continued application of the experimental methods used for 3-pentanone photophysics to toluene would lead to the development of a photophysics database and model for toluene. Combined with CW excitation and high-speed detection, toluene PLIF would be a sensitive, time-resolved, and quantitative diagnostic for flow field imaging in a variety of applications.
### Appendix A 3-pentanone Model Parameters

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Table A.1 Lennard-Jones collision parameters used to calculate the collision frequency. Values for 3-pentanone are from [48], and values for nitrogen and oxygen are from [67].

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Table A.2 3-pentanone vibrational frequencies used to calculate the thermal vibrational energy. These values are from [48]. 3-pentanone
Appendix B  Rayleigh-calibrated FQY Data

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Table B.1 Absorption cross-section for 3-pentanone.
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Table B.2 FQY of 3-pentanone vapor calibrated using Rayleigh scattering (continued).
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Table B.4 3-pentanone FQY in air calibrated using Rayleigh scattering.
# Appendix C 3-pentanone Extended $T \& p$ FQY Data

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Table C.2 3-pentanone FQY in air (continued).

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Table C.2 3-pentanone FQY in air (continued).
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Table C.2 3-pentanone FQY in air (continued).
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Table C.2 3-pentanone FQY in air (continued).
Appendix D  Uncertainty Analysis

This section details the uncertainty analysis for measurements of photophysics performed in the current thesis. In particular, measurements of absorption cross-section and fluorescence quantum yield (FQY) were performed.

D.1 Absorption Cross-Section

Absorption cross-section was determined via equation (D.1):

\[
\sigma = \frac{1}{nL} \left( \ln \left( \frac{I_2}{I_1} \right) - \ln \left( \frac{I_2}{I_1} \right) \right)
\]

The cross-section was calculated with the tracer number density \( n \), the length of the cell \( L \), and two separate measurements of transmission. One measurement was made with tracer in the cell, and one made without (indicated by subscript ‘0’). In this equation, \( n \) is determined by the ideal gas equation

\[
n = \frac{X_{tr} p}{k_b T}
\]

where \( p \) is pressure and \( T \) is temperature. The tracer mole fraction \( X_{tr} \) is one since pure 3-pentanone vapor was used in these measurements.

Because these individual uncertainties are uncorrelated, the overall uncertainty in absorption cross-section can be determined with the root-sum-square (RSS) method.

\[
\frac{\Delta \sigma}{\sigma} = \sqrt{\left( \frac{\Delta p}{p} \right)^2 + \left( \frac{\Delta T}{T} \right)^2 + \left( \frac{\Delta L}{L} \right)^2 + 2 \left( \frac{\Delta (I_2/I_1)}{(I_2/I_1) \ln(I_2/I_1)} \right)}
\]
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Error (%)</th>
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<tr>
<td>Pressure ($p$)</td>
<td>Measurement read to 0.01 mbar resolution</td>
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<td>Temperature ($T$)</td>
<td>Maximum difference between cell surface and gas temperature is 5 K at 690 K.</td>
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</tr>
<tr>
<td>Length ($L$)</td>
<td>Measurement to 0.1 mm resolution using calipers</td>
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<td>Transmission ($I_2/I_1$)</td>
<td>Determined by examining standard deviation of repeated measurements of transmission with no tracer in the cell. Highest uncertainties for 277, 308 nm excitation due to lower beam energies than 248, 266 nm. Average transmission for cross-section measurements is about 0.85 for these wavelengths.</td>
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<th>Parameter</th>
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<td>3-pentanone abs. cross-section ($\sigma$)</td>
<td>RSS calculation</td>
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Table D.1 Uncertainty analysis for 3-pentanone absorption cross-section.

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<td>Temperature ($T$)</td>
<td>Measurement read to 0.1 K at 298 K</td>
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<td>Toluene absorption cross-section ($\sigma$)</td>
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Table D.2 Uncertainty analysis for toluene absorption cross-section.
Table D.1 summarizes the uncertainty for the measurement of the absorption cross-section in 3-pentanone. Table D.2 summarizes the uncertainty for measurements in toluene.

