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Photophysical characterization of toluene and 3-pentanone for quantitative imaging of fuel/air ratio and temperature in combustion systems

Referees: Prof. Dr. Jürgen Wolfrum Prof. Dr. Ulrich Platt

Abstract

Treibstoffvisualisierung mittels laser-induzierter Fluoreszenz (LIF) von Treibstoffmarkern hat sich zu einer wichtigen Technik in der modernen Motorenforschung entwickelt. Um jedoch quantitative Aussagen über das Treibstoff-Luft-Mischungsverhältnis oder die Temperatur zu erhalten, müssen die Abhängigkeiten des Fluoreszenzsignals von Temperatur, Druck und Gaszusammensetzung genau bekannt sein. In dieser Arbeit wurden in einer heizbaren Flusszelle (300 - 900 K) Absorptionsquerschnitt, Fluoreszenzguantenausbeute und die Effizienz der Stoßlöschung durch Sauerstoff für Toluol-LIF sowie absolute Fluoreszenzguantenausbeuten von 3-Pentanon bestimmt. Ein photophysikalisches Modell wurde entwickelt, welches die Fluoreszenzintensität von Toluol in Abhängigkeit von Temperatur, Sauerstoffkonzentration und Anregungswellenlänge vorhersagt. Das Modell für Toluol wurde verifiziert, indem Messungen in einem optisch zugänglichen Motor mit Vorhersagen des Modells verglichen wurden. Das weitverbreitete Modell für 3-Pentanon Fluoreszenz zeigte sich jedoch ungeeignet für Bedingungen mit gleichzeitig hohem Druck und hoher Temperatur. Es konnte gezeigt werden, dass die oft verwendete Annahme, dass das Toluol-Fluoreszenzsignal proportional zum Treibstoff-Luft-Mischungsverhältnis sei (FARLIF), unter motorischen Bedingungen nicht gerechtfertigt ist. Ist die Temperatur jedoch bekannt oder gemessen, kann das Signal mit Hilfe des neuen LIF-Modells quantitativ ausgewertet werden. Neue bildgebende Verfahren basierend auf Toluol-LIF zur Bestimmung von Temperatur und Sauerstoff zusätzlich zum Treibstoff-Luft-Verhältnis wurden entwickelt.

The use of fluorescent tracers for fuel visualization based on laser-induced fluorescence (LIF) has grown to an important engineering tool in modern engine research. However, quantitative interpretation of fluorescence signals in terms of fuel/air ratio or temperature requires sound fundamental knowledge of the compound's photophysical behavior, i.e. the dependence of the LIFsignal on temperature, pressure and bath gas composition. In this work, absorption cross-sections, fluorescence quantum yields and oxygen quenching efficiencies of toluene-LIF were investigated in a heated flow cell (300 - 900 K) and absolute fluorescence quantum yields of 3-pentanone in dependence on excitation wavelength have been determined. A photophysical model that predicts toluene-LIF intensities in dependence on external variables (i.e. temperature, oxygen concentration, excitation wavelength) is developed. This model has been verified by comparison of LIF-signal predictions to data obtained in an optical engine. The well-established model for 3-pentanone LIF, however, has shown significant shortcomings at simultaneously elevated temperatures and pressures. It is shown that the widespread assumption of toluene LIF being proportional to the fuel/air ratio (FARLIF) is wrong at conditions present in the compression stroke of internal combustion engines. With additional temperature information, however, the new LIF model enables quantitative signal interpretation. Novel imaging techniques based on toluene-LIF for the measurement of temperature and oxygen concentration in addition to the fuel/air ratio are demonstrated.

Contents

1 Introduction	1
2 Background	3
2.1 Motivation: Use of fluorescent tracers	3
2.2 The ideal tracer	4
2.3 Typical classes of fuel tracers	5
2.4 Current status of tracer-LIF interpretation	7
2.4.1 Ketones 2.4.2 Aromatics	7 9
3 Photophysics of organic molecules	11
3.1 Absorption	11
3.1.1 Classification of electronic transitions	11
3.1.2 Classification of electronic state	12
3.1.4 Deactivation of excited molecules	16
3.2 Radiative processes	17
3.2.1 Fluorescence	17
3.2.2 Phosphorescence	17
3.3 Non-radiative processes	18
3.3.1 Dependence of the transition probability on the energy difference (energy gap law)	18
3.3.2 Singlet-triplet energy difference	18
3.3.3 Intersystem crossing, ISC	19
3.3.5 Vibrational relaxation	20
3.3.6 Intramolecular vibrational redistribution (IVR)	20
3.4 Kinetics of photo-physical processes	20
3.4.1 Radiative and effective lifetimes	20
3.4.2 Fluorescence quantum yield	21

3.5 Collisional quenching	23
3.5.1 Stern-Volmer-Coefficient	23
3.5.2 Electronic energy transfer	24
3.5.3 Fluorescence resonance energy transfer	24
3.5.4 Short-range energy transfer	25
3.5.5 Fluorescence quenching by molecular oxygen	25
4 Experimental investigation of toluene photophysics	27
4.1 Introduction	27
4.2 Experimental	29
4.3 Absorption	32
4.3.1 Absorption spectrum	32
4.3.2 Absorption at 248 nm and 266 nm	34
4.4 LIF in nitrogen bath gas	35
4.4.1 Fluorescence Spectrum	35
4.4.2 Fluorescence Quantum Yield	36
4.5 Oxygen quenching	39
4.5.1 Background	39
4.5.2 Fluorescence spectra	40
4.5.4 Integrated signals, excitation at 248 nm	41 42
5 Photophysical model for toluene fluorescence	45
5.1 Interpretation of results and the underlying photophysical processes	45
5.2 Model description	48
5.3 Comparison with experimental data	48
6 Experimental investigation of 3-pentanone and acetone LIF	51
6.1 Absolute fluorescence quantum yield measurements	51
6.1.1 Literature review	51
6.1.2 Experimental	53
6.1.3 Measurements	58
6.1.4 Results	61
6.2 Comparison of acetone data with fluorescence quantum yield model	63

7 Validation of model predictions for LIF-signal strength	
in a practical internal combustion engine	67
7.1 Experimental	67
7.2 Validation of the toluene model	68
7.3 Validation of the 3-pentanone model	69
8 Feasibility of fuel/air ratio measurements using toluene LIF	71
8.1 Toluene-LIF signal at engine-related conditions	71
8.1.1 Effect of temperature 8.1.2 Effect of oxygen quenching	71 72
8.2 Signal Interpretation at engine related conditions	73
8.2.1 Fixed fuel mole fraction, varying oxygen mole fraction (i.e. changing ϕ by EGR) 8.2.2 Varying fuel concentration at fixed total pressure (i.e. changing ϕ due to stratified load	74) 76
9 Demonstration of novel imaging strategies	79
9.1 Experimental	79
9.2 Quantitative temperature imaging	80
9.2.1 Single-color detection	81
9.2.2 Two-color detection 9.2.3 Summary of tracer-based temperature imaging strategies	84 89
9.3 Quantitative oxygen concentration imaging	90
9.3.1 Two-color detection using toluene-LIF	90
9.3.2 Two-tracer technique 9.3.3 Summary of tracer-based oxygen imaging strategies	92 93
10 Summary	95
11 References	97
12 Publications	103

1 Introduction

Innovative concepts for internal combustion engines like homogenous charge compression ignition (HCCI) and direct-injected spark-ignition engines (DISI), that promise high efficiency and low emissions, require a detailed knowledge about the gas mixture prior to ignition. Exact control of ignition is crucial for the reliable operation of those engines. Furthermore, the properties of the mixture determine the combustion process and thus effect pollutant formation and the emission of unburned hydrocarbons. It is therefore highly desirable to obtain quantitative information about the endgas conditions prior to ignition, i.e. of fuel/air ratio, oxygen concentration, fuel concentration and temperature distribution.

Laser-based measurement techniques provide time- and spatially resolved in-situ information without influencing the system under study by inserting probes and surfaces. The use of laser-induced fluorescence (LIF) has therefore grown to an important engineering tool over the last two decades. Commercial fuels contain numerous compounds that strongly fluoresce upon illumination with UV light. However, each component exhibits a fluorescence signal that depends not only on the concentration of the fluorescing species but - in its own characteristic way - also on temperature, pressure and local gas composition. With the current knowledge a quantitative interpretation of the total signal that is emitted from a wealth of different species is not feasible. Therefore, LIF measurements from commercial fuels can provide gualitative information at best [1]. For this reason, situations where only single fluorescing components (so-called tracers) are present in an otherwise nonfluorescing fuel (e.g. iso-octane) have been preferred. However, quantitative interpretation of the fluorescence signal in terms of fuel/air ratio or temperature requires sound fundamental knowledge of the compound's photophysical behavior, i.e. the dependence of the LIF-signal on temperature, pressure and bath gas composition.

Several tracer groups have been suggested among which ketones and aromatics have become the most popular. 3-pentanone (a representative of ketones) and toluene (a representative of aromatics) are thereby the most suitable tracers for gasoline engine application. When 3-pentanone LIF was first applied to engines, changes in the fluorescence signal due to varying conditions were pragmatically

neglected [2,3]. With further scrutiny, investigators recognized that the fluorescence signal may change significantly with temperature *T*, pressure *p*, and excitation wavelength λ_{exc} [4-6]. Eventually, a semi-empirical model has been established to predict signal intensities for engine conditions (i.e. high temperature *and* pressure simultaneously), based mainly on cell measurements with either elevated temperature or pressure [7]. Toluene is especially interesting for engine applications as it is a natural component of commercial gasoline. The dominant photophysical processes for the two molecules are significantly different. A study from Reboux et al. [8] showed that the toluene LIF signal at room temperature is directly proportional to the fuel/air ratio. Since then, toluene has quickly become a popular tracer for the investigation of fuel/gas mixing in the compression stroke of an engines (e.g. [9,10]). However, despite its frequent application almost no information has been available about the fluorescence behavior at engine-related conditions, i.e. at elevated temperatures and pressures.

The motivation for this work is to enable quantitative signal interpretation of the toluene-LIF signal at conditions relevant to the precombustion mixing process in internal combustion engines. Cell measurements will provide a large database of fluorescence and absorption data depending on temperature and bath gas. Based on this data, a semi-empirical model for toluene-LIF will be developed. Additional measurements of the fluorescence properties of 3-pentanone will be presented that lead to improved parameters for the photophysical model of this substance. In collaboration with Stanford University and the University of Michigan, Ann Arbor, both models have been validated by comparing signal predictions with data obtained in an optical engine where temperature and pressure are reasonably well known. Novel measurement strategies for fuel/air ratio, temperature and oxygen concentration, based on toluene-LIF, will be discussed and demonstrated.

2 Background

In this section, a summary on the current state-of-the-art of tracer-LIF application to IC engines will be given. This includes a motivation of the concept itself, a review of popular groups of tracer molecules and details on the current status of LIF-signal interpretation.

2.1 Motivation: Use of fluorescent tracers

The safe, clean and reliable operation of combustion devices depends to a large degree on the exact control of the air fuel mixing process prior to ignition. Therefore, quantitative measurement techniques that characterize the state of the fresh gas mixture are crucial in modern combustion science and engineering. The mixture is characterized by a number of key quantities. While the fuel concentration determines the total energy available for the process, the actual chemical process depends mostly on the local ratio of fuel, oxygen and inert gases. The temperature of the mixture in turn has a strong influence on ignition, flame speed and flame orientation. Turbulence, finally, significantly increases the volumetric reaction rates.

In recent years, ignitability and ignition control started to play an important role again in engine research. Since the early eighties, gasoline engines have been run with a homogeneous and stoichiometric mixture of fuel and air. Ignition and ignition timing, provided by a spark plug, was therefore no great deal. This strategy was driven mainly by the operating mode of the three-way catalyst, which requires stoichiometric combustion. However, at low and medium load, the total amount of air and fuel is reduced by a throttle valve. The resulting throttle losses lead to reduced energy efficiency. Modern engine concepts try to circumvent this deficit. In direct-injected spark ignition engines (e.g. Volkswagen FSI), a well-defined stratification of the fuel/air mixture is attempted. Thus, the engine can be run with an overall lean mixture (i.e. less fuel but no or reduced throttling of intake air), as long as a stoichiometric (i.e. ignitable) mixture is present at the spark plug at the time of ignition. However, this is at the same time the crucial challenge in the development of those engines. A HCCI (Homogeneous charge compression ignition) engine is a hybrid of the "classical" spark ignition (Otto) engine and a Diesel engine. Whereas the fuel/gas mixture is typically homogeneous as in the Otto engine, ignition is no longer provided by a spark plug but by self-ignition through compression similar to the Diesel engine. In this concept, control of ignition timing is a challenge. HCCI engines are usually run with a diluted gas mixture, i.e. a high fraction (up to 70%) of hot residual gas. The resulting temperature and oxygen concentration determines the auto-ignition of the fuel.

Fuel visualization strategies based on laser-induced fluorescence (LIF) have provided a great deal of information for the improvement of the above mentioned engine concepts. The LIF signal from commercial gasoline results from a wealth of different species and a quantitative interpretation is currently not feasible. It is therefore popular to use systems with a single, well-defined fluorescence species (so-called tracer) added to a non-fluorescing base fuel. The tracer signal intensities depend on the surrounding conditions, e.g. temperature and gas composition, which must be corrected for when quantitative tracer concentration measurements are desired. Moreover, these interdependencies can be used to assess temperature and residual gas concentrations in addition to the fuel/air ratio. Thus, tracer-based LIF imaging strategies offer the potential to fully characterize the endgas prior to ignition.

2.2 The ideal tracer

The ideal tracer should behave exactly like the fluid to which it is added (i.e. the fuel or the desired component of a multi-component fuel) in terms of droplet formation, evaporation, convection, diffusion, reactivity, and reaction rate. It is obvious that these requirements can not be met in full. However, a practical tracer should be chemically close to the fuel or at best a "natural" component of commercial fuels.

The tracer should yield a fluorescence signal upon excitation with commercially available laser sources (e.g. KrF-excimer at 248 nm, quadrupled Nd-YAG at 266 nm) and therefore requires an absorption feature at those wavelengths.

Critical for the selection of a suitable tracer is a matching boiling point with the base fuel, in order to ensure simultaneous evaporation. Thus, 3-pentanone (boiling point 101°C) and toluene (111°C) have become popular tracers for gasoline-type model fuels (iso-octane: 99°C).

Ideally, the tracer should yield LIF signal intensities that are directly proportional to the desired quantity and should not be influenced by the ambient conditions. Unfortunately, signals from all fluorescent tracers show at least some dependence on local temperature, pressure, and bath gas composition. In IC engines, ambient conditions change with time and space. It is therefore crucial to understand the

underlying interdependencies with the tracer signal in order to enable the quantitative interpretation of signal intensities.

For practical reasons, the tracer should be non-toxic (therefore, e.g. benzene is not suitable) and commercially available at reasonable cost.

Some tracers, like toluene, are components which are present in commercial fuels. Therefore the tracers must not be understood as "added" to the fuel. Rather, the other fluorescing substances are replaced. In general, the modification of the system must be kept to a minimum, and the influence of the tracers on a given experimental situation must be critically reviewed.

2.3 Typical classes of fuel tracers

Aliphatic (saturated, i.e. no double bonds) hydrocarbons that form the major part of combustion fuels are transparent within the wavelength range of commercial UV lasers (e.g. 248 nm KrF* excimer or 266 nm quadrupled Nd:YAG) and therefore do not give any LIF signal at all (see also chapter 3.1). Aromatics or ketones, in turn, do have (weak) transitions in this range and yield LIF signals strong enough to be detected with CCD-cameras. The larger the chromophore (i.e. the active electronic system) responsible for absorption, the more the absorption is shifted toward longer wavelengths. Mainly for this reason and due to their chemical similarity to components of commercial fuel (aromatics are typical components of fuels), two major classes of tracers have been found suitable for gas phase tracer-LIF applications: ketones and aromatics. Comprehensive reviews on the different substances investigated for the application in tracer-LIF is given in [11] and [12].

Acetone (CH₃COCH₃) and 3-pentanone (C₂H₅COC₂H₅), representatives of **ketones**, are popular fluorescence tracers for LIF-based imaging measurements of temperature and mole fraction or species concentration in a variety of flows [4,13-19]. The high vapor pressure makes acetone (bp: 56°C) an ideal tracer for gaseous flows [20,21]. 3-pentanone (bp: 101°C) [2,3,22] or mixtures of 3-pentanone and 3-hexanone [23] were suggested as tracers that mimic the boiling and transport properties of gasoline. High-power UV lasers with wavelengths between 230 and 330 nm excite the electronic $\pi^* \leftarrow$ n transition and result in broadband fluorescence signals between 350 and 550 nm. Such signals are often strong enough to permit detection with unintensified CCD cameras in fundamental fluid and heat transfer studies and they provide good single-shot signal-to-noise using intensified cameras in harsher environments like internal combustion engines. Understanding the pressure, temperature, and excitation wavelength dependencies of ketone LIF is crucial for quantitative measurements. Initially, these dependencies were neglected or poorly

understood, resulting in only qualitative measurements where signals indicated roughly the location of the fluorescence tracers, but concentrations could not be accurately calculated [3,17,24]. With further research, the existence of these dependencies became known, and quantitative concentration experiments could be performed under carefully controlled conditions [13,14]. As the empirical understanding of the fluorescence signal's dependencies on temperature, pressure, and excitation wavelength has further developed [7,22,25,26], new diagnostics strategies have led to improved and more robust quantitative measurements, e.g. temperature imaging in uniformly seeded flows with single-color excitation measurements of temperature and mixture fraction in isobaric flows with two-color excitation [15,16,25,27]. In addition to the development of diagnostics techniques for temperature and mole fraction measurements, the fundamental photophysical data have been used to form a fluorescence quantum yield model accounting for wavelength, temperature, pressure, and bath gas effects on acetone fluorescence [25]. A more preliminary model using the same conceptual framework has also been developed for 3-pentanone [7]. These models help one understand the relevant energy transfer processes and allow the prediction of signal behavior under conditions where experimental data are not available. They thus serve as useful tools for experimental design (e.g. tracer selection, excitation wavelength selection), diagnostic development and data interpretation.

Aromatic hydrocarbons are typical components of commercial fuels. These species are responsible for the strong absorption in the UV and the subsequently emitted fluorescence [28]. Thus, aromatics are a natural choice for the application as fuel tracers. Benzene is typically avoided because of its carcinogenic effects. Toluene is less toxic and not considered carcinogenic. Therefore, it has been most frequently chosen as a fuel tracer. In the early stage of tracer-LIF experiments, toluene was considered not suited for fuel imaging as aromatic fluorescence is strongly quenched by oxygen [6]. The total fluorescence yield therefore not only increases linearly with toluene number density but at the same time decreases with oxygen number density. However, it thus offers the potential to track the fuel/air equivalence ratio ϕ rather than the fuel number density n_{fuel} . Signal interpretation in many applications is currently based on a study by Reboux et al. [8] who found toluene signal to be proportional to the fuel/air ratio for 248-nm excitation, at room temperature and air pressures above 3 bar. As ϕ is an important quantity for ignition and flame development, this study sparked numerous in-cylinder investigations using toluene as a fluorescent tracer [9,10,29]. Despite its frequent use for fuel mixing diagnostics little is known about the behavior of toluene fluorescence at engine-related pressures and temperatures.

According to their boiling points different tracers have been used to represent different volatility classes of multi-component fuels [29]. Larger representatives like

5-nonanone [30] and methylnaphtalene [31] have been suggested as tracers for Diesel or kerosene surrogates.

Recently, the use of *exciplex systems* has become popular [32-35]. Those systems provide the possibility to distinguish between liquid and gas phase of the fuel. This is important in some applications in direct injection engines, when droplets are present during most of the compression stroke, and the LIF signal from the liquid phase dominates the gas-phase signal. The gas-phase signal is thereby often provided by an aromatic molecule. One example for an exciplex system is a mixture of 89% n-hexane, 9% diethylmethylamine (DEMA) and 2% fluorobenzene (FB) [36]. In the liquid phase, the excited FB forms an exciplex when colliding with DEMA. Due to the much lower collision rates, this exciplex does not form in the gas phase. The fluorescence signal from the exciplex is red-shifted and thus, in general, the fluorescence signal from gas phase (monomer) and liquid phase (exciplex) can be spectrally separated. However, a fraction of the light emitted from the liquid phase results from monomers thus leading to cross-talk with the gas phase channel. In addition, little is known on the temperature and pressure dependence of fluorobenzene LIF in the gas phase.

