FUEL TRACER PHOTOPHYSICS
FOR QUANTITATIVE PLANAR LASER-INDUCED
FLUORESCENCE

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Abstract

Temperature, pressure, and excitation wavelength dependencies of the absorption and fluorescence of 3-pentanone ($C_2H_5COC_2H_5$) and toluene ($C_6H_5CH_3$) were studied to support the quantitative imaging of such fuel tracers in a variety of environments. The results of basic photophysical experiments have helped to develop the database needed for successful implementation of two-dimensional temperature and/or concentration measurements under a broad range of conditions. In addition to experimental efforts, semi-empirical photophysical models that account for the change in the fluorescence quantum yield of fuel tracers under a range of experimental conditions have also been developed, providing a physically-based, computationally-tractable framework for data interpretation and a tool for zeroth order experimental design.

Several experimental methods have been used to characterize the photophysical behavior of 3-pentanone in terms of relevant thermal and engineering parameters. Broadband, spectrographic absorption measurements have been made in shock tubes where high temperatures and short time scales enable quantitative measurements without interference from decomposition products. Relative fluorescence measurements in flowing cells at elevated temperatures and static cells at elevated pressures show that 3-pentanone photophysics are qualitatively similar to the well-studied acetone tracer, but quantitative differences can be significant. One finding reveals that 3-pentanone signals per unit mole fraction are virtually independent of temperature for 308 nm excitation below about 600 K, thus enabling straightforward measurements of mole or mixture fractions even in non-isothermal environments. 3-pentanone’s larger temperature dependence for other excitation wavelengths enable sensitive and simultaneous temperature/mole fraction imaging at higher temperatures than were
previously demonstrated using acetone. Absolute fluorescence quantum yield (FQY) measurements reveal that 3-pentanone can provide slightly more signal per molecule than acetone. Pressure and composition studies reveal that oxygen weakly quenches 3-pentanone fluorescence with a clearly noticeable effect when air pressure is above a few bar.

Toluene, like 3-pentanone, is physically similar to iso-octane with a boiling point of around 110 °C. Furthermore, toluene is a representative aromatic, a class of chemicals that form a major component of a wide variety of real and surrogate fuels. Substantial fluorescence signal levels are possible in the UV where toluene absorbs (220-270 nm) and fluoresces (270-350 nm). Unlike 3-pentanone, however, toluene’s high propensity for oxygen quenching has made it attractive as a tracer for the local fuel-air ratio in internal combustion engines (ICE’s) rather than simply a fuel tracer. Because of the importance of identifying regions of ignitability in ICE’s, fuel-air ratio LIF (FARLIF) has high potential for application in the ICE research community. Unfortunately, there has been a lack of experimental evidence for the linear relationship between signal and fuel-air ratio at high temperatures. The basic experiments and modelling efforts of this work show that signal interpretation is not necessarily straightforward under all conditions relevant to combustion research. While there are limited experimental regimes in which signal is directly proportional to the fuel-air ratio, specifically only for 266nm excitation under 500K, general application of FARLIF requires that extra calibrations or flow control measures are necessary in order to ensure accurate signal interpretation. In addition to suggesting refinements for current techniques, the basic experimental studies also suggest the possibility of new and simplified techniques for measuring temperature and concentration.
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Chapter 1

Introduction

Planar laser-induced fluorescence (PLIF) is a spatially-resolved, non-invasive, laser-based diagnostic technique that can be used to visualize one or more properties of a spectroscopically targeted species in a variety of situations. In most cases, the primary property of interest is the concentration of the targeted species, but velocity, pressure, temperature, reaction rates and a number of other properties may also be measured [11–14]. Fields of interest range in size from a several nanometers — like single cells or even single molecules [15] — to fairly large systems, like 100-kW gas flames [16], and they range in speed from static to supersonic [17]. PLIF is a tool applicable to both basic scientific inquiries and development of practical engineering devices, and it has been applied to all classical phases of matter. PLIF and similar fluorescence imaging diagnostics span the fields of engineering, biology, medicine, physics, and chemistry.

A generic PLIF experiment consists of a laser beam (usually a sheet-shaped laser beam to provide a high degree of spatial resolution for planar LIF, but there are also other means of obtaining good spatial resolution) passing through a flow of interest with a lens and camera available to detect the fluorescence. By design, the laser wavelength will correspond to a resonant transition of the targeted molecules in the field of interest. Some of the resonant laser light is absorbed, exciting the targeted molecules, and a fraction of those molecules subsequently fluoresce. A fraction of the emitted fluorescence is collected by the camera, and the resulting signal
is then post-processed and interpreted as an image of the property of interest, like concentration. In some cases, carefully chosen combinations of lasers, fluorescence events, and detection systems can result in measurements of more than one property simultaneously.

Sometimes PLIF measurements take advantage of the nascent molecules in a flowfield, such as visualizing the reaction region of a flame via the OH radical [18, 19]. Often however, photo-active species are not a natural part of the field of interest and are added as tracers in order to enable a measurement of that field. PLIF using such molecular tracers or tags is thus common.

As one might imagine, the best choice of a PLIF tracer depends on the application, the desired measurement quantity, the availability of lasers and detection equipment (in cases of limited resources), and a myriad of other factors that result in the use of tracers ranging from atoms to proteins — a scope too broad to be covered here. In this work, we are chiefly concerned with tracers for non-reactive gas-phase measurements. We thus continue with a historical background on the development of a few of these types of tracers.

1.1 Acetone and 3-pentanone photophysics

In an effort to find an ideal low temperature (sub-combustion temperatures), gaseous, molecular tracer, Lozano surveyed a large number of candidates [20]. He determined that acetone was an optimal tracer for many applications [21] because it was safe, cheap, easy to handle, and it had:

- a high vapor pressure (it was easy to seed into the gas phase),

- a broad and accessible absorption spectrum (where high-powered lasers could be used),

- a strong, non-resonant fluorescence spectrum in the near-UV/visible (where detector quantum efficiencies were high), and
• a short fluorescence lifetime (enabling measurements of fast flows without blurring effects and a high resistance to collisional quenching or bath gas effects).

His discovery lead rapidly to the near-ubiquity of acetone PLIF as a means of studying basic fluid mechanics and a variety of other engineering applications [22–27].

While Lozano initially isolated his search to conditions near room temperature and atmospheric pressure, the range of acetone PLIF applications quickly expanded to incorporate other experimental conditions. As a result, questions naturally arose regarding the possible effects of temperature and pressure on the fluorescence signal. Further confusing the issue was the fact that several excitation wavelengths were popular, and the temperature and pressure behaviors were not necessarily the same for each excitation wavelength. This issue was addressed in part by several researchers [7,28], but the most thorough were the studies of Thurber, who undertook concerted experimental and modelling efforts to evaluate the temperature, pressure, and excitation wavelength dependencies of acetone fluorescence [5, 29]. Combining some of the hypotheses of physical chemists with experimental observations, Thurber developed a reasonably straightforward photophysical model to describe the apparently complex behavior of acetone under various experimental conditions (read more about the details of the model in Chapter 3). Also from Thurber’s and others’ work came the realization that because of the temperature dependencies, one could devise techniques to measure temperature and concentration simultaneously [7,30].

Simultaneous with Thurber’s efforts to quantify the photophysics of acetone, other researchers were realizing that acetone was not the ideal tracer in some situations because it did not necessarily track the property of their interest — that is, the concentration of fuel during mixing in combustion devices. In many such devices, safety dictates that the fuel be injected as a liquid and evaporate and mix with the air a short time before ignition. The mixing process is thus a key to controlling and optimizing various modes of combustion, and PLIF is well-suited for studying such processes. Mixing rates naturally depend on the evaporation and diffusion rates of the fuel. Iso-octane, a typical non-fluorescing surrogate for gasoline, being a much heavier compound than acetone, would tend to remain in the liquid phase much longer than acetone, and PLIF measurements on a system using acetone with or instead of
iso-octane would thus be misleading if they were interpreted as fuel concentration for the operational device. Researchers thus proposed using 3-pentanone, a larger and less volatile member of the ketone (acetone) family, as a more suitable tracer for iso-octane [31, 32]. 3-pentanone has many of the same attractive photophysical characteristics as acetone, but its boiling point is close to iso-octane, roughly indicating that evaporation rates will be similar. One might thus mix a small amount of 3-pentanone with iso-octane in order to obtain a PLIF-ready surrogate fuel that did not significantly alter the combustion process but would yield more accurate information regarding the concentration of the gas-phase fuel. Since then, 3-pentanone has been a preferred tracer for mixing studies in gasoline combustion devices [33–36]. Similar to acetone, questions quickly arose regarding the effects of temperature and pressure on 3-pentanone’s fluorescence signal and the possible systematic errors in concentration measurements. Naturally, researchers set to investigating these dependencies, but similar to early investigations of acetone, the studies before this work filled-in only part of the picture, for example, quantifying only the fluorescence behavior (as opposed to the more fundamental separation of absorption and fluorescence processes) under various conditions for a single excitation wavelength or over a limited range of temperature and pressure [4, 7, 37]. No comprehensive photophysical understanding of 3-pentanone has been developed, and as a result, the general use of quantitative 3-pentanone PLIF in a wide variety of applications is hindered.

A major portion of this work is thus to experimentally investigate the temperature, pressure, and excitation wavelength dependencies of 3-pentanone LIF, and in so doing, assimilate and expand data already available in the literature to form as comprehensive an understanding of 3-pentanone LIF as possible, enabling development of suitable engineering models for fluorescence behavior. With a better understanding of the photophysics and a suitable model, quantitative 3-pentanone measurements will be more easily applied to a wide range of experimental conditions.
1.2 Toluene photophysics

As previously mentioned, Lozano performed a thorough survey of potential PLIF tracers for non-reacting gaseous flows [20]. In his survey, aromatics like toluene were considered disadvantaged in comparison with the ketones because of their proclivity for oxygen quenching from the excited state. For applications that require constant signals proportional only to the local tracer concentration, oxygen quenching is of course a disadvantage. However, for applications where the presence of oxygen is of great importance, toluene’s high sensitivity to oxygen can yield a useful measurement of the local toluene-to-oxygen ratio (see Chapter 4 for photophysical explanation). This significant finding was first noted by Reboux [10] and suggested for measuring the fuel-air ratio in a spark ignition (SI) engine. Subsequent quantitative application of the Fuel-Air Ratio LIF (FARLIF) technique, however, has been hindered by lack of detailed knowledge of toluene photophysics. While Reboux showed that toluene LIF signals are proportional to the fuel-air ratio for 248nm excitation at room temperature above 3 bar, its behavior above room temperature and for different excitation wavelengths (namely 266nm) is not well understood. Hence, in addition to 3-pentanone, this work seeks to expand the photophysical knowledge and understanding of toluene.

1.3 Outline of thesis

The goal of this work is to advance the understanding of 3-pentanone and toluene fluorescence so that quantitative fuel or fuel-air tracer PLIF diagnostics can be applied under a wider range of experimental conditions without systematic errors. Several tools and techniques are described and utilized to do this, including broadband absorption spectra obtained in a shock tube, well-controlled absorption and fluorescence measurements in cells, and physically-based models describing the excited state energy transfer mechanisms and their effects on the fluorescence quantum yield. After presenting some further background on fluorescence and PLIF techniques (Ch. 2), the work on 3-pentanone will be presented in its entirety, followed by toluene. In Chapter 3, experiments are described that isolate and quantify the photophysical
properties of tracers, and results of the experiments and model developments are given for 3-pentanone. Chapter 4 will detail some additional background for tracers strongly quenched by oxygen and give experimental and modelling results for toluene. Conclusions and recommendations for future work will then follow.
Chapter 2

Photophysics and PLIF

Background

The tracer molecules considered in this text are polyatomic broadband absorbers, generally excited by nanosecond lasers in the near UV, and the fluorescence is subsequently collected over a period many times longer than the excited state lifetimes. The following time-integrated form of the fluorescence equation thus describes the observed fluorescence signal, $S_f$ (in number of photons collected), following weak excitation:

$$S_f = \frac{E\lambda}{hc} n\sigma(\lambda, T)L\phi(\lambda, T, p_i)\eta$$  \hspace{1cm} (2.1)

The terms on the right-hand side are:

- $E$ incident laser energy
- $h$ Planck’s constant
- $c$ speed of light
- $\lambda$ wavelength of excitation laser
- $n$ number density of absorbing species
- $\sigma$ absorption cross section of absorbing species
length of the illuminated volume in direction of laser propagation, i.e. path length

fluorescence quantum yield — fraction of excited molecules that fluoresce

collection efficiency — fraction of emitted photons collected by detection system

$E\lambda/hc$ represents the number of incident photons that pass through the imaged volume of length $L$. The fraction of the photons absorbed is $n\sigma L$, a Beer’s Law representation in the optically thin limit. For mole or mixture fraction imaging, the number density may also be written in terms of the mole fraction, $\chi$, of the targeted species.

$$n = \frac{\chi p}{kT}$$  \hspace{1cm} (2.2)

where $p$ is the total pressure, $k$ is the Boltzmann constant, and $T$ is the temperature. The product of incident photons and the fraction absorbed is equal to the number of excited molecules. If one multiplies the number of excited molecules by the fraction that fluoresce, $\phi$, one obtains the number of fluorescence photons. $\eta$ then describes the fraction of the fluorescence photons that are collected by the detector.

Equation 2.1 provides some insight for developing quantitative PLIF diagnostics for properties like concentration or temperature. First, the incident laser energy must either be uniform or known and correctable. The latter is more often the case. The collection efficiency can also be non-uniform and thus requires calibration, either simultaneous with, or separate from, the incident laser energy. While relative changes in these parameters in a given experiment can be removed via established methods [11, 17, 30], the absolute values of the collection efficiency and the photon fluence are often difficult to determine accurately, so relative measurements for a property like number density or mole fraction are usually performed by calibrating the fluorescence signal from a single point of known properties somewhere in the flowfield.

Once a calibration method is established, the fluorescence equation can guide the development of diagnostics. Techniques for number density (or mole or mixture fraction) measurements are greatly simplified if the photophysical parameters, $\sigma$ and $\phi$, 

are constant throughout the flowfield. In many cases, however, $\sigma$ and $\phi$ are not constant because in addition to wavelength dependencies, $\sigma$ depends on temperature $T$, and the fluorescence quantum yield depends on temperature and, to varying degrees, on the collisional environment, represented in Equation 2.1 by the partial pressure of species $i$, $p_i$. Hence, unfortunately, rather than the exception, the norm is that nonuniform temperatures or concentrations cause non-linearity in the relationship between fluorescence signal and concentration.

In general, approaches to diagnostic development for inhomogeneous environments are a) to identify regimes in which the photophysical parameters do not vary in the flowfield of interest (thus restoring the linearity), b) to quantify the photophysical behavior in order to enable corrections, or c) to develop more sophisticated techniques that can measure more than one parameter. Usually, combinations of these options may be used, depending on the application. All of these approaches, and ultimately, the broadest application of PLIF depend on how well we understand the photophysics. Hence, the functional dependence of absorption, $\sigma(\lambda, T)$, and fluorescence, $\phi(\lambda, T, p_i)$ must be known.

For diatomic PLIF tracers like NO or OH, limited degrees of freedom in the molecular structure result in clearly identifiable absorption lines with a relatively straightforward temperature dependence that can be theoretically predicted. For large molecules like acetone, 3-pentanone, and toluene, overlap of rovibronic transitions is so extensive that individual transitions cannot be measured under most conditions. Moreover, first principles calculations of absorption and fluorescence are also generally infeasible, although efforts in this direction continue to show improvement [38]. On the other hand, large tracers with broad spectra enable the use of broadband, high-power lasers at a variety of wavelengths and broadband detectors with large quantum efficiencies. Signals thus tend to be much higher for large tracers than for diatomics. Experiments are also simplified because overlap integrals between laser and absorption lines need not be considered, focussing instead on large scale effects of temperature, pressure, and excitation wavelength. Furthermore, data interpretation does not require knowledge of individual transitions. A qualitative understanding of the excited state deexcitation mechanisms can be used to provide a
framework for understanding empirically measured temperature, pressure, and excitation wavelength effects, and simplified models of the excited state dynamics can be optimized to match observations. Together, models and data provide a qualitative and quantitative description of the fluorescence from large tracers that is otherwise lacking.

\section{Measurement strategies}

If the temperature dependencies can be identified and the composition dependencies are small so that \( p_i \) in equation 2.1 can be replaced by the overall pressure of the flow, \( p \), uniformly seeding an isobaric, non-isothermal flow results in fluorescence signals that can be directly mapped to the temperature.

\[ S_f \propto \frac{1}{T} \sigma(\lambda, T) \phi(\lambda, T, p) \tag{2.3} \]

For the more general case in which tracer concentration and temperature vary, the ratio of two measurements using different excitation wavelengths with different temperature dependencies yields a unique function of temperature.

\[ \frac{S_{f,\lambda_1} E_{\lambda_2}}{S_{f,\lambda_2} E_{\lambda_1}} \propto \frac{\sigma(\lambda_1, T) \phi(\lambda_1, T, p)}{\sigma(\lambda_2, T) \phi(\lambda_2, T, p)} \tag{2.4} \]

In an isobaric flow, one can measure the fluorescence from two spatially overlapping laser pulses, separated in time enough to collect fluorescence following each pulse but not so much as to allow the flow to significantly change. From the ratio of the energy-corrected measurements one can derive temperature, provided the right-hand side of Equation 2.4 is known. Furthermore, having obtained the temperature field, one can correct for the temperature-induced non-linearities via Equation 2.1 and derive mole fractions or number densities from one of the original measurements. This two-line, two-camera technique thus also enables concentration measurements in cases where temperature variations are unknown.
Chapter 3

3-pentanone

This chapter will describe in detail some of the experimental tools utilized to study the photophysics of large polyatomic tracer molecules and how they were applied to 3-pentanone. The tools include broadband absorption measurements, relative LIF temperature dependence measurements using a heated cell, relative LIF pressure dependence measurements using a room-temperature cell, and absolute fluorescence quantum yield measurements in the room-temperature cell using a Rayleigh calibration. Results and implications for the 3-pentanone measurements are included as well as efforts to model the fluorescence quantum yield.

3.1 Broadband absorption measurements

For the large tracers relevant to this work, the near-UV absorption spectra may span several tens of nanometers. Quantifying the entire spectrum is useful for several reasons. First, a broad absorption survey will reveal which high-powered lasers (including those that are not yet available) are suitable for PLIF applications using the tracer in question. Second, the value of the absorption cross section at selected wavelengths is necessary during experimental design stages in order to estimate expected signal levels. The cross section may also be useful during image post-processing where corrections due to laser absorption may be necessary. Finally, since the spectrum may
shift as a function of temperature, survey measurements allow one to consider the effects of radiative trapping of the fluorescence signal in high-temperature applications. This section will describe a method for measuring the vis/UV absorption spectra for large molecules as a function of temperature. Results of measurements performed on 3-pentanone are provided.

3.1.1 Background on 3-pentanone near UV absorption

The near-UV absorption spectrum of 3-pentanone is common to many carbonyl compounds. At ambient conditions, the system is broad and devoid of fine structure, varying slowly from about 230 nm to 320 nm with a maximum absorption cross section of about $6 \times 10^{-20} \text{cm}^2$ around 280 nm and an electronic zero-point around 325 nm. The spectrum corresponds to the symmetry forbidden (or vibronically allowed) electronic $\pi^* \leftarrow n$ transition where an electron from a non-bonding orbital localized near the oxygen atom is excited to an anti-bonding orbital around the CO group. About 3 orders of magnitude smaller than an allowed electronic transition, this system borrows its intensity from Rydberg transitions in the deep UV through vibronic coupling. In other words, the wave functions of vibrational modes that break the $C_{2v}$ symmetric structure of the molecule couple with the electronic wave functions (effectively a breakdown of the Born-Oppenheimer approximation) to produce a non-zero transition dipole moment; even so, the spatial overlap is poor (e.g., 10x weaker than the $\pi \leftarrow \pi^*$ transition for toluene, which is also symmetry-forbidden).

While researchers have measured the absorption at room temperature [2, 3], elevated temperature studies have not previously been performed on 3-pentanone. Work on other ketones like acetone [39], however, indicates that temperature increases will tend to increase the strength of the system and cause the spectrum to redshift, logistically due to stronger vibronic coupling at higher vibrational energies. Increases in pressure, however, will not measurably affect the spectrum because its ambient shape is dominated by extreme congestion of rovibronic transitions that are dominated by doppler broadening in the near UV. Individual lines, even for the smaller and less-congested acetone molecule, can be observed with some difficulty only at temperatures
of a few Kelvin for excitation wavelengths above 315 nm [40–42].

### 3.1.2 Experimental Layout

The experimental schematic shown in Figure 3.1 depicts the key facilities used for measuring the absorption spectra of several gases (ketones, toluene, carbon dioxide, carbon monoxide, water) at elevated temperatures. The experiments were performed in a high-purity, turbo-pumped, stainless-steel shock-tube (15.24 cm in diameter) that has been previously described for use in high-temperature measurements of chemical reaction rates [43]. UV-grade fused silica windows centered 2.0 cm from the shock-tube end wall allowed the optical access necessary for the absorption measurements. Reflected shock wave conditions were calculated from measured incident shock speeds using standard ideal-gas shock wave relations [44].