### D.2 Absolute FQY Measurements

The absolute FQY determined via calibration to nitrogen Rayleigh scattering was calculated using equation (D.4)

\[
\phi = 4\pi \frac{E_{Ray} n_{Ray}}{E_{LIF} n_{LIF}} \left( \frac{\partial \sigma}{\partial \Omega} \right) \frac{1}{\sigma} \int_{\lambda_L}^{\lambda_U} \frac{S_{LIF}(\lambda)}{R_{SR}(\lambda)} d\lambda \int_{\lambda_R}^{\lambda_U} \frac{R_{SR}(\lambda)}{S_{Ray}(\lambda)} d\lambda
\]

where \( S_{LIF} \) is the fluorescence spectrum, \( E_{LIF} \) is the incident laser energy fluence for the fluorescence measurement, \( n_{LIF} \) is the number density of fluorescing tracer, \( \sigma \) is the absorption cross-section, \( S_{Ray} \) is the Rayleigh line, \( E_{Ray} \) is the incident laser energy fluence, \( n_{Ray} \) is the number density of the scatterer, and \( (\partial \sigma/\partial \Omega) \) is the differential Rayleigh cross-section.

The number densities for both the LIF tracer and Rayleigh scatterer are calculated using the ideal gas equation. For measurements of 3-pentanone FQY made in a bath gas, the 3-pentanone mole fraction is determined from the pump and mass-flow-controller flow rates:

\[
X_{3p} = \frac{Q_{3p} \rho_{3p} M_{3p}}{Q_{bath} \rho_{bath} M_{bath} + Q_{3p} \rho_{3p} M_{3p}}
\]

where \( Q_{3p} \) is the pump volume flow rate, \( Q_{bath} \) is the MFC flow rate, \( \rho_{3p} \) is the 3-pentanone liquid, \( \rho_{bath} \) is the bath gas densities, \( M_{3p} \) is the molecular weight of 3-pentanone, and \( M_{bath} \) is the molecular weight of the bath gas.

The FQY uncertainty can be calculated using the RSS combination of errors from the measurements used in the calculation, as shown below. RSR uncertainty was determined as the RSS of the error in ICCD signal measurement and the error in the manufacturer-provided calibration curves. The resulting expression for calculating error is given by
\[
\frac{\Delta \phi}{\phi} = \sqrt{\left(\frac{\Delta S_f}{S_f}\right)^2 + \left(\frac{\Delta S_{ray}}{S_{ray}}\right)^2 + 2\left(\frac{\Delta p}{p}\right)^2 + 2\left(\frac{\Delta T}{T}\right)^2 + 2\left(\frac{\Delta E}{E}\right)^2 + \left(\frac{\Delta Q_{bath}}{Q_{bath}}\right)^2 + \left(\frac{\Delta Q_{3p}}{Q_{3p}}\right)^2}
\]  

(D.6)

Table D.3 summarizes the uncertainty analysis for 3-pentanone FQY.

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<td>Temperature ((T))</td>
<td>Maximum difference between cell surface and gas temperature is 5 K at 745 K.</td>
<td>0.7</td>
</tr>
<tr>
<td>Laser energy ((E))</td>
<td>Calculated from transmission uncertainty assuming both photodiodes are uncorrelated.</td>
<td>0.3</td>
</tr>
<tr>
<td>MFC flow rate ((Q_{bath}))</td>
<td>MFC calibrated against dry test meter</td>
<td>0.1</td>
</tr>
<tr>
<td>Pump flow rate ((Q_{3p}))</td>
<td>Pump calibrated against graduated cylinder</td>
<td>1.0</td>
</tr>
<tr>
<td>Relative spectral response ((RSR))</td>
<td>RSS combination of ICCD uncertainty and manufacturer provided lamp calibration uncertainty of 1.0%</td>
<td>2.2</td>
</tr>
<tr>
<td>Rayleigh differential cross section ((\partial \sigma / \partial \Omega))</td>
<td>From [70]</td>
<td>1.0</td>
</tr>
<tr>
<td>3-pentanone FQY ((\phi))</td>
<td>RSS calculation</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table D.3 Uncertainty analysis for Rayleigh-scattering calibrated FQY measurements with 3-pentanone.

