

Effects of hydrogen addition on soot formation in flames:  
experimental investigation by laser imaging

PhD Thesis

Anshul Nilesch Seecharam

Department of Chemical and Process Engineering  
University of Strathclyde, Glasgow

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# Abstract

Soot emissions from combustion processes have adverse effects on human health and the environment. As a result, much attention has been paid to the reduction of soot in combustion systems. Hydrogen is of increasing interest as an energy carrier for combustion applications, including its use in blends with carbon-containing fuels. Since hydrogen addition may alter the formation of soot particles and their precursors, depending on the operating conditions, it is important to understand its influence on soot nucleation and growth. In this work, the effects of hydrogen addition were studied in an atmospheric-pressure, ethylene-air, premixed flat flame over a range of carbon-to-oxygen (C/O) ratios, spanning from the nucleation condition to highly sooting conditions (C/O = 0.59 - 0.79). Hydrogen-doped flames were obtained by replacing a portion of the premixed gas with hydrogen, thus maintaining a constant C/O ratio and the total molar flow rate of the feed gas.

Laser-induced incandescence (LII) experiments have been carried out to determine how hydrogen affects soot concentration and LII decay times (indicative of primary particle size). In the C/O-ratio measurements, which were carried out at a fixed height above burner (HAB) of 16 mm, hydrogen addition was found to significantly reduce soot concentration and LII decay times in all the flames studied, with the extent of reduction being highly dependent on the C/O ratio. The inhibitory effect of hydrogen on soot concentration and LII decay time was found to increase sharply with increasing C/O ratio from the nucleation condition to C/O = 0.63, before declining more gradually thereafter. Another interesting observation is that the C/O ratio at which the threshold of nucleation was observed in the hydrogen-free flame was found to be only slightly sensitive to the addition of hydrogen, shifting from 0.59 to 0.60. Height-scan

measurements were also carried out in the highly sooting flame ( $C/O = 0.79$ ) and a sparingly sooting flame ( $C/O = 0.69$ ), in which a reduction in soot concentration and LII decay times was observed at all heights, with the extent of reduction being higher at lower HABs.

These observations naturally lead to examining how fluorescence associated with polycyclic aromatic hydrocarbons (PAHs) and related structures responds under corresponding flame conditions. Some of these structures may be linked to soot nucleation. Laser-induced fluorescence (LIF) measurements were therefore carried out using three excitation wavelengths to determine whether the effect of  $H_2$  addition on the fluorescence signal reflects the corresponding reduction in soot concentration. The LIF measurements were radiometrically calibrated. This is an important feature of the present work, since the spectra are corrected for the wavelength-dependent response of the detection system and reported on a quantitatively reproducible basis.

Contrary to the reduction observed in soot concentration, hydrogen addition increased the LIF signal at all three excitation wavelengths in the fixed-height (16 mm HAB) C/O-scan measurements. In the height-scan measurements, hydrogen addition increased the LIF signal at all heights in the nucleation flame ( $C/O=0.59$ ), whereas the response in the rich flame ( $C/O=0.79$ ) was height-dependent, with reductions in LIF signal observed only at lower HABs. Since PAH-related structures are considered to play important roles in soot nucleation and growth, it is therefore surprising that they should be more abundant in the  $H_2$ -doped flames, despite the corresponding reduction in soot volume fraction observed by LII.

Principal component analysis (PCA) was applied to the LIF spectra to identify the dominant modes of spectral variation, which provided a basis for extracting approximate spectral components separately for each excitation wavelength. For 266 and 355 nm excitation, the measured spectra were reproduced well using an approximate UV-visible component and a visible component, whereas the 532 nm spectra were adequately represented by a visible component alone. Fluorescence contributions in the visible emission region have recently been discussed in relation to PAH-related structures potentially involved in soot nucleation, such as resonance-stabilised radicals and

aliphatically bridged dimers of PAHs. A notable finding of the present work is that the extracted visible components from all three excitation wavelengths follow very similar trends with C/O ratio, with broadly similar increases in signal following hydrogen addition. These results suggest that the visible components may arise either from the same underlying emitting population or from different contributions that track each other very closely.

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# Chapter 1

## Literature review: soot formation, hydrogen effects, and optical diagnostics

### 1.1 Impact of soot on environment and health and importance of soot studies

The past several decades have been marked by growing concern over the effects of combustion-generated particles on human health and the environment. Soot particles, in particular, have been identified as a significant public health hazard in numerous scientific studies [5,6]. Soot is produced during the incomplete combustion of hydrocarbon fuels, when fuel-rich regions, insufficient oxidiser, low local temperatures or poor fuel–air mixing prevent complete oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [7]. Under these conditions, carbon-containing intermediates undergo chemical growth and particle formation, producing fine carbonaceous particles. Soot generally consists of aggregates of small primary particles, with size, morphology and composition depending strongly on the fuel and combustion conditions [8]. Its emission contributes to air pollution, smog and haze, while inhaled fine particles can aggravate respiratory and cardiovascular conditions [7]. In addition, soot emissions have received significant attention due to their contribution

to climate change [9–11]. Reduction of soot will not only mitigate global warming but will also save lives and improve people’s health [12]. As a result, much attention has been paid to the reduction of soot generation in combustion systems.

Careful and relevant experimental studies remain necessary both to advance the understanding of soot formation and to improve the predictive capability of numerical models [13]. Consequently, soot formation is often studied in well-controlled laboratory flames, where fuel composition and flame conditions can be controlled more precisely. These configurations provide a simplified framework for generating experimental data, including soot volume fraction, particle size and number density, which are useful for model validation [14–16].

Hydrogen addition is also of practical and scientific interest because it has been shown that the introduction of hydrogen into sooting flames may inhibit the formation of soot particles and their precursors, depending on the operating conditions [15,17,18]. This is relevant to the wider interest in blending green  $H_2$  with low-carbon fuels such as biogas for energy generation and industrial heating [19]. Studying the effects of hydrogen on soot formation is therefore the focus of this work. Before considering how hydrogen may influence soot formation, it is first necessary to review the fundamental stages of soot formation.

## 1.2 Fundamentals of soot formation

Efforts to reduce soot emissions depend on understanding the physical and chemical pathways by which hydrocarbon fuels are converted into soot particles. While the main stages of soot formation are broadly established, the detailed mechanisms remain complex and are still debated, especially the soot inception phase [20–25], which involves the transition from gas-phase precursors to nascent soot particles. Figure 1.1 presents a conceptual schematic of the soot-formation pathway. Soot formation is commonly described as a sequence of fuel pyrolysis, formation of gas-phase soot precursors, particle inception (nucleation), and subsequent surface growth and agglomeration [1, 26, 27].

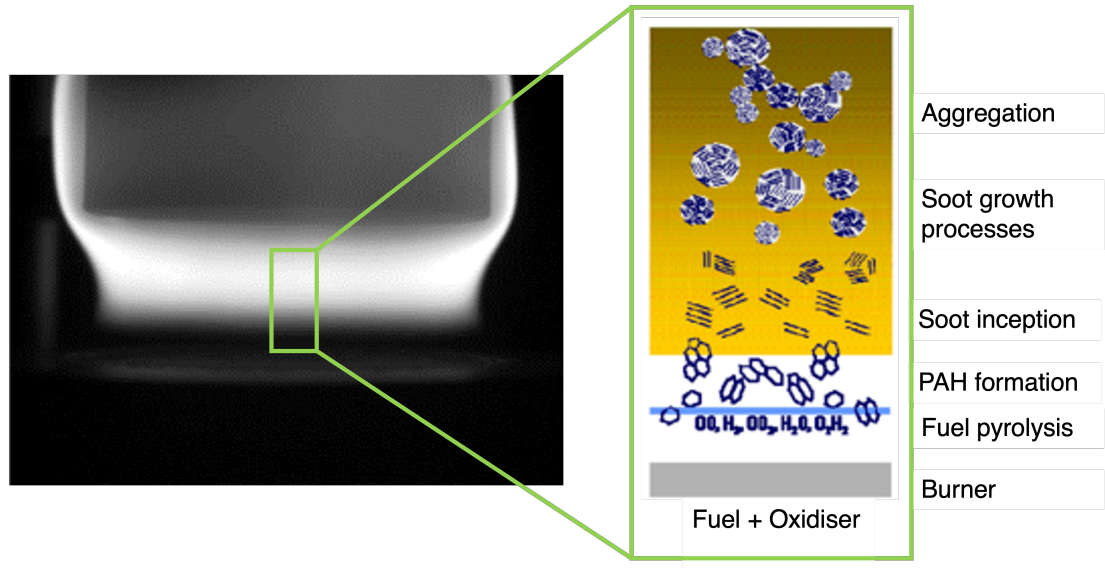


Figure 1.1: Conceptual schematic of the soot-formation pathway in a premixed flat flame, from fuel pyrolysis and PAH formation to soot inception, particle growth, and aggregation. The right-hand schematic is adapted from Wang [1].

### 1.2.1 Fuel pyrolysis and formation of gas-phase precursors

Pyrolysis, the thermal decomposition of hydrocarbons in the absence of oxygen, initiates soot formation by producing unsaturated intermediates such as acetylene ( $C_2H_2$ ) and resonantly stabilised radicals such as propargyl ( $C_3H_3$ ) [28, 29]. These species are widely recognised as important building blocks in aromatic ring formation. In particular, the self-reaction of propargyl radicals has been identified as a key pathway to first-ring formation in flames, leading to benzene formation under flame conditions [1]. Subsequent molecular growth into larger PAHs proceeds mainly through the hydrogen-abstraction–acetylene-addition (HACA) mechanism, which is highly reversible and kinetically controlled [30]. These processes generate larger PAHs that are widely regarded as important intermediates in soot formation, although the specific pathway from gas-phase aromatics to nascent soot particles remains debated, which is discussed next. An example of PAH growth through the HACA mechanism is shown in Figure 1.2.

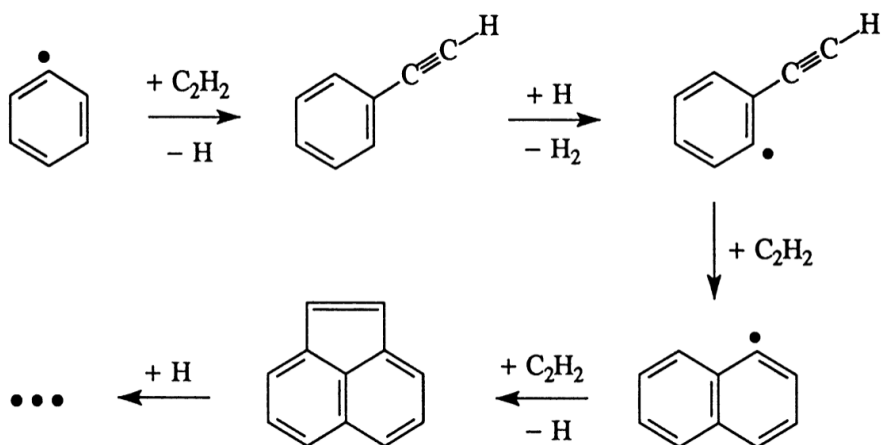


Figure 1.2: Example of PAH growth through the HACA mechanism, illustrating H-abstraction, acetylene addition, and ring closure to form a larger aromatic structure [2].

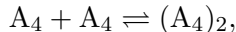
### 1.2.2 Commonly proposed soot nucleation mechanisms

A key bottleneck in soot-formation research is the transition from gas-phase PAHs to condensed carbonaceous particles, commonly referred to as soot inception or nucleation [21]. Incipient soot particles have typically been reported to be approximately 1–6 nm in size and may include a range of structures, from disordered aromatic/aliphatic material to more ordered stacked PAH arrangements [26]. Given the complexity of this transition, several soot-nucleation mechanisms have been proposed in the literature and are discussed below.

#### PAH dimerisation

One of the most widely discussed pathways for soot inception is the dimerisation of PAHs [22,30]. Early soot-inception models treated the initial transition from molecular precursors to particles mainly as a chemical growth process, in which aromatic species increase in size until they begin to exhibit condensed-phase behaviour [31]. However, chemical growth alone was not sufficient to reproduce experimentally observed particle sizes [32]. Subsequent modelling therefore introduced the physical association of aromatic species, with PAH dimerisation often used to represent the transition from gas-phase PAHs to incipient soot particles.

In many soot-formation models, this transition is represented by the association of two moderately sized PAHs, often pyrene, to form a stacked dimer [7, 31, 33]. In this description, two planar aromatic molecules are held together primarily by van der Waals interactions. The process is often represented as reversible:



where  $A_4$  represents pyrene and  $(A_4)_2$  represents the corresponding stacked dimer. Pyrene was proposed because it is a relatively stable four-ring PAH, and its concentration can be comparable to the number density of soot nuclei under some flame conditions [1]. Support for a dimerisation-based interpretation has also been reported experimentally, including observations of a strong relationship between soot volume fraction and the square of pyrene concentration in nucleation-dominated methane flames [18]. Broadband fluorescence in sooting flames had also been interpreted as being consistent with possible contributions from PAH dimers, including pyrene and perylene dimers, whose fluorescence is red-shifted relative to the corresponding monomers [22].

However, the physical stability of simple PAH dimers remains debated. Dimers held only by van der Waals interactions are generally expected to be too weakly bound to survive at flame temperatures, particularly for small and moderately sized PAHs [34, 35]. Although transient pyrene dimers may persist briefly under flame conditions [31], simple physical association alone is unlikely to fully explain the formation of stable incipient soot. This has motivated the proposal that PAH dimers or clusters must be chemically stabilised before they can develop into soot nuclei.

### **Chemically stabilised and bridged PAH structures**

The limited stability of purely van der Waals-bound PAH dimers has motivated alternative descriptions of soot inception in which aromatic units become chemically stabilised through covalent bonding. In this view, the initial association of PAHs is not sufficient on its own; instead, weakly bound aromatic complexes must undergo further reactions, such as hydrogen abstraction and carbon–carbon bond formation, to produce structures



stable enough to act as soot nuclei [30, 34, 36, 37].

One proposed route involves alkylated and aliphatically bridged PAHs. Atomistic studies by Elvati and Violi [35] suggested that aromatics with aliphatic side chains can form more stable molecular complexes than small pericondensed PAHs such as pyrene. These aliphatic groups may promote molecular proximity and provide reactive sites for covalent linking, allowing aromatic units to form more stable three-dimensional structures rather than relying solely on weak intermolecular forces. This interpretation is also consistent with experimental observations of aliphatic material in nascent or young soot particles [38–40]. Direct experimental evidence for alkylated and aliphatically bridged multicore PAHs was reported by Adamson et al. [41] using flame-sampled high-resolution tandem mass spectrometry. They identified structures containing either alkyl substituents attached to a single aromatic core or multiple aromatic cores connected through aliphatic bridges.

### **Resonance-stabilised radicals**

More recent studies have proposed that resonance-stabilised radicals (RSRs) may play an important role in soot inception [23, 42]. These have been proposed as one class of reactive intermediates that may contribute to the formation and growth of chemically linked aromatic precursor structures. Unlike stable PAH molecules in which all electrons are paired, RSRs contain an unpaired electron that is delocalised over the aromatic structure, allowing them to retain radical character during molecular growth. RSR-based reactions have been shown to form chemically bonded aromatic clusters, providing a possible bridge between gas-phase precursors and incipient soot particles [25].

Ex-situ high-resolution microscopy of incipient soot sampled from premixed ethylene–air flames [20] observed aromatic structures containing aliphatic groups and peripheral five-membered rings, and proposed that hydrogen removal from these motifs could generate resonantly stabilised  $\pi$ -radicals. EPR measurements of soot sampled across the inception region also detected persistent carbon-centred aromatic radicals associated with particle nucleation and initial growth [21].

Elias et al. [23, 43] linked these radical-containing structures to visible fluorescence

from soot-inception species. Using excitation–emission matrix (EEM) fluorescence measurements, they identified visible features in the soot-inception region consistent with RSR-like species. Density functional theory (DFT) calculations further supported this assignment by predicting visible electronic transitions for radical PAH-type structures [23].

Overall, RSR-based mechanisms provide a route by which PAH-derived species may form chemically linked, three-dimensional structures during soot inception. However, the involvement of RSRs in soot inception is still at an early stage of investigation and remains a topic of active debate. It remains unclear whether RSR PAHs act as primary soot precursors or transient intermediates in the growth process, and no single soot-inception mechanism has yet been conclusively established.

### 1.2.3 Soot surface growth

After particle inception, soot mass increases mainly through surface growth, while particle coalescence and agglomeration also contribute to particle-size evolution. Surface growth is a heterogeneous process in which gas-phase hydrocarbon species react with active sites on the soot surface and become incorporated into the particle [44]. In premixed ethylene–air flames, early measurements showed that this growth could be accounted for primarily by the reaction of acetylene with soot particles [44].

The H-abstraction–C<sub>2</sub>H<sub>2</sub>-addition (HACA) mechanism is commonly used to describe soot surface growth. In this mechanism, hydrogen abstraction creates an active radical site on the soot surface. Acetylene can then add to this site and, through ring-closure and hydrogen-loss steps, become incorporated into the aromatic surface structure [45]. Numerical simulations have shown that the surface growth rate is proportional to the acetylene concentration [45]. However, acetylene addition occurs only at reactive surface sites, meaning that soot growth also depends on the number and reactivity of available active sites.

Competing surface reactions include oxidation, where active sites react with O<sub>2</sub> or OH, resulting in carbon removal. Thus, soot surface chemistry reflects a balance between HACA-driven growth and oxidation [46]. As soot particles mature, the C/H

ratio increases and the number of hydrogenated surface sites available for further growth decreases [46]. However, alongside surface growth, coalescence and agglomeration contribute to particle-size evolution. Mature soot is typically composed of primary particles 10–50 nm in diameter [26].

### 1.3 Hydrogen addition as a soot-reduction strategy

Hydrogen addition has received attention both as a low-carbon energy carrier and as a component in fuel blends for practical combustion systems, including internal combustion engines [47–49]. H<sub>2</sub>–hydrocarbon blends have also been investigated as a route for reducing soot and gaseous pollutant emissions [50]. In addition, there is growing interest in blending green H<sub>2</sub> with biogas [19, 51], which may be relevant to energy generation and industrial heating.

The effect of hydrogen addition on soot formation is, however, not universal. Some studies have shown that hydrogen can inhibit the formation of soot particles and their precursors, although the magnitude and even the direction of this effect can depend on the flame operating conditions [15, 50]. These effects are therefore often examined in well-controlled laboratory flames, including premixed and diffusion flames, as discussed in the following section.

### 1.4 Influence of hydrogen on soot and its precursors

Hydrogen addition has generally been reported to suppress soot formation in hydrocarbon flames. The influence of hydrogen addition on soot formation has been investigated across a range of flame configurations, including co-flow diffusion flames [52–54], inverse co-flow diffusion flames [13] and counterflow diffusion flames [55].

In diffusion flames, a number of experimental and numerical studies have shown that H<sub>2</sub> addition reduces soot formation, with reduction reported in soot volume fraction, particle number density and precursor signals [13, 52, 54–56]. Among the first experimental works on diffusion flames, Gulder et al. [52] investigated hydrogen and helium addition in a laminar ethylene diffusion flame. As helium shares hydrogen’s thermal and

transport properties but lacks chemical reactivity, their comparison isolated hydrogen’s chemical effects. Despite minimal impact on flame temperature, hydrogen suppressed soot more effectively, indicating a primarily chemical mechanism. Similarly, Ezenwajaku et al. [13] reported reductions in both PAH laser-induced fluorescence and laser-induced incandescence signals in ethylene inverse diffusion flames with increasing  $H_2$  addition, indicating that hydrogen affects both precursor fluorescence and soot formation. Other diffusion-flame studies have also reported reductions in soot concentration with  $H_2$  addition [54–56].

Premixed flames are particularly relevant to the present work, but the literature on hydrogen effects in premixed sooting flames is more limited. An early study by Haynes et al. [57] examined premixed ethylene–air flat flames at atmospheric pressure with up to 3%  $H_2$  added to the unburned gas mixture. Their measurements showed that  $H_2$  addition lowered the critical C/O ratio for soot inception, indicating that soot formation began at leaner conditions.