2.4 Current status of tracer-LIF interpretation

This section describes the current understanding of the LIF-signal behavior from ketones and aromatics under conditions similar to those in internal combustion engines. They form the most widely applied tracer groups. In this work, representatives of both groups have been investigated.

2.4.1 Ketones

Electronic quenching of ketone-LIF by oxygen or other species present in combustion is weak (see section 3.5.5). Its fluorescence signal is therefore generally assumed as proportional to the tracer number density and therefore to directly represent the fuel distribution:

$$S_{fl} \sim n_{tracer} \sigma_{abs}(\lambda_{exc}, T) \phi_{fl}(\lambda_{exc}, T, p)$$
(2-1)

The absorption cross section σ_{abs} and the fluorescence quantum yield ϕ_{fl} (i.e. the fraction of excited molecules that actually fluoresce) depend on the excitation wavelength λ_{exc} , temperature *T* and total pressure *p*. Thus, to interpret ketone LIF in terms of fuel distribution, corrections for these conditions must be undertaken. Therefore, the pressure and temperature dependence of acetone and 3-pentanone

LIF has been subject to many investigations [18,22,25,26,37-43]. Ketone LIF has a pronounced temperature-dependence and a weak pressure-dependence. However, due to experimental restrictions, only one of the two variables has been varied at a time, i.e. the LIF-signal at elevated temperatures was investigated at a total pressure of 1 bar and at increasing pressure mainly for room temperature. Thurber and Hanson [25] have developed a photophysical model that describes this behavior and that is meant to predict signal intensities when both T and p are elevated simultaneously.

Photophysical model for acetone and 3-pentanone

The conceptual model by Thurber [25] was developed for acetone. Koch [39] extended this scheme also to 3-pentanone. In Fig. 1 the basic processes included in the model are shown. Qualitatively, the model can explain the experimentally found dependencies of ketone-LIF on *T*, *p* and λ_{exc} .



Fig. 1: Schematic of acetone photophysics: Simplified model based on a multi-step vibrational decay in the S_1 state and an energy-dependent intersystem crossing rate.

The key variable is the vibrational excess energy. With increasing vibrational excitation, the rate of a non-radiative decay path k_{nr} (here intersystem crossing, ISC) is increasing while the fluorescence rate k_{fl} is approximately constant. Thus, the LIF signal is decreasing with increasing vibrational excitation, i.e. with decreasing λ_{exc} or increasing *T*. Increasing temperature leads to a higher vibrational excitation in the ground state (Boltzmann distribution) and thus, for a constant λ_{exc} , the molecules end up with a larger excess energy in the excited electronic state. Collisions with the bath gas remove vibrational excess energy (i.e. the molecules "thermalize"), leading to an

increase in signal. Thus, increasing pressure will accelerate this process and the LIF signal increases with increasing pressure, until thermalization is reached before fluorescence occurs. A further increase in pressure will then have no influence and a plateau of signal vs. pressure will be found. It is important to note that temperature and pressure effects can generally not be separated. The non-radiative decay rate dependents on vibrational energy and is obtained by a fit to experimental data. The fit parameter of the model is α , the average energy transfer per collision.

With this conceptual model, experimental data available for acetone and 3pentanone can be satisfactorily described. In this work it will be shown that there are significant shortcomings of the model for predictions beyond the data that has been used for model development, i.e. at simultaneously elevated pressure and temperature (e.g. in the compression stroke of the engine).

2.4.2 Aromatics

In contrast to ketone LIF signal which is almost insensitive to collisions with oxygen and therefore is commonly used to determine the fuel number density, aromatic fluorescence is strongly quenched by oxygen. It thus offers the potential to track the fuel/air equivalence ratio ϕ . In fact, as long as oxygen quenching is the dominant deexcitation pathway, the fluorescence signal will be proportional to the fuel/air ratio. This concept was introduced by Reboux et al. [8] who found that this is the case for toluene LIF at room temperature with 248-nm excitation and air pressures above 3 bar. This strategy is known as FARLIF (Fuel/Air Ratio LIF).

The total toluene-LIF signal $S_{\rm fl}$ is proportional to the product of number density $n_{\rm tracer}$ and absorption cross-section $\sigma_{\rm abs}$ (i.e. number of excited molecules) times the fluorescence quantum yield $\phi_{\rm fl}$ (i.e. the fraction of excited molecules that actually fluoresce):

$$S_{fl} \sim n_{tracer} \sigma_{abs}(\lambda_{exc}, T) \phi_{fl}(\lambda_{exc}, T, n_{oxy})$$
(2-1)

A simple rate-equation analysis of a single excited electronic state yields an expression for the quantum yield in the presence of a quenching species (in this case oxygen):

$$S_{fl}(T, n_{oxy}) \sim n_{tracer} \sigma_{abs}(T) \frac{k_{fl}(T)}{k_{tot}(T) + \widetilde{k}_{g}^{oxy}(T) n_{oxy}}$$
(2-2)

with k_{fl} denoting the rate of spontaneous fluorescence [s⁻¹] and k_{tot} the rate for the sum of all intramolecular decay pathways [s⁻¹]. The oxygen-quenching rate is the product of oxygen number density (n_{oxy}) [cm⁻³] and the bimolecular quenching rate

coefficient k_q^{oxy} [cm³ s⁻¹]. If quenching by oxygen is much faster than intramolecular processes, k_{tot} can be neglected and the signal becomes proportional to the fuel/air ratio ϕ :

$$S_{fl}(T, n_{oxy}) \sim g(T) \frac{n_{tracer}}{n_{oxy}} \sim g(T) \phi$$
 if $k_{tot}(T) \ll \widetilde{k}_q(T) n_{oxy}$ (2-3).

The function g(T) includes the temperature-dependent variables. In practical applications, g(T) is often determined by LIF measurements at motored engine operation with known concentrations of the fluorescent species at various crank angles and the assumption that conditions under fired operation are not too different. Thus, the FARLIF technique relies on two assumptions:

- (1) Oxygen quenching is the dominant de-excitation pathway at all temperatures,
- (2) Temperature-dependent variables (like the absorption cross-section and the *T*-dependent parts of the quantum yield expression) can be separated into an experimentally accessible function g(T) which can be used to correct the signal.

It is part of this work to critically review this concept for engine-related temperatures.

3 Photophysics of organic molecules

The tracer techniques discussed here are based on laser-induced fluorescence (LIF) detection. Molecules are electronically excited by absorbing a photon typically in the ultraviolet or visible spectral range. Spontaneous emission (fluorescence) from the excited molecule that occurs within 1 - 100 ns is then detected and is representative of the local tracer concentration. There is, however, a strong influence of the bath gas on absorption, energy transfer in the excited state, and non-radiative relaxation of the excited state that affects signal intensities and spectral distribution. An interpretation of measured signal intensities therefore requires a detailed knowledge of the underlying photophysical processes, as long as significant changes of these processes are expected relative to the calibration system. This section describes the fundamentals of photophysics of small organic molecules. It follows in large parts the textbook from Gilbert and Baggot [44].

3.1 Absorption

3.1.1 Classification of electronic transitions

Absorption of photons in the UV (and with larger molecules also in the visible) populates excited electronic levels. The absorption strength is described by the wavelength-dependent absorption cross-section $\sigma(\lambda)$. In organic molecules it is useful to describe the chemical bonds by linear combinations of so-called s- and p-states (atomic orbitals) giving molecular orbitals with different symmetry: binding σ and π orbitals, anti-binding σ^* and π^* , and neutral (non-binding) n orbitals. Organic molecules typically have closed shells where the highest occupied molecular orbitals (HOMO) are binding σ , π or non-binding n orbitals (localized at the O-atom in ketones, aldehydes and alcohols). The lowest unoccupied molecular orbitals (LUMO) usually are anti-bonding π^* or σ^* orbitals. The following typical optically-active transitions occur:

- $\pi \rightarrow \pi^*$, e.g. in alkenes and aromatics
- n → π^{*}, e.g. in molecules with carbonyl groups (ketones, aldehydes), azo- or thiocarbonylgroups (which are the analogous molecules with O replaced by N or S, respectively)
- $n \rightarrow \sigma^*$, e.g. in amines and alcohols
- $\sigma \rightarrow \sigma^*$, e.g. in alkanes (at vacuum UV wavelengths).

This indicates that according to the photo-active groups or electronic systems (socalled chromophores) the molecules can be sorted in different classes with typical properties shown in Table 1. This is analogous to the classification for functional groups determining the reactivity and classes of chemical reaction of organic molecules.

Chromophore	Transition	λ _{max} [nm]	$\sigma_{ m abs}$ [10–20cm ²]
C=O	$n \rightarrow \pi^{\star}$	280	8
Benzenes	$\pi \rightarrow \pi^{\star}$	260	80
C=N	$n \rightarrow \pi^{\star}$	240	50
C=C-C=C	$\pi \rightarrow \pi^{\star}$	220	8 × 10 ⁴
C=C	$\pi \rightarrow \pi^{\star}$	180	4 × 10 ⁴
C–C	$\sigma \rightarrow \sigma^{\star}$	<180	400
C–H	$\sigma \to \sigma^{\star}$	<180	400

Table 1: Wavelength of maximum absorptivity and absorption cross sections for relevant chromophores [44]

3.1.2 Classification of electronic state

The electronic state of a molecule is characterized by its total spin and the degree of excitation. In the ground state for the most molecules the total spin is S = 0. Here, all electrons (each of them with $S = \frac{1}{2}$) are paired with anti-parallel spin. When exciting a single electron, the two resulting unpaired electrons can either be parallel (S = 1) or anti-parallel (S = 0). According to the resulting multiplicity of the states (number of potential realizations with the same total energy) the S = 0 and 1 states are called singlet (S) and triplet (T), respectively. The level of excitation is indicated by subscript numbers. 0 is the ground state, and 1 and 2 are excited states with increasing

energy. Fig. 2 shows the population and the energy of the ground state and the first excited states for a carbonyl group.



Fig. 2: Population of the molecular orbitals in the ground state and the first excited state of a ketone group. Right: Comparison of the relative energy of the various states.

3.1.3 Transition probabilities

Transition matrix

The probability for the absorption of a photon can be calculated using timedependent perturbation theory. Thereby, the interaction with electromagnetic radiation is regarded as a short perturbation in order to solve the time-dependent Schrödinger equation:

$$\widehat{H}_{total}\psi = i\hbar\frac{\partial}{\partial t}\psi$$
(3-1)

Herein is:

$$\hat{H}_{total} = \hat{H}_0 + \hat{H}' \tag{3-1a}$$

the Hamiltonian of the total system, the sum of the zeroth Hamiltonian (unperturbed system) (\hat{H}_0) and the perturbation Hamiltonian (\hat{H}'), which represents the interaction of the electromagnetic field with the molecule. The wave function Ψ is taken to be a linear combination of the solutions for the zeroth Hamiltonian, i.e. initial (*m*) and final state (*n*) of the respective transition:

$$\psi = \mathbf{a}_m(t)\psi_m + \mathbf{a}_n(t)\psi_n, \qquad (3-1b)$$

with the time-dependent coefficients a_m and a_n . The probability P_n , that the transition $m \rightarrow n$ has occurred at time t, is represented by a_n :

$$\boldsymbol{P}_n = \boldsymbol{a}_n^* \boldsymbol{a}_n = \left| \boldsymbol{a}_n \right|^2. \tag{3-2}$$

Looking at the transition on a short time scale Eq. 3 -1 yields:

$$\frac{\partial}{\partial t}\boldsymbol{a}_{n} = -\frac{i}{\hbar} \langle \boldsymbol{\psi}_{n} | \hat{\boldsymbol{H}}' | \boldsymbol{\psi}_{m} \rangle .$$
(3-3)

This integral represents the coupling of the states to the electromagnetic field. It is called transition matrix.

Transition dipole moment

The interaction of the electromagnetic field with the molecule can be described by the interaction of the field with the total dipole moment of the molecule:

$$\hat{H}' = pE.$$
(3-4)

The solution of the differential equation (3-3) leads to:

$$P_n \approx \frac{E^2 |M_{nm}|^2}{\hbar^2} t^2.$$
 (3-5)

Thus, the transition probability is increasing with the time *t* squared, the amplitude of the electric field *E* squared (i.e. proportional to the intensity of the radiation) and the transition dipole moment M_{nm} squared, where

$$\boldsymbol{M}_{nm} = \left\langle \boldsymbol{\psi}_{n} \left| \boldsymbol{p} \right| \boldsymbol{\psi}_{m} \right\rangle = \int \boldsymbol{\psi}_{n}^{*} \boldsymbol{p} \boldsymbol{\psi}_{m} \mathrm{d} \boldsymbol{\Gamma}$$
(3-6)

is an integral over all spatial electron- and nucleon coordinates, and the electron spin coordinates. *p* denotes the dipole operator. While the intensity of the incoming radiation can be influenced during an experiment, the transition dipole is an intrinsic property of the specific transition. The strength of the transition dipole moment can be calculated in the Born-Oppenheimer-Approximation. This is the assumption that the electronic motion and the nuclear motion of a molecule can be separated. This is a good approximation as long as the motion of the nucleons is significantly slower than that of the electrons. Since the nuclei are much heavier than the electrons, they are generally much slower and the approximation is often valid for molecules.

This leads to a molecular wave function in terms of electron positions and nuclear positions. Ψ can thus be separated into the spatial electronic wave function ϕ , the nuclei wave function *N* and the electronic spin wave function χ .

$$\psi = N\phi\chi \,. \tag{3-7a}$$

Developing the dipole operator yields:

$$\boldsymbol{M}_{nm} = \left\langle \phi_n \left| \boldsymbol{p} \right| \phi_m \right\rangle \left\langle \boldsymbol{N}_n \left| \boldsymbol{N}_m \right\rangle \left\langle \boldsymbol{\chi}_n \right| \boldsymbol{\chi}_m \right\rangle.$$
(3-7b)

With the transition probability being proportional to $|M_{nm}|^2$, three factors determine its magnitude:

- The electronic contribution $|\langle \phi_n | p | \phi_m \rangle|^2$ depends on the spatial overlap and symmetry of the electronic wave functions.
- The Franck-Condon contribution $|\langle N_n | N_m \rangle|^2$ describes the spatial overlap of the wave functions of the nuclei between ground and excited state.
- The spin wave function $|\langle \chi_n | \chi_m \rangle|^2$ is zero for singlet-triplet transitions and unity for singlet-singlet and triplet-triplet transitions due to the orthonormal properties of the spin wave functions.

The combination of these contributions yields the selection rules. n and π^* orbitals in ketones ($S_0 \rightarrow S_1$ transition) for example have a poor spatial overlap. The resulting transition is weak and sometimes called "orbital-forbidden". If the wave functions of ground and excited state have different symmetry, the integral determining the transition moment is zero; the respective transition is called "symmetry forbidden". This selection rule applies to $S_0 \rightarrow S_1$ transitions in ketones and aromatics. The reason that these molecules absorb light in contrast to the selection rules is that the Born-Oppenheimer approximation (which assumes the independence of the movement of electrons and nuclei: the typical timescale of the absorption is on the order of 10^{-15} s, that of vibrations 10^{-12} s) is partially violated. The intra-molecular vibrations couple with the electronic system and therefore distort the electronic wave functions, breaking the perfect symmetry, which then introduces non-zero contributions to the integral. The resulting transitions are called "vibrationally allowed". With increasing vibrational excitation (i.e. temperature) those transition moments increase. This effect explains the relatively small transition moments for aromatic $S_0 \rightarrow S_1$ transitions compared to fully allowed transitions like $\pi \rightarrow \pi^*$ in alkenes (cf. Table 1). In small and highly-symmetric molecules vibrations are responsible for a clear band structure of the absorption spectrum, whose relative intensities depend on the Franck-Condon overlap argument. In organic molecules at room temperature, the large number of degrees of freedom causes broad, only weakly-structured absorption bands. The shape of this spectrum, however, is still determined by Franck-Condon's principle.

These arguments focus on the interaction of the electronic dipole moment with the electric field of a light wave. The respective magnetic interaction is usually negligibly

small. In some cases, however (e.g. $n \rightarrow \pi^*$ transition in formaldehyde HCHO), symmetry-forbidden and vibrationally-forbidden transitions are still observed, because they coincide with allowed magnetic dipole transitions.

Spin-forbidden transitions finally should completely prevent singlet-triplet transitions because of their orthogonal wave functions. The validity of this rule, however, is limited due to coupling of the spin with the orbital's angular momentum. In this case the selection rules are determined by the resulting total angular momentum. In organic molecules the coupling between the orbital and the electronic angular momentum is weak, and the selection rule is strongly obeyed. Coupling, however, increases in the presence of heavy atoms (with the fourth power of the atomic mass). Organic molecules with heavy atoms (i.e. Br, I) show an increased coupling and a limited validity of the spin selection rule.

3.1.4 Deactivation of excited molecules

So far we discussed the excitation of molecules leading to the population of highly excited states well above their thermal equilibrium population. From these states the excess energy can be lost on different paths via chemical (dissociation, photo-induced reaction) and physical processes. The latter fall into three categories:

- Radiative processes. The excess energy (or a part of it) is emitted by spontaneous emission, i.e. fluorescence
- Non-radiative processes: The excess energy is thermalized by vibrational and rotational energy transfer
- Collisional quenching: Electronic excitation of colliding molecules, i.e. electronic energy transfer



Fig. 3: Jablonski diagram showing the photo-physical processes during deactivation of excited organic molecules

The processes of the first two categories are shown in the Jablonski diagram in Fig. 3. Radiative and non-radiative processes are indicated by straight and curved lines respectively. The excited molecule can loose energy by emitting light (fluorescence and phosphorescence) or by exciting vibrations and rotations in colliding molecules (external vibrational relaxation, VR). Radiationless, intra-molecular electronic transitions occur "horizontally" without changing the total energy. When the spin multiplicity changes, the process is called intersystem crossing (ISC), when the multiplicity is maintained: internal conversion (IC).

3.2 Radiative processes

Spontaneous emission has the same dependence on transition moments like the absorption cross-sections and must satisfy the same selection rules. The probability of spontaneous emission, however, increases with the energy difference hv between the coupled states ($\sim v^3$).

3.2.1 Fluorescence

The $S_1 \rightarrow S_0$ transition due to spontaneous emission of light is fast; it is typically observed during an interval of 1 – 100 ns. In ketones the $S_1 \rightarrow S_0$ transition is symmetry and orbital forbidden. The radiative lifetime is therefore on the order of microseconds. The fast depopulation of the excited state due to intersystem crossing, however, limits the effective fluorescence lifetime to ~ 1 ns.

3.2.2 Phosphorescence

Triplet states are significantly longer lived due to the spin-forbidden radiative relaxation to the singlet ground state. Intersystem crossing populating the S₀ state is inefficient due to the large energy difference. The spontaneous transition $T_1 \rightarrow S_0$ is called phosphorescence and has a typical lifetime of milliseconds to seconds.

3.3 Non-radiative processes

3.3.1 Dependence of the transition probability on the energy difference (energy gap law)

The transition probabilities of non-radiative relaxation processes (intersystem crossing and internal conversion) decrease with an increasing energy difference between the involved quantum states. The overlap of the vibrational wave functions decreases with increasing energy difference. This explains why ISC in simple ketones ($\Delta E \sim 20 \text{ kJ/mol} (0.22 \text{ eV})$) is much faster than in benzene and toluene ($\Delta E \sim 120 \text{ kJ/mol} (1.3 \text{ eV})$). This difference in triplet-singlet energy difference is also important for the understanding of quenching processes (section 3.5). Due to this importance, we further discuss the background of the energy gap between the triplet and singlet states.

3.3.2 Singlet-triplet energy difference

When comparing singlet and triplet systems with otherwise identical quantum numbers, the triplet is systematically lower in energy. This reflects Hund's first rule, stating that in open-shell systems the configuration with maximum spin multiplicity is preferred.

A simple interpretation of this effect is based on Coulomb repulsive forces between the electrons. With maximum spin, the spin wave function is fully symmetric, and hence, according to Pauli's law, the spatial wave function must by anti-symmetric. This means, however, that the average distance of the electrons increases (relative to the symmetric case), and the coulomb forces decrease. The result is an overall lowered energy of the triplet compared to the singlet.

