Development of a laser induced phosphorescence technique for the investigation of evaporating two-phase flows

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Abstract

The prospects of utilising the laser induced phosphorescence emission of common ketone tracers in the study of multi-phase (gas-liquid) flows are investigated within the context of this thesis.

The quantification of evaporated fuel concentrations in the vicinity of liquid droplets by means of the laser induced fluorescence imaging technique, and the measurement of fuel concentrations in sprays containing sub-pixel sized droplets by means of the laser induced exciplex imaging technique suffer from well-known limitations; the former is plagued by low vapour phase signal intensities and halation, and the latter by liquid-vapour crosstalk and quenching. Therefore, a literature research was initially carried out, focusing on two main topics: the underlying photophysics of the processes involved in the excitation and deexcitation mechanism of the tracers under investigation, and the relevant optical techniques available for carrying out vaporized fuel concentration measurements in two-phase flow environments.

Following a description of the experimental apparatus, a series of calibration experiments is presented. The liquid phase phosphorescence properties of acetone and 3-pentanone were investigated in the bulk and in liquid streams, and the phosphorescence emission characteristics of both tracers were quantified for different bath gas compositions. The phosphorescence signal of gaseous acetone was calibrated for the excitation energy and concentration dependencies. Based on the calibration data, a new technique was developed for the purpose of investigating the vapour phase concentration in the vicinity of liquid droplets. The proposed technique utilizes the phosphorescence rather than the fluorescence emission of vapour and liquid acetone, and is compared with the well-established laser induced fluorescence technique (LIF), in both evaporative and non-evaporative monodisperse droplet streams. The obtained results suggest that laser induced phosphorescence (LIP) imaging clearly improves upon laser induced fluorescence imaging, by successfully addressing both the high signal intensity disparity between the two phases and the ensuing halation that plague measurements carried out by deployment of LIF.
The fluorescence and phosphorescence emission of acetone and 3-pentanone, the latter considered in order to demonstrate the feasibility of LIP imaging by deployment of other common ketone tracers apart from acetone, were also examined in sprays by means of a high-pressure gasoline direct injection system. Experiments examining the emission from both electronic states and their potential correlation are presented for non-evaporative sprays; in particular, liquid phase corrections are carried out in LIF images by deployment of their corresponding LIP images and the obtained correlation functions, and the ensuing errors are quantified. Finally, mean and median filters are employed in limiting these errors and assessing the feasibility of the proposed technique. The obtained results are rendered encouraging, with suggestions for improvement focusing on reducing the noise observed in the LIP images by both signal augmentation and enhancement in the efficiency of the collection optics.
Declaration of Originality

This work, unless where a reference is provided, is the result of the study carried out by Alexandros Charogiannis

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Alexandros Charogiannis

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I would like to dedicate this thesis to my parents Georgia and Vaggelis for all their love and support
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“A thinker sees his own actions as experiments and questions - as attempts to find out something. Success and failure are for him answers above all”.

Friedrich Nietzsche, The Gay Science
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## Nomenclature

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFR</td>
<td>Air-to-Fuel Ratio</td>
</tr>
<tr>
<td>ASOI</td>
<td>After the Start of Injection</td>
</tr>
<tr>
<td>BSFC</td>
<td>Brake Specific Fuel Consumption</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CI</td>
<td>Compression-Ignition</td>
</tr>
<tr>
<td>DEMA</td>
<td>Diethyl-methyl-amine</td>
</tr>
<tr>
<td>DMA</td>
<td>N,N-dimethylaniline</td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust Gas Recirculation</td>
</tr>
<tr>
<td>ESF</td>
<td>Edge Spread Function</td>
</tr>
<tr>
<td>FB</td>
<td>Fluorobenzene</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half-Maximum</td>
</tr>
<tr>
<td>GDI</td>
<td>Gasoline Direct Injection</td>
</tr>
<tr>
<td>IC</td>
<td>Internal Conversion</td>
</tr>
<tr>
<td>IRO</td>
<td>Intensified Relay Optics</td>
</tr>
<tr>
<td>IDU</td>
<td>Injector Drive Unit</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem Crossing</td>
</tr>
<tr>
<td>LAR</td>
<td>Least Absolute Residuals</td>
</tr>
<tr>
<td>LIEF</td>
<td>Laser Induced Exciplex Fluorescence</td>
</tr>
<tr>
<td>LS</td>
<td>Least Squares</td>
</tr>
<tr>
<td>LSD</td>
<td>Laser Sheet Dropsizing</td>
</tr>
<tr>
<td>LSF</td>
<td>Line Spread Function</td>
</tr>
<tr>
<td>MCP</td>
<td>Micro-Channel Plate</td>
</tr>
</tbody>
</table>
MTF  Modulation Transfer Function
NVH  Noise Vibration and Harshness
OD   Optical Density
PFI  Port Fuel Injection
PLIF Planar Laser Induced Fluorescence
PLIFP Planar Laser Induced Fluorescence and Phosphorescence
PLIP Planar Laser Induced Phosphorescence Imaging
PM   Particulate Matter
PSF  Point Spread Function
PSU  Power Supply Unit
ROI  Region of Interest
SI   Spark-Ignition
SLIPI Structured Laser Illumination Planar Imaging
SMD  Sauter Mean Diameter
SNR  Signal-to-Noise Ratio
SRF  Step Response Function
TDC  Top Dead Centre
TEA  Triethylamine
TMPD N,N,N',N'-tetramethyl-p-phenylenediamine
TTA  Triplet-Triplet Annihilation
UHCs Unburned Hydrocarbons
VR   Vibrational Relaxation

**Tracer Photophysics**

Greek symbols (upper case)

\[ \Psi_i \] Molecular wavefunction of the initial state
\[ \Psi_f \] Molecular wavefunction of the final state

Greek symbols (lower case)

\[ \lambda \] Wavelength [nm]
Absorption cross-section [cm\(^2\)]

Transition dipole moment [Cm]

Transition dipole moment operator

Effective fluorescence lifetime [ns]

Natural fluorescence lifetime [ns]

Phosphorescence lifetime [ns]

Electronic wavefunction of the initial state

Electronic wavefunction of the final state

Fluorescence quantum yield

Fluorescence quantum yield in the absence of quencher

Latin symbols (upper case)

\(\Delta E\) Energy difference between states \(E_1\) and \(E_2\) [J]

\(\Delta E_{ST}\) Energy gap between the between the \(S_1\) and \(T_1\) states of the sensitizer

\(E_{T_1}\) Total excitation energy of two triplet molecules [kcal mol\(^{-1}\)]

\(E_{S_1}\) Total excitation energy of two singlet molecules [kcal mol\(^{-1}\)]

\(I_{ph}(t)\) Phosphorescence signal collected by a detector at time \(t\) following the initial population of \(T_1\)

\(I_{ph\; total}\) Total phosphorescence signal collected between \(t = 0\) and \(\infty\)

\(N_i\) Nuclear wavefunction of the initial state

\(N_f\) Nuclear wavefunction of the final state

\(S_i\) Spin wavefunction of the initial state

\(N\) Ground state acceptor molecule

\(N^*\) Excited state acceptor molecule

\([Q]\) Quencher molar concentration [molecules cm\(^{-3}\)]

\(R\) Ground state donor molecule

\(R^*\) Excited state donor molecule

\(R \rightarrow N\) Exciplex system

\(S, S_0\) Ground singlet electronic state

\(S^*, S_1\) First excited singlet electronic state

\([S]\) Ground singlet state molar concentration [moles cm\(^{-3}\)]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>[S*]</td>
<td>First excited singlet state molar concentration [moles cm(^{-3})]</td>
</tr>
<tr>
<td>[S*] (_0)</td>
<td>First excited singlet state molar concentration [moles cm(^{-3})] at (t = 0)</td>
</tr>
<tr>
<td>[S*] (_t)</td>
<td>First excited singlet state molar concentration [moles cm(^{-3})] at (t)</td>
</tr>
<tr>
<td>(S_f)</td>
<td>Spin wavefunction of the final state</td>
</tr>
<tr>
<td>(S_n)</td>
<td>(n^{th}) excited singlet state</td>
</tr>
<tr>
<td>(T_0)</td>
<td>Ground triplet electronic state</td>
</tr>
<tr>
<td>(T^{*, T_1})</td>
<td>First excited triplet electronic state</td>
</tr>
<tr>
<td>[T*]</td>
<td>First excited triplet state molar concentration [moles cm(^{-3})]</td>
</tr>
<tr>
<td>[T*] (_0)</td>
<td>First excited triplet state molar concentration [moles cm(^{-3})] at (t = 0)</td>
</tr>
<tr>
<td>[T*] (_t)</td>
<td>First excited triplet state molar concentration [moles cm(^{-3})] at (t)</td>
</tr>
</tbody>
</table>

Latin symbols (lower case)

- \(h\): Planck constant [J s]
- \(\hbar_{\text{vis}}\): Absorbed photon energy [J]
- \(\hbar_{\text{ fluorescence}}\): Fluorescence photon emission energy [J]
- \(\hbar_{\text{p} R}\): Monomer photon emission energy [J]
- \(\hbar_{\text{p} R-N}\): Exciplex photon emission energy [J]
- \(h\): Reduced Planck constant [J s]
- \(k_{\text{abs}}\): Absorption rate constant (s\(^{-1}\))
- \(k_f\): Fluorescence rate constant (s\(^{-1}\))
- \(k_{\text{IC}}\): Internal conversion rate constant (s\(^{-1}\))
- \(k_{\text{ISC}}\): Intersystem crossing rate constant (s\(^{-1}\))
- \(k_{\text{NR}}\): Nonradiative rate constant (s\(^{-1}\))
- \(k_{\text{ph}}\): Phosphorescence rate constant (s\(^{-1}\))
- \(k_Q\): Quenching rate constant (cm\(^3\) molecules\(^{-1}\) s\(^{-1}\))
- \(k_{\text{tot}}\): Total deexcitation rate (s\(^{-1}\))
- \(k_{\text{T-T}}\): Triplet-triplet annihilation rate constant (cm\(^3\) molecules\(^{-1}\) s\(^{-1}\))
- \(m_s\): Spin magnetic quantum number
- \(s\): Spin quantum number
- \(v\): Frequency [s\(^{-1}\)]
### Experimental parameters

#### Greek symbols (lower case)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{opt} )</td>
<td>Efficiency of the collection optics</td>
</tr>
<tr>
<td>( \rho_a )</td>
<td>Density of liquid acetone ([ \text{kg m}^{-3} ])</td>
</tr>
<tr>
<td>( \rho_{tracer} )</td>
<td>Tracer number density ([ \text{mol m}^{-3} ])</td>
</tr>
<tr>
<td>( \tau_1 )</td>
<td>Short phosphorescence emission decay component ([ \text{ns} ])</td>
</tr>
<tr>
<td>( \tau_2 )</td>
<td>Long phosphorescence emission decay component ([ \text{ns} ])</td>
</tr>
</tbody>
</table>

#### Latin symbols (upper case)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>Laser sheet cross-sectional area ([ \text{m}^2 ])</td>
</tr>
<tr>
<td>( D_d )</td>
<td>Droplet diameter ([ \text{µm} ])</td>
</tr>
<tr>
<td>( E )</td>
<td>Laser pulse energy ([ \text{mJ} ])</td>
</tr>
<tr>
<td>( E_{pulse} )</td>
<td>Reference pulse energy ([ \text{mJ pulse}^{-1} ])</td>
</tr>
<tr>
<td>( E_0 )</td>
<td>Acetone molar mass ([ \text{kg mol}^{-1} ])</td>
</tr>
<tr>
<td>( M )</td>
<td>Acetone vapour pressure at ( T_{amb} ), ( P_{amb} ) ([ \text{bar} ])</td>
</tr>
<tr>
<td>( P_a )</td>
<td>Ambient pressure ([ \text{bar} ])</td>
</tr>
<tr>
<td>( P_{inj} )</td>
<td>Injection pressure ([ \text{bar} ])</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal gas constant ([8.3144621 \text{ J K}^{-1} \text{ mol}^{-1}])</td>
</tr>
<tr>
<td>( S )</td>
<td>Fluorescence/phosphorescence signal ([ \text{counts} ])</td>
</tr>
<tr>
<td>( S_{LIF} )</td>
<td>Total collected LIF signal ([ \text{counts} ])</td>
</tr>
<tr>
<td>( S_{Flvapour} )</td>
<td>Vapour fluorescence signal</td>
</tr>
<tr>
<td>( S_{0Flvapour} )</td>
<td>Vapour fluorescence signal corresponding to the saturated tracer concentration</td>
</tr>
<tr>
<td>( S_{FlLiquid} )</td>
<td>Liquid phosphorescence signal corresponding to the saturated tracer concentration</td>
</tr>
<tr>
<td>( S_{PhLiquid} )</td>
<td>Liquid phosphorescence signal corresponding to the saturated tracer concentration</td>
</tr>
<tr>
<td>( S_0 )</td>
<td>Reference fluorescence/phosphorescence signal ([ \text{counts} ])</td>
</tr>
<tr>
<td>( S_{0PhVapour} )</td>
<td>Vapour phosphorescence signal corresponding to the saturated tracer concentration</td>
</tr>
<tr>
<td>( S_d )</td>
<td>Inter-droplet separation ([ \text{µm} ])</td>
</tr>
</tbody>
</table>
$T_{amb}$  Ambient temperature [K]  
$V_{pix}$  Imaged volume along the line of laser sheet propagation [m$^3$]  
$X_d$  distance from the droplet centre  

Latin symbols (lower case)  

$c$  Normalized inter-droplet separation parameter  
$n_a$  Acetone number density [m$^3$]  
$n_{a0}$  Acetone number density corresponding to the saturated acetone concentration at $T_{amb}, P_{amb}$ [m$^3$]  
$n_{tracer}$  Tracer number density [m$^3$]  
$r_d$  Droplet radius [µm]  
$x_a$  Acetone vapour mole fractions
1 Motivation

Different engine concepts are generally classified according to the method employed in igniting the air/fuel mixture, effectively yielding two major engine types; compression-ignition (CI) engines which rely on autoignition of the in-cylinder charge, and spark-ignition (SI) engines which utilize spark plugs in order to initiate combustion. CI engines exhibit lower brake specific fuel consumption (BSFC) and hence better fuel economy per unit output power owing to the use of higher compression ratios and unthrottled load management, while SI engines offer a significantly higher engine speed range, and thus increased power output, as well as lower NOx and particulate emissions in combination with reduced NVH (noise vibration and harshness) levels. In response to pressing requirements for increased fuel efficiency and compliance with ever-more stringent emission regulations over the past two decades (see for example the European Emission Standards), the automotive industry developed and commercialized the gasoline direct injection (GDI) engine, essentially an SI unit incorporating certain advantageous attributes of the CI engine.

The commercial prevalence of GDI engines over their predecessor, the port fuel injection (PFI) engine, is mainly attributed to the different methods employed in introducing the fuel into the combustion chamber. Whereas GDI engines operate with direct, in-cylinder fuel injection, mixture preparation in PFI engines involves the injection of fuel in the intake port, often resulting to partial vaporization and the creation of fuel puddles (for example during cold-starting). When the intake valves open, the vaporized fuel enters the cylinder along with the incoming air, with fuel stratification entirely managed by the combustion chamber design and valve timing system. Thus, GDI engines achieve more accurate control of the fuel quantity entering the combustion chamber. Additional fuel economy gains are achieved through more reliable stratification allowing for overall leaner mixtures, the reduction of pumping losses owing to reduced throttling, and the use of higher compression ratios realizable as a result of charge cooling during fuel injection. Finally, superior transient response, lower cycle-to-cycle variations and lower unburned hydrocarbon (UHC) emissions are amongst the comparative advantages afforded by GDI technology [1].

Despite addressing many of the shortcomings of PFI, optimization of GDI technology is on-going. Whereas PFI engines essentially employ pre-vaporizing chambers (intake ports), GDI engines must often achieve spray atomization and droplet evaporation within the short
time interval between the start of injection and ignition. High load operation is realized by homogeneous stoichiometric (or near-stoichiometric) charge combustion, with the fuel injection advanced early during compression or late during intake and the exhaust-gas aftertreatment (three-way catalyst) system operating within its high conversion efficiency regime. At lower loads, for example during urban driving, the lower power requirements allow for greater fuel savings and CO₂ reductions to be sought for by switching to stratified mode. Stratified operation at low and medium loads is realized by the generation, through late injection, of a locally stoichiometric mixture in an extremely lean background, often comprised of large amounts of recirculated exhaust gases (EGR). In that case, the suppression of soot formation, UBHCs and particulate matter (PM), along with the prevention of misfiring present major challenges. The necessary faster atomization and vaporization rates are attained through the utilization of high pressure injection systems, often resulting in fuel film deposits on the piston head or cylinder liner, contributing further UBHC emissions and inducing faster wear of the particular mechanical components. The two aforementioned operation regimes are schematically presented in Fig 1.1.

As a consequence of the challenges encountered by researchers in further improving engine performance while enhancing fuel savings and limiting emissions, the necessity for quantitative information regarding fuel vaporization, mixture formation and in-cylinder fuel
concentration and charge temperature distributions became fully apparent and boosted the application of optical techniques in the field of IC engine research. In particular, the previously discussed shift of IC engine technology towards GDI, which entails the presence of two-phase flows in the cylinder over a wide range of operating conditions, further emphasizes the need for optical methods capable of yielding relevant quantitative information; for example regarding the concentration of evaporated fuel in the presence of both phases.

Laser diagnostics, such as the planar laser induced fluorescence (PLIF) technique, allow for non-invasive real-time imaging and interpretation of the two-dimensional distributions of seeded or naturally occurring tracer components, in both the liquid and vapour phases. Intimate knowledge of their photophysical properties along with carefully designed calibration experiment has allowed researchers to exploit any light emission dependencies on in-cylinder quantities of interest, for example temperature or concentration, yielding relevant quantitative data. Despite providing extremely valuable information, the applicability of optical methods in two-phase flows will always be limited by the photophysics of the employed tracers, the physics of light transmission across a field of varying refractive index, and the capabilities of experimental apparatuses. For example, PLIF is often employed in evaporating droplet stream experiments in order to quantify the vapour field in the vicinity of liquid droplets; such idealized two-phase flow arrangements are commonly employed as they allow for fuel evaporation to be studied in isolation from other physical processes, such as spray breakup and atomization [2]. As the fluorescence emission in the linear regime is proportional to the number of excited molecules, the large density disparity between the liquid and vapour phases introduces a similarly large fluorescence intensity disparity between the two phases. Commonly utilized detectors, such as intensified CCD (charge-coupled device) cameras, offer a limited dynamic range, and any experimental parameters are therefore typically adjusted so that the intense liquid phase signal does not quite saturate the detector. This, in turn, results to a vapour phase signal which is close to or below the camera noise level.

A typical example of how tracer photophysics impact on the applicability of optical diagnostics can be identified in the case of laser induced exciplex fluorescence (LIEF) imaging, a. This two-tracer formulation of PLIF imaging offers the unique ability of discriminating between the vapour and liquid phase signals in a spectral manner owing to the formation of a short-lived excited complex (exciplex) molecule in the liquid phase which
displays red-shifted fluorescence emission relative to the individual molecular emission spectra [3]. The particular technique remains the only source of evaporated fuel concentration data from within spray structures; however, the quantitative interpretation of vapour phase signal is particularly challenging, owing to spectral liquid-vapour cross-talk effects, strong oxygen quenching of both the exciplex and monomer emission, and strong signal degradation with increasing temperature.

The challenges associated with measurements such as the ones discussed earlier will become fully apparent in the course of this thesis, as will the need to further explore and develop alternative optical methods. The significance of expanding the range of available optical diagnostics for two-phase flow investigations, and in particular the quantification of evaporated fuel concentrations in two-phase environments, along with addressing the limitations of any available diagnostics in fulfilling the particular objective, stand for the motivation of the present study. The upcoming section presents the perfect opportunity to introduce laser induced fluorescence imaging, along with the practice on which the present research project is based, namely planar laser induced phosphorescence imaging (PLIP). Within this introductory chapter, the research objectives will be firmly established.
2 Introduction

Within the confines of this introductory section of the report, an overview of the current interpretation of PLIF imaging will presented, the basis and historical background of the proposed phosphorescence imaging technique will be introduced, and the project objectives will be clearly outlined. The association between the two diagnostics is crucial, as the latter will be introduced as an alternative to the former; in other words, the deployment of PLIP concerns experimental investigations for which the application of PLIF is rendered problematic.

2.1 Current interpretation of PLIF imaging by molecular tracers

The PLIF technique has been employed over a wide range of scientific investigations, as it allows for spatially-resolved non-intrusive measurements of flow properties. Depending on the application, the excited species range from diatomic to polyatomic molecules [4] emerging as reaction products or seeded to the flow, on account of their favourable fluorescent properties [5]. A typical LIF setup is comprised of an excitation source used to illuminated the probe volume, and a detection system (Fig 2.1). Upon excitation by a laser source, tracer molecules gain energy which is sometimes dissipated by photon emission. These photons are collected by means of a detector, typically a CCD camera, with the resulting signal quantified in accordance with its dependencies on any relevant flow parameters. The quantification of these dependences necessitates an extensive calibration effort along with an in-depth understanding of the background excitation and deexcitation theory of he employed molecular tracer.
The total collected LIF signal $S_{LIF}$ in the weak (linear with the excitation energy) regime, can be described by the following relationship:

$$S_{LIF} = \eta_{opt} \left( \frac{E_{pulse}\lambda}{A h \nu} \right) V_{pix} n_{tracer} \sigma_{abs} \phi_f$$ \hspace{1cm} \text{Eq 2-1}$$

$\eta_{opt}$ stands for the efficiency of the collection optics and incorporates factors such as the solid angle fraction collected by the detector lens and the spectral responsivity of the detection system. The bracketed term represents the number of excitation photons per laser sheet cross-sectional area, here given as the ratio of excitation energy per laser sheet cross-sectional area $E_{pulse}/A$ (J/cm$^2$), also called the laser fluence, to the energy of the exciting photons $h\nu/\lambda$ (J) of wavelength $\lambda$. The product of the size of the imaged volume along the line of laser sheet propagation $V_{pix}$ (cm$^3$) times the tracer number density $n_{tracer}$ (cm$^{-3}$) gives the number of tracer molecules available for excitation. The last two terms, the absorption cross-section $\sigma_{abs}$ (cm$^2$) and the fluorescence quantum yield $\phi_f$ account for the photophysical dependencies of the fluorescence signal and represent the probability of absorption and the efficiency of fluorescence emission respectively. The fluorescence signal under the particular, commonly employed formulation of the fluorescence equation (see for example [6] and [7]), is expressed in collected fluorescence photons; alternative though equivalent formulations can also be found (for example [8, 9]).
Whereas a wide variety of naturally occurring molecules have been employed in combustion-relevant studies, more complex tracer components, typically hydrocarbons seeded to the inlet air or fuel have dominated the field of modern planar thermometry and mixture formation investigations (an extensive account of which can be found in [10]). For example, the fluorescence properties of aromatic tracers such as toluene [11] and naphthalene [12] have been calibrated and employed in engine-relevant planar air-to-fuel ratio (AFR) as well as thermometry studies [13, 14]. The particular tracer class displays very strong absorption in the UV and very high signal sensitivity to both temperature and oxygen concentration [15]. Planar thermometry is realized on account of the fluorescence spectrum redshift with increasing temperature, allowing for two-colour detection. Ketones, such as acetone and 3-pentanone, are also very popular tracers for fuel vaporization [16] and thermometry [7, 17] studies, the latter conducted by deployment of the two-line excitation technique. Owing to the observed redshift of the absorption spectrum with increasing temperature, two excitation sources are employed in order to obtain an image ratio dependant only upon the quantity of interest. Amongst the shared advantaged of the particular tracer class, the low toxicity and broadband absorption in the UV need essentially be noted. Acetone, in particular, has been widely employed due to its high volatility, which allows for high seeding concentrations already at ambient temperatures. 3-pentanone displays very close photophysical properties to acetone but is less volatile, making it the preferred tracer for isoctane, a common substitute in gasoline-like fuel investigations [18].

As has already been noted, PLIF can be used to visualize both vapour and liquid phases. For example, the laser sheet dropsizing technique (LSD) utilizes the LIF and Mie signals, the latter scattered off dye-doped fuel droplets, in order to generate quantitative SMD measurements [19]. A wide range of strongly fluorescing organic dyes, more commonly known as laser dyes, have been employed in liquid flow diagnostics such as sprays and thin liquid films on account of their extremely high fluorescence quantum yields, high temperature sensitivities and minimal doping concentration requirements [20]. Typical examples are Rhodamine 6G and Rhodamine B. Two-phase flow investigations using dyes are however sparse, mainly owing to the very low volatility of such compounds. Earlier mentioned idealized studies of single droplet or droplet stream evaporation often employ acetone PLIF, exploiting the high volatility and favourable photophysical properties of the particular tracer. LIEF imaging, which as noted earlier allows for spectral discrimination between the vapour and liquid signals, is achieved on the basis of two tracers forming a short-
lived donor-acceptor complex. Typically aromatics such as fluorobenzene [21] and trimethylnaphthalene (1,4,6-TMN) [22] are employed as donors, while amines such as N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) [23], diethyl-ethyl-amine (DEMA) [21] and triethylamine (TEA) [24] are used as acceptors. The applicability of amines to LIF imaging experiments is largely limited to such studies owing to handling difficulties (toxicity and strong unpleasant odour), as well as adverse photophysical characteristics, such as strong oxygen quenching and low resistance against thermal decomposition.

2.2 Introduction to planar laser induced phosphorescence imaging (PLIP)

As has already been noted, the present research project has been motivated by the need to explore alternative methods for studying evaporated fuel concentrations in two-phase flows. In doing so, the utilisation of another radiative deexcitation process was investigated, namely the phosphorescence. A distinction between the fluorescence and phosphorescence can be drawn regarding the nature of the relevant electronic transitions; whereas the former entails no electron spin change, the latter is associated with a spin inversion. Typically molecules reside in a ground singlet electronic state, with laser light absorption resulting to promotion of an electron to a higher energy molecular orbital and excitation to a higher energy state of the same spin multiplicity. The emission of phosphorescence, however, proceeds from excited triplet states, thus necessitating the transfer of population either via intersystem crossing or collisions with other molecules. Hence, the spin multiplicity changes after the absorption and before the emission of phosphorescence. Such processes transpire readily in ketones, owing to strong coupling between states of different multiplicity, with biacetyl and acetone being the most thoroughly investigated compounds. Whether a triplet state has been populated by intersystem crossing or through sensitization, prior occupation of an excited singlet state must always occur, allowing for the fluorescence and trailing phosphorescence signals to be distinguished in a temporal manner, for example using a gated detector.

Another difference between the two radiative processes under consideration is that whereas the fluorescence lifetime is limited by extremely fast energy transfer to just a few nanoseconds [25], the phosphorescence lifetime extends to as much as hundreds or even thousands of microseconds [26, 27]. These values are very strongly dependent upon any collisional deactivation, and hence the rate of collisions and quenching efficiencies of the colliding species. The comparative longevity of the triplet state emission is attributed to
violation of the spin selection rule and the associated spin multiplicity change, a topic which will be discussed more extensively later in the report. The aforementioned dependence of the phosphorescence emission on molecular collisions yields some very interesting characteristics: For example, whereas the observed fluorescence lifetime is nearly identical for both liquid and vapour phases, liquid acetone phosphorescence displays a severely reduced lifetime compared to its gaseous phase counterpart, owing to substantially higher collisional quenching rates by other acetone molecules and dissolved gas molecules. Oxygen, in particular, is an extremely efficient quencher of the triplet state emission, completely consuming the excitation energy in the gaseous phase [28], and limiting the applicability of vapour phase diagnostics in oxygen-free environments (an extensive account regarding the reasons why the particular molecule is such an efficient quencher is provided in Section 3.2.8.1). In contrast, liquid acetone phosphorescence has been shown to persist under the same conditions, yielding a liquid-only signal. Finally, a strong enhancement of the liquid phase phosphorescence signal intensity and lifetime has been observed when reducing the dissolved oxygen content through, for example, nitrogen purging [29]. Exemplary fluorescence and phosphorescence images of a thin acetone liquid stream are hereby presented for demonstration purposes (Fig 2.2).
Fig 2.2 Schematic representation of the fluorescence and phosphorescence emission of a laminar acetone stream in air, presented along with fluorescence and phosphorescence images obtained at different time delays.

The phosphorescence images were collected at different delays relative to the fluorescence emission along the phosphorescence emission decay. In collecting these images, a standard LIF setup comprised of a 308nm XeCl excimer laser and an intensified CCD camera was employed. A schematic diagram of the temporal decay of the fluorescence and phosphorescence signals is also provided.

Knowledge of the phosphorescence emission of ketones dates back to early fluorescence investigations; in fact, the two terms were used interchangeably [26] until Lewis and Kasha [30] postulated and proved that the observed biacetyl emission originated from two different states, the singlet and the triplet. Early acetone and biacetyl photophysical studies were carried out mainly by the same research groups during the 40s and 50s [26, 31-33], providing the first emission decay models and an extensive range of photophysical data. Two discoveries tipped the scales in favour of biacetyl phosphorescence at that time: the high phosphorescence quantum yield (around 15%) and the extremely long lifetime (approximately 1ms) [34]. Employment of biacetyl phosphorescence became common-place in electronic energy transfer investigations, some of which were even reported for acetone-
biacetyl donor-acceptor pairs [35]. Flow investigations emerged during the 80s focusing on molecular mixing [36], flow tagging velocimetry [37, 38] and gaseous phase concentration measurements [39]. It should however be noted, that no studies on evaporating flow investigations were encountered in literature. Regarding acetone, Lozano and Hanson [36] firstly reported turbulent mixing investigations by employing acetone and biacetyl as markers, while a second gas phase investigation emerged later on [40]. More recently, Seiztman and co-workers emphasized on the phosphorescence properties of liquid acetone. A series of publications describing extensive calibration efforts became available [41, 42], supplemented by the introduction of a two-phase flow imaging technique based on combined fluorescence and phosphorescence imaging [43]. The latter, abbreviated PLIFP (planar laser induced fluorescence and phosphorescence), employs the liquid phase phosphorescence signal in order to locate the liquid-vapour boundary and the transition of zone from subcritical to supercritical fluid, and the vapour phase fluorescence in order to measure the evaporated acetone concentration in the purely vapour phase region. Regarding 3-pentanone, or any other ketone tracers, only early fluorescence and photolysis studies have been reported, mostly confined to photophysical characterization efforts [44].

Despite the fact that biacetyl is the most charismatic phosphorescent tracer, its implementation in combustion-related applications has been limited owing to the following considerations: Its vapour pressure at room temperature is quite low resulting in moderate seeding concentrations without preheating, while its strong butter-like odour is particularly unpleasant. Efficient phosphorescence emission is displayed for excitation above 400nm, accessible only by dye lasers. Excitation by the third harmonic of an Nd:YAG (355nm) or a XeF (351nm) laser is possible, however, the absorption is negligible and the triplet dissociation rate quite high [27]. Acetone, instead, can be readily excited by a wide range of commonly utilized UV lasers, evaporates quite readily at room temperature, has been employed throughout a wide range of gaseous and two-phase flow fluorescence visualization studies and its phosphorescence properties are also quite well-documented. It has therefore been selected as the tracer of choice for this investigation, with liquid phase 3-penatnone phosphorescence examined alongside for the first time by direct imaging. 3-pentanone has been extensively employed as an isooctane tracer, a common parent fuel in gasoline-like fuel investigations by laser diagnostic techniques.
2.3 Project Objectives

In order to examine the potential applicability of acetone and 3-pentanone phosphorescence in two-phase flow investigations, it was rendered essential to a) carry out a background theory investigation of the relevant photophysical processes and decay kinetics involved in the excitation/deexcitation mechanism thereof and b) produce an extensive literature review of the available photophysical data. In addition, a state of the art literature review is presented, whereby diagnostics aimed at the quantification of evaporated tracer/fuel concentrations in two-phase flows are discussed and key areas where phosphorescence imaging could potentially prove advantageous are identified. In its entirety, the literature review stands for the first objective of this experimental effort and aims at a) providing a comprehensive review of the phosphorescence properties of acetone and 3-pentanone and b) correctly recognizing key areas in laser diagnostic studies where phosphorescence imaging should be pursued.

The design and development of an experimental facility aimed at investigating acetone and 3-pentanone phosphorescence in isothermal (room temperature) evaporating and non-evaporating flows constitutes the second project objective. An isothermal environment was selected in order to allow for the phosphorescence properties of the aforementioned tracers to be examined in isolation of an additional photophysical dependency, namely temperature. The experimental arrangement was initially developed around the investigation of evaporating droplet streams, and later adapted so as to accommodate a high pressure GDI system, along with an extended (dual-camera) detector setup. Excitation was provided by a 308nm XeCl excimer laser in both cases; for the first time in liquid phase phosphorescence imaging experiments providing the first lifetime calibration data for the particular wavelength.

The final project objective is the feasibility assessment and application of laser induced phosphorescence (LIP) imaging in practical two-phase flow environments. Following a calibration effort aimed at characterizing the emission decay of liquid and vapour phase signals, two study-cases were pursued. The first includes the implementation and comparative assessment to LIF imaging of a novel LIP technique; in particular, evaporated tracer concentration measurements were carried out in close vicinity to liquid droplets. The second involves the development and calibration of a combined PLIFP technique by means of a contemporary automotive GDI injection system. Unlike a previous formulation
encountered in literature, sequential fluorescence and phosphorescence imaging was employed in order to explore the possibility of calibrating the liquid phase fluorescence and phosphorescence signals; the two emissions were compared amongst each other under non-evaporating conditions with the ultimate goal of producing liquid-only LIF corrections using LIP images and calibration results.
3 Background Theory

This section of the report is aimed at providing the relevant theoretical background behind the photophysical phenomena involved in tracer-based LIF and LIP imaging using ketone tracers. In that respect, a concise review rather than an exhaustive study of the photochemistry of organic molecules is presented, based on the textbooks by Gilbert and Baggott [45], Atkins and de Paula [46], and Turro, Ramamurthy and Scaiano [47].