![Figure 3.1: Experimental schematic for time-resolved broadband absorption measurements in the near UV at elevated temperatures.](image)

Argon-diluted mixtures of the studied tracer (less than 4% tracer) were made manometrically in a mixing tank from the room temperature vapor pressure of a
purified (via freeze-pump-thaw) liquid sample. The mixture was then filled into the driven section of the evacuated shock tube to a prescribed pressure, $P_1$, between 60 and 220 mbar with reflected shock pressures, $P_5$, in the range of 1-2 bar. Post-shock gas temperatures ranged from 540 to 1040 K. Nitrogen and helium were used as driving gases.

The optical system was comprised of a deuterium lamp, collimating optics, monochromator, and modified frame-transfer CCD camera. UV light (deuterium lamp – Oriel, 30W) was transmitted through the test gas, focused at f/4 into an imaging spectrometer (Acton SpectraPro 150, 300 line/mm grating), and detected with an unintensified Lumogen-coated EEV 57 frame-transfer CCD camera (Roper Scientific). A modified chip controller and a mechanical mask (installed by Roper) covering all but the first 5 rows of pixels converted the fast-framing EEV 57 chip to a kinetics format. Every $\Delta t$ (a time set by the control software, typically 4 $\mu$sec) the charge in each row of pixels was shifted down one row; with 5 exposed rows, each row was thus exposed for $5 \times \Delta t$, typically 20$\mu$sec. The dispersed light was spread over the 512 pixel columns (6 mm wide) of the CCD chip with a total wavelength coverage of approximately 130 nm (0.25 nm/pixel). The columns were binned into groups no larger than four in order to achieve a better signal-to-noise ratio (SNR) for the subsequent analysis. This did not hinder the spectral resolution; it was 2.6 nm (FWHM), limited by the 120$\mu$m spectrograph entrance slits needed to acquire adequate light signal in the short exposure time. The wavelength calibration was performed by substituting a mercury lamp for the deuterium lamp. The uncertainty in the wavelength calibration, as given by the standard (1$\sigma$) error from a linear fit of six mercury lines, is only 0.2 nm, well within the resolution of the spectrograph.

Because the kinetic spectrograph acquired spectra with time resolution, we were able to determine when pyrolysis or gas kinetic effects began to occur by monitoring the absorption versus time. After ensuring that the time-steadiness of the deuterium lamp was within $\pm 0.2\%$ and background signals were appropriately subtracted, the baseline light intensity in the form of a 2-D array, $I_0(t, \lambda)$, was acquired immediately prior to filling and firing the shock-tube. The transmitted light intensity, $I(t, \lambda)$, captured the arrival of the shock and the post-shock test time. Each data set was
then averaged over a limited number of rows (representing a limited post-shock time interval) to maximize the SNR. For example, when studying 3-pentanone at 1040 K, the integration time interval was limited to about 60 µsec due to thermal decomposition. For lower temperatures, however, the integration time was increased to obtain a better SNR. The resultant 1-D transmitted array $I(\lambda)$ was then divided, member by member, by a similar time-averaged baseline array $I_0(\lambda)$ to give a transmission array $T(\lambda)$. The absorption cross-section, $\sigma(\lambda)$, was then derived from the Beer-Lambert Law,

$$\frac{I(\lambda)}{I_0(\lambda)} = exp(-\sigma(\lambda)n_xL)$$

where $n_x$ represents the number density of the tracer during the post-reflected shock conditions, and L is the path length, 15.24cm. Each shock resulted in a measurement of $\sigma(\lambda)$ at a fixed post-shock temperature, $T$, which was calculated from the velocity and initial conditions via one-dimensional shock-jump equations [44]. Several experiments were performed using various initial pressures in the driven section. The post-shock temperature was thus also varied, resulting in a series of measurements at temperatures between 540 K and 1040K, the group being represented by $\sigma(\lambda, T)$.

### 3.1.3 Results and discussion

Room temperature measurements, taken from a pre-shock fill of the test section, agree well with the data of Martinez [2] as shown in Fig. 3.2. Shock-heated 3-pentanone spectra are shown in Fig. 3.3. The minimum temperature was 540K, limited by the gasdynamic behavior of the shock tube, and the maximum temperature was 1040K, limited by the pyrolysis of 3-pentanone. The strength of the system increases with temperature. Between room temperature and 1000K, the peak absorption increases by almost a factor of two (from $\sigma = 6 \times 10^{-20}$ to $1 \times 10^{-19}$) in addition to shifting to the red by about 10 nm. Below 220 nm, the red tail of the $\pi^* \leftarrow \pi$ system is similarly seen to redshift into the measured range. The blue tail of the $\pi^* \leftarrow n$ transition, between about 220 and 265 nm changes very little in magnitude over the measured temperature range. Above 265 nm, however, the increase in absorption cross section with temperature is dramatic.
The temperature behavior can be interpreted in light of the symmetry-forbidden transition. As the vibrational energy of the ground state increases with temperature, the increased displacement of the symmetry-breaking vibrations improves the Franck-Condon overlap, and the transition strength thus increases with temperature. Also, with added energy in the ground state, the photon energy required to make the electronic transition lessens, leading to a net red-shift in the absorption spectrum. These two effects cause the spectrum to grow and broaden to the red as temperature increases.

The uncertainties in the measured cross-sections vary with their magnitude. In regions of low absorption, the uncertainty is $\pm 0.3 \times 10^{-20} \text{cm}^2$ for the lowest cross-sections shown in Figure 3.3, this due primarily to the 0.2% uncertainty in the steady output of the deuterium lamp. For larger measured cross sections and higher temperatures, other uncertainties contribute. The temperature and pressure uncertainties
3.1. BROADBAND ABSORPTION MEASUREMENTS

Figure 3.3: Absorption spectrum of 3-pentanone measured at elevated temperatures.

from the gas dynamic model are both \( \approx \) 3%. Initial gas mixtures are prepared to better than 98% accuracy. During shock tube filling, some slow loss of the tracer via adsorption to o-ring seals and walls might be expected, but given the strong agreement with independently measured data at room temperature (Fig. 3.2), these losses are decidedly insignificant. Propagation of uncertainties in the fractional absorption and the number density leads to an uncertainty at the largest cross-sections of \( \pm 8\% \). The total assigned experimental uncertainty for these data are thus \( \pm 8\% \) of the measured value with a minimum of \( \pm 0.3 \times 10^{-20} \text{cm}^2 \).

**Representation of the absorption cross section**

Advances in the simulation and prediction of vibronically-allowed, polyatomic spectra have been periodic since the problem was first attacked by Herzberg and Teller [38, 45–47]. Unfortunately, first-principle calculations for molecules relevant to fuel tracers, although informative in many respects, have not advanced enough to resemble experimental observations under ambient conditions [38]. Before the advent of
the computing power necessary for *ab initio* calculations, simpler models were proposed that captured the essential features of electronic systems ranging into the deep UV, [9, 48, 49]; however, corrections were often necessary in order to obtain quantitative agreement, compromising the model’s simplicity.

Given the previous work and the apparent difficulty in modelling highly congested systems, it is more efficient and useful to parameterize the absorption cross section as a function of excitation wavelength and temperature with a least-squares fitting routine and a suitable equation form. The advantage of the fit will be its straightforward application for predicting fluorescence signals from experiments as well as for correcting for laser absorption effects during image post-processing. Unfortunately, because the fit lacks physical basis, extrapolations beyond the range of fitted data are less likely to be accurate. Since the measurement domain spans room to pyrolytic temperatures, probably only low-temperature (e.g., compressible or supersonic) applications are left wanting.

At each temperature, the absorption between 230 and 330 nm can be approximated by a gaussian profile of the form:

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

(3.2)

where $A$ represents the amplitude, $\lambda_c$ represents the system center, and $w$ represents the width. Since the growth and redshift of the feature appears to be smooth, low-order polynomial expressions of the gaussian parameters in terms of temperature should then yield a reasonable fit. Using a least-squares, unweighted optimization, the gaussian parameters with the following linear form match the data shown in Fig. 3.3 reasonably well:

$$
\begin{align*}
A &= A(T) = 4.67 \times 10^{-23} T + 4.84 \times 10^{-20} \\
\lambda_c &= \lambda_c(T) = 0.0184 T + 274 \\
w &= w(T) = 1.41 T + 25.0
\end{align*}
$$

(3.3)

The simulated curves and the residuals are shown in Fig. 3.4. The top portion shows
the calculated curves. The middle portion shows the residual, defined as the data minus the fit at every point, and the bottom plot shows the relative residual, defined as the residual divided by the value of the measured data. The residual is consistently less than $4 \times 10^{-21}$ cm$^2$, which is less than 10% of the measured cross section in the 260 to 320 nm region (recall that the measurement uncertainty is about 8% in this region). In the wings of the spectrum, the disagreement is somewhat larger, but is still on the same order of the measurement uncertainty in these regions. The fit thus introduces little error outside of the measurement uncertainty throughout the spectrum.
3.2 Laser Absorption and Fluorescence Measurements

Quantifying the absorption is the first step toward understanding fluorescence tracers and performing quantitative measurements. Broad spectral surveys as described in the previous section provide part of the necessary information. Methods for obtaining the fluorescence quantum yield (FQY), $\phi(\lambda, T, p_i)$, are described in the following section. Three types of experiments are described. First, the absolute value of the FQY is measured at a reference condition using Rayleigh scattering as a means of calibrating the optical system. Second, the fluorescence temperature dependencies are measured relative to room temperature conditions at atmospheric pressure, and third, the relative fluorescence pressure dependencies are measured at room temperature. Results for 3-pentanone are provided for each experiment.

3.2.1 Absolute fluorescence quantum yield measurements

Literature review

The absolute fluorescence quantum yield of gaseous acetone has previously been published, to the best of the author’s knowledge, by only two sources: Heicklen [50] and Halpern [51]. For 3-pentanone, only Hansen and Lee [3] have published absolute values, but these measurements were made relative to acetone using Heicklen’s value as a calibration standard. We will thus review the sources of the acetone data in greater depth. Each of the two published works on acetone is a measurement of $\phi$ relative to another published fluorescence yield measurement. Figure 3.5 is a diagram showing the chain of relative measurements for each source, ending with a published value of $\phi$ for acetone when excited at 313 nm. Despite the fairly similar conditions, the two values differ by almost a factor of two. One might hypothesize that the differences in temperature and pressure could impact the fluorescence yield significantly; however, the fluorescence yield model developed by Thurber [5] indicates that this would not be the case. Obviously, with consecutive relative measurements, there arises the concern for propagation of systematic errors from one experiment to the next. Little is
Figure 3.5: Diagram of relative measurements leading to two published values of acetone fluorescence quantum yield. Each author measured the behavior of their chemical using the chemical of the previous work as a fluorescence standard.

said by either source about experimental uncertainties. Given the age of the work, we can only speculate into possible sources of error in each chain of measurements based on the published information. For example, Heicklen’s calibration measurements for biacetyl were at a different temperature than when Almy [52] made an absolute measurement; Heicklen also noted that acetone data obtained by comparison to biacetyl is approximate. Similarly, Halpern used a different hexafluoroacetone pressure compared to that of his reference, Gandini [53]. The Gandini work measured the gas-phase properties of hexafluoroacetone relative to liquid quinine sulfate with a published uncertainty of 10%, and the absolute fluorescence yield of quinine sulfate was measured by Eastman [54] with an estimated uncertainty of at least 6%. An accurate value of the fluorescence quantum yield for both acetone and 3-pentanone thus remains an open question. New, more direct measurements may help resolve the disagreement in the published data.

**Theory for Rayleigh-calibrated fluorescence yield measurement**

Rather than calibrate the optical system against another fluorescent species whose fluorescence yield may also be uncertain, we chose to utilize Rayleigh scattering.
Rayleigh scattering has been successfully used previously as a means of absolute calibration for LIF concentration measurements of radical species [55–58]. Since our application is somewhat different, however, we will present the relevant equations below to thoroughly explain our methods.

For this application, the total LIF signal collected from a laser-illuminated volume of a gas, can be predicted by the following form of the fluorescence equation:

\[
S_{LIF} = \frac{I_{laser} A}{\hbar \nu} n \sigma L_\phi \frac{\Omega}{4\pi} R_{LIF}
\]  

(3.4)

Here, the laser energy of Equation 2.1 has been replaced by an intensity \( I_{laser} \) and a cross-sectional area, \( A \), and the optical collection efficiency has been expanded into the collected fractional solid angle, \( \Omega/4\pi \), and the spectral responsivity, \( R_{LIF} \).

The average spectral responsivity is the net efficiency of the conversion of collected photons into photoelectrons; it includes the transmissivity of the optics, the quantum efficiency of the photocathode, and the gain of the intensifier or other electronics. For broadband detection, this responsivity must be weighted by the spectrum being observed, since it may vary with wavelength:

\[
\overline{R_{LIF}} = \frac{\int R'(\lambda)S'_{LIF}(\lambda)d\lambda}{\int S'_{LIF}(\lambda)d\lambda}
\]

(3.5)

where \( R' \) and \( S'_{LIF} \) are the responsivity and measured LIF signal, respectively, at a particular wavelength. Note that in the general case for any candidate tracer, the LIF spectrum may change shape with experimental conditions, e.g. changing pressure or excitation wavelength. Hence, \( \overline{R_{LIF}} \) may need to be calculated for each experimental condition. For ketones like acetone and 3-pentanone, however, the fluorescence spectrum shape is nearly independent of the studied conditions, so \( \overline{R_{LIF}} \) is a constant for all experimental conditions. Thus, \( \overline{R_{LIF}} \) needs only to be measured once for the ketones. This is not true for a molecule like toluene (see Ch. 4).

While the fluorescence quantum yield is the property of interest in this section, quantities like the collection solid angle and the overall responsivity are often difficult
3.2. LASER ABSORPTION AND FLUORESCENCE MEASUREMENTS

to specify, measure, or control during the course of an experiment. Hence, experiments
to measure $\phi$ are often performed on a relative scale where only one quantity is
varied or the change in multiple properties is well-known (e.g., when the fluorescent
tracer is changed and the absorption cross section and number density are altered).
Absolute measurements of $\phi$ were performed by Almy in 1943 [52] for biacetyl and
by Eastman [54] in 1967 for quinine sulfate. Since then, experiments measuring the
change in the fluorescence signal due to changing wavelength and tracer have been
used to find $\phi$ of the ketones.

The Rayleigh signal, if collected orthogonal to the laser’s plane of vibration (the
plane containing the electric field vector and the direction of laser propagation), can
be calculated from the following.

$$
S_{Ray} = \frac{I_{laser} A}{\hbar \nu} n L \frac{d\sigma}{d\Omega} \Omega R_{Ray}
$$

(3.6)

where most of the terms are defined similarly to those in Equation 3.4. Here, the dif-
ferential Rayleigh cross section, $d\sigma/d\Omega$ (cross section per unit solid angle), evaluated
orthogonal to the plane of incident polarization, is calculated from classical theory
based on a widely-spaced group of oscillating dipoles. If the signal is collected over a
small solid angle, $\Omega$, changes in the differential cross section with spatial coordinates
can be neglected. The spectral responsivity of the collection and detection system,
$R_{Ray}$, is evaluated at the laser wavelength, rather than averaged over the broader
fluorescence wavelengths as in Equation 3.5.

A thorough review of the theory behind Rayleigh scattering is provided by Miles
et al. [59]. In short, the differential Rayleigh cross section can be described by Equa-
tion 3.7.

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

(3.7)

New symbols in this equation are $F_K$, the King factor, and $r$, the simple index of
refraction at the wavelength in question ($r$ must be close to 1 for this form of Equa-
tion 3.7). The King factor term quantifies the anisotropic behavior of the scattering
molecule and generally increases the cross section by a few percent. For nitrogen, the
King factor is [60]

\[ F_K = 1.034 + \frac{317}{\lambda^2} \]  \hspace{1cm} (3.8)

The ratio of \( r-1 \) to \( n \) is proportional to the polarizibility of the molecule (in accordance with the Lorentz-Lorenz equation) and is thus an intrinsic property of the molecule in question. Hence, the index and the number density need only be evaluated at a single temperature and pressure. The index of refraction of nitrogen at 0 \( ^\circ \)C and 1.013 bar in the UV is calculated by a fit to data from Griesmann [61], which incorporates the effects of electronic resonances in the deep UV:

\[ r - 1 = \frac{1.966}{22086 - \left(\frac{1000}{\lambda}\right)^2} + \frac{0.02745}{133.86 - \left(\frac{1000}{\lambda}\right)^2} \]  \hspace{1cm} (3.9)

For both Equations 3.8 and 3.9 the units of \( \lambda \) should be nm.

If the same experiment arrangement is used to measure Rayleigh signals from nitrogen and LIF signals from ketones, Equations 3.4 and 3.6 can be ratioed, cancelling several parameters that appear in both equations, to give Equation 3.10.

\[ \frac{S_{\text{LIF}}}{S_{\text{Ray}}} = \phi \frac{n_{\text{ketone}}}{n_{N_2}} \frac{\sigma}{\text{d} \Omega} \frac{4\pi I_{\text{laser}}^{\text{LIF}} RSR_{\text{LIF}}}{I_{\text{laser}}^{\text{Ray}} RSR_{\text{Ray}}} \]  \hspace{1cm} (3.10)

Here, the spectral responsivities from Equations 3.4 and 3.6, have been replaced by the relative spectral response, RSR, a more easily measured quantity defined relative to the peak responsivity of the detection system:

\[ RSR_{\lambda} = \frac{R_{\lambda}}{R_{\text{max}}} \]  \hspace{1cm} (3.11)

where \( R_{\text{max}} \) is the highest responsivity of the detection system. Hence, one needs an \( RSR_{\text{LIF}} \) averaged over the fluorescence wavelengths (weighted by the LIF spectrum) and the \( RSR_{\text{Ray}} \) at the laser wavelength. Equation 3.10 shows that, using a single experimental configuration, we need to measure the LIF signal per ketone molecule and per unit laser energy, the Rayleigh signal per nitrogen molecule per unit laser energy, and the relative spectral response of the collection and detection system. The differential Rayleigh cross section for nitrogen can be determined from Equations 3.7
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through 3.9 with an uncertainty of around one percent (see for example, Naus and Ubachs [60]); good Rayleigh measurements thus have an advantage over using the less certain fluorescence quantum yield of another species as a reference. The absorption cross sections of each ketone have been measured with uncertainties of around six percent [5,62].

It is important to note that the Rayleigh signal from nitrogen is strongly, but not completely, polarized and depends on the polarization of the incoming light. The fluorescence signal from the ketones, if excited by polarized light, will depolarize rapidly compared to the collection time scales in these experiments (several ns for the fluorescence lifetimes). Hence, one must ensure that the collection system is polarization insensitive for this method to work properly.

Experimental Arrangement

Figure 3.6 depicts the experimental arrangement used to measure the fluorescence quantum yield. All experiments were carried out at room temperature, 296 (±2) K. The ketones used were ACS grade acetone (>99.8% assayed) and ACS grade 3-pentanone (>99.0% assayed). Each was placed in a sealed reservoir and subjected to several freeze-pump-thaw cycles in order to remove dissolved air and lighter impurities. The evacuated cell was then filled barometrically by the ketone’s vapor pressure before being diluted with nitrogen to the desired final pressure (between 20 and 1013 mbar). Before each set of measurements, the pressure reading from the MKS Baratron (with 0-1333 mbar range) was monitored for several minutes with ketone alone and with nitrogen diluent in the cell to ensure that potential adsorption losses to walls were negligible.

The cell was a stainless steel cross (made by MDC) with six, orthogonal, flanged ports — 4 for optical access, 1 for gas throughput, and 1 to provide a reservoir in the bottom for a Teflon-coated magnetic stir bar. The intersecting tubes composing the cross were nominally 3.8 cm in diameter while the total length from laser entrance to exit was slightly less than 13 cm; the total volume was close to 0.3 L.

Three different lasers were used, each with less than 2 mJ in a 2 mm diameter (thus easily within the linear excitation regime). A Lambda Physik Compex 102 filled
with a krypton-fluorine excimer mixture delivered 248 nm pulses at 5 Hz to the cell. A Questek model 2220 filled with a xenon-chloride mixture provided 308 nm pulses at 2 Hz. Finally, the quadrupled output of a Spectra-Physics GCR-3 Nd:YAG provided 266 nm light at 10 Hz.

Only the vertically polarized beams were used to measure the Rayleigh and LIF intensities needed to calculate the fluorescence quantum yield. The outputs of the two excimer sources were unpolarized, so the beams were directed through a $\text{MgF}_2$ Rochon polarizing beamsplitter to separate the horizontally and vertically polarized components. For the quadrupled YAG, the 266 nm output was already vertically polarized; however, it was also directed through the Rochon in order to fully separate the quadrupled frequency from a small amount of horizontally polarized 532-nm light that remained after the harmonic separators.