The resulting energy difference depends on the electronic structure of the respective molecule. In single ring aromatic molecules the π and π^* molecular orbitals (that contain the two unpaired electrons) have a larger spatial overlap than the n and π^* orbitals in ketones. Therefore, the above mentioned effect of Coulomb repulsion is more pronounced in benzene and toluene compared to acetone and 3-pentanone, for

example. This effect ultimately contributes to the different susceptibility towards oxygen quenching that is observed in these two classes of molecules (cf. section 3.5.5).

3.3.3 Intersystem crossing, ISC

The non-radiative transition between states of different spin multiplicity is called intersystem crossing. The total energy is typically preserved, which means that after a $S_1 \rightarrow T_1$ transition the molecule gains vibrational excitation. The dependence on the energy gap between the two states was discussed above (energy gap law). Additional geometry-dependent selection rules ("EI-Sayed's rules") must be satisfied. ISC is allowed for $S(n,\pi^*) \rightarrow T(\pi,\pi^*)$ and $S(\pi,\pi^*) \rightarrow T(n,\pi^*)$ and forbidden for $S(n,\pi^*) \rightarrow T(n,\pi^*)$ and $S(\pi,\pi^*) \rightarrow T(n,\pi^*)$ and forbidden for S(n, π^*) and S(π,π^*) transitions. The transition probabilities of forbidden transitions are not exactly zero due to interaction of the electronic wave function with vibrations. They are, however, significantly reduced (cf. Table 2).

Molecule	Transition	Selection rule	Rate for ISC [s ⁻¹]
Anthracene	$S_1(\pi,\pi^*) \rightarrow T(n,\pi^*)$	"forbidden"	1,4 × 10 ⁸
Acetone	$S_1(n,\pi^*) \rightarrow T(n,\pi^*)$	"forbidden"	5×10^8
Benzophenone	$S_1(n,\pi^*) \rightarrow T(\pi,\pi^*)$	"allowed"	10 ¹¹

Table 2: ISC-rates for molecules with similar singlet-triplet energy gaps but different symmetries (8 – 21 kJ/mol, 0.08 – 0.2 eV) [45,46]

For ketones and benzene derivatives (toluene) ISC is symmetry-forbidden. Nevertheless, it is 3 and 1 orders of magnitude faster than the respective rates of spontaneous $S_1 \rightarrow S_0$ emission. ISC can be significantly increased in the presence of oxygen. This is discussed in the collisional quenching section (3.5).

3.3.4 Internal conversion

Internal conversion (IC) is the non-radiative transition between states of the same spin multiplicity. This process is symmetry-allowed. Because of the large energy difference between S_0 and S_1 , according to the energy gap law, at room temperature IC is typically of minor relevance for S_1 deactivation. This argument can be applied to motivate Vavilov's law that states that fluorescence is emitted from the S_1 state only. The energy difference between excited singlet states is small enough to enable fast IC (i.e. $S_2 \rightarrow S_1$) transitions. However, certain vibrational modes can promote fast IC due to a favorable Franck-Condon Factor. Thus, at high vibrational excitation, $S_1 \rightarrow S_0$

IC can become very fast. This plays an important role for toluene at elevated temperatures.

3.3.5 Vibrational relaxation

Vibrational relaxation (VR) occurs through collisions with bath gas molecules with almost unity probability. Therefore, in the liquid phase, VR is very fast. In the gas phase, however, VR does not fully relax the molecules to the vibrational ground state during the fluorescence lifetime, which makes signals pressure-dependent. While VR takes place, competing processes (ISC and spontaneous emission) are active on the same timescale. The entire process, therefore, often requires dynamic modeling for a full explanation of the observed behavior [47].

3.3.6 Intramolecular vibrational redistribution (IVR)

In larger molecules like toluene, optically active and inactive vibrational modes will overlap with the density of states increasing exponentially with vibrational excess energy. Thus, the excitation of an optically active vibrational mode will lead to intramolecular redistribution of the excess energy to optically inactive modes. The rate of this process is dominated by the state density.

3.4 Kinetics of photo-physical processes

3.4.1 Radiative and effective lifetimes

If fluorescence emission of photons h_V is the only pathway of relaxation of the excited molecules M* according to M* \rightarrow M + h_V , the temporal variation of the concentration [M*] of excited molecules is described by a first order differential equation

$$-\frac{d}{dt}\left[\mathsf{M}^*\right] = k_{ff}\left[\mathsf{M}^*\right]. \tag{3-8}$$

leading to an exponential decay with the rate $k_{\rm fl}$ of the fluorescence process and the initial concentration $[M^*]_0$

$$\left[\mathsf{M}^{*}\right] = \left[\mathsf{M}^{*}\right]_{0} \exp^{-k_{\mathrm{fl}}t}.$$
(3-9)

Within the radiative lifetime, τ_{rad} , the concentration of excited molecules decays to 1/e of the initial value.

$$\tau_{rad} = \frac{1}{k_{fl}} \tag{3-10}$$

Typical values are shown in Table 3.

	Dipole allowed	Dipole allowed, vibrationally forbidden	Spin forbidden
σ_{abs} [10 ⁻²⁰ cm ²]	2 × 10 ³	5	5 × 10 ⁻³
τ _{rad} [μS]	1 × 10 ⁻³	5	5 × 10 ³

Table 3: Radiative lifetimes for systems obeying different selection rules.

In practical systems the decrease of $[M^*]$ is increased because non-radiative processes ISC and IC (with rates k_{isc} and k_{ic}) occur simultaneously:

$$-\frac{d}{dt}\left[\mathsf{M}^{*}\right] = \left(k_{fl} + k_{isc} + k_{ic}\right)\left[\mathsf{M}^{*}\right]$$
(3-11)

 k_{tot} is then the total rate of depopulation of the excited state including all individual depopulating processes *i*

$$k_{tot} = \sum k_i \tag{3-12}$$

yielding the experimentally accessible effective fluorescence lifetime:

$$\tau_{eff} = \frac{1}{k_{tot}} \,. \tag{3-13}$$

In 3-pentanone for example the radiative lifetime of approx. 1 µs [48] is reduced to approximately 2 ns mainly due to fast ISC [38].

3.4.2 Fluorescence quantum yield

Non-radiative processes reduce the fraction of excited molecules that actually emit fluorescence. This fraction is called fluorescence quantum yield ϕ_{fl} . ϕ_{fl} is unity in the

absence of non-radiative relaxation and decreases otherwise. It is the ratio of the fluorescence rate $(k_{fl}[M^*])$ over the absorption rate $(k_{abs}[M][hv])$ with [hv] being the photon density

$$\phi_{fl} = \frac{k_{fl} \left[\mathsf{M}^*\right]}{k_{abs} \left[\mathsf{M}\right] \left[h_{\mathcal{V}}\right]}.$$
(3-14)

With the rate coefficient of non-radiative excited state depopulation $k_{nr} = k_{tot} - k_{fl}$ the temporal variation of excited state population

$$\frac{d}{dt}\left[\mathsf{M}^{*}\right] = k_{abs}\left[\mathsf{M}\right]\left[h_{V}\right] - \left(k_{ff}\left[\mathsf{M}^{*}\right] + k_{nr}\left[\mathsf{M}^{*}\right]\right)$$
(3-15)

can be used to substitute [M*] which is experimentally not easily accessible by assuming steady state (i.e. $\frac{d}{dt} [M^*] = 0$ which is actually quickly established within a turning paragraph lager pulse duration).

typical nanosecond laser pulse duration)

$$\left[\mathsf{M}^*\right] = \frac{k_{abs}\left[\mathsf{M}\right]\left[h_{\mathcal{V}}\right]}{k_{fl} + k_{tot}}.$$
(3-16)

This leads to the interpretation of the fluorescence quantum yield as the ratio of the rate coefficients of fluorescence and total depopulation or the inverse ratio of the respective lifetimes.

$$\phi_{\rm fl} = \frac{k_{\rm fl}}{k_{\rm tot}} = \frac{\tau_{\rm eff}}{\tau_{\rm rad}} \tag{3-17}$$

Measurements of the fluorescence quantum yield and the effective fluorescence lifetime yields the radiative lifetimes.

The detected fluorescence signal intensity S_{fl} is proportional to the number of fluorescence photons, which is the product of absorbed photons and the fluorescence quantum yield (times the efficiency of the detection system η and the observed solid angle $\Omega/4\pi$)

$$S_{fl} = (E/h\nu) V N \sigma_{abs} \phi_{fl} \eta \Omega/4\pi$$
(3-18)

 E/h_V is the photon flux (in cm⁻²), n_{fl} the number density of fluorescence molecules in the observed volume V that have the absorption cross-section σ_{abs} (in cm²).

3.5 Collisional quenching

The non-radiative processes leading to depopulation of the excited state discussed so far were intra-molecular processes. Depending on the properties of the colliding molecules, strong inter-molecular deactivating processes can occur. First, we will focus on the kinetics of these processes, and then we will discuss possible mechanisms.

3.5.1 Stern-Volmer coefficient

If quenching collisions occur, an additional term must be added to the denominator of the formulation of the fluorescence quantum yield, ϕ_{fl} (Eq. 3-10), given in section 3.4.2. The probability of fluorescence quenching is proportional to the collision rate with the respective species times a species-specific quenching cross-section. This is usually expressed by the number density of the colliding (quenching) species, n_q , times a rate coefficient, \tilde{K}_q , changing the equation for ϕ_{fl} to

$$\phi_{\rm fl} = \frac{k_{\rm fl}}{k_{\rm tot} + \widetilde{k}_{\rm q} n_{\rm q}} \,. \tag{3-19}$$

Note that it is distinguished between rates of energy transfer processes (like k_{tot} , k_{fl}) and the rate coefficient \tilde{k}_q by adding a tilde on top of k. It becomes a rate by multiplying with the respective number density of quenching molecules n_q .

In some practical applications it can be argued that the denominator is dominated by the quenching term and that ϕ_{fl} is inversely proportional to the quencher concentration. This assumption, however, is limited and must be carefully checked for particular situations. The variation of signal intensity with increasing concentration of quenching molecules is given by:

$$\frac{S_{fi}^{0}}{S_{fi}} = \frac{k_{fi}}{k_{tot}} \frac{k_{tot} + \tilde{k}_{q} n_{q}}{k_{fi}} = 1 + \frac{\tilde{k}_{q}}{k_{fi}} n_{q}.$$
(3-20)

 S_{fl}^{0} is the fluorescence intensity in the absence of quenching. If measurements with varying quencher concentrations under otherwise identical conditions are carried out, this equation can be used to evaluate the ratio of \tilde{k}_{q}/k_{tot} , the so-called Stern-Volmer coefficient k_{SV}

$$\boldsymbol{k}_{\rm SV} = \boldsymbol{k}_q / \boldsymbol{k}_{\rm tot} = \boldsymbol{k}_q \boldsymbol{\tau}_{\rm eff} \quad . \tag{3-21}$$

 k_{SV} indicates the relevance of fluorescence quenching and is therefore experimentally important. The plot for graphical analysis of this relation is called

Stern-Volmer plot (c.f. Fig. 2). The Stern-Volmer coefficient can be temperaturedependent, as will be shown for toluene.



Number Density of Quenching Species, n_q

Fig. 4: Stern-Volmer plot

With the assumption that quenching occurs as a consequence of short-ranging interactions (collisions) the quenching constant can be understood as a product of the collisional frequency, Z_{coll} , as obtained from kinetic gas theory and a probability, $\langle p \rangle$, of an effective collision.

$$k_q = Z_{coll} \langle \boldsymbol{p} \rangle \tag{3-22}$$

3.5.2 Electronic energy transfer

One important process leading to collisional quenching is electronic energy transfer. The ground-state collider Q is electronically excited during the collision according to

$$M^* + Q \rightarrow M + Q^* \tag{3-23}$$

This process can in principle involve the emission of a photon by M with subsequent absorption by Q (radiative energy transfer). The non-radiative process can, however, be much more efficient. In this case M is called donor and Q acceptor. Two fundamentally different processes must be considered.

3.5.3 Fluorescence resonance energy transfer

Fluorescence resonance energy transfer (FRET) was first described by Förster [49]. Dipole-dipole interaction distorts the electronic structure of the donor and acceptor molecules. The dipole oscillation of M* then induces an oscillation in Q without direct physical contact between the two. This interaction depends strongly on the distance between the molecules but allows energy transfer over the distance of several

molecule diameters (up to 10 nm). The probability, dP_n , of the energy transfer within the time interval, dt, is

$$dP_n = \tau_{eff}^{-1} \left(\frac{r_0}{r}\right)^6 dt , \qquad (3-24)$$

with the fluorescence lifetime, τ_{eff} . The "critical radius", r_0 , determines the strength of the interaction and depends on the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor.

Electrons are not exchanged between the molecules. Therefore, the spin selection rules must be satisfied. Possible processes are

$$1M^* + 1Q \rightarrow 1M + 1Q^* \text{ or}$$
 (3-25a)

$$1M^* + 3Q \rightarrow 1M + 3Q^*$$
. (3-25b)

3.5.4 Short-range energy transfer

The mechanism first described by Dexter [50] involves the exchange of electrons between the two molecules. Direct contact leading to spatial overlap of the different molecular orbitals is therefore a requirement. The maximum distance is on the order of 0.5 - 1 nm. The probability of this process depends on the spectral overlap of the two molecules as well. Selection rules, however, do not apply. For this process the following reactions are spin-allowed:

$${}^{1}M^{*} + {}^{1}Q \rightarrow {}^{1}M + {}^{1}Q^{*}$$
 and (3-26a)

$${}^{1}M^{*} + {}^{1}Q \rightarrow {}^{1}M + {}^{3}Q^{*}.$$
 (3-26b)

3.5.5 Fluorescence quenching by molecular oxygen

The ground state of molecular oxygen is a triplet state. It is therefore very efficient in quenching fluorescence of organic molecules by facilitating the transition into triplet states. The energy transfer reactions can be written as [51]:

$${}^{1}M^{*} + {}^{3}O_{2} \leftrightarrow {}^{3}(M,O_{2})^{*} \rightarrow {}^{3}M + {}^{1}O_{2}^{*}$$
(3-27a)

The colliding molecules form a short lived exciplex (transition state). Different states with localized excitation (i.e. ${}^{3}({}^{1}M^{*}, {}^{3}O_{2}), {}^{3}({}^{3}M^{*}, {}^{3}O_{2}), \ldots)$ and charge transfer $({}^{3}M^{\bullet+}, {}^{2}O_{2}^{\bullet-})$ is possible. This coupling between states with different spin multiplicity enables the otherwise spin-forbidden intersystem crossing. Decreasing quenching

rate coefficients \tilde{k}_q with increasing ionization potentials indicate that at least partial charge transfer occurs in the transition state [52]. This process can, however, only happen if the energy difference between M's singlet and triplet state is larger than the energy required for excitation of O₂ into its singlet state (91 kJ/mol, 0.98 eV). This is the case for aromatic molecules, but not for ketones. Therefore, aromatic molecules are efficiently quenched by molecular oxygen, while small aliphatic ketones are only mildly influenced. The effects of collisional quenching in aromatics is, therefore, well described by the mechanism shown above [53].

In ketones, however, it was not clear for a long time whether oxygen has any influence at all. Nau and Scaiano [54] finally found a weak influence and use the above mentioned mechanism also for this class of molecules to describe an "oxygen-enhanced intersystem crossing". The reduced \tilde{k}_q compared to aromatic systems is then motivated with the observation that also in aromatics \tilde{k}_q decreases with a decreasing singlet-triplet energy difference and when the formation of the exciplex $(M,O_2)^*$ is endothermic [53]. Both arguments apply to aliphatic ketones. Furthermore, the fluorescence lifetime of ketones is much shorter than that of aromatics because of faster ISC. The Stern-Volmer coefficient that describes the quenching effect relative to the sum of all depopulation effects therefore is much reduced, making the oxygen quenching influence on ketones almost negligible.
4 Experimental investigation of toluene photophysics

In this chapter, the experimental data of toluene fluorescence and absorption obtained during this work is presented. Absorption has been studied in the temperature range from 300 - 1150 K, fluorescence in a 1 bar nitrogen bath gas from 300 - 950 K. Investigation of oxygen quenching has been performed in a nitrogen/oxygen bath gas mixture at 1 bar total pressure and with oxygen partial pressures ranging from 0 - 400 mbar. The temperature range was restricted by the onset of wall-induced chemistry to 300 - 700 K. Excitation wavelengths for the LIF studies have been 266 and 248 nm.

4.1 Introduction

The photophysical properties of the $S_0 \rightarrow S_1$ (π , π^*)-transition in toluene vapor have been a subject of interest since early in the last century [55,56]. The first highresolution absorption spectrum was published by Madsen [57] and a thorough investigation of the fluorescence properties was performed by Burton and Noyes, Jr. [58]. The absorption around 260 nm is easily accessible with commercially available high-power UV lasers, and the excitation is followed by fluorescence with a high quantum yield. These properties make the toluene molecule (along with similar aromatic molecules) attractive for diverse research fields ranging from the investigation of fundamental processes in larger molecules to practical applications that use toluene as a tracer molecule for flow-field and mixing studies.

Toluene was studied to elucidate the process of collision-induced vibrational energy transfer within the S_0 -state (using UV absorption [59], IR emission [60] or two-photon ionization [61]) and within the S_1 state (by means of dispersed fluorescence spectra [62]) as well as for the investigation of intramolecular vibrational redistribution (again by dispersed fluorescence [63,64]). Its absorption feature is of interest for concentration measurements in the atmosphere [65]. In the field of laser-based measurements in combustion systems, toluene is a promising tracer for visualizing mixing processes. As a major component of commercial gasoline it is especially

attractive to IC engine researchers [15]. The strong fluorescence quenching by oxygen allows one to directly assess the fuel/air equivalence ratio in precombustion mixing [8]. Adding an additional tracer that is oxygen-insensitive enables the simultaneous quantification of fuel *and* oxygen concentrations [30,66]. Despite the frequent application of toluene for fuel concentration diagnostics in the mixing and compression phase of internal combustion engines, no information is available about the variation of absorption cross-sections and fluorescence quantum yields in the relevant pressure and temperature range. As a result, many authors simply assume negligible pressure and temperature effects.

A wealth of toluene spectroscopic data is available in the literature for toluene at or below room temperature. Burton and Noyes measured absolute fluorescence quantum yields as a function of excitation wavelength using benzene as a standard [58] ($\phi_{fl} = 0.3$ for 266.8 nm excitation, room temperature, 23 mbar). Jacon et al. noted that above about 2100 cm⁻¹ excess vibrational energy in the S₁ state (this corresponds to an excitation at 253 nm), the quantum yield decreases rapidly by two orders of magnitude [67]. In this energy range, fluorescence and triplet yields do not add to unity, thus justifying the assumption of a "third-decay-channel", a phenomenon that was explored extensively by Smalley and co-workers [63,68]. Effective lifetimes of the S₁ state have been published by several groups [64,67,69], the most recent value is 86 ns with no vibrational excess energy [64]. The fundamental vibrational modes in both the ground and excited state are specified by Hickman et al. [64].

The $S_0 \rightarrow S_1 \ (\pi, \pi^*)$ absorption spectrum of toluene at room temperature has been well described [57,58]. It extends from about 270 nm to 240 nm featuring various dominant vibrational bands with the strongest transition for the (0,0)-band at 266.8 nm. Etzkorn et al. [65] determined this cross-section to be $1.3 \times 10^{-18} \text{ cm}^2$. At longer wavelengths the spectrum is less structured as a result of the densely-spaced energy levels in the excited state. The electronic transition strength is relatively weak due to symmetry reasons, though the (0,0)-transition is significantly stronger than in benzene because of the symmetry-breaking methyl group.

All of the aforementioned measurements were done at or below room temperature (except for one data set up to 423 K [58]). The motivation for this work therefore is to provide a database of absorption and fluorescence properties at conditions relevant to the conditions of the precombustion mixing process in devices like internal combustion engines. Three main objectives are important: firstly, to permit quantitative interpretation of toluene-LIF signals obtained in the aforementioned applications, secondly, to acquire a deeper understanding of the dominant photophysical processes in order to develop a semi-empirical model for LIF intensity as a function of external variables like pressure, temperature, and excitation wavelength (see chapter 5) and thirdly, to take advantage of the complex

dependence of toluene LIF on temperature and oxygen concentration in order to actually measure those quantities (see chapter 9).