3.1 Electronic excitation

3.1.1 Electronic transitions and electronic states

Electronic transitions are manifested by migration of electrons to molecular orbitals of different energy; they are therefore associated with changes in the molecular configuration and molecular electronic state. In laser diagnostics using ketone tracers, the π* ← n transition is responsible for absorption in the UV. The active chromophore is the C=O group and the transition involves a pair of electrons of the oxygen atom, whereby a non-bonding electron is promoted to an anti-bonding π* orbital. Electronic states are classified according to their total spin and level of excitation. Quantum mechanics dictates that the spin quantum number is always given by $s = 1/2$ and the magnitude of the electron spin (intrinsic angular momentum arising through the motion of the electron about its own axis) is always equal to $(s(s + 1))^{1/2} \hbar$, where $\hbar = h/2\pi$ stands for the reduced Planck constant. The spin vector can only assume two orientations, the spin up ($\uparrow$) and the spin down ($\downarrow$), corresponding to spin magnetic numbers $m_s$ (projection of the spin vector to the specified z-axis) equal to $+1/2$ and $-1/2$. When considering an electron pair, the two individual spin vectra can be arranged either parallel ($\uparrow\uparrow$) or anti-parallel ($\uparrow\downarrow$) to each other; in the first case the total spin vector is equal to one (the total magnetic spin vector $M_s$ can be either $-1, 0$ or $1$), the multiplicity of states (number of different configurations with the same total energy) is equal to three, and the electronic state is called a triplet ($T$). In the second case, the total spin vector equals to zero ($M_s = 0$), the multiplicity is one and the resulting state is identified as a singlet ($S$). The three arrangements allowing for a non-zero total spin resultant and the precise anti-parallel spin arrangement yielding a zero total spin resultant are displayed in Fig 3.1.
excitation refers to the promotion of an electron to a higher energy bound state, while the level of excitation identifies the bound state that the electron occupies. This is typically identified by the subscript following the multiplicity index; for example $S_0, S_1, T_1$ for ground singlet, first excited singlet and first excited triplet.

![Fig 3.1](image)

**Fig 3.1** (Left) Representation of the three possible parallel spin vector arrangements forming a triplet state. Despite the fact that the orientation of the vectors on the cones is not known, the angle with respect to the specified axis is always the same; all three arrangements have the same total spin angular momentum but different total magnetic spin angular momentum. (Right) Anti-parallel electron spin vector arrangement yielding a singlet state. In this case the two spin vectors are oriented ‘precisely’ anti-parallel to each other and both total spin and total magnetic spin numbers are equal to zero.

### 3.1.2 The transition dipole moment

The origin of light absorption and emission is the interaction between two oscillating electric dipoles, light and electrons. This interaction produces a resonance condition provided a common frequency $\nu$ is available such that the Bohr frequency condition is satisfied:
The redistribution of electric charges ensuing from light-matter interactions is described by the transition dipole moment $\mathbf{\mu}$. It follows from time-dependent perturbation theory that the rate of population redistribution associated with a transition is proportional to the square modulus of the transition dipole moment $|\mathbf{\mu}_{fi}|^2$. Hence, if a transition is not associated with dipolar charge redistribution at a molecular level ($\mathbf{\mu}_{fi} \neq 0$), it does not occur. This outcome is referred to as a selection rule, and classifies transitions as dipole allowed or forbidden. It should be noted that forbidden transitions, such as the $n \leftarrow \pi^*$ in ketones, do in fact occur, albeit with severely reduced probability. The term “forbidden”, in the context of quantum mechanics, bears no absolute meaning and rather classifies the nature of the transition in reference to quantum-mechanically derived directives (selection rules).

The quantum-mechanical representation of light-matter interactions is described by Eq 3-2. $\Psi_f$ stands for the wavefunction of the final molecular state, $\Psi_i$ describes the wavefunction of the initial state and $\hat{\mathbf{\mu}}$ represents the dipole moment operator. According to the Born-Oppenheimer approximation, nuclei remain “frozen” during electronic transitions and hence, the nuclear and electronic motions can to be treated independently. The transition dipole moment can be expressed as the product of three contributions; the electronic transition dipole moment $\langle \varphi_f | \hat{\mathbf{\mu}} | \varphi_i \rangle$, the vibrational overlap integral $\langle N_f | N_i \rangle$, and the spin overlap integral $\langle S_f | S_i \rangle$:

$$\mathbf{\mu}_{fi} = \langle \Psi_f | \hat{\mathbf{\mu}} | \Psi_i \rangle = \langle \varphi_f | \hat{\mathbf{\mu}} | \varphi_i \rangle \langle N_f | N_i \rangle \langle S_f | S_i \rangle$$

Eq 3-2

The electronic transition dipole moment places restrictions on the electron distributions of the states participating in the transition. Selection rules are imposed on the change of total orbital angular momentum and symmetry, rendering transitions orbital or symmetry allowed or forbidden. The vibrational overlap integral, also called the transition Franck-Condon factor, describes the spatial overlap of nuclear wavefunctions, while the spin overlap integral accounts for the effect of spin multiplicity changes. Singlet-singlet transitions are not associated with a spin multiplicity change and are thus termed spin-allowed, whereas singlet-triplet transitions are described as spin-forbidden. The latter can become weakly allowed due to spin-orbit coupling. $S_0 \leftrightarrow T(n, \pi^*)$ transitions favour strong spin-orbit coupling as the
orbital momentum change necessitated for the spin flip can be directly compensated by an orbital jump. Molecular configurations involved in $S_0 \leftrightarrow T(\pi, \pi^*)$ transitions, in contrast, inhibit the angular orbital momentum change and therefore, the spin-orbit coupling perturbation is insignificant (for example, in the case of aromatics). This is a general conclusion called El-Sayed’s rule and governs transitions between states of different multiplicity such as the phosphorescence emission.

### 3.1.3 Vibronic coupling

The Franck-Condon principle dictates that transitions occur most readily between vibrational levels in the ground and excited electronic states with maximum vibrational wavefunction overlap; in that way, vibrational levels in the newly occupied electronic state are populated preferentially (Fig 3.2):

![Fig 3.2 Potential energy diagram illustrating the preferential population of vibrational levels with large Franck-Condon factors during vibronic transitions](image)

Such transitions, termed vibronic, arise due to coupling between the electronic and nuclear motion, effectively violating the Born-Oppenheimer approximation. This type of interaction is responsible for rendering originally orbital and symmetry forbidden transitions, such as the $\pi^* \leftrightarrow n$, weakly allowed. Vibronic coupling operates by introducing perturbations to the electronic transition dipole moment by mixing molecular orbitals. Out-of-plane vibrations
allow the $\pi^* \leftarrow \pi$ transition to “borrow” absorption intensity by partially acquiring a $\pi^* \leftarrow \pi$ character (overlap allowed transition).

### 3.2 Electronic deexcitation

Excluding chemical processes such as dissociation, the photo-induced excess energy of excited molecules can be dissipated by a number of different pathways, hereby grouped into three main categories: radiative processes which involve energy dissipation by spontaneous or stimulated emission of photons, non-radiative processes which encompass both the thermalization of excess energy by vibrational energy transfer and intramolecular energy transfer to different electronic states, and collisional quenching which accounts for intermolecular energy transfer to colliding partners. The aforementioned excitation and deexcitation pathways are best introduced by use of a Jablonski diagram (Fig 3.3).

![Jablonski diagram](image)

**Fig 3.3** Jablonski diagram illustrating the radiative and non-radiative processes in ketones following light absorption. Radiative processes are shown as straight lines and non-radiative processes as wavy lines. The $S_0, S_1$ and $T_1$ vibrational manifolds are illustrated as groups of black horizontal lines, each corresponding to a different vibrational level. The density of vibrational levels is shown to increase with increasing energy difference from the state origin (lower vibrational level displayed in bold), as more vibrational modes are become.

#### 3.2.1 The Jablonski diagram

Along with any relevant radiative and non-radiative processes, the former represented by straight arrows and the latter by wavy ones, the Jablonski diagram illustrates the ground state singlet, first excited singlet and first excited triplet vibrational manifolds. Each vibrational
level can be further split into a rotational manifold representative of the rotational transitions that accompany nuclear vibrations; however, the influence of electronic and vibrational excitation on the molecular configuration is far more potent, and any changes to the rotational structure are rendered insignificant in comparison.

3.2.2 Absorption

Before electronic excitation, the molecule lies at some vibrational (and rotational) level at the ground electronic state. Absorption of a photon results to promotion of an electron to a higher energy molecular orbital and excitation, for example to the first excited singlet $S_1$. As has already been noted, this transition (and fluorescence) is both orbital overlap and symmetry forbidden in ketones.

3.2.3 Fluorescence

The radiative decay between an excited electronic state and a ground state of the same multiplicity is termed fluorescence. It is subject to the same dependence on the transition dipole moment as light absorption and, as a result, the same selection rules.

3.2.4 Phosphorescence

Phosphorescence describes the radiative transition from a higher to a lower energy electronic state of different multiplicity. Ketones phosphoresce from the first excited triplet state $T_1$, which is readily populated by a process called intersystem crossing (ISC), following excitation to $S_1$. The emission of phosphorescence is spin-forbidden but becomes weakly-allowed due to spin-orbit coupling.

3.2.5 Vibrational relaxation (VR)

The electronically excited molecule gives up its excess vibrational energy through collisions with other molecules and moves down the vibrational manifold in a stepwise manner. In liquids, fluorescence is mainly emitted from the lowest (thermalized) vibrational levels of $S_1$, as the frequency of molecular collisions within the fluorescence lifetime is high.
In gases, however, VR competes with other processes on a comparable time scale and thus, spontaneous emission can occur from higher up the vibrational manifold. In this manner the pressure dependence of (gas phases) ketone fluorescence emission arises [48].

### 3.2.6 Intersystem crossing (ISC)

Similar to the distinction between fluorescence and phosphorescence, intramolecular non-radiative processes can be classified according to the multiplicity of the states participating in the transition. Intersystem crossing is defined as the transfer of population between states of different multiplicity, which in relation to this study, concerns the $S_1 \rightarrow T_1$ transition. This type of interaction is symmetry-forbidden for ketones but becomes weakly allowed, once again, owing to spin-orbit coupling. By inspection of the potential energy curves of $S_1$ and $T_1$, it is evident that the crossing occurs where the surfaces of vibrational levels of the excited singlet and triplet states coincide. As the transition probability is strongly dependant on the energy difference between the participating states (energy gap law), it follows that ISC progresses more readily for ketones (for which the energy disparity between the $S_1$ and $T_1$ states is markedly low) than aromatics. Another noteworthy observation is that ISC entails a vibrational energy gain as the triplet lies at a lower energy than the singlet.

![Fig 3.4](image)

**Fig 3.4** Excitation to $S_1$ followed by vibrational relaxation down the $S_1$ vibrational manifold, intersystem crossing to $T_1$, vibrational relaxation down the $T_1$ vibrational manifold and finally deexcitation by phosphorescence emission back to $S_0$. 51
3.2.7 **Internal conversion (IC)**

Internal conversion describes the transfer of population between states of the same multiplicity, and like ISC, is subject to symmetry-related selection rules and the energy gap law. When considering the potential energy curves of $S_1$ and $S_0$, the transition can be modelled as a horizontal crossing from one curve to the other. The crossing will occur where the surfaces of a highly excited vibrational level of the ground electronic state and a low vibrational level of the electronically excited state meet (Fig 3.5). By inspection of the displayed wavefunctions of the initial and final states, it is evident that the spatial overlap, and hence the Franck-Condon factor of the vibrational levels involved in IC, are poor. Consequently, the rate of IC will be insignificant and fluorescence and ISC will be dominant; a behaviour characteristic of the ketone deexcitation mechanism.

![Potential Energy vs Internuclear Separation](image)

**Fig 3.5** Illustration of the poor spatial overlap between the vibrational wavefunctions of a highly excited vibrational level of the ground $S_0$ state and a low-lying vibrational level of the excited singlet $S_1$

3.2.8 **Collisional deactivation**

The electronic energy transfer between an excited tracer (donor) and a colliding partner (acceptor) as a result of electron exchange interactions is considered under the terms collisional deactivation and quenching. Unlike dipole-dipole energy transfer arising through the interaction of an oscillating electric field in space with the donor-acceptor pair, electron exchange interactions require the electron clouds of the donor and acceptor molecules to
spatially overlap. The ground state acceptor $M$ gains excitation energy, while the originally excited donor $^*R$ returns to the ground state:

$$^*R + M \rightarrow R + ^*M$$  \hspace{1cm} \text{Eq 3-3}

In the context of the present study, two collisional deactivation mechanisms are of great interest: oxygen quenching and triplet-triplet annihilation (TTA). Oxygen quenching is responsible for very efficiently quenching the phosphorescence emission of ketone tracers; its effect on ketone fluorescence is, however, less pronounced owing to very rapid ISC. TTA, in turn, is another primary phosphorescence quenching mechanism, alongside oxygen quenching.

### 3.2.8.1 Oxygen quenching

Unlike most organic molecules, the ground state of molecular oxygen is a triplet ($T_0$). The first spin-allowed electronic transition is the $T_0 \rightarrow T_1$ ($\sim 140\text{kcal mol}^{-1}$ above $T_0$), while the most “accessible” excited electronic states are the $S_1$ and $S_2$, located at 22.4kcal mol$^{-1}$ and 37.5kcal mol$^{-1}$ above $T_0$ respectively. The interactions between ground state oxygen molecules and excited singlet state organic molecules proceed according to one of the following pathways:

$$^*R(S_1) + ^3O_2 \leftrightarrow ^3[R - O_2]^* \rightarrow ^*R(T_1) + ^1O_2$$  \hspace{1cm} \text{Eq 3-4}

$$^*R(S_1) + ^3O_2 \leftrightarrow ^3[R - O_2]^* \rightarrow ^*R(T_1) + ^3O_2$$  \hspace{1cm} \text{Eq 3-5}

$$^*R(S_1) + ^3O_2 \leftrightarrow ^3[R - O_2]^* \rightarrow ^*R(S_0) + ^3O_2$$  \hspace{1cm} \text{Eq 3-6}

In all three cases, the sensitizer-oxygen interactions are facilitated by the formation of short-lived triplet state encounter complexes and involve energy transfer. The factor determining the dominant deexcitation pathway is the energy gap $\Delta E_{ST}$ between the $S_1$ and $T_1$ states of the sensitizer; if $\Delta E_{ST}$ is larger than the energy gap between the ground state triplet and first excited singlet states of oxygen, the interaction proceeds according to Eq 3-4. If $\Delta E_{ST}$ is smaller than the energy gap between the $T_0$ and $S_1$ states of oxygen, the interaction is manifested either as oxygen-catalysed intersystem crossing (Eq 3-5) or radiationless
deactivation (Eq 3-6). These mechanisms can be used to describe the mild quenching effect of oxygen on ketone fluorescence, for which $\Delta E_{ST}$ is typically below 10 kcal mol$^{-1}$. The interaction of oxygen with triplet state sensitizers generates three possible outcomes:

\[ ^*R(T_1) + ^3O_2 \overset{1/9}{\leftrightarrow} ^1[R - O_2]^* \rightarrow R(S_0) + ^1O_2 \quad \text{Eq 3-7} \]

\[ ^*R(T_1) + ^3O_2 \overset{3/9}{\leftrightarrow} ^3[R - O_2]^* \rightarrow R(S_0) + ^3O_2 \quad \text{Eq 3-8} \]

\[ ^*R(T_1) + ^3O_2 \overset{5/9}{\leftrightarrow} ^5[R - O_2]^* \quad \text{Eq 3-9} \]

The singlet path (Eq 3-7) describes the quenching of triplet sensitizers alongside the production of $S_1$ oxygen, the triplet path (Eq 3-8) results to radiationless deactivation, while the quintet path (Eq 3-9) is dissociative and does not contribute to quenching. The fractions on top of the double arrows represent the probability that the encounter yields the following outcome in accordance with spin statistics. In that respect, triplet state quenching is limited to 4/9 of the diffusion rate.

### 3.2.8.2 Triplet-triplet annihilation (TTA)

TTA is a form of electron exchange interaction attributed to collisions between excited triplet molecules. As the energy difference between the $S_1$ and $T_1$ states is generally smaller than the energy difference between the $S_0$ and $T_1$ states ($\Delta E_{T_1-S_0} > \Delta E_{S_1-T_1}$), the total excitation energy of two triplets ($2 \times (\Delta E_{T_1-S_0})$) suffices to produce one molecule in an excited singlet state, while the other returns to $S_0$. This process can be described by Eq 3-10, while a schematic representation is provided in Fig 3.6. Here, $k_{TTA}$ stands for the TTA rate constant ($M^{-1}s^{-1}$).

\[ ^*R(T_1) + ^*R(T_1) \overset{k_{TTA}}{\rightarrow} ^*R(S_1) + R(S_0) \quad \text{Eq 3-10} \]

Given the fluorescence efficiency of the excited molecule is high, TTA may result in long-lived fluorescence emission, also called “delayed” fluorescence. The longevity of delayed fluorescence relative to the fluorescence emitted by direct deexcitation from $S_1$ is attributed to the substantially longer lifetime of the triplet state; essentially the population of $S_1$
molecules produced by TTA is being replenished throughout the triplet state radiative lifetime. The generation of two singlets, one in an excited and one in a ground state, is spin-allowed but does not constitute the only potential spin arrangement that does not violate the conservation rule. Only one-ninth of such triplet-triplet interaction will produce a singlet pair; three ninths will result in an excited triplet and a ground singlet molecule, and the rest to an overall quintet (Eq 3-11 – 3-13)

\[ ^*R(T_1) + ^*R(T_1) \xleftrightarrow{1/9} [R - R]^* \rightarrow ^*R(S_1) + R(S_0) \quad \text{Eq 3-11} \]

\[ ^*R(T_1) + ^*R(T_1) \xleftrightarrow{3/9} [R - R]^* \rightarrow ^*R(T_1) + R(S_0) \quad \text{Eq 3-12} \]

\[ ^*R(T_1) + ^*R(T_1) \xleftrightarrow{5/9} [R - R]^* \quad \text{Eq 3-13} \]

**Fig 3.6** Energy diagram of the triplet-triplet annihilation interaction yielding an excited singlet molecule. The total excitation energy of the two triplets \(2 \times E_{T_1}\) suffices to excite one of the two molecules to an excited singlet state \(S_n\) as \(E_{S_1} - E_{T_1} < E_{T_1}\)

### 3.3 Kinetics of photophysical processes

#### 3.3.1 Excited singlet formation and decay processes

The principal radiative and non-radiative processes and reaction rates associated with the formation and decay of the first excited singlet state are listed in Table 3-1:
Table 3-1 Processes, reactions and reaction rates associated with the formation and decay of $S_1$ states. The bracketed terms stand for the concentrations of the ground and first excited singlet state populations in molecules\texttimes cm$^{-3}$. The rate constants $k_{abs}$, $k_f$, $k_{IC}$ and $k_{ISC}$ have units of s$^{-1}$.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>$S + h\nu_i \rightarrow S^*$</td>
<td>$k_{abs} \langle S \rangle h\nu_i$</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>$S^* \rightarrow S + h\nu_f$</td>
<td>$k_f \langle S^* \rangle$</td>
</tr>
<tr>
<td>Internal conversion</td>
<td>$S^* \rightarrow S$</td>
<td>$k_{IC} \langle S^* \rangle$</td>
</tr>
<tr>
<td>Intersystem crossing</td>
<td>$S^* \rightarrow T^*$</td>
<td>$k_{ISC} \langle S^* \rangle$</td>
</tr>
</tbody>
</table>

In the absence of any competing deexcitation mechanisms, the temporal variation of the first excited singlet state population is given by:

$$- \frac{d[S^*]}{dt} = k_f \langle S^* \rangle$$  \hspace{1cm} \text{Eq 3-10}

After time $t$, the initially excited state population concentration $[S^*]_0$ has decayed exponentially to a value $[S^*]_t$:

$$[S^*]_t = [S^*]_0 e^{-k_f t}$$  \hspace{1cm} \text{Eq 3-15}

The natural lifetime of the fluorescence emission (time required for the concentration to drop to $1/e$ of its initial value) is:

$$\tau_f = \frac{1}{k_f}$$  \hspace{1cm} \text{Eq 3-16}

If fluorescence is not the only deexcitation pathway, and intersystem crossing and internal conversion are also accounted for, Eq 3-10, 3-11 and 3-12 must be adjusted accordingly:

$$- \frac{d[S^*]}{dt} = (k_f + k_{IC} + k_{ISC}) \langle S^* \rangle = k_{tot} \langle S^* \rangle$$  \hspace{1cm} \text{Eq 3-17}

$$[S^*]_t = [S^*]_0 e^{-k_{tot} t}$$  \hspace{1cm} \text{Eq 3-18}

$$\tau_{eff} = \frac{1}{k_{tot}} = \frac{1}{k_f + k_{IC} + k_{ISC}}$$  \hspace{1cm} \text{Eq 3-19}
\( \tau_{eff} \) stands for the effective or observed lifetime, which due competition with any non-radiative deexcitation processes (here IC and ISC), is substantially limited in comparison to the natural lifetime. Koban [15], for example, quotes a natural lifetime of 1\( \mu \)s and an effective lifetime of 2ns for 3-pentanone as a result of fast intersystem crossing. Hansen and Lee [44] measured \( k_f = 8 \times 10^5 \) and \( k_{ISC} = 8 \times 10^5 \) s\(^{-1} \) for acetone, indicative of the deexcitation mechanism of ketones.

### 3.3.2 Fluorescence quantum yield

The fluorescence quantum yield is defined as the number of molecules fluorescing per unit time per unit volume over the number of light quanta absorbed per unit time per unit volume, and can be interpreted as a fluorescence efficiency term. In the context of the present analysis, \( \phi_f \) can be expressed as the ratio of the fluorescence and absorption rates:

\[
\phi_f = \frac{k_f[S^*]}{k_{abs}[S]hv_i} \quad \text{Eq 3-20}
\]

Assuming steady state excitation, the rates of generation and decay of the excited singlet state population are equal and their sum is zero:

\[
\frac{d[S^*]}{dt} = k_{abs}[S]hv_i - k_f[S^*] - k_{IC}[S^*] - k_{ISC}[S^*] = 0 \quad \text{Eq 3-21}
\]

This expression can then be rearranged to include the fluorescence quantum yield:

\[
\phi_f = \frac{k_f}{k_f + k_{IC} + k_{ISC}} \quad \text{Eq 3-22}
\]

### 3.3.3 Collisional deactivation

Contrary to the intramolecular processes examined so far, collisional deactivation falls under the category of intermolecular emission quenching. The collisional deactivation reaction rate will thus be proportional to the quencher concentration in addition to the molar concentration of the excited state population and the quenching rate constant (Table 3-2):
Table 3-2 Collisional quenching reaction and reaction rate; the bracketed terms \([Q]\) and \([S^*]\) stand for the molar concentrations of the excited singlet state and quencher expressed in molecules\(\times\)cm\(^3\). The rate constant \(k_Q\) has units of cm\(^3\)\(\times\)molecules\(^{-1}\)\(\times\)s\(^{-1}\)

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quenching</td>
<td>(S^* + Q \rightarrow S + Q)</td>
<td>(k_Q [Q][S^*])</td>
</tr>
</tbody>
</table>

If collisional deactivation is included in the definition of the fluorescence quantum yield, Eq 3-18 takes the form:

\[
\phi_f = \frac{k_f}{k_f + k_{IC} + k_{ISC} + k_Q[Q]} \tag{Eq 3-23}
\]

The fluorescence efficiency degradation induced through collisional quenching can be examined by plotting the ratio between the fluorescence quantum yield with and without the quencher \((\phi_f\) and \(\phi_{f,0}\) respectively), against the quencher concentration \((Q)\). Such a plot is referred to as a Stern-Volmer plot and is described by the Stern-Volmer equation:

\[
\frac{\phi_{f,0}}{\phi_f} = 1 + \tau_0 k_Q[Q] \tag{Eq 3-11}
\]

The relationship between \(\phi_{f,0}/\phi_f\) and \([Q]\) is linear and provides a measure of the quenching rate constant \(k_Q\).

### 3.3.4 Phosphorescence quantum yield

In the absence of any competing deexcitation mechanisms, the temporal variation of the first excited triplet state population proceeds according to:

\[
- \frac{dT^*}{dt} = k_{ph}[T^*] \tag{Eq 3-25}
\]

Between \(t = 0\) and \(t\), the triplet state population decays exponentially to a value \([T^*]_t\):

\[
[T^*]_t = [T^*]_0 e^{-k_{ph}t} \tag{Eq 3-12}
\]
The phosphorescence signal \( I_{ph}(t) \) collected by a detector at time \( t \) following the initial population of \( T_i \) is proportional to the initial triplet state population \( [T^*]_0 \); consequently, the total phosphorescence signal \( I_{ph\ total} \) collected between \( t = 0 \) and \( \infty \) will also be a linear function of the initial triplet state population density \( [T^*]_0 \) (here, internal conversion is assumed to be the only alternative deexcitation pathway):

\[
I_{ph\ total} \propto \frac{k_{ph}}{k_{ph} + k_{ic}} [T^*]_0 \quad \text{Eq 3-13}
\]

Including the contribution of TTA, the modified Eq 3-21,3-22, 3-23 are:

\[
- \frac{d[T^*]}{dt} = (k_{ph} + k_{ic})[T^*] + 2k_{TTA}[T^*]^2 \quad \text{Eq 3-14}
\]

\[
[T^*]_t = \frac{(k_{ph} + k_{ic})[T^*]_0}{e^{((k_{ph} + k_{ic})t)(k_{ph} + k_{ic} + 2k_{TTA}[T^*]_0) - 2k_{TTA}[T^*]_0}} \quad \text{Eq 3-15}
\]

\[
I_{ph\ total} \propto \frac{k_{ph}}{2k_{TTA}} \ln \left( 1 + \frac{2k_{TTA}}{k_{ph} + k_{ic}} [T^*]_0 \right) \quad \text{Eq 3-16}
\]

Eq -28 is obtained by introducing a quenching term \( (k_Q(Q)) \) in the decay rate equation of the triplet state population in order to account for TTA. Unlike other quenching mechanisms, TTA is manifested by the interaction of two excited triplets, and therefore the quencher and excited molecule are the same. The quenching rate \( k_Q(Q)[S^*] \) can then be expressed as \( k_Q[S^*][S^*] = k_Q[S^*]^2 \), where \( [S^*] = [T^*] \) and \( k_Q = 2k_{TTA} \). The definition of \( k_{TTA} = k_Q/2 \) accounts for the fact that both quencher and excited molecules contribute equally to the reaction rate. Eq 3-30 suggests that the collected phosphorescence does not correlate linearly with the \( [T^*]_0 \) anymore; the linearity could, however, be restored given the following condition:

\[
[T^*]_0 \ll \frac{k_{ph} + k_{ic}}{k_{TTA}} \quad \text{Eq 3-31}
\]
4 State of the art

This section of the thesis is dedicated to the fulfilment of two objectives: Firstly, a thorough review of the photophysics of acetone and 3-pentanone is carried out. This includes the photophysical characterization of the fluorescence and phosphorescence of both liquid and vapour phases by experimentalists over the latest era of optical diagnostics. The second part of this chapter concentrates on PLIF practices aimed at the characterization of evaporated tracer concentrations in two-phase flows. In discriminating between the vapour and liquid phase signals, three different approaches have been put forward; discrimination based on the signal intensity disparity between the two phases, temporal discrimination achieved by sequential detection of the fluorescence and phosphorescence, and spectral discrimination by simultaneous detection of monomer and redshifted exciplex fluorescence in donor-acceptor tracer systems. The first approach has largely been implemented in droplet stream experiments, the second has been attempted in liquid jets and sprays, while the last one enjoys a long history in automotive spray investigations. The analysis of PLIF imaging in droplet streams includes an experiment set up for demonstrating the challenges associated with this method, and has already been included in a recent publication [49]. Permission to reprint this material has been granted by the publisher as the experiments presented in the publication were carried out by the author of this report.

4.1 Acetone and 3-pentanone Photophysics

4.1.1 Acetone Photophysics

Acetone absorption in the UV is attributed to the symmetry-forbidden $\pi^* \leftrightarrow n$ transition, whereby a non-bonding electron located near the oxygen atom of the C=O chromophore is promoted to a higher energy, anti-bonding orbital. The transition becomes weakly allowed due to vibronic coupling between the electronic and nuclear motions, thus breaking the ground state $C_{2v}$ symmetry. The intensity borrowing mechanism has been assigned to C=O out-of-plane wagging and methyl torsion [50, 51]. Fluorescence emission and intersystem crossing are the dominant depopulation channels of $S_1$, while from $T_1$, the majority of the excitation energy is lost either through collisions or dissociation, while part of it is radiatively dissipated as phosphorescence.
4.1.1.1 The absorption spectrum

The room temperature absorption spectrum of acetone is diffuse and featureless owing to spectral overlap of a plethora of hot vibrational bands. Lozano et al. [52] and Gierczak et al. [53] have quoted maximum room temperature absorption cross-sections of $4.7 \times 10^{-20} \text{ cm}^2$ and $4.94 \times 10^{-20} \text{ cm}^2$ respectively, over a 270-280nm plateau. In comparison, Yujing et al. [54] and Martinez et al. [55] have presented measurements of $4.99 \times 10^{-20} \text{ cm}^2$ and $5.07 \times 10^{-20} \text{ cm}^2$, at 273nm and 278nm respectively. With increasing temperature, the absorption intensity increases throughout the spectrum. An overall broadening, which is more pronounced towards the red side, has also been reported; for example, Gierczak et al. [53] and Hynes et al. [56] detected this trend over the 260-360K and 235-298K ranges respectively. Koch et al. [57] and Thurber et al.[58] investigated the absorption cross-section temperature dependence at engine-relevant temperatures; between 300K and approximately 850K the absorption peak shifts to around 290nm while the maximum cross-section increases by nearly 50%. Löffler et al. [6] reported a more moderate spectral shift but a more pronounced increase in absolute absorption cross-sections over the 298-698K range.

4.1.1.2 The fluorescence spectrum

The room temperature fluorescence spectrum of acetone vapour has been measured by Lozano et al. [52], Bryant et al. [8] and Bogan and Lee [59]. Extending over the 320nm-550nm region, the fluorescence spectrum is red-shifted relative to the absorption spectrum as radiative emission occurs primarily from low-lying vibrationally relaxed $S_1$ levels. This phenomenon, known as a Stokes shift, stems from the disparity between the timescales of spontaneous emission (of the order of $10^{-9}$s) and molecular vibrations ($10^{-12}$s). Two peaks at 445nm and 480nm have been identified by Lozano et al. [52], whereas Bryant et al. [8] and Bogan and Lee [59] have identified a single peak in the 420nm-430nm region. Fluorescence spectrum dependencies have been recognized for both temperature and excitation wavelength; increasing either results to a reduction in the emitted fluorescence and a blueshift mainly on the blue side of the spectrum. The former can be explained on the basis of a vibrational excitation dependant intersystem crossing rate constant; excitation to vibrational levels higher up the $S_1$ vibrational manifold results to enhanced intersystem crossing and fluorescence efficiency degradation. The blueshift ensues as a result of a larger portion of the excited state population being distributed amongst more energetic vibrational levels, with
radiative deexcitation from those levels manifested by the emission of higher energy photons. In addition to temperature and excitation wavelength, pressure has also been shown to influence the fluorescence spectrum; for example, a pressure increase in the absence of oxygen induces a boost in the emission and a slight redshift of the short wavelength side. Both observations can be associated faster vibrational relaxation rates as a result of higher collision frequencies [60]. Liquid acetone fluorescence is emitted over the same spectral region as the vapour, and also peaks in the 420-430nm region [41, 61, 62]. A slight blueshift has been detected when lower excitation wavelengths are employed [41].

4.1.1.3 The phosphorescence spectrum

In oxygen-free rigid glass (amorphous molecular arrangement rather than ordered crystalline as in the case of solids) at 77K, the phosphorescence spectrum peaks at around 455nm, owing to emission from thermal triplets [62]. The phosphorescence spectrum of acetone vapour occupies almost the same spectral region and peaks at 440nm, indicating that radiative deexcitation from $T_1$ in the gas phase also proceeds primarily from levels near the origin [59]. Tran et al. [41] have noted that the spectral shift of liquid acetone phosphorescence relative to the fluorescence varies with detection delay relative to the emission of fluorescence. Starting off at 200ns after the emission of fluorescence and collected over the next 300ns, the liquid phase phosphorescence spectrum peaks at around 380nm (slightly blue-shifted relative to the fluorescence), while the phosphorescence collected over the 2000-3000ns delay range peaks slightly to red of the fluorescence.