A quartz plate was placed into the beam path to separate approximately 10% of the laser; a portion of this was then detected by a photodiode (Thorlabs DET210) whose output was monitored via oscilloscope, so relative changes in energy could be monitored during the experiments and later used to correct the acquired data.

Scattered and fluorescent light from inside the cell was collected orthogonal to the beam path and polarization direction with a Nikon, Nikkor - UV, 105 mm, f/4, achromatic lens. This light was focused onto the slit of an Acton Spectra Pro 150 mm
spectrometer where it was dispersed by a 300 groove/mm grating blazed at 300 nm and detected by a Princeton Instruments I-Max-512-T intensified CCD camera. The spectral resolution of this system was about 3 nm at full-width, half-maximum, and the range was about 250 nm. Using a CCD camera (as opposed to a photomultiplier tube) allowed us to focus the collection system more efficiently and spatially filter some of the background by selecting an optimized region of interest on the chip, which was kept constant for the entire experiment. The camera was controlled by a PC using Roper Scientific’s Winspec version 2.5.12.0. Camera gating was between 200 ns and 1 µs, depending on the amount of timing jitter from the laser. In order to take advantage of the camera’s full dynamic range and optimize the signal-to-noise, at least 64 shots were averaged on-chip. Background signals were taken with the laser running under vacuum conditions (< 0.1 mbar) and subtracted from measurements with ketone and/or nitrogen in the cell.

Measurements

The relative spectral response was obtained via the measurement of several calibration lamps, placed directly behind the cell with one of the windows removed (see Fig. 3.6). The columns of pixels were first calibrated to wavelength between 245 and 490 nm using eight lines of a mercury lamp (Spectronics Corp. Spectroline model Hg/3). Knowing the wavelength calibration, the spectral response could then be calculated with measurements from two other sources: an argon mini-arc plasma (NIST calibrated) for the 245 to 400 nm range and a calibrated tungsten lamp (Optronics Laboratories OL550) in the 350 to 490 nm range. The region of overlap from 350 to 400 nm allowed for normalization of the tungsten lamp’s curve to that of the plasma and ensured internal consistency. The resultant relative spectral response curve \( R(V/\text{photon})/R_{\text{peak}}(V/\text{photon}) \) of each source is shown in Figure 3.7. Measurements were also taken with a broadband, UV polarizer between the achromatic lens and the spectrometer to ensure there was no dependence of the relative spectral response on polarization.\(^1\)

\(^1\)Note that collection systems using gratings can, in general, be polarization-sensitive; however, the reflectivity of relatively coarse gratings like the one used in this experiment (300 grooves/mm)
Figure 3.7: Experimental arrangement for measuring fluorescence quantum yields with respect to Rayleigh signals.

An example of a 3-pentanone spectrum excited with 248 nm is shown in Figure 3.8. For comparison, background levels and the spectrally corrected traces are also shown. Using a fixed grating for all experiments was preferred to changing the grating position between Rayleigh and LIF experiments, which may incorporate changes in grating reflectivity and hysteretic complexities. Hence, the measured fluorescence signal was integrated from 300 to 490 nm, and a correction factor of 1.14 was used to account for the long-wavelength portion of the spectrum (490-580nm) that was not captured by the spectrograph. The correction factor was determined by comparing the measured spectrum to a complete reference spectrum (also shown in Fig. 3.8) that was measured in a separate experiment [62]. For 308 nm excitation, the spectrum was integrated only above 320 nm to avoid incorporation of the Rayleigh signal with an estimated loss of less than 1% of the integrated fluorescence strength.

To ensure that the Rayleigh signal was measured correctly and possible contributions from small particle or surface scattering were excluded, several secondary experiments were performed. First, when the horizontally-polarized component from
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Figure 3.8: Example measured and corrected 3-pentanone fluorescence spectra excited with 248 nm laser light in 1 bar of nitrogen with comparison to background levels and a reference spectrum. The reference spectrum allowed us to calculate the fraction of the emission that was not collected and thus make a correction.
the Rochon was used, the scattered signal was about 1/100 of the vertically-polarized value in accordance with Rayleigh theory. As a further check on the accuracy and reproducibility of our method, the system was used to measure the ratio of methane’s Rayleigh cross section to that of nitrogen at 248 nm and compared with the work of Reckers et al. [63]. Methane’s differential Rayleigh cross section was 2.26 times larger than that of nitrogen in our experiments, in good agreement with Recker’s value of 2.3 ($\pm 0.1$).

As indicated by Equation 3.10, it is the Rayleigh and LIF signal per unit number density (or per molecule) and per unit incident energy that is necessary to determine $\phi$. Small relative corrections in incident laser energy were typically less than 5% from shot-to-shot, but fluorescence measurements were additionally corrected on the order of 10% (depending on absorption cross section and concentration) to account for laser absorption between the cell entrance and the LIF measurement volume. As a means of minimizing the pressure uncertainty and confirming detector linearity, the Rayleigh signals were measured at various pressures of pure nitrogen (before and after the LIF measurements to ensure reproducibility and time-steadiness) and the best-fit slope through the data was used to determine the Rayleigh signal input into Equation 3.10. Similarly, LIF signals were measured at a fixed total pressure (at 507 mbar and 1013 mbar) while using a range of partial ketone pressures.

Examples of integrated Rayleigh and fluorescence signals as a function of pressure are shown in Figure 3.9. Under the lowest pressure conditions, only pure ketone was used between about 7 and 33 mbar. The resultant slope was used to calculate the fluorescence yield at a nominal pressure of 20 mbar.

Results and discussion

The wavelength dependence of the fluorescence quantum yield for 3-pentanone (Fig. 3.10) at the lowest pressure condition is compared with the data of Hansen and Lee [3] (23 °C, 13 mbar 3-pentanone, 2.7 mbar oxygen). The agreement is rather poor. First, our FQY is much lower at all conditions than what is measured by Lee. Lee measured the FQY relative to acetone, using the value of Heicklen $\phi = 0.0021$ as a calibration [50]. Our measurements of acetone indicate that this value is also too high (see App. A).
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Figure 3.9: Example integrated Rayleigh (from 244 to 252 nm) and fluorescence (from 300 to 490 nm) signals versus pressure.

Figure 3.10: 3-pentanone FQY for different excitation wavelengths (296K, 20 mbar pure ketone) and comparison with Hansen and Lee data (296K, 13 mbar ketone, 2.7 mbar $O_2$) [3].
Figure 3.11: Absolute fluorescence quantum yield of 3-pentanone at room temperature as a function of pressure (in nitrogen) and excitation wavelength.

The two works agree well on the relative FQY between acetone and 3-pentanone for excitation near 308nm, so the source of the scaling difference lies in Heicklen’s acetone measurement. In addition to the scaling, however, the relative increase in FQY with excitation wavelength is much greater for our data than is indicated by Hansen and Lee. Given the similarities between acetone and 3-pentanone that have been noted in other studies [4], we expect that $\phi$ should change with excitation wavelength in a similar manner for each molecule.

Figure 3.11 shows the results of our measurements for each excitation wavelength at the three measured pressures. The pressure and wavelength dependencies seem to follow the conceptual model for the FQY developed by Thurber where fluorescence yields increase with pressure and decrease with excitation frequency. The approach of the fluorescence yield to a vibrationally-relaxed, high-pressure limit (independent of the excitation wavelength) is apparent. Estimated experimental uncertainties of our measurements are 10% for the 507 and 1013 mbar data. At low pressures, we assign a slightly higher uncertainty, 15%, due to possible changes in the absorption
cross section at low pressures and possible collected emission from states other than
the excited singlet during the camera integration time that were not thoroughly ex-
plored in this work. Primary sources of the uncertainty were the relative spectral
response calibration (7% for the ratio of the Rayleigh wavelength to the fluorescence
wavelengths), the absorption cross section of the molecule (6%), the value of the col-
lected signal per unit number density (3%), and the correction factor used for the
long wavelength part of the fluorescence spectrum that was not collected (3%).

3.2.2 Fluorescence temperature dependencies

Quantifying the fluorescence quantum yield at a convenient reference condition is one
piece of the puzzle that reveals the complete photophysical properties of a tracer.
Another piece involves characterizing the influence of temperature. While the tem-
perature dependence of absorption is captured by the more complete results from
Section 3.1, laser absorption can be performed simultaneously with fluorescence mea-
surements using a single experimental configuration. The experiment described below
will thus provide verification for the previously reported absorption spectra at dis-
crete wavelengths in addition to shedding new light on the influence of temperature
on the fluorescence quantum yield.

Since absolute measurements of the FQY are available as described in Section 3.2.1,
the experiments below are somewhat simplified because they have only to measure
the change in fluorescence with respect to the room temperature value for the same
excitation wavelengths used in the previous experiment.

Experimental layout

Experiments were undertaken to characterize the temperature dependence of the pho-
tophysical properties beyond the range of current literature using common excitation
wavelengths. Absorption cross sections and relative fluorescence signals between 300
and 875 K at approximately 1 atmosphere were measured using the experiment shown
in Figure 3.12. Nitrogen and air were percolated through a series of chambers con-
taining liquid 3-pentanone until the exiting gas was saturated to the vapor pressure
Figure 3.12: Experimental schematic of system used to measure absorption cross section and relative fluorescence of 3-pentanone at various temperatures.

of the ketone. Since the vapor pressure is a known function of temperature [64], the thermocouple and pressure gage at the exit of this section provided the information necessary to calculate the ketone mole fraction in the flow (about 4%). A water bath surrounding the liquid ketone maintained a constant exit temperature and mitigated the effects of evaporative cooling. The flow then entered a Thermolyne 48000 furnace and was pre-heated to the desired temperature before entering the optically accessible cell. Pyrolysis and photolysis were minimized by keeping the gas residence time in the furnace below about 0.5 seconds.

As a concomitant check for seeding saturation and pyrolysis, the absorption and fluorescence signals were confirmed to be independent of the gas flow rate. The temperature limit of these measurements, 875 K, was determined by monitoring the signals at various flow rates at elevated temperatures. That is, at low flow rates and high temperatures, 3-pentanone begins to decompose, and the signals changed with furnace residence time. For 308 nm excitation, the absorption and fluorescence decreased as the 3-pentanone decomposed. For 248 and 266 nm excitation, the fluorescence and absorption would actually increase with furnace residence time,
indicating that the products of 3-pentanone decomposition may be absorbing and fluorescing more strongly than 3-pentanone. At high flow rates, the gases exiting the percolator were no longer saturated as indicated by a decrease in the absorption and fluorescence.

The optically accessible cell (22.4 cm long, 1 cm diameter, atmospheric pressure) contained a type K thermocouple to measure the gas temperature in the center of the cell where the LIF signal was measured. Further measurements were taken to ensure that the temperature variation along the beam path in the cell was less than 10 K even at the highest operating temperature, thus minimizing errors in the path-averaged absorption measurements. Three sapphire windows (2 mm thick) accommodated the incident and transmitted laser beams and allowed for fluorescence collection orthogonal to the beam path. Three excitation wavelengths were studied: 248 nm from a Lambda-Physik Compex 102 krypton-fluoride (KrF) excimer, 266 nm from a Spectra Physics GCR-300, quadrupled Nd-YAG, and 308 nm from a Questek 2220 multi-gas excimer containing a xenon-chloride (XeCl) mixture. The pulse frequencies were 10 Hz for the 266 and 248 nm beams, 5 Hz for the 308 nm beam, and the pulse lengths were about 30 ns for the excimer lasers and 6 ns for the YAG. Incident energies were kept below 1 mJ, and beam diameters were about 3 mm, thus ensuring linear excitation.

The laser beam was split by a fused silica flat before entering the cell. Photodiode measurements taken from the split beam were used to account for changes in the incident laser energy. The transmitted energy was measured by a second photodiode, and the fluorescence was collected by a photomultiplier tube (PMT, a Hamamatsu 1P-21), located behind a pair of appropriate filters (2 mm Schott BG-28, 2 mm Schott WG-320) to eliminate scattered laser light and other signals outside of the fluorescence band (e.g., the glow of heating wires in the furnace). All detectors were checked to respond linearly with laser energy. The signals were gated, time-integrated, and recorded by boxcar averagers (Stanford Research Systems model SR250) and a PC-based data acquisition system (LabVIEW 5.0). An additional correction to the fluorescence signal was made to account for the fractional absorption of the laser through one-half of the cell’s length. An average of 300 laser shots were taken at each
temperature.

As a result of the spectral response of the PMT and the optical filters, the fluorescence signal in this experiment was integrated over the spectral region between 330 and 550 nm. Other experimental arrangements with different detectors and cameras may have a different spectral response, so to ensure the general applicability of the resultant temperature dependence data, concomitant measurements using a static cell and an imaging spectrograph confirmed that there was no significant change in the fluorescence spectrum as one changed the excitation wavelength from 248 to 308 nm. The measured fluorescence spectra for these two excitation wavelengths are shown in Figure 3.13, graphed as relative numbers of fluorescence photons at a given wavelength, for room temperature 3-pentanone in one atmosphere of nitrogen. The spectrum is slightly narrower for the longer excitation wavelength, likely due to a narrower distribution of emitting states, but the change in width is not sufficient to affect most broadband collection schemes. Additionally, varying the oxygen concentration in the bath gas from 0 to 21% had no measurable effect on the fluorescence spectrum at one atmosphere. We assume that any shift in the fluorescence spectrum with temperature is also negligible, as has been confirmed in acetone [29].

Results and Discussion of Cell Experiments

Absorption Cross Section

By measuring the relative transmitted laser energy with and without 3-pentanone flowing through the cell, one can use the Lambert-Beer relation and the known number density of 3-pentanone in the cell to calculate absorption cross sections. Figure 3.14 shows the measured cross sections for 3-pentanone as a function of temperature using 248, 266, and 308 nm excitation. The measurements agree with the previously presented shock tube work, except for a 10% deviation at 266 nm. Reasons for this are speculative. In the shock tube, the spectral resolution results in averaging over a 3-4 nm spectral region, and the absorption cross section changes rapidly with wavelength near 266 nm. Averaging over a spectral region where the change in cross section is large may result in artificial broadening, and the absorption cross section may thus be biased. Alternatively, the 266 nm pulse from the Nd-YAG was the most spectrally
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Figure 3.13: Fluorescence spectra of 3-pentanone when excited with 248 and 308 nm. Curves are corrected for the relative spectral response of the detection system. Varying the partial pressure of oxygen in the bath gas from 0 to 21% also had no significant effect on the shape of the spectrum.
Figure 3.14: 3-pentanone absorption cross section as a function of temperature for 248, 266, and 308 nm excitation. Filled points indicate laser-measured values. Hollow points indicate spectrograph-measured values (see Section 3.1). Uncertainties are typically under 10% with a minimum of $\pm 3 \times 10^{-20} \text{cm}^2$.

Fluorescence

There are two interesting ways to map relative fluorescence to temperature. 1) In order to examine the molecule’s photophysical behavior, one should look at the relative fluorescence signal per mole or per molecule, as shown in Figure 3.15 or 3.16. Visualizing absolute concentrations may also be useful for quantifying parameters like the potential heat release in a pre-combustion environment. 2) In other diagnostic applications, one may be more interested in how the mole fraction of the tracer varies in space, taking into account the change in overall number density due to temperature at constant pressure. Such interpretation requires examining the fluorescence per unit
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Figure 3.15: Relative 3-pentanone fluorescence signal per molecule, denoted by $S_f^*$, for three excitation wavelengths at atmospheric pressure in nitrogen and comparison with past work. Fluorescence lifetime data from Ossler and Aldén [4] has been converted to show comparison at 266 nm.

Figure 3.15 shows the temperature dependence of 3-pentanone fluorescence per mole fraction, shown in Figure 3.17.

Figure 3.15 shows the temperature dependence of 3-pentanone fluorescence per molecule between 300 and 875 K using excitation at 248, 266, and 308 nm in 1 atmosphere of nitrogen. Data below 600 K agree well with the previous work of others [4, 7, 36, 37, 65] with an exception at 308 nm where the line approximating the data of Tait and Greenhalgh [66] shows systematic deviation from our measurements and those of Wolff et al. Although each trend is fairly linear up to about 600 K, Tait’s fluorescence sensitivity to temperature is significantly less than our and Wolff’s data show. The cause of this discrepancy is not immediately evident to us.

It is also useful to compare the quantitative behavior of acetone and 3-pentanone. While qualitative similarities are expected, the quantitative photophysical differences may cause one tracer to be preferred over another in applications where the physical properties are not the primary selection criterion. Acetone data from Thurber [5] is shown in comparison with the 3-pentanone data in Figure 3.16. 3-pentanone temperature dependencies are generally stronger than acetone. No common excitation wavelengths result in temperature-independence over the entire range; however a few
smaller regions of relative temperature-independence are noticeable. In these regions, if the temperatures of a flowfield are sufficiently constrained, a judicious choice of tracer and excitation wavelength makes for straightforward imaging of concentration without the need for temperature corrections. 308nm-excited 3-pentanone signal per molecule is relatively independent of temperature from 500K to 700K. Acetone is temperature-independent at higher temperatures, 700-900K, for the same excitation wavelength. Such temperatures may correspond to the conditions near top-dead-center in reciprocating engine cycles. At lower temperatures (300-450K), neither tracer signal varies greatly for 266nm excitation.

The trends in Figure 3.17 indicate the relative change in signals when using 3-pentanone PLIF for mixture or mole fraction imaging as one might do when making equivalence ratio measurements in flows with uniform oxygen concentrations. Again, for comparison, acetone data are also included on the plot. Excited with 248 nm, 3-pentanone signal decreases rapidly with increasing temperature until it
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Figure 3.17: Relative 3-pentanone fluorescence signal per unit mole fraction, denoted by $S_f^+$, and comparison with acetone. This mapping takes into account the decrease in overall number density due to changes in temperature and could be useful when mole or mixture fraction is the parameter of interest.

is only about 5% of its room temperature value at 700 K. With 308 nm excitation, however, the relative temperature insensitivity of 3-pentanone fluorescence below 600 K indicates the potential for single-line imaging of mole fraction without the need for temperature corrections when thermal gradients are moderate. For acetone, the condition of temperature-independence does not exist for any of the common excitation wavelengths. Uncertainties in 3-pentanone fluorescence measurements are estimated at about 3%, due mainly to the temperature measurement used to calculate 3-pentanone’s vapor pressure.

By dividing the relative fluorescence signal per molecule by the absorption, one can observe trends in the fluorescence quantum yield with temperature, shown in Figure 3.18. The uncertainties here are somewhat larger than the individual absorption and fluorescence measurements, since the uncertainties of both measurements propagate into this quantity (not exceeding +/-7%). It is apparent that the quantum yield decreases with temperature for all excitation wavelengths, and it does so more
Figure 3.18: Relative fluorescence quantum yield for 3-pentanone at 1 atm excited with 248, 266, and 308 nm.

quickly for the shorter excitation wavelengths. This agrees qualitatively with the current understanding of ketone photophysics in that the upper vibrational levels of the excited state are subject to faster non-radiative decay than the lower levels. Such behavior shows promise for modelling 3-pentanone behavior in a manner similar to what has been done with acetone [5].

In situations where temperature and/or mixing information is desired but neither is uniform, the ratio of fluorescence signals from two different excitation wavelengths results in a unique temperature dependence, independent of local concentration. The temperature mapping for 3-pentanone in nitrogen using a 308/248 and 308/266 nm fluorescence signal ratio is shown in Figure 3.19, normalized to room temperature values for each curve. The calculations of Einecke et al. [36] are shown for comparison (renormalized to our data near 383 K) as well as similar ratios for acetone from the work of Thurber et al. [5]. It is clear that for similar excitation wavelengths, 3-pentanone’s temperature sensitivity is superior to that of acetone and the ratio using 248 nm is more sensitive than that of 266 nm.
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Figure 3.19: Temperature trends of the fluorescence signal ratio of 3-pentanone and comparison with acetone data taken by Thurber [5]. All ratios are normalized to 300 K. P = 1 atm. nitrogen.

Imaging demonstration: application of measured temperature dependencies

To demonstrate 3-pentanone’s temperature sensitivity and to explore the opportunity for imaging at high temperatures, we measured the properties of a heated turbulent jet with a room temperature coflow, depicted in Figure 3.20. 4.5% 3-pentanone in air was heated electrically in a Sylvania air heater (model 014683) to about 650 K and injected through a nozzle with a 1.7 mm orifice at about 70 m/s into a slow (0.16 m/s) coflow of 1.5% 3-pentanone/air at room temperature. Since the jet is heated and contains a different amount of 3-pentanone from its surroundings, this flow provides an unsteady (Re \( \approx 4000 \)), non-uniform field by which to demonstrate and evaluate simultaneous temperature and mole-fraction imaging.