4.2 Experimental

4.2.1 Shock-tube measurements

The temperature-dependent variation of toluene absorption spectra in the 240-290 nm range were measured using a deuterium lamp and kinetic spectrograph in shock-heated, argon-diluted toluene. These measurements where performed within a collaboration on toluene absorption from Jon Koch at the high temperature gas dynamics laboratory at Stanford University. Toluene (concentrations between 0.25% and 0.50% in argon) was shock-heated in a 15.24 cm diameter shock tube for 1 to 2 ms to pressures between 0.9 and 2.4 bar and temperatures between 600 and 1200 K. Absorption measurements were taken using a collimated deuterium lamp and a lumogen-coated (for UV-sensitivity) kinetic spectrograph with ~10 µs time-resolution and ~1 nm spectral-resolution (FWHM). The kinetic spectrograph measured transmitted light levels during the passage of the incident and reflected shock waves, as well as changes in transmission due to decomposition at high temperatures. Using the reference signal from the evacuated shock, and having confirmed the stability of the lamp, the fractional transmission could be calculated and averaged over the steady-state post-shock test time. The post-shock temperature and pressure were calculated from measurements of the initial test gas pressure and shock wave velocity using ideal one-dimensional shock equations. The temperature, pressure, toluene concentration, and fractional transmission were then used to calculate the absorption cross-section using the Beer-Lambert law.

4.2.2 Flow-cell measurements

Laser absorption and fluorescence experiments were conducted at atmospheric pressure between room temperature and 950 K in an optically accessible, stainless steel flow-cell placed in a Thermolyne 48000 furnace. The setup is depicted in Fig. 5. Nitrogen was percolated through two bottles of liquid toluene to produce a toluene-saturated gas. A thermocouple and a pressure gauge at the exit of the second bottle allowed for the calculation of the toluene concentration using the temperature-vapor pressure relation from Yaws [70]. A water bath surrounding the bottles maintained a constant toluene temperature and mitigated the effects of evaporative cooling.

Absorption cross-section and fluorescence measurements were confirmed to be independent of the applied gas flow rate (0.3 - 2.5 l/min) and served as a check for saturation. Toluene (0.2% - 2%) and oxygen (0 - 400 mbar) concentration were controlled with additional co-flows of pure nitrogen (1 - 8 l/min) and oxygen (1 - 8 l/min). The flow was preheated in a metal tube section before it entered the cell. A type K thermocouple in the center of the cell measured the gas temperature. Residence times were kept below 0.5 s to minimize the influence of pyrolysis. This was checked by varying the flow rate (i.e. the residence time) and confirming that absorption and fluorescence remained constant. Above 700 K the fluorescence signal in the presence of oxygen became dependent on the flow rate, and laser absorption was significantly reduced compared to the results with pure nitrogen, indicating the onset of chemical degradation of the tracer.



Fig. 5: Experimental setup of absorption and fluorescence measurements in a heated flow cell.

The cell (22.4 cm length, 1 cm diameter) was equipped with three sapphire windows to transmit the laser beam and detect the fluorescence at 90°. Laser light was provided at 248 nm by a Lambda-Physik Compex 102 krypton fluoride (KrF) excimer laser (30 ns pulse length, 5 Hz) and at 266 nm by a Spectra Physics GCR 300, quadrupled Nd:YAG (6 ns pulse length, 10 Hz). Incident energies were kept at about 0.1 mJ with beam diameters of about 2 mm, thus ensuring weak (linear) excitation. Quartz plates separated a part of the laser light to measure incident and transmitted energy by means of two photodiodes. A MgF-Rochon prism polarized the laser beam to ensure that the reflectivity of the quartz plate was constant for every pulse. Both photodiodes were thoroughly checked to respond linearly with laser energy. The signals were time-integrated and recorded by boxcar averagers (Stanford Research Systems model SR250) and a PC-based data acquisition system (LabView 6.0).

Absorption cross-sections σ_{abs} were calculated using Beer-Lambert's law. Toluene concentrations were varied to provide several data points from 30% to 90% total

absorption at each temperature thus minimizing uncertainty in the absolute toluene number density. 100 laser shots were averaged for each concentration.

The fluorescence signal was collected with an achromatic lens (f = 100 mm), spectrally resolved with an Acton Research Spectra Pro 150 mm spectrometer (300 lines/mm grating, blazed at 300 nm) and detected with a Princeton Instruments I-Max-512-T intensified CCD camera. Our spectral resolution was ~1 nm. This resolution allowed us to detect significant shifts in the shape of the emission spectrum that may be important for typical applications that collect broadband signals. It was not, however, sufficient to accurately record the fine structure of the emission spectrum. At each temperature, fluorescence was measured for several toluene concentrations and 100 laser shots were averaged for each concentration.

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

Before integrating, spectra were corrected for the relative response of the detection system in order to properly account for the red-shift in the emission spectrum with increasing *T*. This correction changed relative quantum yields by a few percent at high *T*. The relative spectral response of our detection system (maximum around 270 nm decreasing smoothly to ~50% at 400 nm) was determined by measuring the emission from an argon mini-arc plasma (NIST calibrated). More details on the relative spectral response can be found in [42].

The relative fluorescence quantum yield ϕ_{fl} at temperature *T* and excitation wavelength λ_{exc} was calculated as the ratio of the integrated LIF signal *S* per molecule per unit laser energy and the absorption cross-section σ_{abs} :

$$\phi^{rel}(\lambda_{exc},T) = \frac{S(\lambda_{exc},T)}{nE} \frac{1}{\sigma_{abs}(\lambda_{exc},T)},$$
(4-1)

with *n* being the toluene number density and *E* the (relative) laser energy. In general, *S* also depends on the total pressure *p* even though total pressure was kept constant at 1 bar in the presented work. A considerable source of uncertainty in our experiments was the toluene number density as we calculated it based on the vapor pressure and did not measure it directly. To minimize this uncertainty we performed measurements with various concentrations for each temperature. The slope of a fit through zero from the energy-corrected signal vs. tracer concentration (i.e. the signal

per tracer number density) as illustrated in Fig. 6 was the used to calculate the fluorescence yield:

$$\phi^{rel}(\lambda_{exc},T) = \frac{d(S(\lambda_{exc},T)/E)}{dn} \frac{1}{\sigma_{abs}(\lambda_{exc},T)}$$
(4-2)

Incident laser energy was corrected for fractional absorption of the laser light through one half of the cell (2 - 20%).



Fig. 6: Integrated fluorescence signal, corrected for incident laser energy, vs. toluene number density, 248 nm excitation, 296 K.

Results from the absorption measurements in shock-heated toluene were used to estimate signal absorption that may become important at elevated temperatures. Toluene concentrations were then chosen to keep absorption at 280 nm (emission maximum) below 1%, so no further correction of the detected signal was necessary.

4.3 Absorption

4.3.1 Absorption spectrum

The spectrally-resolved absorption in shock-heated toluene in the 240 - 290 nm range is displayed in Fig. 7 together with data from the literature.

Room-temperature measurements were also made within the shock-tube setup and compared to the spectrum published by Burton and Noyes [58]. Although our spectral

resolution was limited, the same structure was evident, and values of the crosssection in the weakly structured blue region of the spectrum agreed well.



Fig. 7: Solid lines: absorption spectra, this work (shock tube); dotted line: room temperature spectrum from [58]; • 850 K, \blacksquare 1200 K from [71]; vertical lines illustrate the laser wavelengths used in the flow-cell experiments.

At the lowest accessible temperatures in our shock tube experiments (~600 K) the fine structure is no longer evident. The spectrum becomes a broadband continuum with a maximum at 261 nm ($\sigma_{abs} = 5.6 \times 10^{-19} \text{ cm}^2$) and a FWHM of ~20 nm. Due to the thermal population of vibrationally-excited ground state levels, absorption on the red side of the (0,0) band becomes energetically possible and broadens the absorption feature. At 1100 K the absorption cross-section at 300 nm increases to $1.0 \times 10^{-19} \text{ cm}^2$ from <1×10⁻²⁰ cm² at room temperature and the FWHM increases to ~40 nm. The absorption maximum also shifts with temperature and is found at ~268 nm at 1125 K.

On the blue side of the feature the stronger (symmetry allowed) $S_0 \rightarrow S_2$ transition centered at ~200 nm [72] shows a very pronounced increase with temperature and overlaps with the $S_0 \rightarrow S_1$ transition [73].

Our results can be compared to two other publications [71,74]. The work by Hippler et al. focused on the $S_0 \rightarrow S_2$ transition but additionally published absorption cross-section data at 280 nm. The agreement is within 10% for the high-temperature measurement (with an 80 K temperature difference between our measurements and the Hippler data). The spectra published by Richardson et al. (not shown in Fig. 7) show similar relative behavior, i.e. loss in structure and the red-shift with increasing temperature. However, their absolute numbers are lower at all temperatures by ~30%.

4.3.2 Absorption at 248 nm and 266 nm

The low-temperature absorption spectra contain fine structure that is not fully resolved with our spectrometer setup. Absorption of laser light may show a strong variation with temperature due to the broadening of the structure, e.g. the laser line at 266 nm is located in the valley next to the peak at 266.8 nm that is observed in the room-temperature spectra, as can be seen in Fig. 7. Therefore, we measured the absorption cross-sections in the intermediate temperature-range in the flow cell (300 - 950 K) with laser radiation at 248 and 266 nm in order to generate data relevant for laser diagnostics experiments. Results of these measurements are shown in Fig. 8 and Fig. 9 along with data from the literature.



Fig. 8: Toluene absorption cross-section at 248 nm as a function of temperature. ■ this work, flow cell; □ this work, shock tube; + from [74]; × from [58].

Absorption at 248 nm is fairly independent of temperature up to 950 K. The cell data agrees very well with our shock-tube measurements in the temperature range accessible to both experiments. Agreement with literature data, that is the room temperature measurement of Burton and Noyes and the shock tube data from Richardson et al., is evident. For all further calculations, the absorption cross-section of toluene at 248 nm is assumed to be $3.1 \pm 0.2 \times 10^{-19}$ cm² for 300 – 950 K. The steep increase in absorption at temperatures above 1000 K corresponds to the strong increase of the red side of the S₂ absorption feature.

Absorption at 266 nm increases linearly from 300 - 550 K by a total factor of 2.5. Above 550 K, the increase continues more slowly. At room temperature, 266-nm absorption occurs in the valley between two dominant vibrational bands (cf. Fig. 7). Broadening of the bands initially leads to a quick rise of absorption with increasing *T*. At ~600 K the fine structure is completely lost and the remaining increase in absorption is due to the overall rise of the S_1 absorption feature.



Fig. 9: Toluene absorption cross-sections at 266 nm as a function of temperature. \blacksquare this work, flow cell; \Box this work, shock tube; + from [74]; × from [58].

In the temperature range where flow-cell and shock-tube measurements overlap, results show the same relative trend, but absolute numbers for the latter are about 15% lower. The precision of the cell experiments is about ± 7 %. Major contributions to the error result from the uncertainty of the toluene concentration in the cell or, at the high toluene concentrations, from the low transmitted signal intensity. Precision of the shock-tube data is about ± 10 %. The difference in absolute values may also be a result of the different spectral resolution. However, the different data sets are still within experimental error. As mentioned above. values obtained from Richardson et al. are significantly lower, whereas the room temperature value from Burton and Noyes is well reproduced by our cell measurements. For all further calculations we used the values from the cell measurement.

4.4 LIF in nitrogen bath gas

4.4.1 Fluorescence Spectrum

Fluorescence was investigated in a bath of nitrogen at total pressures of 1 bar. Fig. 10 displays the temperature dependence of the toluene fluorescence spectrum following 248-nm excitation. The total fluorescence decreases rapidly with temperature (see below), so the spectra are normalized to compare the shape.

Emission (at room temperature) extends from roughly 260 nm to 400 nm with a maximum around 280 nm. With increasing temperature a slight shift of the fluorescence maximum of roughly 2 nm per 100 K to the red is observed. The tail on the red side of the spectrum becomes stronger relative to the peak emission.



Fig. 10: Normalized fluorescence spectra; 5 mbar toluene in nitrogen, 248 nm excitation, 1 bar total pressure.

The room-temperature emission spectrum probably possesses more structure than was resolved with our setup. Evidence for this can be seen at low pressures (e.g. [58]). In the same reference it is reported, that the addition of hexane results in even sharper spectra (due to vibrational relaxation). However, since applications with toluene as a tracer molecule typically use broadband filters (e.g., a long-pass filter), knowledge of the fine structure is not critical to this work. The structure that can be seen on the 750 K and 925 K spectra is noise due to the low signal intensities at these temperatures.

Spectra at room-temperature have identical shape for 266 nm and 248 nm excitation. The red-shift for the latter is slightly more pronounced.

4.4.2 Fluorescence Quantum Yield

Fluorescence was confirmed to increase linearly with toluene concentration within the range covered by our experiment. The seeding at room temperature restricted us to a maximum concentration of 30 mbar. Measurements at higher concentrations may be desirable to thoroughly investigate the potential effect of self-quenching, especially at higher temperatures, where absorption and fluorescence spectra overlap to a greater extent.



Fig. 11: Toluene fluorescence quantum yield: ■ 266 nm excitation, 5-20 mbar toluene in 1 bar nitrogen; straight line: Exponential best-fit; × from [58] 266.8 nm excitation, 23 mbar pure toluene.

Details on the calculation of the fluorescence quantum yields are described in the experimental section. Dependence of ϕ_{fl} on temperature after excitation at 266 nm normalized to room temperature is shown in Fig. 11. It decreases exponentially by three orders of magnitude within our 600 K temperature range. The single exponential best-fit is given by:

$$\frac{\phi_{ff}(T)}{\phi_{ff}(296\,\mathrm{K})}\Big|_{266\,\mathrm{nm}} = 22.5 \times \exp(-0.0105 \times T) \tag{4-3}$$

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

A decrease in the fluorescence yield with temperature is expected since ϕ_{fl} is known to decrease with increasing vibrational excitation [58,67]. Raising the temperature increases the vibrational energy of the ground state and thus also increases vibrational energy of the S₁ state for a fixed excitation wavelength. We estimated the expected loss in signal due to this effect by calculating the relative level populations (thereby assuming a Boltzman distribution and using the level density from [67]) and using the quantum yield data from [58,67] that was obtained at room temperature but for different excitation wavelength. We found that this approach is not sufficient to explain the steep signal fall-off at increasing *T*. Additional lifetime measurements are thus desirable in order to investigate the kinetics of the excited electronic state more thoroughly. For now, we can only conclude that changes in vibrational excitation in

thermal equilibrium do not seem to justify the magnitude of the temperaturedependent decrease seen in Fig. 11.

Fig. 11 also shows the data from Burton and Noyes, whose measurements were performed at lower pressures (~20 mbar pure toluene). Within the overlapping temperature range, no effect of our additional 1 bar nitrogen is observable, and both series show the same temperature dependence.

The results for 248-nm excitation are shown in Fig. 12. The dependence of the fluorescence yield on temperature can be described by a double-exponential function:

$$\frac{\phi_{ff}(T)}{\phi_{ff}(296 \text{ K})}\Big|_{248 \text{ nm}} = 171 \times \exp(-0.0175 \times T) + 0.337 \times \exp(-0.0068 \times T)$$
(4-4)

with *T* in K, valid for 300 - 950 K and 1 bar nitrogen bath gas. The initial decrease at 300 - 500 K is steeper than that found for 266-nm excitation. The signal decreases more slowly at higher temperatures. The total variation in fluorescence quantum yield within the 600 K interval exceeds by three orders of magnitude.



Fig. 12: Toluene fluorescence quantum yield: ■ 248-nm excitation, 5-20 mbar toluene in 1 bar nitrogen; solid line: Double-exponential best-fit; × from [58] 250-nm excitation, 23 mbar pure toluene.

The absolute fluorescence quantum yield for 248-nm excitation in 1 bar of nitrogen can only be estimated. Burton and Noyes [58] give a value of 0.09 for low total pressures (23 mbar). But little research has been done on the pressure-dependence of the quantum yield. Our own (unpublished) measurements suggest that the quantum yield increases with N₂ pressure; thus, at 1 bar it may be somewhere between 0.1 and 0.3. Experiments are currently under way to study the pressure-dependence of toluene fluorescence quantum yield in more detail. Fig. **12** also shows results from Burton and Noyes at a similar wavelength but at lower pressures

(23 mbar) than our experiments. Apparently, the difference in total pressure (i.e. vibrational relaxation) has no observable effect on the *relative* temperature dependence between 300 K and 450 K.

Precision of the results is about $\pm 10\%$ resulting from uncertainties in the correction for laser absorption and the calculation of toluene concentration. Accuracy may be somewhat limited by the measured absorption cross-sections.

4.5 Oxygen quenching

4.5.1 Background

Quenching of the fluorescence from aromatic molecules by molecular oxygen is a well-known phenomenon (e.g. [52]). For toluene this behavior was first published by Burton and Noyes [58] for 266.8 nm excitation at room-temperature. They found that the inverse fluorescence signal increases linearly with the oxygen number density (Stern-Volmer behavior) and calculated a quenching efficiency of approximately unity, i.e. almost every (hard-sphere) gas-kinetic collision leads to electronic deexcitation.

Reboux et al. [8] suggested the use of toluene LIF to measure fuel/air ratios in the compression stroke of IC engines. While the LIF signal from acetone, 3-pentanone and biacetyl [75] are relatively immune to quenching and thus are commonly used to represent the fuel distribution, toluene fluorescence is additionally sensitive to oxygen. It thus offers the potential to directly assess the fuel/air ratio Φ . The concept suggested by Reboux et al. is intriguing and simple: when oxygen quenching is the dominant de-excitation pathway and intra-molecular de-excitation can be neglected, the signal from an excited molecular state is proportional to the tracer number density and inversely proportional to the oxygen number density, i.e. proportional to Φ . They found this to be true for toluene at air pressures above 3 bar for room temperature and 248-nm excitation. This concept is known in the literature as FAR-LIF (Fuel-Air Ratio LIF) [76]. The same concept has been applied to other tracer molecules like benzene [33] and THT [77].

Until now, the toluene LIF-signal behavior at elevated temperatures was not quantified. It was assumed that the concept of oxygen quenching as the dominant de-excitation process and the resulting proportionality of signal and fuel/air ratio can be adapted for all pressures and temperatures within the compression stroke of IC engines. However, as shown in section 4.4, the non-radiative, intra-molecular decay

rates feature a strong dependence on temperature *T*, most noticeable in the rate for internal conversion (i.e. radiation-less transition to the ground state), which is known in the literature as the "third-decay-channel" [67,78] – but also possibly in the rates of fluorescence and intersystem crossing (i.e. transition to the triplet state). The collision rate *Z*, in turn, is only a weak function of temperature ($Z \propto \sqrt{T}$) because density and velocity have opposite effects. It will be shown in this work that these combined effects lead to a breakdown of the FARLIF-concept under many practical conditions.

4.5.2 Fluorescence spectra

For 248 nm, the normalized spectrum initially shifts to the red with increasing oxygen partial pressure, an indication that some of the transitions that contribute to the longer wavelengths in the emission spectrum experience a weaker relative quenching effect (smaller Stern-Volmer factor). This red-shift has been found at all temperatures under study but is limited to relatively low oxygen partial pressures. Above ~200 mbar O_2 , no change in the spectrum could be observed with further increasing oxygen partial pressures (c.f. Fig. 13).



Fig. 13: Toluene-LIF spectra with 248-nm excitation at room temperature for different oxygen partial pressures. The spectra are corrected for instrumental spectral response.

Similar behavior is found at all investigated temperatures with the strongest effects at room temperature. An increase in temperature also results in a red-shifted spectrum (see section 4.4.1). Thus, when varying both temperature and oxygen number density, the two effects overlap.

In a room-temperature, nitrogen bath gas, the spectral shape of the emission is identical for 248- and 266-nm excitation. However, for 266-nm excitation, no change

in spectral shape due to added oxygen could be observed within the investigated range of conditions.