4.1.1.4 The near-isolated molecule deexcitation mechanism

Two different deexcitation mechanisms have been proposed for acetone; one applicable to near collision-free environments (jet-cooled molecular beams and low pressure samples), and one relevant to typical LIF experimental conditions; in the latter case, molecular collisions are frequent within the time scale of radiative emission and the excited molecules possess an appreciable degree of vibrational excitation. In order to a priori resolve any discrepancies that may arise regarding quoted fluorescence and phosphorescence lifetimes and relevant deexcitation channels, the first mechanism will also be briefly discussed.
The decay pattern of acetone in near collision-free environments involves the emission of light from states of mixed singlet and triplet character in addition to fluorescence and phosphorescence. Near the $S_1$ origin, the density of states is low, and each state is strongly coupled to the much denser $T_1$ manifold. The coupling results to fast dephasing (non-radiative transition to a mixed state) and subsequently photon emission, or to collisionally-induced deactivation of the mixed states, and generation of “hot” triplets with much weaker $S_1$ coupling. Direct light emission from $S_1$ is also possible, resulting to a fast component emitted near-concurrently with the laser pulse, and attributed to pure fluorescence from $S_1$. For jet-cooled samples excited to states up to 900-1200cm$^{-1}$ above the $S_1$ origin, the fast component is not detected and deexcitation proceeds either through radiative emission from the mixed states or internal conversion arising from weak $S_1 - S_0$ coupling [63, 64]. The mixed state emission is prominent near the $S_1$ origin but subsides with increasing excess vibrational energy [63, 65, 66]. As the sample pressure increases from below 1mTorr (0.1333 Pa) to a few mTorr, the emission from the mixed state dies out due to extremely efficient collisional quenching (by either acetone molecules or other colliding partners), and two new radiative components emerge [66]; the faster component emanates from hot triplets, while the slow component is ascribed to thermal triplet phosphorescence. With decreasing excitation wavelength, the hot triplet emission increases in the 330-312nm range, but then falls off and completely disappears below 305nm due to the activation of a strong dissociation channel [67]. Within the 330-312nm band, further increasing the sample pressure to a few Torr results to near-complete quenching of the hot triplet component, and a slight reduction in the radiative lifetime of thermal triplet phosphorescence [66]. A list of the measured lifetimes of each of the four distinct radiative components is presented below:

<table>
<thead>
<tr>
<th>Study</th>
<th>Singlet emission (μs)</th>
<th>Mixed $S - T$ emission (μs)</th>
<th>Hot triplet emission (μs)</th>
<th>Thermal triplet phosphorescence (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenblatt et al. [66]</td>
<td>&lt;0.02</td>
<td>5</td>
<td>30-50</td>
<td>200</td>
</tr>
<tr>
<td>Copeland and Crosley [67]</td>
<td>-</td>
<td>8</td>
<td>15</td>
<td>225</td>
</tr>
<tr>
<td>Costela et al. [68]</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>150-200</td>
</tr>
<tr>
<td>Anner et al. [65]</td>
<td>&lt;0.02</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.1.1.5 Vapour acetone fluorescence decay

Vapour acetone fluorescence is governed by extremely fast intersystem crossing, which limits the effective lifetime to a few nanoseconds. The lifetime itself varies depending on the sample pressure and temperature. A list of fluorescence lifetimes, quantum yields and rate constants encountered in literature, along with any relevant experimental conditions, is provided below:

<table>
<thead>
<tr>
<th>Study</th>
<th>$k_f$ ($s^{-1}$)</th>
<th>$\phi_f \times 10^{-3}$</th>
<th>$\tau_f$ (ns)</th>
<th>Exp. conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halpern and Ware [25]</td>
<td>$5 \times 10^5$</td>
<td>1.2</td>
<td>2.4</td>
<td>313nm excitation, ambient air</td>
</tr>
<tr>
<td>Heicklen [32]</td>
<td>-</td>
<td>1.7-2.1</td>
<td>-</td>
<td>280-313nm excitation, 40°C, air</td>
</tr>
<tr>
<td>Breuer and Lee [69]</td>
<td>$(5.2-8.8) \times 10^5$</td>
<td>1.7-2.1 [32]</td>
<td>$&lt;1.6-2.7$</td>
<td>260-313nm excitation, 23°C, O$_2$ present</td>
</tr>
<tr>
<td>Hansen and Lee [44]</td>
<td>$8 \times 10^5$</td>
<td>1-2.1</td>
<td>1.6-2.6</td>
<td>325nm excitation, 23°C, O$_2$ present</td>
</tr>
<tr>
<td>Koch et al. [70]</td>
<td>-</td>
<td>0.25-0.84</td>
<td>-</td>
<td>248, 266 and 308nm excitation, 296K, 4kPa-105.3kPa, N$_2$ bath gas</td>
</tr>
<tr>
<td>Ossler and Aldén [71]</td>
<td>-</td>
<td>-</td>
<td>0.5-2.5</td>
<td>266nm excitation, 323-723K, 0.002-1Mpa, air/N$_2$ bath gas</td>
</tr>
</tbody>
</table>

Hansen and Lee [44] have quoted an intersystem crossing rate constant of $3.88 \times 10^8$ s$^{-1}$ and a fluorescence rate constant of $8 \times 10^5$ s$^{-1}$. Using the fluorescence efficiency and lifetime data presented by Halpern and Ware [25] and Breuer and Lee [69], the previously quoted disparity of the order of $10^3$ between the two rate constants is confirmed. This calculation was performed on the basis of insignificant contributions by vibrational relaxation or collisional deactivation, both in accordance with literature. The rate of internal conversion was also rendered insignificant, reflecting the weak coupling between the populated $S_1$ vibrational levels and highly excited $S_0$ vibrational levels.

From the absolute fluorescence quantum yield measurements of Koch et al. [70], the following conclusions can be deduced: Firstly, the promotion of acetone molecules higher up the $S_1$ vibrational manifold by deployment of lower excitation wavelengths results to lower fluorescence efficiencies. The same trend applies to measurements carried out for higher...
temperature samples. Relative fluorescence quantum yield measurements carried out at different excitation wavelengths and sample temperatures also support this finding [58], and the trend has been attributed to an excess energy dependent ISC rate constant. Secondly, for the same excitation wavelength, higher nitrogen bath gas pressures enhance the fluorescence quantum yield. This effect can be explained on the basis of enhanced vibrational relaxation contributions; higher bath gas pressures result to higher rates of molecular collisions, which in turn force the excited molecule towards lower-lying vibrational levels. According to the previously proposed mechanism, these levels are associated with lower intersystem crossing rates, thus favouring the emission of fluorescence. This pressure-induced fluorescence quantum yield dependence is well-documented and bath gas specific [48, 72, 73]. The bath gas composition dependence arises as a result of the different effectiveness of collisional energy transfer between excited acetone singles and different colliding partners [45]. For example, for a given total pressure and acetone partial pressure, acetone-acetone collisions have been shown to be more effective at vibrationally relaxing excited acetone molecules compared to acetone-nitrogen collisions. Further, as a result of the bath gas dependency arising through the pressure-induced vibrational relaxation contribution, a slight oxygen quenching effect on the fluorescence quantum yield has also been identified.

It is noteworthy at this point to draw attention to a modelling effort of the fluorescence quantum yield dependencies of acetone. Only a brief reference is made here, while a more detailed account can be found in the relevant literature. Initially, only the effects of pressure, temperature and excitation wavelength on acetone fluorescence quantum yield were modelled [58], while subsequently Thurber and Hanson [48] also accounted for the bath gas composition dependency. Koch [74] and later Rothamer [75] adapted and advanced the model for application to 3-pentanone. Under the model formulation, the bulk of excited molecules are treated as a single average molecule. The vibrational energy distribution is approximated by a cascade of energy steps, while the excited state energies are treated as continuous. Four deexcitation processes are included: inter-system crossing, vibrational relaxation, fluorescence and collisional quenching. The total fluorescence quantum yield is calculated by summing up all fluorescence quantum yield contributions from $N$ vibrational levels occupied during the decay (Eq 4-1). Each contribution is determined as the probability that the molecule fluoresces from that level rather than decaying by some competitive mechanism, times the probability that this level has been occupied through vibrational
relaxation. Once the thermalized level is reached, only fluorescence and intersystem crossing are feasible and the sequence is terminated.

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

**Eq 4-1**

### 4.1.1.6 Liquid acetone fluorescence decay

The deexcitation mechanism of liquid acetone resembles closely that of the vapour phase; however, owing to the higher density of the liquid medium, vibrational relaxation is assumed to be complete prior to the emission of fluorescence. As a result, the bath gas pressure dependence of liquid acetone fluorescence is insignificant [42]. The close agreement between the fluorescence lifetimes and emission spectra of liquid and vapour acetone supports the notion that even for acetone vapour, fluorescence is mainly emitted from vibrational levels near the $S_1$ origin.

**Table 4-3** Liquid acetone fluorescence lifetimes, quantum yields and rate constants encountered in literature, and presented along with any relevant experimental conditions

<table>
<thead>
<tr>
<th>Study</th>
<th>$k_f (s^{-1})$</th>
<th>$\phi_f \times 10^{-3}$</th>
<th>$\tau_f (ns)$</th>
<th>Experimental considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halpern and Ware [25]</td>
<td>$8.3 \times 10^5$</td>
<td>1.4</td>
<td>1.7</td>
<td>280nm excitation</td>
</tr>
<tr>
<td>Wilkinson and Dubois [76]</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>320nm excitation, 25°C, in solution</td>
</tr>
<tr>
<td>Borkman and Kearns [62]</td>
<td>$4 \times 10^5$</td>
<td>$10 \pm 3$</td>
<td>25</td>
<td>313nm excitation, 25°C, neat acetone or in solution</td>
</tr>
</tbody>
</table>
4.1.1.7 Vapour acetone phosphorescence decay

In air, acetone vapour phosphorescence is completely quenched by oxygen and can, thus, only be detected in oxygen-free environments. Early studies of the phosphorescence lifetime of acetone vapour should be interpreted with caution, as was the population and depopulation mechanism of the $S_1$ and $T_1$ states [26, 31, 77]. The originally established phosphorescence lifetime of acetone vapour was 200µs [26], and its suppression by oxygen was immediately observed [26, 32, 77]. A rough estimate of the phosphorescence rate constant is given by Groh et al. [77] (5×10^5 s^{-1}). The phosphorescence efficiency is of the order of 10^{-2}-10^{-3} for rigid solutions excited at 313nm [62], while in the gas phase, pressure, temperature and excitation wavelength dependencies have been identified [26, 31, 77] and associated with an energy-dependent decomposition mechanism. Excitation higher up the triplet vibrational manifold, either as a result of higher sample temperatures or lower excitation wavelengths, favours the dissociation of acetone triplets rather than the emission of phosphorescence, thus reducing the phosphorescence efficiency. This excess vibrational energy dependence is analogous to the one observed for the intersystem crossing rate of acetone singlets. The gas phase phosphorescence data of Luckey and Noyes [31], Kaskan and Dunkan [26], Groh et al. [77] and Heicklen [32] have been incorporated in the pressure-dependent dissociation mechanism proposed by O’Neal and Larson [78], who reported phosphorescence quantum yields of approximately 0.042-0.002 for the 25-200°C temperature range at 20torr acetone pressure, and 0.0289-0.0005 for the same temperature range at 200torr acetone pressure. The corresponding dissociation rates are of the order of 10^{-6}sec^{-1} in the 25-75°C range, in good agreement with Cundall and Davies [79]. The decomposition products are methyl and acetyl radicals [80]. At temperatures below 100°C, the acetyl radicals can combine to form biacetyl molecules which act as sensitizers and emit phosphorescence in the green region [27]. This particular phenomenon has been observed in closed-cell acetone vapour experiments and can be avoided by utilizing flow cells instead.

Owing to the long phosphorescence emission lifetime, collisional deactivation is a very important deexcitation pathway. In the absence of molecular oxygen or any molecular species that can form a donor-acceptor pair with acetone, any collisionally-induced quenching would have to be attributed to collisions with bath gas molecules, ground state acetone molecules (self-quenching) or acetone triplets (triplet-triplet annihilation). The quenching rates of thermalized acetone triplets by different bath gases has been investigated
by Borge et al. [81], and their results suggest that neither nitrogen, nor self-quenching provide appreciable deactivation rates. Instead, the rate constant of oxygen quenching is two to three orders of magnitude higher.

<table>
<thead>
<tr>
<th>Quencher</th>
<th>Rate constant (l/mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>9.2×10^6</td>
</tr>
<tr>
<td>O2</td>
<td>8×10^6</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.2×10^7</td>
</tr>
</tbody>
</table>

Table 4-4 Quenching rate constants of thermalized acetone vapour triplets by different bath gases [81]

The effect of TTA has been investigated for biacetyl vapour by Badcock et al. [82], and has been described as an excitation energy-dependant phosphorescence lifetime shortening mechanism; as the number of light quanta absorbed by the tracer increases with increasing laser intensity, the triplet state population number density also increases and the probability of triplet-triplet collisions rises. At 25°C, following excitation at 436.5nm, the reported triplet-triplet annihilation rate constant is 4.2±1.7×10^{11} l/mol/sec; in comparison, the oxygen quenching rate constant for biacetyl is 5.5±0.2×10^8 l/mol/sec [83]. This lifetime shortening effect has also been identified in studies employing liquid biacetyl [37], whereby it was illustrated that despite the lifetime degradation, an increase in the laser fluence also results to a boost in the phosphorescence emission. Despite the fact that an analysis of the TTA mechanism for acetone has not been found in literature, the close similarity between the photophysical properties of acetone and biacetyl suggests that triplet-triplet annihilation will affect the triplet state emission of acetone in a very similar manner. In addition, the associated excitation energy density dependence implies that any lifetime measurements will be specific to the particular experimental conditions (for example, through the laser fluence and detection delay dependencies). For example, lifetime decay measurements carried out at higher fluences (higher excitation energy densities) will result in reduced phosphorescence lifetimes compared to lower fluence measurements given identical collection optics settings (detection delay and gate time). Similarly, as the TTA process is intermolecular and involves collisions between excited triplets, lifetime decay measurements carried out at longer delays are expected to result in increased lifetimes; as the TTA reaction consumes the excited triplet state population, the probability of triplet-triplet interactions and thus phosphorescence
quenching falls, allowing for higher phosphorescence quantum yields and effective lifetimes. In contrast to the early acetone vapour phosphorescence studies, the reported lifetimes encountered in recent studies are substantially lower (Table 4-5). This can probably be attributed to the combined effects of utilizing intensified CCD cameras instead of photomultipliers to reproduce the phosphorescence decay curves, which might be unable to visualize the late long tail of the emission, and the selection of experimental conditions suitable for LIF imaging rather than photophysical characterization purposes, such as high excitation energy densities, higher sample pressures. Both promote fast quenching through enhanced TTA, allowing only for the stronger and faster-decaying early emission to be resolved.

**Table 4-5** Acetone vapour phosphorescence lifetimes encountered in recent literature and presented along with any relevant experimental conditions

<table>
<thead>
<tr>
<th>Study</th>
<th>$\tau_{ph}$ (µs)</th>
<th>Experimental considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hu and Koochesfahani [40]</td>
<td>13</td>
<td>Nitrogen bath gas, 308nm excitation, ambient conditions</td>
</tr>
<tr>
<td>Hu and Koochesfahani [40]</td>
<td>~0.01</td>
<td>Air bath gas, 308nm excitation, ambient conditions</td>
</tr>
<tr>
<td>Weckenmann et al. [28]</td>
<td>&lt;3</td>
<td>Nitrogen bath gas, 320nm excitation, ~18mJ/cm² laser fluence, 5bar, 60°C</td>
</tr>
<tr>
<td>Weckenmann et al. [28]</td>
<td>~0.1</td>
<td>8% oxygen in nitrogen bath gas, 320nm excitation, ~18mJ/cm² laser fluence, 5bar, 60°C</td>
</tr>
</tbody>
</table>

4.1.1.8 Liquid acetone phosphorescence decay

Unlike the vapour phase, liquid acetone phosphorescence is observable in oxygenated, as well as oxygen-free environments. In addition, the decay rate has been shown to depend on the concentration of dissolved oxygen within the liquid, and consequently, aerated and de-aerated acetone solutions display very different phosphorescence lifetimes. Apart from quenching by any dissolved oxygen, the deexcitation pathways limiting the phosphorescence emission are not well defined. No radiative or non-radiative quantum yield data or decay rate constants were encountered in literature, while the effects of collisional deactivation of any form are expected to be even more pronounced than for acetone vapour, as a result of the substantially higher frequency of molecular collisions. Such a scenario is supported by
evidence of a biexponential, instead of single exponential, decay of the triplet state emission [29, 84] and the different temporal evolution over different detection wavelengths [41]. The phosphorescence of liquid acetone has been shown to decrease substantially with temperature, possibly due decomposition as has been reported for acetone vapour, as well as enhanced collisional deactivation. Any liquid acetone phosphorescence lifetimes encountered in literature are presented in in Table 4-6. The large variability in the lifetime data reflects the dependence of the measurement in the experimental conditions and the complexity of the deexcitation mechanism of the triplet state.

Table 4-6 Liquid acetone phosphorescence lifetimes encountered in literature and presented along with any relevant experimental conditions

<table>
<thead>
<tr>
<th>Study</th>
<th>( \tau_{ph} ) (µs)</th>
<th>Experimental considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wilkinson and Dubois [76]</td>
<td>0.4</td>
<td>320nm excitation, de-aerated hexane solution, 25°</td>
</tr>
<tr>
<td>Bortolus et al. [61]</td>
<td>30 ±2</td>
<td>337.1nm excitation, de-aerated neat acetone, 20°C</td>
</tr>
<tr>
<td>Borkman and Kearns [85]</td>
<td>1</td>
<td>300-330nm excitation, 25°C, de-aerated hexane solution</td>
</tr>
<tr>
<td>Ritchie and Seitzman [84]</td>
<td>0.244</td>
<td>266nm excitation, aerated acetone</td>
</tr>
<tr>
<td>Ritchie and Seitzman [84]</td>
<td>39.5</td>
<td>266nm excitation, nitrogen-purged acetone</td>
</tr>
<tr>
<td>Tran et al. [42]</td>
<td>( &lt;0.175 – 0.975±0.15 )</td>
<td>266nm excitation, room temperature, nitrogen-purged acetone</td>
</tr>
<tr>
<td>Tran et al. [41]</td>
<td>1.1±0.15</td>
<td>285nm excitation, room temperature, nitrogen-purged acetone</td>
</tr>
<tr>
<td>Tran et al. [43]</td>
<td>1.1±0.1 – 0.5±0.07</td>
<td>266nm excitation, 295-395K, 30-60atm, nitrogen-purged acetone</td>
</tr>
</tbody>
</table>

4.1.2 3-pentanone photophysics

Compared to acetone, less is known regarding the photophysics of 3-pentanone; despite extensive characterization efforts on gaseous 3-pentanone fluorescence, no characterization of the triplet state emission was found in literature for either liquid or vapour phases, while no liquid phase fluorescence data were available either. Despite the numerous early studies of the photolysis of 3-pentanone [86-88], the investigation of the emission characteristics was neglected. Weir [89], for example, noted the presence of a weak emission in the 385-470nm...
spectral region, and due to the spectral similarity with acetone fluorescence, assigned to 3-pentanone the same deexcitation mechanism. In the presence of oxygen, a slight shortening of the long wavelength side of the emission spectrum was observed, possibly due to quenching of the triplet state population. In addition, the strong sensitization of biacetyl triplets by excited 3-pentanone was reported.

4.1.2.1 The absorption spectrum

The room temperature absorption spectrum of 3-pentanone has been measured by numerous researchers [55, 57, 90-92]. Extending over the 230-325nm range and peaking at approximately 280nm, the spectrum is devoid of fine structure, while the measured absorption cross-sections are slightly higher than for acetone. Martinez et al. [55], for example, quoted a maximum absorption cross-section of $6.2 \times 10^{-20}$ cm$^2$ at 280nm, while Koch [74] reported a value of $6 \times 10^{-20}$ cm$^2$. Similar to acetone vapour, the absorption spectrum of 3-pentanone vapour is temperature dependent, with higher temperatures boosting the absorption intensity and red-shifting the spectrum, in particular on the long wavelength side.

4.1.2.2 The fluorescence spectrum

The fluorescence spectrum extends over 330-550nm range, peaking at around 420nm [70, 92]. The temperature, pressure, and excitation wavelength effects are analogous to the ones reported for acetone [71, 91-93].

4.1.2.3 3-pentanone vapour fluorescence

The deexcitation mechanism of 3-pentanone vapour can be identified with that of acetone. Fluorescence is emitted within a few nanoseconds, while intersystem crossing is once again responsible for readily depopulating the $S_1$ state ($k_{ISC} = 3.88 \times 10^8$ s$^{-1}$), and transferring the excited population to $T_1$. The fluorescence quantum yield dependencies on temperature, pressure, excitation wavelength and bath gas composition have been extensively investigated [70, 92, 93], and can be explained in an identical manner to those of acetone [7, 74]. A list of fluorescence lifetimes, quantum yields and rate constants encountered in literature, along with any relevant experimental conditions, is provided below:
### Table 4-7 3-pentanone vapour fluorescence lifetimes, quantum yields and rate constants encountered in literature, and presented along with any relevant experimental conditions

<table>
<thead>
<tr>
<th>Study</th>
<th>$k_f (s^{-1})$</th>
<th>$\phi_f \times 10^{-3}$</th>
<th>$\tau_f (ns)$</th>
<th>Exp. conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hansen and Lee [44]</td>
<td>$1.1 \times 10^6$</td>
<td>2.8-2.3</td>
<td>2.1-2.7</td>
<td>325nm excitation, 23°C, $O_2$ present</td>
</tr>
<tr>
<td>Ossler and Aldén [71]</td>
<td>-</td>
<td>-</td>
<td>0.5-2.5</td>
<td>266nm excitation, 323-723K, 0.002-1Mpa, air/$N_2$ bath gas</td>
</tr>
<tr>
<td>Koch et al. [70]</td>
<td>-</td>
<td>0.5-1.5</td>
<td>-</td>
<td>248, 266 and 308nm excitation, 296K, 40-1053mbar, $N_2$ bath gas</td>
</tr>
<tr>
<td>Cheung and Hanson [92]</td>
<td>3.7$^a$</td>
<td>0.05-0.95</td>
<td>-</td>
<td>248, 266, 277 and 308nm excitation, 295-693K, 1.3bar, air/$N_2$ bath gas</td>
</tr>
<tr>
<td>Cheung and Hanson [93]</td>
<td>-</td>
<td>0.05-0.95</td>
<td>-</td>
<td>248, 266, 277 and 308nm excitation, 295-745K, 1-25bar, air/$N_2$ bath gas</td>
</tr>
</tbody>
</table>

$^a$ Model fitted by authors

### 4.2 Vapour phase concentration measurements in two-phase flows

Having provided a comprehensive account of the photophysics and relevant experimental results encountered in literature for acetone and 3-pentanone, the last part of the literature review concentrates on PLIF imaging practices aimed at the characterization of evaporated tracer concentrations in two-phase flows. In discriminating between the vapour and liquid phase signals, three different approaches have been put forward; discrimination based on the signal intensity disparity between the two phases, temporal discrimination achieved by sequential detection of the fluorescence and phosphorescence, and spectral discrimination by simultaneous detection of monomer and redshifted exciplex fluorescence in donor-acceptor tracer systems. The first tactic has been extensively implemented in droplet stream experiments, the second has been attempted in liquid jets and sprays, while the last enjoys a long history in automotive spray investigations.

#### 4.2.1 Acetone PLIF in two-phase flows

As has already been noted, acetone PLIF has been extensively employed in monodisperse, mono-size droplet investigations, owing to its favourable photophysical characteristics and
“user-friendly” attributes. A major challenge in visualizing the vapour field in close vicinity to liquid droplets by acetone PLIF imaging, is that the liquid phase fluorescence is more than two orders of magnitude stronger than the gas phase [94], mainly as a consequence of the large number density disparity between the two phases. Since the commonly utilized intensified CCD cameras have a limited dynamic range, the experimental parameters are typically adjusted so that the intense liquid phase signal does not quite saturate the detector. This, in turn, results to a vapour phase signal which is close to the noise level of the camera. An additional problem in discriminating between the two phases is intense halation. The very strong signal from the liquid introduces a crosstalk with neighbouring pixels (which contain the weak vapour phase signal), resulting in an apparent increase in the spatial extent of the liquid or in an over-prediction of the vapour phase concentration near the interface [95]. It has been reported, for example, that reliable measurement of vapour concentrations is not feasible to within one droplet diameter away from the droplet surface for 235μm and 122μm droplets [96]. Other studies have reported that for 230μm droplets the extent of halation is of the order of 1-1.5 droplet diameters [95], and up to 10 droplet diameters for 173μm and 238μm droplets [97].

The emergence of optical halation using intensified cameras can be traced back to two causes, both associated with the micro-channel plate (MCP); namely optical and electron scattering [98, 99]. Both effects are schematically represented in Fig 4.1. In the first case (photon 2), a small fraction of the collected light is transmitted through the photocathode and reflected from the interstices of the glass structure. Upon reencountering the photocathode, photoelectrons are released, accelerated and multiplied in adjacent pores. Approximately 20% of the halation phenomenon can be attributed to this mechanism [100] with the ensuing halo being highly localized. The remaining 80% originates from primary photoelectron collisions with the MCP interstices (photon 3). The scattered photoelectrons are accelerated back towards the MCP, enter through neighbouring pores, and give the impression of a spurious event. In that case, an extended symmetric halo over several pixels is observed [101, 102].
Fig 4.1 Schematic representation of photoelectron generation at the photocathode and multiplication at the MCP without halation (photon 1) with halation due to optical scattering (photon 2) and with halation due to electron scattering (photon 3).

Since halation is a detector-induced artefact, a non-intensified camera or electron multiplying CCD (EMCCD) sensitive to the spectral range of acetone fluorescence would suffer less from the particular effect [103, 104]. However, intensified cameras are commonly employed in studies such as the ones cited earlier, in order to enhance the low vapour phase fluorescence signal. In addition, non-intensified cameras suffer from substantially higher jitter, offer limited control of the exposure time (which is generally much larger compared to the timescale of fluorescence emission) and provide limited adjustability of the intensity of the strong liquid phase signal, which in the case of intensified cameras, can be fine-tuned by adjusting the gain. In that way, the dynamic range of the detector can be fully exploited and the dynamic range over which the weak vapour signal is imaged can be boosted.

In tackling halation, the practice of establishing a cut-off signal to distinguish between the vapour and liquid phase plus halation signals has been introduced [105]. Other researchers have adopted this method [104, 106], most commonly by calibrating the saturated acetone vapour signal independently. The location, near a droplet, where the collected signal drops to the saturated vapour fluorescence level is, however, shifted away from the droplet surface due to halation. Consequently, the spatial extent of the droplet is overestimated. Alternatively, the use of Mie scattering images from ethanol droplets in order to obtain the radial profile of halation, and thus the location of the interface, has also been proposed and practiced [95]. Frackowiak and co-workers [97] have adopted an entirely different approach.
in locating the liquid-vapour interface. They have shown that by masking the liquid phase fluorescence, an uncontaminated vapour phase signal up to a certain distance away from the liquid-vapour interface can be obtained. The fluorescence emission from the droplet and its subsequent collection by the detector is then modelled based on the Lorenz-Mie theory and geometric optics. Knowledge of the droplet size and acquisition of both masked and unmasked images of the droplet stream allow for extrapolation of the vapour field in close proximity to the droplet surface, as well as accurate location of the interface. This method, however, presents some severe drawbacks. Apart from the inherent complexity of its setup (which necessitates the utilization of a physical mask) and the application of numerical methods in order to correct for halation effects, this tactic cannot be applied in a measurement field where the droplets are not arranged so that the liquid phase can be effectively masked, for example in a spray.

In order to demonstrate the aforementioned effects of halation and large signal disparity between the two phases, a single fluorescence image of an acetone droplet stream in saturated acetone vapour in air is presented for two different dynamic ranges (Fig 4.2(c) and 4.2(d)). Excitation was provided by a RadiantDyes 308nm XeCl excimer laser, while images were recorded using a state of the art LaVision Imager Intense CCD camera system optically coupled to an image intensifier (S20 multi-alkali photocathode, P43 phosphor screen). For comparison, the droplet stream was also imaged using diffuse white light illumination from the background (Fig 4.2(b)), while experimental parameters relevant to the presented images are included in Fig 4.2(a). The laser sheet thickness $t$ is approximately $400\mu m$, the average droplet diameter $D_d$ is $330\mu m$ and the average inter-droplet separation $S_d$ is approximately $1\text{mm}$. In Fig 4.2(c) the droplet stream fluorescence image is presented with a high dynamic range, and only the liquid phase is visible as a consequence of the weak vapour phase fluorescence. The same image is presented in Fig 4.2(d) with a much lower dynamic range, allowing both vapour phase and halation to be visible.
Fig 4.2 Results from a stream of acetone droplets in saturated acetone vapour in air. (a) Schematic of the illuminated droplet stream. (b) White light image of a droplet stream under diffuse background illumination. (c) Fluorescence image of the stream with 0-1000 counts dynamic range. (d) The same fluorescence image presented with 0-100 counts dynamic range

The challenges induced due to halation in determining the location of the liquid-vapour interface and the evaporated tracer concentration near the droplets are: The droplets appear to be approximately 1.5 times larger than they actually are (around 500μm instead of 330μm), whilst the regions surrounding the droplets appear brighter, suggesting locally higher acetone vapour concentrations. However, since the image is obtained in a saturated acetone vapour environment, the vapour phase concentration is spatially constant and this apparent increase is purely an artefact attributed to halation. The same effect can also be observed in the “shadow” region to the right and in the immediate vicinity of the droplets. Due to strong absorption of the laser pulse by the liquid phase, the local vapour phase fluorescence intensity is expected to drop abruptly but still remain effectively constant. However, a locally brighter signal extending to approximately one droplet diameter away from the apparent droplet surface is once more observed. An uncontaminated vapour acetone signal corresponding to the real fluorescence intensity within the droplet shadow area can be obtained further away from the droplet surface.

In an attempt to overcome these challenges and provide an improved imaging approach, a series of experiments aimed at characterizing the fluorescence and phosphorescence emission from both phases were set up and will be presented. These measurements reveal the potential for better visualizing acetone vapour concentrations in the presence of liquid droplets by addressing the two aforementioned shortcomings associated with two-phase flow acetone LIF. Therefore, visualization experiments of evaporative and non-evaporative acetone droplet streams and their surrounding vapour fields by both LIF and
LIP will be presented for demonstrative purposes, while the vapour field around evaporating droplet streams will be quantified by both optical techniques, in an attempt to quantitatively address the suitability of laser induced phosphorescence for two-phase flow imaging.

4.2.2 Acetone Planar Laser Induced Fluorescence and Phosphorescence (PLIFP)

Aimed at the study of mixture fractions in subcritical, transcritical and supercritical two-phase flows, this technique is based on the temporal discrimination of liquid phase phosphorescence (in air bath gas) and combined liquid and vapour fluorescence signals [29]. Originally, PLIFP was developed and employed in the following manner: The phosphorescence signal from a nitrogen-purged liquid acetone jet was used to delineate the liquid-vapour boundary as well as the subcritical/supercritical interface, whereas the vapour fluorescence was employed in quantifying the evaporated tracer number density and mixture fraction in regions occupied exclusively by the gaseous tracer. Since even trace amounts of oxygen can quench the vapour phase phosphorescence very efficiently, phosphorescence images provide “uncontaminated” liquid phase signals, allowing for the two-phase boundary to be located. The subcritical/supercritical interface was identified on the basis of increased oxygen diffusivity in the supercritical fluid, manifested by a large drop in the phosphorescence intensity through enhanced oxygen quenching. In comparison, the fluorescence signal remained unaffected. In developing this imagining tactic, the phosphorescence and fluorescence of liquid acetone were calibrated, following 266nm and 285nm excitation, over a wide temperature (approximately 300-400K) and pressure range (up to 60atm). While the former was shown to be independent of both temperature and pressure, liquid acetone phosphorescence was invariant only with pressure and decreased exponentially with temperature [42, 43, 107]. In addition, owing to its longer lifetime, the dependence of liquid acetone phosphorescence on camera delay and gate settings was also assessed [41, 84].

A practical implementation of simultaneous fluorescence and phosphorescence imaging is hereby presented using a high-pressure ($P_{inj}=150$bar) GDI injector in order to introduce an acetone spray in ambient air ($T_{amb}=297$K, $P_{amb}=1$bar). Combined vapour and liquid phase fluorescence, liquid-only phosphorescence and evaporated acetone mole fraction images are presented (Fig 4.3) for two instances during the 1.5ms injection duration: $0.2\pm0.1$ms and $1.0\pm0.1$ms after the start of injection (ASOI). The fluorescence was captured using a non-
intensified LaVision Imager Intense CCD camera, while the phosphorescence (collected at 20ns after the fluorescence emission with 200ns gate and 70% gain) was imaged using the previously employed IRO (intensified relay optics) plus intensified camera setup. The laser pulse propagates from left to right in these images, while only the left half of the spray is displayed, as the right hand side suffers from substantial attenuation.

**Fig 4.3** Combined vapour and liquid phase fluorescence (left), liquid-only phosphorescence (middle) and evaporated acetone mole fraction (right) single-shot images of a pressure-atomized GDI spray injected in ambient air. The presented images correspond to two instances during the 1.5ms injection duration: 0.2±0.1ms and 1.0±0.1ms after the start of injection (ASOI).

By deployment of both imaging tactics, a thin (1.5-2mm) shear mixing layer can be identified immediately adjacent to the liquid boundary at 0.2ms ASOI, while 0.8ms later, the extent of the vapour region rises to as much as 10mm. In both cases, evaporated tracer mole fractions of approximately 0.20 were observed prior to detection of liquid phase phosphorescence. The efficacy of the technique in correctly identifying the two-phase boundary and allowing for correct evaluation of evaporated tracer concentrations is essentially dependent upon the threshold level distinguishing between intensifier noise and liquid acetone phosphorescence, and consequently the sensitivity of the optical setup in detecting phosphorescing liquid droplets. Hence, small droplets could still be present within
the vapour region and be treated as evaporated acetone. Under the particular experimental conditions, the size of a single droplet contributing the same fluorescence signal as a pixel containing saturated acetone vapour can be approximated by equating the gaseous tracer mass with the mass of a spherical droplet. The assumptions involved in this crude calculation are that the fluorescence yields of liquid and vapour acetone are the same, and that scattering is negligible:

\[
\frac{P_a V_{pix} M_a}{RT_{amb}} = \frac{4}{3} \rho_a \pi r_d^3
\]

\(V_{pix}\) stands for the illuminated volume imaged by a single pixel (optical magnification times laser sheet thickness), \(T_{amb}\) is the temperature, \(P_a\) is the acetone vapour pressure at \(T_{amb}\), \(P_{amb}\) (FLUIDAT® on the Net by Bronkhorst High-Tech B.V.), \(\rho_a\) is the density of liquid acetone (FLUIDAT® on the Net by Bronkhorst High-Tech B.V.), \(M_a\) is the acetone molar mass (FLUIDAT® on the Net by Bronkhorst High-Tech B.V.) and \(r\) is the droplet radius. The result suggests that a 20μm diameter droplet would produce the same fluorescence intensity as the incremental illuminated volume (\(V_{pix}\)) filled with saturated acetone vapour; hence the unidentified liquid volume within the air/acetone mixing region corresponds to approximately a fluorescing liquid tracer volume equivalent to that of a 20μm diameter spherical droplet.

An alternative approach regarding the utilization of acetone PLIFP was proposed by Kiel et. al. [108]. The authors argue that since the phosphorescence, similar to the fluorescence, is emitted from the droplet volume rather than the droplet surface (which is the case for the Mie scattering signal), it should be possible to correlate the two signals and implement liquid phase fluorescence corrections in evaporating sprays using the phosphorescence liquid phase signature. In that way, evaporated tracer concentrations could be extracted from within the spray break-up zone. Encouraging results were presented for both hollow-cone and solid conical core sprays, with spray fluorescence and phosphorescence images shown to correlate well with each other (upon subtraction by random scaling factors). The second formulation of combined PLIFP is believed to provide a promising approach regarding the utilization of phosphorescence imaging in spray investigations, and in order to examine its potential, a suitable experiment was designed and will be presented in Section 7 of the report. This decision stemmed in part from the encouraging data generated in developing the LIP
technique for evaporated acetone concentration measurements in the vicinity of liquid droplets, as well as the significant challenges encountered in literature regarding the quantitative implementation of LIEF imaging (Subsection 4.2.3).

4.2.2.1 Critical evaluation of the applicability of PLIFP in two-phase flow experiments

Despite offering an effective way for discriminating between the two phases, PLIFP does not present significant advantages over the use of, for example, Mie-scattering in locating the liquid-vapour boundary. The latter is stronger as well as insensitive to oxygen and temperature quenching, potentially proving superior in that role. However, the results of Kiel et. al. [108] suggest otherwise, at least regarding the investigation of polydisperse droplet structures. Delineating the subcritical/supercritical boundary is unique to PLIFP, however, the transition region cannot be clearly defined as the effect of oxygen quenching (through enhanced oxygen diffusivity), temperature-induced phosphorescence degradation and liquid density reduction cannot be separated. Nevertheless, a droplet thermometry technique based on combined PLIFP imaging (through fluorescence/phosphorescence ratios) should be feasible. Regarding the challenges discussed earlier with respect to vapour concentration measurements in the periphery of evaporating liquid droplets, namely the low signal intensity and halation contamination, PLIFP imaging cannot be used to address them directly. However, the liquid-only phosphorescence signal from non-evaporating liquid droplets could be employed in tandem with the fluorescence in order to obtain a halation profile; the latter could then be used to correct fluorescence images. The particular procedure, albeit with the use of Mie signals, has already been successfully implemented [95].