Hydrogen effects have also been examined in richer premixed ethylene–air flames. Using three-angle light scattering (TALS), light extinction, and transmission electron microscopy (TEM), De Iuliis et al. [15] investigated flames with 20% and 40%  $H_2$  substitution and observed significant reductions in soot volume fraction and particle size. This suppression was attributed to inhibited growth of soot precursors, leading to a reduction in soot concentration. More recently, Do et al. [18, 50] investigated nucleating and slightly sooting premixed methane flames using a combination of gas chromatography (GC), jet-cooled laser-induced fluorescence (JCLIF), laser-induced incandescence (LII), cavity ring-down spectroscopy (CRDS), and scanning mobility particle sizing (SMPS). They showed that the effect of hydrogen depends strongly on whether it is added or substituted:  $H_2$  substitution inhibited soot formation, whereas  $H_2$  addition promoted the formation of nascent soot particles.

Several explanations have been proposed for the soot reduction observed with  $H_2$  substitution. In the premixed methane flames studied by Do et al. [18, 50],  $H_2$  substitution mainly reduced the formation of aromatic soot precursors, including benzene, naphthalene and pyrene. The authors interpreted this within a HACA-based framework:

under substitution conditions,  $\text{H}_2$  was proposed to favour the branching reaction



with the increased laminar flame speed used as evidence for this enhanced pathway. This conversion of H atoms into O and OH was suggested to increase the oxidation of aromatic species and reduce the H atoms available for PAH growth through HACA, thereby lowering aromatic precursor concentrations and, consequently, soot formation. Numerical studies of premixed flames have also reported similar soot-reduction trends with  $\text{H}_2$  addition, generally linking the reduction to lower concentrations of soot precursors such as  $\text{C}_2\text{H}_2$  and PAHs, together with inhibited inception and surface-growth processes [58–60].

The available premixed-flame studies also suggest that the observed changes in soot formation may not be primarily driven by large thermal changes. De Iuliis et al. [15] reported that, in rich premixed ethylene flames, 40%  $\text{H}_2$  substitution reduced the calculated adiabatic flame temperature by only about 50 K, despite producing a marked reduction in soot. Similarly, Do et al. [18, 50] reported that, in nucleating and slightly sooting premixed methane flames, the introduction of only a small amount of hydrogen caused little change in peak flame temperature, typically less than about 20 K, even though  $\text{H}_2$  substitution strongly inhibited soot formation. In these studies, hydrogen substitution shifted the temperature profile closer to the burner, which was attributed to an increase in laminar flame speed, whereas hydrogen addition caused little change in the temperature profile. These observations suggest that, under the premixed-flame conditions, the effect of hydrogen on soot and precursor formation may be more likely to arise from chemical and kinetic effects than from temperature changes alone.

Previous studies have generally focused on specific regimes, such as rich sooting flames or nucleation/slightly sooting flames. Information remains limited on how hydrogen affects soot formation across a broader range of flame conditions.

## 1.5 Measurement techniques for soot and precursors

Soot and precursor measurements in flames can be broadly divided into intrusive sampling methods and non-intrusive optical diagnostics. Intrusive approaches, such as probe sampling followed by SMPS or TEM, can provide detailed information that is difficult to obtain optically. SMPS is commonly used to measure particle size distributions [61], while TEM provides information on soot morphology, primary particle size and aggregate structure [15]. However, these methods require material to be extracted from the flame, which can perturb the flow and may alter the sampled species.

In-situ laser diagnostics are therefore particularly useful for flame studies because they can probe soot and precursor species without physically disturbing the flame. Several optical techniques have been applied to soot measurements, including light extinction for soot volume fraction, elastic light scattering for particle or aggregate sizes, photoacoustic detection for soot volume fraction, and laser-induced incandescence (LII) for spatially and temporally resolved soot measurements, providing information on soot concentration and, through time-resolved signal decay, particle size [26, 62–64].

Precursor species and incipient soot material can also be investigated using a range of sampling-based and spectroscopic techniques. Molecular-beam mass spectrometry can provide species concentration profiles and identify gas-phase intermediates and PAHs [65], while jet-cooled LIF can provide quantitative measurements of selected aromatic species [50]. AFM/STM can also resolve the molecular structures of soot precursors and incipient soot after sampling [66]. However, these methods also require physical sampling. In contrast, LIF is an in-situ optical technique: it generally cannot provide direct molecular identification, but can provide spatially, spectrally or temporally resolved measurements of precursor fluorescence within the flame.

The present work therefore focuses on LII and LIF as complementary non-intrusive diagnostics, with LII used to quantify soot volume fraction and decay times related to soot particle size, and LIF used to examine changes in precursor fluorescence intensity and spectral shape with excitation wavelength, flame condition and hydrogen addition.

## 1.6 Laser-Induced Incandescence (LII)

Laser-induced incandescence (LII) has been used extensively for measurements of soot concentration in a wide range of applications, including laboratory burners and practical, more challenging environments such as high-pressure flames and aero-engine combustors [67, 68].

### Theory of LII

In LII, a short, energetic nanosecond laser pulse is used to heat soot particles within the flame. 1064 nm Nd:YAG lasers are commonly used for excitation because this wavelength is not sufficiently energetic to induce significant fluorescence from soot precursors such as polycyclic aromatic hydrocarbons (PAHs) [69]. The illuminated soot particles absorb the laser energy and are rapidly heated to high temperatures (around 4000 K), which is much higher than the surrounding gas temperature.

As a consequence of this rapid temperature rise, the soot particles emit thermal radiation, commonly referred to as incandescence. After the laser pulse, the particles cool back towards the local gas temperature. The cooling behaviour is governed by several heat-transfer processes, including conduction to the surrounding gas, radiative emission and sublimation/vaporisation at sufficiently high fluence [11]. These processes are shown schematically in Figure 1.3. Under atmospheric-pressure, low-to-moderate fluence conditions, the main cooling mechanism is typically conduction to the surrounding gas, while radiative heat loss is comparatively small. Since the cooling rate depends on the soot particle surface-area-to-volume ratio, primary particle sizes can also be extracted from appropriately modelled heat-transfer processes [11, 70].

The emitted incandescence depends strongly on the particle temperature and can be described using Planck's law:

$$I(\lambda, T) = \frac{2hc^2}{\lambda^5} \left( \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \right), \quad (1.2)$$

where  $I(\lambda, T)$  is the spectral radiance,  $T$  is the particle temperature,  $\lambda$  is the emission

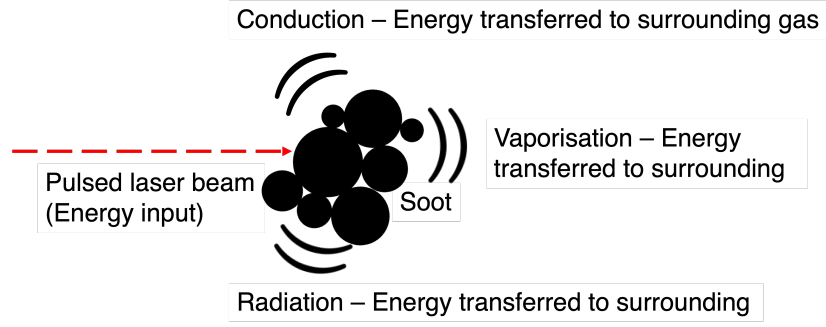


Figure 1.3: Heat-transfer processes taking place during laser-induced heating and cooling of soot particles.

wavelength,  $h$  is Planck's constant,  $c$  is the speed of light and  $k_B$  is Boltzmann's constant.

Melton [71] showed that, when soot particles are heated close to their vaporisation temperature, the peak LII signal can be related to the soot particle number density and diameter as

$$S_{\text{LII}}(T_{\text{max}}) \propto N_p d_p^{3+0.154/\lambda_{\text{det}}}, \quad (1.3)$$

where  $N_p$  is the soot particle number density,  $d_p$  is the soot particle diameter and  $\lambda_{\text{det}}$  is the detection wavelength expressed in microns. Thus, the laser-induced peak thermal radiation is nearly proportional to the local soot volume fraction [14]:

$$f_v \simeq C_{\text{cal}} S_{\text{LII}}(T_{\text{max}}). \quad (1.4)$$

The calibration constant is determined independently under equivalent LII measurement conditions. In this work, this is done using the light-extinction method [14], which is explained next. Alternative approaches, such as two-colour pyrometry, can also be used, but require knowledge of the soot temperature [72].

### Calibration to soot volume fraction

In the extinction method, a laser beam is passed through the soot-laden region of the flame. The presence of soot attenuates the laser intensity, and the transmissivity is



defined as

$$\tau = \frac{I}{I_0}, \quad (1.5)$$

where  $I_0$  is the incident laser intensity measured without the flame and  $I$  is the transmitted intensity measured after the beam has passed through the soot-laden region, as shown in Figure 1.4. According to the Beer–Lambert law, the transmissivity can be

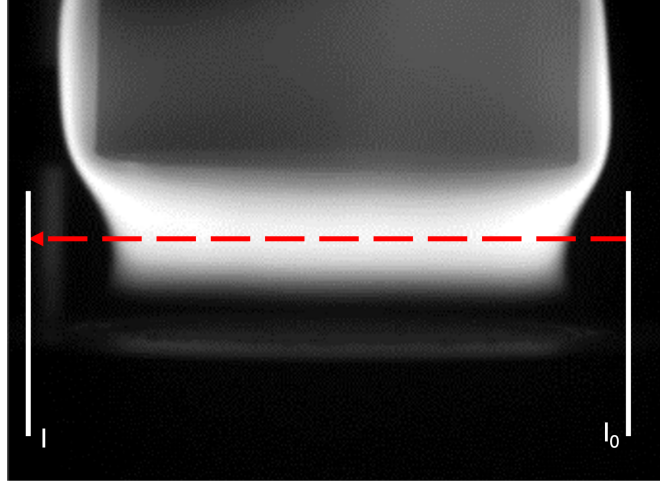


Figure 1.4: Light-extinction measurement through the soot-laden region of the premixed flat flame. The dashed red line indicates the laser path, where  $I_0$  is the incident laser intensity and  $I$  is the transmitted intensity after passing through the flame.

expressed as

$$\frac{I}{I_0} = \exp \left( - \int_0^L K_{\text{ext}} dl \right), \quad (1.6)$$

where  $K_{\text{ext}}$  is the local extinction coefficient and  $L$  is the optical path length through the absorbing medium. If the extinction coefficient is assumed to be uniform along the beam path [73, 74], this reduces to

$$\ln \left( \frac{I_0}{I} \right) = K_{\text{ext}} L. \quad (1.7)$$

For soot particles much smaller than the laser wavelength, the measurement lies within the Rayleigh limit and scattering is small compared with absorption. This is commonly expressed using the scattering parameter,  $\pi D / \lambda_{\text{LEM}}$ , which should remain below approximately 0.3 [74]. Under this condition, the extinction coefficient can be

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approximated by the soot absorption coefficient,

$$K_{\text{ext}} \approx K_{\text{abs,soot}}, \quad (1.8)$$

which is related to soot volume fraction by

$$K_{\text{abs,soot}} = \frac{6\pi E(m)}{\lambda_{\text{LEM}}} f_v, \quad (1.9)$$

where  $E(m)$  is the soot absorption function,  $\lambda_{\text{LEM}}$  is the extinction laser wavelength and  $f_v$  is the soot volume fraction.

Combining this expression with the Beer–Lambert law gives

$$f_v = \frac{\lambda_{\text{LEM}}}{6\pi E(m)L} \ln \left( \frac{I_0}{I} \right). \quad (1.10)$$

The soot volume fraction obtained from extinction is then used to calibrate the LII signal. Assuming a linear relationship between the LII signal and soot volume fraction,

$$f_v(x, y) = C_{\text{cal}} S_{\text{LII}}(x, y), \quad (1.11)$$

where  $S_{\text{LII}}(x, y)$  is the measured LII signal and  $C_{\text{cal}}$  is the calibration constant. The calibration constant is obtained by comparing the integrated LII signal with the soot volume fraction inferred from extinction [14]:

$$C_{\text{cal}} = \frac{\lambda_{\text{LEM}} \ln(I_0/I)}{6\pi E(m) \int_0^L S_{\text{LII}}(x) dx}. \quad (1.12)$$

The main uncertainty in this calibration arises from the soot absorption function  $E(m)$ , which depends on wavelength and soot properties [75]. The value of  $E(m)$  used in this work is discussed in the next chapter.

## 1.7 Laser-Induced Fluorescence (LIF)

As discussed in Section 1.2.2, it is well established that PAHs are the main precursors of soot and play an important role in soot formation, and different soot nucleation mechanisms have been proposed that involve PAHs as key intermediates, however, this mechanism is still poorly understood. Laser-induced fluorescence (LIF) is a non-intrusive spectroscopic technique widely used to detect aromatic species such as PAHs [22, 23, 76, 77], as well as radicals [78], even at very low concentrations (ppm or sub-ppm levels). LIF has therefore been widely used to investigate fuel effects on PAH measurements, with the aim of validating soot models [79]. In most works involving LIF in sooting flames, low laser energies are typically used to avoid interference from LII signals [80].

### Theory of LIF

Fluorescence is the process by which a radical or molecule in the flame is excited by a laser of a specific wavelength; its low-energy state (usually ground state) is changed to a higher-energy state (excited state). While relaxing back from the excited to the ground state, the energy difference between the two states may be released in the form of photons (fluorescence) [81].

As shown in Figure 1.5, following excitation, the molecule first undergoes a non-radiative relaxation (vibrational and rotational energy transfer) to lower ro-vibrational energy levels within the higher electronic energy state, which is subsequently followed by fluorescence emission. The energy of this emission is usually less than the energy absorbed by the molecule, leading to emission at a longer wavelength (redshift). However, under high-temperature conditions, molecules can occupy elevated vibrational levels of the ground electronic state ( $S_0$ ) due to thermal excitation. In such cases, absorption may occur from these thermally populated levels to  $S_1$ , requiring less photon energy. After internal relaxation in the excited state, fluorescence can occur to a vibrational level lower than the initial one. This results in the emission of a photon with higher energy than the absorbed one, producing anti-Stokes-shifted fluorescence. Such anti-Stokes-shifted

fluorescence has been reported in PAH-LIF studies under flame conditions, although its occurrence depends on the excitation wavelength and the contributing molecular species [76, 80].

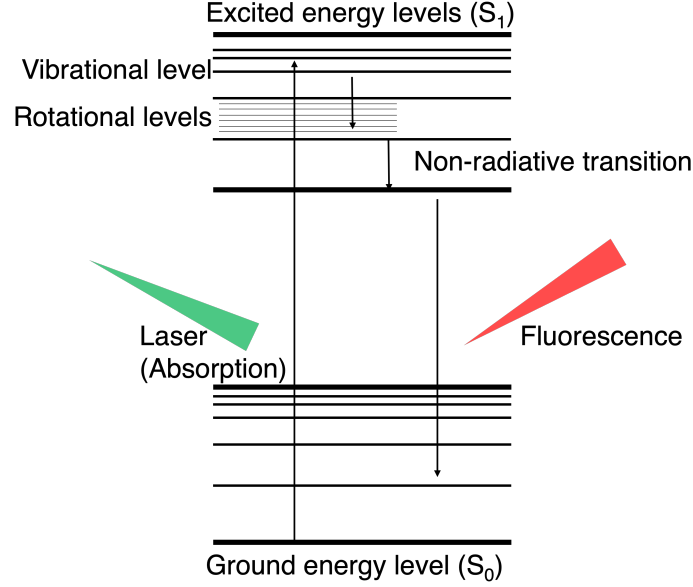


Figure 1.5: Energy-level diagram illustrating laser excitation from the ground electronic state  $S_0$  to the excited electronic state  $S_1$ , followed by non-radiative relaxation and fluorescence emission.

### 1.7.1 Interpretation of LIF spectra

A measured LIF spectrum can be viewed as a weighted sum of contributions from all species that absorb at the excitation wavelength and fluoresce within the detection range. In schematic form [22, 82]:

$$I_{\text{calc}}(\lambda) = I_L \sum_i y_i \sigma_i(\lambda_{\text{exc}}) N_i S_i(\lambda), \quad (1.13)$$

where  $I_{\text{calc}}(\lambda)$  represents the calculated fluorescence energy density spectrum,  $I_L$  is the laser fluence in  $\text{J m}^{-2}$ ,  $y_i$  is the effective fluorescence quantum yield of species  $i$ ,  $\sigma_i(\lambda_{\text{exc}})$  is the absorption cross-section at the excitation wavelength in  $\text{m}^2$ ,  $N_i$  is the number density of species  $i$  in  $\text{m}^{-3}$ , and  $S_i(\lambda)$  is the normalised emission spectrum and has units of  $\text{nm}^{-1}$ , and  $I_{\text{calc}}(\lambda)$  has units of  $\text{J m}^{-3} \text{nm}^{-1}$ .

In principle, if  $\sigma_i$ ,  $y_i$  and  $S_i(\lambda)$  were known at flame conditions for all relevant precursor species, the measured spectrum could be reconstructed as a sum of individual molecular contributions. In practice, however, high-temperature gas-phase fluorescence data remain incomplete and substantial spectral overlap is expected. A measured PAH-LIF signal cannot generally be converted directly into PAH concentration. The fluorescence intensity depends not only on species concentration, but also on temperature-dependent absorption cross-sections and Boltzmann population factors, collisional quenching, and the spectral overlap of multiple emitting species [83–85]. The recorded spectrum therefore represents a composite signal from several PAHs rather than the concentration of an individual species. While the choice of excitation and detection wavelengths can favour different PAH size classes, the resulting LIF signal still represents a mixture of multiple species. As a result, selective identification and quantification of individual PAHs generally require more advanced techniques, such as jet-cooled LIF or photoionisation coupled with time-of-flight mass spectrometry [18].

### 1.7.2 Excitation wavelength selection and spectral characteristics

LIF measurements are typically carried out using UV and visible excitation wavelengths [80]. The general understanding is that, as the PAH aromatic system becomes larger, the  $\pi-\pi^*$  energy gap decreases and the wavelength of the lowest-energy transition increases, shifting the absorption bands to longer wavelengths [76]. Excitation in the UV can therefore produce fluorescence from a broad range of PAH species, since many size classes absorb in this region [76]. In general, smaller PAHs tend to emit at shorter wavelengths, while larger PAHs emit at longer wavelengths. This has led to the common use of broad emission ranges to group PAH-LIF signals according to aromatic size. In particular, LIF signals from UV excitation detected at 320–380 nm are commonly associated with 2–3 ring aromatics, whereas emission above 400 nm is more often attributed to larger species with four or more rings [23, 76, 82], as well as clustered structures. This trend is illustrated in Figure 1.6, which shows gas-phase fluorescence spectra of naphthalene, phenanthrene, pyrene and fluoranthene measured in an optical cell at 1073 K by Zhang et al. [3].

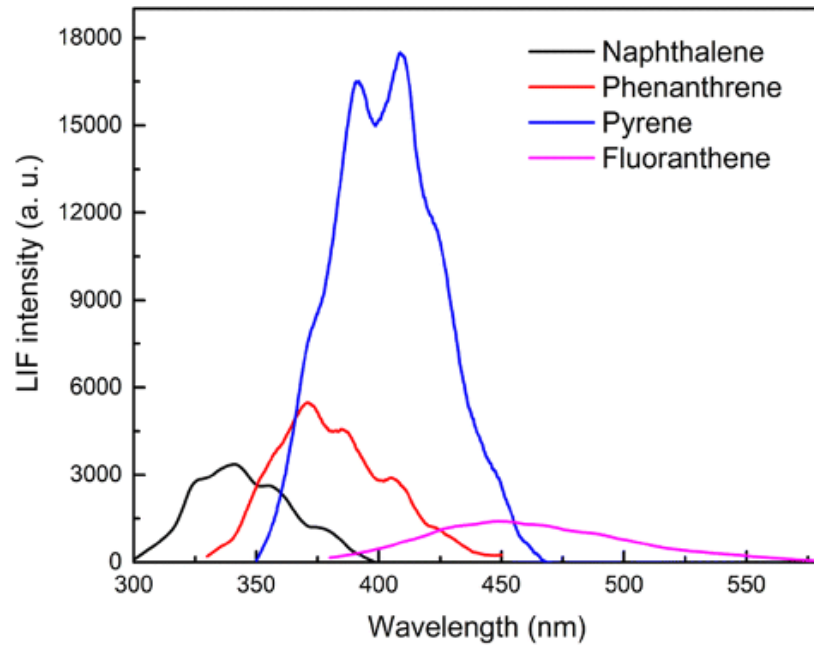


Figure 1.6: Example gas-phase fluorescence spectra of selected PAHs measured in an optical cell at 1073 K: naphthalene, phenanthrene, pyrene and fluoranthene. (Taken from Zhang et al. [3]).