For measurements of toluene FQY, the mole fraction was determined using pressure measurements, so MFC and pump flow rate uncertainties are not included in the calculation. Table D.4 summarizes the uncertainty analysis for toluene FQY.
### Table D.4 Uncertainty analysis for Rayleigh-scattering calibrated FQY measurements with toluene.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICCD ($S_F, S_{LIF}$)</td>
<td>Estimated uncertainty of ICCD collection</td>
<td>2.0</td>
</tr>
<tr>
<td>Pressure ($p$)</td>
<td>Pressure transducers calibrated against MKS Baratron reading resolution of 1 mbar</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature ($T$)</td>
<td>Maximum difference between cell surface and gas temperature is 5 K at 745 K.</td>
<td>0.03</td>
</tr>
<tr>
<td>Laser energy ($E$)</td>
<td>Calculated from transmission uncertainty assuming both photodiodes are uncorrelated.</td>
<td>0.6</td>
</tr>
<tr>
<td>Relative spectral response (RSR)</td>
<td>RSS combination of ICCD uncertainty and manufacturer provided lamp calibration uncertainty of 4.0%</td>
<td>4.5</td>
</tr>
<tr>
<td>Rayleigh differential cross section ($\partial \sigma / \partial \Omega$)</td>
<td>From [96]</td>
<td>1.0</td>
</tr>
<tr>
<td>Toluene FQY ($\phi$)</td>
<td>RSS calculation</td>
<td>8.1</td>
</tr>
</tbody>
</table>

FQY can also be calculated using

$$\phi = \frac{S_{LIF}}{S_{LIF,0}} \frac{E_n}{E} \frac{\phi_0}{\phi_0}$$  \hspace{1cm} (D.7)

where $S_{LIF}$ is fluorescence signal, $E$ is laser energy, and $n$ is number density. The ‘0’ subscript indicates a reference measurement. The uncertainty can then be calculated using equation (D.8).
\[
\frac{\Delta \phi}{\phi} = \sqrt{2 \left( \frac{\Delta S_f}{S_f} \right)^2 + 2 \left( \frac{\Delta p}{p} \right)^2 + 2 \left( \frac{\Delta T}{T} \right)^2 + 2 \left( \frac{\Delta E}{E} \right)^2 + 2 \left( \frac{\Delta \theta_0}{\theta_0} \right)^2 + 2 \left( \frac{\Delta Q_{bath}}{Q_{bath}} \right)^2 + 2 \left( \frac{\Delta Q_{3p}}{Q_{3p}} \right)^2 + \left( \frac{\Delta Q_{3p}}{Q_{3p}} \right)^2}
\] (D.8)

Table D.5 summarizes the uncertainties for absolute FQY measurements made using this method.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICCD (S_f, S_LIF)</td>
<td>Estimated uncertainty of ICCD signal measurements</td>
<td>2.0</td>
</tr>
<tr>
<td>Pressure (p)</td>
<td>Pressure transducers calibrated against MKS</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Baratron reading resolution of 1 mbar</td>
<td></td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>Maximum difference between cell surface temperature and gas temperature is 5 K at 745 K.</td>
<td>0.7</td>
</tr>
<tr>
<td>Laser energy (E)</td>
<td>Calculated from transmission uncertainty assuming both photodiodes are uncorrelated.</td>
<td>0.3</td>
</tr>
<tr>
<td>MFC flow rate (Q_{bath})</td>
<td>MFC calibrated against dry test meter</td>
<td>0.1</td>
</tr>
<tr>
<td>Pump flow rate (Q_{3p})</td>
<td>Pump calibrated against graduated cylinder</td>
<td>1.0</td>
</tr>
<tr>
<td>3-pentanone FQY (\phi)</td>
<td>RSS calculation</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table D.5 Uncertainty analysis for fluorescence calibrated FQY measurements with 3-pentanone.
Appendix E  3-pentanone FQY Model
Sample MATLAB Script