4.2.3 Laser Induced Exciplex Fluorescence LIEF

The basis of LIEF imaging, introduced in the early 80s by Prof L.A. Melton, is that charge transfer processes between excited state “donor” and ground “acceptor” molecules result to the formation of exciplex systems which produce spectrally distinct fluorescence compared to either monomers. In the liquid, charge transfer processes occur readily owing to frequent collision events within the radiative lifetime of the excited donor (of the order of 10-100ns); thus, exciplex fluorescence serves as the liquid phase signature. In the vapour phase, the number density of donor and acceptor molecules is low, and monomer emission dominates.
The photophysical processes resulting to monomer excitation and radiative deexcitation, exciplex formation and subsequent radiative decay are represented by Eq 4-3 – Eq 4-6.

\[ R + h\nu_{\text{laser}} \rightarrow R^* \quad \text{Eq 4-3} \]

\[ R^* \rightarrow R + h\nu_{R^*} \quad \text{Eq 4-4} \]

\[ R^* + N \rightarrow R -* -N \quad \text{Eq 4-5} \]

\[ R -* -N \rightarrow R + N + h\nu_{R-->N} \quad \text{Eq 4-6} \]

\(h\nu_{\text{laser}}\) is absorbed by the ground state monomer \(R\) resulting to electronic excitation (\(R^*\)). Upon colliding with an acceptor \(N\), the exciplex system \(R -* -N\) is formed. Radiative deexcitation of the \(R -* -N\) exciplex results to the emission of a photon of energy \(h\nu_{R-->N}\), and the breakup of the excited complex to its constituent molecules. The strength of the interaction between \(R^*\) and \(N\) determines the energy of the emitted photon \(h\nu_{R-->N}\). Alternatively \(R^*\) deexcitation proceeds by radiative emission of energy \(h\nu_{R^*}\) (monomer fluorescence).

4.2.3.1 LIEF application to two-phase flows

The first LIEF [3] system employed a 10% naphthalene/1% TMPD tracer pair seeded in cetane and excited at 313nm, while a spray visualization technique employing the same components, albeit at different concentrations (2.5% naphthalene/1% TMPD), was introduced shortly afterwards [109]. Amongst the challenges associated with the implementation of LIEF, the liquid/vapour cross-talk (liquid phase fluorescence contributions to the vapour phase signal and vice versa) and its dependencies on the mixture spectral properties, the strong oxygen quenching of both monomer and exciplex fluorescence and finally the relative tracer concentrations and appropriate filter selection were brought forward. The strong dependence of exciplex fluorescence on temperature and its potential employment for liquid phase thermometry were also examined during these early studies [110]; the exciplex to monomer emission ratio remained almost invariant up to 140 °C, but from that point on and up to 265 °C, the emission was shown to shift almost entirely to the monomer side. In order
to improve the interpretation of LIEF data for quantitative two-phase measurements, absolute quantum yields were obtained and published for four different exciplex-forming systems [111], whereby the original naphthalene/TMPD mixture was awarded the highest suitability (quantum yield of 0.13% at 308nm and 337nm excitation) and modest temperature response. A first direct calibration effort for a 1% TMPD/10% naphthalene in decane mixture was later carried out by Rotunno et al. [112]. In contrast to the tactic brought forward by Melton and co-workers, the in situ liquid/vapour ratio calibration of known quantities of evaporated and non-evaporated tracers was preferred by the particular research group and employed in a quantitative spray analysis.

Up until that point, research on exciplex systems focused on tracer components most relevant to diesel sprays; Melton [113] first performed an assessment of mixtures comprised of tertiary amines, fluorine-substituted aromatics (toluene and benzene) and hexane or isooctane, better matching the volatility range of gasoline-like fuels. All “recommended” systems necessitated excitation below 266nm, and despite the fact that they were assigned “excellent” coevaporation, they all displayed a strong shift towards monomer emission at higher temperatures. As a consequence of the observed spectral shift, the liquid/vapour cross-talk increased dramatically, rendering the interpretation of detected signals problematic. However, the particular behaviour was subsequently exploited in the development of liquid fluorescence thermometers capable of generating temperature measurements with near-degree accuracy up to 400°C [114].

Following, this initial attempt by Melton to expand LIEF imaging to tracers better matching the volatility range of gasoline-like fuels, the potential of the fluorobenzene (FB)/DEMA/isoctane system for quantitative liquid/vapour concentration measurements was explored by Felton [115], while Ghandhini et al. [116] were the first to access the possibility of quantitative vapour phase LIEF imaging of gasoline-like fuels directly in an engine. Their results (tenfold drop in FB emission over the 300-600K range) indicated that quantitative interpretation of vapour phase signals was precluded by strong temperature-induced quenching, and that quantitative studies are only feasible in single-phase (vapour) regions with small temperature gradients. A similar behaviour was reported for the N,N-dimethylaniline (DMA)/1,4,6-trimethylnaphthalene(1,4,6-TMN)/isoctane system examined by Kim et al. [23], and later calibrated for quantitative two-phase spray visualization [117]. Fröba et al. [24] calibrated the TEA/benzene/isoctane system for the purpose of conducting fuel measurements in SI engines. Unlike previous researchers, the oxygen quenching effect
on monomer fluorescence was employed in obtaining quantitative fuel-to-air ratio data during compression, while the effects of pressure and temperature on the system emission were accounted for using previously conducted calibration measurements. Signal cross-talk was not completely eliminated, but having obtained exciplex/monomer fluorescence image pairs, subtractions of liquid phase contributions to vapour images were performed. Qualitative results of two-phase fuel distributions inside a PFI engine were also presented by Kelly-Zion et al. [118] using two exciplex systems representative of the light and heavy components of commercial gasoline.

Despite the fact that the capabilities and limitations of LIEF became fully apparent from research published over the course of almost two decades, interest on the technique persisted owing to its unique capability of simultaneously visualizing both liquid and vapour phases, thus yielding qualitative or semi-quantitative results of mixture formation studies of both diesel [119-122] and gasoline [123] sprays in a relatively straightforward manner. However, in order to reduce the errors associated with quantitative measurements, a complete assessment of the dependencies of both exciplex and monomer fluorescence was rendered necessary. For this purpose, a comprehensive investigation of the TMPD/α-methylnaphthalene (1-Me-Np) system, its application in diesel sprays and an assessment of the most significant errors sources were carried out by Desantes et al. [124]. Their work clearly highlights the complexity associated with the successful quantitative implementation of LIEF and emphasizes on the limitations of its applicability. Based on independent calibration experiments, both cross-talk and quenching corrections were proposed and later implemented in LIEF investigations of diesel sprays [125].

An alternative approach towards accounting for liquid-vapour cross-talk was put forward by Wieske et al. [126, 127]. The employed mixture was the FB/DEMA/hexane, while an optical setup allowing for fourfold imaging of the two-dimensional field of interest was employed. Two images were used to perform two-line liquid phase (exciplex) thermometry, and one to collect the vapour phase emission. Since a direct measurement of liquid temperature became available, corrections for temperature-dependent crosstalk were incorporated. The monomer emission was also calibrated for oxygen mole fraction, yielding air-to-fuel ratio measurements. The simultaneous quenching effects of temperature and oxygen to monomer emission were, however, not addressed. A complete temperature dependence characterization of the same exciplex-forming pair was later carried out [21], whilst an attempt to characterise the liquid and vapour fuel distributions in a GDI spray can
be found in [22]. Based on the preceding study, a direct in situ calibration of the LIEF technique was performed, while double illumination was employed in order to address both laser attenuation and scattering effects, characteristic of dense sprays. The cross-talk correction was much improved, but as the authors admit, still remained imperfect.

**4.2.3.2 Critical evaluation of the applicability of LIEF in two-phase flow experiments**

Despite offering the unique capability of spectrally discriminating between the liquid and vapour phase signals, exercising the LIEF technique involves a series of challenges. The fluorescence of both aromatic and amine tracers used in exciplex-forming systems is strongly quenched by oxygen, and consequently, LIEF experiments are often limited to nitrogen environments. Selecting air as the bath gas for such experiments allows for air-to-fuel ratio measurements, an approach that entails two severe limitations; the emission from the quenched vapour phase becomes very weak, thus producing noisy signals, whilst any temperature variations induce additional uncertainties. These arise from the sensitivity of monomer emission to temperature variations, effectively making the discrimination between any temperature-induced signal drop and oxygen quenching extremely cumbersome. The temperature-dependent behaviour of monomer emission cannot be employed for thermometry purposes either, as this would necessitate the simultaneous knowledge of vapour phase concentrations. Thus, some other means for correcting for temperature-induced effects must be available; either through the employment of computational methods or by liquid phase temperature measurements (two-colour detection of the exciplex fluorescence). Neither of the two approaches, however, guarantees reliable corrections.

Another limitation stemming from the photophysics of LIEF is the spectral overlap between the monomer and exciplex emission, manifested as liquid-vapour signal cross-talk. This hampers the vapour phase measurement more severely due to the substantially higher number density of the liquid phase, at least at lower temperatures at which temperature-induced quenching of the exciplex emission is limited. Moreover, the liquid-vapour cross-talk is strongly temperature-dependent and thus, any calibration effort must include a temperature-dependent correction. Even if such a correction is implemented, literature data suggest that substantial uncertainties are unavoidable. The extent of cross-talk is associated with the choice of the exciplex-forming components, their relative concentrations and the interference filters used in the two detection channels. Optimization of these parameters
allows for suppression, but not elimination, of the particular phenomenon. A final practical
difficulty associated with the quantitative interpretation of LIEF-based measurements is the
coevaporation of the tracer components and base fuel. This criterion must be satisfied by
appropriate selection of all three constituents of the mixture. So far the challenges inherent to
the application of LIEF have been discussed; however, it should essentially be noted that the
difficulties generally associated with laser diagnostics in optically dense media, such as laser
light extinction, signal attenuation and multiple scattering also persist.

The literature research analysis on ketone excitation and deexcitation has revealed that the
phosphorescence emission in air bath gas is limited to the liquid phase only, whereas the
fluorescence emission is common to both phases. Thus, quantitative knowledge of the
correlation, if any, between the prompt fluorescence and trailing phosphorescence emission
could, in theory, allow for liquid phase fluorescence contributions to be accounted for in a
two-phase flow experiment, such as an automotive spray, by sequential visualization of both
light-emitting processes. As has already been noted, this idea was brought forward by Kiel et
al who attempted such corrections by subtracting acetone spray phosphorescence images
from their fluorescence counterparts. If attainable, this combined PLIFP technique would
allow for vapour phase concentrations to be extracted from within a spray, and provide an
alternative to LIEF. In order to access the feasibility of this idea, an experimental
investigation was developed around a high pressure GDI spray. Based on the present ketone
phosphorescence investigation, the experimental conditions were optimised for the particular
study and an appropriate methodology was developed and adopted. The main objectives of
this investigation are the extraction of liquid phase acetone and 3-pentanone fluorescence
data from within the spray structure, the generation of correlation functions between the two
emissive processes and the implementation and assessment of the efficacy of liquid phase
signal corrections.
5 Development of an Experimental Facility

Two principal experimental configurations are described in this section of the report. The first, entitled *Droplet Stream Experiments*, is dedicated to ketone emission lifetime measurements carried out in a quartz cuvette, as well as in liquid and gas flows, and ultimately measurements performed in droplet streams. The second, labelled *Spray Investigations*, was designed with the ultimate goal of conducting spray measurements that entail the near-simultaneous imaging of fluorescence and phosphorescence signals by use of two separate detectors and was implemented as an extension of the former.

5.1 Droplet Stream Experiments

The experimental facility described in the following pages was developed in order to conduct three sets of experimental measurements; the temporal emission decay curves of liquid and vapour acetone and 3-pentanone in air and nitrogen, a comparative evaluation of fluorescence and phosphorescence images of acetone droplet streams and the surrounding vapour, and quantitative measurements of the vapour field around an evaporating acetone droplet stream by both laser induced fluorescence and phosphorescence. Temporal decay measurements were originally conducted in bulk liquid acetone and 3-pentanone in a quartz cuvette, and later in thin liquid streams inside an in-house designed and purpose-built flow cell. The arrangements employed in both cases were similar, albeit with a few important alterations; the latter was, however, also employed throughout the course of droplet streams experiments, and is therefore presented first (Fig 5.1).

A Radiant Dyes XeCl excimer laser (308nm) was used for excitation of the liquid and vapour tracer flow set up inside a cell equipped with optical access. Fluorescence and phosphorescence images were collected using a CCD camera (LaVision Imager Intense) attached to an image intensifier with an S20 multi-alkali photocathode and a P43 phosphor screen, and equipped with an 85mm f/1.4D IF Nikon Nikkor lens. The magnification was approximately 28μm/pixel owing to the utilization of extension rings (6.6cm). The linearity of the combined intensifier-CCD camera system was confirmed using a set of neutral density filters of different optical densities (ODs). Three Ø2" neutral density (grey) filters were also employed during imaging in order to prevent saturation of the collected signal when
necessary. The quoted transmittance and optical densities of these filters are 20% (OD 0.7), 1% (OD 2.0) and 0.1% (OD 3.0) respectively. No high-pass filter was used to block any elastically scattered light from the excitation pulses, as the employed lens is non-transmissive in the UV.

![Fig 5.1 Schematic of the optical setup used throughout the laminar stream and vapour phase emission decay experiments, as well as droplet stream imaging experiments](image)

A beam sampler was placed at 45° to the plane of propagation of the laser sheet, directing approximately 10% of the excitation energy to a pyroelectric energy sensor (ES245C from THORLABS) connected to a power meter (PM100D from THORLABS). Pulse energies were recorded for all collected images, while the pulse-to-pulse energy variation and overall performance of the laser at different high voltage (HV) discharge settings were also assessed. A cylindrical f=500mm plano-convex lens was used to focus the laser sheet down to a thickness of 400μm, while the height of the laser sheet was adjusted to 25mm by means of an iris and an f=−500mm plano-concave lens. A custom-made droplet generator equipped with a piezo-electric oscillator was set up on top of the cell. The droplet generator electronics were comprised of a Thurby Thandar Instruments TG210 2MHz function generator and an amplifier, allowing for different frequency and of adjustable intensity signals to be applied to the piezoelectric crystal. Depending on the acetone flow rate to the droplet generator and the input signal frequency, droplet streams of different droplet sizes and different inter-droplet separations were obtained. Four gas lines were used for purging the cell with nitrogen,
saturated acetone vapour in air or saturated acetone vapour in nitrogen. Acetone vapour was supplied from a seeder purged with air or nitrogen. When conducting the liquid phase phosphorescence decay measurements, a smooth continuous stream rather than a droplet stream was set up by switching the droplet generator electronics (frequency generator and amplifier) off, and adjusting the nitrogen pressure to the vessel. Three pinholes of 600μm, 200μm and 100μm diameter were used, the first two in the emission decay experiments and the second and third in the droplet stream experiments.

As has already been noted, the original setup developed for examining the emission decay of acetone and 3-pentanone employed a quartz cuvette in place of the flow cell. The characterization of emission properties in this manner, and in particular in the liquid phase, is substantially less cumbersome and more practical than in liquid streams for a plethora of reasons. For example, the size of the illuminated volume can be clearly identified, allowing for a more precise determination of the effect of laser fluence to the phosphorescence decay rate, with far better repeatability compared to the liquid stream experiments, which were sometimes plagued by the instabilities developing over the course of an experimental run. In addition, the effect of nitrogen purging and deoxygenation on the phosphorescence intensity, along with the proximity to completion of the process, could be monitored in real time. The main disadvantage of the particular setup is that any photodissociation products remain in the probe volume and possibly act as sensitizers (in the case of the liquid). For acetone, the principal dissociation process is disintegration to acetyl radicals and methyl groups, effectively producing biacetyl. For static cells, even in the gas phase, the emergence of sensitized biacetyl phosphorescence has been reported for excitation at 308nm \cite{27}. Meanwhile, Seitzman and co-workers. \cite{41, 84} have reported an additional artefact associated with lifetime measurements carried out using a similar setup. In an attempt to measure the phosphorescence lifetime of acetone in the liquid phase by illuminating bulk acetone in a cuvette, the researchers reported the presence of an intense background signal emanating from the cuvette itself, and resulting to an unrealistic measurement of the liquid phase phosphorescence lifetime (39.5μs) \cite{84}. The particular phenomenon was, however, not apparent in the current attempts, as images collected with the laser firing but with no tracer displayed near-noise background signal intensities. Despite the aforementioned drawbacks, the characterization of acetone and 3-pentanone phosphorescence in the bulk allows for qualitative evaluation of the lifetime dependencies, providing valuable insight that is
otherwise missing from studies employing modern 2-D tracer-based diagnostics. The modified cuvette experimental setup is presented below (Fig 5.2):

The employed cuvette (purchased from Hellma-Analytics) is made of quartz glass and has a capacity of 7ml. A modified lid was designed in order to accommodate inlet and outlet gas lines for nitrogen and vapour tracer purging, while a versatile mounting base allowing for retrofitting a mask in order to block any reflections was designed and manufactured out of black Delrin (polyoxymethylene). Other modifications compared to the setup shown in Fig 5.1 include the introduction of a rectangular aperture in order to extract a relatively homogeneous section of the laser pulse, and rail-mounted carriers on which the laser sheet optics were installed. By translating the lenses along the laser sheet direction of propagation, the focal point was shifted away from the probe volume, thus allowing for variable laser fluences to be obtained without changing the laser-out energy. In the particular arrangement, the liquid tracer emission is monitored at right angles relative to the laser sheet direction of propagation. The light-emitting volume corresponds to a thin layer (few hundred micrometres) immediately adjacent to the cuvette wall, owing to the strong extinction displayed by the dense light-absorbing medium. The mirror closest to the cuvette was also installed on a rail carriage, allowing for illumination of the front, rather than the side cuvette surface at an angle of around 45º relative to the collection optics. Decay measurements were conducted using both aforementioned arrangements.

**Fig 5.2** Schematic of the optical setup used in the emission decay experiments carried out by deployment of a quartz cuvette
5.1.1 **Droplet Generator and Gas Line Setup**

A schematic of the droplet generator and gas line setup is presented in Fig 5.3. A PTFE line emanating from a 2 litre capacity reservoir was responsible for supplying the droplet generator with liquid tracer. Two tracers were employed in these measurements; acetone (≥99.5%, purchased from VWR) and 3-pentanone (≥99.0%, purchased from Sigma-Aldrich). Prior to an experimental run, the reservoir was filled with approximately 1.0 litre of liquid tracer. The tracer output flow rate was controlled by adjusting the inlet N\textsubscript{2} pressure in the 0.5-1.0 bar range. When the generation of a continuous laminar stream was desired, the reservoir was pressurized to 1.5 bar (absolute) and the droplet generator electronics were switched off, while in producing droplet streams, the pressure was set to 2.0 bar absolute and the electronics were operated. N\textsubscript{2}, rather than air, was used to pressurize the reservoir on account of safety reasons. When purging the liquid tracer inside the reservoir, N\textsubscript{2} was allowed to flow through the purging line with the reservoir pressure relief valve open and the purging line connected to the laboratory exhaust. The purging line steel pipe which was immersed inside the liquid was equipped with a T-section and a pair of sintered bronze caps, thus increasing the contact surface area between the gas/liquid interface. The N\textsubscript{2} flow rate was set to 1.0L/min, while the deaeration procedure was carried out for approximately 40 minutes.

![Fig 5.3 Schematic of the droplet generator and gas line setup employed throughout the droplet stream experiments](image-url)
The droplet generator operates on the basis of ultrasonic excitation. The principal component is a mild-steel tube, which effectively acts as a fluid reservoir. Two piezoelectric blocks attached to flat recesses on the tube outer surfaces are responsible for transmitting vibrations along the transverse axis of the steel body to the fluid. The fluid exits the droplet generator through a thin laser-drilled pinhole housed within a brass end-cap. A brass ring is placed atop the pinhole, providing firm seating and alignment. Owing to the small thickness of the employed pinholes (approximately 25µm), plastic deformation ensued upon application of even minute mechanical stresses, for example, when fixing the end-cap onto the droplet generator body. As a result, stream irregularities and divergence would ensue. Extreme care was, therefore, taken when handling or exchanging the particular component. Stream divergence also arose when solid impurities present in the reservoir or piping were trapped in the pinhole aperture. Under such circumstances, an ultrasonic bath was employed in order to eliminate the blockage. The generated droplet sizes can be calculated analytically by volume conservation provided the liquid flow rate and excitation frequency are known [128].

Saturated acetone vapour was supplied to the fluorescence cell via an in-house designed and manufactured seeder. The seeder body and top plate were both made of aluminium, while the inlet air/N₂ pipe was equipped with an identical pair of sintered bronze caps, as the ones installed in the reservoir purging line. The flow rate of air/N₂ gas to the seeder was set to 1.0 l/min for all experiments. In selecting the particular flow rate, the fluorescence emission of acetone vapour was monitored. The flow rate to the seeder was increased in 0.1 l/min steps over 10 minute intervals while averaged signals were collected. For flow rates below 0.6 l/min, the signal kept rising while between 0.7 l/min and 2.0 l/min the fluorescence intensity was effectively constant, suggesting that the cell was saturated with the vapour tracer. The use of an aluminium seeder was preferred to the employment of a gas washing bottle owing to the robustness of the former. In saturating the fluorescence cell with nitrogen or evacuating it of any vapour residuals using the shop air supply, the same gas lines responsible for delivering saturated vapour in air/N₂ were employed. In that case, the line leading to the seeder outlet was isolated. All gas lines were made of PTFE.
5.1.2 *Fluorescence Cell*

An exploded view of the fluorescence cell employed throughout the emission decay and droplet stream experiments is presented below:

![Exploded view of the fluorescence cell](image)

**Figure 5.4** Exploded view of the fluorescence cell two-piece body plus windows assembly. The design and engineering drawings were produced in SolidWorks.

The fluorescence cell was machined from black Delrin in order to minimize reflections. It is comprised of a top plate allowing for optical access, droplet generator entry and gas purging, and a bottom plate through which the liquid stream exits. Together, they form a cylindrical chamber. A large chamber diameter (90mm) was selected so that fluorescence and phosphorescence images of evaporating droplet streams could be collected in succession without any significant gaseous tracer build-up. Two AR-coated fused-silica Ø1” windows were installed in the laser entrance and exit apertures, while a Ø1” uncoated CaF$_2$ window was installed in the front window aperture. The gas supply was split twice, forming four separate lines; these were connected to four pneumatic fittings installed on the cell top surface. The liquid exiting the cell was directed via a PTFE line fixed to a pneumatic fitting located at the bottom of the cell to a collection bottle.

When purging the cell, for example with N$_2$ or acetone-seeded N$_2$, it is essential to allow enough time for any residual oxygen to be completely evacuated. As has already been noted, the vapour phase phosphorescence is completely quenched at ambient air conditions; however, at lower oxygen concentrations, a faint signal emerges and grows until the ambient gas is completely devoid of quencher molecules [28]. As even trace quantities of oxygen are
capable of significantly affecting the observed signal intensity, it is crucial to verify that no oxygen remains in the cell. In doing so, both the fluorescence and phosphorescence emission of acetone-seeded nitrogen were monitored over time. In measuring the temporal evolution of acetone vapour build-up by laser induced phosphorescence, the intensifier gate was moved away from the fluorescence and into the phosphorescence emission regime, the gate was set to 1.2µs and the gain was adjusted to 70%. The nitrogen flow rate to the seeder was set to 1.0 l/min, and 10-image sets were collected every 30s over a 15min period. Average phosphorescence signals were extracted from a 50x50pixel ROI and plotted against the acquisition period (Fig 5.5).

![Fig 5.5 Average acetone vapour fluorescence and phosphorescence plotted against the cell purging time for a seeder N_2 flow rate of 1.0 l/min](image)

The same procedure was repeated with the delay advanced so as to monitor the vapour phase fluorescence, with the gain now set to 50%. While the phosphorescence signal appears to settle to a constant value after approximately 11 minutes of purging, the fluorescence signal reaches a saturation value within only 7min. This lag was anticipated owing to the different decay kinetics of the two processes. When conducting emission decay or droplet stream experiments and an environment devoid of oxygen is desired, the proposed phosphorescence imaging test is rendered an accurate and extremely useful tool in ensuring that enough purging time has been allowed. It should, however, be noted that the result of such an experiment is only applicable to the particular setup and gas flow rate and hence, the
same flow rate (1.0 l/min) was employed when purging the cell throughout the range of experiments presented in the thesis.

5.1.3 **Synchronization**

In synchronizing the different components of the setup, the XeCl excimer laser was used as the ‘master clock’. The laser produces 130µs TTL pulses concurrently with the initiation of the thyratron (high voltage switch) charge, dedicated to driving externally other devices. This signal was used to trigger a) the programmable time unit (PTU) of the LaVision computer and b) the Stanford Research Systems DG535 delay generator dedicated to driving the IRO. The time delay between the laser trigger rising edge and the light pulse, measured using a photodiode (DET10A from THORLABS) and a Tektronix DPO 4054 oscilloscope, was 720ns. There are two reasons for triggering the Stanford clock and using its output to trigger the IRO rather than directly triggering the IRO from the PTU. Firstly, in order to amplify (to 4V) the 2V TTL laser output signal, and secondly, to isolate the IRO delay and gate timing from the strong PTU jitter. This is of the order of a few µs, the same as the lifetime of the emission process to be studied. It should finally be noted that the laser was run at 5Hz, while the camera was recording at 2.5Hz, as every second pulse was used to pre-trigger the PTU. A schematic of the timing setup is presented below:

**Fig 5.6** Schematic of the timing setup employed in synchronizing the laser, Stanford clock, camera and IRO
The intensifier delay and gate settings are supplied by the IRO controller and can be monitored by dedicated output BNC output channels. The minimum delay between the IRO Trigger In pulse and the shutter is approximately 140ns, allowing for the intensifier gate to be set by as much as 580ns in advance of the laser pulse emission. The camera exposure was set to 20000µs in order to accommodate the entire P43 phosphor decay (a few µs).

5.1.4 Optical Setup

5.1.4.1 Resolution Measurements

Despite the fact that the real resolution of imaging systems cannot always be accurately described by measuring the optical magnification, the latter is often straightforwardly quoted as a measure of the former. As the projected image of an object is given by the convolution of the irradiance distribution of the object and the point-spread function (PSF), the intensity distribution produced by imaging an infinitesimally small light source [129], the inadequacy of the approach noted above is evident. The size of the PSF, also called the blur spot, is exacerbated particularly when low f# optics are employed owing to greater aberrations, and effectively limits the minimum object/structure sizes that can be resolved. The use of standard resolution test targets, for example the USAF 1951 chart, enables the researcher to obtain an improved characterization of the real resolution of the imaging system by determining the line pattern for which sufficient contrast is preserved. However, the adoption of the particular approach may generate misleading results owing to aliasing. Instead, a measurement of the step response function (SRF) by means of the scanning edge technique can be devoid of such issues, and is therefore recommended [130]. The SRF represents the monitored pixel intensity as a function of knife edge translation. The line spread function (LSF), the 1-D equivalent of the PSF, can be obtained by differentiating the SRF, provided the latter can be approximated analytically. Typically the PSF is adequately approximated by an error function, the derivative of which is a Gaussian with a known standard deviation σ. The Fourier transform of the LSF is also a Gaussian and corresponds to the modulation transfer function (MTF). The latter describes the amplitude response of a system to a sine wave pattern and can be used to infer the contrast distortion induced by the optical system during imaging. This loss of contrast over different frequency ranges can be employed as a measure of the system resolution.
The down-side of the scanning edge approach is that in order to satisfy the Nyquist sampling theorem, a very small translation step must be adopted making the measurement extremely time-consuming. For the employed camera (LaVision Imager Intense), the pixel pitch is 6.45μm, and the Nyquist frequency corresponds to 77.5 lines pairs/mm. A micrometre stage with a step as low as 10μm would allow for sampling at 100 lines/mm, and the measurement would still suffer from aliasing effects. For this reason, the slanted edge technique was adopted in the present study. In this case, a single image of a tilted knife edge can be employed in order to obtain the edge spread function (ESF), the derivative of which is once again the LSF. A hypothesis implicit to this tactic is that the imaged pixels display identical response. The incline angle determines the sampling frequency, and consequently, the number of sampled points in the ESF [131]. In measuring the ESF, a setup similar to the one described in [129] was employed, albeit with the knife edge inclined at approximately 2.5° with respect to the z axis (Fig 5.7). An LED torch was used to illuminate a white foam screen at an angle of around 20°, while a diffusion screen was set up between the former and the knife edge. The knife edge was mounted on an x-y micrometre stage in order to allow for precise translation. The intensifier gain was set to 70%, the same value employed in the imaging experiments.

![Fig 5.7](image.png)

Fig 5.7 Schematic representation of the setup employed in measuring the ESF. The knife edge is mounted onto an x-y translation stage and inclined at an angle θ relative to the z-axis, while an LED torch was used for back-illuminating a diffusion screen.

100 images were collected and averaged, and a 60x40 pixel ROI was selected and processed in Matlab in order to generate the ESF. The two-dimensional data extracted from the ROI were projected onto a one-dimensional trace; the projection angle (2.5°) was
obtained and used to calculate the distance of each projected sample point from the reference position (first column in the ROI) along the line of projection [132]. The measured and curve-fitted ESF were plotted along with the analytically calculated LSF (Fig 5.8). The same procedure was also carried out for smoothed images, as a 3x3 mean filter was employed when conducting quantitative vapour concentration measurements (Fig 5.9). The system resolution (wavelength of a sine wave that can be resolved at a given loss of contrast) at 10% and 50% contrast reduction obtained by plotting the MTF, along with the characteristic width of the LSF (full width at half-maximum or FWHM) for both smoothed and unsmoothed average images are presented in Table 5-1. The FWHM is obtained from the standard deviation σ of the LSF using the $FHW M = 2.35\sigma$ relation [130].

**Fig 5.8** Measured ESF (1.3μm sub-pixel step), fitted error function and calculated LSF for the 85mm-f/1.4D lens plus intensified camera setup employed in the droplet stream experiments
Measured ESF, fitted error function and calculated LSF for images obtained using the same setup and subsequently smoothed (3x3 mean filter)

Table 5-1 FHWM and resolution measurements at 10% and 50% contrast reduction for smoothed and unsmoothed images (droplet stream experiments)

<table>
<thead>
<tr>
<th></th>
<th>FWHM (σ)</th>
<th>Resolution at 10% contrast reduction (μm)</th>
<th>Resolution at 50% contrast reduction (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Smoothing</td>
<td>111</td>
<td>103.1</td>
<td>40.2</td>
</tr>
<tr>
<td>3x3 Smoothing</td>
<td>127.3</td>
<td>117.6</td>
<td>46.1</td>
</tr>
</tbody>
</table>

5.1.4.2 Neutral Density Filters

The transmission of a series of neutral density filters was examined for two purposes: Firstly, neutral density filters were employed in both the emission decay experiments and droplet stream LIF measurements in order to prevent saturation while preserving a single intensifier gain throughout the entire series of calibration and vapour phase concentration measurements. Secondly, the linearity of the intensifier response over the camera dynamic range had to be verified; in doing so, a procedure based on the use of different OD grey filters was developed and adopted. The first step was to experimentally verify the ODs of a range of grey filters and compare them to the manufacturer’s claims. For this purpose the cuvette was purged with acetone vapour in air, and the fluorescence signal was monitored using a non-intensified camera (LaVision Imager Intense), for which the response was assumed to be linear. The camera was equipped with the same 85mm f/1.4D IF Nikon Nikkor lens and no grey filters, while the laser fluence was adjusted so that the observed fluorescence signal...
(nearly 3600 counts) approached the saturation signal level (approximately 4000 counts). 50-image sets were collected for grey filters of different ODs, ranging from 0.1 to 2.0. A 50x50 pixel region of interest (ROI) was extracted from each image and an average signal was calculated for each image set. A table of the calculated and quoted transmittance values is presented in Table 5-2. The transmittance of all filters (apart from the OD 2.0) was measured to be higher by 3-8% compared to the quoted values; measurements carried out using liquid acetone and a photodiode (DET10A from THORLABS), also confirmed these results, with average transmittance values varying to within 2%. Unlike the rest of the examined filters, the thickness of the OD 2.0 filter was 5mm compared to 1.6mm, and the quoted transmittance matched the measured value. Despite the fact that the precision of this measurement (±0.001) is comparatively low owing to the low signal intensity, the excellent agreement with the photodiode measurement renders the result trustworthy. The agreement between the quoted and measured transmittance in this case is attributed to the larger thickness of the particular filter.

<table>
<thead>
<tr>
<th>Quoted OD</th>
<th>Quoted Transmittance</th>
<th>Measured Transmittance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.79</td>
<td>0.870</td>
</tr>
<tr>
<td>0.2</td>
<td>0.63</td>
<td>0.668</td>
</tr>
<tr>
<td>0.3</td>
<td>0.50</td>
<td>0.558</td>
</tr>
<tr>
<td>0.6</td>
<td>0.25</td>
<td>0.307</td>
</tr>
<tr>
<td>0.7</td>
<td>0.20</td>
<td>0.243</td>
</tr>
<tr>
<td>0.9</td>
<td>0.13</td>
<td>0.150</td>
</tr>
<tr>
<td>2.0</td>
<td>0.01</td>
<td>0.010</td>
</tr>
</tbody>
</table>

An identically sized OD 3.0 filter was also purchased, and widely employed in the emission decay experiments. As the dynamic range of both the camera and photodiode did not suffice in verifying the filter transmittance, the latter was measured on a relative manner. As a result, this procedure serves as a rather rough check of the transmittance of the particular optical component. The fluorescence emission of acetone vapour was monitored with the OD 2.0 filter, while the IRO gain was increased until an average signal of approximately 3000 counts was obtained. The OD 2.0 filter was then replaced by the OD 3.0, and its transmittance was determined to be 11.2% relative to the former. The agreement with the
manufacturer’s claim is rendered satisfactory, and therefore the latter will be used when treating the emission decay data.