Linearly excited with 50 mJ laser sheets at 266 and 308 nm (0.7 mm thick, 3.5 cm high), the fluorescence was captured with a fast (f/1.2) lens and an interline-transfer, unintensified CCD camera (Princeton Instruments MicroMAX 1300 YHS) with gate times of 1\( \mu \)s per frame and 500 ns between frames. Although the use of 248 nm
Figure 3.20: Experiment used to demonstrate simultaneous temperature and mole fraction imaging using 3-pentanone.
Figure 3.21: Single-shot images of 3-pentanone temperature and jet fluid fraction in a heated, turbulent jet using 308/266 nm excitation.

excitation would provide better temperature sensitivity according to Figure 3.19, the signal levels from 248 nm excitation are quite low near 650 K as evidenced by the fluorescence quantum yield measurements and Figure 3.17. Hence, some sensitivity was sacrificed in favor of a better SNR. The laser pulses were separated by 1.0±0.2 µs. By binning the 1300 x 1050 pixels into groups of two by two, the movement of a packet of fluid even at 70 m/s was on the order of one binned pixel, thus minimizing blurring effects due to fluid motion between the two laser pulses.

The images were processed in Matlab on a per-pixel basis using methods similar to those described by Thurber [30]. Figure 3.21 shows a temperature image and a mole fraction image mapped as the fraction of jet fluid in the flow (0 in the coflow to 1 in the core). Dimensions of the images are about 3.0 cm high and 1.7 cm wide.

As a figure of merit for the capabilities that this technique offers for a nearly instantaneous measurement, one can examine the RMS variations of temperature and mole fraction over small, relatively uniform regions of the flow. RMS temperature fluctuations are ±15 K in both the coflow, around 298 K, and in the jet core, around
670 K. For the image of jet fluid fraction, the RMS values primarily follow the temperature corrections made to the original 308 nm image and are thus highest in jet core: ± 5% for the same region of the jet core that was analyzed in the temperature field. Since the jet fluid mapping represents a difference of only 3% 3-pentanone, the detection limit, calculated by taking the ratio of the RMS fluctuation to the range of 3-pentanone concentrations, is about 0.15% 3-pentanone at 650 K.

3.2.3 Fluorescence pressure dependencies

So far, fluorescence measurements have been described to obtain a tracer’s absolute fluorescence quantum yield and the change in the FQY with temperature for a given set of excitation wavelengths. For tracers in systems where the collision frequency is comparable to or faster than the fluorescence lifetime, the fluorescence quantum yield will also depend on the pressure and the composition of the bath gas. Mechanistically, inelastic collisions change the optically-excited population of tracer molecules, either through quenching of the electronic state or through vibrational energy transfer to other excited states with different probabilities of fluorescence. For aliphatic ketones like acetone and 3-pentanone, the pressure dependencies are much weaker than many other PLIF candidates, but they can be significant depending on the range of conditions [29]. The following section describes experiments to measure the relative change in fluorescence with pressure for a few common bath gases. Results for 3-pentanone are provided.

Experimental arrangement

The experiment is similar to the one used to perform the absolute measurements of the FQY of acetone and 3-pentanone (see Fig. 3.6). The lowest pressure was 1 mbar, limited by the uncertainties in the pressure gage, a 1330-mbar baratron. The highest pressure was 6 bar, following the advice of the viewport manufacturer. A second pressure gage (Setra 280E 0-500 psi) measured pressures above 1 bar. A photodiode before and after the cell a) allowed correction for incident laser energy, b) verified that transmission measurements were consistent with known absorption cross sections and
did not change with pressure, and c) verified that the ketone concentration in the cell was steady without the development of significant photolytic products or other interferences.

Ketone was filled using the evaporated component from a liquid reservoir. Bath gases were then added slowly to avoid condensation when total pressures exceeded the vapor pressure (about 45 mbar). Additionally, a magnetic stir bar in the bottom of the cell accelerated the mixing process. Measurements were typically made with 10 mbar of ketone in the cell, well below the dew point for these room-temperature experiments.

Several concomitant experiments were performed to eliminate possible systematic errors. Fluorescence signal was measured as a function of laser energy (Fig. 3.22) and confirmed to be linear. The effects of photolysis were measured by examining the change in fluorescence signal after more than ten thousand laser shots (Fig. 3.23). Mixing time was not an issue because signal levels did not vary by more than 1% when measurements were taken between 0.5 and 15 minutes after preparation.

Fluorescence spectrum shape

Significant changes in the shape of the fluorescence spectrum can make the pressure dependence of the integrated signal depend on the detection system. In other words, if the shape of the spectrum changes, different experimentalists are likely to measure different pressure dependencies, or, conversely, different experiments will require different corrections for pressure effects on the signal. Because these measurements have been spectrally resolved, we can examine the magnitude of this effect for 3-pentanone.

Figure 3.24 shows the shape of 3-pentanone’s fluorescence spectrum for the range of conditions (10 mbar-6 bar) covered in these experiments. A slight narrowing of the spectrum occurs as pressure and excitation wavelength are increased, likely because the distribution of emitting molecules is narrower when using long wavelengths or when vibrational relaxation is most rapid. Further measurements at various pressure between 10 mbar and 6 bar using 248nm excitation show that the shift is gradual and continuous as pressure is increased. For most broadband detection systems that capture the bulk of the spectrum between 350 and 500nm, this 15 nm (≈10%) change
Figure 3.22: Linearity of fluorescence signal with incident laser energy for 296K, 10mbar pure 3-pentanone. Points are averages of 256 laser shots. Lines are best fits to data and are forced through the origin. Incident laser energy was measured on a relative basis with a photodiode and calibrated to an approximate absolute scale with the use of a thermal energy meter. Errors (Err) represent 95% statistical confidence in the slope of the best-fit line. Other experiments were carried out within the range of the measurements shown here.
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Figure 3.23: Effects of photolysis on the fluorescence signal. Each point is an average of 64 laser shots. A reduction in signal is evident but minor for 248nm and 266nm excitation. All other experiments were limited to less than 2000 laser shots per mixture in order to keep the photolytic effects below 1%. Larger scatter in the 308 nm data is due to the large pulse-to-pulse instabilities of the laser, resulting in significant variations in spatial and temporal profile that were not averaged-out over 64 pulses. Using 256-shot averaging for other experiments mitigated this effect.
Figure 3.24: Shape of 3-pentanone’s fluorescence spectrum (spectrally corrected) for the range of pressures studied in this experiment: room temperature, 10mbar 3-pentanone. Increasing pressure and excitation wavelength cause a slight narrowing of the spectrum.

in the FWHM will not be significant. Detection systems that are solely or especially sensitive to the areas where the spectrum’s shape is rapidly changing - between 310nm and 375nm and again above 500nm - will show different pressure effects than what are presented here. If the pressures are consistently high, however, or if the excitation wavelength is long, this effect is again minimized.

Results

The measurements presented below were obtained from the spectrally-resolved data by numerically integrating the signal between about 330 and 540 nm. The most common bath gases used in 3-pentanone PLIF are nitrogen and oxygen. Additionally, the collisional effects of large molecules are examined via studies of pure 3-pentanone. Results for nitrogen, air, oxygen, and pure 3-pentanone gases are thus presented below.
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Nitrogen

Although the data measured in these experiments were relative, their wavelength dependence can be calibrated to the previous absolute measurements of Section 3.2.1. The previous measurements and the normalized data from added nitrogen are shown in Figure 3.25 with the difference between these and previous data being less than 10%. As pressure is increased, the fluorescence quantum yield increases, and it does so more dramatically for short excitation wavelengths. The same value of the FQY appears to be approached at high pressures by all three excitation wavelengths, indicating that collision-induced vibrational relaxation is nearly complete at 6 bar.

Air and Oxygen

Oxygen has been shown to have a small but measurable quenching effect on the fluorescence of acetone [29], and one should expect a similar trend for 3-pentanone. The results of our measurements for 248, 266, and 308 nm excitation are shown in Figures 3.26, 3.27, and 3.28, respectively (maintaining consistent normalization across}

Figure 3.25: Dependencies of 3-pentanone FQY on added nitrogen pressure and comparison to previous data.
Figure 3.26: Effect of oxygen on the FQY of 3-pentanone for 248nm excitation.

wavelengths provided by the absolute data where 1.0 is approximately the high pressure limit). Oxygen shows the capacity to both increase and decrease the FQY when the wavelength is short, as shown for 248 and 266nm excitation. For 308nm, near the zero-point of the electronic state, oxygen only decreases the signal. Oxygen thus plays a two-fold role in affecting excited state processes, both vibrationally relaxing and weakly quenching the excited ketones. At six bar, the FQY depends on the amount of oxygen but is nearly independent of the excitation wavelength since each figure shows that the FQY is about 65% of its high pressure limit. Using air as a bath gas instead of nitrogen seems to result in nearly negligible decreases in signal at 1 bar but causes a 10% decrease in signal at 6 bar.

Pure 3-pentanone

Vibrational relaxation efficiency has been shown to increase with the size/complexity of the colliding molecule for acetone and other molecules [29,67]. We might thus guess that vibrational relaxation of excited 3-pentanone is efficient when the collision partner is another pentanone molecule. While we are limited by the vapor pressure to about 40 mbar, the effect is nonetheless observable as shown in Figure 3.29. Similar
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Figure 3.27: Effect of oxygen on the FQY of 3-pentanone for 266nm excitation.

Figure 3.28: Effect of oxygen on the FQY of 3-pentanone for 308nm excitation.
to acetone, 3-pentanone self-relaxation is most dramatic for short excitation wavelengths, changing the FQY by 20% between 1 and 35mbar for 248nm excitation. For comparison, acetone’s FQY changes by 20% over a much greater pressure range, from 10 to 250mbar. For 266nm excitation 3-pentanone’s increase in FQY is somewhat less dramatic, and at 308nm, no change in the FQY is observable outside of the scatter in the data.

### 3.3 Modelling the Fluorescence Quantum Yield

Fluorescence experiments thus far quantify the effects of pressure, temperature, and excitation wavelength on 3-pentanone’s fluorescence quantum yield. The general trends are similar to those of acetone:

1. Increases in temperature tend to lower the FQY, especially for short wavelength excitation.
2. Increases in pressure tend to increase the FQY, approaching a high pressure limit. *Exception:* Oxygen has the capacity to both increase and decrease the FQY, depending on the conditions.

3. Decreases in excitation wavelength tend to decrease the FQY, unless one is in the high pressure limit.

Because of their qualitative similarity, the photophysical model first proposed by Thurber [39] for acetone would appear to apply equally well to 3-pentanone with different numerics. We thus adapt the formulation of Thurber’s model as a starting point for a more general ketone photophysical model.

### 3.3.1 Ketone model

For molecules as large as 3-pentanone, the dephasing time for the optically prepared eigenstates is much faster than the length of a nanosecond-scale excitation laser. (Measurements for acetone have confined it to $<50$ fs [68].) Hence, for the pulses common to typical excitation sources, rate equation analysis can be used in lieu of more complex methods involving density matrices or Bloch equations.

The key to modelling the FQY with rate equations is to identify and quantify the important energy transfer channels and how they vary among the relevant excited states. For the aliphatic ketones, the dominant channels are either intersystem crossing ($S_1 \rightarrow T_1$) or internal conversion ($S_1 \rightarrow S_0$). (For other molecules, predissociation may also play a role, but the effective mechanism of collisionless, nonradiative decay still applies). Researchers have long known that such processes sometimes dominate excited state decay, but their rates may not be constant, depending specifically on the prepared rovibronic states and more generally upon the amount of vibrational energy in the excited electronic state, [3, 69]. Multistep, multi-energy decay models have been used to describe the pressure dependence of fluorescence [70]. Such models are also an important component in understanding activation and deactivation in chemical and photochemical reactions [71–73]. For acetone, Thurber was the first to adapt a multi-step decay model that parameterizes a few rate constants in terms of the excess energy of the excited vibrational state [5]. Fitting model parameters
to available fluorescence data indicated that the overall changes in excited state processes were captured and that the model could be useful to compare acetone PLIF diagnostic strategies.

Following Thurber’s formulation, the most important channels for decay of an excited singlet ketone are fluorescence, intramolecular nonradiative decay (which reflects the combined effects of intersystem crossing, internal conversion, or predissociation), and oxygen quenching. In addition, intermolecular vibrational energy transfer may change the vibrational energy in the electronic manifold.

The fluorescence quantum yield, the fraction of the excited molecules that fluoresce, can be viewed as a branching ratio representing the fraction of molecules leaving the excited state via fluorescence. The numerator in such ratio is the first-order rate coefficient for fluorescence while the denominator is the sum of all possible rates of decay. For a given excited state or energy level, n:

$$\phi_n = \frac{k_{f,n}}{\sum_i k_{i,n}} \quad (3.12)$$

where the subscript $i$ represents a single decay channel, and the sum is over all available channels. Equation 3.12 applies to a single excited state or a group of excited states with all of the same $k_i$. If multiple excited states with varying rates of decay contribute to the emission, then the total FQY is the sum over the states contributing to the fluorescence:

$$\phi = \sum_n \phi_n \quad (3.13)$$

If the contributing states can be characterized, this basic formulation can be used to calculate the fluorescence contribution from a range of states for a range of temperatures, pressures, and excitation wavelengths. Thurber has parameterized the range of states and their decay rates through the excited molecule’s vibrational energy, as shown schematically in Figure 3.30. The energy levels contributing to the fluorescence are determined by the experimental conditions. Following Figure 3.30, the molecule begins the process in the ground electronic state, containing some thermalized vibrational energy, $E_{\text{thermal}}$ (calculated from a Boltzmann distribution using harmonic
oscillator vibrational frequencies, listed in Appendix B.) Depending on the excitation wavelength, an amount of energy, $\Delta E_{laser}$, is added to the molecule, sending it to the excited electronic singlet. From this initial excited state energy level, the molecule may fluoresce, or it may undergo a nonradiative process, like intersystem crossing or predissociation or an electronically quenching collision with oxygen. Additionally, the molecule may collide with a nonreactive partner, losing some of its excess vibrational energy and moving to a lower energy level in the excited singlet. From this lower energy level, the competition between fluorescence and nonradiative decay continues, except the nonradiative rate is reduced at lower energies. Hence, starting from the initial excited state, each decreasing energy level has a finite probability of fluorescing and makes some contribution to the fluorescence quantum yield.

The total probability of fluorescence from the mechanism described above is the
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sum of the probability of fluorescence from each energy level and is captured by Equation 3.14.

\[ \phi = \frac{k_f}{k_f + k_{vib} + k_{aox}[O_2] + k_{NR,1}} \]

fluorescence probability from level 1

\[ + \sum_{i=2}^{N-1} \left[ \frac{k_f}{k_f + k_{vib} + k_{aox}[O_2] + k_{NR,i}} \prod_{j=1}^{i-1} \left( \frac{k_{vib}}{k_f + k_{vib} + k_{aox}[O_2] + k_{NR,j}} \right) \right] \]

fluctuation probability from i probability of getting to i

\[ + \frac{k_f}{k_f + k_{aox}[O_2] + k_{NR,N}} \prod_{j=1}^{N-1} \left( \frac{k_{vib}}{k_f + k_{vib} + k_{aox}[O_2] + k_{NR,j}} \right) \]

fluorescence probability from N probability of getting to N

(3.14)

where the sum starts at initially excited energy level 1 and continues in a downward direction to the thermalized energy level N, from which no further vibrational relaxation will occur.

With the mechanism and framework given by Equation 3.14, one must next quantify the relevant reaction rate coefficients, \( k_{NR}, k_f, k_{vib}, \) and \( k_{aox} \), and their energy dependencies in order to successfully model the FQY. Ideally, one would like to derive rate coefficients for each deexcitation pathway from experiments in regimes where that pathway is isolated. Practically, however, direct measurements of each rate under all conditions is not feasible. The approach then, is to use experimental data to constrain the parameters as more complex effects are incrementally considered for a progressively wider range of conditions. At each step, model parameters must be optimized by minimizing the weighted root-sum-squared difference between the model and the data, a solution which results in potentially non-unique but satisfactory agreement between model and data. The following sections will describe how one can constrain or measure values of \( k_{NR}, k_f, k_{vib}, \) and \( k_{aox} \).

In addition to the data already presented in this chapter, there are also several sources of data under unique conditions in the literature. Some of these data were
also used to optimize the variable parameters of the model. They include converted fluorescence quantum yield or fluorescence lifetime data from Hansen and Lee [3] and Ossler and Aldén [4] and relative fluorescence data with varying nitrogen and air pressure at higher temperatures and pressures [7,74]. Wherever possible, comparison between published data and measurements performed in this work have been made to ensure consistency among the data sets.

Model assumptions

The model considers four energy transfer processes: an irreversible, intramolecular, nonradiative decay dependent upon excited state energy (internal conversion and/or intersystem crossing), fluorescence, a downward collisional relaxation, and collisional quenching due to oxygen. Other processes are assumed unimportant or much slower. The model also considers only the average energy of a population of molecules in the ground state and adds to this the excitation wavelength energy. Relaxing this assumption by considering the distribution of energies would require a ”master equation” analysis with considerable increase in computational cost and complexity. While such an analysis may be feasible with the aid of high-powered computing, significant assumptions would remain that are not solved by increased computing power – that is the possible change in the energy distribution of initially excited upper state due to energy level dependence of the absorption cross section and the approximate parameterization of the excited state decay as a function of total vibrational energy rather than considering state-specific lifetimes. In the current model, the possible variations in state-specific lifetimes are likely mitigated by the averaging effects of the thermal distribution.

Model development and results

\( k_{NR} \):

At sufficiently low pressures, collisions do not occur frequently enough to significantly affect the energy of the excited molecules before they decay nonradiatively. Setting the collisional terms in Equation 3.14 to zero results in 
\[ \phi = \frac{k_f}{k_f + k_{NR,1}}, \]

a much simplified relationship between the FQY, fluorescence rate, and the nonradiative decay rate. Low pressure data thus serve as a starting point for the model analysis. As shown in section 3.2.1, the maximum fluorescence quantum yield of the studied ketones is on the order of one part in a thousand, indicating that $k_{NR} \gg k_f$ and $\phi \approx k_f/(k_{NR,1})$ at low pressures. The fluorescence lifetime, $\tau_f$, is thus controlled by the nonradiative decay, and time-resolved fluorescence measurements at low pressures then provide initial insights into the nonradiative decay rate, $k_{NR} \approx 1/\tau_f$. By varying the excitation wavelength or the temperature, the energy level at which the lifetime is measured can also be varied. Such data then provide initial estimates of the energy functionality of $k_{NR}$.

For high pressures without oxygen, Equation 3.14 again simplifies because vibrational relaxation dominates.

$$\phi \approx \frac{k_f}{k_{NR,N}} \text{ when } k_{vib} \gg k_{NR}$$

(3.15)

In this case, the fluorescence lifetime is determined by the decay from the thermalized energy level, and $k_{NR,N} \approx 1/\tau_f$. For 3-pentanone, the liquid-phase fluorescence lifetime, $\tau_f$ presents a good approximation to this high pressure limit.

Low pressure 3-pentanone lifetime measurements have been made by Ossler and Aldén [4] and Hansen and Lee [3] and have been converted to values of $k_{NR}$ in Figure 3.31. There is marked disagreement in the value of the decay rate around 10,000 cm$^{-1}$. Upon further review, Hansen and Lee’s high energy data was determined to be in a regime of low signals and was obtained with a ns-scale flashlamp whose pulse length was likely as long or longer than the fluorescence lifetime. No deconvolution of the lamp pulse was performed for their time-resolved measurements. The Ossler data, in contrast, were obtained with the use of a picosecond YAG laser, and a deconvolution of the laser pulse was performed on the data. The Ossler data would thus seem to be the more reliable in the ten thousand wavenumber energy range. For the low pressure data, the ordinate, $E$, of Figure 3.31 is calculated from the experimental
3.3. MODELLING THE FLUORESCENCE QUANTUM YIELD

excitation wavelength and the temperature via

\[ E = E_{\text{thermal}} + \Delta E_{\text{laser}} - E_{\text{elec}} \]  (3.16)

where \( E_{\text{elec}} \) is the zero-point energy difference between the ground and excited electronic states, 30770 cm\(^{-1}\) (325 nm) for 3-pentanone [3]. \( E_{\text{thermal}} \) is the average thermal vibrational energy, calculated from the vibrational frequencies in Appendix B. (To give an example, thermal vibrational energy is 1070 cm\(^{-1}\) at room temperature and 7330 cm\(^{-1}\) at 800 K). Hansen and Lee’s data correspond to wavelength-dependent lifetime measurements at room temperature between 250 nm (10,270 cm\(^{-1}\)) and 325 nm (1,070 cm\(^{-1}\)). Ossler and Aldén’s data represent temperature-dependent data from 266nm excitation between 323K (8,050 cm\(^{-1}\)) and 723K (12,860 cm\(^{-1}\)). The laser energy is the energy of the exciting photon, \( hc/\lambda \). The decay rate of Figure 3.31 could alternatively be expressed as a function of a vibrational temperature by accounting for the vibrational heat capacity.