Although these broad wavelength ranges are useful for interpreting PAH-LIF signals, the species responsible for the visible part of UV-excited LIF remain under debate. This emission should therefore not be attributed only to larger PAH monomers. Mercier et al. [22] selected a number of PAHs preferentially formed in a sooting diffusion flame, and fitted them to experimental LIF spectra measured at a range of heights. PAH monomer fits were only satisfactory at the lower heights. Since dimers of moderate-sized PAHs had been proposed as soot-nucleation intermediates and are known to form excimers with broad, red-shifted visible fluorescence, selected PAH dimers were also included in the fitting procedure. This produced a better agreement with the measured spectra, suggesting that visible fluorescence following UV excitation can be consistent with contributions from moderate-sized PAH dimers or excimers. This interpretation was also supported by time-resolved LIF measurements, which showed that fluorescence decay times in the high-temperature soot-inception region were much longer than expected for gas-phase molecular PAHs [22, 86]. This suggested that much of the detected LIF signal could indeed be originating from dimers since they have much longer fluorescence

lifetimes than PAH monomers [87].

However, as discussed in Section 1.2.2, since purely van der Waals-bound PAH dimers are unlikely to remain stable under flame conditions, chemically stabilised dimer-like structures have also been proposed as more stable soot-precursor species. These may include covalently bonded PAH units or aliphatically bridged PAH structures. Theoretical calculations have shown that aliphatically-bridged PAH complexes containing small-to-moderate PAHs can produce visible-range fluorescence [88]. UV-excited visible fluorescence has therefore been linked to aliphatically bridged dimers of PAHs.

Elias et al. [23] used excitation-emission matrix measurements to distinguish different fluorescence contributions during soot formation. In addition to the spectral region attributed to PAH monomers, they identified a separate contribution observed by UV excitation and emission in the visible range, observed in the soot inception zone. The UV-excited visible contribution was therefore interpreted as arising from clusters or aliphatically bridged PAH dimers. This interpretation was supported by DFT calculations, which showed that PAH dimers and aliphatically bridged dimer-like structures are expected to absorb mainly in the UV, close to the corresponding monomer absorption wavelengths.

Visible-excited fluorescence requires separate consideration. In early interpretations, this was treated as a way of probing a more limited group of visible-absorbing precursors, including PAH dimers. However, recent studies have started associating visible-excited fluorescence with resonance stabilised aromatic radicals (RSRs), including RSR PAHs and related aliphatically substituted aromatic radicals formed during soot inception [23]. Although spectroscopic data for RSRs remain limited, gas-phase, jet-cooled radical spectroscopy has shown visible absorption by aromatic RSRs, including trans-1-phenylallyl at about 521 nm and naphthylmethyl radicals in the 580 nm region [89, 90]. Elias et al. [23] used EEM measurements to identify a distinct visible-excited, visible-emitting fluorescence feature that could not be reproduced by reference EEMs of neutral PAH monomers. Since this feature was strongest near the soot-inception region, and TD-DFT calculations showed that radical PAH-type structures can have visible electronic transitions, it was associated with RSR-type aromatic species as possible contributors

to the visible LIF signal.

Although the assignment of LIF signals to specific molecular species remains uncertain, different excitation wavelengths provide sensitivity to different parts of the soot-precursor fluorescence response, including species that may be involved in soot inception. This would make LIF useful for examining how precursor fluorescence changes with  $H_2$  addition, and whether these changes follow the same trend as the measured soot volume fraction.

## 1.8 Research gap

Soot measurements have previously been performed over a range of premixed ethylene–air flame conditions [14, 75]. These studies demonstrated a significant increase in soot volume fraction as flame richness increased, showing power-law-like relationships with the C/O ratio. However, equivalent studies examining hydrogen addition across a comparable range of premixed flame conditions have not been reported. Instead, previous studies of hydrogen effects have often focused either on strongly sooting flames or on near-nucleation regimes [15, 18, 50]. As a result, there remains limited experimental evidence on how hydrogen addition affects the onset of soot formation, soot volume fraction and particle-growth behaviour across a wider range of premixed flame conditions. A similar limitation applies to precursor measurements. Although PAHs and related aromatic structures are central to many proposed soot-nucleation mechanisms, little is reported on how hydrogen addition affects these structures alongside soot formation over a wide range of flame conditions.

This thesis addresses these gaps by combining LII and LIF measurements in atmospheric ethylene–air premixed flat flames, spanning conditions from nucleation to highly sooting regimes. LII is used to determine how hydrogen affects soot volume fraction and obtain decay times (related to soot particle size), while LIF is used to examine how radiometrically calibrated precursor fluorescence intensity and spectral shape change with excitation wavelength, flame condition and hydrogen addition. The LIF measurements are performed using excitation wavelengths of 266, 355 and 532 nm. As the excitation wavelength increases, larger aromatic structures are generally expected to



contribute more strongly to the fluorescence signal, providing scope for detecting fluorescence from PAH monomers as well as recently discussed soot-inception species such as resonance-stabilised radicals or aliphatically bridged PAH structures [23, 80]. Since PAH-LIF spectra are broad and overlapping, individual species cannot usually be quantified directly. The measured spectra can however be treated in terms of broader spectral features or grouped precursor contributions, whose responses to hydrogen addition can then be compared with corresponding changes in soot concentration. Together, the LII and LIF measurements are intended to clarify how hydrogen addition affects soot onset, soot volume fraction, LII decay behaviour and precursor fluorescence over a range of flame conditions, with particular focus on how hydrogen influences soot nucleation.

## 1.9 Thesis organisation

The remainder of this thesis is organised into four experimental chapters. Chapters 2 and 3 focus on LII measurements of soot, while Chapters 4 and 5 focus on LIF measurements of PAH fluorescence.

- **Chapter 2** describes the LII experimental methodology used for soot measurements. This includes the flame conditions, optical arrangement for planar LII imaging and time-resolved LII measurements, detection systems used, checks to ensure that the detected LII signals remain within the linear response range of the detection systems, data processing procedures for soot volume fraction and LII decay-time measurements, and soot volume fraction calibration using the light extinction method.
- **Chapter 3** presents the LII results on the effect of hydrogen addition on soot formation in atmospheric ethylene–air premixed flat flames. The chapter examines how hydrogen affects soot onset, soot volume fraction and LII decay behaviour across a range of C/O ratios, from nucleation to highly sooting conditions. Height-scan measurements are also presented for a rich flame and a sparingly sooting flame.

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- **Chapter 4** describes the LIF experimental methodology used to investigate fluorescence associated with PAHs and related structures. This includes the optical arrangement for all excitation wavelengths (266, 355 and 532 nm excitation), radiometric calibration, and data processing steps for PAH-LIF spectra.
- **Chapter 5** presents the LIF results on the effect of hydrogen addition on fluorescence associated with PAHs and related structures. Measurements using 266, 355 and 532 nm excitation are used to examine how radiometrically calibrated fluorescence intensity and spectral shape vary with C/O ratio, height above the burner and hydrogen addition. The chapter also uses component-based analysis to identify grouped spectral features, examine how they are affected by hydrogen addition, and compare their behaviour with the soot trends observed from LII in Chapter 3.
- **Chapter 6** summarises the main findings and overall conclusions of the study. The chapter also outlines recommendations for future work.

## Chapter 2

# Laser-induced incandescence (LII) experimental set-up, data processing, and methodology validation

### 2.1 Introduction

Following the overview of LII in the previous chapter, this chapter describes the implementation of LII in the present work to investigate the effect of  $\text{H}_2$  addition on soot formation in premixed ethylene flames. Planar LII imaging is used for spatially resolved soot volume fraction measurements with an intensified CMOS camera, while time-resolved LII measurements using a photomultiplier tube (PMT) are point measurements that are used to measure soot volume fraction and track changes in LII signal decay times, used here as a proxy for soot primary particle size [11, 70].

The chapter is therefore organised as follows. First, the flame parameters are described, including the choice of burner, fuel, and experimental conditions, which include the different flow rates for different mixtures with and without  $\text{H}_2$  addition. The LII experimental set-up is then presented, followed by the laser sheet and detector configurations for planar and time-resolved measurements, including checks for reliable LII

Chapter 2. Laser-induced incandescence (LII) experimental set-up, data processing, and methodology validation

measurements, such as prompt LII timing and operating within the linear response of detectors. The associated data-processing procedures are then described, including the calibration of LII measurements into soot volume fraction and the extraction of decay times from time-resolved LII measurements. Having established the flame conditions and LII methodology, the resulting LII measurements with and without hydrogen addition are then presented in the next chapter.

## 2.2 Flame parameters

### 2.2.1 Flame type and choice of burner

Flat premixed laminar flames (reactants are premixed prior to combustion) generated by flat-flame burners (e.g., McKenna burners) are widely studied to investigate soot formation using both optical diagnostics and sampling methods [15, 74].

Importantly, soot nucleation remains the least understood stage of soot formation [91], and studying the effects of hydrogen addition on soot nucleation is therefore one of the core aims of this work. In premixed flat flames, the well-defined inlet composition makes the flame conditions, such as the carbon-to-oxygen (C/O) ratio of the fuel-air mixture, easier to characterise than in diffusion flames [92]. In diffusion flames, fuel and oxidiser mix locally by molecular diffusion, so soot formation is inherently coupled to mixing and residence-time effects [93]. The one-dimensional nature of the premixed flat flame also allows soot evolution to be resolved systematically as a function of height above the burner, from nascent soot particles near the burner to more mature soot further downstream [1, 94, 95]. This has been shown to be useful for interpreting soot-formation kinetics, since height above the burner can be treated as a proxy for reaction time in the soot formation process [14]. As a result, a premixed flame configuration was chosen for this work.

The burner of choice for this work was therefore a capillary hole burner with a diameter of 64 mm, and is shown in Figure 2.1. It incorporates a premixing chamber upstream of a perforated burner plate, with ball bearings used to homogenise the reactant flow. The premixed gases exit through small capillary holes in the burner plate, producing a

stable and one-dimensional (flat) laminar premixed flame, with temperature and soot concentrations approximately uniform in the radial direction and varying predominantly with height above the burner. A stainless steel stabilisation plate with a diameter of 60 mm was positioned 21 mm above the burner surface [73, 74, 96] to stabilise the flame and prevent flame flickering, thereby defining the maximum height above the burner (HAB). The flame geometry was therefore consistent with that employed in numerous previous studies of soot formation in laminar flat flames, including configurations recommended within the LII workshop framework [14–16, 18]. The burner assembly was mounted on a vertical translation stage, enabling precise vertical movement relative to the laser probe, with an accuracy estimated to be approximately 0.1 mm.

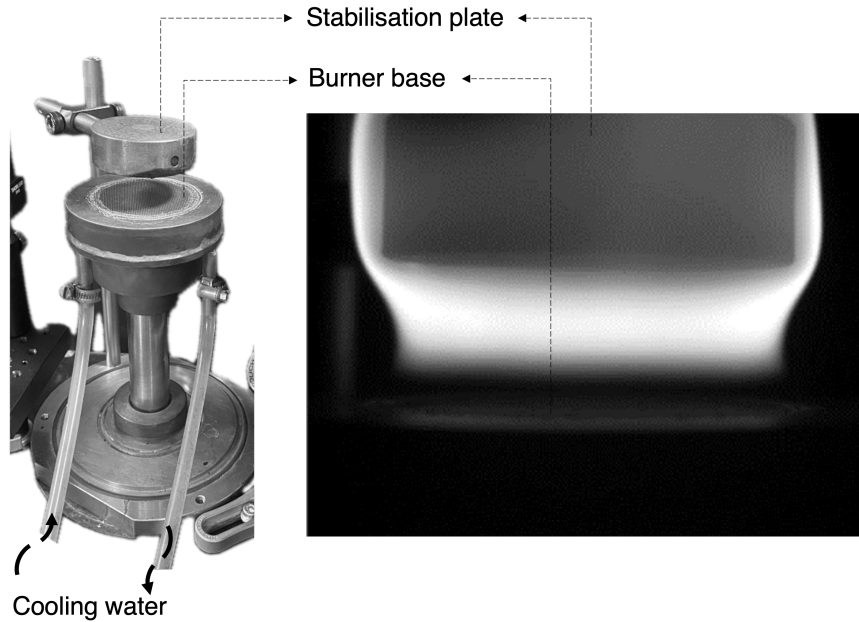


Figure 2.1: Capillary-hole burner used to generate a flat premixed flame. Left: photograph of the burner assembly, including the stabilisation plate, burner base and water-cooling connections. Right: image of the flat flame during operation, with the stabilisation plate and burner base visible.

### 2.2.2 Selection of fuel

Ethylene was selected as fuel of choice for this study because it is moderately sooting, widely used in soot-formation studies, and strongly PAH/soot-prone, can be considered

as a surrogate for fuels that contain higher order carbon-carbon bonds [14]. Ethylene is common in practical fuel blends (e.g. LPG) and is a key product/intermediate from the high-temperature breakdown of larger hydrocarbons, including jet fuels under pulse-detonation and scramjet conditions [97]. It also has several detailed kinetic mechanisms that have been extensively validated against large cross-study datasets, so its chemistry is well studied [98–100]. This makes ethylene a suitable reference fuel for examining how  $\text{H}_2$  addition affects soot formation under well-defined premixed flame conditions.

### 2.2.3 Selection of operating flow conditions

As discussed in the literature review, the effects of hydrogen in premixed flames have often been investigated either in highly sooting or nucleation flames [15, 18, 50]. In comparison, studies examining hydrogen addition across a wide range of premixed flame conditions, from nucleation to richer sooting flames, have not been reported. The present work therefore extends the investigation of hydrogen addition across a wider range of flame conditions (C/O ratios), from nucleation to highly sooting conditions, so that its effects on the onset of soot formation can be studied; soot volume fraction and particle-growth behaviour over a wide range can also be examined.

The operating flow conditions used in this work were based on a key reference involving hydrogen addition in a rich premixed ethylene–air flame at a single C/O ratio, using scattering/extinction measurements [15]. In their study, hydrogen-doped flames were obtained by substituting a portion of the ethylene–air reactant mixture with hydrogen. For each hydrogen addition level, the ethylene and air flow rates were adjusted to maintain both the total flow rate and C/O ratio. Hydrogen addition was found to reduce both soot concentration and particle size significantly. Since changes in carbon concentration with  $\text{H}_2$  addition were found to be small, and flame-temperature changes were also small, the reduction in soot was attributed to the chemical effect of hydrogen rather than simply to dilution [15].

In the present work, the same basis of comparison was applied at each selected C/O ratio. Soot concentration which is highly dependent on C/O ratio [14, 94] was kept fixed when hydrogen was added. A constant cold-gas velocity was also maintained,

since changes in reactant velocity can alter heat loss to the burner and the stabilisation position of a burner-stabilised premixed flame [101]. Flame richness was therefore varied by adjusting the ethylene and air flow rates while keeping the total molar flow rate constant. Starting from a nucleation flame to a highly sooting flame, this gave a selected range of  $C/O = 0.59\text{--}0.79$ , corresponding to an equivalence-ratio range of  $1.77\text{--}2.36$  in the  $H_2$ -free flames. In a nucleation flame, soot nuclei are formed but do not grow with flame height. The condition for a nucleation flame was therefore determined by adjusting the  $C/O$  ratio of the ethylene-air flame until no growth in particle size was observed along the flame height [16, 91]. In this work, this was assessed using time-resolved LII measurements, with the results presented in Chapter 3. A  $C/O$  ratio of 0.59 was thus identified as the nucleation flame condition, in agreement with the value reported by Bladh et al. [16].

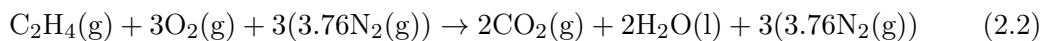
A cold-gas velocity of  $5.84\text{ cm s}^{-1}$  was selected for the premixed reactants, which is comparable with several premixed ethylene-air flat-flame studies [14–16, 64, 75]. It is also consistent with standard flat-flame configurations discussed within the International LII and International Sooting Flame Workshop communities [96, 102]. For the 64 mm diameter capillary-hole burner used here, this corresponded to a total flow rate of 11.39 normal litres per minute (NLPM), referenced to the mass-flow-controller calibration conditions of 293 K and 1 atm. The following section describes how the flow rates were calculated at each  $C/O$  ratio using the constraints outlined above.

#### 2.2.4 Calculation of $H_2$ -free and $H_2$ -doped reactant flow rates

For hydrogen-free cases, at each  $C/O$  ratio, the air and ethylene flow rates were determined from the definition of equivalence ratio,  $\phi$  (where  $\phi = 3(C/O)$  for  $H_2$ -free ethylene-air flames):

$$\phi = \frac{(\text{fuel/air})_{\text{mixture}}}{(\text{fuel/air})_{\text{stoichiometric}}}. \quad (2.1)$$

From the balanced reaction, the stoichiometric fuel/air ratio for ethylene is  $1/14.28$  (i.e. 0.0700).



Therefore, for a specified value of  $\phi$  in the  $H_2$ -free case and a fixed total flow rate of 11.39 NLPM, the individual flow rates can be obtained from:

$$\frac{V_{C_2H_4}}{V_{air}} = 0.0700 \times \phi, \quad (2.3)$$

$$V_{C_2H_4} + V_{air} = 11.39. \quad (2.4)$$

where  $V_{C_2H_4}$  and  $V_{air}$  are the flow rates of ethylene and air, respectively, in normal litres per minute (NLPM, reference conditions of 293 K and 1 atm).

However, for the hydrogen-doped cases, the individual flow rates of ethylene, air and hydrogen were calculated by applying the operating constraints mentioned in Section 2.2.3. For the  $H_2$ -doped cases, the following constraints were therefore applied at each C/O ratio:

$$V_{total} = V_{C_2H_4} + V_{air} + V_{H_2} = 11.39 \text{ NLPM}, \quad (2.5)$$

$$\frac{V_{H_2}}{V_{C_2H_4}} \in \{0\%, 20\%, 40\%\}, \quad (2.6)$$

$$\frac{V_{C_2H_4}}{V_{air}} = \text{constant}. \quad (2.7)$$

where  $V_{total}$  is the total flow rate (NLPM) of the  $H_2$ -doped reactant mixture, and  $V_{H_2}$  is the flow rate of hydrogen (NLPM). During  $H_2$  addition,  $V_{C_2H_4}/V_{air}$  was kept constant so that the C/O ratio remained constant for each selected flame condition.

A C/O ratio of 0.79, corresponding to  $\phi = 2.36$  in the  $H_2$ -free case, was selected as the rich base condition. This condition is close to that examined by De Iuliis et al. (C/O = 0.78) [15] and provides sufficiently strong soot signals for LII measurements even when hydrogen is added, thus justifying the choice of this starting case C/O ratio. A second condition at C/O = 0.69, corresponding to  $\phi = 2.07$  in the  $H_2$ -free case, was also defined. The flow rates for the resulting six flame conditions used for a height-scan measurements are shown in Table 2.1. LII measurements were taken for each of these conditions at different heights above the burner. A separate C/O-ratio scan was then performed at a fixed height of 16 mm HAB for the  $H_2$ -free and 40%  $H_2$ -doped cases. The corresponding flow rates are listed in Table 2.2.



| % $H_2$ | Flowrate<br>$C_2H_4$<br>(NLPM) | Flowrate<br>$H_2$<br>(NLPM) | Flowrate<br>Air<br>(NLPM) | C/O ratio |
|---------|--------------------------------|-----------------------------|---------------------------|-----------|
| 0       | 1.62                           | 0                           | 9.77                      | 0.79      |
| 20      | 1.57                           | 0.31                        | 9.50                      | 0.79      |
| 40      | 1.53                           | 0.61                        | 9.25                      | 0.79      |
| 0       | 1.44                           | 0                           | 9.95                      | 0.69      |
| 20      | 1.41                           | 0.28                        | 9.70                      | 0.69      |
| 40      | 1.37                           | 0.55                        | 9.47                      | 0.69      |

Table 2.1: Flow rates used for the height-scan LII measurements in the rich flame (C/O = 0.79,  $\phi = 2.36$  in the  $H_2$ -free case) and sparingly sooting flame (C/O = 0.69,  $\phi = 2.07$  in the  $H_2$ -free case). Flows are quoted in normal litres per minute (NLPM), referenced to 293 K and 1 atm.