Having measured the transmittance of a wide range of neutral density filters using a non-intensified camera, the response of the intensifier plus CCD camera setup to different signal intensities was evaluated. Three different aperture settings were employed, yielding three different signal level ranges over which neutral density filters were used. The resulting average signals were plotted against signal intensities calculated using the average signal intensity prior to application of any filter and the filter transmittances determined earlier (Fig 5.10). In essence, filter transmittance values were compared amongst two different detectors and three different signal levels. The results clearly confirm the linearity of the intensifier plus camera response.

![Fig 5.10 Intensifier plus CCD camera response over the 0-3000 counts signal level range](image)

5.2 Spray Investigations

In order to study the fluorescence and phosphorescence emission of acetone and 3-pentanone sprays, the setup developed previously for the study of evaporated tracer concentrations in the vicinity of liquid droplets was appropriately modified. An overview of the revised experimental facility is presented below (Fig 5.11), while the fuel injection assembly and imaging system are discussed extensively in the following subsections.
In modifying the previously employed setup, the flow cell and droplet generator were replaced by an injection chamber on which a prototype, single-hole GDI injector was installed. The injection time and duration were controlled by dedicated trigger and control electronics. Liquid tracer (acetone or 3-pentanone) was supplied to the injector by means of a fuelling system comprised of a fuel tank, an air-driven fuel pump and a high-pressure fuel line. Vapour tracer was supplied to the cell using the previously employed seeder. The excitation source and energy monitoring arrangement were also carried over from the previous setup. The spray and evaporated tracer fluorescence and phosphorescence were imaged near-simultaneously by an intensified and a non-intensified CCD detector pair. The former was also carried over from the droplet stream experiments, but was operated at a different magnification. The latter was a LaVision Imager Intense camera, the same as the one attached to the image intensifier. The two detectors were placed at right angles to each other, while a 75mm x 75mm 50R/50T plate beamsplitter was installed at 45° relative to both cameras. In that way, 50% of the emitted light was directed to the non-intensified camera dedicated to the collection of fluorescence images, while the rest was collected by the intensified CCD camera. The intensifier was fitted with an 85mm-f/1.4D Nikon Nikkor lens and a set of extension rings (15mm), whereas the non-intensified camera was equipped with a 50mm-f/1.8D Nikon Nikkor lens and an OD 0.6 neutral density filter. The optical magnification of the two cameras (99μm for the intensified and 98μm for the non-intensified
camera) prior to calibration for image distortion and magnification mismatch, was measured using a THORLABS micrometre grid target.

5.2.1 Injection System

The fuel injection system is comprised of a fuel tank, an air-driven fuel pump, a single-hole prototype injector and the injector control and trigger electronics. A schematic of the fuel system is presented in Fig 5.12. A shop air supply line was connected to the fuel pump inlet air regulator, dedicated to the inlet air pressure adjustment and consequently also determining the fuel pressure. The latter could be monitored via a manometer installed in the high-pressure fuel line. The fuel itself was supplied from a fuel tank installed on top of the fuel pump assembly. Two tracers were employed in the spray measurements; acetone (≥99.5% purchased from VWR) and 3-pentanone (≥99.0% purchased from Sigma-Aldrich). Prior to filling up the injection system fuel tank with either tracer, both tracers were thoroughly aerated in order to prevent any aeration and ensuing phosphorescence quenching from occurring during injection. An increase in the oxygen content of the liquid tracer is expected to induce a reduction in the phosphorescence efficiency, and therefore phosphorescence signal intensity, in a similar fashion as has been reported for the phosphorescence enhancement of nitrogen-purged acetone liquid streams [29]. The aeration was carried out by purging the liquid tracers with air at a flow rate of 0.5L/min, inside a gas wash bottle. The employed 1000ml borosilicate glass Drechsel type bottle was purchased from VWR, and was equipped with a porosity grade 1 (90-150μm average pore size) sintered glass disc. The total purged liquid volume was 1.5L, while the total purging air volume was 150L; 100 times the volume of the purged liquid. The room temperature was continuously monitored during experimental runs; the vapour pressures of acetone and 3-pentanone at ambient conditions (296K, 1bar) are 0.2475bar and 0.03498bar respectively (fluid property database FLUIDAT by Bronkhorst High-Tech B.V.).
The pressurized fuel leaving the pump was directed, via stainless steel piping through a pressure vessel, to the injector. In depressurizing both air and fuel lines, pressure relief valves were installed in appropriate locations. Additional valves were installed in order to isolate the high-pressure fuel line leading to the injector and the shop air supply line leading to the pump. These were used when depressurizing the system, as well as for draining the fuel lines in order to change fuel.

The fuel pump operates by deployment of the pressure intensifier principle. It is comprised of a larger area air piston charged with low pressure and mated to a smaller area plunger on which high pressure is generated. The pressure ratio which is 1:28 for the particular pump (MAXIMATOR MSF22(L)), reflects the ratio of the air and plunger pistons areas, and can be used to calculate the maximum outlet (fuel line) pressure available. In controlling the outlet pressure, an inlet air regulator was used; the product of the pump pressure ratio and the set air pressure gives the nominal fuel pressure. As the drive piston ascends, the liquid fuel is drawn by suction. In turn, the down-stroke movement of the piston builds up the pressure in the liquid side. This process is repeated until the pre-set pressure is reached; if the liquid fuel pressure drops, for example by repeated injections, the pump restarts automatically in order to compensate for the pressure drop.
The maximum fuel pressure available is determined by the maximum available inlet air pressure; for the particular pump and shop air supply it corresponds to around 180bar. An increase in the injection pressure is associated with an improvement in fuel atomization, smaller droplet diameters and faster evaporation [1]. Typical images of acetone sprays at 50bar, 100bar and 150bar injection pressures in saturated acetone vapour in air are presented below. Considering the objectives of this experiment, higher injection pressures are rendered desirable as the ensuing finer droplet distributions will result to only sub-pixel sized droplets with no independent droplets being detectable.

![Acetone spray LIF images in saturated acetone vapour in air, injected at 50bar, 100bar and 150bar](image)

**Fig 5.13** Acetone spray LIF images in saturated acetone vapour in air, injected at 50bar, 100bar and 150bar

The injector electronics are comprised of two components, an Injector Drive Unit (IDU) and the injector control and power supply unit (PSU). The latter is designed to work along with the injector drive unit. It is responsible for providing power (14V at 20mA) to the IDU, along with a variable control output signal (5V TTL active low). The control signal duration can be manually adjusted between 0.00ms and 9.99ms, and determines the injection duration. The control box itself can be externally triggered to the rising edge of a 5V TTL pulse (as is the case here), or operated manually. The delay between the external trigger and the output trigger signal going low is approximately 10-11μs according to the manufacturer.

A photograph of the injection chamber as incorporated in the experimental arrangement is presented in Fig 5.14. The backbone of the chamber is made of six Aluminium plates; four walls, the bottom and top plates (Fig 5.15). The bottom plate was designed so as to act as a mounting platform, whereas the top plate accommodates the injector holder and four gas inlet connectors. Two gas outlet connectors were located at the lower half of the rear wall plate, while a draining port for any liquid deposits was fitted to the centre of the bottom plate. Three apertures, one on each of the left, right and front panels were incorporated in the design.
for optical access. The fitted 50x50x4mm windows were made of UV-grade fused silica and were supplied by Edmund Optics. All contact surfaces were grooved and fitted with PTFE flanges in order to seal against leakage. The inside surfaces of the front and side panels were sand-blasted in order to reduce their reflectivity, while the inside surface of the rear plate was hard black anodised (40μm coating thickness). The injector holder was positioned centrally on the top plate whereas the injector itself was fixed at angle of 20°, the spray angle relative to the injector longitudinal axis, thus allowing the spray to propagate vertically downwards.

Fig 5.14 Schematic of the optical setup used throughout the spray imaging experiments

Fig 5.15 Exploded view of the injection chamber assembly. The design and engineering drawings were produced in SolidWorks
A 25mm thick spacer was placed between the top plate and main body with the intension of reducing the signal disparity between the liquid and vapour phase fluorescence signals. The near-nozzle region is dominated by the primary break-up zone, characterized by high ligament and droplet densities. In order to avoid saturating the camera, grey filters were used, simultaneously moderating the fluorescence intensities of both phases. While this presents no issue when imaging the liquid as the observed fluorescence signals span over the entire dynamic range of the detector, the maximum (saturated) vapour signal under the particular experimental conditions corresponded to only 35 counts (Fig 5.16, left). Further downstream, within the secondary breakup zone, the spray becomes more dilute; the density of the liquid tracer within the probed volume reduces, and consequently, the peak liquid phase fluorescence diminishes. The saturated vapour signal can therefore be imaged over a wider range, of the order of 150 counts (Fig 5.16 right).

![Fig 5.16 Acetone spray LIF images in saturated acetone vapour in air (150bar injection pressure) without the spacer (left) and with the spacer (right). Both images are presented over the same dynamic range](image)

### 5.2.2 Synchronization

The synchronization of the experimental arrangement was carried over from the previous setup, albeit with the addition of two components; the second camera and the injector trigger electronics. Following the installation of a second frame-grabber to the LaVision computer, the second camera was triggered in an identical manner to the one coupled to the intensifier. Apart from triggering the IRO, the Stanford delay generator was also used to externally trigger the injector control unit. The output signal delay relative to the input (laser) signal was determined by the laser frequency, the injection duration and the injection timing. The laser was run at 4Hz with the recording frequency adjusted to 2Hz, so that every second pulse was used to pre-trigger the PTU. The injector control unit delay was tuned to the 499.30-
497.80ms range (for a pre-set injection duration of 1.5ms), in order to match the setup recording frequency and account for any delays between the input trigger signal and the injection process. The delay corresponding to the start of injection was identified by direct imaging; initially set to 500ms, it was gradually reduced in 0.1ms steps until the fluorescence/phosphorescence signal from the spray tip was detectable.

5.2.3 Optical Setup

A major difference between the experiments described in the following pages and the ones carried out by Kiel et al [108] can be identified regarding the employed fluorescence and phosphorescence detection apparatus. Kiel et al [108] argue that the use of a dual-frame camera employed for the acquisition of both fluorescence and phosphorescence images constitutes the optimal choice, as it eliminates a plethora of potential error sources such as any alignment mismatch, magnification, lens aberration, sensitivity and response differences between two independent detectors.

Despite the validity of the aforementioned arguments, the employment of a dual frame camera for the particular application entails severe disadvantages which render the collection of phosphorescence signals problematic. Owing to the large signal strength disparity between the liquid phase fluorescence and phosphorescence emission (approximately 3-4 orders of magnitude), any imaging parameters such as the gain, gate and delay settings of the IRO, should ideally be adjusted independently. The same argument applies regarding the selection of appropriate collection optics (neutral density filters and camera lenses). Whereas the collection of fluorescence images requires very low gain factors and is not dependent upon the delay timing and gate duration, imaging the phosphorescence emission necessitates the use of very high gains, with the delay and gate settings significantly affecting the collected signal level, and consequently, the signal-to-noise ratio. As the phosphorescence decay rate of ketone tracers is very fast, monitoring the phosphorescence as early as possible results to substantial augmentation of the collected signal. The earliest phosphorescence collection delay for a dual frame camera is essentially dependent upon the inter-frame duration, and hence, the collection of phosphorescence signals is pushed away from the optimum timing. In order to make up for the ensuing signal degradation, a higher gain setting will need to be employed, further compromising the quality of the measurement. Provided that the same gain is employed for the collection of fluorescence images, the gating time of the first frame must
now be pushed ahead of the fluorescence emission with only a small fraction of it being monitored in order to avoid saturating the detector. This, in turn, means that the fluorescence measurements will be subjected to strong jitter, with the first frame representing a different fraction of the total fluorescence emission for every acquisition (Fig 5.17).

![Fig 5.17 Schematic representation of the fluorescence and phosphorescence emission, imaged by a dual frame camera and separate detector pair.](image)

In contrast, an independent detector pair can fully exploit the temporal decay characteristics of liquid phase phosphorescence, with the delay and gate settings of the phosphorescence camera adjusted so as to monitor the strongest part of the emission. The other camera, dedicated to the collection of fluorescence, would not suffer from any jitter effects as the exposure could be sufficiently high so as to accommodate the entire emission.
5.2.3.1 Resolution Measurements

The resolution of the detector pair employed in the spray measurements was examined in an identical manner to the droplet stream setup. It should be noted that the ESF measurements for both detectors were carried out with the beam splitter in place, for images processed with and without smoothing (5x5 mean filter). The measured and curve-fitted ESF, plotted along with the analytically calculated LSF for both intensified and non-intensified cameras, are presented in Fig 5.18 and 5.19 respectively. The resolution of the intensified camera at 10% and 50% contrast reduction, along with the characteristic width of the LSF with and without smoothing are presented in Table 5-3. The same measurements are also presented for the non-intensified camera in Table 5-4.

![Graph showing ESF and LSF](image)

**Fig 5.18** Measured ESF for a 2.6μm sub-pixel step, fitted error function and calculated LSF for the 85mm-f/1.4D lens plus intensified camera setup
Fig 5.19 Measured ESF for a 2.6μm sub-pixel step, fitted error function and calculated LSF for the 50mm-f/1.8D lens plus non-intensified camera setup

Table 5-3 FHWM and resolution measurements at 10% and 50% contrast reduction for smoothed and unsmoothed images (intensified camera, spray measurements)

<table>
<thead>
<tr>
<th></th>
<th>FWHM (σ)</th>
<th>Resolution at 10% contrast reduction (µm)</th>
<th>Resolution at 50% contrast reduction (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Smoothing</td>
<td>229.1</td>
<td>212.0</td>
<td>84.1</td>
</tr>
<tr>
<td>5x5 Smoothing</td>
<td>445.8</td>
<td>417.1</td>
<td>161.2</td>
</tr>
</tbody>
</table>

Table 5-4 FHWM and resolution measurements at 10% and 50% contrast reduction for smoothed and unsmoothed images (non-intensified camera, spray measurements)

<table>
<thead>
<tr>
<th></th>
<th>FWHM (σ)</th>
<th>Resolution at 10% contrast reduction (µm)</th>
<th>Resolution at 50% contrast reduction (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Smoothing</td>
<td>158.2</td>
<td>147.1</td>
<td>57.5</td>
</tr>
<tr>
<td>5x5 Smoothing</td>
<td>431.9</td>
<td>400</td>
<td>156.5</td>
</tr>
</tbody>
</table>
5.2.3.2 Beamsplitter

Two beamsplitters were tested when developing the presented setup; a 75mm x 75mm, 50R/50T and a 75mm x 75mm 25R/70T, both dielectric-coated on the front surface and antireflective-coated on the back. The latter allows for a 50% boost in the collected phosphorescence over the former, and was therefore preferred; an increase in the collection efficiency of the weak phosphorescence signal is rendered favourable as it enables for the intensifier gain, and consequently measurement noise, to be reduced. However, upon conducting preliminary resolution measurements by deployment of a 1951 USAF target, strong ghosting effects were observed in the non-intensified camera images (Fig 5.20). These were attributed to the reflectivity/transmissivity ratio of the particular glass component and the antireflective coating quality. The typical glass reflectivity is approximately 4% per surface, while a MgF₂ coating such as the one applied to the particular component reduces reflections to around 1%. However, the antireflective-coated surface was observed to contribute a double image shifted by approximately 1.5mm; in theoretical agreement with a contribution coming from an uncoated surface. No such issues were observed for the 50R/50T beamsplitter, which was consequently employed in the measurement setup.

![Fig 5.20](image)

**Fig 5.20** 1951 USAF target images obtained by the non-intensified camera using two beamsplitters. Regions of interest were selected and magnified in both images in order to clearly illustrate the ghosting effect

5.2.3.3 Intensifier Jitter

Electronic jitter may influence the collected phosphorescence signals on a shot-to-shot basis, thereby inducing strong variability in the observed fluorescence to phosphorescence signal intensities. In these experiments, the delay relative to the prompt fluorescence emission was minimized in order to boost the phosphorescence signal, with the former monitored as
close as possible to the latter. Owing to the extremely fast decay rate of the liquid tracer, even a small advance or retardation of the camera gate could result to substantial fluctuations in the collected signal intensity. In order to assess the intensifier jitter, the following arrangement was set up (Fig 5.21): The injection chamber was saturated with acetone vapour in air, and the fluorescence emission was monitored by a non-amplified photodiode purchased from THORLABS (200-1100nm wavelength range, 1ns rise time) and connected to a Tektronix DPO 4054 oscilloscope. Meanwhile, the intensifier gate was also tuned to capture the vapour fluorescence emission. The IRO delay was then increased in 5ns steps until no fluorescence could be detected over an ensemble of images (phosphorescence emission regime). The intensifier gate was also monitored on the oscilloscope screen via the corresponding IRO port, and the delay between the two signals was calculated and recorded using the Tektronix interface software.

![Diagram of measurement setup](image)

**Fig 5.21** Intensifier jitter measurement setup: the relative delay between the IRO gate and acetone vapour fluorescence emission monitored by a photodiode, was recorded by an oscilloscope over 500 laser pulses

After collecting a total of 500 relative delay measurements, the mean delay was calculated and subtracted from all measured values in the data set. The processed data were then fitted to a normal distribution and the probability distribution function was generated (Fig 5.22) The full-width at half maximum, defined as $FWHM = 2.35 \times \sigma$, was 3.76ns; hence the intensified camera jitter is not expected to induce significant variability in the
characterization of the phosphorescence against the fluorescence emission given the presently employed setup.

**Fig 5.22** Probability distribution function of the observed jitter values about the mean delay between the photodiode and the intensifier gate signals
6 Laser Induced Fluorescence and Phosphorescence Imaging in Droplet Streams

The first aim of this study is to characterize and compare the emission decay of vapour and liquid acetone, excited at 308nm, in both air and nitrogen bath gases. In doing so, two different experimental arrangements were employed (cuvette and droplet generator/flow cell) yielding results for liquid acetone in the bulk and in liquid streams, as well as acetone vapour. In addition, complementary results for liquid 3-pentanone laser induced phosphorescence emission are reported for the first time. The particular tracer was, however, not employed in demonstrating the proposed technique owing to its comparatively low vapour pressure and consequently vapour phase concentration at ambient conditions, effectively preventing the collection of vapour phase phosphorescence with acceptable signal to noise ratios.

Apart from providing valuable information regarding the nature and temporal evolution of the triplet state emission, lifetime measurements reveal the potential for better visualizing vapour concentrations around liquid droplets by addressing the two major shortcomings associated with two-phase flow acetone LIF; the extreme fluorescence intensity disparity between the two phases and the ensuing halation. The validity of these claims is demonstrated by comparative visualization experiments carried out using both laser induced fluorescence and phosphorescence imaging of evaporative and non-evaporative acetone droplet streams. The final objective of this study is the quantification of the vapour tunnel forming around evaporating droplet streams, again by deployment of both optical techniques, in an attempt to quantitatively address the suitability of laser induced phosphorescence for two-phase flow imaging. The imaging results are discussed, while suggestions for improvement and future work are also provided. Large part of the material presented in this thesis has been published in [49]; permission to reprint this material, along with relevant tables and figures has been granted by the publisher, as the experiments presented in the publication were carried out by the author of this thesis.
6.1 Emission Decay Measurements in the Cuvette

The main advantages of the cuvette setup when characterising the phosphorescence emission decay are the increased practicality and enhanced repeatability of experimental conditions, and therefore, the obtained results. The aforementioned argument does not apply to vapour phase measurements; in the case of liquid tracers, however, the deployment of a contained liquid volume allows for the fluence and nitrogen-purging dependencies of the phosphorescence emission to be readily evaluated. On the downside, and contrary to the vapour phase, no liquid flow is established, with inaccuracies potentially arising due to the emergence of sensitized phosphorescence; decomposition products, mainly acetyl radicals combining to form biacetyl, may act as energy acceptors reemit.

The decay of acetone vapour in nitrogen was examined by purging the cuvette at a flow rate of 1.0 L/min, and imaging the emission through an unmasked aperture over a 2.5μs range following the fluorescence emission. The cuvette was illuminated at right angles to the collection optics, with the average excitation energy over the entire measurement run being approximately 30mJ. The laser profile distribution, obtained by averaging the acetone vapour fluorescence signal over 100 pixels along each row and normalizing the results to the maximum average signal, is shown in Fig 6.1. Measurements were carried out for three different laser fluence values (25mJ/cm², 50mJ/cm² and 250mJ/cm²), obtained by translating the focusing lenses along the laser sheet direction of propagation and adjusting the laser power (from 30mJ/pulse to 15mJ/pulse). The laser sheet thicknesses for the low (25mJ/cm² and 50mJ/cm²) and high (250mJ/cm²) excitation energy studies were approximately 5mm and 0.8mm respectively.

In supplying the cuvette with the respective liquid tracers (acetone/3-pentanone) a 5ml capacity glass syringe (purchased from VWR) was employed. Approximately 4.5ml of liquid tracer were introduced prior to each measurement run, in order to allow enough space between the liquid surface and the cuvette lid for a purging flow (nitrogen flow) to be established. As nitrogen flows through the cell, it diffuses into the liquid tracer and removes any dissolved oxygen, thus boosting the phosphorescence efficiency and consequently signal intensity [29]. For example, following excitation at 266nm, an increase in the liquid acetone phosphorescence lifetime from 175ns to nearly 1μs has been reported for complete degassing. This process can be imaged in real time by deployment of the cuvette setup, with the reported
lifetime measurements for nitrogen-purged liquid acetone and 3-pentanone corresponding to complete deaeration.

![Diagram](image)

**Fig 6.1** Cuvette setup and laser profile distribution employed in the liquid acetone and 3-pentanone, as well as acetone vapour emission decay experiments. The cuvette is fixed on a Delrin mounting base, while a Delrin sheet mask (here displayed as semi-transparent), was placed between the cuvette and the collection optics in order to minimize any reflections or cuvette emission.

Two different optical arrangements were examined; illumination from the side and detection at right angles, as in the flow experiments, and illumination at 45° relative to the collection optics. In the first case, the emitting volume corresponds to a thin strip appearing adjacently to the cuvette wall, while in the second, to a rectangle of similar size to the laser pulse. The measurements performed using the first arrangement are presented in the following pages; however, it should be noted that the results obtained from both setups agreed closely.

### 6.1.1 Acetone Vapour Emission Decay

In measuring the decaying phosphorescence intensity following the prompt fluorescence emission, the detection delay was varied from -100 to 2400ns in 100ns intervals. The IRO gate and gain were set to 200ns and 70%, necessitating the use of an OD 2.0 neutral density filter for the fluorescence measurements. The first set of phosphorescence images was collected at a delay of 200ns after the start of fluorescence emission in order to ensure the
fluorescence signal would not affect the phosphorescence measurements through electronic jitter. Before each measurement run, 50-image sets were collected over the examined delay range with the same optics and IRO settings, with the laser firing but no tracer inside the probed volume. The collected background images for each delay were then averaged and subtracted from the corresponding image sets during post-processing. Each data point on the normalized emission decay curves corresponds to the average signal obtained from a 300×200 pixel region of interest (9.62x5.5mm viewing area) located immediately adjacent to the cuvette wall, over 50 images per image set (or equivalently per delay setting). All data points were normalized to the average fluorescence intensity, while their position on the plot relative to the x-axis corresponds to the IRO delay setting plus half of the gate time (Fig 6.2).

No results are presented for acetone vapour in air, as no phosphorescence was observed. The average fluorescence varied to within 3% compared to the equivalent value in nitrogen, in qualitative agreement with literature results, suggesting that oxygen quenching of the first excited singlet is insignificant at ambient conditions.

Bi-exponential (Eq. 6-1) as well as single exponential (Eq. 6-2) functions were fitted to the phosphorescence emission decay curves, the former yielding short $\tau_1$ and long $\tau_2$ decay components (Table 6-1):

$$S_{ph}(t) = S_{ph1}e^{-t/\tau_1}+S_{ph2}e^{-t/\tau_2}$$

Eq 6-1

$$S_{ph}(t) = S_{ph0}e^{-t/\tau_1}$$

Eq 6-2

The short components account for the faster decay rates observed early during the emission, while the slower ones fit the longer delay data. The presented uncertainties correspond to mean deviations from the fitted values calculated with 95% confidence bounds. Previous studies of liquid acetone phosphorescence also indicated that single exponential functions do not adequately describe the decay [29, 43], as the emission appeared to evolve over time. Longer detection wavelengths displayed longer lifetimes, or equivalently, the phosphorescence emission spectrum shifted to the red with increasing detection delay [41]; a trend most probably associated with the emission from lower vibrational levels populated by vibrational relaxation. This multi-exponential decay has been attributed to collisional interactions between acetone molecules resulting in quenching; when working with pure acetone, self-quenching or triplet-triplet annihilation are the two candidate processes. In the
present study, the following interpretation is offered and supported by a series of observations, some of which are clearly identifiable in Fig 6.2: Increasing the excitation energy density is shown to reduce both lifetime components, as well as to force the entire phosphorescence decay curve towards lower percentage values compared to the prompt fluorescence emission. In addition, the collected data from both 25mJ/cm² and 50mJ/cm² laser fluence experiments can be adequately described (R² higher than 0.99) by single exponentials. The emergence of triplet-triple annihilation (TTA) as a primary deexcitation mechanism at higher excited state populations (higher excitation energy densities) is believed to be the reason for the observed behaviour, as well as the one encountered in literature and discussed earlier in the case of liquid acetone. No explicit account of the particular deexcitation mechanism has been found for acetone triplets, however, for biacetyl, the TTA rate constant is approximately three orders of magnitude higher than oxygen quenching and has been shown to affect the emission lifetime in an identical manner to the presently observed one [82, 83]. For aromatics in solution, triplet-triplet annihilation displays rate constants of the same order as molecular diffusion [47]. Instead, self-quenching has been attributed a very low quenching efficiency, suggesting that the observed phenomena are very unlikely to be attributable to the particular process [27].

![Graph](image)

**Fig 6.2** Saturated acetone vapour emission decay in nitrogen bath gas for 25mJ/cm², 50mJ/cm² and 250mJ/cm² laser fluences
Table 6-1 Measured fast and slow lifetime components of gaseous acetone in nitrogen bath for different excitation energy densities

<table>
<thead>
<tr>
<th>Laser Fluence (mJ/cm²)</th>
<th>Fitted function</th>
<th>Fast Decay Component Lifetime (ns)</th>
<th>Slow Decay Component Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>Bi-exponential</td>
<td>292 ± 21</td>
<td>2297 ± 162</td>
</tr>
<tr>
<td>50</td>
<td>Bi-exponential</td>
<td>948 ± 432</td>
<td>4211 ± 1003</td>
</tr>
<tr>
<td>50</td>
<td>Exponential</td>
<td>-</td>
<td>3012 ± 204</td>
</tr>
<tr>
<td>25</td>
<td>Exponential</td>
<td>-</td>
<td>4250 ± 218</td>
</tr>
</tbody>
</table>

The reproducibility of the above results was examined by comparing the 50mJ/cm² and 250mJ/cm² emission decay curves calculated from four different experiments; two conducted by deployment of illumination from the cuvette side and two from the cuvette front (Fig 5.2). The results of Fig 6.2 were then re-plotted over a shorter dynamic range (Fig 6.3) in order to emphasize on the size of the error bars corresponding to the standard deviation of the normalized decay points. It can be observed that the trends identified previously are clearly reproduced, thus highlighting their validity.

![Graph showing acetone vapour emission decay in nitrogen bath gas for 50mJ/cm² and 250mJ/cm² laser fluences. The displayed error bars correspond to the standard deviation of normalized decay points calculated from four different experimental runs.](image)

**Fig 6.3** Saturated acetone vapour emission decay in nitrogen bath gas for 50mJ/cm² and 250mJ/cm² laser fluences. The displayed error bars correspond to the standard deviation of normalized decay points calculated from four different experimental runs.
6.1.2 **Liquid Acetone and 3-pentanone Emission Decay**

The decay measurements of liquid acetone and 3-pentanone were carried out in the same manner as described earlier for acetone-seeded nitrogen. The same gain, gate and delay values were carried over from the previous experiment, however, O.D. 3.0 and 0.7 filters were employed when monitoring the fluorescence emission, while phosphorescence images at 200ns after the start of fluorescence emission were also collected using an O.D. 0.7 filter. The normalized emission decays of liquid acetone and nitrogen-purged liquid acetone for 50mJ/cm² and 250mJ/cm² laser fluences are presented in Fig 6.4, while corresponding results for 3-pentanone are shown in Fig 6.5. All generated phosphorescence decays curves were fitted to bi-exponential functions, with the obtained slow and fast decay component lifetimes enlisted in Table 6-2. It should be noted that the overall decay rates observed for liquid tracers are substantially higher than their vapour counterparts, with the majority of the phosphorescence emitted during the initial stages of the decay. The significance, in terms of imaging, of the fast decay components in comparison to the slower ones is therefore rendered superior, with the present and future analysis focusing on the former.

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Laser Fluence (mJ/cm²)</th>
<th>Fast Decay Component Lifetime (ns)</th>
<th>Slow Decay Component Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>250</td>
<td>102 ± 3</td>
<td>975 ± 148</td>
</tr>
<tr>
<td>Acetone</td>
<td>50</td>
<td>112 ± 7</td>
<td>614 ± 160</td>
</tr>
<tr>
<td>Nitrogen-purged Acetone</td>
<td>250</td>
<td>220 ± 20</td>
<td>1002 ± 129</td>
</tr>
<tr>
<td>Nitrogen-purged Acetone</td>
<td>50</td>
<td>194 ± 10</td>
<td>1087 ± 88</td>
</tr>
<tr>
<td>3-pentanone</td>
<td>250</td>
<td>101 ± 6</td>
<td>1093 ± 298</td>
</tr>
<tr>
<td>3-pentanone</td>
<td>50</td>
<td>107 ± 3</td>
<td>886 ± 98</td>
</tr>
<tr>
<td>Nitrogen-purged 3-pentanone</td>
<td>250</td>
<td>112 ± 3</td>
<td>1024 ± 180</td>
</tr>
<tr>
<td>Nitrogen-purged 3-pentanone</td>
<td>50</td>
<td>112 ± 4</td>
<td>1040 ± 80</td>
</tr>
</tbody>
</table>
Fig 6.4 Normalized liquid acetone and nitrogen-purged liquid acetone emission decay curves for 50mJ/cm$^2$ and 250mJ/cm$^2$ laser fluence

Fig 6.5 Normalized liquid 3-pentanone and nitrogen-purged liquid 3-pentanone emission decay curves for 50mJ/cm$^2$ and 250mJ/cm$^2$ laser fluence
The emission decays of liquid acetone and 3-pentanone display very similar rates, with the fast decay components in extremely close agreement for both laser fluences (within 5%). Slightly higher deviations are observed regarding the slower decay components, with 3-pentanone displaying slightly higher values. Increasing the laser fluence from 50mJ/cm$^2$ to 250mJ/cm$^2$ results to a shift of the entire phosphorescence decay curve (relative to the fluorescence) by almost a decade for both tracers; a result that further supports the proposed primary role of TTA in the deexcitation mechanism of excited triplets. It should essentially be noted at this point that any heating of the liquid tracer owing to laser energy absorption is also expected to introduce phosphorescence signal and lifetime degradation when comparing the 50mJ/cm$^2$ to the 250mJ/cm$^2$ excitation energy density results. The clear emergence of TTA as a primary deexcitation mechanism in the gas phase measurements where no heating effects are present, however, suggests that a similar phenomenon should also play a primary role in liquid phase kinetics. Observations made in preliminary low excitation energy density trials carried out in thin liquid streams also support this thesis, as early (short delay) phosphorescence to fluorescence signal ratios were found to vary significantly (by nearly as much as one order of magnitude) when the excitation energy was varied by a factor of approximately seven.

In the case of acetone, nitrogen-purging is observed to both shift the phosphorescence emission closer to the fluorescence, as well as to boost the lifetimes for both examined fluence values; 3-pentanone phosphorescence, in comparison, appears almost completely unaffected. This phenomenon is most probably attributed to higher solubility values of oxygen/nitrogen in acetone compared to 3-pentanone, rather than a deviation between the oxygen quenching rate constants of the two ketones. $O_2$ solubility values of $2.4 \times 10^{-3}$M, $1.8 \times 10^{-3}$M [133] and $1 \times 10^{-3}$M [42] (25ºC and 1bar) were encountered in literature for acetone, while the equivalent values for $N_2$ were approximately half. No data were found for 3-pentanone, and therefore, the above stated speculative proposal could not be verified.

As has already been noted, the main disadvantage associated with conducting emission decay measurements in static cells is that any decomposition products may themselves absorb and reemit part of the excitation energy, thus introducing additional contributions to the collected light not emanating from the originally excited tracer. Biacetyl has been attributed this role following decomposition of acetone triplets, so in order to examine the possible emergence of biacetyl phosphorescence in these measurements, a Chroma D440/90 filter (transmission band extends from 390nm to 480nm) was employed in reproducing the
nitrogen-purged liquid acetone emission measurement. Biacetyl first excited singlets are produced following excitation in the 350-480nm range, coincident with the fluorescence/phosphorescence emission spectrum of acetone, while the fluorescence and phosphorescence spectra extend from approximately 430nm to 520nm and 490nm to 650nm respectively [27]. The employed filter should therefore block any unwanted biacetyl phosphorescence. The obtained results displayed excellent agreement, with only a slight deviation observed for the lower intensity measurements. It is therefore believed that biacetyl phosphorescence was not present in the above experiment series; however, as will be shown later, the liquid phase lifetimes measured in the cuvette are substantially higher than the equivalent measurements in the liquid streams, particularly the ones carried out in air. Possible explanations are the sensitization of other decomposition products, as well as the emergence of delayed biacetyl fluorescence, rather than phosphorescence. The emission spectrum of the latter coincides with the spectrally transmissive range of the Chroma filter, and if present, should be collected along with the phosphorescence of acetone.