Section 2.5 describes the structure of the FQY model, and expressions for the
model parameters were optimized using measurements in Chapter 3 and Chapter 4. To
compare the model to FQY data, this MATLAB code was utilized.

```matlab
function phitot = getYield(lambda,T,p,XO2,X3P)

kb = 1.38054E-16;       %Boltzmann constant [erg/K]
close = 1;              %Terminate summation when within 1 cm^-1
XN2 = 1 - X3P - XO2;    %Nitrogen mole fraction
n = p*1e6/(kb*T);       %Total number density (cm^3)
nN2 = XN2*p*1e6/(kb*T); %N2 number density [cm^-3]
n3P = X3P*p*1e6/(kb*T); %3P number density [cm^-3]
nO2 = XO2*p*1e6/(kb*T); %O2 number density [cm^-3]

%Calculate collision rates using Lennard-Jones parameters
[kcoll, Z3PN2, Z3PO2, Z3P] = LJ3pent(T,n3P,nN2,nO2);

%Calculate initial vib. Energy of excited state, thermal energy [cm^-1]
[Ehigh,Eth] = getenergy(T,lambda);
```

163
%Calculate vibrational energy cascade from relaxation
i = 1;      %Initialize counter
E = zeros(30000,1); %Initialize energy cascade array
E(1) = Ehigh; %Start vib energy at initial state in S1

while (E(i)-Eth > close) || (i == 1)
    dEav = deactivate(E(i),Eth,T,n3P,nN2,nO2);
    E(i+1) = E(i) - dEav;
    i = i+1;
end

inum = i;
E = E(1:inum);  %Resize energy array

kf = 3.70e5;    %Fluorescence rate [s^-1]
knr = 4.0e8 ... %Non-radiative rate [s^-1]
+ (1.8E7)*exp(-(E-1175).*(E-1175)/(500*500)) ... 
+ 2*1.13e12/pi*(2650./((4*(E-10340).^2+2650^2)) ... 
+ (5.18e13/5490)*1/((sqrt(pi/2))*exp(-(E-8700).^2)) ... 
+ 2*1.13e12/pi*((E-11608).^2)*exp(-(E-11608)/(2037).^2)) ... *nN2^0.28;

kN2 = 1.789*T^0.28*exp(T/190) ... %N2 quenching rate [s^-1]
* (exp(-2*((E-8700)./2379).^2) ... 
+ 1.1*exp(-2*((E-11608)./2379).^2))*nN2^0.28;

kO2 = 19.0E-04*exp(4.9e-05.*E)*Z3PO2*nO2;   %O2 quenching rate [s^-1]

prob = kcoll./(kcoll + kN2 + kO2 + knr + kf);  %Prob. of relaxation
phi = kf/(kcoll + knr + kf + kN2 + kO2); %Phi for vib energy E
phi(inum) = kf/(knr(inum) + kf + kN2(inum) + kO2(inum)); %Lowest vib

%Sum contributions weighted for relaxation probability
phitot = phi(1);
for i = 1:inum-1
    phitot = phitot + phi(i+1)*prod(prob(1:i)); %Add contr. from step i
end

%**********************************************************************
%   LJ3pent.m
%   Calculates collision frequencies using L-J theory
%   
%   [kcoll [s^-1], Z3PN2 [cm^-3 s^-1], Z3PO2 [cm^-3 s^-1],
%    Z3P [cm^-3 s^-1]] = LJ3pent(T [K], n3P [cm^-3],
%    nN2 [cm^-3], nO2 [cm^-3])
%   
%   Written by: Brian Cheung
%   Date: 8/20/10
%   
%**********************************************************************

function [kcoll, Z3PN2, Z3PO2, Z3P] = LJ3pent(T,n3P,nN2,nO2)
R = 8.314E+7; % Gas constant [erg/mol-K]

% Lennard-Jones coll diam [cm]
sigma3P = 6.05E-8; % 3-pentanone
sigmaN2 = 3.798E-8; % N2
sigmaO2 = 3.4678E-8; % O2

% L-J well depth epsilon/kb [K]
epsilon3P = 432; % 3-pentanone
epsilonN2 = 71.40; % N2
epsilonO2 = 106.7; % O2

% Molecular weight [g/mol]
m3P = 86.016; % 3-pentanone
mN2 = 28.02; % N2
mO2 = 32.00; % O2