In addition to the low pressure data, the room temperature liquid phase value of the decay rate constant, converted from Breuer [75], is also plotted in Figure 3.31 and is shown to agree well with Hansen and Lee’s measurements at low pressures and low excitation energies. Also shown in Figure 3.31 is the optimized model curve for the nonradiative decay rate. While lifetime data provide insight into the nonradiative decay rate up to energies around 12,000 cm\(^{-1}\), initial excitation energies for 248 nm, room temperature experiments are around 10,500 cm\(^{-1}\) and extend to around 17,000 cm\(^{-1}\) at 800K. With no other available data, the 248nm data at atmospheric pressure and high temperature (shown in Fig. 3.36) help predict the shape of this curve at high energies. The best-fit curve takes the form of a double exponential:

\[ k_{NR} = 3.78 \times 10^8 + 8.15 \times 10^6 \exp(E/2466) + 216 \exp(E/10220) \]  (3.17)

where \( E \) is in units of cm\(^{-1}\).

\( k_f \):

The fluorescence rate from the excited singlet state may vary with excitation
Figure 3.31: Nonradiative decay rate of 3-pentanone and its change with energy in the S$_1$ electronic state.
3.3. MODELLING THE FLUORESCENCE QUANTUM YIELD

energy due to changing Frank-Condon factors across the vibrational manifold. Without detailed information on the optically-coupled potential energy surfaces, however, there is little information on whether the fluorescence rate generally increases or decreases with increasing vibrational energy (precedents for both behaviors are set by smaller molecules like OH and NO). Lacking such a priori insight, we can still use measurements of the fluorescence quantum yield combined with the \( k_{NR} \) or lifetime data to interpret the fluorescence rate \( (k_f = \phi k_{NR}) \). Values of each parameter have been measured at a few energies by varying the excitation wavelength or temperature (lifetime data from Lee [3] and Aldén [4], FQY data from this work). We can thus empirically test one of the original model assumptions made by Thurber [5] – that \( k_f \) is a constant. Calculated values for 3-pentanone are shown in Figure 3.32.

Variations in the two- to ten-thousand wavenumber range are on the order of 10% (well within the combined experimental uncertainties of \( \phi \) and \( k_{NR} \)) and show no consistent trend. \( k_f \) is thus set to a constant value of \( 4.2 \times 10^5 \text{sec}^{-1} \) for 3-pentanone. A few comments on this value are warranted. First, it is of course much lower than typical values for an allowed electronic transition because of the symmetry selection rule. Second, the rate is significantly lower than previously recommended by Hansen who assigned a value of \( k_f = 1.1 \pm 0.2 \times 10^6 \text{sec}^{-1} \) based on fluorescence yield and lifetime measurements [3], the reason being Hansen’s use of acetone as a fluorescence standard. This work is in better agreement with a Strickler-Berg calculation from the room temperature absorption spectrum (\( \approx 10^5 \text{sec}^{-1} \)), but because the absorption spectrum has been shown to increase in strength with increasing temperature, the Strickler-Berg calculation is also likely to underpredict the fluorescence rate, again abetting our assignment of a slightly higher value.

\( k_{vib} \):

So far, it has been shown that model parameters like \( k_{NR} \) and \( k_f \) can be measured or calculated directly from experimental data in some regimes. Estimating the effect of vibrationally relaxing collisions, represented by \( k_{vib} \), is less straightforward, and, despite the fact that such processes play key roles in the broader field of chemical

\footnote{At the time, Thurber could only use the fluorescence yield and lifetime measurements of previous workers in order to estimate one value of the fluorescence rate constant. Multiple absolute measurements were not available.}
Figure 3.32: Fluorescence rate constant calculated from measurements of $\phi$ and $\tau_f$ under similar conditions. Variations with energy are within the propagated experimental uncertainty, so the modelled rate is set to a constant value of $4.2 \times 10^5 \, \text{sec}^{-1}$. 
3.3. MODELLING THE FLUORESCENCE QUANTUM YIELD

kinetics, fundamental understanding of their nature in general remains illusive [73]. The pseudo-first order rate constant, \( k_{\text{vib}} \), shown in Equation 3.14, is given by

\[
k_{\text{vib}} = Z_{\text{coll}}[M]
\]  

(3.18)

where \( Z_{\text{coll}} \) is the collision frequency and \([M]\) is the concentration of the surrounding bath gas.

The levels (1 to \( N \)) over which the summation of Equation 3.14 is carried out depends on the average amount of energy transferred per collision, \( \Delta E_{\text{coll}} \). While the mechanism of vibrational energy loss dictates that the rate scale with collision frequency, there are several choices for the energy levels over which to sum the model, depending on the amount of energy transferred per collision event. The most commonly adapted forms are a constant or linearly increasing energy loss per collision as a function of the excited molecule’s energy. While studies specific to the ketones have not been performed, indirect measurements of other molecules indicate that the linear energy dependence works well for energies up to several thousand wavenumbers [73,76–78]. For acetone, Thurber also found that experimental data were well-predicted by a linear relationship between the transferred energy and the amount of excess vibrational energy in the excited molecule [29] or

\[
\Delta E_{\text{coll}} = \alpha(E - E_{\text{thermal}})
\]  

(3.19)

where \( \alpha \) is an optimized parameter and depends on the collision partner. The qualitative similarities between acetone and 3-pentanone indicate that such a model should apply equally well to 3-pentanone, probably with a slightly higher energy transfer efficiency, \( \alpha \), for a given collision partner.

The optimized parameter, \( \alpha \), is most sensitive to the short excitation wavelength, pressure-dependence data. For 3-pentanone collisions with itself (termed self-relaxation), the optimal solution occurred for \( \alpha_{3p} = 0.15 \) (Fig. 3.33) while for nitrogen, \( \alpha_{N_2} = 0.05 \) (Fig. 3.34) at room temperature. While the relaxation efficiency of 3-pentanone may be three times stronger than nitrogen, nitrogen’s and other diluent’s effects remain the primary consideration for cases of moderate pressure and low
Figure 3.33: Data (points) and model (lines) of the effect of 3-pentanone self-relaxation on the fluorescence quantum yield. The slight increase in the FQY with pressure for short wavelength excitation is well-predicted by the use of $\alpha = 0.15$. It is useful to compare the values of $\alpha$ found for 3-pentanone with similar results from acetone because Thurber and others have found that the value of $\alpha$ generally increases with the number of atoms of the collision partner [39, 76, 78]. For acetone and nitrogen, $\alpha = 0.021$, slightly less than half of the best-fit value for 3-pentanone and nitrogen. For acetone self-relaxation, $\alpha = 0.08$, again about half of the value for 3-pentanone. These results undergird the general correlation between energy transfer efficiency and the number of atoms in the colliding molecules.

use of literature data to further develop photophysical model

So far, model development has been analogous with that of acetone and has shown similarly successful results. Temperature dependencies measured at atmospheric pressure and pressure dependencies measured at room temperature have combined with the model framework and optimization to provide a better qualitative and quantitative concept of ketone fluorescence behavior. For acetone, fluorescence data at
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simultaneously high temperature and pressure were not considered because, for the most part, measurements do not exist for such conditions. For 3-pentanone, data are not as sparse because a major motivation for study has been for application in internal combustion engines, i.e. in high temperature, high pressure environments. As a result, there is a significant source of literature data from researchers who aim to quantify in-cylinder images using laboratory experiments [4,7,37,74]. Individually, each study contributes partly to the larger picture of 3-pentanone photophysical behavior, but interpretation of the published data can be hindered by the predominance of relative data sets that neglect or misinterpret potentially important effects like the temperature dependence of the absorption cross section. The conglomerate, however (after incorporating corrections for the effects of absorption and calibrating relative data sets to measured absolute values of the FQY), can provide further insight into the photophysical behavior of ketones under a wider range of conditions.

Figure 3.34: Comparison of modelled (lines) and measured (points) fluorescence quantum yield of 3-pentanone with added nitrogen. For nitrogen, $\alpha = 0.05$. 

![Figure 3.34: Comparison of modelled (lines) and measured (points) fluorescence quantum yield of 3-pentanone with added nitrogen. For nitrogen, $\alpha = 0.05$.](image-url)
temperature dependence of collisional relaxation rates

As temperature increases \( \alpha \), or equivalently, \( \Delta E_{\text{coll}} \), may increase, decrease, or stay the same for large molecules, depending on the nature of the interaction and the species involved [73]. While no detailed vibrational energy transfer studies have been performed for 3-pentanone or other ketones, Brown et al. found that \( \Delta E_{\text{coll}} \) decreased with temperature between 340 K and 850 K for the similarly structured ethyl acetate (\( CH_3CH_2OCOCH_3 \)) [79]. For other molecules, a positive temperature dependence has been shown to be a better predictor of reaction rates [80]. Measured pressure-induced changes in the FQY at high temperature for 266 nm excitation and the model developed so far provide a means of observing a similar effect in 3-pentanone. As can be seen in Figure 3.35, the constant value of \( \alpha = 0.05 \) results in predictions that are significantly higher than the data at high pressures and 723 K. Agreement improves, however, if one substitutes a temperature-dependent collisional transfer efficiency:

\[
\alpha = 0.05 \left( \frac{T}{300} \right)^{-1.2} \tag{3.20}
\]

where \( T \) is the temperature in Kelvin. (Published data at 423 K and 623 K were also used to optimize the temperature dependence of \( \alpha \).) Close to room temperature, the temperature-dependent transfer efficiency changes from the constant value only slightly, and as seen by the 323K data, results in no significant alteration of model predictions. Note also that while the high-T, high-p data of Figure 3.35 indicate that collisions may be less effective at removing excess energy at high temperatures, they also support a basic tenet of the model – that nitrogen vibrationally relaxes excited ketones without significant collisional quenching. That is to say, increasing the nitrogen pressure can only increase the fluorescence quantum yield.

A potential alternative explanation for the slower-than-predicted increase in the FQY as a function of pressure at high temperature may be that \( \Delta E_{\text{coll}} \) is less than linear with energy at high energies, i.e. the energy transferred per collision may plateau at high energies rather than continuing to increase linearly. A parabolic collisional relaxation model (of the form \( \Delta E_{\text{coll}} = a_1(E - E_{th}) + a_2(E - E_{th})^2 \) where \( a_1 \) and \( a_2 \) are optimized parameters) was investigated, but optimization for the pressure...
Figure 3.35: Fluorescence quantum yield data from 3-pentanone in nitrogen converted from the work of Ossler and Aldén [4] indicate that $\alpha$ may decrease at high temperatures. Solid lines represent $\alpha = 0.05$. Dashed lines represent $\alpha = 0.05 \times (T/300)^{-1.2}$. Error bars on data points represent the original authors’ estimate of ±15%.
Figure 3.36: Temperature dependence data in nitrogen reflect the combined effects of pressure relaxation and an increasing excitation energy. Relative T-dependent measurements have been calibrated to absolute measurements at 300K, 1 bar.

dependencies of different excitation wavelengths (Fig. 3.34) did not result in significant curvature of the $\Delta E_{\text{coll}}(E)$ curve. It should be noted, however, that such roll-off has been observed for other large molecules [77].

At atmospheric pressure, the rates of vibrational relaxation are on the same order as the nonradiative decay. (Collision rates are $\sim 10^{10} \text{sec}^{-1}$ per 3-pentanone molecule in 1 bar of nitrogen at room temperature and scale with $1/\sqrt{T}$ while intersystem crossing is $\sim 10^8$ to $10^{10} \text{sec}^{-1}$ between 1000 and 15000 cm$^{-1}$.) The data of Figure 3.36 thus represent an intermediate regime in which fluorescence may come from both the initially excited and the thermalized energy levels. The model’s relatively good agreement with the data for all three excitation wavelengths support its basic soundness.
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**Effect of oxygen**

So far, the pressure effects of nitrogen or 3-pentanone diluent have been modelled and discussed with no evidence for a quenching effect, i.e. increases in the concentration of 3-pentanone or nitrogen will not decrease the fluorescence quantum yield. Oxygen, however, shows the capacity to both vibrationally relax and measurably decrease the fluorescence signal, generally in proportion to its concentration (see Figs. 3.26-3.28). In addition to the possibility of chemical reaction or oxidation, a variety of non-reactive channels may be responsible for this behavior, including electronic energy transfer to the oxygen molecule (resulting in singlet oxygen production), oxygen-enhanced intersystem crossing, and oxygen-enhanced internal conversion [81]:

\[
\begin{align*}
1^3\text{Pent}^* (S_1) + ^3\text{O}_2 & \rightarrow 3^3\text{Pent}^* (T_1) + ^3\text{O}_2 \quad (3.21) \\
& \rightarrow 1^3\text{Pent}^* (S_0) + ^3\text{O}_2 \quad (3.22) \\
& \rightarrow 3^3\text{Pent}^* (T_1) + \text{O}_2(1^\Delta_g) \quad (3.23) \\
& \rightarrow 3^3\text{Pent}^* (T_1) + \text{O}_2(1^\Sigma_g^+) \quad (3.24)
\end{align*}
\]

Unfortunately, detailed vapor phase oxygen quenching studies have not been performed for any ketones to the best of our knowledge, and fluorescence yield data without simultaneous measurements of other products like singlet oxygen or triplet ketone provide no additional insight into which pathways dominate. Fortunately, the possible pathways are all similar and likely to have a bimolecular, gas-kinetic character. A simple, collision-theory formulation for the rate of oxygen quenching would be

\[k_{\text{ox}} [\text{O}_2] = \langle P \rangle Z_{\text{O}_2} [\text{O}_2]\quad (3.25)\]

where \(Z_{\text{O}_2}\) is the collision frequency for 3-pentanone/oxygen collisions, \([\text{O}_2]\) is the oxygen number density, and \(\langle P \rangle\) is the quenching efficiency or the probability that a collision will result in a quenching event. This term appears in the denominator of the terms in Equation 3.14. \(\langle P \rangle\) is the variable parameter that is optimized for the model to match the oxygen-containing experimental data.

Despite the lack of true mechanistic knowledge, we can gain some further insight
by looking at the change in electronic energy of the oxygen molecule in the aforementioned potential processes. The above reagents and products are shown in a Jablonski diagram in Figure 3.37. The pathways of processes 3.21 and 3.22 require no excess energy above the electronic states in order to reach the product state. However, for electronic energy transfer to oxygen, the 3-pentanone or oxygen reactant must have significant vibrational energy. We might thus expect an energy dependence for $\langle P \rangle$, with new channels opening at higher energies. Using the model thus far developed and optimizing the oxygen quenching coefficient to the room temperature fluorescence results in air and oxygen from Figures 3.39, 3.40, and 3.41 resulted in the best agreement when using an exponential energy dependence with a sudden increase in quenching efficiency at energies above $11,000 \text{ cm}^{-1}$ (corresponding to the initial energy for 248nm excitation around 350K or 266nm excitation near 600K).

$$\langle P \rangle = 0.0023 \exp(5 \times 10^{-5}E) \text{ for } E < 11,000 \text{ cm}^{-1}$$

$$\langle P \rangle = 0.25 \text{ for } E \geq 11,000 \text{ cm}^{-1}$$  \hspace{1cm} (3.26)
Figure 3.38: Optimized oxygen quenching efficiency as a function of excited state vibrational energy for 3-pentanone. The large increase in quenching efficiency around $11,000 \text{ cm}^{-1}$ is likely a result of electronic resonance with low-lying excited oxygen states.

This function is shown in Figure 3.38. The numerical functionality is rudimentary, but the likely resonant behavior in light of oxygen’s low-lying electronic states is obvious, and the simple formulation adequately captures the behaviors in the data shown below. Further photophysical (integrated signal and lifetime) studies in this high-energy regime may help to refine the formulation and further investigate this resonant-quenching hypothesis.

As can be seen by the 248nm data with pure oxygen diluent in Figure 3.39, oxygen collisions can also increase the fluorescence quantum yield. Unfortunately, it is difficult to separate the relaxation effect from the quenching effect for these experiments other than to say that the rate of increase in the FQY with added oxygen is similar to the rate for added nitrogen. Since similar oxygen and nitrogen relaxation rates have been noted for other molecules [76, 77], $\alpha_{O_2}$ has been set to the same value as $\alpha_{N_2}$, incorporating the same temperature dependence.

Pressure dependence measurements at somewhat higher temperature with and
without oxygen have been made using 248nm excitation by Großmann et al. [7] and are shown in Figure 3.40. In the figure, the nitrogen data, which were originally published only on a relative scale, have been calibrated to the absolute measurements in this work via the atmospheric temperature dependence measurements in nitrogen. The air and oxygen data have been calibrated to the nitrogen data by setting the signals at nearly zero pressure as equal (corresponding to conditions of a small, fixed, amount pure 3-pentanone in the measurement volume). The 473K data was also scaled by the temperature dependence data at one bar. Model predictions for data at 383K show a relatively well-captured behavior overall. The oxygen data, while underpredicted by 15-25%, agree on a relative scale. The disagreement may result from the propagation of errors in the relative measurements that were used to calibrate the data, but probably they reflect the higher order complexities of the combined effects of temperature and excitation energy on the specific decay channels for oxygen/3-pentanone interactions. It is nonetheless encouraging to see that most of the effect of added oxygen can be captured at the level of collision theory without consideration of the detailed mechanisms, structures of the excited 3-pentanone molecule, or the
structures of possible transition states.

In addition to the data so far presented, Frieden et al. have measured the relative fluorescence signal of 3-pentanone following 248nm excitation in air through a range of temperature and pressure conditions by uniformly seeding the charge of a motored internal combustion engine (ICE) [74]. Having characterized the in-cylinder temperatures and pressures, the LIF data provide a reference for conditions ranging from about 330K, 1 bar to 600K, 8 bar. The high-energy excitation frequency and presence of oxygen at high temperature and high pressure make this a particularly complex system by which to test the FQY model. FQY model results (the absorption cross section for 248nm is nearly temperature-independent as shown in Fig. 3.14, making \( S_f \propto \phi \) in this case) and LIF signals per molecule (normalized to -90°ATDC) are shown as a function of crank angle in the bottom half of Figure 3.41. For reference, the top half of the figure shows the temperature and pressure conditions during the cycle. The trends between -90°ATDC and top-dead center are well-captured by
Figure 3.41: FQY data and model for 248nm excitation of 3-pentanone in air in a motored ICE cylinder.

The absorption and fluorescence characteristics of 3-pentanone under a variety of conditions, quantified in this work, will enable better quantitative PLIF measurements for temperature and concentration in a variety of applications, potentially for basic fluid and heat transfer studies, but more likely for experimental investigations of research combustion devices where the physical properties of 3-pentanone are more desirable. The acquired photophysical data underscore the general similarities among the aliphatic ketones even though quantitative differences can be significant.
3.4. KETONE CONCLUSIONS

For example, 3-pentanone’s fluorescence signal per unit mole fraction has proven to be temperature-independent below 600K for 308 nm excitation. Such a condition does not exist for a common acetone excitation scheme. A semi-empirical fluorescence quantum yield model, first developed for acetone, has been shown to apply to 3-pentanone and also shows promise for predictive capability. Comparison of model and data at high temperatures and pressures indicate that a few adjustments to the original model formulation are necessary. For example, vibrational relaxation effects tend to decrease with increasing temperature. Also, oxygen quenching or oxidation reactions may be complex at high energies due to the multiplet of deactivation mechanisms. Unfortunately, there remains a dearth of experimental data in this regime, and fluorescence measurements alone cannot fully describe the detailed mechanisms.

Despite the model’s apparent ability to represent a wide range of conditions, its development still ultimately depends upon the experimental data. Use of the model under simultaneous high-temperature, high-pressure conditions would thus be aided by experimental data in this regime that would differentiate between the proposed mechanisms, e.g., oxygen quenching, vibrational relaxation, and temperature or excitation wavelength effects. Such data (both fluorescence yield and accurate lifetime data) may enable a better understanding of the relevant processes, but more importantly, a complete survey of the parameter space of excitation wavelength, temperature, pressure, and bath gas concentration will have a direct impact on quantitative 3-pentanone PLIF applications in the harsh mixing environments of practical combustion devices.

For better mechanistic understanding of the ketone excited state dynamics, more sophisticated approaches are required in addition to a full experimental fluorescence survey. Fluorescence data could provide useful model benchmarks, for example, measurements of the fluorescence high pressure limit as a function of temperature. However, fluorescence data alone may not illuminate the mechanistic detail needed to quantitatively understand the ketone excited state, as exemplified by the multiple possible pathways for oxygen quenching. Simultaneous product formation measurements, e.g., of singlet oxygen, would thus provide additional insight. In addition to studying oxygen-induced decay mechanisms, more direct vibrational energy transfer
studies would serve to better constrain the vibrational energy transfer model. A variety of techniques are available that would isolate and constrain this critical variable in the model, including infrared fluorescence (IRF) [82], ultraviolet absorbance (UVA) [9] or kinetically controlled selective ionization (KCSI) [83].
Chapter 4

Toluene

The experimental methods described in Chapter 3 are generally applicable to study a wide range of potential PLIF tracers. One such tracer with exceptional potential for the development of quantitative diagnostics in fuels or fuel surrogates is toluene \((C_6H_5CH_3)\). Below, the reader will be provided with an introduction and motivation for studying toluene as a PLIF tracer. Results of experiments similar to those described in Chapter 3 will provide a means of exploring toluene’s strengths and weaknesses as a PLIF tracer.