4.5.3 Integrated signals, excitation at 266 nm

The dependence of the total (integrated) toluene-LIF signal on the oxygen number density is shown in Fig. 14 for selected temperatures. At room temperature it shows a Stern-Volmer behavior. The Stern-Volmer factor is determined for $p_{O_2} = 0 - 350$ mbar, $p_{total} = 1$ bar as:

$$k_{SV}^{O_2}(296 \text{ K}) = 1.39 \times 10^{-23} \text{ m}^3 = 340 \text{ bar}^{-1}$$
 (4-5)

This is within experimental error of the value published by Burton et al. [58] who found a Stern-Volmer factor of 1.65×10^{-23} m³ (402 bar⁻¹). Their measurements are conducted for a toluene / oxygen mixture with up to 90 mbar oxygen.



Fig. 14: Stern-Volmer plots for selected temperatures, 266-nm excitation. Maximum oxygen partial pressure is 350 mbar for all T. The slope (e.g. k_{SV}) decreases strongly with increasing temperature (left). At elevated temperatures a systematic deviation from linearity can be observed (right). This behavior can be observed above ~500 K. It indicates the increasing relevance of a state that features fast internal conversion (see text). Error bars of 5% result from the variation of repeated measurements.

With increasing temperature the slope of the Stern-Volmer plot, k_{SV} , decreases dramatically (c.f. Fig. 14). As k_{SV} is the ratio of $\tilde{k}_q^{O_2}$ and k_{tot} , this can be caused by a decreasing quenching rate coefficient $\tilde{k}_q^{O_2}$ and/or by an increasing intramolecular deactivation rate k_{tot} ($k_{SV}^{O_2} = \tilde{k}_q^{O_2} / k_{tot} = \tilde{k}_q^{O_2} / (k_{fl} + k_{nr})$). In 4.4 it has been found that toluene's fluorescence quantum yield in nitrogen ($\phi_{fl}^{N_2} = k_{fl} / k_{tot} = k_{fl} / (k_{fl} + k_{nr})$) also

decreases strongly with T. Thus, from the ratio of these quantities we can learn about the T-dependence of the quenching and the radiative rate:

$$\frac{k_{SV}^{O_2}(T)}{\phi_{fl}^{N_2}(T)} = \frac{\widetilde{k}_q^{O_2}}{k_{fl}}(T) = \frac{e\widetilde{k}_{coll}}{k_{fl}}$$
(4-6)

The results of this calculation are displayed in Fig. 15.



Fig. 15: Temperature-dependence of the ratio of quenching rate and radiative rate, calculated according to Eq. 4-6. The ratio and thus likely the quenching efficiency and the radiative rate themselves feature a moderate dependence on T. Data normalized to room temperature.

The weak *T*-dependence for temperatures below 500 K can be explained with the *T*-dependence of the collision rate coefficient $\tilde{k}_{coll}^{O_2}$. Although the effect of temperature can not be evaluated separately for the radiative and the quenching rate, the fact that the ratio is approximately constant suggests that both parameters do not depend strongly on *T*. We thus infer that the dominant *T*-dependence underlying the decrease of k_{SV} and $\phi_{fl}^{N_2}$ with increasing *T* is a strong increase of the intramolecular non-radiative decay rate k_{nr} (e.g. intersystem crossing).

The deviation from linearity in the Stern-Volmer plots (Fig. 14) at higher temperatures will be discussed in detail in the following section.

4.5.4 Integrated signals, excitation at 248 nm

The results for 248-nm excitation are surprising (Fig. 16). Overall, the relative strength of quenching decreases with increasing temperature as is the case for 266-nm excitation. However, the dependence of the toluene-LIF signal on oxygen pressure does not show a Stern-Volmer behavior even at room temperature. Since

this behavior strictly applies only to a single vibrational state (or to a group of states with similar behavior), it can be hypothesized that vibrational states with significantly different $k_{\rm fl}$, $\tilde{k}_a^{O_2}$ and/or $k_{\rm nr}$ contribute to the emission process.



Fig. 16: Stern-Volmer plots for selected temperatures with 248-nm excitation. The graphs are clearly non-linear at all temperatures. This shows that a more comprehensive model than a simple Stern-Volmer plot is required for the discussion of toluene LIF.

This effect becomes more important with increasing vibrational excitation in the S_1 state and hence, the deviation of the Stern-Volmer plot from linearity increases with increasing temperature and with decreasing excitation wavelength. In chapter 5 a model will be presented to describe the experimental data and to predict signal strengths for higher oxygen concentrations.

5 Photophysical model for toluene laser-induced fluorescence

The model presented below is a compromise between a complete representation of the physical processes involved in toluene LIF and a simple numerical fit to the presented experimental data. Although it does not attempt to characterize the statespecific behavior of excited toluene, this model allows the prediction of toluene LIF at oxygen pressures that are relevant for IC engine applications.

In chapter 8 the breakdown of the FARLIF concept and implications for combustion diagnostics are discussed based on this model.

5.1 Interpretation of results and the underlying photophysical processes

The slope of the Stern-Volmer (SV) plot, k_{SV} , indicates the strength of oxygen quenching *relative* to intramolecular decay. As temperature increases, k_{SV} decreases, and from Fig. 15 it can be concluded that this is mainly caused by an increasing intramolecular decay rate with increasing temperature, probably dominated by intersystem crossing (ISC) as determined by measurements of triplet yields [58].

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

Evidence for simultaneous emission from states with significantly different SV factors is found in several publications [67,78-83]. Jacon et al. [67] found biexponential fluorescence decay in toluene at room temperature for excitation wavelengths shorter than 250 nm. The long-lived component was similar to those measured at lower energies, probably dominated by ISC. The short-lived component indicates a "third-

decay-channel" (in addition to fluorescence and intersystem crossing) with a significant energy threshold. Such a decay channel has been documented for many aromatic compounds [78-81,83] and has commonly been assigned to internal conversion (IC), the radiationless transition to the S_0 state. At high vibrational excitation, decay from this channel can become extremely fast; Farmara et al. [82] reported a lifetime of 4 ps for 202 nm excitation. Further complexity occurs because IC does not seem to have a fixed energy threshold but a threshold that depends on the vibrational modes involved¹ [67,68]. Without going into the details of which modes are most responsible for the decay processes, we simply name two types of states in terms of their non-radiative intramolecular deactivation pathways: 1) the short-lived, least-oxygen-sensitive states noted heretofore as IC, and 2) states with a longer lifetime, and thus more oxygen-sensitive, hereby labeled ISC.

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

In addition to direct absorption, states may be populated via Intramolecular Vibrational Redistribution or Randomization (IVR), i.e. a "horizontal" intramolecular process that redistributes vibrational energy from selectively excited vibrational states to an ensemble of vibrational states within the same electronic state and similar vibrational energy. In a review of excited state dynamics, Smalley [68] indicates that the onset of IC in aromatics coincides with the onset of rapid IVR. IVR rates depend on both the density of states and the nature of the coupling between the optically populated modes and the "dark" modes into which some of the excess vibrational energy flows (e.g. methyl-rotors and rotational Coriolis coupling have been suggested as especially efficient promoters of IVR in some cases [84,85]). In general, IVR rates increase with the density of states and the degree of energy localization within the molecule. Hence, IVR may occur rapidly if only a few modes are optically active or highly excited but more slowly once the energy is dissipated to the other vibrational modes of the molecule.

Regardless of whether the combination of temperature and excitation wavelength leads to a population of the "IC-states" through direct absorption or rapid IVR (probably both occur), the population of the excited state is effectively divided into states with rapid IC and states without IC (that decay through the slower ISC-

¹ As a simple example, IC may be "triggered" when two vibrational quanta are in v_x with a total energy of 600 cm⁻¹ but will not be triggered if 3 vibrational quanta are in v_y with a total energy of 900 cm⁻¹. Thus, while IC rates tend to increase with energy, it also depends on the mode in which the energy is stored.

channel), The fluorescence is then the combined signal from states with two different lifetimes and two different sensitivities to oxygen quenching (SV factors); the fraction of the population within each type of state depends on temperature and excitation wavelength.

The modeled energy-transfer processes are depicted in Fig. 17. Fluorescence and oxygen quenching-rate constants are assumed to be constant. At low excitation energies, the SV factor is determined primarily by the temperature dependent ISC rate. For these conditions, the fluorescence behavior as mapped on a SV plot is still linear. At high energies, however, fluorescence occurs from some states with IC. Because of their short effective lifetimes, emission from these states is less sensitive to oxygen. Thus, the SV plot combines two processes with different SV factors and the graph is no longer linear. The deviation from linearity increases when these short-lived states receive a larger fraction of the excited population with increasing vibrational energy. The model determines the fraction of molecules that goes into each type of state.



Fig. 17: Simple photophysical scheme of the important decay processes for toluene LIF. Intersystem crossing (ISC) and fluorescence are the dominant non-collisional processes for low vibrational excitation. Internal conversion (IC) becomes important for selected states at higher energies. ISC and IC states may be populated either directly via absorption or via intramolecular vibrational redistribution (IVR) following absorption. The model yields values for the fraction of the population that goes to each kind of state; it does not differentiate between direct population and IVR. For details refer to the text.

Since almost every collision with oxygen leads directly to electronic de-activation [58] (oxygen quenching involves a charge-transfer complex and results in either triplet or ground-state toluene) while collisions with nitrogen are not likely to change the electronic state, it is a reasonable approximation to regard oxygen as the only important colliding species and the effect of collisional relaxation and total pressure small in comparison.

5.2 Model description

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

We consider fluorescence from two types of vibrational states within the electronically-excited state, distinguished by their Stern-Volmer factor, to represent states with ISC (1) and with IC (2) occurring. The total signal then is the sum of the signal emitted from the two types (Eq. 11).

$$S(T, n_{O_2}) \sim \sigma_{abs}(T) \phi_{ff}(T, n_{O_2}) \sim \sigma_{abs}(T) \left(\frac{A_1(\lambda_{exc}, T)}{1 + k_{SV,1}(T) n_{O_2}} + \frac{A_2(\lambda_{exc}, T)}{1 + k_{SV,2}(T) n_{O_2}} \right)$$
(5-1)

Fit parameters are the temperature-dependence of $k_{SV,i}(T)$ and the (temperatureand excitation-wavelength-dependent) relative contribution of each type of state (i.e. A_1 and A_2). A_i is the product of the relative population a_i and the fluorescence quantum yield $\phi_{fl,i}^{N_2}$ of the respective state in pure nitrogen as bath gas. In the limit of zero quencher concentration, Eq. 5-1 must agree with the data in nitrogen from section 4.4. This is ensured by:

$$A_{1}(T) + A_{2}(T) = \phi_{f}^{N_{2}}(T)$$
(5-2)

As the oxygen concentration influences the quantum yield only, this section focuses on the quantum yield. The absorption cross-section is also *T*-dependent (see section 4.4) and has to be included when discussing implications on combustion diagnostics in chapter 8.

5.3 Comparison with experimental data

Experimental data together with the fits from the model for both excitation wavelengths are shown in Fig. 18. The model can consistently quantify the fluorescence behavior; data and model agree within 10% for all conditions. For all temperatures the data are normalized to the quantum yield in pure nitrogen (section 4.4).



Fig. 18: Comparison of the modeled (lines) with experimental (symbols) fluorescence quantum yields, normalized to T = 296 K and $n_{oxy} = 0$. The total signal intensity would be the product of quantum yield and absorption cross-section (c.f. chapter 8).

In this section we focus on the variation of the *quantum yield*. The *total toluene*–*LIF signal* additionally varies due to the *T*-dependence of the absorption cross-section. The best-fit parameters are (T in K):

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

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

$$A_{2}^{266nm} = \frac{1}{0.0241T^{2} - 25.12T + 7029}$$

$$A_{2}^{248nm} = \frac{1}{0.0371T^{2} - 3.012T + 691.5}$$
(5-3)

with $A_1(T) = \phi_{fl}^{N_2}(T) - A_2(T)$ and $\phi_{fl}^{N_2}(T)$ from section 4.4:

$$\frac{\phi_{f1}^{N_2}(T)}{\phi_{f1}^{N_2}(296 \text{ K})}\Big|_{266nm} = 22.5 \exp(-0.0105 T)$$
$$\frac{\phi_{f1}^{N_2}(T)}{\phi_{f1}^{N_2}(296 \text{ K})}\Big|_{248nm} = 171 \exp(-0.0175 T) + 0.337 \exp(-0.0068 T)$$

Absolute values of the fluorescence yield can also be calculated or estimated from these equations by calibrating the above equations to the low-pressure measurements of Burton [58]. For 266.8 nm, room temperature, $\phi_{fl} = 0.30$ and for 248 nm, room temperature, $\phi_{fl} = 0.09$ [58].

As motivated above, the importance of the IVR+IC channel increases with increasing temperature. The rate for ISC also increases with temperature, interpreted as a relaxing of the spin selection rule. Additional lifetime measurements of toluene at elevated temperatures are highly desirable to better interpret the underlying

processes, to determine decay rates more precisely, and to improve predictions from the model.

Not included in the fitting procedure is the data published by Reboux et al. [8]. In Fig. 19 we compare their data with the predictions from our model. Excitation wavelength is 248 nm. Results agree within 15%.



Fig. 19: Comparison of experimental data from Reboux et al. [8] (symbols) with model predictions (lines) for the slope of LIF signal vs. Φ for various total air pressures. The model predicts adequately the experimental results. It can also be seen that whereas at room-temperature the LIF signal becomes proportional to Φ above \approx 3 bar (i.e. a horizontal line in this representation), this approximation breaks down at higher temperatures. Data is normalized at 8 bar.

Experimental data is published as the slope of LIF signal vs. Φ , the fuel / air ratio, at various total pressures of air. When this slope becomes independent of total pressure, the FARLIF approximation (see section 2.4) is fulfilled and the signal is proportional to Φ . Experimental data is available only for room temperature. We show it along with predictions for higher temperatures. We confirm the finding of Reboux et al. [8] that the toluene-LIF signal is proportional to Φ above ~ 3 bar at room temperature. At higher *T*, however, this proportionality is incorrect. The consequences of this finding for fuel/air ratio measurements are discussed in chapter 8.

6 Experimental investigation of 3-pentanone and acetone LIF

Despite the rather large database on the fluorescence properties of acetone and 3pentanone, a couple of open questions remain.

During this work, absolute fluorescence quantum yields $\phi_{\rm fl}$ of acetone and 3pentanone as a pure gas and with nitrogen diluent were measured at room temperature at 20, 507, and 1013 mbar using 248, 266, and 308-nm excitation by calibrating the optical collection system with Rayleigh scattering from nitrogen. On top of the fundamental insight, the data is valuable for the improvement of the photophysical model for ketones discussed in section 0. It enables to compare on an absolute scale data sets obtained with different excitation wavelength. This work was done in collaboration with Jon Koch and Prof. Ron Hanson during a recent visit at Stanford University.

Our directly-measured values for the fluorescence quantum yield are significantly lower than earlier ones found in the literature that were based on a chain of relative measurements. Therefore, an extensive review on the literature of $\phi_{\rm fl}$ measurements of acetone and 3-pentanone will be given. The experimental technique of calibrating the experimental system using Rayleigh scattering is novel in this context and will be presented in detail. Results will be employed to improve the photophysical model for acetone.

6.1 Absolute fluorescence quantum yield measurements

6.1.1 Literature review

The absolute fluorescence quantum yield of gaseous acetone has previously been published by two sources: Heicklen [86] and Halpern [87]. For 3-pentanone, only Hansen and Lee [48] have published absolute values, but these measurements were

made relative to acetone using Heicklen's value as a calibration standard. Thus the sources of the acetone data will be reviewed in greater depth.

Each of the two published works on acetone is a measurement of $\phi_{\rm fl}$ relative to another published fluorescence yield measurement. Fig. 20 is a diagram showing the chain of relative measurements for each source, ending with a published value of $\phi_{\rm fl}$ for acetone when excited at 313 nm.



Fig. 20: Diagram of relative measurements leading to two published values of acetone fluorescence quantum yield. Each author measured the behavior of a species using the species of the previous work as a fluorescence standard.

Despite the fairly similar conditions, the two values differ by almost a factor of two. One might hypothesize that the differences in temperature and pressure in the two measurements could impact the fluorescence yield significantly; however, the fluorescence yield model developed by Thurber [25] indicates that this would not be the case. Furthermore, according to the model, Halpern should have measured a slightly higher value of ϕ_{fl} than Heicklen. Obviously, with consecutive relative measurements, there arises the concern for propagation of systematic errors from one experiment to the next. Little is said by either source about experimental uncertainties. Given the age of the work, we can only speculate into possible sources of error in each chain of measurements based on the published information. For example, Heicklen's calibration measurements for biacetyl were at a different temperature than when Almy [90] made an absolute measurement; Heicklen also noted that acetone data obtained by comparison to biacetyl is approximate. Similarly, Halpern used a different biacetyl pressure compared to that of his reference, Gandini [88]. The Gandini work measured the gas-phase properties of biacetyl relative to liquid quinine sulfate with a published uncertainty of ±10%, and the absolute fluorescence yield of quinine sulfate was measured by Eastman [89] with an estimated uncertainty of at least 6%. An accurate value of the fluorescence quantum yield for both acetone and 3-pentanone thus remains an open question. Our new, more direct measurements may help resolve the disagreement in the published data.

6.1.2 Experimental

Measurement strategy

Rather than calibrate the optical system against another fluorescent species whose fluorescence yield may also be uncertain, we chose to utilize Rayleigh scattering as a standard. Rayleigh scattering has been successfully used previously as a means of absolute calibration for LIF concentration measurements of radical species [91-94]. Since our application is somewhat different, however, we will present the relevant equations below to thoroughly explain our methods.

For this application, the collected LIF signal from a laser-illuminated volume of a gas with broadband absorption and fluorescence (like the ketones), in the limit of weak excitation, can be predicted by the following form of the fluorescence equation:

$$S_{fl} = \frac{I_{laser}A}{h_V} n_{abs} I \sigma_{abs} \phi_{fl} \frac{\Omega}{4\pi} R_{fl}$$
(6-1)

where

fluorescence signal (integrated over the fluorescence wavelength region) [V] S_{fl}: laser fluence passing through the illuminated volume [J/cm²] I_{laser}: area of the probed volume (orthogonal to direction of laser propagation) $[cm^{2}]$ A: Planck's constant times frequency of laser (or laser energy per photon) [J] hv. number density of absorbing species [cm⁻³] n_{abs}: length of absorbing medium (in direction of laser propagation) [cm] 1: absorption cross-section of absorbing molecule [cm²] σ_{abs} : fluorescence quantum yield $\phi_{\rm fl}$: $\Omega/4\pi$: fraction of solid angle collected by lens/detector spectral responsivity of the optics and detector system averaged over the R_{fl}: collected wavelength region [V/photon].

The number of excited molecules is equal to the number of laser photons entering the probed volume, $I_{laser}A/h_V$ times the fraction of the photons absorbed by the targeted species, n_{abs}/σ_{abs} . The number of fluorescence photons emitted is equal to the number of excited molecules times the probability of fluorescence emission, ϕ_{fl} . Assuming these photons emit isotropically into 4π steradians and are not subsequently absorbed, a fraction of them are collected by a lens ($\Omega / 4\pi$), focused, converted into photoelectrons and finally into a digitized voltage. The average spectral responsivity, R_{fl} reflects the net efficiency of this conversion process; it includes the transmissivity of the optics, the quantum efficiency of the photocathode, and the gain of the intensifier or other electronics. While the fluorescence quantum yield is the key property in this paper, quantities like the collection solid angle and the overall responsivity in the above equation are often difficult to specify, measure, or control during the course of an experiment. Hence, experiments to measure $\phi_{\rm fl}$ are often performed on a relative scale where only one quantity is varied or the change in multiple properties is well-known (e.g., when the fluorescent tracer is changed and the absorption cross-section and number density are altered). Absolute measurements of $\phi_{\rm fl}$ were performed by Almy in 1943 [90] for biacetyl and by Eastman [89] in 1967 for quinine sulfate. Since then, experiments measuring the change in the fluorescence signal due to changing wavelength and tracer have been used to find $\phi_{\rm fl}$ of the ketones.

The Rayleigh signal, if collected orthogonal to the laser's plane of polarization (the plane formed by the oscillating electric field vector and the direction of laser propagation), can be calculated from the following.

$$S_{Ray} = \frac{I_{laser}A}{h\nu} n I \frac{d\sigma}{d\Omega}\Big|_{90^{\circ}} \Omega R_{Ray}$$
(6-2)

where most of the terms are defined similarly to those in Eq. 6-1. Here, the differential Rayleigh cross section, $d\sigma/d\Omega|_{90^{\circ}}$ (cross section per unit solid angle), evaluated orthogonal to the plane of incident polarization, is calculated from classical theory based on a widely-spaced group of oscillating dipoles, and the signal is collected over a small solid angle, Ω . The spectral responsivity of the collection and detection system, R_{Ray} , is evaluated at the laser wavelength, rather than at the fluorescence wavelengths as in Eq. 6-1.