The calculated flow rates were set using the gas delivery system described in Figure 2.2 . For this project, laboratory-grade ethylene and hydrogen (99.96% purity) were used as the gaseous fuels. Fuel and air delivery was metered with Cole-Parmer Masterflex MC-Series mass-flow controllers for air and ethylene (accuracy:  $\pm 0.8\%$  of reading +  $\pm 0.2\%$  of full scale). Over our operating range, the error was small, typically around 1%.

| C/O  | Flowrates with 0% H <sub>2</sub> (NLPM) |       | Flowrates with 40% H <sub>2</sub> (NLPM) |      |                |
|------|-----------------------------------------|-------|------------------------------------------|------|----------------|
|      | C <sub>2</sub> H <sub>4</sub>           | Air   | C <sub>2</sub> H <sub>4</sub>            | Air  | H <sub>2</sub> |
| 0.59 | 1.26                                    | 10.13 | 1.20                                     | 9.71 | 0.48           |
| 0.60 | 1.27                                    | 10.12 | 1.21                                     | 9.67 | 0.49           |
| 0.61 | 1.29                                    | 10.10 | 1.23                                     | 9.67 | 0.49           |
| 0.62 | 1.31                                    | 10.08 | 1.26                                     | 9.63 | 0.50           |
| 0.63 | 1.33                                    | 10.06 | 1.27                                     | 9.62 | 0.51           |
| 0.65 | 1.36                                    | 10.03 | 1.30                                     | 9.57 | 0.52           |
| 0.67 | 1.40                                    | 9.99  | 1.33                                     | 9.52 | 0.53           |
| 0.71 | 1.47                                    | 9.92  | 1.40                                     | 9.43 | 0.56           |
| 0.75 | 1.54                                    | 9.85  | 1.46                                     | 9.34 | 0.59           |
| 0.79 | 1.62                                    | 9.77  | 1.53                                     | 9.25 | 0.61           |

Table 2.2: Flow rates used for the fixed-height C/O-ratio scan at 16 mm HAB. Values are given in NLPM, referenced to 293 K and 1 atm, for C<sub>2</sub>H<sub>4</sub>, air, and H<sub>2</sub> at different C/O ratios under 0% and 40% H<sub>2</sub> conditions. The H<sub>2</sub>-free case at C/O = 0.59 corresponds to the nucleation flame condition identified in the present work.

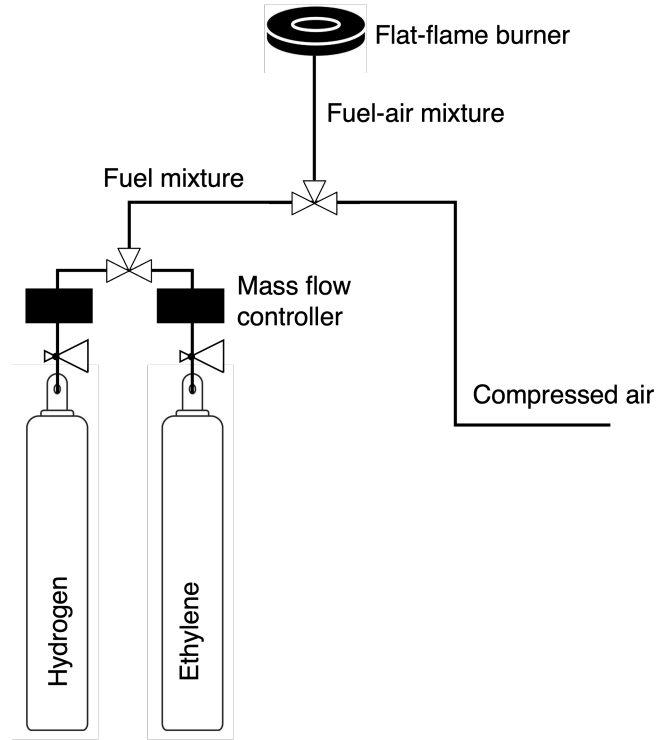


Figure 2.2: Schematic of the gas supply and mixing system used to deliver premixed reactants to the flat-flame burner. Ethylene, hydrogen, and air flow rates are independently controlled using mass flow controllers prior to mixing and injection into the burner.

Having defined the flow conditions used in this work, the following section describes the LII experimental setup used for these measurements.

## 2.3 LII experimental set-up

Figure 2.3 shows the general schematic of the LII setup used throughout this project to acquire planar LII images and time-resolved LII signals. The laser employed in this work for LII measurements is the Continuum Surelite SL II-10, operating at a fundamental wavelength of 1064 nm, in the infrared. This Nd: YAG 1064 nm laser produces a Gaussian beam with a  $1/e^2$  diameter of approximately 7 mm [103], operating at a frequency of 10 Hz. LII measurements were performed using 1064 nm excitation to minimise interference from laser-induced fluorescence of PAHs [96]. The pulse energy of the SureLite laser can be adjusted by varying the Q-switch–flashlamp delay (in  $\mu\text{s}$ ); at its optimum delay (187  $\mu\text{s}$ ), it delivered  $\sim 250$  mJ per pulse.

As shown in Figure 2.3, the laser beam was directed towards the centre of the burner using two Nd:YAG laser-line mirrors (Thorlabs NB1-K13). The first Nd:YAG mirror was positioned at 45 degrees to the laser beam, reflecting the beam towards the second Nd:YAG mirror, which was also positioned at 45 degrees to direct the beam towards the centre of the burner. A plano-concave square cylindrical lens (Thorlabs LK1743L1-C) with a negative focal length ( $f = -100$  mm) expanded the light in one dimension, and a second plano-convex round cylindrical lens (Thorlabs LJ1363RM-C) with a positive focal length ( $f = 400$  mm) collimated the light in one direction, as shown in the upper part of Figure 2.3.

The centre of the collimated laser sheet then passed through a rectangular slit of 2 mm width and 10 mm height. The slit was oriented perpendicular to the laser-sheet direction, used to shape the laser sheet to a near top-hat profile, and placed as close as practicable to the centre of the burner ( $\sim 10$  cm) to minimise diffraction effects. Finally, a beam dump was placed at the back of the burner.

Soot particles in the flame illuminated by the laser sheet absorb the incident radiation and are rapidly heated, producing the incandescence signal for LII measurements. In this work, the emitted signal was collected using two detection methods: time-gated

planar imaging with an intensified CMOS camera and time-resolved point detection with a photomultiplier tube (PMT), as shown in Figure 2.3. The laser-sheet orientation was different for these two detection methods, as described next.

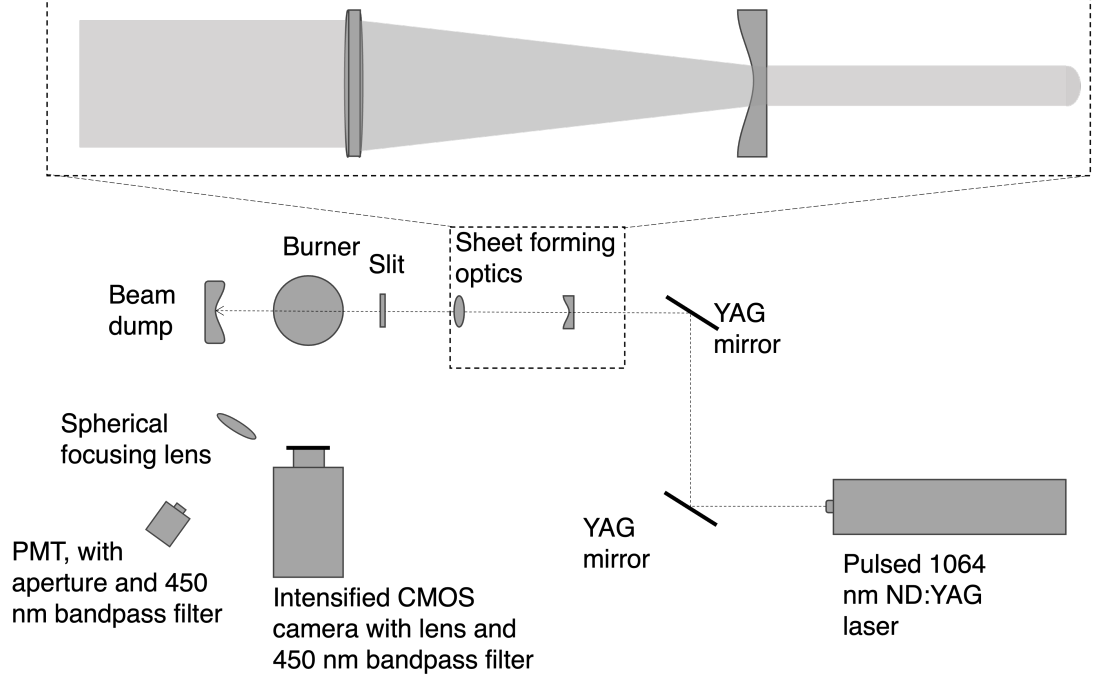


Figure 2.3: Schematic of the experimental LII set-up showing the Nd:YAG laser, beam-steering mirrors, sheet-forming optics, flat-flame burner and detectors used for planar and time-resolved measurements.

## 2.4 Excitation of laser-induced incandescence

Two laser-sheet configurations were used in this work. The choice of configuration depended on whether the measurement required time-resolved point detection with the PMT or planar imaging with the intensified camera.

Time-resolved LII measurements with the PMT were required for the C/O-ratio scan, particularly because the scan extended to the nucleation regime. In time-resolved LII, the signal is collected from a defined measurement volume at a selected height above the burner [104]. In nucleation-flame studies, this approach has been used with a horizontal laser sheet to increase the illuminated volume contributing to the detected signal, allowing measurable time-resolved signals to be obtained under very weakly soot-

ing conditions [16,91]. In the present work, the cylindrical lenses and slit were therefore rotated by  $90^\circ$ , producing a horizontal laser sheet of  $2\text{ mm} \times 10\text{ mm}$  before passing through the flame. However, for planar LII imaging, the cylindrical lenses and slit were instead oriented to produce a vertical laser sheet of  $2\text{ mm} \times 10\text{ mm}$ . The reasoning for using two different laser sheet configurations is explained in the next section. However, since different laser-sheet and detection configurations were used, planar LII images and time-resolved PMT measurements were not acquired simultaneously.

## 2.5 LII detection equipment and techniques

### 2.5.1 Planar LII imaging

Planar LII imaging consisted of taking images of the region of the flame illuminated by the vertical laser sheet, since this would allow a two-dimensional soot distribution to be recorded and enable spatially resolved soot volume fraction measurements over a range of heights above the burner in a single image. For imaging experiments, an intensified 16-bit CMOS camera (PCO DiCam C1), with a Nikkor lens (105 mm; f/4.5) and a 450 nm band-pass filter (10 nm FWHM; Edmund Optics: #86-999), imaged the LII signal on an axis perpendicular to the light sheet. The 450 nm filter was selected to reduce interference from flame emission associated with  $\text{C}_2$  Swan bands by isolating a window with minimal  $\text{C}_2$  emission [105]. The collection lens was positioned approximately 40 cm from the centre of the burner to obtain a desired magnification ( $M \approx 0.14$ ). A ruler (with known markings) was placed at the measurement plane to adjust the camera focus.

Planar LII imaging was used for the selected rich and sparingly sooting flames (From Table 2.1). Planar LII imaging was not used for the C/O-ratio scan, since even with the horizontal laser-sheet configuration (which increases LII signal collection volume), the camera signal became too weak for reliable imaging before reaching the nucleation C/O ratio.

The intensified camera operation was controlled through three main settings in the PCO Camera Control software: intensifier gain, gate duration and gate timing. The

gain setting determines the degree of signal amplification, while the gate duration and timing define the temporal window over which the LII signal is collected. These settings are described in the following sections.

### Camera gain

The camera gain is controlled by the image intensifier, which amplifies LII signals before it is recorded by the CMOS sensor. The operation of the intensified camera is shown in the schematic in Figure 2.4. Incident photons first reach the photocathode, a photo-sensitive layer a few  $\mu\text{m}$  thick, where they are converted into photoelectrons. These photoelectrons are then accelerated towards the microchannel plate (MCP), located behind the photocathode, where signal amplification occurs.

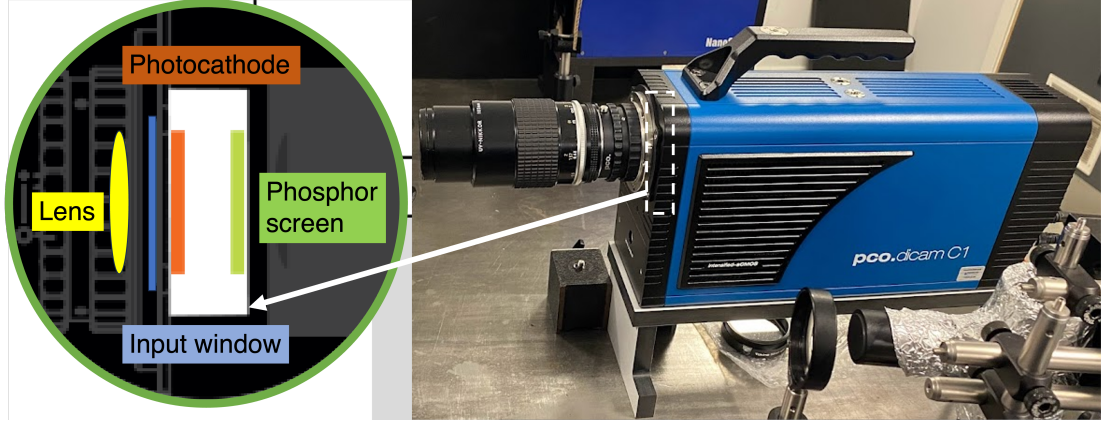


Figure 2.4: CMOS camera and image intensifier features, adapted from the PCO DiCam C1 manual [4].

The MCP amplifies the electrons through an electron avalanche, as demonstrated in Figure 2.5. The amplified electrons are incident on the phosphor screen, and the phosphor screen emits light, which is then imaged onto the CMOS sensor. This corresponds to the pixels displayed in the readout. The MCP gain (intensifier voltage) ranges between 750 V to 1100 V. By increasing the intensifier voltage, the number of output electrons from each channel is increased. This makes the CMOS camera optimal for low-light applications. Throughout this thesis, the image intensifier was operated at a gain setting of 1100 V to ensure sufficient sensitivity given the low soot volume fraction

in some of the flames under study. The recorded images were checked to ensure that the signal remained below the 16-bit saturation limit of 65,535 counts, thereby avoiding saturation of the LII signal.

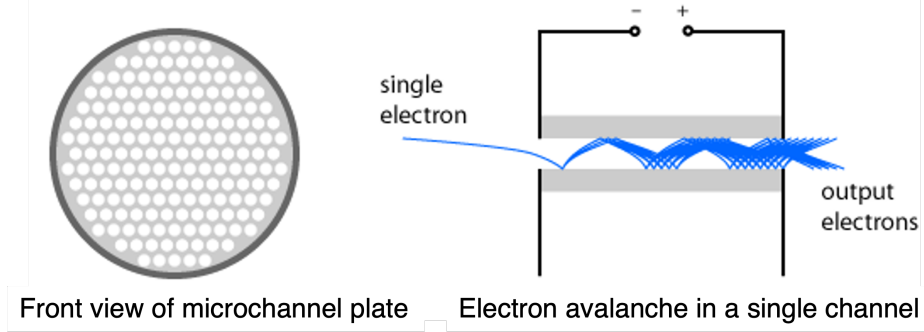


Figure 2.5: Electron avalanche through the microchannel plate (MCP) [4].

### Prompt LII

One of the advantages of an intensified CMOS camera is its ability to record images over very short exposure times. In this context, the exposure time is defined by the intensifier gate duration, i.e., the time over which the intensifier remains open. The PCO DiCam C1 supports a minimum gate duration of 4 ns, with the gate delay adjustable in 1 ns increments [4]. The gate delay determines when the camera gate opens relative to the trigger, while the gate duration determines the length of the detection window (exposure).

In prompt LII, the incandescence signal is evaluated at the earliest times following laser irradiation, corresponding approximately to the peak of the temporal LII profile, which is commonly used to determine soot volume fraction [14]. At the peak, all soot particles, in principle, have been heated to approximately the same temperature [71], so that the measured LII signal (and thus evaluation of soot volume fraction) is not dependent on particle size. At later detection times, size-dependent conductive cooling, associated with the particle surface-to-volume ratio  $\propto 1/r$ , causes smaller particles to cool more rapidly than larger ones, biasing the LII signal towards larger particles [96, 106]. Short, prompt detection gates of 60 ns or less have typically been used [14, 74, 96]. In this work, a camera gate duration of 50 ns was selected as a compromise between

maximising signal-to-noise ratio and maintaining a sufficiently short detection window to minimise size-dependent cooling effects.

To achieve prompt LII detection, the camera gate was synchronised with the laser pulse using an SRS DG535 delay generator. The delay generator was used to invert the negative polarity TTL output from the pulsed Nd:YAG laser, allowing the camera to be triggered on the required rising edge of a TTL pulse. The same delay generator also triggered the oscilloscope (Tektronix DPO2024 (200 MHz bandwidth, 8-bit vertical resolution)). A BNC output from the camera was connected to the oscilloscope so that the camera gate could be monitored relative to the same trigger signal. The temporal position of the laser pulse was monitored on the oscilloscope using a Thorlabs DET10A/M photodiode placed close to the burner centre ( $\sim 10$  cm). The photodiode has a bandwidth of 280 MHz and a rise time of approximately 1 ns, making it sufficiently fast to resolve the temporal profile of the Nd:YAG laser pulse. Using this arrangement, the pulse duration of the 1064 nm Nd:YAG laser was measured to be approximately 6.8 ns, as shown in Figure 2.6 (traces were averaged over 128 shots). By monitoring both the laser pulse and the 50 ns camera gate relative to the same oscilloscope trigger, the camera gate delay was adjusted so that the laser pulse lay within the camera gate. Before recording LII measurements, the effect of the gate delay on the raw LII signal counts was also observed directly during live acquisition in the PCO DiCam software. The delay setting giving the maximum LII signal count was selected, confirming that the camera gate was positioned to capture the prompt LII signal. Once this delay had been set, 100 single-shot LII images were recorded for each measurement.



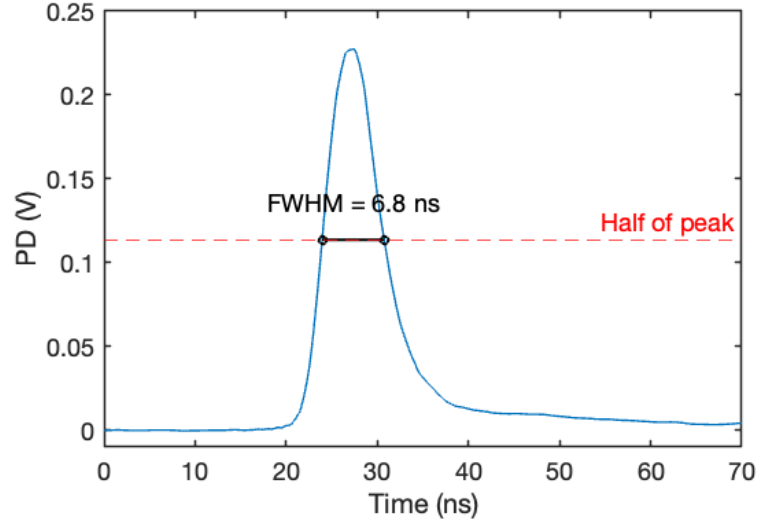


Figure 2.6: Temporal profile of a single Nd:YAG laser pulse measured using a Thorlabs DET10A/M photodiode, showing a pulse width of 6.8 ns FWHM. The horizontal axis represents time and the vertical axis represents the photodiode output voltage.