4.1 Background and Motivation for Toluene LIF

Toluene and similar aromatics are a focus of diverse research fields ranging from the investigation of fundamental processes in large molecules to use as a PLIF tracer for flow-field and mixing studies. On a fundamental level, the photophysical properties of the \(S_0 \rightarrow S_1(\pi, \pi^*)\) transition in toluene vapor have been a subject of interest to chemists since early in the last century [84,85]. Its absorption is also relevant to concentration measurements in the atmosphere [86]. For PLIF, toluene is also a promising tracer for visualizing mixing processes. As a major component of commercial gasoline and its research surrogates, toluene is especially attractive to reciprocating IC engine researchers [36]. The strong fluorescence quenching by oxygen potentially allows one to directly visualize the fuel-air or equivalence ratio during pre-combustion.
mixing [10], and, if combined with an oxygen-insensitive tracer, it may enable the simultaneous quantification of fuel and oxygen concentrations [74,87]. In addition to gasoline applications, typical aeropropulsion fuels like JP-8 and their surrogates consist of n-paraffins, iso-paraffins, napthenes, aromatics, and alkenes [88]. Of these groups, aromatics are the only major components that produce large fluorescence signals after near-UV excitation. Toluene is thus a primary candidate for advanced diagnostic development for a wide range of fuels and fuel surrogates and also for a wide range of combustion applications. However, as with acetone and 3-pentanone, the photophysics must be well-understood in order to realize toluene’s potential for quantitative PLIF.

Since toluene has been a topic of interest to chemists for almost a century, there is a wealth of data at and below room temperature from which to learn about its photophysical properties. The \( S_0 - S_1 (\pi, \pi^*) \) absorption spectrum of toluene at room temperature has been well described [8,89]. It extends from about 240 nm to 270 nm featuring a dominant vibrational sequence with the strongest transition for the \((0,0)\) band at 266.8 nm with a peak absorption cross section of \(1.3 \times 10^{-18} \text{cm}^2\) [86]. At shorter wavelengths the spectrum loses most of its structure as a result of the increasing state density in the excited electronic manifold. Similar to ketones, the electronic transition strength is relatively weak due to symmetry reasons, though slightly better vibronic coupling results in absorption cross sections that are approximately ten times larger than acetone or 3-pentanone. From the previous studies, we know that absorption is easily accessible with commercially available high-power UV lasers at 248 nm and 266 nm.

A thorough investigation of the fluorescence properties at room temperature was performed by Burton and Noyes, Jr. [8]. The fluorescence quantum yield is high (about 30\%\(^1\)) at low pressures in the absence of oxygen for 266nm excitation. Jacon et al. further noted that above about 2100 cm\(^{-1}\)vibrational energy in the \( S_1 \) state (corresponding to excitation with 253 nm) the quantum yield decreases rapidly by two orders of magnitude [90]. Furthermore, around this energy level, fluorescence

\(^1\)Similar to previous ketone measurements, the FQY cited here is based on a series of relative measurements that may contain systematic errors. Work is ongoing to determine the Rayleigh-calibrated FQY of toluene for 266nm and 248nm excitation at ambient conditions.
4.1. BACKGROUND AND MOTIVATION FOR TOLUENE LIF

and triplet yields do not add to 1.0, thus justifying the existence of a "third decay channel", a phenomenon that was explored extensively by Smalley and co-workers [91,92]. Effective lifetimes of the $S_1$ state have been published by several parties, the most recent being $86\text{ns}$ at low vibrational energy levels [75,90,93]. The frequencies of vibrational modes in both the ground and excited state have been specified by Hickman et al. [93].

Oxygen quenching of the fluorescence from toluene and other aromatics is also a well-known phenomenon [94]. The fluorescence signal at room temperature is inversely proportional to the oxygen number density (Stern-Volmer behavior) with an oxygen quenching efficiency of approximately one, i.e. almost every (hard-sphere) gas-kinetic collision leads to electronic deexcitation. Toluene has also been studied to elucidate the process of collision-induced vibrational energy transfer within the $S_0$ state using UV absorption [76], IR emission [67], and two-photon ionization [95]. Within the $S_1$ state, both inter- and intra-molecular vibrational energy transfer have been studied by means of dispersed fluorescence spectra [91,93,96].

With keen insight for application, Reboux et al. were the first to show that as long as oxygen quenching is the dominant deexcitation pathway, the fluorescence signal from toluene will be proportional to the fuel-air ratio [10]. This concept, known in the literature as FARLIF, was experimentally confirmed for toluene LIF at room temperature with 248 nm excitation and air pressures above 3 bar. Similar results have been found for benzene [97] and tetrahydrothiophene (THT) [98]. Because of the importance of measuring the fuel-air ratio for ignitability and flame development in combustion systems, the FARLIF technique rapidly became popular in reciprocating IC engines [74,99].

Despite the plethora of basic studies and frequent use of toluene for diagnostics in the mixing and compression phase of internal combustion engines, little information about absorption cross sections and fluorescence quantum yields at high pressure and elevated temperature has been available. As a result, PLIF measurements must assume negligible pressure and temperature effects when interpreting fluorescence signals under such conditions. Maintaining an emphasis on fundamental understanding, we thus have two objectives for toluene PLIF development: to study the photophysics
in order permit better quantitative interpretation of toluene PLIF, and to acquire a
deeper understanding of the dominant processes in the $S_1$ state with the goal of de-
veloping a model for tracer-LIF intensities as a function of pressure, temperature,
and excitation wavelength in practical situations.

\section{4.2 Toluene photophysics background – the potential for fuel-air ratio imaging}

For toluene LIF, the fluorescence equation (Eq. 2.1) generally applies, and again,
the key to signal interpretation and diagnostic development lies in understanding $\sigma$
and $\phi$. For broadband absorbers in the UV, the absorption cross section depends on
excitation wavelength and temperature. The quantum yield depends on temperature,
excitation wavelength, and on the concentration of collider species. Whereas collisions
with nitrogen and toluene may affect the FQY via vibrational relaxation, collisions
with oxygen can also lead directly to electronic deexcitation. As with the ketones, the
effect of oxygen quenching of an excited state (or similar group of states) is thought
to occur via a charge-transfer complex. The FQY can thus generically be described
by:

\[ \phi = \frac{k_f}{k_f + k_{NR} + k_{ox}[O_2]} = \frac{k_f}{k_{tot} + k_{ox}[O_2]} \] (4.1)

For toluene, the oxygen quenching term is traditionally considered the dominant
pathway, and for convenience, we combine the intramolecular decay channels into a
single term: $k_{tot} = k_f + k_{NR}$.

A direct measurement of the quenching rate coefficient is difficult, so the impact of
$O_2$ quenching is typically measured relative to the total intramolecular deexcitation
rate, leading to a ratio called the Stern-Volmer factor ($k_{SV}$):

\[ k_{SV} = \frac{k_{ox}}{k_{tot}} \] (4.2)

The Stern-Volmer factor can be deduced as the slope from a Stern-Volmer plot,
i.e. the slope of the inverse signal, normalized to the signal $S_0$ in absence of the
4.2. TOLUENE PHOTOPHYSICS BACKGROUND

quencher, plotted versus the quencher concentration, according to Equation 4.3.

\[
\frac{S_0}{S} - 1 = \frac{k_f}{k_{tot}} \left( k_{tot} + k_{ex}[O_2] \right) = k_{SV}[O_2]
\]  

(4.3)

Substituting \( k_{SV} \) into Equation 4.1, the decrease in the fluorescence yield with added oxygen may be expressed as

\[
\phi = \frac{k_f/k_{tot}}{1 + k_{SV}[O_2]} = \frac{\phi_0}{1 + k_{SV}[O_2]}
\]  

(4.4)

where \( \phi_0 \) is the FQY in the absence of oxygen. Substituting Equation 4.4 into the fluorescence equation, it becomes obvious that in the limit of strong oxygen quenching (\( k_{SV}[O_2] \gg 1 \)), the fluorescence signal is approximately proportional to the toluene-to-oxygen ratio:

\[
S_f \propto \frac{n_{toluene}}{[O_2]}
\]  

(4.5)

Assuming toluene directly represents the fuel and oxygen represents air, the fluorescence signal is thus also proportional to the fuel-air or equivalence ratio. A single measurement of a fluorescence signal with a known equivalence ratio, \( \Phi \), will account for the other multiplicative factors in the fluorescence equation and result in a linear calibration curve for signal vs. \( \Phi \) that goes through the origin of such a plot, resulting in a straightforward interpretation of fluorescence signal in terms of an important parameter for ignitability in combustion applications.

The FARLIF technique as described so far relies on two assumptions for practical applications (e.g., combustion engines):

1. Oxygen quenching is the dominating deexcitation pathway at all temperatures.

2. Temperature dependencies (like the absorption cross-section and the temperature-dependent parts of the quantum yield expression) are either negligible or separable into an experimentally accessible function, which can be used to correct the signal.

Reboux et al. first supported the strong oxygen quenching approximation experimentally by finding it valid for 248nm excitation at room temperature for air pressures
above 3 bar [10]. The validity of this approximation (and the promise of a straightforward fuel-air ratio diagnostic) for other conditions has remained a matter of conjecture. As will be shown with the aid of experimental results below, Equation 4.5 can be significantly erroneous, especially at high temperatures, meaning that FARLIF measurements may not be as straightforward as first hoped. While the photophysical complexities of toluene LIF may at first seem inhibitive to diagnostic development, the experimental results will also lead us toward the necessary solutions for equivalence ratio imaging and suggest a richer variety of potentially useful diagnostics.

4.3 Toluene absorption cross section

Toluene’s absorption spectrum was measured with an absorption spectrograph in a shock tube and with lasers in a cell using methods similar to those described for 3-pentanone (see Ch. 3). The spectrally-resolved absorption in shock-heated toluene in the 240 - 290 nm range is displayed in Figure 4.1 together with data from the literature. Room-temperature measurements were also made within the shock-tube and spectrograph and compared to the spectrum published by Burton and Noyes [8]. Although our spectral resolution was limited, the same structure was evident, and values of the cross section in the weakly structured blue region of the spectrum agree well. At the lowest accessible temperatures in our shock tube experiments (600 K) the fine structure is no longer evident. The spectrum becomes a broadband continuum with a maximum at 261 nm ($\sigma = 5.6 \times 10^{-19} \text{cm}^2$) and a FWHM of 20 nm. Due to the thermal population of vibrationally excited ground state levels, absorption on the red side of the (0,0) band becomes energetically possible and broadens the absorption feature. At 1100 K the absorption cross section at 300 nm increases to $1.0 \times 10^{-19} \text{cm}^2$ from $< 1 \times 10^{-20} \text{cm}^2$ at room temperature and the FWHM increases to 40 nm. The absorption maximum also shifts with temperature and is found at 268 nm at 1125 K. On the blue side of the feature the stronger (symmetry allowed) $S_0 \rightarrow S_2$ transition centered at 200 nm [100] shows a pronounced increase with temperature and overlaps with the $S_0 \rightarrow S_1$ transition [49]. Our results can be compared to two other publications. The work by Hippler et al. focused on the
4.3. TOLUENE ABSORPTION CROSS SECTION

Figure 4.1: Toluene absorption spectra. Solid lines: this work (shock tube); dotted line: room temperature spectrum from [8]; data points at 850 K and 1200 K from [9]; vertical lines illustrate the laser wavelengths used in cell experiments.

The agreement is within 10% for the high-temperature measurement (with an 80 K temperature difference between our measurements and the Hippler data). The spectra published by Richardson et al. (not shown in Fig. 4.1) show similar relative behavior, i.e. loss in structure and the red-shift with increasing temperature [101]. However, their absolute numbers are lower at high temperatures by 30% for 266-nm excitation (see Fig. 4.3).

4.3.1 Laser absorption measurements

The low-temperature absorption spectra contain fine structure that is not fully resolved with our spectrometer. Absorption of laser light may show a strong variation with temperature due to the broadening of the vibrational bands within the system, especially for the laser line at 266 nm, located in the valley next to the peak at 266.8
Figure 4.2: Toluene absorption cross section at 248 nm is nearly constant with temperature until the red-shifting $S_0 \rightarrow S_2$ system begins to dominate around 1000K.

Therefore, we measured the absorption cross sections in the intermediate temperature range in a flowing cell (300 - 950 K) with laser radiation at 248 and 266 nm in order to generate data relevant for laser diagnostics experiments. Results of these measurements are shown in Figure 4.2 and Figure 4.3 along with data from the literature. Absorption at 248 nm is independent of temperature up to 950 K. The cell data agrees well with our shock tube measurements in the temperature range accessible to both experiments. Agreement with literature data, that is the room temperature measurement of Burton and Noyes and the shock tube data from Richardson et al., is evident. For all further calculations, the absorption cross section of toluene at 248 nm is set to $3.1 \pm 0.2 \times 10^{-19} \text{cm}^2$ for 300 - 950 K (the straight line in Fig. 4.2). The steep increase in absorption at temperatures above 1000 K corresponds to the strong increase of the red side of the $S_0 \rightarrow S_2$ feature.

Absorption at 266 nm increases linearly by a factor of 2.5 from 300 - 550 K. Above 550 K, the increase continues more slowly. At room temperature, 266nm absorption occurs in the valley between two dominant vibrational bands (see Fig. 4.1). Broadening of the bands initially leads to a quick rise of absorption with increasing temperature. At 600 K the fine structure is lost; the remaining increase in absorption
4.3. TOLUENE ABSORPTION CROSS SECTION

Figure 4.3: Toluene absorption cross section at 266nm increases temperature, likely as a result of broadening of the (0,0) band. Line represents Eq. 4.3

is due more to the overall increasing system strength. In the temperature range where flow-cell and shock tube measurements overlap, results show the same relative trend, but absolute numbers for the latter are about 15% lower. Uncertainty of the cell experiments is ±7% with major contributions to the error consisting of uncertainty of the toluene concentration in the cell or, at the high toluene concentrations, from the low transmitted signal intensity. Uncertainty in the shock tube data is estimated at ±10% due also to possible concentration errors and due to the potential for unresolved but remaining structure, especially near the (0,0) band around 600K. Hence, the different data sets are within experimental error. As mentioned above, the room temperature value from Burton and Noyes is well-reproduced by our cell measurements, but values from Richardson et al. are significantly lower. Unfortunately, no other basis of comparison, including a room temperature spectrum, is available from Richardson’s work. The 266nm absorption cross section can be represented within 5% of the data between 295K and 920K by the following expression, with T in Kelvin.

\[
\frac{\sigma(266nm, T)}{10^{-19} cm^2} = -3.57 + 0.022T - 1.22 \times 10^{-5}T^2
\]  (4.6)
4.4 Fluorescence temperature dependencies without oxygen

As with the ketones, it is important to first isolate and quantify the temperature behavior without oxygen in the system. Hence, fluorescence results at elevated temperatures will first be presented for nitrogen baths before discussing the results with oxygen.

4.4.1 Fluorescence spectrum

Fluorescence was investigated in a bath of nitrogen at a total pressure of 1 bar using a heated, flowing cell and methods similar to those for the 3-pentanone investigations (Fig. 3.12). In these experiments, however, a spectrometer and ICCD camera were used as the detection system in order to fully understand the temperature dependence of the entire fluorescence spectrum. Further details can also be found in [102]. Figure 4.4 displays the temperature dependence of the toluene fluorescence spectrum following 248 nm excitation. The total fluorescence decreases rapidly with temperature (see below), so the spectra are normalized to compare the shape. Emission (at room temperature) extends from roughly 260 nm to 400 nm with a maximum around 280 nm. With increasing temperature, a slight shift of the fluorescence maximum of roughly 2 nm per 100 K to the red is observed. The tail on the red side of the spectrum becomes stronger relative to the peak emission. The red-shift of the fluorescence spectrum with increasing temperature has also been noted in investigations of other aromatic molecules [103,104]. A plausible explanation involves the difference between ground and excited state vibrational frequencies. The transitions in question are bonding orbital to anti-bonding orbital transitions of polyatomic molecules. With less electronic bonding energy, the excited-state vibrational frequencies tend to be smaller than those of the ground state. Vibronic sequences of the fluorescence spectrum (e.g., (0,0), (1,1), (2,2)...for a single vibrational mode) thus have lower transition energies and tend to progress toward the red in an emission spectrum. The higher transitions in a given sequence become more noticeable with increases in
4.4. TEMPERATURE DEPENDENCIES WITHOUT $O_2$

Figure 4.4: Normalized fluorescence spectra (relative numbers of collected photons); 5 mbar toluene in nitrogen, 248 nm excitation, 1 bar total pressure.

The room temperature emission spectrum shown in Figure 4.4 also possesses more structure than was resolved with our measurements. Evidence for this can be seen at low pressures (e.g. [8]). Burton and Noyes reported that the addition of hexane results in even sharper spectra due to vibrational relaxation. However, since applications with toluene as a tracer molecule typically use broadband filters (e.g., a long-pass filter), knowledge of the fine structure is not critical to this work. Spectra at room-temperature have identical shape for 266 nm and 248 nm excitation with the red-shift for the latter slightly more pronounced, likely because of incomplete relaxation for the atmospheric conditions studied.
4.4.2 Temperature dependence of the fluorescence quantum yield

Relative fluorescence quantum yields were calculated by spectrally integrating the signal. For 248 nm excitation, the integration area between 260 and 400 nm accounted for 99.9% of the total emission. For 266 nm excitation, signals between 270 and 400 nm were integrated, so about 3% of the total emission was not captured by our integration. This was necessary to avoid integrating the Rayleigh signal (primarily from toluene) at the laser wavelength. Errors in the relative quantum yield due to this emission omission are negligible.

Dependence of the FQY on temperature after excitation at 266 nm normalized to room temperature is shown in Figure 4.5. The FQY decreases exponentially by three orders of magnitude within our 600 K temperature range. The single-exponential best-fit is

\[
\frac{\phi(T)}{\phi(296K)}|_{266\text{nm}} = 22.5 \exp(-0.0105T)
\]  

with T in K, valid for 300 - 950 K and 1 bar nitrogen bath gas. To obtain an approximate absolute scale, one may calibrate results to the room temperature value of 0.3 determined by Burton and Noyes (for excitation at 266.8 nm, 23 mbar pure toluene). The difference in wavelength and pressure between their and our measurements should be negligible due to the small vibrational excess energy deposited in the molecule.

Similar to the ketones, a decrease in the fluorescence yield with temperature is expected since it decreases with vibrational energy [8, 90]. Raising the temperature increases the vibrational energy of the ground state and thus also increases vibrational energy of the $S_1$ state for a fixed excitation wavelength. Conversely, decreasing the excitation wavelength at room temperature also raises the vibration energy in $S_1$. We might thus expect that toluene photophysics might be modelled similarly to 3-pentanone. Using previously measured lifetime data for various excitation energies to predict our measured temperature dependencies, however, did not explain the steep signal fall-off. Additional lifetime measurements are desirable in order to investigate the kinetics of the excited electronic state more thoroughly. For now, we can only
4.4. TEMPERATURE DEPENDENCIES WITHOUT $O_2$

Figure 4.5: Toluene fluorescence quantum yield: solid squares indicate 266 nm excitation, 5-20 mbar toluene in 1 bar nitrogen; straight line indicates exponential best-fit; ×-marks are data from [8], 266.8 nm excitation, 23 mbar pure toluene.

conclude that changes in average vibrational energy due to temperature do not seem to justify the magnitude of the decrease seen in Figure 4.5. Figure 4.5 also shows the data from Burton and Noyes, whose measurements were made at lower pressures. Within the overlapping temperature range, no effect of our additional 1 bar nitrogen is observable, and both series show the same temperature dependence.

The results for 248 nm excitation are shown in Figure 4.6. The dependence of the fluorescence yield on temperature can be described by a double exponential function:

$$\frac{\phi(T)}{\phi(296K)}_{248nm} = 171 \exp(-0.0175T) + 0.337 \exp(-0.0068T)$$

with $T$ in Kelvin, valid for 300 - 950 K and 1 bar nitrogen bath gas. The initial decrease at 300 - 500 K is steeper than that found for 266 nm excitation, but the signal decreases more slowly at higher temperatures. The total variation in fluorescence quantum yield within the 600 K interval exceeds three orders of magnitude. The absolute quantum yield for 248 nm excitation in 1 bar of nitrogen can currently only be estimated. Burton and Noyes give a value of 0.09 for low total pressures (23
Figure 4.6: Toluene fluorescence quantum yield. This work represents 5-20 mbar toluene in 1 bar nitrogen; Burton and Noyes [8] data is from 250 nm excitation, 23 mbar pure toluene.