### 6.2 Emission Decay Measurements in a Flow Cell

#### 6.2.1 Acetone Vapour Emission Decay

In examining the saturated acetone vapour emission decay in air and nitrogen, the cell was purged with the respective gases and the emission was imaged over the same 2.5μs delay range. The laser settings were readjusted and the average excitation energy reaching the imagining area was now approximately 20.5mJ per pulse. This was calculated using the Beer-Lambert law:

$$ T = e^{\sigma l N} $$  \hspace{1cm} \text{Eq 6-3}

The acetone number density $N$ ($6.9116 \times 10^{18}$ molecules/cm$^3$) at 297.15K and 1bar respectively was obtained from the fluid property database FLUIDAT (by Bronkhorst High-Tech B.V.), while the absorption cross-section $\sigma$ at 308nm ($1.603 \times 10^{-20}$ cm$^2$) was obtained from Lozano [27]. Given the laser sheet dimensions (approximately 400μm thickness and 25mm height), the laser fluence corresponds to 205mJ/cm$^2$. The laser sheet profile distribution obtained by averaging 50 fluorescence images is displayed below:
Acetone vapour emission decay data were once again collected by varying the detection delay from -100ns to 2.400ns after the start of fluorescence emission. The IRO gate and gain were set to 200ns and 70%, necessitating the use of an OD 2.0 neutral density filter for the fluorescence image collection. Similar to the experiments described earlier, the first set of phosphorescence images was collected at a delay of 200ns after the start of fluorescence emission, while the rest of the phosphorescence measurements were performed in 100ns steps throughout the examined delay range. 50 images were collected at each delay setting, with each data point on the decay curves obtained by averaging the signal observed in a 200x350 pixel region of interest located in the middle of the imaging region. All data points were normalized to the averaged fluorescence intensity, and their position on the plot relative to the x-axis corresponds to the IRO delay setting plus half of the gate time. The normalized acetone vapour in air and acetone vapour in nitrogen emission decay data are presented in Fig 6.7.
Fig 6.7 Normalized vapour acetone emission decay in nitrogen and air bath gas

The measured fluorescence intensities agree to within 2%, an outcome that fits the theoretical description of vapour acetone deexcitation from the $S_1$, as well as the cuvette measurement. For acetone vapour in air, no emission was observed for delays other than the first, an effect attributed to very effective oxygen quenching of the triplet emission. In contrast, the early phosphorescence signal of acetone vapour in nitrogen is clearly detectable and approximately two orders of magnitude lower than the prompt fluorescence signal. Over the examined delay range the vapour phase phosphorescence drops to approximately one sixth of the initially measured value. The fast and slow decay component lifetimes, calculated in the same manner as earlier, are presented below:

<table>
<thead>
<tr>
<th>Laser Fluence (mJ/cm$^2$)</th>
<th>Fitted function</th>
<th>Fast Decay Component Lifetime (ns)</th>
<th>Slow Decay Component Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>Bi-exponential</td>
<td>366 ± 62</td>
<td>2658 ± 496</td>
</tr>
</tbody>
</table>
The obtained results agree closely with the cuvette measurement conducted for the 250mJ/cm² average fluence, and lie in between that and the 50mJ/cm² fluence measurement. Acetone vapour emission decay data in both in air and nitrogen have recently been published for the same delay range, following excitation at 320nm [28]. Although a direct quantitative comparison cannot be made between the current and aforementioned study on account of the higher excitation wavelength (320nm), lower fluence (4.46 mJ/cm²) and the lower gating time (100ns) employed in the latter, it should be noted that nearly identical trends were observed amongst the two studies. Another account of the phosphorescence lifetime of acetone vapour in air and nitrogen, following excitation at 308nm and measured by direct imaging, has been reported by Hu and Koochesfahani [40]. Their reported value of 15µs is substantially higher compared to the ones observed in this study or the study of Weckenmann and co-workers [28]. As no information regarding either the imaging or excitation energy settings were provided by the authors, the validity of their measurement cannot be assessed and a comparison cannot be pursued.

6.2.2 Liquid Acetone and 3-pentanone Emission Decay

Three sets of experiments will be presented in this section of the report for each of the two tracers; the emission decay of a thin liquid stream in air, a liquid stream in nitrogen bath gas and a previously nitrogen-purged liquid stream in nitrogen bath gas. In generating the liquid flows, a 600µm pinhole was installed on the droplet generator yielding a relatively thick (approximately 560µm diameter determined according to optical magnification) smooth stream. This decision was made on the basis of obtaining a probed volume largely occupied by the liquid tracer, thus allowing for direct signal strength comparisons between the two phases. Typical fluorescence and phosphorescence images are displayed below:
Fig 6.8 Fluorescence (left) and phosphorescence (right) images of an acetone stream (air bath gas, no purging) employed in the emission decay experiments. The presented phosphorescence image was acquired at a 200ns after the prompt fluorescence emission using a gate of 200ns and a gain of 70%

Acetone/3-pentanone degassing was performed by repeatedly bubbling nitrogen through the supply vessel via a pipe equipped with a sintered end cap. This procedure has been shown to boost the phosphorescence emission by replacing any dissolved oxygen with nitrogen. For liquid acetone introduced in a nitrogen environment, the diffusion of oxygen out of the liquid is on-going within the imaging region and as will be shown later, causes a noticeable variation in the phosphorescence intensity along the stream. In contrast, 3-pentanone did not display such behaviour; an outcome that was anticipated following the lifetime measurements in the cuvette. Despite the fact that the particular experimental condition is not well-defined for imaging experiments owing to the ensuing dependence of the phosphorescence emission on the residence time within the ambient gas, the obtained direct imaging evidence of oxygen diffusion out of liquid stream is relevant to this study and, therefore, worth presenting.

The emission decay measurements of liquid acetone and 3-pentanone were once again performed by collecting images in 100ns steps using 70% intensifier gain. For nitrogen-purged liquid acetone in nitrogen bath gas, data were collected in 200ns steps as the decay time is substantially longer and the stream stability could not be maintained over the duration necessary to perform a complete measurement run. As before, each data point on the decay curves corresponds to a 50 image average (this time of a 200x10 pixel region of interest), and its position on the plot relative to the x-axis corresponds to the IRO delay plus half of the gate time. A 200ns exposure time starting at 100ns before the laser pulse was used to collect the prompt fluorescence signals, while the gating for all IRO delays was also set to 200ns. A list
of the neutral density filters employed in the liquid acetone and 3-pentanone fluorescence and phosphorescence experiments, along with the phosphorescence delay settings (range and steps) corresponding to each measurement run, is provided in Table 6-4. The same average excitation energy (20.5mJ) was used as before. No appreciable vapour build-up was observed inside the cell, and therefore, any uncertainties induced by the vapour emission and laser light attenuation were rendered insignificant.

Table 6-4 List of the optical setup parameters used in the emission decay measurements presented in this section of the report. The fluorescence and phosphorescence gate and gain settings (200ns, 70%) were identical for all decay measurements. The phosphorescence delay values are expressed relative to the start of fluorescence

<table>
<thead>
<tr>
<th>Emission Decay Study</th>
<th>Fluorescence Filters</th>
<th>Phosphorescence Delay Range</th>
<th>Phosphorescence Filters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid acetone in air</td>
<td>OD 3 &amp; OD 0.7</td>
<td>200-900ns in 100ns steps</td>
<td>(OD 0.7 for 200ns delay)</td>
</tr>
<tr>
<td>Liquid acetone in N₂</td>
<td>OD 3 &amp; OD 0.7</td>
<td>200-1400ns in 100ns steps</td>
<td>(OD 0.7 for 200ns delay)</td>
</tr>
<tr>
<td>N₂-purged liquid acetone in N₂</td>
<td>OD 3 &amp; OD 0.7</td>
<td>200-2400ns in 200ns steps</td>
<td>(OD 0.7 for 200ns and 400ns delays)</td>
</tr>
<tr>
<td>Liquid 3-pentanone in air</td>
<td>OD 3 &amp; OD 0.7</td>
<td>200-900ns in 100ns steps</td>
<td>(OD 0.7 for 200ns delay)</td>
</tr>
<tr>
<td>Liquid 3-pentanone in N₂</td>
<td>OD 3 &amp; OD 0.7</td>
<td>200-1400ns in 100ns steps</td>
<td>(OD 0.7 for 200ns delay)</td>
</tr>
<tr>
<td>N₂-purged liquid 3-pentanone in N₂</td>
<td>OD 3 &amp; OD 0.7</td>
<td>200-2400ns in 200ns steps</td>
<td>(OD 0.7 for 200ns and 400ns delays)</td>
</tr>
</tbody>
</table>

Normalized emission decay curves for liquid acetone are presented in Fig 6.9; for comparison, the vapour phase emission decay in nitrogen and the vapour phase fluorescence in air are also included. All data points are normalized to the maximum liquid phase fluorescence signal observed in the measurements, that of liquid acetone in air. It should be noted that all three liquid fluorescence signals agree to within 5% of each other, reflecting the impotency of oxygen quenching. In fact, liquid acetone fluorescence has been shown to be independent of bath gas composition for pressures up to 15bar [42]. The intensity of acetone vapour fluorescence is two orders of magnitude lower than that of liquid acetone under the particular experimental conditions. At 300ns after the start of fluorescence emission, the intensity of liquid acetone phosphorescence in air is only 2.7 times higher than the vapour, while 100ns later, the vapour phosphorescence is already stronger. The nitrogen-purged
liquid acetone phosphorescence remains higher than the vapour throughout the entire delay range; however, the liquid to vapour signal ratio drops from around 100 for the fluorescence to only around 10 at 300ns delay and to 2 at 1μs delay. The liquid acetone in nitrogen decay lies between the other two curves.

![Graph](image)

**Fig 6.9** Normalized nitrogen-purged liquid acetone in nitrogen bath gas, liquid acetone in nitrogen bath gas, liquid acetone in air bath gas, vapour acetone in nitrogen bath gas and vapour acetone in air bath emission decay curves

The phosphorescence of liquid acetone in air was approximated by a single exponential function ($R^2 \approx 0.99$), yielding a 74ns lifetime, whilst the other decays curves were fitted with bi-exponential functions (Table 6-5).
Table 6-5 Measured fast and slow lifetime components of liquid acetone and 3-pentanone for different excitation energy densities and dissolved oxygen concentrations

<table>
<thead>
<tr>
<th>Emission Decay Study</th>
<th>Fast Decay Component Lifetime (ns)</th>
<th>Slow Decay Component Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid acetone in air</td>
<td>74 ± 8</td>
<td>-</td>
</tr>
<tr>
<td>Liquid acetone in N₂</td>
<td>98 ± 4</td>
<td>661 ± 111</td>
</tr>
<tr>
<td>N₂-purged liquid acetone</td>
<td>127 ± 15</td>
<td>825 ± 164</td>
</tr>
<tr>
<td>Liquid 3-pentanone in air</td>
<td>72 ± 9</td>
<td>-</td>
</tr>
<tr>
<td>Liquid 3-pentanone in N₂</td>
<td>78 ± 16</td>
<td>-</td>
</tr>
<tr>
<td>N₂-purged 3-pentanone in N₂</td>
<td>58 ± 2</td>
<td>567 ± 232</td>
</tr>
</tbody>
</table>

The fast decay component of nitrogen-purged liquid acetone in nitrogen bath gas is nearly double the single lifetime component of the measurement carried out in air, while the longer one is more than tenfold higher. It is believed that longer purging could result to even longer lifetimes; however, the phosphorescence intensity along the nitrogen-purged stream is reasonably constant, suggesting that the liquid is nearly depleted of all oxygen. This is clearly not the case for liquid acetone in nitrogen, for which the effect of oxygen diffusion out of the stream can be visualized in the phosphorescence images. In order to demonstrate this effect, two average phosphorescence images are presented (Fig 6.10); one showing a 200µm liquid acetone stream in air, and one in nitrogen. Close inspection of the liquid acetone in air image reveals that the emission intensity distribution along the stream is fairly constant. In comparison, the emission intensity of liquid acetone in nitrogen bath gas already starts off at a higher value, as the topmost part of the imaged area corresponds to a location approximately 1cm downstream of the droplet generator pinhole, and increases all the way to the bottom of the image. The emission decay data of liquid 3-pentanone (Fig 6.11) validate the observation made earlier in the cuvette measurements regarding the effect of deaeration on the phosphorescence emission. In air, the single-component lifetime matches that of acetone very well, while in nitrogen, the lifetime increases only marginally, suggesting that any deaeration effect observed for acetone is far less potent. In addition, the clear identification of the particular phenomenon presented in Fig 6.10 was lacking in these experiments. Nitrogen-purged 3-pentanone in nitrogen phosphoresces nearly as much as its unpurged counterpart; however, the decay in this case was better fitted to a bi-exponential function. The large relative uncertainty of the slow component reflects the fact that the emission is nearly exponential. Regarding the fluorescence, once again an excellent
agreement amongst the different experiments was observed, with the average signal varying to within 4%.

**Fig 6.10** Phosphorescence images of a liquid acetone stream collected at 300ns delay (a) in air and (b) in nitrogen. The phosphorescence is constant along the length of the liquid stream set up in air, whereas in nitrogen, the phosphorescence increases downstream due to on-going removal of dissolved oxygen and subsequent degradation of oxygen quenching.

**Fig 6.11** Normalized nitrogen-purged liquid 3-pentanone in nitrogen bath gas, liquid 3-pentanone in nitrogen bath gas and liquid 3-pentanone in air emission decay curves
In comparing the liquid stream measurements to the 250mJ/cm² cuvette emission decay data, the following remarks are discussed. The observed disparities between the lifetime components (single exponentials and fast decay components) for aerated and deaerated studies are well-matched. For example, the liquid acetone lifetime nearly doubles following nitrogen purging in both the cuvette and liquid stream experiments, whereas for 3-pentanone, it stays nearly the same. Hence, it can be inferred that the effect of oxygen diffusion out of the liquid is correctly identified and interpreted using either experimental methodology. When inspecting the relative disparity between the prompt fluorescence and early phosphorescence measurements, the results also appear agreeable. For example, the acetone phosphorescence at 200ns delay accounts for approximately 0.025% for aerated and 0.08% for deaerated acetone, while in liquid streams, the equivalent values are 0.017% and 0.06% respectively. In contrast, at longer delays, the phosphorescence signals observed in the cuvette measurements display substantially less degradation. This is particularly clear in the unpurged acetone and 3-pentanone measurements. Possible explanations are the enhanced oxygen quenching from the interface regions, as well as the inability of the detection system to image these signals as a consequence of the relatively small light emitting volume. Thus, the regions excited by reduced energy density (due to absorption) may be responsible for the longer tails observed in the cuvette measurements. Finally, the possibility of late sensitized emission is once again brought forward. The last two suggestions render the liquid stream setup more suitable for studying the potential of using laser induced phosphorescence for two-phase flow visualizations; however, the qualitative agreement between the two sets of experiments, along with the increased practicality associated with the utilization of the cuvette setup, render it a useful tool for the particular application.

6.3 Two-Phase Flow Imaging by Acetone Laser Induced Phosphorescence

For the purposes of two-phase flow imaging using acetone phosphorescence, and additionally for providing a well-defined boundary condition (with respect to the dissolved oxygen content within the liquid), the use of nitrogen-purged liquid acetone in a nitrogen atmosphere is considered to be the optimal choice. The signal disparity between the two phases can be adjusted by selecting appropriate delay and gate settings to a large enough value so as to clearly identify the liquid/vapour interface, but simultaneously sufficiently small to prevent the emergence of any halation. In order to demonstrate the improvements
this technique introduces in two-phase flow visualization experiments, two cases are examined. Firstly, a non-evaporating acetone droplet stream (330μm average droplet diameter) is set up in a saturated acetone vapour in nitrogen environment. The fluorescence is initially collected and the same instantaneous image is presented in Fig 6.12 with two dynamic ranges (0-1000 counts in Fig 6.12 (b) and 0-100 counts in Fig 6.12 (c)) as the intense halation and large signal disparity between the two phases prevent the saturated vapour and real droplet sizes to be observed simultaneously. Phosphorescence, in this example, is collected over 400ns, starting off at 300ns after the fluorescence with a gain of 70%. A single dynamic range suffices as the signal disparity is sufficiently reduced and no halation is observed (Fig 6.12 (d)). A lower gain setting (50%) along with an OD 2.0 filter was employed in the fluorescence image collection. The excitation energy was set to 23.5mJ. Both fluorescence and phosphorescence images were background-subtracted and corrected for laser sheet inhomogeneities and dark noise. For comparison, a white light image of the of the same droplet stream with diffuse background illumination is also presented, indicating their real sizes and inter-droplet distances (Fig 6.11(a)).

![Fig 6.12](image)

**Fig 6.12** Results from a non-evaporating stream of acetone droplets in saturated acetone vapour in nitrogen. (a) White light image of a droplet stream under diffuse background illumination. (b) Fluorescence image of the stream (0-1000 counts dynamic range). (c) The same fluorescence image presented with 0-100 counts dynamic range. (d) Phosphorescence image of the droplet stream

The effects of halation have already been discussed earlier; an apparent increase in the vapour phase concentration around the droplets is observed, along with an increase in the spatial extent of the droplets by at least 50% (Fig. 6.12(c)). When increasing the dynamic range, the glow around the droplets subsides, but the vapour phase is now completely
indiscernible due to the low fluorescence signal level (Fig 6.12(b)). Instead, when monitoring the phosphorescence, no halation around the droplets is observed and the saturated vapour is clearly visible and discernible from the liquid (Fig 6.12(d)). The droplet sizes also match those of the shadow image (Fig 6.12(a)). The liquid phase intensities range between 1000 and 2000 counts for both fluorescence and phosphorescence images, whilst the vapour phase fluorescence to the left of the stream has an average intensity of 19 counts and the phosphorescence an average intensity of 420 counts.

The two imaging techniques are also compared under evaporating conditions, with fluorescence and phosphorescence images of a free-falling monodisperse droplet stream in pure nitrogen bath gas presented in Fig 6.13. It should be noted that the excitation energy, collection optics settings and dynamic ranges were carried over from the previously presented non-evaporative study. In this case, it is impossible to evaluate the vapour phase signal from the fluorescence image (Fig 6.13(c)), as the majority of the evaporated tracer lies within the spatial extent of halation. In contrast, when monitoring the phosphorescence, a vapour cloud forming around the droplet stream and expanding further downstream is clearly observed.

![Fig 6.13 Results from a stream of evaporating acetone droplets in pure nitrogen. (a) White light image of the droplet stream under diffuse background illumination. (b) Fluorescence image of the stream (0-1000 counts dynamic range). (c) The same fluorescence image presented with 0-100 counts dynamic range. (d) Phosphorescence image of the droplet stream](image)

### 6.4 Quantitative two-phase flow imaging

Following the comparative analysis of acetone two-phase flow imaging by laser induced fluorescence and phosphorescence on a qualitative basis, a quantitative examination is hereby
presented. While experiments were once again carried out around an isothermal evaporative droplet stream, an additional step was necessary; the calibration of both laser induced fluorescence and phosphorescence with acetone vapour concentration and excitation energy.

### 6.4.1 Vapour phase concentration and Excitation Energy Calibration

It has been firmly established that for low fluences, vapour acetone fluorescence varies linearly with both excitation energy and concentration [8, 27]. This, however, may not be the case for laser induced phosphorescence, as collisions with either ground state or excited triplet state acetone molecules result to quenching. The probability that such a collision event will occur is clearly time-dependent and hence, both energy and vapour phase concentration calibrations will apply to particular delay and gate settings. In comparison, the excited singlet state is extremely short-lived due to rapid inter-system crossing, and hence, laser induced fluorescence is hardly affected by molecular collisions at ambient pressure.

#### 6.4.1.1 Excitation Energy Calibration

The excitation energy calibration experiments were performed by saturating the cuvette with acetone vapour in nitrogen and varying the excitation energy between 7.8 and 22.1mJ. The cuvette was employed in this calibration in order to prevent the large energy drop occurring within the flow cell when the latter is saturated with the vapour tracer due to strong absorption of the laser beam prior to the imaging region. This energy drop would substantially limit the energy exciting the tracer within the imaging region, and thus, the obtained calibration would not be applicable to an evaporating droplet stream such as the one presented in Fig 6.13 (in this case the laser beam propagates unobstructed until the middle of the cell where it encounters and excites the droplet stream and surrounding vapour). Following both dark current and background signal corrections, 100 images were collected and a 250x100 region of interest was extracted and averaged for each pre-set energy setting. The energy drop within this region corresponds to approximately 5%. Vapour acetone fluorescence was collected using a delay of -100ns relative to the start of emission, a gate of 500ns, a gain of 50% and an OD 2.0 filter. The vapour phase radiative decay results (Fig 6.7) indicate that the contribution from any collected phosphorescence when using the particular delay and gate settings will be insignificant. Vapour phase phosphorescence was collected by
setting the delay to 200ns after the start of fluorescence emission, maintaining the 500ns gate, setting the gain to 70% and removing the neutral density filter. The average fluorescence and phosphorescence signals, as well as excitation energies, were normalized to their respective maxima and are presented in Fig 6.14:

![Normalized fluorescence and phosphorescence signals](image)

**Fig 6.14** (Left) Normalized fluorescence signal plotted against normalized excitation energy. (Right) Normalized phosphorescence signal plotted over the same excitation energy range. The maximum pulse energy was 22.1mJ corresponding to a fluence of 221mJ/cm². The laser sheet thickness and height are 400µm and 2.5cm respectively.

The linearity between fluorescence and excitation energy was confirmed in these measurements. Laser induced phosphorescence, however, was shown to vary non-linearly with excitation energy, and the obtained data were better fitted with both power and second order polynomial functions. In both cases the observed R² and rmse values were nearly identical (0.9974 and 0.0008), signifying that either could be implemented in correcting for pulse-to-pulse variation.

\[
\frac{S}{S_0} = -0.3802 \times (E/E_0)^2 + 1.1800 \times (E/E_0) + 0.1897
\]

**Eq 6-4**

The pulse-to-pulse variation of the XeCl excimer laser was investigated simultaneous by deployment of two different tactics; by utilizing the THORLABS power meter to measure the average energy and standard deviation over 1000 consecutive pulses, and by monitoring the fluorescence emission of acetone vapour using a non-intensified LaVision Imager Intense camera over the same run. In the latter case, the mean fluorescence of a 50x50 pixel ROI was calculated for all 1000 collected images, and the average and standard deviation over the
entire run were subsequently obtained. In both cases, the standard deviation values accounted for less than 3% of the mean measurements, signifying that the error induced due to fluctuations in the excitation energy is relatively small.

### 6.4.1.2 Number Density Correction

Acetone vapour laser induced fluorescence and phosphorescence were also calibrated against acetone vapour concentration. For this purpose, the flow cell was saturated with known acetone vapour concentrations obtained by adjusting the flow rates of two independent gas lines mixed prior to entering the cell. One line provided saturated acetone vapour in nitrogen (with the acetone number density corresponding to the saturated value at ambient temperature and pressure), whilst the second provided pure nitrogen. An extensive account of how the acetone number density can be calculated by employing such a setup can be found in literature [8]. The energy drop due to laser sheet absorption within the cell was calculated using the Beer-Lambert law, and the collected fluorescence and phosphorescence signals were corrected using the previously derived fluorescence and phosphorescence against excitation energy relationships. In order for these corrections to be valid, the collection optics settings were carried over from the excitation energy calibrations. For both fluorescence and phosphorescence experiments 100 images were collected, while the same 250x100 region of interest was extracted and averaged for each measurement run (number density setting). The corrected average signals and number densities were then normalized to their respective maxima and plotted (Fig 6.15).

![Graphs](image.png)

**Fig 6.15** (Left) Normalized fluorescence plotted against normalized number density. (Right) Normalized phosphorescence plotted over the same number density range. The average pulse energy was 20.5mJ
corresponding to a fluence of 205mJ/cm². The saturated acetone vapour number density is $6.916 \times 10^{18}$ molecules/cm³ at the ambient temperature and pressure of 297.15K and 1bar respectively.

The results indicate that whereas the fluorescence signal varies linearly with number density, as expected, laser induced phosphorescence signals are once again better fitted to either a power function or a second order polynomial ($R^2$ and rmse of 0.9982 and 0.001428 respectively). The observed linearity between fluorescence and acetone number density serves as a validation for the procedure. The second order polynomial function describing the phosphorescence against number density trend is presented below:

$$\frac{n_a}{n_{a0}} = 0.6899 \times (S/S_0)^2 + 0.2826 \times (S/S_0) + 0.008521 \quad \text{Eq 6-5}$$

The observed non-linearities in the phosphorescence calibration experiments with both increasing excitation energy density and concentration are attributed to competition between a higher light-emitting population and increased phosphorescence quenching via triplet-triplet annihilation. The saturation-like behaviour at both high laser fluences (Fig 6.14) and high tracer concentrations (Fig 6.15) probably signifies the onset of triplet-triplet annihilation as a strong deexcitation channel. In contrast, lower fluence/tracer concentration regions indicate that for lower triplet state population densities, the vapour phase phosphorescence signal behaviour approaches linearity. Within the context of the present study, a lower excitation energy could have been adopted in order to perform the quantitative analysis within the regime for which the effects of triplet-triplet annihilation are not so prominent; however, this would be done at the expense of noisier measurements (given a short gating time is adopted), an outcome that is clearly unwanted.

### 6.4.2 Quantitative acetone vapour measurements

Both laser induced fluorescence and phosphorescence imaging techniques were employed in order to determine the vapour distribution around an evaporative droplet stream set up in nitrogen bath gas. A schematic diagram of the imaged region along with a shadow image of the examined 161m droplet stream obtained under diffuse background illumination are presented below:
Prior to an experimental run, the cell was saturated with acetone vapour in nitrogen and average saturated concentration fluorescence and phosphorescence signals were obtained using the calibration optical setup settings. In doing so, 100 images were collected and the same 250x100 pixel region of interest, now coincident with the droplet stream location, was selected and processed. Regarding the fluorescence measurements, the ROI mean signal was corrected for absorption effects through the cell using the Beer-Lambert law, and then used as the cut-off level between the vapour and liquid phase plus halation signals, following the procedure introduced by Bazile and Stepowski [105] and later adopted by other researchers [104, 106]. Subsequently, the vapour cloud forming around the droplets was quantified using this measurement and the number density calibration. A phosphorescence threshold value was calculated in an identical manner; however, the threshold signal was corrected using both the Beer-Lambert and previously derived phosphorescence against excitation energy relation. Prior to image acquisition, dark current, background and white image corrections were implemented, while both fluorescence and phosphorescence images were corrected for pulse energy variation using the energy calibration results. Single-shot raw and quantified acetone mole fraction image obtained by both laser induced fluorescence and phosphorescence are presented below (Fig 6.17 and 6.18), while 20-image averages are displayed in Figs 6.19 and 6.20 respectively:
Fig 6.17 Raw phosphorescence and calculated acetone mole fraction images of an evaporating acetone droplet stream in nitrogen. The theoretically calculated mean droplet diameter is 161 µm

Fig 6.18 Raw fluorescence and calculated acetone mole fraction images of the same (Fig 6.17) evaporating acetone droplet stream in nitrogen. Note the difference when the mole fraction image is derived from a raw fluorescence rather than a phosphorescence image

Fig 6.19 Raw average phosphorescence and calculated acetone mole fraction images of an evaporating acetone droplet stream in nitrogen. The theoretically calculated mean droplet diameter is 161 µm
In producing the examined droplet stream, a 100µm pinhole was fitted to the droplet generator. The liquid acetone flow rate was adjusted to 3.3 ml/sec, whilst the resonance frequency of the generator electronics was set to 25 kHz; the respective theoretically calculated average droplet size was 161µm [128]. Measured diameters from both shadow and phosphorescence images are virtually identical and in good agreement with the calculations. The fluorescence images, instead, are plagued by strong halation that forces the location of the liquid-vapour interface away from the actual droplet surfaces. Hence, it provides no realistic information regarding the location of the liquid-vapour interface or droplet sizes. The vapour distribution obtained from the phosphorescence image suggests that a low concentration (mole fraction of up to 0.05) vapour tunnel surrounds the droplet stream, while adjacent and in between the droplets, the acetone mole fraction rises to beyond 0.10. A saturated or near-saturated acetone vapour concentration is only encountered immediately adjacent to the droplets.

In order to examine more closely the extent of halation in LIF images and compare the vapour fields obtained by both techniques, amongst each other, as well as with those obtained by other researchers, radial profiles of acetone vapour distributions emanating from droplet surfaces have been collected and averaged over 10 droplets. As the droplet size and shape showed periodic variations with the distance from the droplet generator tip, equidistant droplets from 10 different fluorescence and phosphorescence images were selected. The results are presented in Fig 6.21:
Fig 6.21 Averaged radial profiles of acetone vapour mole fractions \( (x_a) \) plotted against the distance from the droplet centre normalized to the average droplet diameter \( (X_d/D_d) \). Results by both laser induced fluorescence and phosphorescence imaging are presented in tandem.

The radial profile obtained from the phosphorescence images suggests that the vapour tunnel formed around the droplet stream extends radially to nearly 10 droplet diameters away from the droplet surfaces and represents the radial diffusion and forced convection (owing to the relative motion between the droplet and the ambient gas) of the evaporated tracer. In the immediate vicinity of liquid droplets, the vapour mole fraction increases rapidly towards the saturated value. The profile obtained from the fluorescence images indicates that a vapour phase measurement is not feasible to within 1.5 droplet diameter away from the droplet surfaces. At greater distances, the effect of halation results to an overestimation of the entire vapour field which extends to more than 7 droplet diameters. Orain and co-workers [95] have studied the radial profile of the vapour tunnel forming around a 230\( \mu \)m monodisperse droplet stream at 298K. They present results with and without a halation correction; the former obtained by quantifying the spatial extent and intensity of halation by means of the Mie scattering signal from ethanol droplets. From the uncorrected profile, mole fractions can be first evaluated at a distance of slightly more than half a droplet diameter away from the droplet surfaces, whilst the mole fraction distribution coincides with the one obtained from the corrected images at a distance slightly longer than 2 droplet diameters away from the droplet surfaces. The spatial extent of halation is shorter than the one observed in the present study, an outcome that can be attributed to the following two reasons. Despite the fact that
similar inter-droplet separations are encountered in the present study and that of Orain and co-workers (around 3.5 droplet diameters), in the latter case the droplets are larger and hence, the radial distribution measurement across a particular droplet suffers less severely from halation contributions from the other two neighbouring droplets. Secondly, the implemented halation correction is incomplete, as the authors admit. This is also evident from the fact that the first mole fraction measurement is not attained immediately adjacent to the droplet surface but approximately 0.2 droplet diameters away from it. Comparing the corrected profile with the one obtained presently by means of the laser induced phosphorescence technique, it also becomes apparent that the former is not completely free of halation; despite the fact that the overall trend is very similar, it appears that the corrected profile consistently overestimates the acetone vapour mole fraction measurement. However, both experimental and numerical results presented in another study by Castanet and co-workers [134] for 170µm droplets injected in ambient air agree very well with the mole fraction profile obtained presently by laser induced phosphorescence imaging. In an attempt to account for halation effects, Castanet and co-workers have successfully utilized the technique previously introduced by Orain and co-workers.

Another quantitative account of the radial acetone vapour distribution around a droplet stream is provided by Frackowiak and co-workers [97, 135]. In this study, the halation is suppressed by masking the droplets using an aperture in the field of view, thus obtaining the vapour field directly from a fluorescence measurement in the interval between approximately 1.5 droplets diameters away from the droplet surfaces up to more than 10 droplet diameters away from the stream. A comparison of the radial profiles obtained with and without the mask reveals that the blooming effect extends as far as 10 droplet diameters for 173µm and 238µm droplets. The present study confirms this observation for up to at least 7 droplet diameters away from the liquid-vapour interface. For 173µm droplets at 22.4 ºC, the agreement between measured radial profiles by Frackowiak and co-workers (with the implementation of the mask) and the present study is satisfactory. The numerical results, however, overestimate the experimental measurements of both studies. Additionally, the phosphorescence results suggest a much sharper increase in the acetone vapour concentration near the droplet stream (0.5 droplet diameters away from the droplet surface) than the numerical results under consideration. The experiments by Castanet and co-workers [134] also appear to support the former.
In order to demonstrate the feasibility of laser induced phosphorescence imaging over a wider droplet diameter range, further experiments were conducted for two evaporative droplet streams of 124μm and 226μm theoretically calculated droplet diameters. The vapour phase quantification procedure for both droplet streams was identical to the one adopted before, as were all optical setup parameters. Once again, no halation effects were detected with the observed droplet sizes closely matching those of the theoretical calculation. Single-shot images of both droplet streams are presented in Figs 6.22 and 6.23, while average (10-droplets) acetone vapour radial profiles are presented in Figs 6.24 and 6.25. The error bars represent the standard deviation of the acetone mole fraction measurement.

![Image](image1)

**Fig 6.22** Raw and quantified phosphorescence images of an evaporating acetone droplet stream in nitrogen. The theoretically calculated mean droplet diameter is 124μm

![Image](image2)

**Fig 6.23** Raw phosphorescence and calculated mole fraction images of an evaporating acetone droplet stream in nitrogen. The theoretically calculated mean droplet diameter is 226μm
Fig 6.24 Average radial profile of acetone vapour mole fractions ($x_a$) around a 124µm (theoretically calculated value) droplet stream obtained by laser induced phosphorescence imaging

Fig 6.25 Average radial profile of acetone vapour mole fractions ($x_a$) around a 226µm (theoretically calculated value) droplet stream obtained by laser induced phosphorescence imaging

A comparison amongst the radial profiles obtained by laser induced phosphorescence imaging for 124µm, 161µm, and 226µm droplets reveals that the extent $x/D_d$ of the vapour distribution increases with decreasing droplet size; from less than 3.5 droplet diameters for 226µm droplets to around 6 droplet diameters for 161µm droplets and 9 droplets diameters for 124µm droplets. The results of Castanet and co-workers [134] support this finding as the
absolute special extent for 144m and 170m droplets is shown to remain almost identical. The results of Sahu [96] for 235µm and 122 µm also display the same affect; however; no halation correction was carried out and, consequently, their validity is undermined.

Vapour distribution profiles were also generated between consecutive droplets for the 161µm and 124µm streams. In this case, the axial distance z was normalized to the droplet diameter, while average mole fractions were calculated from 10 droplet pairs from different images located roughly at the same axial location. Care was also taken in selecting droplet pairs for which the inter-droplet separation was very similar, as the observed dispersion along the axial direction was imperfect. For 161µm droplets, the average mole fraction drops from the saturated value immediately adjacent to the liquid-vapour interface to approximately 0.08 in the mid distance between the two droplets, and then quickly rises again to the saturated value Fig 6.26:

![Fig 6.26 Average axial profile of acetone vapour mole fractions (xₐ) between two adjacent 161µm droplets (theoretically calculated value) obtained by laser induced phosphorescence imaging](image)

The vapour fraction at the same distance away from the droplet surface but in the radial direction was earlier shown to be around 0.04, with the resulting vapour concentration distribution around a droplet being uneven. For the 124µm droplet stream, the normalized inter-droplet separation is smaller (approximately 2.3 droplet diameters) and the concentration in the mid distance rises to nearly 0.13, with the equivalent value in the radial
direction being 0.09 (Fig 6.27). The normalized inter-droplet separation parameter, often denoted \( c = z/D_d \) in literature, has been shown to be a decisive factor with respect to both evaporation rate and vapour distribution development. Connon and co-workers [136] emphasize that for \( c < 3 \), convective entrainment in the inter-droplet region is severely reduced with local concentrations rising as a consequence. These results emphasize the efficacy of the LIP technique, as despite the very small inter-droplet separations, imaging of evaporated concentrations was possible.