### 2.5.2 Time-resolved LII

The time-resolved LII detection setup consisted of a photomultiplier tube (PMT) (Hamamatsu Photonics R3788 [107]) used to monitor the temporal evolution of the LII signal. A simplified schematic diagram of a photomultiplier tube is shown in Figure 2.7.

A single photon ejects an electron upon hitting the photocathode. Electric fields in the PMT accelerate the electron into another surface called a dynode. Upon collision with the dynode, several new electrons are released, which are then accelerated to another dynode. The multiplied electrons emitted from the last dynode are finally collected by the anode. This gives rise to an electric current that can be measured. The magnitude of the output signal depends on the PMT gain, which is controlled by the applied high voltage. Increasing the high voltage increases the electron multiplication at the dynode stages, thereby increasing the sensitivity of the detector to weak LII signals.

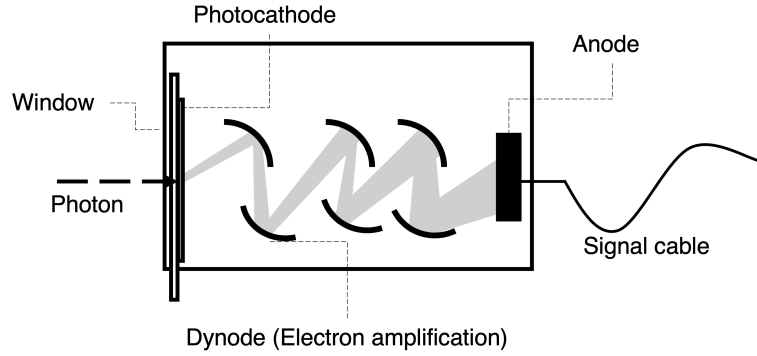


Figure 2.7: Description of a photomultiplier tube (PMT).

A bandpass filter centred at 450 nm (Thorlabs FBH450-10, 10 nm FWHM) was placed in front of the PMT, matching the detection wavelength used for planar LII imaging. The LII signal was collected using a spherical lens with a focal length of 15 cm, arranged in a  $2f-2f$  configuration between the burner centre and the PMT aperture. This gave a total distance of 60 cm between the burner centre and the PMT aperture and provided approximately 1:1 magnification. The aperture was placed close to the photocathode, approximately 4 cm in front of the PMT housing, so that the photocathode was roughly filled, but not overfilled.

With an approximately 1:1 magnification, a rectangular aperture of  $2\text{ mm} \times 10\text{ mm}$ , together with the horizontal laser sheet of the same dimensions, defined an effective collection volume of  $2 \times 10 \times 10 = 200\text{ mm}^3$ , as shown in Figure 2.8. This larger collection volume improved the signal-to-noise ratio, which was particularly important for detecting weak LII signals near the nucleation flame condition. It was therefore used for the wider C/O ratio scan, from the nucleation condition to the richest flame. PMT height-scan measurements were also performed for the rich and sparingly sooting flames, allowing comparison with the planar LII measurements. These measurements required the PMT gain to be adjusted to measure signals over a wide range of flame conditions. Therefore, it was necessary to verify that the PMT remained within its linear response range. The following subsections assess the PMT response in terms of both the DC signal level and the peak transient LII signals.

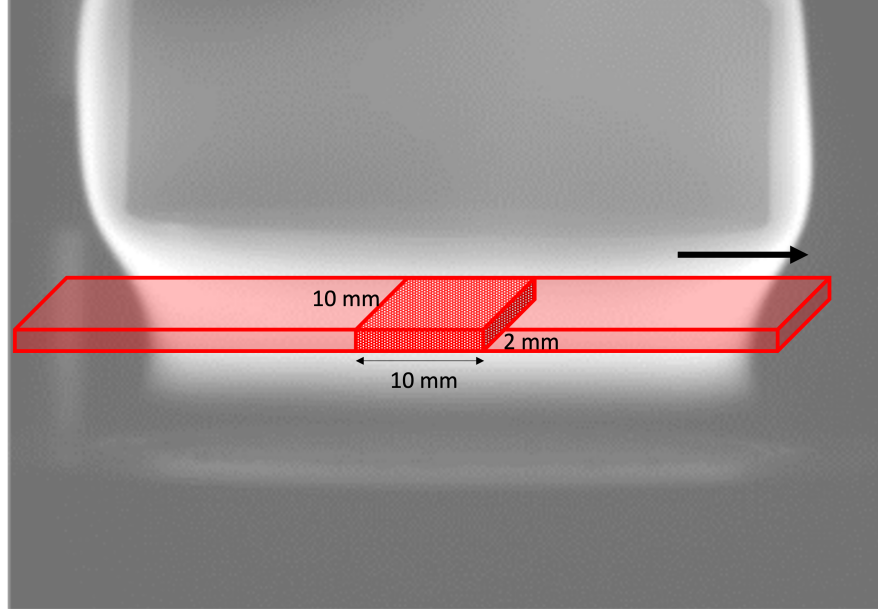


Figure 2.8: Schematic representation of the horizontal laser sheet used for time-resolved LII measurements with the PMT, shown overlaid on a representative flame image for visual context. The textured red region indicates the effective PMT collection volume within the laser sheet, defined by the overlap between the  $2\text{ mm} \times 10\text{ mm}$  laser sheet and the  $2\text{ mm} \times 10\text{ mm}$  rectangular aperture. The black arrow denotes the propagation direction of the laser sheet.

### DC-level saturation

In a rich flame condition ( $C/O = 0.79$ ), the PMT high voltage was scanned over a wide range in order to assess the extent of the DC level linear operating regime. The corresponding DC level measured on the oscilloscope (with a  $50\ \Omega$  termination) is shown in Fig. 2.9 and plotted against the PMT high voltage, with both axes on logarithmic scales. A straight-line trend indicates that the measured DC level follows a power-law dependence on PMT high voltage over the range considered. Over the measured range, the DC signal increased approximately linearly with PMT high voltage, with no clear evidence of saturation up to the highest recorded level of about 10 mV. The PMT manual [107] specifies a maximum average anode current of 0.1 mA, which corresponds to a DC level of approximately 5 mV across a  $50\ \Omega$  termination. In the measurements reported in this thesis, the DC signal was kept well below this limit; even in the worst cases it remained below 1 mV, and was much lower in most conditions.

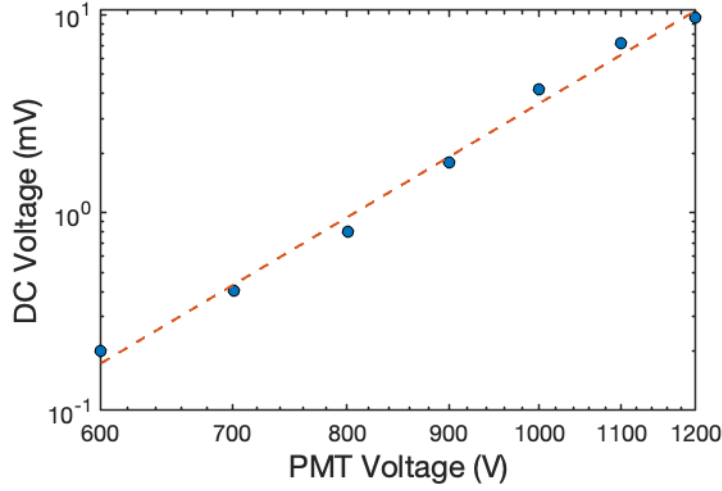


Figure 2.9: PMT DC level measured on the oscilloscope as a function of PMT voltage in a rich flame ( $C/O = 0.79$ ). Both axes are plotted on a logarithmic scale. The dashed line indicates the linear trend.

### Transient saturation threshold and characterisation of the PMT

The PMT must also be operated below its transient saturation threshold, where the measured signal remains linearly proportional to the incident light intensity photon flux at the photocathode. This threshold is separate from the DC saturation limit because there is a capacitor within the PMT which allows a current much greater than the DC maximum to be drawn for a short interval. Figure 2.10 presents the PMT response to the peak transient LII signals over a wide range of supply voltages for several flame conditions. The data are plotted on logarithmic axes to assess the power-law dependence of the measured signal on the applied PMT high voltage, such that the response appears as an approximately linear trend whose gradient can be directly compared across flame conditions. As shown, nearly identical gradients were obtained in each case, indicating a reproducible gain scaling behaviour. Figure 2.10 shows that, within the linear-response range, the peak transient LII signal scales with PMT high voltage as a power law that is independent of flame condition, with an average slope of about 7.44 on log-log axes. We therefore treat the PMT gain as  $G \propto V_{HV}^{7.44}$  up to a peak transient level of  $\sim 70$  mV, above which saturation occurs; signal levels above this threshold were avoided during experiments. The 'typical' gain-voltage characteristic was 6.46, as shown in the PMT

datasheet [107]. The difference demonstrates the importance of determining the gain experimentally, rather than relying on the quoted value from the datasheet. Across the flame conditions listed in Table 2.2, the LII signal varied over a large dynamic range because of the large change in soot volume fraction between nucleation and rich flame conditions. To measure this range while keeping the PMT within its linear response regime, the PMT high voltage was increased for weak signals, whereas neutral-density (ND) filters were used to attenuate stronger signals.

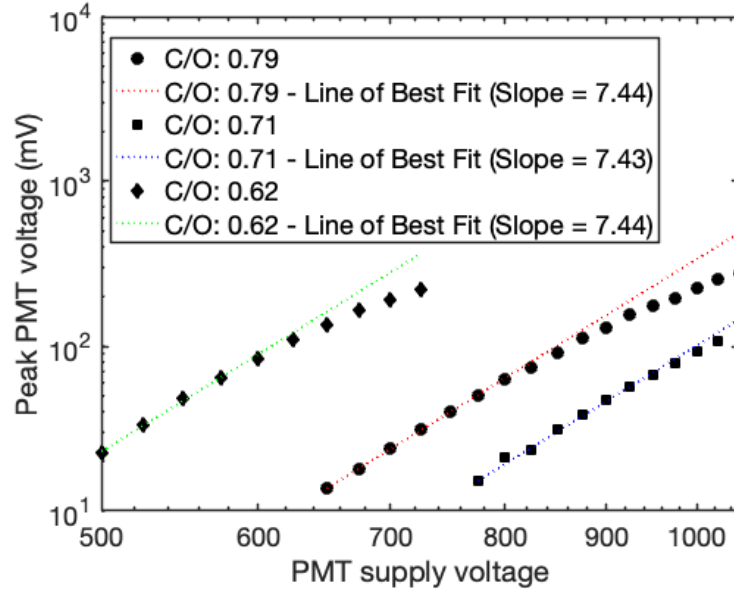


Figure 2.10: Peak transient LII signal as a function of PMT supply voltage for several flame conditions, plotted on logarithmic axes. Dashed lines show best fits within the linear-response range, indicating a power-law dependence of PMT gain on supply voltage. Neutral density (ND) filters were used for the richer flames to attenuate the stronger signals, with the attenuation held constant across the full PMT-voltage range for each flame condition; consequently, the richer-flame traces appear at higher PMT voltages than the leaner-flame traces. Deviation from linearity above a peak signal level of approximately 70 mV marks the onset of saturation.

As illustrated in Fig. 2.11, time-resolved LII profiles obtained for the same flame condition at different PMT voltages exhibit the same overall shape when superimposed, although the peak signal at the higher PMT voltage lies above the identified linear operating range of the transient signal ( $> 70$  mV). In the left subplot, operation at 800 V yields a peak signal of approximately 115 mV, whereas operation at 700 V

produces a peak of about 45 mV. After normalisation (right subplot) by their respective peak values, the two profiles overlap closely, preserving the time-resolved profile shapes. Nevertheless, all measurements reported in this thesis were acquired within the identified linear portion of the transient response ( $< 70$  mV).

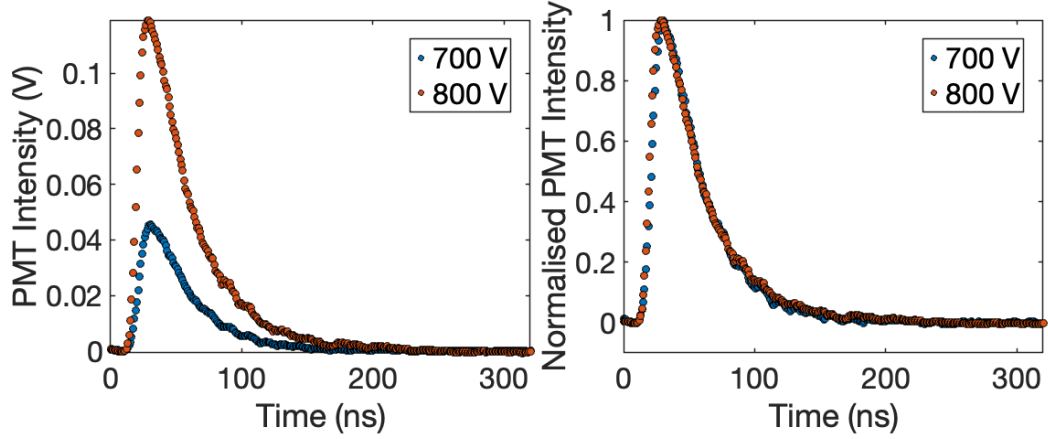


Figure 2.11: Temporal LII profiles measured at two PMT voltages for a  $C/O = 0.60$  flame. Left: raw signals in volts (V). Right: the same traces normalised to their respective peak amplitudes, illustrating preservation of the temporal profile shape despite differences in peak signal level.

## 2.6 LII data processing

Once LII measurements had been taken, the recorded signal counts from planar LII imaging and voltage signals from time-resolved PMT measurements had to be calibrated to soot volume fraction. This section describes the processing of the raw LII signal data and their calibration to soot volume fraction using the light extinction method, as introduced in Chapter 1. The steps used to extract LII decay times from PMT time-resolved measurements, which are used as an indicator of soot particle size, are also described. Planar LII image processing is described first.

### 2.6.1 Planar LII image processing

Data processing steps include background subtraction, pixel-to-physical length calibration and extraction of radial and centreline vertical SVF profiles, calibrated from LII

signal in pixel counts to soot volume fraction. All processing steps were done in MATLAB.

### Image averaging and background subtraction

For each LII measurement, 100 single-shot images were recorded and averaged. A corresponding set of 100 background images was also recorded with the laser off, but with the flame on. These background images were averaged and then subtracted from the averaged LII image. In practice, the background level was low and spatially uniform relative to the LII signal intensity, such that this correction has a negligible effect on the results. An example of a background-subtracted LII image obtained in a rich flame at  $\phi = 2.36$  ( $C/O = 0.79$ ) is shown in Fig. 2.12.

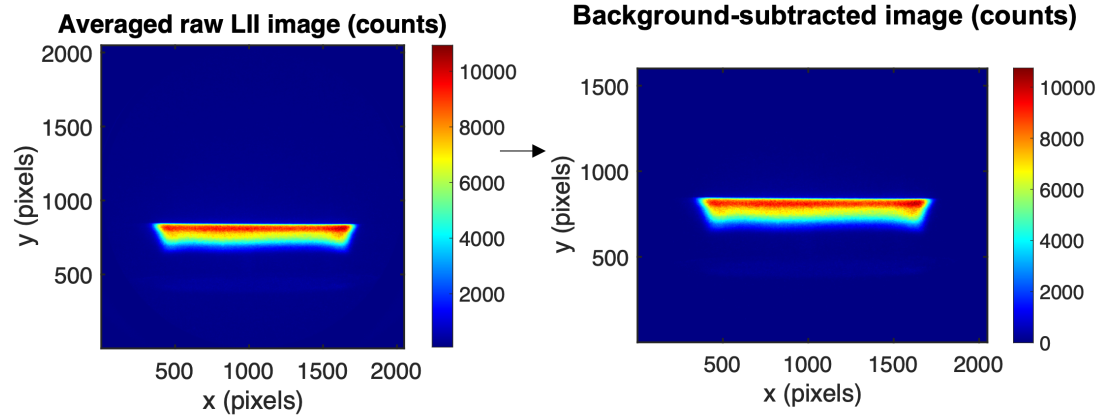


Figure 2.12: Averaged planar LII image before (left) and after (right) background subtraction and cropped for a rich ethylene flame at an equivalence ratio of  $\phi = 2.36$  ( $C/O = 0.79$ ).

### Conversion from pixel coordinates to physical length scales

To establish the physical length scale for the LII images, a calibration object of known dimensions was imaged in the laser-sheet plane. In this case, a ruler was positioned in the measurement plane, as shown in Figure 2.13. The known spacing between the ruler markings was used to convert pixel distance to physical distance in the flame; in this case, 10 mm corresponded to 232 pixels. The same calibration image was also used to

identify the reference pixel locations corresponding to the burner base and the burner centreline.

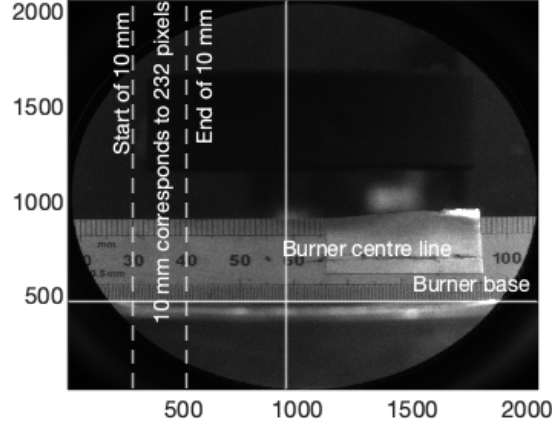


Figure 2.13: Calibration image used to convert pixel coordinates to physical length scales. A ruler placed in the LII image plane provides a known spatial reference, allowing determination of the pixel-to-length conversion. The image is also used to identify the burner base and burner centreline.

The same LII image from Fig. 2.12, converted to physical length scales, is shown in Fig. 2.14. The LII signal was subsequently calibrated using the light extinction method for the quantitative determination of soot volume fraction ( $f_v$ ), as described in the following section.

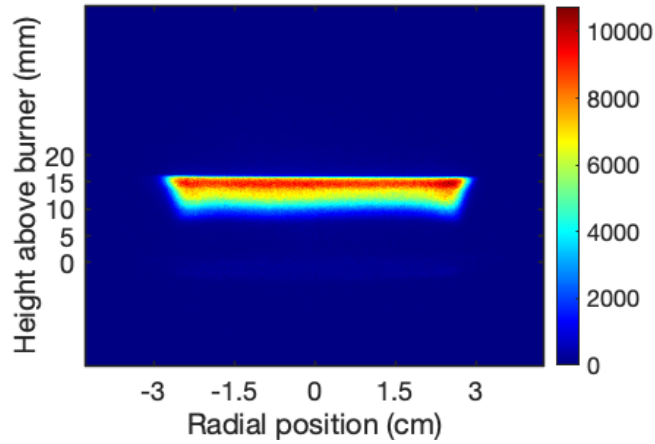


Figure 2.14: Planar LII image after conversion from pixel coordinates to physical length scales, showing the same dataset as Fig. 2.12 prior to spatial calibration.



### Calibration of LII pixel to soot volume fraction

The broad principle of soot-volume-fraction calibration using light extinction has been outlined in Chapter 1. This calibration required a 1060 nm pulsed fibre-laser (SPI re-dEnergy G4 20 W EP-Z; repetition rate: 30 kHz), with transmitted intensity monitored by a fast photodiode (Thorlabs PDA36A-EC) and a lock-in amplifier (SRS, SR 860). Using this wavelength minimises absorption by polycyclic aromatic hydrocarbons in the flame [96]. The experimental setup is depicted in Figure 2.15. A monitor signal from the laser device was used as the reference for the lock-in amplifier. The lock-in amplifier measures the amplitude of modulation at the reference frequency and is therefore insensitive to dc background such as the signal arising from flame emission.

A focussing lens was used to ensure that the laser beam was tightly focused when passing through the burner, such that it occupied only a small height (around 200 microns). This allowed the beam transmission at different heights to be determined. After reflection from a mirror, a second focussing lens was used to refocus the transmitted beam onto the photodiode. Since the photodiode had a large active surface area, small angular changes in the beam direction, which could result from the beam passing through the flame, would still fall within the active surface. As a result, the measured transmittance,  $T = I/I_0$ , was not affected. As a safety precaution, a very low pulse energy was used (corresponding to a power of about 10 mW), and a 25GN ND filter was used to avoid damaging the active surface of the photodiode.