A thorough review of the theory behind Rayleigh scattering is provided by Miles et al. [95]. In short, the differential Rayleigh cross-section can be described by Eq. 6-3.

$$\frac{d\sigma}{d\Omega}\Big|_{90^{\circ}} = \frac{4\pi^2}{\lambda^4} \left(\frac{3+7F_{\kappa}}{10}\right) \left(\frac{\widetilde{n}-1}{n}\right)^2$$
(6-3)

 λ is the wavelength, $F_{\rm K}$ is the King factor, \tilde{n} is the index of refraction at the wavelength in question (\tilde{n} must be close to 1 for this form of Eq. 6-3), and *n* is the number density of the scattering molecule. The King factor term quantifies the anisotropic behavior of the scattering molecule and generally increases the cross-section by a few percent. For nitrogen, the King factor is [96]:

$$F_{\kappa} = 1.034 + \frac{3.17 \times 10^{-12}}{\lambda^2}$$
(6-4)

The ratio of $\tilde{n}-1$ to *n* is proportional to the polarizibility of the molecule (in accordance with the Lorentz-Lorenz equation) and is thus an intrinsic property of the molecule in question. Hence, the index and the number density need only be

evaluated at a single temperature and pressure in order to be applied to our experiments. The index of refraction at 0 °C and 1.013 bar is calculated by a fit to data from Griesmann [97],²⁵ which incorporates the effects of electronic resonances in the deep UV in addition to the typical λ^4 behavior:

$$\widetilde{n} - 1 = \frac{1.966}{22086 - (1000/\lambda)^2} + \frac{0.02745}{133.86 - (1000/\lambda)^2}$$
(6-5)

For both equations 6-4 and 6-5 the units of λ are nm.

If the same experimental setup is used to measure Rayleigh signals from nitrogen and LIF signals from ketones, equations 6-1 and 6-2 can be ratioed, canceling several parameters that appear in both equations, to give eq. 6-6.

$$\frac{S_{ff}}{S_{Ray}} = \phi_{ff} \frac{n_{ketone}}{n_{N_2}} \frac{\sigma_{abs}}{d\sigma/d\Omega|_{90^{\circ}} 4\pi} \frac{I_{laser}^{ff}}{I_{laser}^{Ray}} \frac{RSR_{ff}}{RSR_{Ray}}$$
(6-6)

Here, the spectral responsivities from equations 6-1 and 6-2, have been replaced by the relative spectral response, *RSR*, a more easily-measured quantity defined relative to the peak responsivity of the detection system:

$$RSR(\lambda) = R(\lambda) / R_{max}$$
(6-7)

where R_{max} is the highest responsivity of the detection system (in units of V/photon). Hence, one needs an RSR_{fl} over the fluorescence wavelengths and the RSR_{Ray} at the laser wavelength. As the LIF signal is broadband, a correction for the spectral response has to be done before the signal is integrated, yielding the signals corrected for the RSR:

$$S_{fl}^{RSR} = \int S_{fl}(\lambda) RSR(\lambda) d\lambda \quad \text{and} \quad S_{Ray}^{RSR} = S_{Ray} RSR(\lambda_{Ray})$$
(6-8)

Rearranging eq. 6-6 reveals our method for determining the fluorescence quantum yield:

$$\phi_{fl} = \frac{S_{fl}^{RSR} / (n_{ketone} I_{laser}^{LIF})}{S_{Ray}^{RSR} / (n_{N_2} I_{laser}^{Ray})} \frac{d\sigma / d\Omega|_{90^{\circ}} 4\pi}{\sigma_{abs}}$$
(6-9)

Using a single setup, we thus need to measure the LIF signal per ketone molecule and per unit laser energy, the Rayleigh signal per nitrogen molecule per unit laser energy, and the relative spectral response of the collection and detection system. The differential Rayleigh cross-section for nitrogen can be determined from equations 6-3 through 6-5 with an uncertainty of around one percent (see for example, Naus and Ubachs [98]; good Rayleigh measurements thus have an advantage over using the less certain fluorescence quantum yield of another species as a reference. The absorption cross-sections of each ketone have been measured with uncertainties of around six percent [25,39,40].

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

Experimental setup

Fig. 21 depicts the experimental arrangement used to measure the fluorescence quantum yield. All experiments were carried out at room temperature, 296 (±2) K. The ketones used were ACS grade acetone (>99.8% assayed) and ACS grade 3-pentanone (>99.0% assayed). Each was placed in a sealed reservoir and subjected to several freeze-pump-thaw cycles in order to remove dissolved air and lighter impurities. The evacuated cell was then filled barometrically by the ketone's vapor pressure before being diluted with nitrogen to the desired final pressure (between 20 and 1013 mbar). Before each set of measurements, the pressure reading from the MKS Baratron (with 0-1333 mbar range) was monitored for several minutes with ketone alone and with nitrogen diluent in the cell to ensure that potential adsorption losses to walls were negligible.



Fig. 21: Experimental setup for measuring fluorescence quantum yields with respect to Rayleigh signals.

The cell was a stainless steel cross (made by MDC) with six, orthogonal, flanged ports; 4 for optical access, 1 for gas throughput, and 1 to provide a reservoir in the

bottom for a Teflon-coated magnetic stir bar. The intersecting tubes composing the cross were nominally 3.8 cm in diameter while the total length from laser entrance to exit was slightly less than 13 cm; the total volume was close to 0.3 l.

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

Only the vertically polarized beams were used to measure the Rayleigh and LIF intensities needed to calculate the fluorescence quantum yield. The outputs of the two excimer sources were unpolarized, so the beams were directed through a MgF_2 Rochon polarizing beamsplitter to separate the horizontally and vertically polarized components. For the quadrupled YAG, the 266-nm output was already vertically polarized; however, it was also directed through the Rochon in order to fully separate the quadrupled frequency from a small amount of horizontally polarized 532-nm light that remained after the harmonic separators.

A quartz plate was placed into the beam path to separate approximately 2% of the laser; a portion of this was then detected by a photodiode (Thorlabs DET210) whose output was monitored via oscilloscope, so relative changes in energy could be monitored during the experiments and later used to correct the acquired data.

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

6.1.3 Measurements

The relative spectral response was obtained via the measurement of several calibration lamps, placed directly behind the cell with one of the windows removed (see Fig. 21). The columns of pixels were first calibrated to wavelength between 245 and 490 nm using eight lines of a mercury lamp (Spectronics Corp. Spectroline model Hg/3). Knowing the wavelength calibration, the spectral response could then be calculated with measurements from two other sources: an argon mini-arc plasma (NIST calibrated) for the 245 to 400 nm range and a calibrated tungsten lamp (Optronics Laboratories OL550) in the 350 to 490 nm range. The region of overlap from 350 to 400 nm allowed for normalization of the tungsten lamp's curve to that of the plasma and ensured internal consistency. The resultant relative spectral response curve ($R[V/photon]/R_{peak}[V/photon]$) of each source is shown in Fig. 22. Measurements were also taken with a broadband, UV polarizer between the achromatic lens and the spectrometer to ensure there was no dependence of the relative spectral response on polarization.



Fig. 22: Relative spectral response of the detection system measured with respect to a calibrated tungsten lamp and an argon mini-arc plasma. Note, standard lamp data is often expressed as W/cm^2 and must be converted to photons/(s cm^2) to be used as a standard for ICCD's whose output is proportional to the number of detected photons.

An example of a 3-pentanone spectrum excited with 248 nm is shown in Fig. 23. For comparison, background levels and the spectrally corrected traces are also shown. Using a fixed grating for all experiments was preferred to changing the grating position between Rayleigh and LIF experiments, which may incorporate changes in grating reflectivity and hysteretic complexities. Hence, the measured fluorescence signal was integrated from 300 to 490 nm, and a correction factor of 1.14 was used to account for the long-wavelength portion of the spectrum that was not captured by the spectrograph. This factor was determined from a complete spectrum that was

measured in a separate experiment [39] and is also shown in Fig. 23. The shape of acetone's spectrum was similar enough to use the same correction factor without introducing significant errors. For 308-nm excitation, the spectrum was integrated only above 320 nm to avoid incorporation of the Rayleigh signal with an estimated loss of less than 1% of the integrated fluorescence strength.



Fig. 23: Example measured and corrected 3-pentanone fluorescence spectra excited with 248-nm laser light in 1 bar of nitrogen with comparison to background levels and a reference spectrum. The reference spectrum allowed us to calculate the fraction of the emission that was not collected and thus make a correction.

We noted a slight narrowing of the spectrum when pressure or excitation wavelength is increased. This effect occurred predominantly on the blue side of the fluorescence spectrum; however, it was small (at most, a 15 nm broadening at half-maximum) compared to the full-width at half-maximum for the entire feature (130 nm). Such broadening resulted in an error estimated at less than 3% in $\phi_{\rm fl}$ by assuming a constant correction factor for the long-wavelength part of the spectrum that was not collected.

To ensure that the Rayleigh signal was measured correctly and possible contributions from small particle or surface scattering were excluded, several secondary experiments were performed. First, when the horizontally-polarized component from the Rochon was used, the scattered signal was about 1/100 of the vertically-polarized value in accordance with Rayleigh theory. As a further check on the accuracy and reproducibility of our method, the system was used to measure the ratio of methane's Rayleigh cross section to that of nitrogen at 248 nm and compared with the work of Reckers et al. [99] Methane's differential Rayleigh cross-section was 2.26 times larger than that of nitrogen in our experiments, in good agreement with Recker's value of $2.3 (\pm 0.1)$.

As indicated by Eq. 6-5, it is the Rayleigh and LIF signal per unit number density (or per molecule) and per unit incident energy that is necessary to determine $\phi_{\rm II}$. Small relative corrections in incident laser energy were typically less than 5% from shot-to-shot, but fluorescence measurements were additionally corrected on the order of 10% (sometimes more or less depending on absorption cross-section and concentration) to account for laser absorption between the cell entrance and the LIF measurement volume. As a means of minimizing the pressure uncertainty and confirming detector linearity, the Rayleigh signals were measurements to ensure reproducibility and time-steadiness) and the best-fit slope through the data was used to determine the Rayleigh signal input into Eq. 6-9. Similarly, LIF signals were measured at a fixed total pressure (at 507 mbar and1013 mbar) while using a range of partial ketone pressures. Examples of integrated Rayleigh and fluorescence signals as a function of pressure are shown in Fig. 24.



Fig. 24: Example Rayleigh and integrated fluorescence (from 300 to 490 nm) signals versus pressure.

Under our lowest-pressure conditions, only pure ketone was used between about 7 and 33 mbar. No non-linearities in signal with increasing pressure were measurable in this pressure range, i.e. the molecule made few effective collisions on fluorescent timescales even at 33 mbar, so the resultant slope was used to calculate the fluorescence yield at a nominal pressure of 20 mbar. Furthermore, time-resolved examinations of the emission signal using a photomultiplier tube confirmed that the fluorescence signal was completely captured during the 200-1000 ns gating of the

camera, and emission from possible mixed singlet-triplet, hot triplet, and thermalized triplet states was negligible [100,101].

6.1.4 Results

Table 4 shows the measured fluorescence quantum yield for acetone excited with 308 nm and its comparison with data from the literature excited with 313 nm light. By our methods, $\phi_{\rm fl}$ is significantly lower than suggested by the work of Heicklen [86]. Agreement is much better with the data from Halpern [87] although the difference is still significant (almost 40%).

	Heicklen [86]	Halpern[87]	This work
Quantum yield (×10 ³)	2.07	1.2	0.71 - 0.84*
Excitation wavelength	313 nm	313 nm	308 nm
Pressure	103-271 mbar ketone, "oxygen present"	267 mbar ketone, 733 mbar air	4-40 mbar ketone, 0-1013 mbar N ₂
Temperature	40 °C	24 °C	23 °C

*(no N₂ to 1013 mbar N₂, resp.)

Table 4: Measured acetone fluorescence quantum yields;

Using the pressure conditions of Halpern did not significantly change our measured fluorescence quantum yield for acetone, though we must note that we were less confident in the ketone's number density when we operated close to acetone's vapor pressure (this was evidenced by a pressure reading that decreased over several minutes after filling the ketone and then increased over time after filling the diluent). It is conceivable that the change in excitation wavelength would result in an increase in the fluorescence yield. Copeland notes that a significant dissociative channel may increase rapidly for excitations below 312 nm [101]. Excitation wavelengths on either side of this value may thus provide different fluorescence quantum yields. Unfortunately, it was not possible to exactly match the conditions of either Heicklen or Halpern due to lack of a 313 nm source.

Ignoring for the moment Heicklen's value of the fluorescence quantum yield as a calibration standard, we can compare our measured relative behavior of $\phi_{\rm fl}$ as a function of excitation wavelength with the work of Hansen and Lee [48]. Fig. 25 shows the wavelength-dependence of the fluorescence quantum yield for acetone

(left) and 3-pentanone (right) at our lowest-pressure condition and compares them with the relative data of Hansen and Lee (23°C, 11 mbar acetone, 5 mbar oxygen, 67 mbar cyclohexane).



Fig. 25: Relative acetone and 3-pentanone fluorescence quantum yield as a function of excitation wavelength (T = 296 K, $p \sim 20 \text{ mbar}$) and comparison with Hansen and Lee [48].

For acetone the overall trend agrees well. However, this is not the case for 3pentanone. While our data indicates behavior similar to acetone, Hansen's (23 °C, 13 mbar 3-pentanone, 3 mbar oxygen) shows relatively little wavelength-dependence. Given the similarities between acetone and 3-pentanone that have been noted in other studies [38], we expect that $\phi_{\rm fl}$ should change with excitation wavelength in a similar manner for each molecule.

Fig. 26 shows the results of $\phi_{\rm fl}$ for acetone (left) and 3-pentanone (right) for each excitation wavelength at the three measured total pressures. The results for acetone generally seem to be lower than that of 3-pentanone under similar conditions, in qualitative agreement with the work of Hansen, and the pressure and wavelength-dependencies seem to follow the conceptual model developed by Thurber, even for 3-pentanone whose wavelength-dependence was previously considered negligible, due to the work from Hansen and Lee. For 3-pentanone, the approach of the fluorescence yield to a vibrationally-relaxed, high-pressure limit (independent of the excitation wavelength) is apparent. For acetone, the trend is less obvious, possibly indicating a less efficient vibrational relaxation of the excited singlet state.


Fig. 26: Acetone and 3-pentanone fluorescence quantum yield as a function of pressure and excitation wavelength.

Estimated experimental uncertainties of our $\phi_{\rm fl}$ measurements are ±10% for the 507 and 1013 mbar data. At low pressures, we assign a slightly higher uncertainty, ±15%, due to possible changes in the absorption cross-section at low pressures and possible collected emission from states other than the excited singlet during the camera integration time that were not thoroughly explored in this work. Primary sources of the uncertainty were the relative spectral response calibration (±7% for the ratio of the Rayleigh wavelength to the fluorescence wavelengths), the absorption cross section of the molecule (±6%), the value of the collected signal per unit number density (±3%), and the correction factor used for the long wavelength part of the fluorescence spectrum that was not collected (±3%).

6.2 Comparison of acetone data with fluorescence quantum yield model

As reviewed in section 0, parameters of the Thurber model are optimized to describe the relative pressure and temperature dependence for acetone LIF. However, no data was available for the relative signal behavior as a function of excitation wavelength. Thus, comparison of the model predictions with our data serves as a first check for the model.

In Fig. 27, our data is shown along with model predictions on a relative scale. It can be seen, that the model is in good agreement with experimental data. Its absolute predictions, however, are almost three times higher than our measurements.



Fig. 27: Comparison of relative acetone fluorescence quantum yield with model predictions.

The absolute predictions of Thurber's model pivot on the value of the fluorescence rate coefficient, k_{fl} , since the fluorescence yield from an excited state or energy level is given by

$$\phi_{\rm fl} = \frac{k_{\rm lf}}{\sum_{i} k_{i}} = k_{\rm f} \tau_{\rm eff} \tag{6-10}$$

where the denominator represents the sum of the rate coefficients for all possible decay processes from the excited state, a number measurable by the natural lifetime, τ_{eff} . Thurber originally took k_{fl} to be $8.0 \times 10^5 \text{ s}^{-1}$ based on the recommendation of Hansen [48]. Hansen determined the value of k_{fl} from fluorescence yield and natural lifetime measurements and the reader may recall from the literature review that Hansen's work is relative to Heicklen's measurement of the fluorescence quantum yield. In sum, Thurber's model is ultimately calibrated to Heicklen's measurement of the fluorescence quantum yield through the assignment of k_{fl} . Since we find Heicklen's measurements to be much higher than ours, the value of k_{fl} and thus the model predictions are also too high. Reassigning the value of k_{fl} based on our fluorescence quantum yield measurements will recalibrate the model without changing the relative behavior with pressure or temperature. Whereas Thurber originally used a fluorescence rate of $8 \times 10^5 \text{ s}^{-1}$, we recommend this value be changed to $3 \times 10^5 \text{ s}^{-1}$, based on the best fit of his model to our data at one bar for the three different wavelengths.

Using the new value of $k_{\rm fl}$ and keeping all other parameters the same as in [25] the modeled fluorescence quantum yield as a function of pressure and excitation wavelength can be reexamined. Fig. 28 shows the modeled pressure-dependence of acetone's fluorescence quantum yield using a constant $k_{\rm fl} = 3 \times 10^5 \, {\rm s}^{-1}$ in comparison with our data and the relative data of Thurber (Thurber's data is normalized by a

best-fit constant constrained to be within our $\pm 10\%$ uncertainty at one bar). Although there is little overlap, the trends in the relative data of Thurber at high pressures and our absolute data at lower pressures match well, as does the model's prediction of both. Differences between all data and the model predictions are less than 10% of the modeled values for any pressures at or above 1 bar. The combination of the low and high pressure data at 308 nm may indicate slightly more pressure-dependence than the model predicts. Nonetheless, since experimental uncertainties are approximately the same as the differences between model and data, no further changes to the model are currently warranted.



Fig. 28: Comparison of absolute acetone data measured in this work with the model of Thurber using the modified value of $k_{fi} = 3 \times 10^5 \text{ s}^{-1}$.

Although the fluorescence quantum yield for acetone can change by almost an order of magnitude depending on the conditions, it approaches a limiting, constant value at high pressure, independent of excitation wavelength (evident in Fig. 28). This high-pressure limit provides a convenient figure by which to gage acetone's behavior (for comparison to other molecules). The new high pressure limit of $\phi_{\rm fl}$ for acetone at 297 K in nitrogen is 1.0×10^{-3} , a significant reduction from Thurber's value of 2.7×10^{-3} .

In the next chapter, model predictions for simultaneously elevated temperatures *and* pressures will be validated by comparison to data obtained in an optically accessible IC engine.

7 Validation of model predictions for LIF-signal strength in a practical internal combustion engine

The model for toluene-LIF described in chapter 5 was tested by comparison of predicted signal intensities to experimental data that was obtained from in-cylinder measurements in an optically accessible engine where temperature and pressure were reasonably well known. In the same study, predictions from the model for 3-pentanone LIF, developed from Koch et al. [39] (see section 2.4.1 and chapter 6) have been validated. Toluene and 3-pentanone are the most frequently used fuel tracers. This study provides the first systematic comparison of data and model predictions for situations where *T* and *p* are both elevated.