Little research has been done on the pressure dependence of the quantum yield. Using ketones as a basis of comparison, the quantum yield may increase with $N_2$ pressure; thus, at 1 bar it may be somewhere between 0.1 and 0.3. Experiments are currently under way to study the pressure dependence of toluene fluorescence quantum yield in more detail. Also shown in Figure 4.6 are results from Burton and Noyes at a similar wavelength but at low pressures (23 mbar). Apparently, the difference in total pressure (i.e. vibrational relaxation) has no observable effect on the relative temperature dependence between 300 K and 450 K for either 248nm or 266nm excitation. A further discussion of the temperature dependence is more difficult than in the case of 266 nm excitation, since quantum yield data for the shorter wavelengths is sparse. Precision of the results is about $\pm10\%$ resulting from uncertainties in the correction for laser absorption and the calculation of toluene concentration. Accuracy may be somewhat limited by the measured absorption cross sections.
4.4.3 Possible temperature measurements using toluene

Similar to single-line temperature diagnostics for acetone and 3-pentanone, the distinct temperature dependence of the toluene fluorescence in nitrogen makes this molecule a promising tracer for LIF temperature imaging. In homogeneously mixed, constant pressure systems, fluorescence from either 248 or 266 nm excitation is a function of temperature only. Relative calibration curves can be calculated from the results presented above, and one region or condition of known temperature is sufficient to obtain absolute temperatures. The over-all dependence on temperature is exponential since the quantum yield is the dominant factor.

In the case of inhomogeneous systems, one might take advantage of the temperature-dependent red-shift of the fluorescence spectrum to measure temperature by measuring fluorescence simultaneously in two different wavelength regions using two cameras and appropriate filters after excitation at a single wavelength. Evaluating the ratio of the 2D-signals, number density and laser intensity will cancel at each point and the result is sensitive solely to temperature. The temperature sensitivity depends on the chosen combination of filters. Figure 4.7 shows the signal ratio of fluorescence with 266 nm excitation detected around the emission peak (280 ± 5 nm, called "BP280" to represent a 10-nm bandpass filter) and the signal in the long wavelength tail (> 335 nm, called "WG335" according to the filter suggested for this purpose). The temperature sensitivity is similar to that of 3-pentanone two-line thermometry [62]. At room temperature, almost one third of the signal can be collected in the 280±5nm bandpass while only about 15% of the signal is in the same spectral region at 900 K. As can be seen in Figure 4.7, the signal intensities from the two suggested detection channels are the same order of magnitude at higher temperatures.

The temperature sensitivity of the ratioing technique is one figure of merit, but one must also consider the expected signal intensities from each detector during experimental design. As such, the rapid decrease in quantum yield may at first seem disappointing. However, the room temperature quantum yield is on the order of 500 times stronger than that of 3-pentanone or acetone [105]. Additionally, toluene features slightly larger absorption cross sections. Hence, signal levels at elevated temperatures, even using partial spectra, are likely to be similar to ketone signals, whose
Figure 4.7: Signal ratios using two bands within toluene’s fluorescence spectrum (see text) may offer the opportunity for one-laser, two-camera temperature and concentration measurements.

measurability has been demonstrated in this work. Furthermore, since only one excitation source is required for this technique, it potentially represents a significant experimental simplification compared to two-line 3-pentanone thermometry.

4.5 Fluorescence dependencies on oxygen

Having revealed the temperature dependencies of toluene LIF without the complicating behavior of oxygen quenching, we are now in a better position to interpret the oxygen-induced dependencies. We will first describe the behavior of the toluene LIF emission spectrum with varying oxygen concentration and then the results for total (integrated) signals at 266- and 248-nm excitation when oxygen is present.

4.5.1 Fluorescence spectra

For 248 nm, the normalized spectrum initially shifts to the red with increasing oxygen partial pressure, an indication that some of the transitions that contribute to the
longer wavelengths in the emission spectrum experience a weaker relative quenching effect (smaller Stern-Volmer factor). After this initial red-shift, the spectrum approaches a high pressure limit beyond where the shape does not change with added oxygen - in the case of room temperature and 248-nm excitation above 200 mbar $O_2$ (Fig. 4.8). Similar behavior is found at all investigated temperatures with the strongest effects at room temperature. As previously shown, an increase in temperature also results in a red-shifted spectrum. Thus, when varying both temperature and oxygen number density, the two effects are additive. For 266-nm excitation, no change in shape due to added oxygen could be observed within the investigated range of conditions.

4.5.2 Integrated signals, 266nm excitation

The dependence of the total (spectrally integrated) toluene LIF signal on the oxygen number density is shown in Figure 4.9 for selected temperatures. At room temperature toluene LIF exhibits Stern-Volmer behavior. The Stern-Volmer factor is
Figure 4.9: Stern-Volmer plot for selected temperatures, 266nm excitation. Maximum oxygen partial pressure is 350 mbar for all temperatures. The slope, i.e., $k_{SV}$ decreases strongly with increasing temperature.

Our value of $k_{SV}$ is within experimental error of the value published by Burton and Noyes who found a Stern-Volmer factor of $1.6 \times 10^{-23} \text{m}^3 (402 \text{ bar}^{-1})$ [8]. Their measurements were conducted for a toluene / oxygen mixture with up to 90 mbar oxygen. With increasing temperature the slope of the Stern-Volmer plot, $k_{SV}$, decreases dramatically as shown in Figure 4.9. According to Equation 4.2, this can be caused by a decreasing quenching rate coefficient $k_{ox}$ and/or by an increasing intramolecular deactivation rate $k_{tot}$. We have already shown that toluene’s fluorescence quantum yield in nitrogen decreases strongly with temperature (Sec. 4.4.2). Taking the ratio of the
4.5. FLUORESCENCE DEPENDENCIES ON OXYGEN

Figure 4.10: Temperature dependence of the ratio of quenching rate and radiative rate, calculated according to Eq. 4.10. The ratio and thus likely the quenching efficiency and the radiative rate themselves feature a moderate dependence on temperature. Data are normalized to room temperature.

Stern-Volmer coefficient to the FQY in nitrogen reveals the temperature-dependence of the quenching and the radiative rate:

\[
\frac{k_{SV}(T)}{\phi^{N_2}(T)} = \frac{k_{ox}(T)}{k_f} = \frac{\langle P \rangle Z_{O_2}}{k_f}
\] (4.10)

Here, \(k_{ox}\) is substituted by a probability and a collision rate as a means of illustrating an expected weak temperature dependence due to an increasing collision frequency with temperature. The results of this calculation are displayed in Figure 4.10. The weak temperature dependence for temperatures below 500 K can be explained with the temperature dependence of the collision frequency. Although the effect of temperature can not be evaluated separately for the radiative and the quenching rate, the fact that the ratio is approximately constant suggests that both parameters do not depend strongly on temperature. We thus infer that the dominant temperature dependence underlying the decrease of \(k_{SV}\) and \(\phi\) with increasing temperature is a strong increase of the intramolecular nonradiative decay rate \(k_{NR}\) (e.g. intersystem crossing or internal conversion).
Figure 4.11: At elevated temperatures a systematic deviation from linearity becomes evident in the Stern-Volmer plot. This behavior can be observed above 500 K. It indicates the increasing relevance of a state that features fast internal conversion (see text). Error bars of 5% result from the variation of repeated measurements.

Figure 4.11 shows a magnified Stern-Volmer (SV) plot for 625K. For sufficiently high oxygen concentrations, some downward curvature becomes apparent, indicating non-SV behavior. The same trend is evident for all temperatures in our measurements using 248 nm excitation, so we will discuss this further as our 248nm results are presented below.

4.5.3 Integrated signals, 248nm excitation

The results for 248nm excitation indicate the limits of Stern-Volmer behavior (Fig. 4.12). Overall, the relative strength of quenching decreases with increasing temperature, as is the case for 266nm excitation. However, the dependence of the toluene LIF signal
on oxygen pressure does not show a Stern-Volmer behavior over the entire concentration range even at room temperature, i.e. the signal does not obey Equation 4.3. However, Equation 4.3 strictly applies only to a single vibrational state or to a group of states with similar behavior. We might still hypothesize that vibrational states with significantly different $k_f$, $k_{ox}$, and/or $k_{NR}$ contribute to the emission process. Presented below is a model to describe the experimental data and to predict signal strengths for higher oxygen concentrations.
4.6 Semi-empirical model for toluene LIF in the presence of oxygen

The model presented below is a compromise between a complete representation of the physical processes involved in toluene fluorescence and a simple numerical fitting to the presented experimental data. Although it does not attempt to characterize the state-specific behavior of excited toluene, this model shows promise for predictive capabilities for toluene LIF at oxygen pressures that are relevant for IC engine and other tracer PLIF applications.

Interpretation of results and the underlying photophysical processes

The slope of the Stern-Volmer plot, $k_{SV}$, indicates the strength of oxygen quenching relative to intramolecular decay. As temperature increases, $k_{SV}$ decreases, and from Figure 4.10 we conclude that this is primarily caused by an increasing intramolecular decay rate with increasing temperature, probably dominated by intersystem crossing (ISC) as indicated by measurements of triplet yields [8].

The increasing decay rate explains the decreasing $k_{SV}$; however, it does not explain the nonlinearity in the SV plots at high excitation energies, e.g., above 500 K for 266 nm excitation and above at least 300 K for 248 nm. To explain the nonlinearity, we hypothesize that at high energies, toluene fluorescence can be attributed to two types of vibrational states with different sensitivities to oxygen quenching.

Evidence for simultaneous emission from states with significantly different SV factors is found in several publications [90, 106–111]. Jacon et al. [90] found biexponential fluorescence decay in toluene at room temperature for excitation wavelengths shorter than 250 nm. The long-lived component was similar to those measured at lower energies, probably dominated by ISC. The short-lived component indicates a "third-decay-channel" (an intramolecular process in addition to fluorescence and intersystem crossing) with a significant energy threshold. Such a decay channel has been documented for many aromatic compounds [12, 16–18, 20] and has commonly been assigned to internal conversion (IC), the radiationless transition to the $S_0$ state [106–109, 111].
4.6. TOLUENE FLUORESCENCE MODEL

Further complexities occur because IC does not seem to have a fixed energy threshold but a threshold that depends on the vibrational modes involved. At extremely high energies, decay from this channel can become very fast; Farmanara et al. reported a lifetime of 4 ps for 202 nm excitation [110]. Without going into the details of which modes are most responsible for the decay processes, we simply name two types of states in terms of their non-radiative intramolecular deactivation pathways: 1) the short-lived, less-oxygen-sensitive states noted heretofore as IC, and 2) more oxygen-sensitive states with a longer lifetime, hereby labelled ISC.

The IC and ISC states might be populated in a number of different ways. First, each kind of state may be prepared via direct optical coupling from the ground states. In large molecules at room temperature, monochromatic light will excite multiple vibronic bands, the character of which depends on the excitation energy and the Boltzmann distribution in the ground state. Anharmonic coupling and high state densities further allows the direct optical population of vibronic levels that would be otherwise forbidden by symmetry.

In addition to direct absorption, states may be populated via intramolecular vibrational redistribution or randomization (IVR). That is, vibrational energy is redistributed among various modes (e.g., from optically excited vibrational modes to optically inactive modes) while the total vibrational energy of the molecule remains constant. In a review of excited state dynamics, Smalley indicates that the onset of IC in aromatics coincides with the onset of rapid IVR [92]. IVR rates depend on both the density of states and the nature of the coupling between the optically populated modes and the "dark" modes into which some of the excess vibrational energy flows (e.g. methyl-rotors and rotational Coriolis coupling have been suggested as especially efficient promoters of IVR in some cases [112, 113]) In general, IVR rates increase with the density of states and the degree of energy localization within the molecule. Hence, IVR may occur rapidly if only a few modes are optically active or highly excited but more slowly once the energy is dissipated to the other vibrational modes of the molecule. Regardless of whether the combination of excitation wavelength and temperature results in direct population or rapid IVR (probably both occur), the population of the excited state is effectively divided into states with rapid IC and
states without IC (only a slower ISC). We can thus model the fluorescence as the combined signal from states with two different lifetimes and two different sensitivities to oxygen quenching (SV factors); the fraction of the population within each type of state depends on temperature and excitation wavelength.

The modelled energy transfer processes are depicted in Figure 4.13. We assume constant fluorescence and oxygen quenching rate constants. At low excitation energies, the SV factor is determined primarily by a changing ISC rate. For these conditions, the fluorescence behavior as mapped on an SV plot is linear. At high energies, however, fluorescence occurs from some states with IC. Because of their short effective lifetimes, emission from these states is less sensitive to oxygen. Thus, the fluorescence signal represents two processes with different SV factors, and the graph is no longer linear. The deviation from linearity increases as these short-lived states receive a larger fraction of the excited population. The model determines the fraction of molecules that goes into each type of state.

Since almost every collision with oxygen leads directly to electronic de-activation [8] (oxygen-quenching involves a charge-transfer complex and results in either triplet or ground-state toluene) while collisions with nitrogen are not likely to change the electronic state, we currently think it a reasonable approximation to regard oxygen as the only important colliding species with the effect of collisional relaxation and total pressure small in comparison. Hence, vibrational relaxation is neglected.

Model formulation

The discussion above gives a qualitative understanding of what we treat as the important photophysical processes. While the form of the model below follows this discussion, the complete mechanism and values of key rate constants – including their temperature, energy level, or state dependencies – remain unknown. Thus, the rate constants in the model are ultimately established through fits to the experimental data.

We consider fluorescence from two types of vibrational states within the electronically excited state, distinguished by their Stern-Volmer factor, to represent states with ISC (1) and with IC (2) occurring. The total fluorescence signal is the sum of
4.6. TOLUENE FLUORESCENCE MODEL

Figure 4.13: Simple photophysical scheme of the important decay processes for toluene LIF. Intersystem crossing (ISC), $S_1 \rightarrow T_1$, and fluorescence are the dominant non-collisional processes for low vibrational excitation. Internal conversion (IC), $S_1 \rightarrow S_0$, becomes important for selected states at higher energies. ISC and IC states may be populated either directly via absorption or via intramolecular vibrational redistribution (IVR) following absorption. The model numerics give the fraction of the population that goes to each kind of state; they do not differentiate between direct population or IVR. For details refer to the text.
the signal emitted from the two types (Eq. 4.11).

\[ S_f(\lambda, T, [O_2]) \propto \sigma(\lambda, T)\phi(\lambda, T, [O_2]) = \sigma(\lambda, T) \left[ \frac{A_1(\lambda, T)}{1 + k_{SV,1}[O_2]} + \frac{A_2(\lambda, T)}{1 + k_{SV,2}[O_2]} \right] \]  

(4.11)

Fit parameters are the temperature dependence of \(k_{SV,i}\) and the (temperature- and excitation wavelength-dependent) relative contribution of each type of state (i.e. \(A_1\) and \(A_2\)). \(A_i\) is the product of the relative population \(a_i\) and the fluorescence quantum yield in nitrogen, \(\phi_i^{N_2}\) of the respective state. In the limit of zero quencher concentration, Equation 4.11 must agree with the data in nitrogen from Section 4.4.2. This is ensured by:

\[ A_1(\lambda, T) + A_2(\lambda, T) = \phi_i^{N_2}(\lambda, T) \]  

(4.12)

Since the oxygen concentration influences the quantum yield only, we will focus on the quantum yield in this section. The absorption cross-section is also temperature-dependent and will be included in the discussion in the next section in order to explain the implications for diagnostics.

Experimental data together with the fits from the model for both excitation wavelengths are shown in Figures 4.14 and 4.15. The model can consistently quantify the fluorescence behavior; data and model agree within 10% for all conditions. For all temperatures the data are normalized to the quantum yield in pure nitrogen known from literature [102]. The best-fit parameters are:

\[ k_{SV,1}[m^3] = 7.69 \times 10^{-25} + 2.57 \times 10^{-22}\exp(-0.010T) \]  

(4.13)

\[ k_{SV,2}[m^3] = 8.8 \times 10^{-26} - 4.0 \times 10^{-28}(T - 500) \text{ for } T > 500K \]  

(4.14)

\[ k_{SV,2}[m^3] = 0 \text{ for } T < 500K \]  

(4.15)

\[ A_2^{266nm} = \frac{1}{0.0241T^2 - 25.12T + 7029} \]  

(4.16)

\[ A_2^{248nm} = \frac{1}{0.0371T^2 - 3.012T + 691.5} \]  

(4.17)

with \(A_1(\lambda, T) = \phi_i^{N_2}(\lambda, T) - A_2(\lambda, T)\) and \(\phi_i^{N_2}\) calculated by Equations 4.7 and 4.8. Absolute values of the fluorescence yield can also be calculated or estimated by calibrating the above equations to the low-pressure measurements of Burton. For 266.8
Figure 4.14: Comparison of the modelled (lines) and experimental (symbols) fluorescence quantum yield of toluene for 266 nm excitation. The total signal-intensity would be the product of quantum yield and absorption cross-section.
Figure 4.15: Comparison of the modelled (lines) and experimental (symbols) fluorescence quantum yield of toluene for 248 nm excitation.
4.6. TOLUENE FLUORESCENCE MODEL

Figure 4.16: The predicted fraction of fluorescence signal that comes from short lifetime states (those that undergo internal conversion) that are relatively insensitive to oxygen quenching.

Of the two types of emitting states, those that decay via IC are less sensitive to oxygen quenching. The fraction of the fluorescence that comes from these states is given by \( \frac{A_2}{A_1 + A_2} \) or \( \frac{A_2}{\phi N_2} \). This prediction is shown for each excitation wavelength in Figure 4.16. At low temperatures, the amount of signal coming from these states is expected to be small. At high temperatures, their contribution can approach 10% of the total signal, thus resulting in an increasing immunity to oxygen quenching at high temperatures. The importance of the IC channel thus increases with increasing temperature. Note, however, that the rate for ISC also logically increases with temperature, interpreted as a relaxing of the spin selection rule, and the integrated fluorescence signal data are not sufficient to determine the fractional populations of each state (that is, determining \( a_1 \) and \( a_2 \) rather than \( A_1 \) and \( A_2 \)).

Additional lifetime measurements of toluene at elevated temperatures are highly desirable to better interpret the underlying processes, to determine decay rates, and to
Figure 4.17: Comparison of experimental data from Reboux et al. [10] (symbols) with model predictions (lines) for the change in LIF signal, $S$, per unit equivalence ratio, $\Phi$, for various total air pressures. The model predicts adequately the experimental results. Note that at room temperature the LIF signal becomes proportional to $\Phi$ above 3 bar, but this approximation breaks down at higher temperatures. Data are normalized at 8 bar.

Not included in the fitting procedure is the data published by Reboux et al. [10]. In Figure 4.17 we compare their data (248 nm excitation) with the predictions from our model via the slope of LIF signal versus the equivalence ratio, $\Phi$ at various total pressures of air. When this slope becomes independent of total pressure, Equation 4.5 is satisfied. Experimental data has, until now, been available only for room temperature. We show it along with predictions for higher temperatures. Results agree within 15%, so we confirm the finding of Reboux et al. that the toluene LIF signal is proportional to $\Phi$ above about 3 bar at room temperature. At higher temperatures, such a proportionality is incorrect for the exhibited pressures. This finding will be further discussed in the next section.

Drawing on toluene fluorescence data from the same engine cycle presented for 3-pentanone, model predictions of signal intensities are shown in Figure 4.18 as a function of crank angle in the range of 1bar/350K to 8bar/600K with representative
Figure 4.18: Model predictions and measurements of toluene LIF signals in a motored engine. The engine cycle is the same as the one displayed for 3-pentanone (Fig. 3.41).

error bars of ±10%. Under reciprocating engine conditions for a constant $\Phi$, an increasing temperature will lower the signal of an oxygen-toluene mixture. Increasing density, however, leads to stronger signals through an increase in the toluene number density. During compression, these effects mitigate the signal variation with crank angle, and the change in signal shown in Figure 4.18 is thus moderate. Our model describes the signal behavior sufficiently well, confirming that influences of total pressure are likely small compared to oxygen quenching. Predicted signal intensities are scaled to engine data at -90°ATDC at 0.82bar and 360K, close to conditions covered by the atmospheric flow-cell experiments.

### 4.6.1 Implications for diagnostics

**FARLIF**

The toluene fluorescence quantum yield (FQY) dependence on the inverse oxygen concentration is displayed for various temperatures in Figures 4.19 and 4.20 for two common excitation wavelengths. The tracer concentration is constant, and thus the
Figure 4.19: Toluene-LIF signal vs. inverse oxygen pressure or relative fuel-air ratio. Total signals are corrected for the temperature dependence of the absorption cross section. Symbols are experimental data, solid lines are extrapolations based on the photophysical model. The premise of the FARLIF technique, that the signal is proportional to fuel-air ratio, is applicable only in the case of moderate temperatures and 266 nm excitation. Note that in this case the slope still depends strongly on temperature.