![Graph](image)

**Fig 6.27** Average axial profile of acetone vapour mole fractions \((x_a)\) in between two adjacent 124\(\mu\)m droplets (theoretically calculated value), obtained by laser induced phosphorescence imaging

### 6.5 Discussion and further work

Having provided an account of the applicability of laser induced phosphorescence imaging for the investigation of evaporative acetone droplet streams, suggestions on how the technique can be improved in order to obtain higher signal to noise ratios will be set forth. The potential application of the LIP technique to different studies is also discussed, both using tracers other than acetone, as well as tracer/fuel blends.
6.5.1 Suggestions for improvement

A major drawback associated with the employment of intensified cameras in optical diagnostics is the high noise originating from the MCP. Higher gains induce more noise, and unlike non-intensified CCD cameras, the observed noise level can vary with the signal level. An assessment of the noise associated with the vapour phase concentration measurements presented earlier has been carried out by means of the following methodology: The phosphorescence emission of acetone vapour was monitored over a wide range of signal levels by preserving the imaging gain and delay settings, increasing the gate time and adjusting the lens aperture. 50-image sets were collected at different aperture settings, and the mean signals and standard deviations within a 50x50 pixel ROI were calculated and plotted (Fig 6.28):

![Fig 6.28](image_url)

**Fig 6.28** ROI mean and standard deviation values representative of the intensified camera noise at different signal levels

The signal-to-noise ratio at the saturated concentration signal level is approximately 14, dropping to around 11 at 400 counts and around 8 at 200 counts. Methods allowing for boosting the signal-to-noise ratio when conducting LIP measurements can be broadly categorized in two groups; improving the efficiency of the collection optics and tweaking the excitation parameters. Generally, longer excitation wavelengths result in increased phosphorescence efficiency and longer liquid and vapour phase lifetimes as the excited triplet state acetone molecules migrate closer to the thermalization level for which the excess vibrational excitation energy and dissociation quantum yield are very low. As has been noted
in literature, the phosphorescence quantum yield has been associated with an excess vibrational energy dependant dissociation mechanism. Hence, lower excitation wavelengths promote dissociation, with the fraction of excited triplets radiatively decaying back to the ground state being reduced. Excitation at 320nm, for example, is highly recommended when employing the particular technique \[28\]. Increasing the excitation energy results to higher phosphorescence signals; however, unlike the fluorescence emission, the observed signal gain will not be proportionally higher. In this context, the employment of a beam homogenizer is highly recommended, as a homogeneous laser sheet distribution will be obtainable while minimizing the available excitation energy wastage \[137\]. An additional benefit that need essentially be noted is that any temporal fluctuations in the spatial excitation profile would also be moderated.

High gains can also be obtained by tweaking the collection efficiency of the optical setup. Owing to the different decay rates of the liquid and vapour phases, the gate and delay settings can be adjusted in order to allow for imaging with lower intensifier gain, while still preserving sufficient signal strength disparity. The presented measurements should therefore be interpreted as a “worst case scenario” in the sense that a very small gate time (500ns) was employed. Unlike pressure-atomized spray investigations, the low droplet velocities observed in monodisperse droplet streams allow for a substantial increase in the gate time without introducing blurring. Thus, the gain can then be reduced while maintaining similar vapour phase signal levels, effectively boosting the signal-to-noise ratio. An example whereby this practice was exercised is provided in Fig 6.29.

\[28\]

\[137\]

**Fig 6.29** Raw phosphorescence (left) and fluorescence (right) images of an evaporating acetone droplet stream in nitrogen. The theoretically calculated mean droplet diameter is 228µm, while the IRO delay (relative to the start of fluorescence emission), gate and gain settings are 150ns, 1500ns and 63% for the phosphorescence and -
100ns, 500ns and 50% for the fluorescence images. An OD 2.0 filter was employed in collecting the fluorescence emission.

This phosphorescence image was collected at a delay of 150ns following the prompt fluorescence emission, with the gate and gain set to 1500ns and 63% respectively. The theoretically calculated droplet size is 228μm and the inter-droplet separation parameter is roughly equal to 2. The mean saturated acetone vapour phosphorescence signal (around 670 counts) closely matches to the value achieved using the previous IRO settings, as does the liquid phase signal; however, the signal-to-noise ratio at the saturated concentration signal level is now approximately 32. This corresponds to a more than twofold increase compared to the previous imaging settings. The same droplet stream was imaged by standard LIF using the same IRO settings employed previously. Owing to the very small inter-droplet separation, a high dynamic range was necessitated in order for the individual droplets to be displayed in isolation.

The utilization of an IRO system better suited for phosphorescence imaging is also believed to contribute substantial gains. For example, the photocathode installed in the currently employed IRO is an S20 multialkali type; its quantum efficiency over the acetone phosphorescence emission (350-500nm peaking at around 420nm), varies in the 10%-20% range. Switching to an IRO system equipped with a GaAsP photocathode is recommended, owing to the considerably higher quantum efficiency (20-50%) over the same spectral range. Regarding the processing of phosphorescence images, stronger spatial averaging, for example 5x5, would improve the observed signal-to-noise ratio, albeit at the expense of imaging resolution.

Another important aspect that must be considered prior to expanding the LIP technique to more general experiments is the effect of reduced laser fluence on vapour phase concentration measurements as a result of absorption across a flow field. As has already been noted, in the case of phosphorescence, a lower fluence will enhance the phosphorescence efficiency and hence the signal drop cannot be straightforwardly calculated on the basis of the Beer-Lambert law. Assuming a flow field that is imaged across 5cm, the maximum energy drop would result for a fully saturated acetone vapour environment. Under the present experimental conditions (temperature of 297K, excitation at 308nm) the laser energy would drop to approximately 57% of its original value. In the case of fluorescence, this corresponds
to a 43% decrease in the vapour signal intensity. In order to quantify the corresponding
decrease in the vapour phase phosphorescence signal, the phosphorescence against excitation
energy curve can be used (Fig 6.14). In this case, the phosphorescence signal corresponding
to 57% of the original excitation energy is only reduced to approximately 74% of its original
value. This 17% disparity between the fluorescence and phosphorescence measurements
represents the maximum error that could be induced for a measurement carried out under the
particular conditions. If the vapour concentration varies across the flow field, and hence the
laser pulse is not so strongly absorbed, this error would be substantially reduced. The use of
longer excitation wavelengths would help diminish this inaccuracy even further, as a result of
reduced absorption; for example, at 320nm, the absorption cross-section is reduced to 32% of
the equivalent value at 308nm [27]. Additionally, reducing the laser fluence by either
reducing the excitation energy or increasing the laser sheet thickness would also assist
towards the minimization of the particular error.

6.5.2 Tracer/fuel blends

In internal combustion engines, spray diagnostics are often conducted by doping a base
fuel, which is “transparent” for the employed excitation wavelength, with a co-evaporating
tracer. Acetone, for example, has been employed in the design and experimental
investigation of a multi-component mixture comprised of three tracers and three base fuels of
different volatilities in an attempt to match the volatility range of commercial automotive
gasolines [138, 139]. In particular, acetone was the low-volatility fuel tracer, with the low
volatility base fuel component being isopentane. Acetone/ethanol and acetone/2-propanol
blends have also been employed in droplet stream experiments similar to the ones presented
earlier, in order to assess the effects of asymmetric radiant heating on vaporization [103], and
provide experimental data for modelling. The applicability of LIP imaging in such cases is
subject to the doping concentration of acetone, which should be high enough to ensure
adequate signal levels from both vapour and liquid phases. The phosphorescence properties
of the acetone/solvent mixture would also have to be calibrated in a similar manner to this
study, in order to account for the different triplet-singlet and triplet-triplet quenching rates.
TTA rates are expected to diminish for lower doping concentrations, resulting to enhanced
phosphorescence efficiency and reduced saturation effects with respect to both excitation
energy and tracer concentration. Hence, the signal reduction anticipated as a result of the
reduced acetone number density will be partially restored as a result of reduced frequency of molecular collisions between excited triplets. Both vapour and liquid phase lifetimes are therefore expected to rise, also allowing for signal augmentation by increasing the gating time.

6.5.3 LIP using different tracers

Direct imaging results of the triplet emission of 3-pentanone have been reported for the first time in this study. The LIP technique was, however, not introduced by deployment of the particular tracer owing to the very low (near-noise) vapour phase phosphorescence and fluorescence signals. This comes as no surprise, as the vapour pressure of 3-pentanone at ambient conditions (293.15K, 1bar) is approximately seven times lower than that of acetone. However, at higher temperatures, LIP diagnostics would be readily feasible. Moreover, compared to acetone, 3-pentanone is rendered as a more “relevant” tracer for fuel vaporization studies, often utilized in tracing isooctane [140]. With regard to LIP, it offers the additional advantage of near-negligible nitrogen purging dependence. As a result, it can be readily employed without the necessity to perform any deaeration, offering reduced experimental complexity. Very little is known regarding the phosphorescence properties of 3-pentanone and thus, a spectroscopic study is rendered useful. However, close agreement with acetone, much like in the case of fluorescence spectroscopy is expected. A setup such as the current one or one incorporating the improvements suggested earlier could be readily employed.

The ideal tracer for conducting LIP experiments is believed to be biacetyl. With respect to volatility, it lies between acetone and 3-pentanone (boiling point of 88°C). Biacetyl phosphorescence has been extensively studied in literature, and has been implemented in diagnostics, particularly in velocity tracking [37] as well as molecular mixing studies [36]. A complete account of biacetyl photophysics can be found in [27]. Its phosphorescence efficiency and lifetime are approximately 1.5ms and 15% respectively (independent of excitation wavelength above 400nm), suggesting that very high signal gains should be expected compared to acetone. In addition, biacetyl phosphoresces in the green, thus allowing for full deployment of the spectral response characteristics of a GaAsP photocathode. Biacetyl excitation is somewhat less practical than for the other two ketones, as its absorption spectrum (350nm-460nm) is mainly accessible by excimer laser or Nd:YAG pumped dye
lasers. A frequency-tripled Nd:YAG (355nm) or a XeF excimer could still be employed; however, at the cost of substantial excess vibrational energy and high dissociation rates and thus, reduced phosphorescence efficiency.
7 Laser Induced Fluorescence and Phosphorescence Imaging in a Spray

A major challenge in realizing fuel vapour concentration measurements in a spray by PLIF is discriminating between the fluorescence contributions from the two phases. LIEF imaging tackles this problem by spectrally discriminating between the vapour and liquid phase signals, with the vapour-liquid crosstalk identified as the major source of uncertainty in the vapour phase concentration measurement. In oxygen-containing environments, where the adoption of the LIEF method is rendered problematic due to strong oxygen quenching, isolating a liquid-only signal can be achieved by monitoring either the Mie scattering signal from liquid droplets, or the phosphorescence. The liquid phase Mie scattering signal has been extensively employed along with the redshifted fluorescence emission in yielding two-dimensional droplet size measurements in sprays [19, 141, 142]. The ratio between the fluorescence emitted by illuminated spherical droplets and the light scattered off their surfaces is fundamentally assumed to be proportional to the Sauter Mean Diameter (SMD), which when calibrated using known droplet sizes [143], and can generate quantitative information regarding the droplet size distribution. Typically such measurements are plagued by laser sheet extinction effects, often tackled by utilizing bi-directional illumination [144], as well as signal attenuation between the measurement plane and the detector [145]. In addition, dependences between the scattered light intensity and droplet surface area, fluorescent dye concentration and scattering angle have been identified, rendering the interpretation of the LIF/Mie ratio challenging for smaller droplet sizes [146, 147].

Another significant challenge associated with the interpretation of both fluorescence and Mie scattering signals in optically dense media such as sprays is multiple scattering. Due to the high density of liquid droplets interacting with the probing laser light, the long path length of the latter within the probed medium and the large acceptance detection angle of the collection optics, a large number of photons reaching the detectors have experienced more than one scattering event. This breakdown of the single scattering approximation introduces significant uncertainties (through blurring and attenuation) to both planar Mie scattering and LIF signals. The recently introduced Structured Laser Illumination Planar Imaging (SLIPI) technique [148, 149] offers an effective way in moderating the unwanted contributions of multiple scattering, albeit with important limitations and at a considerable cost.
Despite the fact that the phosphorescence emission of ketones in air is also attributed to the liquid phase only, no attempt to calibrate it against the fluorescence has been found in literature. However, the possibility of utilizing liquid phase phosphorescence data in order to quantitatively account for the liquid phase contribution in liquid-vapour fluorescence images has been discussed in two separate studies. In the first case, the possibility of calculating droplet masses by combined fluorescence and phosphorescence imaging was considered, but was rendered inaccurate compared to the deployment of fluorescence signals [29]. The authors of the second study suggested that on account of the similarities observed between spray fluorescence and phosphorescence images with respect to both secondary emission and scattering effects, it should be possible to directly account for the liquid phase fluorescence contribution in a spray fluorescence image using the phosphorescence image. In that way a measurement of the evaporated fuel concentration [108] could be obtained. The proposed technique was examined by fitting different scaling factors to the subtracted phosphorescence images; however, no attempt was made to investigate the relationship between the two liquid phase signals or quantify any uncertainties.

The experiment described in this section has been designed in order to investigate and build upon the idea put forward by Kiel and co-workers [108], harvesting the knowledge obtained from the phosphorescence lifetime calibration experiments in the cuvette and laminar stream experiments. In doing so, the experimental conditions have been optimised for the particular study and an appropriate methodology has been developed and adopted. The first part of the forthcoming analysis aims at establishing the fundamental assumptions on which the experimental investigation is based. The experimental methodology and image processing approach will be discussed right after, with the experimental results and a relevant discussion completing this section of the report.

### 7.1 Fundamental Assumptions

In order to establish the fundamental assumptions behind the experiment, a fictional experiment comprised of a probed volume saturated with a gaseous tracer in air, an excitation source and a detector pair is proposed. The tracer component is assumed to display similar singlet and triplet emission characteristics to acetone and 3-pentanone, with the vapour and liquid phase fluorescence virtually insensitive to oxygen quenching, the vapour phase phosphorescence completely quenched, and the liquid phase phosphorescence still detectable.
The first detector is dedicated to the collection of fluorescence signals only, while the second is responsible for imaging the phosphorescence emission. Both imaging systems are assumed to be identical and perfect (uniform response throughout the CCD, absence of noise and blurring, etc.), as well as perfectly aligned with each other. Upon excitation, the tracer fluoresces and the fluorescence intensity at each pixel of the detector corresponds to the saturated vapour phase signal $S_{0\text{Fl\ Vapour}}$, while no phosphorescence emission is observed ($S_{0\text{Ph\ Vapour}} = 0$). A schematic representation of the proposed scenario is presented in Fig 7.1.

If droplets are introduced to the flow-field, the collected fluorescence signals in regions where both tracer phases coexist will be comprised of two separate contributions: the vapour phase fluorescence $S_{\text{Fl\ Vapour}}$, and the liquid phase fluorescence $S_{\text{Fl\ Liquid}}$. The phosphorescence image obtained at a slight delay will be comprised of only the liquid phase phosphorescence $S_{\text{Ph\ Liquid}}$ (Fig 7.2).

**Fig 7.1** Schematic representation of the proved volume and the fluorescence and phosphorescence signals corresponding to the saturated vapour phase concentration.

**Fig 7.2** Schematic representation of the proved volume, and the fluorescence and phosphorescence signals corresponding to the saturated vapour phase concentration plus the liquid tracer.
Subtracting the vapour-only fluorescence (saturated vapour concentration image) from the vapour plus liquid fluorescence provides an estimate of the liquid phase fluorescence:

\[(S_{FlVapour} + S_{FlLiquid}) - S_{0FlVapour} \approx S_{FlLiquid}\]  Eq 7-1

An absolute equality cannot be assigned to this relationship as the fluorescence contribution of the vapour volume that has been substituted by a droplet or multitude of droplets is not been accounted for. The resulting uncertainty, however, is expected to be small due to the large density disparity, and consequently fluorescence intensity disparity between the two phases. In real two-phase flow systems, such as sprays, larger deviations may ensue as a result of laser light scattering, reabsorption and reemission effects, multiple scattering and signal attenuation. The liquid-only fluorescence signal obtained in this manner can then be plotted against the phosphorescence \(S_{PhLiquid}\), and a correlation function between the liquid phase fluorescence and phosphorescence can be extracted. Following this calibration procedure, the phosphorescence images obtained in an experimental evaporative or non-evaporative run can be used to simultaneously locate the liquid phase and correct for the liquid phase fluorescence contribution in fluorescence images.

### 7.2 Experimental Considerations

In order to obtain a correlation function between the liquid phase fluorescence and phosphorescence signals, calibration experiments were carried out under non-evaporative conditions for both acetone and 3-pentanone sprays. Prior to each experimental run, the injection system fuel tank was filled with aerated acetone or 3-pentanone, while the injection chamber was saturated with the respective gaseous tracer in air. The injection duration and pressure were set to 1.5ms and 150bar respectively, while imaging experiments were carried out for two injection timings: 0.4ms and 1.4ms after the start of injection. Instantaneous acetone spray fluorescence images corresponding to the two aforementioned injection timings are presented in Fig 7.3. Prior to presenting the image processing procedure, two aspects of the experiment necessitating particular attention will be discussed; the excitation energy non-uniformity, and the selection of appropriate phosphorescence imaging settings.
7.2.1 **Laser sheet profile non-uniformity**

The excitation energy dependence of the phosphorescence emission has been observed in the cuvette lifetime measurements, and has been attributed to quenching effects by excited triplets. In order to address the issue of variable TTA rates across the imaging region as a result of laser sheet profile non-uniformities, the laser sheet excitation energy distribution was examined. In doing so, the laser sheet was focused down to approximately 500μm, the injection chamber was saturated with acetone vapour, and 100 fluorescence images were collected and averaged. A 440x100 pixel region of interest was extracted and the fluorescence signals along each row were summed, averaged and normalized (Fig 7.4).

The normalized laser sheet profile indicates that the excitation energy varies by as much as 60% within the interrogation window (the effect that such excitation energy diversity induces to the phosphorescence efficiency is discussed in the following subsection). In an attempt to
further homogenize the excitation energy distribution, provided a beam homogenizer was not available, a 1cm portion of the laser sheet was extracted (the rest was blocked using an iris) and expanded; the resulting profile is presented in Fig 7.5.

![Region of Interest](image)

**Fig 7.5** Region of interest from which the laser sheet profile distribution was calculated, presented along with the expanded light sheet profile

The clear disadvantage associated with adoption of the particular tactic is the overall reduction in the available excitation energy. The original laser sheet energy (500-pulse average), was 25.2mJ. As the spray calibration experiments are carried out by saturating the injection chamber with the gaseous tracer, laser sheet attenuation due to absorption results to only approximately 55% of the original excitation energy reaching the spray in the case of acetone (Beer-Lambert law calculation). Upon expanding the laser sheet, the available excitation energy drops by nearly 8mJ, with the average pulse energy reaching the spray now only approximately equal to 10mJ. For 3-pentanone, this value is significantly higher (approximately 16mJ) as a result of the much lower saturated vapour concentration.

### 7.2.2 Emission decay measurements

In order to optimize the IRO delay and gate settings, emission decay measurements were carried out for both tracers. As a result of the combined effects of aeration and low liquid phase density within the probed volume, the spray phosphorescence signal is substantially weaker compared to the droplet stream experiments; it is therefore imperative to capture the phosphorescence as early as possible. In doing so, the transition to the pure liquid phase phosphorescence regime was identified using the vapour phase fluorescence signal as reference. Prior to introducing the spray, the injection chamber was saturated with the vapour
tracer while the IRO delay was increased, shifting the gate out of the fluorescence and into the pure phosphorescence emission regime. Due to the presence of oxygen in the ambient gas, the vapour phase phosphorescence is completely quenched; by advancing now the intensifier gate in 5ns steps, the IRO delay setting at which the vapour phase fluorescence reemerges was identified and associated with the end of the singlet state emission from both tracer phases. In order to prevent the collection of any liquid phase fluorescence in the phosphorescence images as a result of intensifier jitter, the earliest phosphorescence image acquisition delay was set to 10ns after the end of fluorescence emission. The spray was then introduced to the saturated vapour in air environment, and 50 phosphorescence images were collected with the IRO gate and gain set to 100ns and 70% respectively. The procedure was repeated in 100ns steps for delays up to 610ns after the end of fluorescence emission, at which point no phosphorescence signal was discernible. The same procedure was also carried out with the laser firing but without injection, in order to collect background signals for each delay setting over the examined phosphorescence decay range. The collected background signals were then averaged for each IRO delay, and subtracted from the corresponding raw phosphorescence images during post-processing. Following the image acquisition and background subtraction steps, a 200x20 interrogation window corresponding to the spray region was extracted from each processed image (Fig 7.6).

The data from all 50 extracted rectangles per measurement run were averaged and emission decay data points were generated. The emission decay measurements were finally normalized to the prompt fluorescence signal and plotted (Fig 7.7), in an identical manner as
practiced in previous lifetime measurements. Fluorescence images were collected using identical gain and gate settings (70%, 100ns), while an OD 3.0 and OD 0.7 neutral density filter combination was employed in order to avoid saturating the camera. During post-processing, the vapour phase fluorescence contribution to the total fluorescence was accounted for, providing a liquid-only spray fluorescence signal. The vapour phase subtraction was carried out in the same manner as the background signal subtraction.

The emission decay results for the aerated acetone spray indicate that the majority of the phosphorescence is emitted immediately following the fluorescence, as approximately 90% of the integrated phosphorescence signal is collected during the first 100ns. Moreover, the total phosphorescence signal corresponds to approximately 0.01% of the fluorescence, which is lower in comparison to the liquid stream experiments despite the lower fluence employed in the spray measurements. This decrease is probably attributed to the higher oxygen content of the spray droplets, and hence, boosted oxygen quenching.

![Graph](image.png)

**Fig 7.7** Aerated 3-pentanone and acetone spray emission decay in saturated vapour in air. All phosphorescence data points are normalized to their respective prompt fluorescence emission signals.

The phosphorescence decay of aerated 3-pentanone resembles closely that of acetone, with most of the phosphorescence once again emitted during the first 100ns of pure triplet state emission. Owing to the substantial disparity between the saturated concentrations of acetone
and 3-pentanone vapour at ambient conditions (mole fractions of around 0.28 and 0.04 respectively), exciting both tracers using the same laser-out pulse energy results to 60% higher excitation energy reaching the 3-pentanone spray. A comparison between the resulting decay curve (16mJ average pulse energy) and one obtained by adjusting the laser settings so as to halve that excitation energy (8mJ average pulse energy) allows for a qualitative evaluation of the phosphorescence efficiency degradation attributed to TTA; the ratio between the total fluorescence and phosphorescence drops by a factor of approximately two when doubling the laser fluence. The particular observation agrees qualitatively with the conclusions derived from the cuvette and liquid stream experiments.

Single exponential functions were fitted to all three phosphorescence decay curves and the emission lifetimes were calculated from the exponent constants. The excellent agreement between the collected data and the fitted curves is reflected in the very low uncertainties associated with the lifetime calculations. The results are presented in Table 7-1.

<table>
<thead>
<tr>
<th>Emission Decay Study</th>
<th>Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerated Acetone Spray (10mJ/pulse)</td>
<td>42 ± 3</td>
</tr>
<tr>
<td>Aerated 3-pentanone Spray (8J/pulse)</td>
<td>41 ± 4</td>
</tr>
<tr>
<td>Aerated 3-pentanone Spray (16mJ/pulse)</td>
<td>44 ± 4</td>
</tr>
</tbody>
</table>

The decay curves of both liquid acetone and 3-pentanone indicate that collecting any phosphorescence past 200ns after the end of fluorescence emission results to insignificant signal augmentation; consequently the gating time during imaging will be limited to this delay value. The IRO delay of 10ns after the end of fluorescence emission, along with the 70% gain utilized in the emission decay measurements were also carried over to the calibration experiments.
7.3 Image Processing

7.3.1 Image Acquisition Settings

The first step of the image acquisition procedure was subtraction of dark current contributions. The IRO delay, gate and gain settings were then adjusted to 10ns after the end of fluorescence emission, 200ns and 70% respectively. Background signals were then collected with the laser firing but with no vapour or liquid tracer inside the probed volume. The vapour tracer was introduced, and a 15 minute interval was allowed in order to fully saturate the injection chamber. Next, 100 white images were collected and stored in order to provide a measurement of the laser sheet distribution for the particular measurement run, followed by the acquisition of 100 non-evaporative spray images. Prior to processing the fluorescence and phosphorescence images in Matlab by means of an in-house developed algorithm, a 440x400 pixel rectangle with the spray centred across its width was extracted from each image. The size of the extracted rectangles was estimated at 4.3x3.8cm using a measurement of the geometrical magnification (approximately 98μm/pixel). Even though no pulse-to-pulse variation corrections were imposed to the collected fluorescence and phosphorescence images, excitation energy measurements were carried out concurrently with the image acquisition. These serve two purposes; firstly to confirm that near identical average excitation energies are utilized amongst different measurement runs, and secondly, to certify that no systematic trends are observed with the respect to the excitation energy variability during experimental measurements.

7.3.2 Vapour phase fluorescence subtraction

One of the main challenges towards calibrating the fluorescence against the phosphorescence emission from raw image pairs is obtaining liquid-only spray fluorescence images (Fig 7.8). In doing so, the first step is identification of the spatial boundary between the liquid plus vapour and the purely saturated vapour regions in each fluorescence image. As the emission of phosphorescence is attributed purely to the liquid phase under the particular experimental conditions, the phosphorescence image can be used to map this boundary back to the fluorescence image [29]. Signals below 20 counts are treated as noise and set to zero in the phosphorescence image, with the same pixels also set to zero in the fluorescence image since any collected fluorescence from those regions emanates from the vapour tracer.
Fig 7.8 Instantaneous raw spray fluorescence and phosphorescence image pair collected at 0.4ms after the start of injection. The non-evaporative spray is injected in saturated acetone vapour in air at 296K and 1bar. The laser sheet direction of propagation is from left to the right.

The vapour phase contribution to the fluorescence image pixels which have not been set to zero is now accounted for by subtraction of an appropriate vapour phase fluorescence signal. Rather than deducting a single vapour fluorescence value, the vapour phase fluorescence to the left of the spray was averaged over 100 pixels along each row, and a vapour fluorescence column vector was produced and subtracted. This tactic was preferred in order to account for the excitation energy variation across the laser sheet direction of propagation. In addition, the pulse-to-pulse excitation energy variation is accounted for, as the correction is performed on a per image basis. A liquid-only spray fluorescence/phosphorescence image pair processed in that manner is presented in Fig 7.9:

Fig 7.9 Instantaneous liquid phase spray fluorescence and phosphorescence image pair (processed images corresponding to the raw images presented in Fig 7.8)
7.3.3 **Spray phosphorescence/fluorescence ratio**

As the laser sheet propagates through the spray and is consequently attenuated, the phosphorescence to fluorescence ratio is expected to vary in a similar fashion as discussed earlier for the laser sheet distribution non-uniformity, resulting to spray regions subjected to different TTA rates. Additionally, the vapour phase subtraction from the fluorescence image becomes increasingly inaccurate; owing to scattering and absorption effects by the spray and vapour tracer within the spray region, the vapour fluorescence subtraction accounts for an increasingly larger than the appropriate fluorescence contribution, resulting to underestimated liquid-only fluorescence signals. In order to investigate both effects along with any other issues that may potentially arise when correlating the two emissions, 100 image pairs collected at 1.4ms after the start of injection were processed and averaged. Each instantaneous image pair was also used to generate an instantaneous ratio (phosphorescence/fluorescence) image, with the resulting 100 ratio images also averaged. Single-shot fluorescence, phosphorescence and ratio image triplets are presented below (Fig 7.10). Along the left hand side ridge of the spray, the observed ratio values are substantially higher compared to the core on account of very low SNR’s that plague low phosphorescence signals. Further inside the spray, the ratio settles to a value of approximately 0.3. Moving on to the right, and on account of the two aforementioned error sources, the ratio rises once again, peaking prior to the processing routine setting any negative fluorescence intensity pixels to zero. The latter emerge as a result of the vapour phase subtraction, and are manifested by the appearance of a crest-like, rather than diffuse boundary in that region of the ratio image. Any shot-to-shot variability is most likely attributed to IRO jitter.
The aforementioned effects can also be examined by observing the correlation between the fluorescence and phosphorescence emission from a spray section. For this reason, a region of interest was extracted from 100 averaged fluorescence and phosphorescence images, and the fluorescence and phosphorescence data were plotted against each other (Fig 7.11). The upper part of the plot represents the spray region between the initially excited region and spray core where the maximum fluorescence and phosphorescence signals are encountered, whereas the lower part of the curve describes the spray region to the right hand side of the spray core. Past the maximum, the ratio (phosphorescence/fluorescence) increases abruptly, reflecting the sudden reduction in the excitation energy.
Fig 7.11 Fluorescence against phosphorescence correlation obtained from a cut-out section through the spray averaged images

7.3.4 **Spray fluorescence and phosphorescence profile extraction**

The ratio between the imaged phosphorescence and fluorescence emissions has been shown to vary across the spray; for this reason, only spray profiles were considered in the calibration. In extracting the profiles, the processed liquid-only fluorescence images rather than the phosphorescence images were utilized. Unlike the phosphorescence, the fluorescence signal intensity reflects the excitation energy level only through the excitation energy dependence and not through the quantum yield. For an isothermal field, the fluorescence signal imaged by a single pixel $S_0$ at point 0 along a line is proportional to the locally available excitation energy $E_0$, the local tracer density $\rho_0$, and a product of experimental and photophysical constants, here denoted $C$.

\[ S_0 \propto E_0 \rho_0 C \quad \text{Eq 7-2} \]

The fluorescence signal $S_i$ at $i = 0 + l$ is then:

\[ S_i \propto E_i \rho_i C \quad \text{Eq 7-3} \]

The ratio of the fluorescence intensities is only a function of the excitation energies at 0 and $i$, provided the tracer density remains invariant, for example, in a saturated environment:

\[ S_i/S_0 \propto E_i/E_0 \quad \text{Eq 7-4} \]

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The vapour fluorescence across the spray, therefore, correlates with the laser light extinction across the spray, an estimate of which can be obtained directly from the unprocessed fluorescence images. Averaging the vapour fluorescence along each row over 100 pixels to the left and right hand side of the spray, and dividing pixel by pixel the resulting column vectors provides a measure of the laser light transmission (Fig 7.12). Typical values range between 40% and 65% for both tracers, with the laser light extinction attributed purely to absorption by the vapour tracer amounting to approximately 10% for acetone and 2% for 3-pentanone. The average transmission for acetone and 3-pentanone sprays, calculated from raw fluorescence image sets each comprised of 100 images and corresponding to 5 different injection timings, is approximately 55% and 65% respectively.

In order to match the excitation energy variation along the spray (due to laser sheet distribution non-uniformities) with that across the spray (extinction due to absorption and scattering), a spray profile thickness limit corresponding to one fourth of the total liquid phase fluorescence was selected for both tracers. The imposition of profile thickness limits to the processed images was performed on a per image pair basis by summing up the liquid phase fluorescence signal along each row, identifying the maximum sum corresponding to the maximum extinction for the particular image, calculating the fluorescence sum limit, and discarding all pixels which upon summation exceed that limit. The non-zero data from the liquid-only fluorescence profile were then mapped onto the phosphorescence image generating the phosphorescence profile. A typical spray profile image pair is shown below:

![Fig 7.12 Instantaneous fluorescence image of a non-evaporative acetone spray. The vapour phase fluorescence to the left and right hand side of the spray is employed in calculating the average laser light transmission](image-url)
7.4 Calibration Results

Once the spray fluorescence/phosphorescence image pairs have been acquired and processed, the next step in the calibration procedure is to obtain a correlation function between the two emissions. In doing so, data points from processed image pairs were plotted against each other and a correlation function was fitted to the plotted data. A fluorescence against phosphorescence emission plot corresponding to a single-shot image pair and fitted to a power function is presented in Fig 7.14.

Apart from any factors associated with the utilization of two separate detection systems, the scatter observed in such plots is also attributed to IRO noise and jitter, spatial inhomogeneities in the phosphorescence efficiency due to excitation energy distribution...
inhomogeneities, and locally enhanced phosphorescence oxygen quenching (in case of partially complete aeration of the liquid tracer). In order to isolate and examine some of the aforementioned potential errors sources, the correlation procedure was firstly carried out for fluorescence signals only.

7.4.1 Acetone Fluorescence/Fluorescence Correlation

The intensified camera noise is substantially higher than that of the non-intensified camera. In addition, higher IRO gains induce more noise, a feature of the light intensification process that exacerbates the imaging of low intensity signals such as the phosphorescence. Fluorescence imaging using the intensified camera can be practiced by adopting a substantially reduced IRO gain, and in that way, a lower limit for the statistical uncertainty involved in fitting a correlation function when visualizing light emitting processes by deployment of the particular detector pair can be obtained. In addition, such a correlation study is expected to serve a multitude of supplementary roles. For example, the linearity between the two detectors can be verified, whilst the intensifier noise can be isolated from uncertainty sources such as the ones noted before, and a lower limit for its contribution can be estimated.

In approximately matching the fluorescence intensities from both cameras, the IRO gain was set to 37%, while the gate and delay were set to 300ns and -100ns respectively. In that way all of the fluorescence emission is collected while any camera jitter will not affect the measurement. Additionally, the liquid phase fluorescence emission of acetone and 3-pentanone is not affected by oxygen quenching, thus eliminating another potential source of uncertainty associated with the phosphorescence measurement. A typical single-shot spray fluorescence image pair is presented in Fig 7.15.
In processing the spray fluorescence images (collected under non-evaporative conditions at 1.4ms ASOI) so as to yield liquid phase fluorescence data, vapour fluorescence contributions were subtracted in an identical manner as described before. The non-zero data points form 100 spray images were extracted and plotted (Fig 7.16). Prior to collecting the fluorescence image set, dark current and background contributions were subtracted.