7.1 Experimental

The engine data used in this study was acquired within the group from Prof. Volker Sick at the University of Michigan, Ann Arbor. The experiment was conducted in a direct-injection optical engine using a KrF*-laser for excitation at 248 nm. The engine was motored at 600 rpm, coolant temperature was kept at 80°C. A mixture of 82% isooctane, 15% 3-pentanone and 3% toluene was injected into the cylinder during the intake stroke to provide enough time for mixing of fuel and air for a stoichiometric mixture. Injection ended at -270 crank angle degrees (CAD) [30,102]. The tracer mixture was chosen for a combined application to determine the in-cylinder oxygen concentration [30]. Cross-talk and mutual energy-exchange processes between the tracer molecules were found unimportant for our operating conditions [66]. The intake air was delivered at a manifold pressure of 0.45 bar and a temperature of 318 K. The trapped mass at IVC can then be calculated from the ideal gas law. However, the gas temperature at IVC inside the cylinder can be affected by heat transfer from the cylinder walls and the cylinder head, frictional heating, and cooling due to fuel evaporation. Fuel was injected only every 6th cycle, during which LIF data were acquired, to ensure that no residual fuel was trapped during following cycles, thus affecting the equivalence ratio. As there is no combustion and thus no hot residual exhaust gas, the overall effect on the temperature at IVC is expected to be small. In comparison to full-metal engines it seems reasonable to assume the gas temperature at IVC may be 10 K higher than the intake temperature [103]. Uncertainties in the temperature at the chosen reference point will have an impact on the evaluated temperature history. A 10 K increase in the intake temperature would result in approximately 20 K higher temperature at top dead center (TDC). For the conditions given, the temperature evolution and the in-cylinder number of molecules are shown along with the measured in-cylinder pressure in Fig. 29.



Fig. 29: Measured pressure (dashed line), calculated temperature (solid line), and number of molecules (dotted line) for the motored engine. The higher temperature curve and the associated lower molecule number curve are obtained when including an estimated 10K temperature increase due to heat transfer from the engine to the intake air.

Peak temperatures in the engine were around 600 K. Though the tracers are not completely stable at these temperatures, chemical breakdown during the cycle was not significant as evidenced by the approximately symmetric signals around TDC.

7.2 Validation of the toluene model

The comparison of engine data and predicted toluene-LIF signal intensities for the incylinder engine conditions are shown in Fig. 30 as a function of crank angle in the range of 1 bar/350 K to 8 bar/600 K. The agreement of model predictions and experimental data is good and indicates that influences of total pressure are small compared to oxygen quenching and that the model describes the signal behavior sufficiently well. Experimental uncertainties of 10%, resulting from data correction, e.g. laser energy and absorption corrections, are displayed. Uncertainties resulting from in-cylinder temperatures and number densities (cf. Fig. 29) are less important. Predicted signal intensities are scaled to engine data at about 1 bar. This is close to conditions in the flow-cell experiment.



Fig. 30: Comparison of model predictions and measured toluene signal intensities for engine conditions after excitation with 248 nm.

Predicted signal intensities are too high around TDC (i.e. when total pressure is high) and too low for early and late stages of the cycle (i.e. when total pressure is below 1 bar). This systematic deviation may be attributed to effects of total pressure that are currently neglected in the model.

7.3 Validation of the 3-pentanone model

The model prediction is shown (as the flattest line) in Fig. 31 as a function of the crank angle (normalized to –90CAD ATDC at 0.82 bar and 360 K).



Fig. 31: Comparison of engine LIF data and predictions for 3-pentanone with 248-nm excitation. The engine data show that the fluorescence per molecule continues to decrease at high temperatures, despite the presence of high pressure, a trend not predicted by the photophysical model. Correcting only for temperature, using exp. data at 1 bar yields much better agreement.

The prediction from the model, that includes pressure and temperature effects, shows a marked difference from the engine data. A second simulation can be obtained by looking at the change in signal due only to temperature based on 1 bar cell data [22,39]. This curve in Fig. 31 is systematically low compared to the engine data, but the agreement is much better than for the photophysical model. The disagreement between the model and the engine data, however, may indicate a gap in the current understanding of the relevant photophysical processes in 3-pentanone LIF. Again, the lack of sub-ns lifetime measurements results in uncertainties about fast decay processes. Neglecting these processes in the current approach may explain the shortcomings in signal prediction of the ketone model.

8 Feasibility of fuel/air ratio measurements using toluene LIF

The fluorescence model from chapter 5 allows to describe toluene-LIF signal behavior at simultaneously elevated temperatures and pressures. In the following, signal interpretation of toluene in terms of fuel/air ratio will be discussed. Thereby, the widespread FARLIF technique (see section 2.4) will be critically reviewed.

8.1 Toluene-LIF signal at engine-related conditions

In Fig. 32 expected signal intensities for engine-relevant pressures and temperatures based on this model are shown. The LIF-signal is displayed for a fuel/air mixture with a constant $\phi = 1.0$.



Fig. 32: Map of the expected toluene-LIF intensity from a mixture with a constant fuel/air ratio of $\phi = 1.0$ for engine-related pressures and temperatures, normalized to 1 bar, 296 K for each wavelength.

8.1.1 Effect of temperature

The presence of oxygen moderates the relative effect of temperature. According to section 2.4, if collisional quenching is stronger or in the order of intramolecular decay, the influence of k_{tot} and hence its change with temperature is less important. This is

demonstrated in Fig. 33. For example at 248-nm excitation in 8 bar of air, the total signal is barely changing with temperature below 420 K. The reason is that oxygen quenching is strong (i.e. $k_{tot}(T) < \tilde{k}_q(T)n_{oxy}$) in this range and hides the strong temperature-dependence of k_{tot} . With 266-nm excitation, the LIF signal in air follows the increase of the absorption cross-section below ~500 K. For higher temperatures, collisional quenching is no longer dominant and the decrease of k_{tot} is observable in total signal. Note that normalized signals are displayed in order to demonstrate the *relative* effect of temperature. The absolute signal is always decreasing with increasing air pressure. It is important to point out that Fig. 33 demonstrates that temperature and oxygen (or air pressure) effects are *not* separable based on time-and wavelength integrating measurements. The temperature behavior of the signal depends on the present oxygen concentration.



Fig. 33: The relative effect of temperature on the total LIF signal for a constant mole fraction of toluene shown for various pressures of air. Signal is normalized for each pressure at 300 K. The signal-dependence on temperature in the presence of oxygen is moderated compared to a nitrogen atmosphere (denoted 0 bar air) due to oxygen quenching.

Data is shown for a constant mole fraction x. Mole fraction, number density n, temperature T and total pressure p are linked by the ideal gas law $x \sim n p/T$. A practical situation where Fig. 33 applies would be e.g. a homogenous fuel/gas mixture (HCCI engine) with local temperature inhomogeneities. The temperature-dependence of the signal can potentially be used to investigate local temperature inhomogeneities.

8.1.2 Effect of oxygen quenching

As already discussed along with the experimental data, the relative effect of oxygen quenching becomes weaker at elevated temperatures. As a result, the basic approximation for FARLIF, $k_{tot}(T) \ll k_q(T)n_{oxy}$, is not valid for most of the pressure and temperature range found in an engine. In Fig. 34, the relative strength of oxygen quenching in percentage of total depopulation of the excited state is displayed. It can

be regarded as a quenching yield or the relative influence of quenching to the overall depopulation of the excited state. If quenching is the only relevant process this number is 1.0 (i.e. 100%). A deviation from this situation is expressed with quenching yields below 1.0. The additional relaxation pathway is then due to intramolecular processes (i.e. k_{tot}). A value of 0.9 thus means that 90% of the initially excited toluene molecules are deactivated through collisionally-induced quenching by molecular oxygen. High values of the quenching yield represent conditions where the approximation of toluene-LIF signal ~ fuel/air ratio (i.e. the FARLIF approach) is justified. The deviation from 1.0 gives the error made when assuming oxygen quenching to be the dominating decay channel. On the other hand, small values of the quenching yield signify that oxygen quenching is barely playing a role and in this case toluene signal behaves simply as proportional to the tracer number density as opposed to the fuel/air ratio. In other words, at those conditions toluene LIF becomes similar - with regard to oxygen quenching - to tracers like acetone or 3-pentanone that are mostly insensitive to oxygen quenching. For most conditions relevant in ICengines, toluene is in an intermediate state of these two extreme cases (i.e. neither is oxygen quenching dominant nor is the signal insensitive to oxygen). Consequences for signal interpretation will be outlined in the next section.



Fig. 34: The fraction of toluene molecules that are de-excited through oxygen quenching. It can be seen that oxygen quenching is not dominant for most conditions present in the compression stroke of an engine.

8.2 Signal Interpretation at engine related conditions

In most practical applications, the toluene-LIF signal is calibrated with a homogenous mixture (e.g. early injection) at a series of different detection times. This calibration curve is than used to correct signal intensities at the respective crank angles with the assumption that calibration conditions are not too different from the actual measurement situation. Therefore signal interpretation will be discussed on the basis of an exemplary pressure-temperature curve as it can be found in an IC engine (Fig. 35). Temperature covers the range of 350 - 600 K and pressure from 0.8 - 8 bar.



Fig. 35: An exemplary T, p-curve as it can be found in the cylinder of an IC engine. These values will be used to discuss toluene-LIF signal interpretation for engine conditions.

In general, two fundamentally different cases must be considered, when discussing fuel/air ratio measurements. The ratio can be changed by varying either the fuel concentration (i.e. stratified load) or by varying the oxygen concentration (i.e. exhaust gas recirculation). Signal interpretation will be discussed for these two distinct cases separately.

8.2.1 Fixed fuel mole fraction, varying oxygen mole fraction (i.e. changing ϕ by EGR)

As a first example, fuel mole fraction is kept fixed, whereas the oxygen mole fraction varies. In a practical application, this corresponds to the case where residual gas (or recirculated exhaust gas) replaces air, thus changing the oxygen mole fraction, whereas the amount of injected fuel is constant. In Fig. 36a the expected total toluene signal for a pure fuel/air mixture (no exhaust gas present) with $\phi = 1.0$ along with the corresponding curves where ϕ equals 1.33, 1.66 and 2.0 is displayed. This corresponds to an amount of (oxygen free) residual gas of 25%, 40% and 50% respectively. The total signal is increasing with crank angle (CA), i.e. with increasing temperature, due to the increase of the absorption cross-section. The signal increases slower than the absorption cross-section, most noticeably around TDC, because oxygen quenching is no longer dominant at these conditions (cf. Fig. 34) and intramolecular decay plays a role in addition to oxygen quenching. In Fig. 36b, the toluene LIF signal relative to the signal at $\phi = 1.0$ is shown. According to FARLIF, horizontal lines with the value of the respective equivalence ratio would be expected. However, a deviation from this assumption is observable mainly around TDC, i.e. where temperatures are high.



Fig. 36: Toluene-LIF signal for the conditions from Fig. 35 and 266-nm excitation shown for various oxygen mole fractions (i.e. various amounts of residual gas). The right plot shows signal intensities relative to the ϕ = 1 case. Around TDC, a significant deviation from the FARLIF assumption is obvious.

This deviation is even stronger in the case of 248-nm excitation. Total and relative signal intensities are shown in Fig. 37. As explained in the background section, the toluene-LIF signal is proportional to ϕ as long as oxygen quenching is the dominant de-excitation pathway. As can be seen in Fig. 34, this is not the case for the (exemplary) conditions investigated here. As a result, the relative signal change is not proportional to the change in the fuel/air (equivalence) ratio. When oxygen quenching is not dominant, the intramolecular decay plays a role as an additional decay path and signal is thus lower than in the FARLIF assumption. This means that fuel/air ratios are underestimated at these conditions.



Fig. 37: Toluene-LIF signal for the conditions from Fig. 35 and 248-nm excitation shown for various oxygen mole fractions (i.e. various amounts of residual gas). The lower plot shows signal intensities relative to the $\phi = 1$ case. The assumption of LIF signal ~ fuel/air ratio proves invalid for the complete range of conditions.

8.2.2 Varying fuel concentration at fixed total pressure (i.e. changing ϕ due to stratified load)

The situation is different when the fuel concentration varies significantly (stratified load). Let's consider the case of a fixed total pressure, a varying fuel concentration and no exhaust gas present (i.e. only fuel and air mixing). That means that ϕ is changed by replacing air with fuel. A practical situation would be a measurement in a fuel/air mixture (i.e. homogenous pressure distribution) with highly stratified load. In this case, the fuel/air ratio is predominantly changed by the fuel concentration while the oxygen concentration barely changes. This situation is displayed in Fig. 38. In the range of up to $\phi \sim 10$, fuel concentration and fuel/air ratio are proportional. As a consequence, the measurement does not distinguish between ϕ and the fuel concentration itself. For this reason, the signal appears to be proportional to the fuel/air ratio. This interpretation, however, is misleading as the signal in this region is simply proportional to the fuel concentration. This proportionality is limited to as soon as the fuel starts to replace air at a significant level. A further increase in fuel then leads to a significant decrease in oxygen concentration. As a result, the signal is no longer proportional to ϕ . That is also shown in Fig. 38 for conditions of 5 bar total pressure, 600 K and 248-nm excitation. As it can be seen in Fig. 34, oxygen quenching is far from dominant for these conditions. This is, however, only observable when the oxygen concentration is significantly changed, as it is the case for very rich mixtures. The dotted line displays the FARLIF assumption. For $\phi > 10$, a deviation from this assumption is observable.



Fig. 38: Change of fuel and oxygen concentration as a function of the fuel/air ratio under the limiting conditions of fixed total pressure (p = 5 bar). ϕ is predominantly changed by the fuel concentration while the oxygen concentration barely changes. Toluene LIF-signal thus appears to be proportional to ϕ over a wide range. The dotted line displays the proportionality (FARLIF assumption).

In order to give an estimate the resulting errors in very rich regions, Fig. 39 displays the LIF-signal strength for several equivalence ratios relative to the ϕ = 1 case, for the conditions from Fig. 35. For ϕ = 10 (i.e. 15% fuel and 85% air) at 248-nm excitation

and $\phi = 20$ (i.e. 30% fuel and 70% air) for 266-nm excitation the deviation from the FARLIF assumption (i.e. from the expected values of 10 and 20, respectively as relative signal strength) is <10% at all conditions. For $\phi = 30$ (i.e. 38% fuel and 62% air) a significant deviation from the proportionality (i.e. from 30) is observable. The deviation is increasing with increasing crank angle (i.e. temperature). Again, the fuel/air (equivalence) ratio will be underestimated as intramolecular decay in addition to oxygen quenching leads to a decrease in signal strength.



Fig. 39: Toluene-LIF signal (relative to signal at $\phi = 1$) for rich conditions. A significant amount of air is replaced by fuel leading to a deviation from the proportionality of ϕ and LIF signal.

9 Demonstration of novel imaging strategies

The complex dependencies of toluene LIF on the surrounding conditions provide the basis for the development of new measurement strategies for temperature and oxygen distributions in addition to the measurement of the fuel/air ratio. In this chapter, several quantitative techniques will be presented that allow imaging measurements of temperature and oxygen concentration: (1) a single-color-detection strategy for temperature measurements, requiring only one camera and one laser, but a homogenous tracer distribution, (2) a two-color-detection strategy (i.e. simultaneous detection of two different wavelength regions of the fluorescence spectrum) enabling temperature measurements for flows with inhomogenous tracer distribution, requiring two cameras but only a single laser, (3) a two-color-detection technique and (4) a two-tracer technique for oxygen concentration imaging in isothermal, inhomogeneously seeded flows.

9.1 Experimental

To demonstrate the temperature sensitivity of toluene and to explore the opportunity for imaging, the temperature distribution of a heated, turbulent free jet with a room temperature co-flow has been measured. The setup is depicted in Fig. 40. The jet was electrically heated in a Sylvania heater (model 014683) and injected into quiescent gases through a nozzle with a 1.7 mm orifice. The flow exit velocity was varied from 10 to 35 m/s by means of different flow rates. Toluene was seeded to a nitrogen gas flow through a Bronkhorst CEM (controlled evaporation and mixing). The toluene concentration (0.5 - 2%) was controlled by a Bronkhorst liquid flow controller. The nitrogen co-flow was seeded with toluene by percolating through a bubbling system in order to obtain fluorescence signal throughout the entire observed area. Exit velocity of the co-flow was about 0.9 m/s and can thus be regarded quiescent in comparison to the exit velocity of the jet. Flow and seeding rates could by varied in order to obtain either homogenous (i.e. the same toluene concentration in the jet as in the co-flow) or inhomogenous seeding (i.e. different concentrations of toluene in jet and co-flow). Varying the applied heating voltage allowed to investigate different exit temperatures of the flow. With the heated jet and the room-temperature co-flow mixing, an inhomogenous temperature field was provided. In order to demonstrate the two-camera technique for oxygen concentration measurements, the co-flow consisted of toluene-seeded air. With the jet being pure nitrogen and toluene, an inhomogenous oxygen distribution was provided. In this case an isothermal system was chosen, i.e. the central flow was not heated.



Fig. 40: Setup of the two-camera experiment for temperature measurements in a heated turbulent jet.

Laser light from a KrF* excimer laser (248 nm) was formed to a light sheet about 2.5 cm high and 0.5 mm thick with about 25 mJ pulse energy. The toluene-LIF signal detection was detected by two intensified CCD cameras (FS2, LaVision) with f = 105 mm, $f_{\#} = 4.5$ lenses (Nikkor UV). Data processing was done with the DAVIS software from LaVision. Appropriate filters (see next section) in front of the camera enabled the two-color detection.

9.2 Quantitative temperature imaging

The distinct dependence of total toluene-LIF signal on temperature can be used to visualize temperature distributions in homogeneously seeded flows using a one-laser, one-camera setup (9.2.1). The *T*-dependence of the signal hereby results from the factors absorption cross-section, fluorescence quantum yield and density. This approach, however, is restricted to systems with a homogeneous tracer distribution (i.e. homogeneous mole fraction), e.g. a seeded gas flow over a heated surface when investigating heat transfer phenomena in non-reacting non-mixing flows. In inhomogeneously seeded flows (e.g. mixing studies) where the tracer concentration varies spatially, the LIF signal depends on both, the local tracer number density and the local temperature. To extract temperature information, at least two pieces of

information are required. In this case, one can take advantage of the red shift of the emission spectrum with increasing temperature. A two-color detection technique (i.e. simultaneous detection of two different wavelength regions of the fluorescence spectrum), using a single-laser, two-camera setup, will provide local temperatures in this situation (9.2.2). The *T*-dependence of the signal ratio then results from the respective fluorescence quantum yields only, as tracer concentration and absorption cross-section cancel. Results are discussed for both nitrogen and air as bath gas

9.2.1 Single-color detection

The toluene-LIF signal S_{fl} at each point (x,y) is proportional to the product of the number density n_{tol} , the absorption cross-section σ_{abs} and the fluorescence quantum yield ϕ_{fl} of the fluorescing species:

$$S_{f}(T, x, y) \sim n_{tol}(T, x, y)\sigma_{abs}(T)\phi_{f}(T)$$
(9-1)

where *T* may be a function of the spatial coordinates (x,y). In homogeneouslyseeded, constant-pressure systems, n_{tol} depends on 1/T only. LIF from either 248 or 266-nm excitation is then a function of temperature only. One region or condition of known temperature is then sufficient for calibration in order to obtain absolute temperatures.

$$T(x,y) = f(S_{ij}(x,y))$$
 (9-2)

Measurements in nitrogen

In a nitrogen bath gas, the temperature-dependence of the LIF signal is dominated by the fluorescence quantum yield that exponentially decreases with increasing temperature. Due to this strong dependence, temperature can be measured with high accuracy and resolution. Note that for the evaluation of average temperatures, as a result of the non-linear T-S_{fl} relation, data must be processed on a single shot basis before averaging the individual T values.

From the cell measurements described in chapter 4 , calibration curves can be obtained for the determination of temperature from the toluene-LIF signal (cf. Fig. 41).



Fig. 41: Calibration curves for the determination of temperature from the toluene-LIF signal in a homogeneously seeded nitrogen gas flow at 1 bar. Symbols: exp. data, lines: fit.

A fit through the cell data yields the following calibration curves:

 $T = -3.3046x^2 + 116.21x + 301.02$ with $x = \ln(1/S_{f}(266 \text{ nm}))$ and T in K (9-3a) $T = -4.3631x^2 + 34.745x + 303.05$ with $x = \ln(1/S_{f}(248 \text{ nm}))$ and T in K (9-3b)

The sensitivity to temperature is stronger for 248-nm excitation because the absorption cross-section at 266 nm increases with increasing temperature whereas it stays constant at 248 nm.

Imaging experiments have been conducted using 248-nm excitation. Data processing is straight forward and exemplary results are shown in Fig. 42.



Fig. 42: Temperature field of the heated jet for different heating voltages (i.e. exit temperatures, cf. Fig. 49). The gas flow consists of nitrogen homogeneously seeded with 10 mbar toluene. Excitation occurs at 248-nm with approximately 12 mJ pulse energy. Exit velocity of the flow is set to 30 m/s.