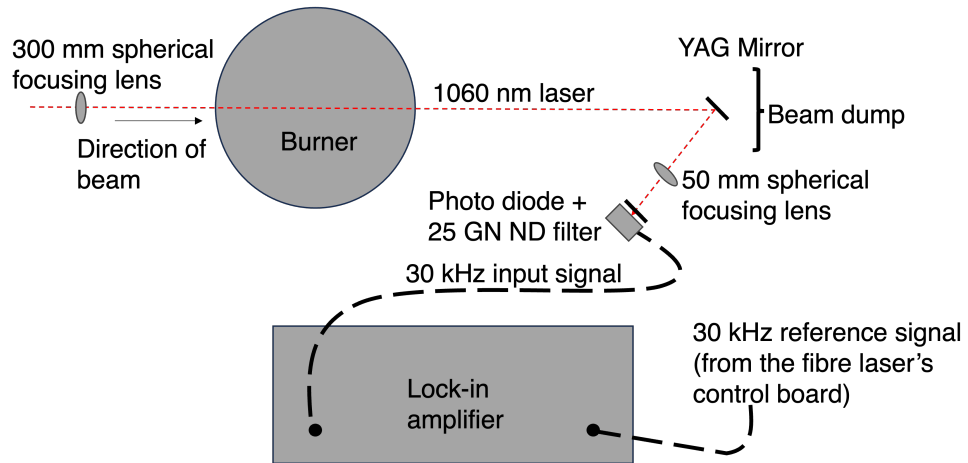


Figure 2.15: Experimental setup used for soot volume fraction (SVF) calibration by light extinction. A 1060 nm laser beam is transmitted through the flame and focussed onto a photodiode. The transmitted intensity is measured using a lock-in amplifier referenced to the 30 kHz laser modulation signal.

From Figure 2.16, a clear proportional relationship between  $R$  (the signal magnitude extracted by the lock-in amplifier) and the laser pulse energy is demonstrated, indicating that a linear change in pulse energy shows a linear change in the signal on the lock-in amplifier. Therefore, it would be suitable to measure changes in the pulse energy after passing through the flame.

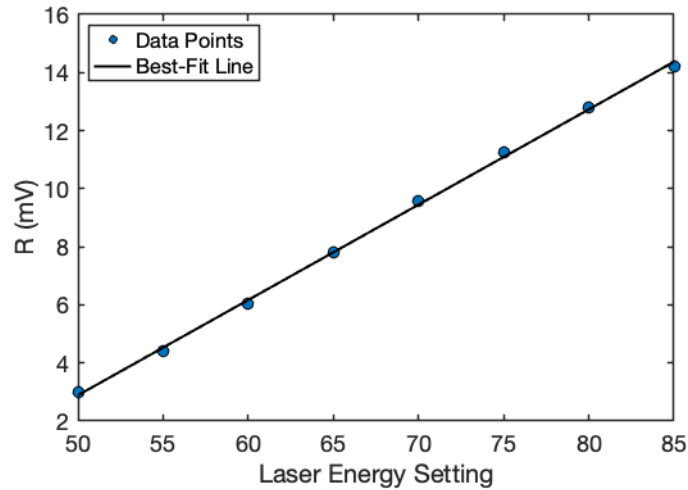


Figure 2.16: Relationship between the lock-in amplifier output  $R$  and the incident laser pulse energy. The linear proportionality demonstrates that the lock-in-based detection accurately tracks changes in laser pulse energy.

Figure 2.17 shows the measured transmission of the laser beam as a function of height above the burner (HAB), calculated from changes in the lock-in amplifier output  $R$ . A reduction in transmission is observed with increasing height, consistent with increased soot concentration at higher HABs. As explained in Chapter 2, to calculate the soot volume fraction ( $f_v$ ) from the measured transmission values, the following expression was used [108]:

$$f_v = \frac{\ln\left(\frac{I_0}{I}\right) \lambda_L}{6\pi L E(m)}, \quad (2.8)$$

where  $I_0$  is the incident light intensity,  $I$  is the transmitted light intensity,  $L$  is the path length (burner diameter),  $\lambda_L$  is the laser wavelength, and  $E(m)$  is the soot absorption function. The value of  $E(m)$  depends on soot maturity, particle size, and wavelength at which extinction is measured, and is therefore not strictly universal [75,109]. Recent in situ studies combining laser-induced incandescence and absorption measurements in premixed ethylene–air flames have shown that  $E(m)$  increases with soot maturity, showing values of approximately 0.15–0.25 for incipient or very small soot particles and approaching  $E(m) \approx 0.35$ –0.36 for mature soot in rich flames [75]. In this work, a value of  $E(m) = 0.36$  [75,110] was adopted for all heights and flame conditions. Since the inferred soot volume fraction is inversely proportional to  $E(m)$ , this assumption would lead to an underestimation of the absolute soot volume fraction wherever the actual value of  $E(m)$  is lower. This may apply at lower HABs in the selected rich flame here ( $\phi = 2.36$ ), where the soot is less mature, and smaller in size, and even at larger HABs in the lower-C/O flames investigated in this work. Figure 2.17 therefore shows the calculated soot volume fraction at different HABs. As would be expected, an increase in soot concentration is observed with height [14].

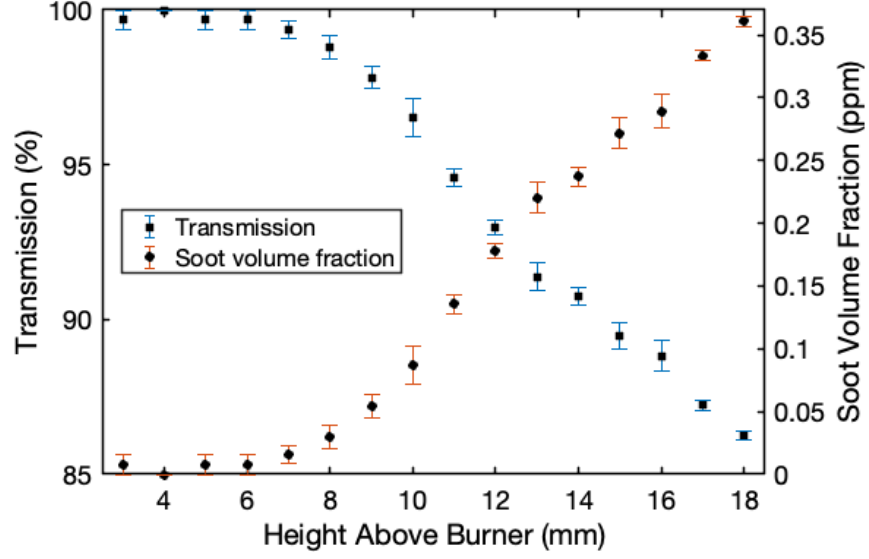


Figure 2.17: Measured transmission (%) at 1060 nm and the corresponding soot volume fraction (ppm), derived from light extinction, as a function of height above the burner (HAB).

To compare the LII results with those of the extinction measurement, centreline vertical profiles were extracted from the processed LII image shown in Fig. 2.14. At each height above the burner, the LII signal was spatially averaged over a narrow region centred at the burner centre line, with a radial width of 1 mm and a vertical extent of about 0.4 mm. Based on the spatial calibration of  $0.0418 \text{ mm pixel}^{-1}$ , this corresponded to 24 pixels in the radial direction and 10 pixels in the vertical direction.

The resulting LII-derived centreline profiles are compared with soot volume fraction profiles obtained from light extinction measurements (Fig. 2.17). Figure 2.18 shows good agreement in the trend between the two techniques for a flame at  $\phi = 2.36$  ( $C/O = 0.79$ ), with SVF referenced to the value at 15 mm HAB.

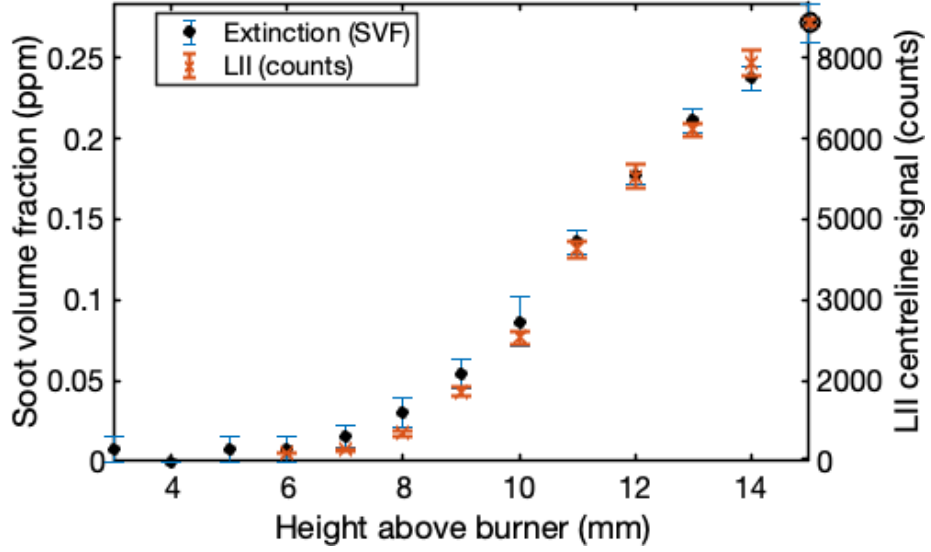


Figure 2.18: Comparison of soot volume fraction derived from light-extinction measurements and centreline LII signals extracted from LII images for a rich flame at  $\phi = 2.36$  ( $C/O = 0.79$ ). The LII images were acquired using a vertical laser sheet ( $2 \times 10$  mm), and the centreline signals were obtained by averaging over a 0.4 mm vertical band ( $\pm 0.2$  mm) and a 1 mm radial width centred on the burner centreline.

The proportionality constant relating LII pixel counts to soot volume fraction was obtained by matching the centreline LII signal at 15 mm HAB to the corresponding soot volume fraction derived from light extinction, as shown in Fig. 2.18. This soot concentration to pixel count calibration constant was then applied to the entire background-subtracted LII image (Fig. 2.14), thereby converting the measured LII signal from pixel counts to SVF. A processed LII image calibrated to SVF is shown in Fig. 2.19.

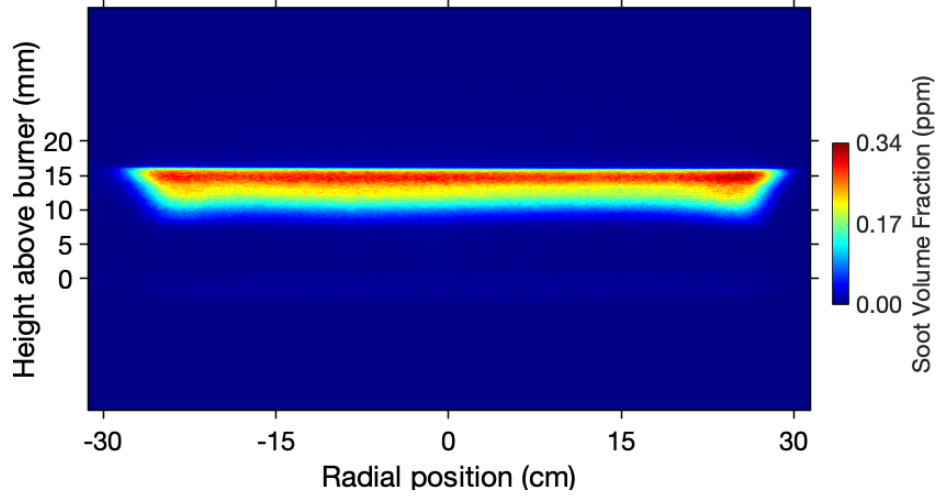


Figure 2.19: Soot volume fraction field obtained from LII measurements in a rich ethylene-air flame at  $C/O = 0.79$ .

SVF-calibrated centreline vertical profiles were then extracted directly from the calibrated LII images using the same spatial-averaging procedure described above, i.e. averaging over a region at the burner centre line with a radial width of 1 mm and a vertical extent of approximately 0.4 mm. Figure 2.20 presents the resulting centreline vertical profile for a rich flame at  $\phi = 2.36$  ( $C/O = 0.79$ ).

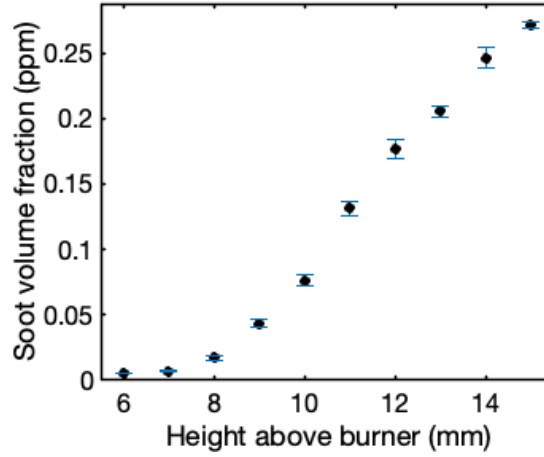


Figure 2.20: Centreline soot volume fraction profiles extracted from SVF-calibrated LII images for a rich flame at  $\phi = 2.36$  ( $C/O = 0.79$ ). The profiles were obtained by averaging the LII signal over a vertical band of thickness 0.4 mm ( $\pm 0.2$  mm) at each height above the burner and over a radial width of 1 mm centred on the burner centreline.

Radial profiles were obtained at fixed heights above the burner by averaging the calibrated SVF over a vertical band of thickness 0.4 mm ( $\pm 0.2$  mm), corresponding to approximately 10 pixels. This produced a one-dimensional SVF profile as a function of radial pixel position. The radial pixel positions were then converted to physical distance from the burner centreline using the spatial calibration, giving SVF as a function of radial position. As shown in Figure 2.21, the soot volume fraction was nominally axisymmetric across the central portion of the flame, but with a slight increase towards the edges of the controlled flow field. This phenomenon, common in flat-flame burners such as McKenna burners, could arise from the local gas composition and temperature gradients near the periphery, as well as non-uniform cooling across the burner surface [111]. Attempts to mitigate the edge peaks using a broader 80 mm stabilisation plate did not yield any improvement under the same flame conditions. The 80 mm stabilisation plate broadened the flame but further heightened edge peaking in the radial profile. The 60 mm plate was therefore used for the experiments in this work.

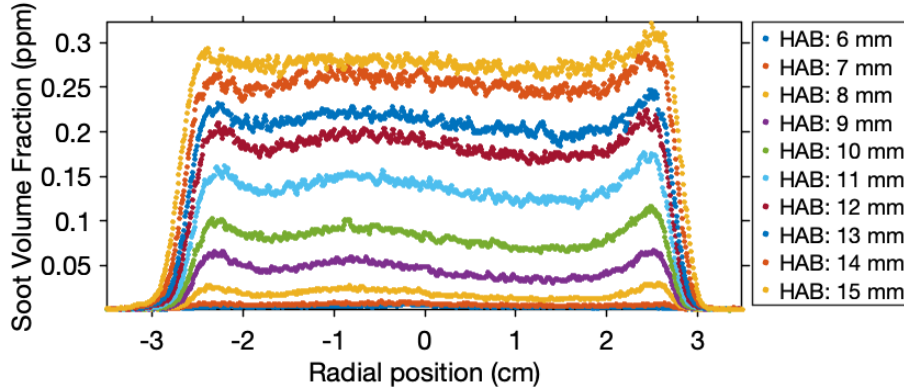


Figure 2.21: Radial soot volume fraction profiles extracted from LII images at heights between 6 and 15 mm HAB for a rich flame with  $C/O = 0.79$ . Profiles were obtained at fixed heights by averaging the LII signal over a vertical band of thickness 0.4 mm ( $\pm 0.2$  mm). The resulting one-dimensional radial signal was then averaged every 2 pixels, corresponding to approximately 0.1 mm, before conversion to physical distance using the spatial calibration.

## 2.6.2 Time-resolved LII signal processing

### Soot volume fraction from time-resolved LII measurements

The peak of the time-resolved LII signal can be used to infer soot concentration from the PMT measurements. For the PMT comparison, the peak PMT LII signal was normalised to the light extinction derived SVF at 16 mm HAB. This provided a calibration factor for the PMT measurements, which was then applied to the PMT peak signals at the remaining heights. Figure 2.22 shows good agreement between the centreline soot volume fraction profiles obtained from time-resolved PMT measurements with corresponding laser-sheet camera measurements at  $\phi = 2.36$  ( $C/O = 0.79$ ). The PMT measurements were taken at 2 mm intervals from 6 to 16 mm HAB using the horizontal laser-sheet configuration, whereas the camera measurements were obtained using the vertical laser-sheet configuration described earlier.

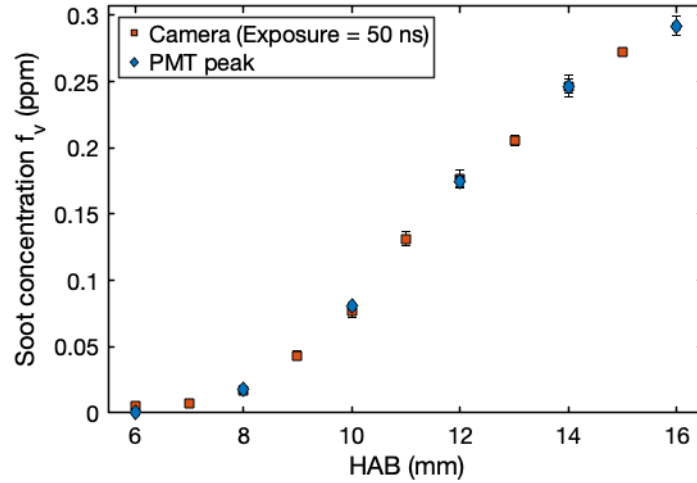


Figure 2.22: Centreline soot volume fraction as a function of height above the burner, comparing peaks of time-resolved PMT measurements and camera measurements at  $\phi = 2.36$  ( $C/O = 0.79$ ). The PMT measurements were performed using a horizontally oriented laser sheet ( $2 \text{ mm} \times 10 \text{ mm}$ ), while the camera measurements employed a vertically oriented laser sheet of same dimensions.



### Extracting decay times from time-resolved profiles

The LII decay times are considered as indicators of primary particle size, since LII decay times are mainly governed by conductive cooling, which depends on the specific surface area of the particle, and thus the primary particle size [11,91]. Decay times were extracted from the time-resolved LII signals by fitting the exponential decay region of the signal (linked to conduction-dominated cooling). To identify the appropriate fitting region, the signals were plotted on a logarithmic scale. The approximately linear region of the signal was selected for fitting, while the initial steeper decay was excluded. This was important because the early steep decay, particularly for more mature soot at high fluence, may be associated with soot sublimation rather than conduction-dominated cooling.

The decay follows:

$$I(t) = A \exp\left(-\frac{t}{\tau}\right), \quad (2.9)$$

where  $A$  is the amplitude,  $t$  is time, and  $\tau$  is the decay time of the fitted segment. Taking the natural logarithm gives

$$\ln I(t) = \ln A - \frac{t}{\tau}. \quad (2.10)$$

The gradient of the linear fit is therefore  $-1/\tau$ , so the decay time was obtained from the reciprocal of the fitted gradient magnitude. In MATLAB, this was done by applying a least-squares first-degree polynomial fit to  $\ln(I)$  within the selected fitting window.

Figure 2.23 shows the straight line fits for two time-resolved profiles at the same flame condition,  $\phi = 2.36$  ( $C/O = 0.79$ ), at 8 and 16 mm HAB on a log scale. For the 16 mm HAB case, representing more mature soot, the fitting region was started approximately 80 ns after the signal peak, after the initial steep decay had passed. For less mature soot, this initial region was less pronounced, allowing the fit to be applied closer to the signal peak. Decay times of 59 ns and 146 ns were thus obtained for the early-stage and more mature soot, respectively. The longer decay time at 16 mm HAB indicates larger soot particles, since larger particles cool more slowly due to their lower

surface-area-to-volume ratio. A direct conversion of decay time to particle diameter is not attempted, as other soot properties, such as heat capacity, thermal accommodation coefficient and density, are also expected to vary with height above the burner, complicating quantitative size determination.