The ordinate is directly proportional to the fuel-air ratio, Φ. The solid lines are model extrapolations to higher oxygen pressures. For 266 nm excitation the LIF signal is proportional to Φ for temperatures up to 500 K even though the slope varies with temperature. Above 500 K, a deviation from linearity is obvious. Above 650 K, more than 4 bar of oxygen (i.e. 20 bar of air) is required to make signal proportional to fuel-air ratio (e.g. where the deviation is <10%). Thus, for 266 nm the FARLIF concept works only for T < 500 K and only with additional temperature corrections. For 248 nm excitation the FARLIF concept breaks down even at moderate temperatures. At room temperature the signal is proportional to Φ for pressures above 400 mbar of oxygen (or about 2 bar of air, corresponding to the literature [10]). This minimum oxygen pressure required to make the FARLIF concept work increases significantly with increasing temperatures. It is 2 bar oxygen (10 bar air) at 500 K and 5 bar oxygen (25 bar of air) at 625K. In the extreme case of high temperature and low
oxygen concentrations the signal is actually *insensitive* to oxygen; that is to say, the signal intensity is simply proportional to the tracer number density as is the case for tracers like 3-pentanone. For many reciprocating engine-related pressures and temperatures, say 300-700K and 1-10 bar, the signal behavior is between the two cases of $S \propto \Phi$ and $S \propto n_{\text{tracer}}$, but it is not directly proportional to either.

While Figures 4.19 and 4.20 reveal the overall nonlinear relationship between signal and inverse oxygen concentration, approximate linearity can be achieved over small ranges of $[O_2]$ (or $p_{O_2}$). Quantitative interpretation is then enabled through the use of two calibration points (signal measurements at known $\Phi$) and a linear approximation. The slope of each line would still be sensitive to temperature, so isothermal conditions are required.

Results have shown that the original FARLIF technique can lead to erroneous signal interpretation for temperatures and pressures in the compression stroke of IC engines. Given the use of the technique for ICE applications, its discovery at this point is somewhat surprising. A possible reason for this oversight is given with the aid of Figure 4.21. Ultimately, the variation of $\Phi$ lies in changing either the fuel (Fig. 4.21a or case a) or the oxygen concentration (Fig. 4.21b or case b). Both might
correspond to situations of practical interest. Figure 4.21a displays the LIF signal versus $\Phi$ behavior when fuel concentration is changing and oxygen pressure is nearly constant (decreasing only slightly to accommodate the increase in fuel with a fixed total pressure). Figure 4.21b shows the analogous behavior for the case where fuel concentration is fixed and the oxygen partial pressure varies. Case b) could apply in an engine environment with exhaust gas recirculation or in a flow with a diluent other than air. In cases where the FARLIF concept was critically examined at elevated temperatures, investigators have primarily looked at cases more akin to a) [99, 114]. The apparent linearity between $\Phi$ and LIF signal in this case is somewhat misleading because changes in $\Phi$ are dominated by changes in the fuel number density. The proportionality found in Figure 4.21a is the linear relation of tracer number density and LIF signal in the presence of uniform oxygen concentrations. Almost any tracer (even oxygen-insensitive tracers like 3-pentanone) could be applied in this case with the same result. The strength of the FARLIF concept would be its applicability to a case where the oxygen concentration varies significantly, e.g. when significant amounts of exhaust gas are present. The behavior of toluene LIF under these conditions is shown in Figure 4.21b where the LIF signal will only be proportional to $\Phi$ for moderate temperatures with 266 nm excitation (e.g. low vibrational excitation of toluene). On the other hand, in the case of 650 K / 248 nm excitation (e.g. high vibrational excitation) the signal is relatively insensitive to oxygen at moderate pressures. For experiments using 248 nm or those which cover a wide range of conditions, i.e. a more general case, the effects of temperature and oxygen on the total signal cannot be separated; both quantities must be known to enable a quantitative interpretation of the toluene LIF signal.

Despite its apparent complexities, toluene LIF diagnostics are still applicable under controlled conditions and may even offer simplified experimental arrangements when compared to alternative techniques. Well-established techniques like single-line temperature imaging in an otherwise homogeneous flowfield will be extremely sensitive to temperature variations. Anaerobic temperature imaging using two collection bands with a single laser source has already been mentioned. Since oxygen also causes
Figure 4.21: Two possible cases of measurements in an engine environment: a) represents mixing of fuel and air only, b) mixing of fuel, air, and residual gas. In case a) variations of the fuel-air ratio are dominated by variations in the fuel concentration since the oxygen concentration barely changes. In case b) the oxygen concentration changes significantly and the FARLIF technique is valid only for low vibrational excitation (e.g. low temperatures, long excitation wavelength). Total pressure is 8 bar. Signals are normalized to 1.0 at $\Phi = 1$. Predictions are calculated from the toluene model.
a shift in the fluorescence spectrum, a similar technique might be possible for isothermal oxygen imaging. In both cases, the two-color measurement technique should also allow for the simultaneous determination of inhomogeneous toluene concentration, resulting in a two-parameter measurement using a single excitation pulse. Since these techniques have yet to be demonstrated, they are a primary target for future efforts.

### 4.7 Toluene conclusions

With the described work, it is apparent that a single-point calibrated FARLIF technique applies only in controlled isothermal environments: a) at high pressures (> 0.6 bar oxygen) and low temperatures for 248 nm excitation, and b) at moderate pressures (> 0.2 bar oxygen) and moderate temperatures (< 500 K) for 266 nm excitation. If temperature is high or the field is non-isothermal, however, the effect of oxygen concentration may not be accurately quantifiable using a single point calibration. Two measurements under isothermal conditions may allow for a linear calibration of signal versus fuel-air ratio. In the general case of a nonisothermal flowfield of varying oxygen concentration, LIF measurements do not result in unique solutions of the fluorescence equation.

The studies presented above have shown that experimental calibrations must be slightly more complex than single measurements, and even then, they will work only under limited conditions. The studies have also indicated the potential for new diagnostic strategies, e.g., one-laser, two-camera measurements of oxygen or temperature in addition to toluene. Demonstrating the feasibility of such strategies could be accomplished using well-characterized bench-top flows that are experimentally straightforward. As such, they present the most obvious next step in toluene PLIF development.

A few additional measurements would also help to confirm or extend the description of toluene photophysics given here. First, since previous fluorescence quantum yield data have been made relative to benzene as a fluorescence standard, Rayleigh-calibrated FQY measurements are warranted to confirm the values of 0.30 for 266nm
excitation and around 0.10 for 248nm excitation at room temperature. Second, pressure dependence measurements for non-oxygen bath gases would confirm the hypothesis that the effects of common colliders are small in comparison to oxygen, and would permit unambiguous anaerobic PLIF measurements under a range of temperatures and pressures.
Chapter 5

Conclusions and Future Work

Since brief conclusions and recommendations specific to each of the two studied tracers were provided at the end of Chapters 3 and 4, the following section will review the broader picture of tracer PLIF development as it now stands and suggest a number of possible future directions.

The optimal choice of PLIF tracer is largely determined by its desired application and the conditions of that application. Acetone was first recommended by Lozano [21] for nonreactive gas phase mixing applications because of its attractive photophysics and high vapor pressure. 3-pentanone, because of its physical similarity to iso-octane and its photophysical similarity to acetone, has been a primary candidate for fuel PLIF in ICE’s. Toluene, because of its prevalence in a variety of fuels and fuel surrogates, is also a primary candidate for a range of combustion-related mixing applications. Regardless of the specific tracer and application, the key to quantitative interpretation of fluorescence signals is to understand and quantify the behavior of the absorption cross section and fluorescence quantum yield for the desired conditions. The choice of tracer for a given application can be driven largely by physical requirements, but their successful implementation is still limited by the availability of fundamental photophysical data.

The experimental approaches described in Chapter 3 outline systematic methods for exploring and exploiting a wide variety of tracers that exhibit broad UV absorption and UV or visible fluorescence. As has been shown by the comparison of acetone
and 3-pentanone, even tracers within a given class, while qualitatively similar, may be quantitatively different, and this sometimes leads to the discovery of regimes in which PLIF techniques are quite straightforward, e.g., mole fraction imaging of 3-pentanone using 308 nm, even in nonisothermal flowfields. Hence, careful parametric studies of each tracer within a family of compounds are needed, and there are a number of tracer classes like aromatics, ketones, diketones, other carbonyls, and amines that absorb and subsequently fluorescence with broad spectra. Many have been thoroughly studied at or below room temperature during the latter half of the last century. For those studies, higher temperature data was not often a concern for either absorption or fluorescence, but the photophysical mechanisms were of great interest. The studies thus provide starting points for experimental extensions to other conditions and for model development. Techniques described in this work provide a means of obtaining the high-temperature data while avoiding systematic errors due to pyrolysis. Tracer comparisons may be achieved through measurements of absolute fluorescence quantum yields by calibrating the optical system using Rayleigh or other scattering methods. These methods are immediately applicable to many tracer candidates. Development of fundamental understanding for a range of tracers will then provide for optimal tracer/technique selection in a variety of applications for both gas and liquid phases.

With the aid of semi-empirical models, a few sets of data can be used to describe the tracers’ measured behavior throughout the multidimensional parameter space of excitation wavelength, temperature, pressure, and concentration. The models represent a middle ground between rigorous first-principles calculations and a simple fitting of experimental data, attempting to provide a broader framework by which to understand the changes in fluorescence caused by changes in the environmental conditions while accurately accounting for the observed dependencies. Despite the promise of predictive capability, however, the models have been shown to require adjustments and new parameters when new sets of data are introduced that are outside of the previously covered range. The models are thus best used to interpret and interpolate between data sets that span the parameter space of interest. The broadest possible
range of conditions should thus be covered via experimental work, including studying the effects of various bath gases at simultaneous high pressure and temperature. While this presents a significant increase in experimental cost compared to the high temperature or high pressure regimes covered by experiments presented in this work, it is the only way to ensure accurate predictions under the broadest possible array of conditions.

Acetone was chosen by Lozano for non-reacting flows in part because of its high room-temperature vapor pressure. "Heavier" tracers, like 3-pentanone and toluene, are physically more similar to iso-octane. A great many fuels, including diesel and jet fuels, contain major constituents that are even heavier, with boiling points near or above 200 °C. Higher aliphatic ketones like heptanone and nonanone are obvious candidates for tracking the heavy fuels, and so are multi-ring aromatics like naphthalene. Currently, there is virtually no detailed photophysical knowledge on the behavior of any of these candidates (sometimes even at room temperature). Although the experimental challenges of seeding and controlling the vapor phase concentration of such candidates must be overcome, any photophysical data gathered from such tracers will be unique.

While the study of single tracers provides a large area for exploration, the use of combinations of tracers expands the field of investigation even further. The potential use of oxygen-sensitive and oxygen-insensitive tracer combinations for oxygen imaging has been proposed [87]. Exciplex molecules have also been utilized for vapor and liquid phase differentiation [97]. For the broad application of such concepts, one not only needs the basic photophysical understanding of each tracer but also an understanding of the energy transfer processes between tracers since electronic resonances are likely to exist.

As previously mentioned, the optimal choice of tracer or tracers depends to a high degree on the application. While large signals are generally desirable for any application, Lozano narrowed his search according to needs for non-reacting, economical, non-toxic tracers with short lifetimes, high vapor pressures, a linear concentration dependence, and accessible absorption and emission bands. His original survey explored
atoms, diatomics, and polyatomics (both organic and a few inorganic candidates) be-
fore settling upon acetone and biacetyl as optimal tracers for making concentration
measurements in turbulent non-reacting gaseous flows. Thurber then developed the
photophysics of acetone in more detail, enabling multi-parameter visualizations with
two-laser, two-camera experiments. With this work, one can foresee new approaches
to tracer development, starting with a new way of looking at the list of candidates
surveyed by Lozano. For example, investigating tracers that are particularly suscep-
tible to quenching by a single type of molecule may provide in-roads for visualizing
molecules that are otherwise inaccessible. Oxygen quenching by aromatics, studied
for the case of toluene in this work, is only one example. If quenching proclivities for
fuels, water, or carbon dioxide could be isolated with another tracer, it would be a
highly desirable property.

At higher temperatures, this work has shown that oxygen quenching of aromat-
ics can become negligible due to the onset of rapid intramolecular decay processes.
Revisiting the use of candidate aromatic compounds (surveyed by Lozano) for high-
temperature applications may lead to the development of aromatic tracers that di-
rectly track fuel concentrations under relevant pre-combustion conditions. Because
the absorption and emission tend to steadily red-shift with the number of rings in a
compound, one could choose a candidate tracer based on available laser and detec-
tion sources, e.g., selecting an aromatic that fluoresces strongly in the visible where
unintensified camera efficiencies are highest.

The models presented for 3-pentanone and toluene are of a decidedly different
nature. The ketone model would at first appear to be more elegant, combining tem-
perature, pressure, and excitation wavelength into one coherent explanation. This
worked, in part, because measured temperature dependencies could be described with
a reasonable fit to the sparse available lifetime data for various excitation energies.
For toluene, lifetime data is more comprehensive and does not increase with energy
enough to explain the steep fall-off in signal due to rising temperature. Furthermore,
the strong bi-exponential fluorescence behavior had been thoroughly documented.
The elegance of the ketone model was thus sacrificed in order to better match the
observed behavior in toluene. A sufficiently fundamental and correct physical model,
however, may not require more than numerical adjustments to match both molecules. This would likely mean that current algebraic simplicity is sacrificed, but a more sophisticated model may provide a more useful tool for understanding and quantifying the photophysics of other classes of tracers.
Appendix A

Acetone Fluorescence Quantum Yield Results

The fluorescence quantum yield for acetone was measured simultaneously with that of 3-pentanone using the methods outlined in Chapter 3. The results of those measurements and their implications for further development of the acetone fluorescence quantum yield model that was first developed by Thurber [39] are given here.

Table A.1 shows our measured fluorescence quantum yield for acetone excited with 308 nm and its comparison with data from the literature excited with 313 nm light. By our methods, $\phi$ is significantly lower than suggested by the work of Heicklen [50]. Agreement is much better with the data from Halpern [51], although the difference is still significant (almost 40%). Using the pressure conditions of Halpern did not significantly change our measured fluorescence quantum yield for acetone, though we must note that we were less confident in the ketone’s number density when we operated close to acetone’s vapor pressure (this was evidenced by a pressure reading that decreased over several minutes after filling the ketone and then increased over time after filling the diluent). It is conceivable that the change in excitation wavelength would result in an increase in the fluorescence yield. Copeland notes that a significant dissociative channel may increase rapidly for excitations below 312 nm [115]. Excitation wavelengths on either side of this value may thus provide different fluorescence quantum yields. Unfortunately, it was not possible to exactly match the conditions
of either Heicklen or Halpern due to lack of a 313 nm source.

<table>
<thead>
<tr>
<th>Author</th>
<th>Quantum yield ($\times 10^3$)</th>
<th>Exciting wavelength</th>
<th>Pressure</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heicklen [50]</td>
<td>2.07</td>
<td>313 nm</td>
<td>103-271 mbar ketone, &quot;oxygen present&quot;</td>
<td>40 $^\circ$C</td>
</tr>
<tr>
<td>Halpern [51]</td>
<td>1.2</td>
<td>313 nm</td>
<td>267 mbar ketone, 733 mbar air</td>
<td>24 $^\circ$C</td>
</tr>
<tr>
<td>This work</td>
<td>0.71 (no N2) to 0.84 (1 bar N2)</td>
<td>308 nm</td>
<td>4-40 mbar ketone, 0-1013 mbar N2</td>
<td>23 $^\circ$C</td>
</tr>
</tbody>
</table>

The wavelength dependence of the fluorescence quantum yield for acetone (Fig. A.1) at the lowest pressure condition is compared with the relative data of Hansen and Lee [3] (23 $^\circ$C, 11 mbar acetone, 5 mbar oxygen, 67 mbar cyclohexane). While the absolute values differ due to the calibration standard (Heicklen), the relative trend agrees well.

Figure A.1: Relative acetone $\phi(\lambda, 296K, 20$ mbar) and comparison with Hansen and Lee [3]

Figure A.2 shows the results of our measurements for acetone for each excitation
Figure A.2: Acetone fluorescence quantum yield as a function of pressure and excitation wavelength.

wavelength at the three measured pressures. The pressure and wavelength dependencies seem to follow the conceptual model developed by Thurber where fluorescence yields increase with pressure and decrease with excitation frequency.

**Comparison of Acetone Data with Fluorescence Yield Model**

The relative pressure and temperature behavior of acetone has already been well-reproduced and demonstrated by the kinetics model of Thurber [39]. The model’s excitation wavelength predictions can now also be compared with experimental data. As seen in Figure A.3, model predictions are also in close agreement with our data on a relative scale, but Thurber’s absolute predictions are almost three times higher than our measurements.

The absolute predictions of Thurber’s model pivot on the value of the fluorescence rate coefficient, $k_f$, since the fluorescence yield from an excited state or energy level


Figure A.3: Relative comparison of acetone fluorescence quantum yield with model predictions for various excitation wavelengths.

is given by

\[
\phi = \frac{k_f}{\sum_i k_i} = k_f \tau
\]  

(A.1)

where the denominator represents the sum of the rate coefficients for all possible processes from the excited state, a number measurable by the natural lifetime, \( \tau \). Thurber originally took \( k_f \) to be \( 8.0 \times 10^5 \text{sec}^{-1} \) based on the recommendation of Hansen (see ref. [3], Table 1). Hansen determined the value of \( k_f \) from relative fluorescence yield and natural lifetime measurements, but was calibrated to Heicklen’s measurement [50]. Thurber’s model is thus ultimately calibrated to Heicklen’s measurement of the fluorescence quantum yield through the assignment of \( k_f \). Since we find Heicklen’s measurements to be much higher than ours, the value of \( k_f \) and thus the model predictions are also too high. Reassigning the value of \( k_f \) based on our fluorescence quantum yield measurements will recalibrate the model without changing the relative behavior with pressure or temperature. Whereas Thurber originally used a fluorescence rate of \( 8 \times 10^5 \text{sec}^{-1} \), we recommend this value be changed to
$3 \times 10^5 \text{sec}^{-1}$, based on the best fit of his model to our data at one bar for the three different wavelengths. Such a change in the spontaneous emission rate also brings this experimental value into better agreement with predictions from the Strickler-Berg relation, where $k_f \approx 10^5 \text{sec}^{-1}$ [3].

Using the new value of $k_f$ and keeping all other parameters the same as in reference [5] (Table 1) and using the model formulation of Equation 2 in that reference, we can reexamine the modelled fluorescence quantum yield as a function of pressure and excitation wavelength. Figure A.4 shows the modelled pressure dependence of acetone’s fluorescence quantum yield using a constant $k_f = 3 \times 10^5 \text{sec}^{-1}$ in comparison with our data and the relative data of Thurber. Thurber’s data is normalized by a best-fit constant, constrained to be within experimental uncertainty (10%) of our data at one bar. Although there is little overlap, the trends in the relative data of Thurber at high pressures and our absolute data at lower pressures match well, as does the model’s prediction of both. The combination of the low and high pressure data at 308 nm may indicate slightly more pressure dependence than the model predicts. Nonetheless, since experimental uncertainties are approximately the same as the differences between model and data, no further changes to the model are currently warranted.

Although the fluorescence quantum yield for acetone can change by almost an order of magnitude depending on the conditions, it approaches a limiting, constant value at high pressure, independent of excitation wavelength (evident in Fig. A.4). This high-pressure limit provides a convenient figure by which to gage acetone’s behavior (for comparison to other molecules). The new high pressure limit of $\phi$ for acetone at 297 K in nitrogen is $1.0 \times 10^{-3}$, a significant reduction from Thurber’s value of $2.7 \times 10^{-3}$.
Figure A.4: Acetone fluorescence quantum yield as a function of pressure and excitation wavelength.
Appendix B

Vibrational Frequencies of 3-pentanone

Experimental data for the vibrational frequencies of 3-pentanone are not yet available, however, quantum mechanical calculations for a wide variety of molecules using a variety of basis sets are available from NIST’s Computational Chemistry Comparison and Benchmark Database [1]. Calculations in this database matched acetone experimental data well, indicating that the methods used provide reasonably good estimates. Because of its relatively good match between predictions and experimental data of acetone, the results from the Quadratic Configuration Interaction (QCISD) calculation method using the 6-31G* basis and the recommended scaling factor of 0.954 were used to estimate the vibrational frequencies of 3-pentanone. For completeness, these values are listed in Table B.1. When other calculation methods and other basis sets were tried, resulting calculations of average thermal energies changed slightly, but it did not significantly affect the overall performance of the model. In a similar study, the lowest four vibrational frequencies given below were also treated as fully excited rotations rather than vibrations (representing the extreme case of the methyl and ethyl hindered rotor modes). This resulted in internal energy decreases of 10-20% for the 300-900K temperature range. The intersystem crossing rate, however, could be re-optimized with only minor adjustments, and the overall performance of the model was again not significantly affected.
Table B.1: Vibrational frequencies of 3-pentanone used for calculating the thermal energy of the ground state molecule as a function of temperature. Data taken from [1]

<table>
<thead>
<tr>
<th>Mode Number</th>
<th>Scaled Frequency $cm^{-1}$</th>
<th>Mode Number</th>
<th>Scaled Frequency $cm^{-1}$</th>
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Bibliography