Varying the heating voltage allows to change the exit temperature of the jet. The coflow remains unheated. Thus, an inhomogenous temperature field is provided. Temperatures ~2 mm above the nozzle have been measured with a thermocouple. Temperatures obtained by LIF thermometry show excellent agreement with the thermocouple measurements (cf. Fig. 49).

Measurements in air

In some cases, temperature diagnostics in air is required where the gas can not be replaced by nitrogen. In Fig. 43 calibration curves for the temperature-dependence of the toluene-LIF signal in air are shown as obtained from the cell-measurements described in chapter 4.



Fig. 43: Calibration curves for the determination of temperature from the toluene-LIF signal in a homogeneously seeded 1-bar air flow. Left: 248-nm excitation, right: 266-nm excitation, symbols: experimental data, line: fit. For 266-nm excitation the function is not unique and thus only applicable for a limited temperature-range.

In comparison to the signal in nitrogen (cf. Fig. 41), temperature sensitivity is significantly reduced in air. The reason for this is that oxygen quenching reduces the influence of temperature. In general, when oxygen quenching is the dominant de-excitation process, temperature effects on the fluorescence quantum yield can be neglected. This can be seen in the case of 266-nm excitation where the LIF signal at the lower temperatures is increasing with increasing temperature as a combined effect of increasing absorption cross-section and strong oxygen quenching (i.e. weak *T*-dependence of the fluorescence quantum yield). At higher temperatures, oxygen quenching is no longer dominant and the LIF signal (i.e. the fluorescence quantum yield) starts to decrease even though the absorption cross-section is still increasing.

For the demonstration experiment, 248-nm excitation has been used. Exemplary results are shown in Fig. 44. The calibration curve obtained from the cell-measurements is:

$$T = -21.944x^2 + 194.94x + 298.96$$
 with $x = \ln(1/S_{i}(248 \text{ nm}))$ and T in K (9-4)



Fig. 44: Temperature field of the heated jet for various heating voltages (i.e. exit temperatures, cf. Fig. 49) obtained with one-line toluene thermometry in a homogeneously seeded 1-bar air flow and 248-nm excitation. Toluene concentration is ~1% and laser pulse energy around 12 mJ. Exit velocity of the flow is set to 30 m/s.

Results obtained in air agree well with the results in nitrogen. The temperature resolution is slightly reduced due to the weaker temperature-dependence of the toluene-LIF signal in air as compared to a nitrogen bath gas.

9.2.2 Two-color detection

In the case of inhomogeneously seeded systems, one can take advantage of the temperature-dependent red-shift of the fluorescence spectrum to measure temperature (cf. Fig. 10). The idea is to measure fluorescence simultaneously in two different wavelength regions with two cameras and appropriate filters after excitation at a single wavelength (cf. Fig. 45). Spectra in Fig. 45 are normalized. Note that the total signal decreases for all emission wavelengths. However, the longer wavelengths show a weaker temperature-dependence.

Evaluating the signal ratio of two different wavelength regions, number density and laser intensity will cancel at each point and the result depends solely on the local temperature T(x,y):

$$\frac{S_{f_{1}}^{1}(x,y,T)}{S_{f_{1}}^{2}(x,y,T)} = \frac{\eta^{1} E_{laser}(x,y) n_{tol}(x,y) \sigma_{abs}(T(x,y) \phi_{\pi}^{1}(T(x,y))}{\eta^{2} E_{laser}(x,y) n_{tol}(x,y) \sigma_{abs}(T(x,y)) \phi_{\pi}^{2}(T(x,y))} = c \frac{\phi_{\pi}^{1}(T(x,y))}{\phi_{\pi}^{2}(T(x,y))} = f(T(x,y))$$
(9-5)

where η_i denotes the detection efficiency.



Fig. 45: Scheme for the two-color-detection stategy based on toluene-LIF.

The temperature-sensitivity depends on the bath gas and the combination of filters. Detection of the long wavelengths ("red" part of the spectrum) can easily be implemented by a commercially available long-pass filter. A band-pass for the detection of the shorter wavelengths ("blue" part of the spectrum) around the peak emission of 280 nm must be custom-made. As such a band-pass was not available for this demonstration experiment, a long-pass filter (WG 280, i.e. transmission of wavelengths longer than 280 nm) was therefore used for the "blue" detection channel.

Measurements in nitrogen

Fig. 46 shows the signal ratio of different parts of the emission spectrum calculated from the cell measurements (chapter 4) for various filter transmissions.



Fig. 46: Temperature-dependence of the signal ratio of different parts of the toluene-LIF emission spectrum in nitrogen, calculated for various filter combinations (see text).

The WG 280, 305, 320 and 335 filters are common, relatively cheap, commercially available (Schott), long-pass absorption filters that transmit wavelengths longer than

the respective number in the name. BP 280 denotes an interference band-pass for the detection of the peak fluorescence of 280 ± 5 nm. This filter can be purchased custom-made (Laseroptik) but was not available at the time of this experiment. For this experiment we chose to employ a WG 280 with the transmitted signal dominated by the peak fluorescence in combination with another long-pass filter. The longer the wavelength region transmitted by this second filter, the better the temperature sensitivity of the signal ratio (cf. Fig. 46). However, total signal intensity is decreasing at the same time. For this reason we decided to use a WG 320. Temperature sensitivity of the signal ratio in nitrogen is significantly more pronounced for 248-nm excitation than for 266-nm excitation. A fit of the data for the filter combination used in this experiment (WG320 and WG280) yields:

$$\frac{S_{fl}^{WG320}}{S_{fl}^{WG280}} = 8 \times 10^{-6} T^2 - 0.0013T + 0.6677 , \quad T \text{ in K}$$
(9-6)

Exemplary results are shown in Fig. 47.



Fig. 47: Temperature field of the heated jet for different heating voltages (i.e. exit temperatures, cf. Fig. 49) evaluated by the two-color technique. Jet and co-flow contain different toluene concentrations, thus providing an inhomogeneous tracer distribution. Excitation occurs at 248-nm with approximately 12 mJ pulse energy. Exit velocity of the flow is set to 30 m/s. Shown are exemplary single shots and 50-shot averages.

For this experiment, co-flow and heated jet are seeded with different tracer concentrations (~0.3 and 1%, respectively) thus providing an inhomogenous tracer distribution over the imaged area. Temperature distribution in the heated jet, the

unheated co-flow and the mixing area is well represented by the two-color technique. The accuracy of two-color technique can be compared to the one-color technique when evaluating temperature fields with both methods from a homogeneously seeded flow. Results are shown in Fig. 48.



Fig. 48: Comparison of one-color and two-color thermometry by calculating the temperature fields with both techniques for the same single shot of a homogenously seeded flow (cf. Fig. 49).

Results of both techniques agree well. The temperature resolution of the two-color technique is somewhat reduced due to the weaker temperature-dependence of the signal ratio. Spatial resolution of the ratioed images is limited due to the use of image intensifiers. Using unintensified UV sensitized cameras may improve the spatial resolution.

Right above the exit (~2 mm) of the nozzle, temperatures are steady as the flow does not yet mix. Temperatures can therefore be measured with a thermocouple and compared to average temperatures measured by the different toluene-LIF strategies at this point. Results are shown in Fig. 49. Agreement of the various techniques is satisfactory.



Fig. 49: Comparison of temperatures ~2 mm above the nozzle determined by one-color and two-color toluene-LIF thermometry and thermocouple measurements.

Measurements in air

The toluene-LIF spectrum with 248-nm excitation exhibits a red-shift with increasing oxygen partial pressure (cf. Fig. 13). This effect, however, is saturated for oxygen partial pressures at about 200 mbar oxygen and a further increase of oxygen partial pressure does not result in any change of the spectral shape. For this reason, the two-color technique can also be applied in air flows of 1 bar or higher total pressure. However, temperature sensitivity will be reduced compared to the case of a nitrogen flow. Fig. 50 displays the temperature sensitivity for the same filters as in Fig. 46. In air, temperature sensitivity of the signal ratio is slightly more pronounced for 266-nm excitation than for 248-nm excitation. In general, for applications in a rough environment as in an engine, a good band-pass for the detection of the peak fluorescence will be needed in order to achieve a distinct temperature-dependence of the signal ratio.



Fig. 50: Temperature-dependence of the signal ratio of different parts of the toluene-LIF emission spectrum in air, calculated for various filter combinations.

The temperature-dependence of the WG 320 / BP 280 filter combination in air is close to the one observed in the nitrogen experiment (WG 320 / BP 280). It is

therefore reasonable to expect the technique to work well in an air atmosphere. Assuming independence of the spectral shape on total pressure, this technique can also be applied in an engine environment.

9.2.3 Summary of tracer-based temperature imaging strategies

The temperature-imaging strategies based on toluene-LIF developed above should be compared to the established techniques that use ketone tracer-LIF. One-color thermometry with acetone [13] or 3-pentanone [40] is based on the same principles. One major advantage of using toluene LIF is its strong sensitivity to temperature allowing for high-accuracy temperature measurements. The two-line temperature imaging based on ketones (i.e. 3-pentanone [22,39] or acetone [43]) is using two different excitation wavelengths (e.g. 266 nm and 308 nm). The temperaturedependence of the total LIF signal is different for different excitation wavelengths. Thus, the ratio of the signals can be used to measure temperatures in inhomogeneously seeded flows. In Fig. 51, the temperature sensitivity of the twocolor-detection strategy presented in this work and the two-line-excitation technique based on ketone-LIF is compared. Both temperature-imaging strategies feature a similar sensitivity with the toluene-LIF-based strategy being somewhat better suited for the 300 – 600 K temperature range and the ketone-LIF-based strategy being a little more sensitive at the higher temperatures. However, an important advantage of the two-color technique based on toluene-LIF is that it requires only one excitation wavelength (i.e. only one laser) thus significantly reducing experimental cost compared to the two-line-excitation strategy.



Fig. 51: Comparison of the temperature sensitivity of the two-color-detection strategy based on toluene LIF presented in this work with the two-line-excitation technique based on ketone LIF demonstrated from Koch et al. [39] and Thurber et al. [43].

While the temperature sensitivity is one figure of merit, one must also consider the expected signal intensities during experimental design. Therefore, Toluene-LIF signal intensities detected through the WG320 will be estimated in comparison to 3pentanone-LIF signal at room temperature and for 248-nm excitation. Toluene fluorescence quantum yield at these conditions is ~0.1 [58] and for 3-pentanone 8×10^{-4} (this work). The absorption cross-section is 3×10^{-19} cm² (this work) whereas 2×10^{-20} cm² for 3-pentanone [39]. Thus, the total LIF-signal from toluene in nitrogen is about 1500× stronger than that from 3-pentanone. In air, the toluene-LIF signal decreases by a factor of 50 and through a WG320 approximately 1/15 of the total signal are detected. Thus, the signal from the long wavelength part of the two-color detection is still about two times stronger than total 3-pentanone LIF at roomtemperature and 1 bar air. Whereas the temperature sensitity of the two signals is similar (decreasing about 1 order of magnitude from 300 to 600 K), 3-pentanone LIF increases stronger with increasing air pressure as toluene-LIF is quenched by oxygen (see chapter 4.5). It can thus be concluded, that the toluene-LIF signal from the "blue" detection channel is much stronger than total 3-pentanone LIF whereas signal from the "red" detection channel is within the same order of magnitude for engine-related conditions. Additionally, toluene may be better suited for engine applications as it is a component of commercial gasoline.

9.3 Quantitative oxygen concentration imaging

Two different techniques will be presented for the measurement of oxygen concentration in inhomogeneously seeded, isothermal flows. In this case, the LIF-signal depends on both, the local tracer concentration and the local oxygen concentration. Therefore, at least two pieces of information are required to evaluate oxygen concentration. One option is to take advantage of the red-shift of the toluene-LIF spectrum with increasing oxygen concentration and to detect two different parts of the emission spectrum (section 9.3.1). The other option is to use two different tracers with a different response of the LIF signal on the presence of oxygen 9.3.2.

9.3.1 Two-color detection using toluene-LIF

The toluene-LIF spectrum is shifted to the red with increasing oxygen partial pressure when excited with 248 nm (cf. Fig. 13), i.e. the longer emission wavelengths are less susceptible to oxygen quenching. Similar to the two-color technique employed for temperature measurements (see section 9.2.2), this red-shift can be used to detect oxygen concentrations in iso-thermal, inhomogeneously seeded flows. The sensitivity of different filter combinations is shown in Fig. 52. It can be seen that sensitivity is

best below 200 mbar oxygen. From Eq. Note, that the sensitivity of the spectral shape to oxygen is decreasing with increasing temperature and this technique yields therefore best results for room-temperature flows.



Fig. 52: Signal ratio of different parts of the toluene-LIF spectrum as a function of oxygen partial pressure at 296 K; calculated for various filter combinations.

The setup of the demonstration experiment is the same as in Fig. 40. The co-flow consisted of air seeded with approximately 0.3% toluene; the jet consisted of nitrogen seeded with about 1% toluene. The jet was unheated is this case. The flow field thus provided an isothermal situation, with inhomogenous oxygen and tracer concentration. Exemplary results of the oxygen distribution measurements are shown in Fig. 53.



Fig. 53: Oxygen concentration in an isothermal flow (296 K) measured by the two-color-detection technique. The jet consists of toluene-seeded (\sim 1%) nitrogen, the co-flow of toluene-seeded (\sim 0.3%) air. Exit velocity is set to 30 m/s.

Mixing of the oxygen-free jet with the surrounding air can be well observed. Uncertainty for values of $n_{oxy} > 180$ mbar is relatively high as the sensitivity of this technique is limited in this range. The technique is therefore best suited for the detection of small amounts of oxygen.

9.3.2 Two-tracer technique

Oxygen concentrations can also be obtained by combining two different fuel tracers that respond differently to oxygen quenching and can be detected separately upon excitation with a single laser wavelength. A suitable tracer pair is toluene and 3-pentanone. Details on this technique can be found in [66,104]. To give a complete overview on tracer-imaging strategies, a brief review will be presented here.

LIF signals from 3-pentanone (centered at 420 nm) and toluene (centered at 280 nm) can easily be spectrally separated. Oxygen quenching of 3-pentanone (3P) LIF can be neglected whereas it is strong for toluene LIF. Basically, the 3P-LIF signal gives the tracer concentration, whereas the toluene-LIF signal is a function of both, tracer and oxygen number density. Starting from Eq. (2-2)

$$S_{fl}(n_{oxy}) \sim n_{tracer} \sigma_{abs} \frac{k_{fl}}{k_{tot} + \tilde{k}_{q}^{oxy} n_{oxy}}$$
(2-2)

it is easily deducted that the signal ratio S^{R} is given by:

$$S^{R} = \frac{S_{fl}^{3p}}{S_{fl}^{tol}} = c(k_{tot}^{tol} + \widetilde{k}_{q}^{oxy} n_{oxy})$$
(9-7)

If oxygen quenching is the dominant de-excitation process for toluene (i.e. $k_{tot} \ll k_q n_{oxy}$), the signal ratio is proportional to the oxygen number density. In general (i.e. for elevated temperatures or short excitation wavelength), the data presented in chapter 4 can be used to obtain a calibration curve.

This technique was demonstrated for room temperature flows [104] and has been later extended to engine measurements [10]. In Fig. 54 exemplary results are shown.



Fig. 54: Local oxygen concentration (single shot) for laminar (left) and turbulent (right) mixing, measured with the two-tracer technique. In each image, the left beam consists of nitrogen, the right one of air, both seeded with toluene and 3-pentanone.

9.3.3 Summary of tracer-based oxygen imaging strategies

Both techniques presented in this chapter allow tracking oxygen concentrations in isothermal flows with similar experimental expense. However, the two-color-detection technique is restricted to relatively low oxygen partial pressures, where sensitivity of this technique is best. The two-tracer technique works best at high oxygen partial pressures, where oxygen quenching of the toluene-LIF signal is strong. The techniques can thus be employed complementary.

10 Summary

In recent years toluene has been a popular tracer for fuel visualization using laserinduced fluorescence (LIF). Despite its frequent application for in-cylinder mixing studies in the compression stroke of IC engines, little has been know on the LIF signal dependence on engine-related temperature and bath gas conditions. Thus, a quantitative signal interpretation has been impossible.

In this work, absorption cross-sections, fluorescence quantum yields and fluorescence quenching efficiencies by oxygen after excitation at 266 nm and 248 nm has been investigated in the temperature range of 300 – 950 K in nitrogen, and from 300 – 700 K when oxygen was present. With increasing temperature, the absorption spectrum exhibits significant broadening, an increasing absorption cross-section, and a red-shift with increasing temperature. Absorption cross-sections at 266 nm show strong temperature-dependence due to the broadening of the two adjacent absorption features at 266.8 and 263.5 nm. Absorption at 248 nm is temperatureindependent up to 950 K. Fluorescence quantum yields show a strong dependence on temperature decreasing by three orders of magnitude for both 266-nm and 248nm excitation. The relative strength of oxygen quenching is decreasing with increasing temperature. For higher vibrational excitation (e.g. short excitation wavelength or elevated temperature) the oxygen quenching of toluene fluorescence does not show Stern-Volmer behavior. This has been attributed to the increasing importance of an intramolecular, non-radiative decay process, namely internal conversion.

A semi-empirical model based on photophysical considerations has been developed, that satisfactorily describes the available experimental data. It can predict signal intensities for higher oxygen partial pressures (up to 10 bar of air) within the investigated temperature range (300 - 700 K). The intramolecular non-radiative decay is modeled as a biexponential decay. The slower component is attributed to intersystem crossing (ISC), the faster one to internal conversion (IC). With raising temperature IC shows an increasing impact.

The fluorescence of ketones had been widely investigated in other studies in the context of combustion related tracer-LIF-based mixing diagnostics. A photophysical model for acetone and 3-pentanone had been available. In this work, absolute

fluorescence quantum yields for pure acetone and 3-pentanone have been measured using 308, 266, and 248-nm excitation by calibration of the optical system with Rayleigh scattering from nitrogen. At 20 mbar using 308-nm excitation, the fluorescence quantum yields for acetone and 3-pentanone are $7\pm1\times10^{-4}$ and $1.1\pm0.2\times10^{-3}$ respectively, and each value decreases with decreasing excitation wavelength and increases with increasing bath gas (nitrogen) pressure. These results allow absolute calibration of the model and provide new data on the LIF-signal intensity as a function of excitation wavelength and pressures below one bar. The model in its original form was able to predict the relative signal-dependence on both parameters. However, model parameters had to be adjusted in order to allow absolute signal predictions.

The predictive capability of the toluene and the 3-pentanone-LIF model for enginerelated conditions (i.e. simultaneously elevated pressure *and* temperature) has been evaluated. This was done by comparison of predicted toluene-LIF signal intensities with experimental data obtained in an optically accessible engine where pressure and temperature are reasonably well known. Whereas the toluene model was in good agreement with the experimental data, the 3-pentanone model showed significant shortcomings. Lifetime measurements at elevated temperatures with subns resolution have been suggested to improve the understanding and hence modeling of ketone-LIF.

Toluene LIF was further investigated as a means for in-cylinder fuel/air ratio measurements. It is shown that the popular assumption of toluene LIF being proportional to the fuel/air ratio ϕ (FARLIF) breaks down for most of the pressure and temperature conditions present in the compression stroke of internal combustion engines. The FARLIF technique assumes that collisional quenching by oxygen is the dominant de-excitation channel. However, for most conditions intramolecular non-radiative decay, which increases strongly with temperature, can not be neglected. With increasing vibrational excitation the characteristic behavior of toluene LIF shifts from *signal* ~ *fuel/air ratio* towards *signal* ~ *fuel number density*. With additional temperature information, however, the new toluene-LIF model enables quantitative signal interpretation.

The distinct temperature- and oxygen-dependence of toluene fluorescence opens a number of possibilities for quantitative measurements of temperature and oxygen concentration in addition to the fuel/air ratio. New imaging strategies have been demonstrated in a heated, turbulent, free jet. In the case of homogenous tracer distribution, a one-color detection strategy provides temperature fields with high resolution. For systems with inhomogenous tracer distribution (e.g. mixing studies), a two-color-detection technique (i.e. using two cameras but a single excitation wavelength) is developed and demonstrated for the measurement of temperature and oxygen distribution.

11 References

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