Owing to the small spatial extent of the spray profiles, the majority of extracted data points correspond to low liquid phase fluorescence and phosphorescence intensity regions; close inspection of the population distribution (Fig 7.17) of fluorescence spray profiles corresponding to a spray profile thickness of one half of the total liquid phase fluorescence reveals that more than half of the processed liquid phase fluorescence data do not exceed the
average vapour phase intensity of approximately 150 counts. As typical fitting methods (such as the least squares and least absolute residuals) generate a fit based on the minimization of the global deviation between the observed values and the fitted function, the influence of higher intensity data to the fit may be undermined. Similarly, the goodness of fit criteria, for example the $R^2$ and rmse, will be heavily affected by the large number of data representative of only a small fraction of the dynamic range of the collected signals. For both aforementioned reasons, the statistical analysis was carried out twice: once utilizing all data points identified as liquid phase fluorescence (Fig 7.17 (a)), and once utilizing only data points exceeding the average vapour contribution (Fig 7.17 (b)). Only least-squares power fits were employed in this part of the analysis, though when correlating the fluorescence against the phosphorescence, a range of different functions and fitting methods were attempted. The $R^2$ and rmse are 0.9933 and 59.58, and 0.9892 and 88.46 for the complete (threshold of 20 counts) and partial (threshold of 150 counts) data sets respectively. The rms error increases by nearly 50% when the low intensity data are discarded, thus better describing the larger uncertainties encountered at higher fluorescence intensities.

\[ \text{Fig 7.17 Population distribution of liquid phase fluorescence data extracted from 100 non-evaporative acetone spray profiles and imaged by the intensified and non-intensified camera detector pair, with the threshold set to} \]

(a) 20 counts (b) 150 counts
7.4.2 Acetone Fluorescence/Phosphorescence Correlation

Similar to the data employed in correlating the fluorescence signals from the two cameras, the data obtained from the fluorescence/phosphorescence spray profiles are unevenly distributed within the observed signal dynamic range. The liquid phase fluorescence and phosphorescence noise threshold values were set approximately equal to the corresponding noise levels of the two cameras: For the non-intensified camera, the noise level was estimated by collecting 100 acetone vapour fluorescence images, extracting a 20x20 pixels ROI, and calculating the standard deviation of the observed intensities (below 10 counts). For the intensified camera, the same procedure was repeated over a range of signal levels representative of the phosphorescence intensities encountered in the spray experiments, in order to address any non-linearity in the signal-noise response. In doing so acetone vapour phosphorescence imaging (in nitrogen) allows for the 70% phosphorescence imaging gain setting to be preserved, with the desired signal range obtainable by adjusting the IRO delay and gate, as well as lens aperture. In the particular experiment, the gate was set to 2μs, while the aperture was varied in order to adjust the collected signal level. Following the collection of the first image set, the aperture was gradually closed and additional image sets were collected and processed. The results are presented in Fig 7.18:

![Graph](image)

**Fig 7.18** ROI mean and standard deviation values representative of the intensified camera noise at different signal levels

For average signals of around 50 counts the standard deviation is approximately 25 counts, while for average signals of nearly 100 counts, the error increases to around 35 counts. The phosphorescence signal noise threshold value was set to 30 counts, the mean value of the
two, whereas for the fluorescence images the noise threshold was set to 20 counts in order to filter out correspondingly noisy pixels in the phosphorescence measurements.

Fluorescence against phosphorescence data sets extracted from 100 image pairs were fitted with two different functions: a power fit and a first order polynomial, while for each function, the effect of forcing the fit through zero by eliminating the constant was also investigated. Higher order polynomial functions were also attempted but were discarded, as the higher order term coefficients were consistently being set to zero by the fitting routine. The fit results for acetone sprays imaged at 1.4ms ASOI are presented in Table 7-2.

<table>
<thead>
<tr>
<th>Function</th>
<th>Fitting Method</th>
<th>rmse</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ax^b$</td>
<td>LAR</td>
<td>98.8</td>
<td>0.964</td>
</tr>
<tr>
<td>$ax^b$</td>
<td>LS</td>
<td>134.0</td>
<td>0.9337</td>
</tr>
<tr>
<td>$ax^b + c$</td>
<td>LAR</td>
<td>93.1</td>
<td>0.968</td>
</tr>
<tr>
<td>$ax^b + c$</td>
<td>LS</td>
<td>131.8</td>
<td>0.9359</td>
</tr>
<tr>
<td>$ax$</td>
<td>LAR</td>
<td>103.3</td>
<td>0.968</td>
</tr>
<tr>
<td>$ax$</td>
<td>LS</td>
<td>134.0</td>
<td>0.9337</td>
</tr>
<tr>
<td>$ax + b$</td>
<td>LAR</td>
<td>94.2</td>
<td>0.9672</td>
</tr>
<tr>
<td>$ax + b$</td>
<td>LS</td>
<td>133.5</td>
<td>0.9343</td>
</tr>
</tbody>
</table>

A comparison of the goodness of fit results amongst the two different fitting methods for the same fitted functions indicates that the LAR method consistently displays higher $R^2$ and lower rmse values. This comes as no surprise, as the effect of the small number of high intensity data, which are treated as outliers, is moderated. In other words, the reduction in the global rmse is achieved by better adjusting the fit to the large population of low intensity data points. For example, when fitting the data with a $ax + b$ function, the rmse observed for the LS fit is nearly 50% higher compared to the LAR fit, a percentage increase that is consistently encountered amongst all fitted functions. Despite reducing the global rmse, the employment of LAR introduces ever-increasing errors to the interpretation of stronger signals. The $R^2$ and rmse values observed for all fitted functions when the fit is not forced through zero are of the order of 0.93 and 130 counts respectively when the LS fitting method is employed, whilst by deployment of the LAR method, values of approximately 0.96 and 94
counts were respectively achieved. The best goodness of fit results were obtained when a $a x^b + c$ function is fitted using the LAR fitting method (Fig 7.19).

![Graphs showing fluorescence/phosphorescence data sets for 0.4ms and 1.4ms ASOI](image)

**Fig 7.19** (Left) Power $(a x^b + c)$ function fitted to the acetone fluorescence/phosphorescence data set obtained at 1.4ms ASOI by deployment of the LAR fitting method. (Right) Power $(ax)$ function fitted fitted to the acetone fluorescence/phosphorescence data set obtained at 0.4ms ASOI by deployment of the LS fitting method.

The rmse errors associated with the best fit studies can be used as an estimate of the average errors associated with the correction of instantaneous fluorescence images for liquid phase fluorescence contributions by means of their paired phosphorescence images. Two functions have been selected in order to investigate such corrections; a power function $(a x^b + c)$ fitted using the LAR method and a first order polynomial $(ax)$ fitted using the LS method. In the first case, the goodness of fit is optimized over the entire data range by accounting for the inhomogeneity in the calibration data population distribution, thus providing the best mathematical interpretation of the examined data set. In the second case, the resulting relative errors will be distributed more evenly across the range of calibration values owing to the adoption of the LS fitting method.

The same calibration procedure was repeated for 100 non-evaporative spray images collected at 0.4ms ASOI. The reasons for not directly adopting the previous calibration in correcting image pairs obtained at that injection timing are the following: The trigger signals for both the injection system and IRO were generated using the Stanford clock, and when the injection timing was switched to 0.4ms ASOI, the IRO timing was also readjusted in order to monitor the same phosphorescence range. Owing to the short emission decay of acetone
triplets and aforementioned timing adjustments, it wasn’t possible to guarantee that the exact same portion of the phosphorescence emission is monitored. The fluorescence/phosphorescence calibration data fitted to a first order polynomial function are plotted in Fig 7.19 (Right). The previously selected functions were fitted to the current calibration data range and are presented in Table 7-3.

<table>
<thead>
<tr>
<th>Function</th>
<th>Fitting Method</th>
<th>rmse</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ax^b$</td>
<td>LAR</td>
<td>128.2</td>
<td>0.9076</td>
</tr>
<tr>
<td>$ax^b$</td>
<td>LS</td>
<td>148.7</td>
<td>0.8757</td>
</tr>
<tr>
<td>$ax^b + c$</td>
<td>LAR</td>
<td>131.3</td>
<td>0.9032</td>
</tr>
<tr>
<td>$ax^b + c$</td>
<td>LS</td>
<td>148.7</td>
<td>0.8758</td>
</tr>
<tr>
<td>$ax$</td>
<td>LAR</td>
<td>115.2</td>
<td>0.9254</td>
</tr>
<tr>
<td>$ax$</td>
<td>LS</td>
<td>149.4</td>
<td>0.8746</td>
</tr>
<tr>
<td>$ax + b$</td>
<td>LAR</td>
<td>118.7</td>
<td>0.9209</td>
</tr>
<tr>
<td>$ax + b$</td>
<td>LS</td>
<td>148.8</td>
<td>0.8756</td>
</tr>
</tbody>
</table>

It is clear by observing and comparing the goodness of fit results and data scatter in the plots describing the emission correlation for the two injection timings that in the case of the second data set (0.4ms ASOI), the IRO noise in not the only source of uncertainty. The observed rmse and $R^2$ values are consistently degraded in this study compared to the previous one throughout the range of examined fitted functions, while the percentage reduction in the rmse when employing an LAR rather than an LS fit is substantially diminished (25%-15%). The origin of this additional data scatter will be examined in the following section where corrections are carried out for non-evaporative acetone sprays.

7.4.3 3-pentanone Fluorescence/Phosphorescence Correlation

The signal correlation investigation for 3-pentanone sprays was carried out in an identical manner to that of acetone sprays and the obtained correlation plots are presented in Fig 7.20:
Owing to the stronger absorption of 3-pentanone at 308nm, slightly higher liquid phase signals were observed compared to acetone sprays. Instead, the saturated vapour signal was limited to approximately 34 counts (compared to 150 for acetone) owing to the lower vapour pressure, and hence lower saturated vapour concentration. It should be noted that the collection optics settings were unaltered compared to the acetone experiments. When fitted to the same range of functions as the ones selected in investigating acetone sprays, the observed $R^2$ and rmse values were nearly identical. For example, for $ax$ polynomials fitted using the LS fitting method, the observed rmse values are approximately 142 and 148 counts at 0.4ms and 1.4ms ASOI respectively. Corrections to non-evaporative 3-pentanone spray images by means of the obtained correlation functions were not performed, on account of the similarity of the results with the acetone sprays, and the relative size of the error associated with the fits, which exceed the vapour signal by three to four times.

7.5 Non-evaporative Acetone Spray Corrections

The first order polynomial and power fit functions were employed in order to correct randomly selected instantaneous fluorescence and phosphorescence image pairs collected under non-evaporative conditions (Fig 7.21 and 7.22). Such corrections provide a measure of the deviation of the obtained result from an already known outcome; ideally upon subtraction
of a correlation image calculated using the fluorescence/phosphorescence correlation function and the liquid phase phosphorescence image, the remainder should be zero. The particular practice is used as the key factor in determining the effectiveness of the proposed technique. As it is evident in all corrected fluorescence images, large absolute deviations (as much as 500 counts) emerge. The average absolute deviation (calculated on a per image basis) ranges from approximately 69 to 87 counts in the three presented image pairs, with the average value calculated over 100 corrected images being 82 counts. Similar errors were encountered when performing corrections using the power fit, with the average absolute error calculated over 100 image pairs being 84 counts.

Close inspection of corrected single-shot images such as the ones presented here shed light over the error sources associated with the correction process. For example, the corrected fluorescence image corresponding to the middle image pair displays higher positive deviations compared to the other two image pairs. The particular effect is most probably attributable to electronic jitter between the laser pulse and the IRO; the gate in this image is advanced compared to the rest of the image set allowing for the collection of stronger phosphorescence signals. In the other presented images, as well other examined image throughout the collected set, the deviation appears to be random with no apparent systematic effects.

The correlation plot obtained from spray images collected at 0.4ms ASOI was shown earlier to suffer from stronger scatter compared to the 1.4ms ASOI study. Upon correcting single-shot images for liquid phase fluorescence contribution, the larger rmse is reflected in the larger absolute deviations obtained in this study. These range from 91 to 114 counts for the presented images, while for an entire 100 image set, the average error amounts to approximately 101 counts. In addition to the random error associated with the intensified camera noise that evidently plagues the corrected images, a systematic overestimation of the corrected fluorescence signal near the spray tip can clearly be identified. This observation is consistent throughout the corrected as well as ratio images for both tracers, and can be attributed to either local quenching of the triplet state emission or the collection of fluorescence from spray regions ahead and behind the excitation plane. Reabsorption of scattered laser light could result to remission from those regions; owing to the narrower collection angle and longer depth of field of the non-intensified camera, the emission from out-of-focus regions would be imaged as nearly in-focus, whereas in the case of the intensified camera would be imaged as a blur.
Fig 7.21 Single-shot liquid phase fluorescence (left) and phosphorescence (middle) spray profiles collected at 1.4ms ASOI, and presented along with their corresponding corrected fluorescence images (right). The first order polynomial coefficient employed in correcting the particular sample images is 3.1470
Fig 7.22 Single-shot liquid phase fluorescence (left) and phosphorescence (middle) spray profiles collected at 0.4ms ASOI, and presented along with their corresponding corrected fluorescence images (right). The first order polynomial coefficient employed in correcting the particular sample images is 3.1128
7.6 Discussion

Provided the saturated acetone vapour fluorescence signal is only 150 counts under the particular experimental conditions, the average signal-to-noise ratio for instantaneous vapour concentration measurements is at best 2:1 (1.4ms ASOI), rendering the technique, under its present formulation, ineffective. The intensifier noise and jitter have been identified as probable limiting factors with regard to the applicability of the technique and will, therefore, be discussed in the following paragraphs. In particular, the application of tactics such as hardware and software binning, along with the implementation of individual calibration constants per corrected image in order to eliminate the effect of camera jitter from the calibration procedure, will be presented. Finally suggestions on improving upon the present results will also be provided.

7.6.1 Binning

A well-known practice for noise reduction is on-chip binning. In these experiments, 2x2 binning was employed, resulting to a 4:1 improvement in the SNR. As a result, the image resolution was halved. The adoption of stronger binning was considered, but the resulting resolution degradation was rendered unsatisfactory as the spray was poorly resolved. The calibration and image correction procedures were instead repeated by application of 5x5 mean (Fig 7.23) and median filtering (Fig 7.24). The clear downside is blurring, described in this report by the loss of contrast compared to the unsmoothed images. Single-shot acetone fluorescence, phosphorescence and corrected fluorescence images captured at 0.4ms and 1.4ms ASOI and processed using both filters are presented in Fig 7.25 and 7.26. The observed erroneous values are clearly reduced compared to unsmoothed images; from 98 to 54 (median filter) and 33 (mean filter) counts (Fig 7.25), and from 81 to 49 (median filter) and 28 (mean filter) counts (Fig 7.26). Average absolute errors calculated over 100-image data sets are enlisted in Table 7-4, along with the first order polynomial coefficients employed in the corrections.
Fig 7.23 First order polynomial ($ax$) functions fitted to the acetone fluorescence/phosphorescence data sets obtained at 0.4ms (left) and 1.4ms (right) ASOI and processed using 5x5 spatial averaging.

Fig 7.24 First order polynomial ($ax$) functions fitted to the acetone fluorescence/phosphorescence data sets obtained at 0.4ms (left) and 1.4ms (right) ASOI and processed using a 5x5 median filter.

Table 7-4 Fit coefficients for first order polynomial $ax$ fits presented along with average absolute errors for corrections carried over 100-image sets collected at 0.4ms and 1.4ms ASOI.

<table>
<thead>
<tr>
<th>Injection Timing (ASOI)</th>
<th>Coefficient of proportionality (5x5 median filter)</th>
<th>Coefficient of proportionality (5x5 mean filter)</th>
<th>Average Absolute Error (5x5 median filter)</th>
<th>Average Absolute Error (5x5 mean filter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4ms</td>
<td>3.1816</td>
<td>3.1693</td>
<td>66</td>
<td>41</td>
</tr>
<tr>
<td>1.4ms</td>
<td>3.2041</td>
<td>3.1937</td>
<td>51</td>
<td>28</td>
</tr>
</tbody>
</table>
Fig 7.25 Single-shot liquid phase fluorescence (left) phosphorescence (middle) and corrected fluorescence (right) spray profiles collected at 0.4 ms, and presented without spatial filtering (top), with 5x5 median filtering (middle) and 5x5 mean filtering. The first order polynomial coefficients employed in correcting the particular sample images are enlisted in Table 7.4
Fig 7.26 Single-shot liquid phase fluorescence (left) phosphorescence (middle) and corrected fluorescence (right) spray profiles collected at 1.4ms, and presented without spatial filtering (top), with 5x5 median filtering (middle) and 5x5 mean filtering. The first order polynomial coefficients employed in correcting the particular sample images are enlisted in Table 7-4
7.6.2 **Single image correlations and corrections**

The effect of camera jitter in the observed uncertainty values can be assessed by generating correlation functions from individual fluorescence/phosphorescence image pairs and back-calculating the remainder. This procedure was carried out for individual image pairs, as well as their smoothed (5x5 mean filter) counterparts, by fitting $\alpha x$ functions to the respective fluorescence/phosphorescence correlation data. Despite the fact that different images displayed slightly different gradients (Table 7-5), the observed average absolute errors were very similar to corrections implemented using the correlation coefficients obtained from 100-image data sets. It can therefore be inferred that camera jitter is not the primary source of data scatter.

**Table 7-5** Fit coefficients and average absolute error corrections performed for individual acetone spray image pairs collected at 0.4ms and 1.4ms ASOI. The fluorescence/phosphorescence data from each image pair were fitted using the LS fitting method to first order polynomial ($\alpha x$) functions.

<table>
<thead>
<tr>
<th>Image Pair/Injection Timing</th>
<th>Coefficient of proportionality</th>
<th>Coefficient of proportionality (5x5 mean filter)</th>
<th>Average Absolute Error</th>
<th>Average Absolute Error (5x5 mean filter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(01)/0.4ms ASOI</td>
<td>2.9292</td>
<td>3.001</td>
<td>93</td>
<td>40</td>
</tr>
<tr>
<td>(02)/0.4ms ASOI</td>
<td>3.4551</td>
<td>3.5226</td>
<td>118</td>
<td>49</td>
</tr>
<tr>
<td>(03)/0.4ms ASOI</td>
<td>2.9004</td>
<td>2.9558</td>
<td>88</td>
<td>38</td>
</tr>
<tr>
<td>(01)/1.4ms ASOI</td>
<td>2.9298</td>
<td>2.9835</td>
<td>77</td>
<td>25</td>
</tr>
<tr>
<td>(02)/1.4ms ASOI</td>
<td>3.4492</td>
<td>3.5096</td>
<td>84</td>
<td>31</td>
</tr>
<tr>
<td>(03)/1.4ms ASOI</td>
<td>2.8363</td>
<td>2.8975</td>
<td>74</td>
<td>27</td>
</tr>
</tbody>
</table>

7.6.3 **Suggestions for improvement**

The applicability of the proposed technique is currently limited due to the combined effects of low phosphorescence efficiency, and correspondingly low phosphorescence signal intensity, and high vapour and liquid phase fluorescence signal intensity disparity. As the purpose of this section of the experimental investigation is to examine and assess the potential for utilizing ketone phosphorescence from the liquid phase in quantitative laser diagnostics, the following discussion will be focus on methods for improving phosphorescence imaging within the confines of the proposed imaging technique. It has been illustrated, for example, that binning can greatly reduce the errors associated with
fluorescence image corrections, albeit at the cost of reduced resolution and loss of contrast. This kind of treatment is ultimately unavoidable when imaging low SNRs, and despite any ensuing drawbacks, it is encouraged. In particular, the adoption of 4x4 on-chip binning in tandem with moderate (for example 3x3) spatial averaging, is proposed for future investigations. Apart from any attempts to achieve higher SNRs by image post-processing, it is also essential to further enhance the collected phosphorescence by suitable alterations to the experimental setup. The acquisition of higher phosphorescence signals can be achieved through two different routes; improving the collection efficiency of the optical setup and boosting the phosphorescence signal itself.

The P43 phosphor installed in the currently utilized IRO provides an ideal trade-off between high electron-light conversion efficiency and decay time (90% and approximately 1ms to 10% according to the manufacturer). However, a slower phosphor with an even higher efficiency, such as the P20, would allow for slight improvement of the conversion efficiency provided that measurements are carried out at low recording frequencies. More importantly, the use of a higher quantum efficiency photocathode over the phosphorescence emission spectrum could result to substantial improvements. The utilization of an IRO system equipped with a GaAsP photocathode was discussed earlier and is hereby recommended once more. Finally, an alternative approach towards splitting the imaged signal amongst the two cameras must essentially be adopted. As has already been noted in the presentation of the experimental apparatus, a 50R/50T beamsplitter was employed following a failed attempt to utilize a 25R/75T beamsplitter owing to strong ghosting effects. In both cases the non-intensified camera was equipped with neutral density filters (OD 0.6 and OD 0.3 respectively), as the fluorescence measurement was plagued by saturation effects. In other words, substantial signal intensity was sacrificed which could have been otherwise diverted to the intensified camera allowing for IRO gain moderation. For the future, the use of a pellicle type beamsplitter is proposed in order to simultaneously prevent ghosting, whilst adopting a very high transmissivity/reflectivity ratio, for example 8R/92T. The particular modification would allow for a near two-fold boost in the collected signal, albeit at the expense of reduced practicality associated with the sensitivity of the particular component.

In improving the phosphorescence efficiency of liquid acetone, but not 3-pentanone, nitrogen purging can be adopted. The particular approach has been shown to simultaneously enhance the phosphorescence intensity and lifetime, allowing for substantially higher integrated phosphorescence signals to be captured. However, implementing this approach
would entail either a) carrying out experiments in nitrogen bath gas, in which case no liquid-only signal can be generated, or b) carrying out experiments in air bath gas, while running the risk of introducing additional scatter and severe uncertainties through varying oxygen diffusion and phosphorescence quenching. Instead, a more suitable approach towards boosting the phosphorescence signal would be excitation at higher wavelengths, for example 320nm \[28\]. Unfortunately, no experimental investigation aimed at developing laser diagnostics by deployment of the phosphorescence properties of ketones has been encountered following excitation near the singlet origin. Such a study would provide valuable insight with regard to the applicability of phosphorescence-based laser diagnostics in general. Finally, additional gains could be achieved by increasing the excitation energy and/or reducing the excitation energy density. The latter can be achieved by increasing the laser sheet thickness, for example to 1mm, as is often encountered in spray investigations. The former is limited by the requirement for a relatively homogeneous laser sheet distribution over an extended field of view; thus, the utilization of a beam homogenizer in simultaneously minimizing the excitation energy waste and obtaining the desired distribution is encouraged. Unfortunately, the particular piece of equipment was not available in these experiments.

Another very important aspect associated with the viability of the proposed technique, is the potential implementation using different tracers and tracer/fuel blends. In addition to acetone, liquid 3-pentanone phosphorescence was introduced in the present investigation, and was shown to display very similar phosphorescence properties to acetone in air bath gas. It was proposed earlier that biacetyl instead of acetone phosphorescence could be employed in evaporative droplet stream experiments, owing to its substantially superior vapour phase triplet emission characteristics. The same suggestion is here put forward and supported by the following arguments: The vapour phase fluorescence of biacetyl vapour has already been employed in calibration \[150\], as well as in-cylinder measurements \[151\], thus being considered a well-investigated tracer with regard to laser diagnostic applications. Regarding its phosphorescence properties, extensive investigations have been carried out, suggesting a much higher yield compared to acetone \[27\]. By applying the current knowledge of acetone and 3-pentanone phosphorescence with regard to, for example, the effects of nitrogen purging, aeration and excitation energy density dependence, calibration experiments could be conducted in order to reveal any relative signal gains attainable by use of the particular tracer. It should also be noted that biacetyl phosphorescence is emitted mainly in the green, thus
fully harvesting the highest photocathode efficiencies observable in the particular spectral regions.
8 Conclusions

Fast fuel vaporization and air-fuel mixing stand at the forefront of automotive GDI development, with multi-phase (gas-liquid) flows arising as a consequence of the introduction of fuel directly into the combustion chamber. In optimising GDI operation, laser diagnostics have been extensively employed, representing an invaluable source of experimental data. Despite this, the applicability of optical methods in two-phase flows is limited by the photophysics of employed tracers, the physics of light transmission across a field of varying refractive index, and the capabilities of experimental apparatuses. The limitations associated with such measurements along with the significance of expanding the range of available optical diagnostics for two-phase flow investigations, and specifically the quantification of evaporated fuel concentrations in two-phase environments, have fuelled the undertaking of the present investigation. In particular, the potential development and implementation of diagnostics utilizing the phosphorescence emission of common ketone tracers such as acetone and 3-pentanone was brought into focus. Unlike previous attempts which employed acetone phosphorescence imaging only for detection purposes, such as mixing layers, this project aims at utilizing the triplet state signal in extracting 2-D quantitative tracer concentration measurements in two-phase flows. In that respect, this is an entirely novel effort.

A literature review of the relevant background theory of ketone excitation and deexcitation, along with an extensive research on previously published photophysical data revealed that contrary to the fluorescence emission of acetone, the phosphorescence displays different decay rates amongst the liquid and vapour phases, favouring the simultaneous visualization of both over a narrower signal dynamic range. Collisonal quenching, and in particular oxygen quenching and TTA were identified as key photophysical processes determining both the effective lifetime and phosphorescence quantum yield from both phases. Moreover, it was found that the phosphorescence emission is fully quenched in the presence of oxygen in the vapour phase, while in the case of the liquid, a fast-decaying triplet state component still persists. TTA, which manifests itself as a triplet-state population dependant quenching mechanism has been shown to introduce an excitation energy density dependence in the phosphorescence efficiency and decay rate of liquid and vapour biacetyl. A similar trend was therefore anticipated for the presently examined tracers, owing to their similar photophysical characteristics. Oxygen quenching from dissolved oxygen molecules has been
identified as a key limiting factor of the phosphorescence emission and lifetime of liquid acetone in recent photophysical studies, with extensive nitrogen purging enhancing both.

Based on the knowledge gained from the literature review, further research was carried out in identifying suitable two-phase flow investigations for which imaging of the phosphorescence rather than the fluorescence could prove advantageous. As such, the investigation and quantification of evaporated tracer concentrations in the vicinity of liquid droplets was selected as an ideal candidate study case. Two-phase flow visualization using acetone fluorescence has been shown in literature and demonstrated in the present study to suffer from two significant challenges; the large intensity disparity between the two phases that forces the vapour phase signal to near noise levels and the ensuing effect of halation around liquid droplets. In an attempt to overcome these obstacles, a strategy using the phosphorescence rather than the fluorescence emission of liquid and vapour acetone was attempted. In doing so, a suitable experimental facility was developed. Phosphorescence lifetime data were collected by examining the emission decays of liquid and vapour acetone under different conditions, following excitation at 308nm. Investigations of the former were carried out both in the bulk (quartz cuvette), as well as in laminar liquid streams (droplet generator). Complementary phosphorescence data were also presented for 3-pentanone (to the researcher’s knowledge, for the first time). Emission decay data were fitted to biexponential functions reflecting the fact that the phosphorescence evolves over time as a result of the decaying triplet state population, with fast components describing the early, strong emission and slow components describing the late, weak region. In the case of cuvette measurements, the emission decays of liquid acetone and 3-pentanone displayed very similar rates, with the fast components in extremely close agreement (around 100ns). Slightly higher deviations were observed regarding the slower components, with 3-pentanone displaying slightly higher values (for both tracers these were approximately 6-10 times higher than the fast ones). Decreasing the laser fluence from 250mJ/cm² to 50mJ/cm² resulted in a shift of the entire phosphorescence decay curves relative to the prompt fluorescence emission by almost a decade for both tracers, owing to the proposed primary role of TTA. In the case of acetone, nitrogen-purging was observed to both shift the phosphorescence closer to the fluorescence, as well as to boost the lifetime; 3-pentanone phosphorescence, in comparison, was almost entirely unaffected. This observation can most probably be attributed to higher solubility values of oxygen/nitrogen in acetone compared to 3-pentanone rather than a deviation of the oxygen quenching rate constants between the two ketones; however, no solubility data
backing up this hypothesis were encountered in literature. Phosphorescence lifetime data obtained in the liquid stream experiments also suggested that in air, liquid acetone and 3-pentanone phosphorescence decay fast (72ns and 74ns respectively). Both decay data sets were fitted to single exponential functions. By purging liquid acetone with nitrogen, the effect of oxygen quenching from any dissolved oxygen was once again reduced, and the decay in a nitrogen atmosphere was again better resolved using two exponential components with similar lifetimes as observed in the cuvette experiments. The insensitivity of liquid 3-pentanone phosphorescence to nitrogen purging was also confirmed. Any deviations observed between the cuvette and laminar stream experiments were attributed to either the inability of the detection system to image the slow (late and weak) part of delay as a consequence of the relatively small light emitting volume, or late sensitized emission. The phosphorescence decay rate of acetone vapour was shown to decrease with increasing laser fluence (from 25mJ/cm² to 50mJ/cm² and 250mJ/cm²), while the low fluence data were better fitted to a single exponential rather than a biexponential function. For the 205mJ/cm² laser fluence employed in the imaging experiments, the nitrogen-purged liquid acetone (540μm stream diameter, 400μm laser sheet thickness) in nitrogen bath gas to vapour signal disparity dropped from around 100 for the fluorescence to only around 10 at 300ns delay and to 2 at 1μs delay for the employed 200ns gate time. At 300ns delay, the unpurged liquid acetone phosphorescence in air was only 2.7 times higher than the vapour, whilst 100ns later, the vapour phosphorescence was already stronger.

In order to demonstrate the advantages of phosphorescence imaging, two study-cases were examined on a qualitative basis; a non-evaporating droplet stream in saturated acetone vapour in nitrogen and an evaporating droplet stream in pure nitrogen. These experiments clearly indicate that by employing laser induced phosphorescence, the intense signal disparity between the liquid and vapour phases, as well as the halation effect are overcome. In addition, the location of the liquid-vapour interface is clearly identified. Therefore, direct visualization of the vapour cloud is shown to be greatly improved. Following this qualitative comparison, a quantitative analysis of an isothermal evaporative droplet stream was carried out. In response to the potential emergence of triplet-triplet annihilation as a major deexcitation channel of acetone triplets, the vapour phase phosphorescence was calibrated for both excitation energy and tracer number density. Whereas a direct proportionality was observed between the aforementioned quantities and laser induced fluorescence, laser induced phosphorescence calibrations were better fitted with second order polynomial
functions. The quantitative two-phase flow measurements by LIP indicate the formation of a diffusion-driven, low concentration vapour tunnel along the droplet stream. Comparing (amongst the two techniques) the vapour fields obtained from radial profiles emanating from droplet surfaces (161μm nominal droplet diameters) and extending to nearly 10 droplet diameters away from the interface, it was shown that halation effects, at least in the particular experiment, were present almost throughout this entire range. Literature data also support this finding. Both the presented fluorescence data as well as literature data appear to overestimate the acetone mole fractions in the vicinity of liquid droplets obtained by the phosphorescence measurement. In addition, in the present experiments as well as in literature, the quantification of the vapour field by LIF was impossible to within one droplet diameter away from the interface. A single comprehensive study that has successfully performed a halation correction by means of the Mie scattering signal from ethanol droplets was shown to closely agree with the laser induced phosphorescence results, thus supporting their validity. Further LIP imaging experiments were presented for 124μm and 226μm droplet streams, in order to verify the feasibility of the technique over a wider droplet diameter range. In all presented droplet streams, the normalized inter-droplet separation was kept low (below 3) in order to challenge the boundaries of the technique, while vapour field profiles were generated along both the radial and axial directions. A signal-to-noise ratio of approximately 14 was achieved for the saturated concentration; however, it was demonstrated that owing to the different decay rates of the liquid and vapour phases, the gate and delay settings can be adjusted in order to allow for imaging with lower intensifier gain while still preserving sufficient signal strength disparity for phase discrimination. The potential expansion of the technique regarding the employment of different tracers, such as 3-pentanone and biacetyl, as well as tracer blends, is discussed, with the need for recalibration (as any given tracer concentration results to different TTA rates) being emphasized.

A major challenge in realizing fuel vapour concentration measurements in a spray by PLIF is discriminating between the fluorescence contributions from the two phases. LIEF imaging is therefore typically employed allowing for spectral discrimination between the two phases; however, literature suggests that the technique is plagued by significant drawbacks such as the simultaneous strong sensitivity of both monomer and exciplex emission on temperature and oxygen concentration along with the vapour-liquid cross-talk. The literature research analysis on ketone excitation and deexcitation along with the previously described experimental effort have revealed that the phosphorescence emission in air bath gas is limited
to the liquid phase only, whereas the fluorescence emission is common to both phases. Thus, quantitative knowledge of the correlation, if any, between the prompt fluorescence and trailing phosphorescence emission could allow for liquid phase fluorescence contributions to be accounted for in a two-phase flow experiment, such as an automotive spray, by sequential visualization of both light-emitting processes. In order to investigate this idea, an experiment was set up around non-evaporative acetone and 3-pentanone sprays generated by deployment of an automotive, prototype GDI injector. The injection pressure was set to 150bar in order to achieve fast atomization resulting to sub-pixel size droplet distributions. An appropriate experimental setup was developed and an experimental methodology was generated whereby vapour phase contributions from within the spray regions were subtracted from LIF images, and liquid-only signals from fluorescence and phosphorescence spray profiles were plotted against each other. Spray profiles rather than the entire spray region along with the homogenisation of the laser profile were employed in order to prevent the inclusion of data subjected to varying TTA rates. In that way, the energy variation both across and along the field of view of the employed images was kept below 15%. The statistical analysis of the correlated fluorescence and phosphorescence data indicated that either power or first order polynomial functions could be employed in describing the relationship between the two signals for both tracers. Subsequently, liquid phase corrections were carried out for non-evaporative acetone sprays by use of the generated correlations and collected fluorescence and phosphorescence image pairs in order to obtain a measurement of the resulting error, readily calculable from an already known outcome; upon subtraction of a correlation image calculated using the fluorescence/phosphorescence correlation function and the liquid phase phosphorescence image, the remainder should be zero. Given the saturated acetone vapour fluorescence of only 150 counts under the particular experimental conditions, the average signal-to-noise ratio for instantaneous vapour concentration measurements was at best 2:1, rendering the technique, under its present formulation, ineffective. The procedure was repeated by application of 5x5 median and mean filters, with the latter displaying the best results. The average absolute errors, calculated over 100-image sets, were reduced from 101 and 82 counts at the two investigated injection timings to 41 and 28 counts respectively. However, large deviations of the same or even higher magnitude than the saturated signal were still encountered in sample corrections. Correlations generated from single image pairs and employed in correcting for liquid phase contributions in LIF images displayed similar average absolute deviations per image pair, suggesting that the combined effects of IRO noise and low dynamic range over which the vapour phase is measured, rather than electronic jitter,
constitute the main source of uncertainty. Thus, suggestions for improvements focusing on boosting the phosphorescence intensity and allowing for the employment of lower gains were brought forward. Amongst others, the adoption of stronger on-chip binning along with the use of a pellicle type beamsplitter with as much as 90% transmission (for signal collection by the phosphorescence camera) constitute readily applicable improvements. Once again, the employment of different phosphorescing compounds was discussed, with biacetyl presenting the most attractive tracer based on its favourable photophysical properties.