% Solve for Lennard-Jones collision parameters and collision frequency
sigma3PN2 = ((sigma3P + sigmaN2)/2.0); % 3p-N2 coll diam [cm]
sigma3PO2 = ((sigma3P + sigmaO2)/2.0); % 3p-O2 coll diam [cm]
epsilon3PN2 = sqrt(epsilon3P*epsilonN2); % 3p-N2 well depth [K]
epsilon3PO2 = sqrt(epsilon3P*epsilonO2); % 3p-O2 well depth [K]
mu3PN2 = m3P*mN2/(m3P + mN2); % 3p-N2 reduced mass [g/mol]
mu3PO2 = m3P*mO2/(m3P + mO2); % 3p-O2 reduced mass [g/mol]
mu3P = m3P*m3P/(m3P + m3P); % 3p-3p reduced mass [g/mol]
omega3PN2 = 1/(0.636 + 0.567*log10(T/epsilon3PN2)); % 3p-N2 coll integ.
omega3PO2 = 1/(0.636 + 0.567*log10(T/epsilon3PO2)); % 3p-O2 coll integ.
omega3P = 1/(0.636 + 0.567*log10(T/epsilon3P)); % 3p-3p coll integ.

Z3PN2 = pi*sigma3PN2^2*sqrt(8*R*T/(pi*mu3PN2))*omega3PN2;
Z3PO2 = pi*sigma3PO2^2*sqrt(8*R*T/(pi*mu3PO2))*omega3PO2;
Z3P = pi*(sigma3P*sigma3P)*sqrt(8*R*T/(pi*mu3P))*omega3P;
kcoll = Z3PN2*nN2 + Z3PO2*nO2 + Z3P*n3P;

% getenergy.m
% Function calculates Eth based on known vibrational frequencies
% assuming harmonic oscillator behavior
% [energy [cm^-1],Etherm [cm^-1]] = getenergy(temp [K], lambda [nm])
% Written by: Brian Cheung
% Date: 30 Sep 2008

function [energy,Etherm] = getenergy(temp,lambda)
E0 = 30770;  %0-0 energy gap [cm^-1]
Etherm = 0;  %Initialize variable

freq = ... %Vibrational mode frequencies [cm^-1]
[21.53, 69.49, 203.10, 217.84, 239.51, 324.61, 423.84, 489.00, 652.08, ...
739.86, 821.13, 851.84, 1009.17, 1038.96, 1057.23, 1066.22, 1165.67, ...
1185.07, 1196.65, 1313.31, 1357.95, 1414.97, 1455.98, 1471.05, 1477.77, ...
1500.03, 1513.69, 1540.67, 1540.95, 1546.58, 1548.44, 1887.78, 3119.43, ...
3128.77, 3145.22, 3146.12, 3159.21, 3170.53, 3230.63, 3230.96, 3240.69, 3241.11 ...];

for i = 1:length(freq)
    Etherm = Etherm + freq(i)/(exp((1.44*freq(i))/temp)-1);
end

energy = 1/lambda*1e7 + Etherm - E0;

% % % deactivate.m % % Function calculates energy decrease per collision % % dEav [cm^-1] = getenergy(temp [K], lambda [nm]) % % Written by: Brian Cheung % Date: 30 Sep 2008 % %******************************************************************************
function dEav = deactivate(E,Eth,T,n3P,nN2,nO2)

%Calculate collision frequencies
[kcoll, Z3PN2, Z3PO2, Z3P] = LJ3pent(T,n3P,nN2,nO2);

%Alpha for N2, O2, 3-pentanone
alphaN2 = (0.89985*exp(-T/82.18)+0.0035).*(0.95+0.0027*exp(E./2150));
alphaO2 = (3.341*exp(-T/59.22)+0.00503).*(0.95+0.0027*exp(E./2150));
alpha3P = 16.4*exp(-T/65.55)+0.00238;

%Collision weighted alpha
alpha = alphaN2*(Z3PN2*nN2)/kcoll + alphaO2*(Z3PO2*nO2)/kcoll + alpha3P*(Z3P*n3P)/kcoll ... + alpha3P*(Z3P*n3P)/kcoll;

dEav = alpha.*(E - Eth);
Bibliography


172