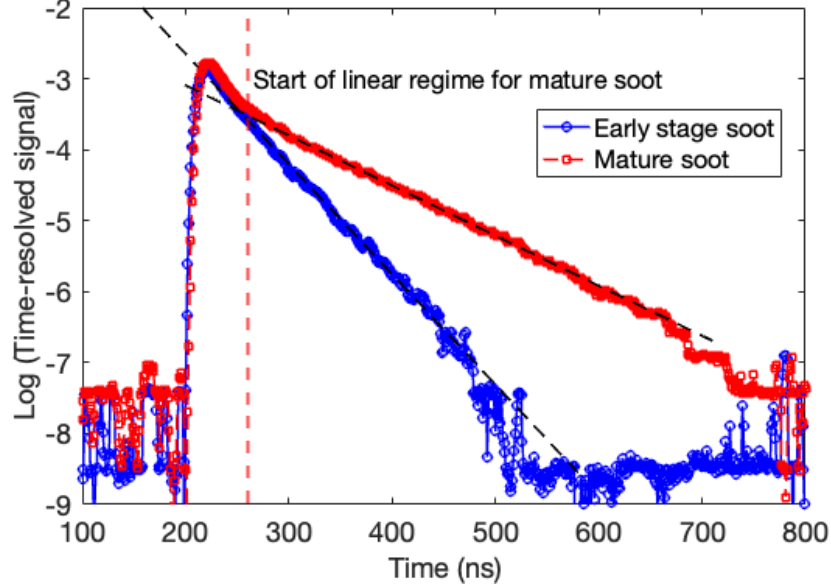


Figure 2.23: Time-resolved LII decay profiles for the same rich flame condition ( $C/O = 0.79$ ), comparing early-stage soot at 8 mm HAB and more mature soot at 16 mm HAB. The signal is plotted on a logarithmic scale,  $\ln(S)$ , on the vertical axis. The initial steeper decay is excluded, and the subsequent conduction-dominated cooling regime is identified for exponential fitting; the dashed black lines show the linear fits to  $\ln(S)$  over the selected time windows.

## 2.7 Choice of laser fluence and fluence curve

When performing laser measurements in a flame, one of the primary considerations is selecting the appropriate fluence. To identify the optimal operating range, a fluence curve was constructed by plotting the LII signal intensity as a function of fluence. The laser pulse energy was adjusted by varying the Q-switch delay. A Coherent PM10V1 thermopile power meter was used to measure the pulse energy for the fluence calculations. Figure 2.24 shows the peak PMT LII signals together with the corresponding signals from planar LII images, both at a height of 16 mm above the burner (HAB).

The camera data were processed following the procedure described in Section 2.6.1. From both measurements, the LII signal increases with laser fluence. However, at the highest fluences, where particle sublimation starts becoming significant, the PMT peak signal shows a later levelling off, whereas the camera signal, which is integrated over a fixed 50 ns gate, has already plateaued. This may occur because, at higher fluence, soot vaporisation removes soot mass, leaving smaller particles that cool more rapidly and therefore produce a more rapidly decreasing post-peak LII signal. Since the camera measurement is averaged over a fixed 50 ns gate, this reduction in the post-peak signal causes the gated camera signal to level off more clearly than the PMT peak signal. A closer agreement is observed between the PMT and camera-based measurements when the PMT signal is averaged over a 50 ns temporal window positioned after the peak, thereby mimicking the camera gate, as shown in Figure 2.25. For LII measurements, it is preferable to operate just beyond the onset of the plateau, where the signal is less sensitive to shot-to-shot pulse energy fluctuations. Figure 2.25 shows that this region is reached at approximately  $235 \text{ mJ cm}^{-2}$ , which was therefore selected for all LII measurements in this work.

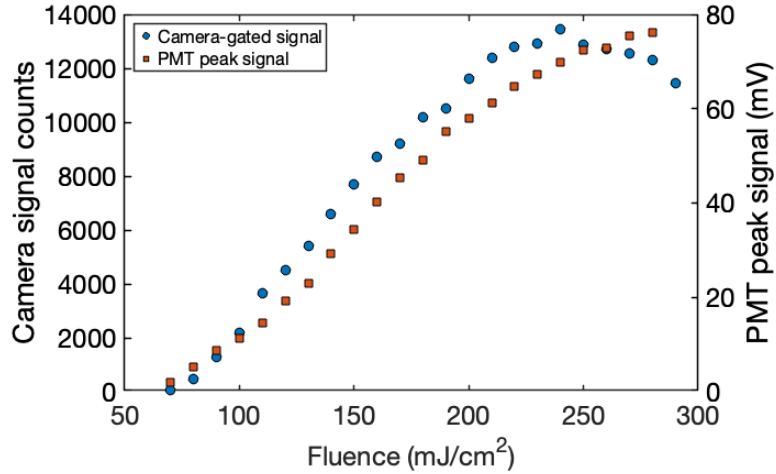


Figure 2.24: Fluence curve at 16 mm HAB for a rich flame at  $\phi = 2.36$  ( $\text{C/O} = 0.79$ ), constructed from the peak values of the time-resolved PMT signals at different laser fluences. Equivalent prompt LII camera signals, averaged over the 50 ns gate duration, are also shown for comparison.

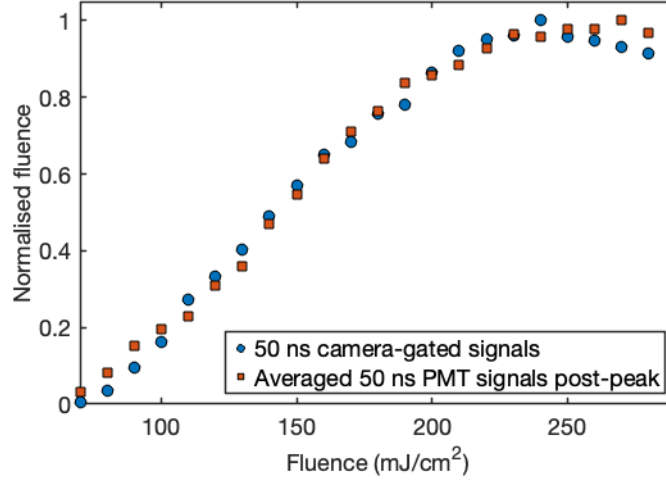


Figure 2.25: Normalised fluence curves at 16 mm HAB for a rich flame at  $\phi = 2.36$ , comparing 50 ns post-peak averaged time-resolved PMT measurements with LII camera measurements acquired using a 50 ns gate duration. The agreement between the two curves confirms the consistency of the PMT-based and camera-based LII measurements under comparable flame and gating conditions.

## Chapter conclusion

In this chapter, the experimental conditions for this work were established based on selected operating constraints. Measurements were therefore defined over a range of C/O ratios, from nucleation (C/O=0.59) to rich sooting conditions (C/O=0.79), at a fixed height of 16 mm HAB, with and without hydrogen addition, and as a function of height in a rich flame (C/O=0.79) and a sparingly sooting flame (C/O=0.69), allowing the effects of hydrogen addition to be studied with height above the burner.

The experimental methodology used to perform these measurements was also established. Planar laser-induced incandescence and time-resolved LII were implemented to track soot volume fraction and LII decay times. It was established that the C/O-ratio scan would be performed using PMT-based time-resolved LII measurements. For these measurements, a horizontal laser sheet was used to increase the LII collection volume, allowing measurable signals with good signal-to-noise ratio to be obtained across the whole range. This enabled soot volume fraction and LII decay time to be tracked as a function of C/O ratio.

For studying the effects of hydrogen addition as a function of height in the rich and sparingly sooting flames, planar LII imaging was used with a vertical laser sheet to obtain a two-dimensional distribution of soot volume fraction over the illuminated region. Separate time-resolved PMT measurements were also taken at selected heights under the same flame conditions, allowing the LII decay behaviour to be also examined.

Checks were carried out to ensure reliable LII measurements, including adjusting the camera delay for prompt LII detection, and making sure LII signals were not saturated by operating the detectors within their linear response. The data-processing procedure was then described, including background subtraction, image averaging, calibration of raw LII signal counts to soot volume fraction using the light extinction method, and extraction of centreline and radial SVF profiles. A fluence curve was constructed for fluence selection.

The processing of the time-resolved LII measurements was also described. The PMT peak signals were used to infer soot volume fraction, while decay times were extracted from the decay profiles using selected fitting windows. In this work, the LII decay times are used as a proxy for soot primary particle sizes. The next chapter therefore applies this methodology to the established flame conditions to study the effects of hydrogen addition on soot volume fraction and LII decay times.

## Chapter 3

# Results: Studying the effects of hydrogen addition on soot formation using laser-induced incandescence

### 3.1 Introduction

In this chapter, we present experimental results for the effect of hydrogen addition on soot formation in atmospheric premixed ethylene-air flat flames across a broad range of flame conditions, with a focus on nucleation flames and the effect of  $H_2$  on the onset of soot formation. Laser-Induced Incandescence (LII) is used to measure soot volume fraction and to track changes in LII signal decay, which provides insight into particle growth.

The study first examines the effects of hydrogen in a base case of a rather rich and strongly sooting flame ( $C/O = 0.79$ ). A sparingly sooting flame with a  $C/O$  ratio of 0.69 was also defined. Experiments were performed for zero, 20% and 40%  $H_2$  addition. The flow rates for the resulting six flame conditions are listed in Table 2.1 in Chapter 2. LII images were recorded for each of these conditions. The laser configuration for planar LII imaging was a vertical laser sheet of  $2\text{ mm} \times 10\text{ mm}$ .

Time-resolved LII measurements were performed in the same strongly sooting and sparingly sooting flames using a horizontally oriented laser sheet of the same dimensions. Measurements were taken at heights of 6–16 mm above the burner, in 2 mm increments, for 0%, 20%, and 40% H<sub>2</sub> addition, thereby cross-validating the soot concentration measurements obtained from LII imaging. In addition, signal decay times were evaluated by fitting an exponential decay to the part of the TiRe-LII signals associated with conduction-dominated cooling.

This study also examines the onset of soot formation in a nucleation flame, to determine how hydrogen addition affects soot formation thresholds. Nucleation flames are characterised by nascent soot, where the LII signal decay rate remains invariant with increasing height above the burner, indicating an absence of soot growth [16,91]. Beyond nucleation, we investigate the soot concentration and decay times evolution across a range of C/O ratios to establish trends in hydrogen’s influence on nucleation and soot growth. The different C/O ratios and the corresponding flow rates in the hydrogen-free and hydrogen-doped mixtures are listed in Table 2.2 in Chapter 2. Given the scarcity of studies on hydrogen’s effect on soot nucleation and growth over a wide range of C/O ratios in laminar premixed flames, this chapter aims to assess how hydrogen influences both soot inception and the subsequent growth process. These insights gained could contribute to a more comprehensive understanding of soot formation mechanisms in hydrogen-enriched flames and aid in the validation of kinetic models [60,112,113].

## 3.2 Study of the influence of hydrogen addition in a highly sooting and sparingly sooting flame

### 3.2.1 Effects of hydrogen addition on soot volume fraction

Prompt LII images were recorded at a fluence of 235 mJ cm<sup>-2</sup> using a 50 ns camera exposure gate. Under the experimental conditions established for the rich flame at C/O = 0.79 ( $\phi = 2.36$  for the H<sub>2</sub>-free case) and the sparingly sooting flame at C/O = 0.69 ( $\phi = 2.07$  for the H<sub>2</sub>-free case), the changes in soot concentration induced by hydrogen addition are shown in Figure 3.1. These were calibrated to soot vol-

ume fraction using the light extinction method described previously (see Section 2.6.1). Changes in soot concentration due to hydrogen addition are clearly visible. The laser sheet propagated from the left to the right of these images. It can be seen that the 2D maps of soot volume fraction are axisymmetric and are radially uniform in the central portion of the flame. There is an increase in  $f_v$  towards the very edges of the flames with  $H_2$  addition. Similar edge-effects have been noted in flat-flame burners by other authors [111] and could arise from the local gas composition and temperature gradients near the periphery.



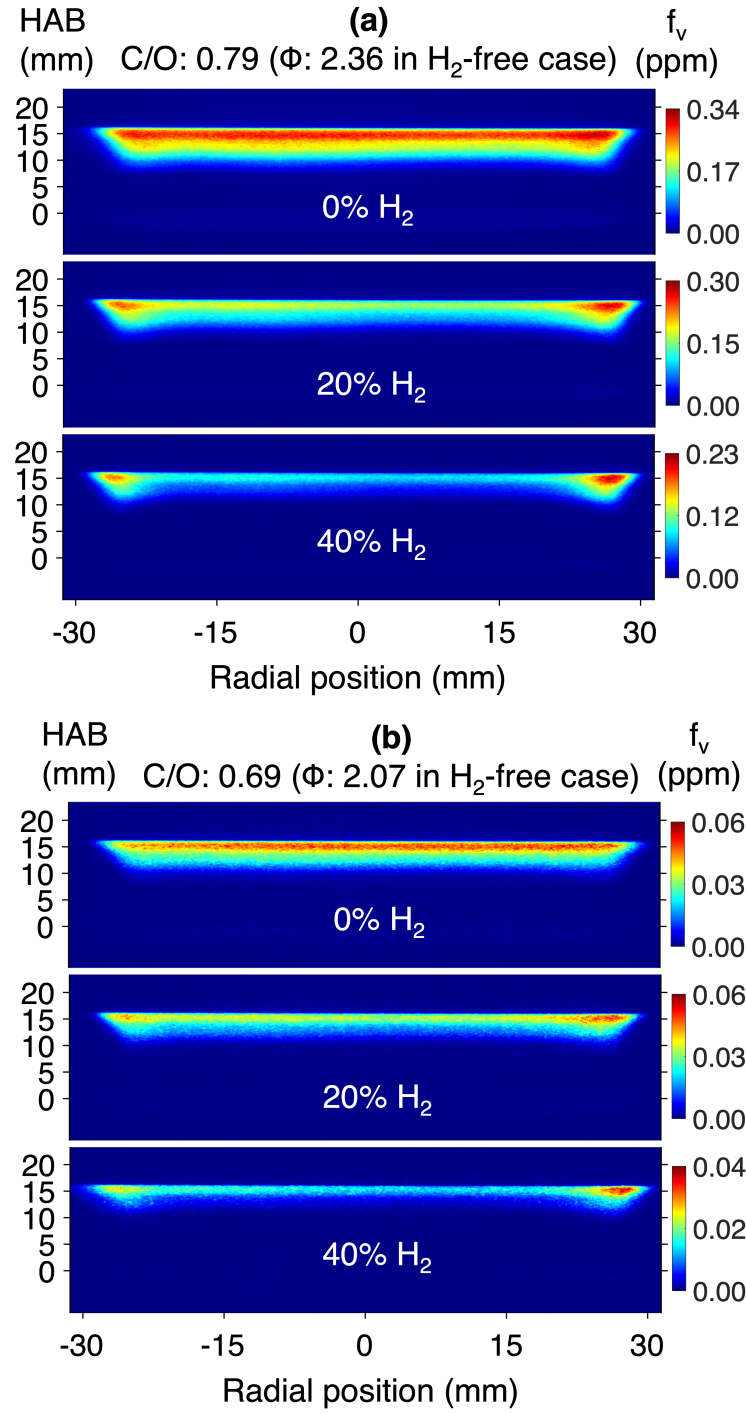


Figure 3.1: LII spatial images with  $H_2$  addition in (a) a fuel-rich flame of C/O ratio of 0.79 and (b) a sparingly sooting flame of C/O ratio of 0.69 (equivalence ratio of  $\phi = 2.36$  and  $\phi = 2.07$  in  $H_2$ -free cases respectively) calibrated to soot volume fraction (ppm).

For both flames at  $C/O = 0.79$  and  $C/O = 0.69$ , Figure 3.2 shows centre-line vertical profiles from which changes in soot concentration induced by hydrogen addition are further illustrated. Data points were obtained from Figure 3.1 by averaging LII signals radially over 1 mm and vertically over 0.4 mm at each height. Peak intensities extracted from PMT time-resolved LII traces are also shown, which are consistent with those from LII images. These demonstrate a similar reduction in soot concentration due to  $H_2$  addition. The centreline vertical profiles shown in Figure 3.2 cover heights from 6 to 15 mm above the burner. Without any  $H_2$  in the flame mixtures, the difference in soot concentration between the rich ( $C/O = 0.79$ ) and sparingly sooting ( $C/O = 0.69$ ) flame is approximately a factor of six at a height of 15 mm HAB, which is in agreement with Hadeef et al [14]. It is clear that with  $H_2$  addition (20% and 40%), soot is reduced in both flames, with a stronger inhibitory effect at 40%  $H_2$ . Increasing amounts of hydrogen addition appear to shift the sharp increase in  $f_v$  further downstream.

The observed differences in soot concentration, as a result of  $H_2$  addition cannot be attributed to merely dilution of carbon concentration, since the initial carbon-oxygen balance is preserved in  $H_2$ -doped mixtures, and the total carbon concentration  $[C]_{\text{tot}}$  changes only marginally across the  $H_2$ -doped cases, as calculated next for the rich flame condition of  $C/O = 0.79$ :

Each mole of  $C_2H_4$  contains two carbon atoms, so the carbon-atom concentration in the unburned mixture is

$$[C]_{\text{tot}} = 2 y_{C_2H_4} c_{\text{tot}} = \left( 2 \frac{Q_{C_2H_4}}{Q_{\text{tot}}} \right) \frac{p}{RT} \quad [\text{mol m}^{-3}]. \quad (3.1)$$

where  $c_{\text{tot}}$  is the total molar concentration of the premixed mixture,  $y_{C_2H_4}$  is the mole fraction of ethylene in the mixture,  $Q_{C_2H_4}$  is the ethylene flow rate,  $Q_{\text{tot}}$  is the total mixture flow rate,  $p$  and  $T$  are the flow-rate reference pressure and temperature, here 1 atm and 293 K, and  $R$  is the universal gas constant. Therefore, using the flow rates in Table 2.1 for the  $C/O = 0.79$  case, a molar carbon concentration of  $11.83 \text{ mol m}^{-3}$  is obtained for the  $H_2$ -free case. For the 20% and 40%  $H_2$  cases, this decreases to 11.48 and  $11.17 \text{ mol m}^{-3}$ , respectively, corresponding to a maximum reduction of approximately

6%. This reduction in carbon concentration is small compared with the much larger decrease in soot concentration observed when  $H_2$  is added.

Changes in flame temperature are also considered unlikely to account for this. Our highly sooting flame case is also close to the ethylene/air premixed flat-flame conditions studied by De Iuliis et al. [15], making their temperature data a useful reference. In that work, even with 40%  $H_2$  addition, the maximum measured temperature difference was only about 50 K relative to the  $H_2$ -free flame. Do et al. [18] likewise reported negligible temperature-profile changes for smaller  $H_2$  additions.

It has however been proposed that adding  $H_2$  lowers the effective availability of H atoms for PAH/soot growth through the HACA mechanism, through preferential channelling of H into O/OH-driven branching and oxidation, leading to less HACA-based soot formation and growth [15, 18, 114].

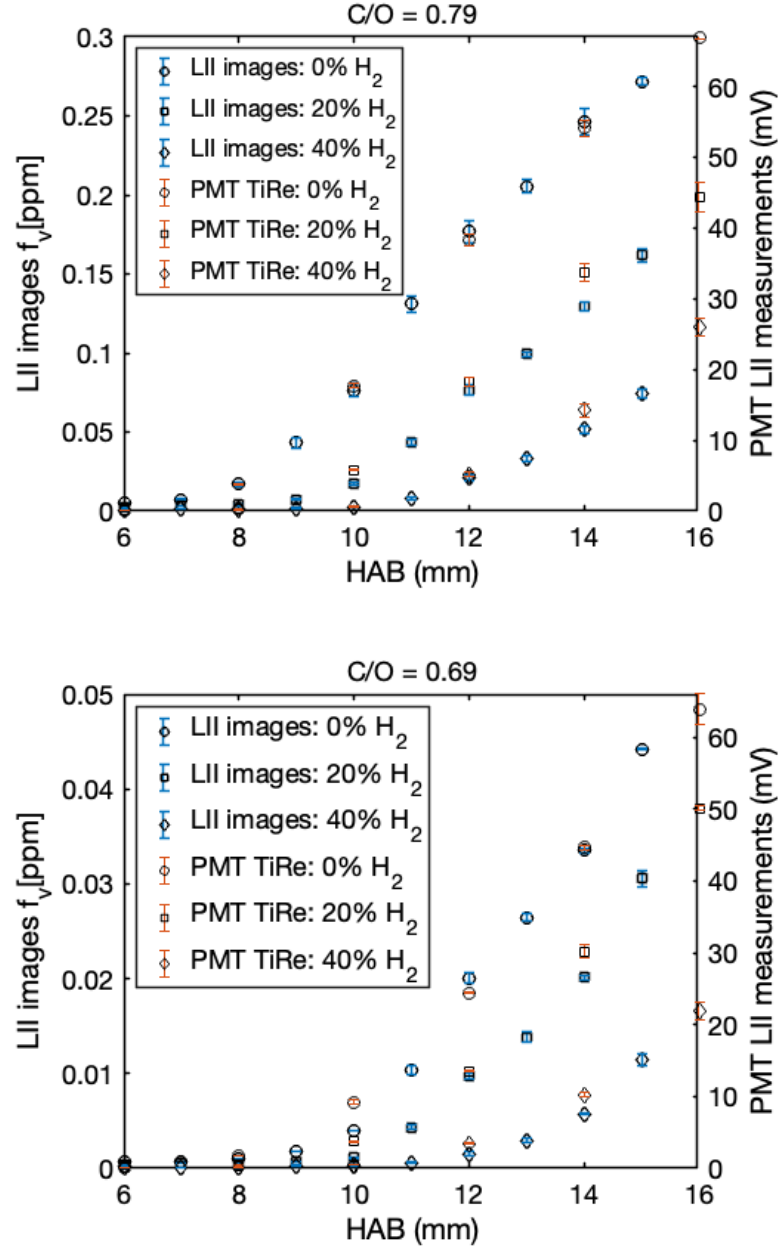


Figure 3.2: Centre-line vertical profiles of soot concentration ( $f_v$  [ppm]) measured using LII images and peaks of PMT TiRe LII signals as a function of height above the burner (HAB) for flames with C/O ratios of 0.79 (top) and 0.69 (bottom). Data are shown for 0%, 20%, and 40% hydrogen addition. Error bars represent the standard error calculated from three independent repetitions.

Figure 3.3 compares PMT-derived soot-volume-fraction ratios,  $f_v(\text{H}_2)/f_v(\text{no H}_2)$ , for the two flame conditions at different HABs. Expressing the data as  $f_v(\text{H}_2)/f_v(\text{no H}_2)$  shows the extent of suppression, such that values  $< 1$  indicate reduced soot with  $\text{H}_2$ , and smaller values show a stronger effect.

In both flames,  $\text{H}_2$  reduces soot at all measured heights, and the reduction is stronger for 40%  $\text{H}_2$  than for 20%  $\text{H}_2$ . The strongest fractional reduction is observed at the lowest HAB, where soot nucleation is expected to dominate [91,115]. The inhibitory effect then becomes less pronounced with increasing HAB, as soot surface growth increases with height above burner [15,16,91].

With 20%  $\text{H}_2$ , the reduction is slightly more pronounced in the highly sooting flame ( $C/O = 0.79$ ) than in the sparingly sooting flame ( $C/O = 0.69$ ) at all heights. 40%  $\text{H}_2$  addition leads to an increase in the suppression in both flames, although the fractional reductions are very similar. However, a weak height dependence is observed: below 12 mm HAB, the highly sooting flame shows a slightly larger reduction, whereas above 12 mm HAB, the sparingly sooting flame becomes slightly more suppressed. Previous reference data is available only for the highly sooting flame: the fractional reductions in soot concentration observed here are consistent with light-scattering data reported by De Iuliis et al [15] for flames of similar composition.

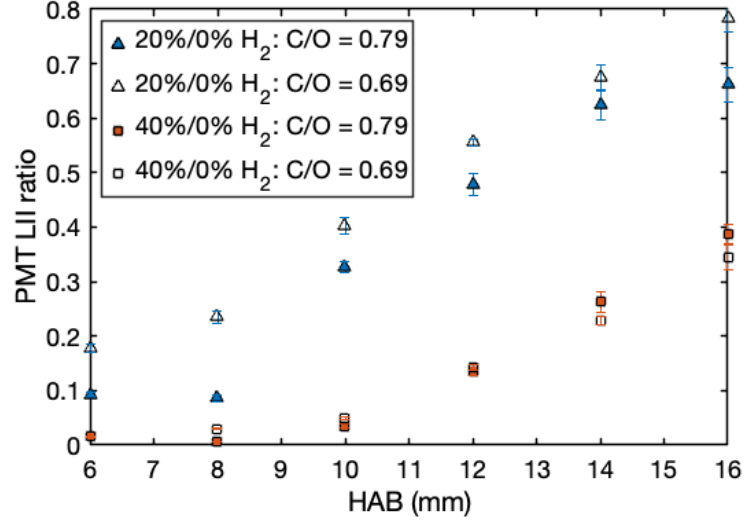


Figure 3.3: Comparison of PMT-derived soot concentration ratios (0% H<sub>2</sub> and 40% H<sub>2</sub> relative to the H<sub>2</sub>-free case) at different HABs for flames with C/O ratios of 0.79 and 0.69. Filled markers denote C/O = 0.79 and open markers denote C/O = 0.69. Error bars represent the standard error of the ratios calculated from three independent repetitions.

De Iuliis et al. had also reported that the addition of H<sub>2</sub> shifts soot nucleation downstream [15]. In contrast, our PMT data shown in Figure 3.2, but replotted on a logarithmic scale (and calibrated to SVF) in Figure 3.4, show that the LII signals, although reduced, remain detectable at the lowest HAB for the rich flame (C/O = 0.79) even when hydrogen is added to the mixture. Therefore, the presence of a measurable LII signal at the lowest HAB indicates that the detectable onset of soot (believed to be the soot inception region [15]) is not shifted downstream.

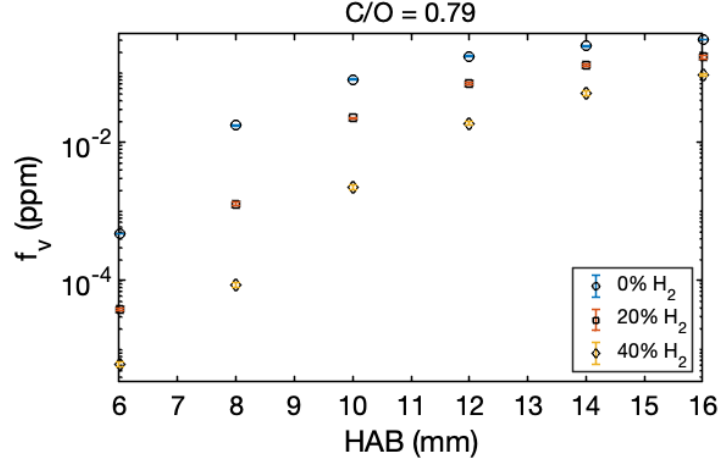


Figure 3.4: PMT-derived vertical LII profiles for  $C/O = 0.79$  plotted on a logarithmic scale. Symbols denote 0%, 20% and 40%  $H_2$  addition at fixed total flow. Showing the data on a logarithmic scale demonstrates that LII is already present at the lowest HAB for all cases but reduced in magnitude with  $H_2$  addition.

Possible additional effects of  $H_2$  on soot particle size, which may further influence soot concentration at different heights, are examined in the next section by analysing changes in decay times from time-resolved LII profiles as a result of  $H_2$  addition. Decay times here serve as indicators of primary particle size [11,91].

### 3.2.2 Effects of hydrogen addition on decay times

To extract decay times from time-resolved LII measurements, an exponential function was fitted to each time-resolved profile, as described in Chapter 2 (Section 2.6.2). The resulting decay-time profiles for the highly ( $C/O=0.79$ ) and sparingly sooting ( $C/O=0.69$ ) flames, both with and without  $H_2$  addition, are presented in Figure 3.5. The decay times increase gradually with height, reflecting the growth of soot particles. Without  $H_2$ , the decay time appears to reach a plateau at about 14 mm HAB, indicating halted soot growth. This is consistent with previous observations reported by Mouton et al. [91]. A possible explanation is that surface growth becomes less effective at higher HAB due to reduced hydrogen-atom availability, which limits HACA-driven growth [14]. The decay times decrease with  $H_2$  addition, and the plateau observed in the hydrogen-free case becomes less evident with 40%  $H_2$  addition. At all heights, 40%  $H_2$  causes a larger

reduction in decay times than 20%  $\text{H}_2$ . This is consistent with suppressed precursor formation and weaker HACA-driven surface growth, leading to smaller particles and hence shorter decay times [15, 18]. In addition, at 6 mm HAB, the decay times are similar for  $\text{H}_2$ -doped and  $\text{H}_2$ -free mixtures in both flame conditions. This suggests that at a height lying close to the onset of soot nucleation, soot size is less affected by  $\text{H}_2$  addition.



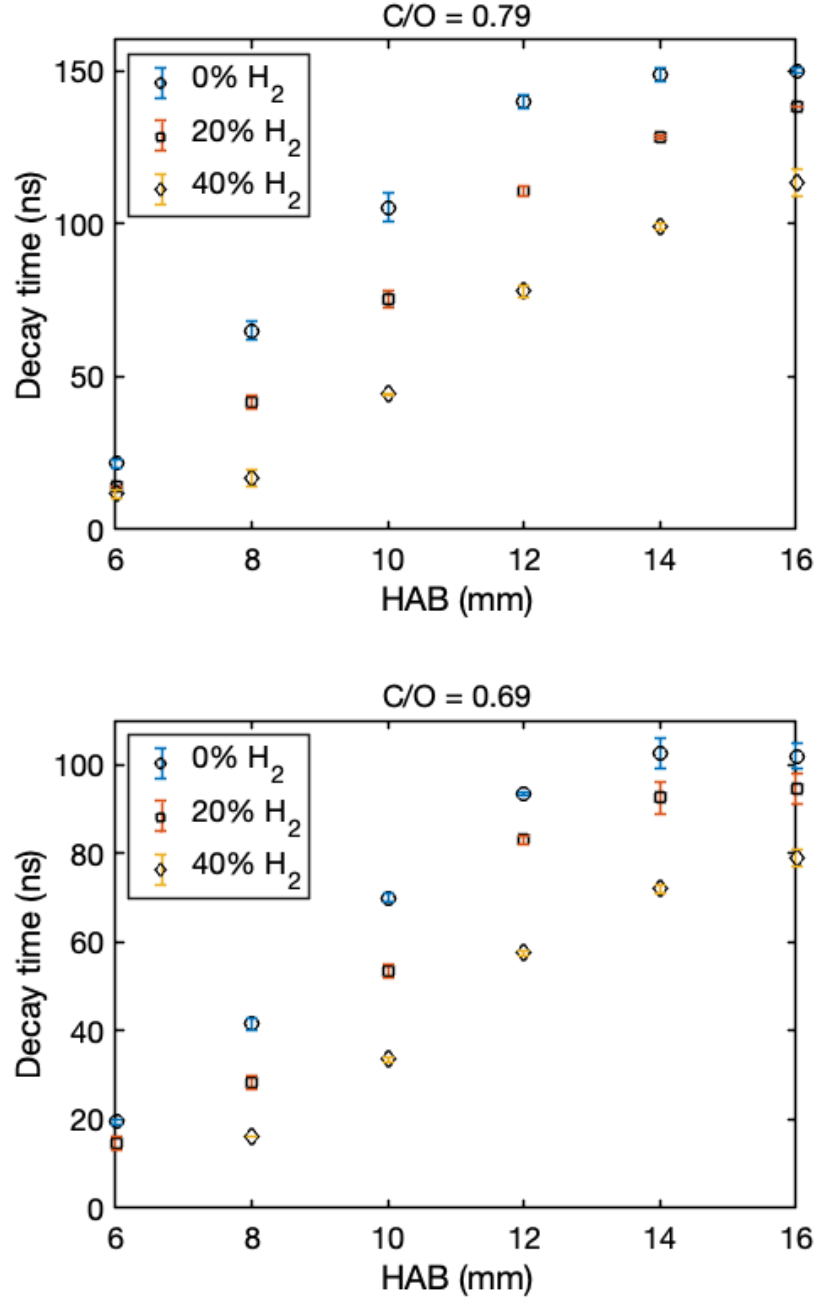


Figure 3.5: Decay times ( $\tau$ ) versus height above the burner (HAB) in flames with C/O ratios of 0.79 (top) and 0.69 (bottom), for 0%, 20%, and 40% hydrogen addition. Error bars indicate the standard error in the extracted decay times from three independent repetitions.

Figure 3.6 compares decay time ratios for 20% and 40%  $H_2$  addition at the different HABs for both C/O ratios, derived from Figure 3.5. Similar to the previous interpretation of soot concentration ratio (Figure 3.3), values  $< 1$  indicate reduced LII decay time with  $H_2$ , and smaller values show a larger effect. The decreasing ratios at lower heights suggest an even stronger effect where soot particles are smaller. Reaching higher heights, as surface growth increases,  $H_2$ 's effect on soot size reduces. A local spike appears at 6 mm HAB, consistent with a reduced  $H_2$  effect on soot size near soot inception, where soot size is at its smallest.

At 16 mm HAB, for both the rich and sparingly-sooting flame, 40%  $H_2$  reduces decay times to approximately 75% of those measured in the  $H_2$ -free case. Decay times reach only 26% of the  $H_2$ -free value at 8 mm HAB in the rich flame and 39% in the sparingly-sooting flame, demonstrating a larger effect on the richer flame. This larger relative reduction in the richer flame is observed for both 20% and 40%  $H_2$  addition. However, it can be observed that with increasing HAB, the ratios for the two flame conditions converge towards similar values for any given doping level (i.e. the 20%/0% ratios at  $C/O = 0.69$  and  $0.79$  become similar; the same convergence is observed for the 40%/0% ratios). These observations indicate that, in similarly rich flames, at a sufficiently high HAB, where soot is already mature, the same level of  $H_2$  doping (e.g. 20 or 40%) produces a similar reduction in particle size.

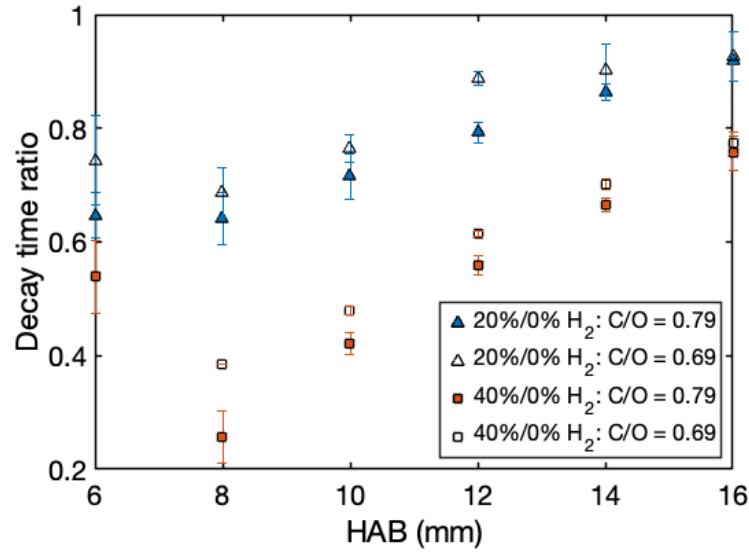


Figure 3.6: Decay-time ratios as a function of height above the burner (HAB) for flames with C/O ratios of 0.79 and 0.69 at 0%, 20%, and 40% hydrogen addition. Filled markers denote the richer flame (C/O = 0.79), while open markers denote the sparingly sooting flame (C/O = 0.69). Error bars indicate the standard error calculated from the ratios of three independent repetitions at each height.

### 3.3 Study of the influence of hydrogen addition over a range of C/O ratios

As established in the previous chapter, the effects of hydrogen addition in premixed laminar flat flames have either focused on rich sooting flames or nucleation flames [15, 18, 50]. Studies examining hydrogen addition across a wide range of C/O ratios have not been reported. This section of this work therefore examines the effects of hydrogen addition over a range of C/O ratios, from the soot nucleation threshold (referred to here as the nucleation flame) to strongly sooting flames at a height of 16 mm HAB.

#### Identifying the nucleation flame

The condition for a nucleation flame is considered to be the highest C/O ratio for which no growth was observed in the LII decay time along the flame height, meaning the size of the soot particles remains constant. A C/O ratio of 0.59 was thus identified as the

threshold for nucleation for the  $\text{H}_2$ -free flame, which agrees with the value presented previously by Bladh et al [16]. The flow rates for the nucleation flames are listed in Table 2.2 in Chapter 2. The corresponding PMT TiRe-LII signals at different heights above burner are reported in Figure 3.7. As shown in the non-normalised plot (a), signal intensity increases, indicating that the concentration of soot nuclei increases with HAB. This could be due to sustained PAH production along the flame height, which can continue to feed the formation of recently nucleated particles [16]. However, in the normalised plot (b), the decay times are invariant with HAB, indicating no particle growth. This C/O ratio was therefore treated as the nucleation flame condition.

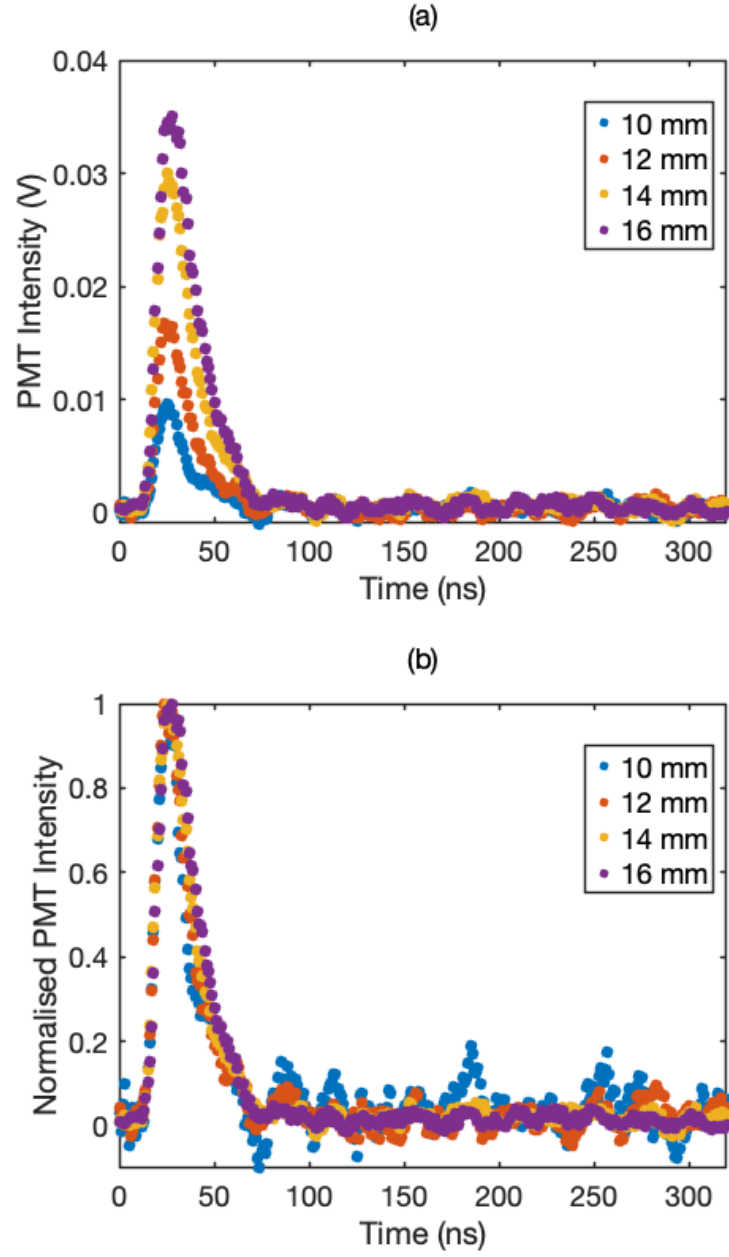


Figure 3.7: (a) Background-subtracted time-resolved LII profiles and (b) normalised time-resolved LII profiles for the nucleation flame ( $C/O = 0.59$ ) without  $H_2$  addition at different heights above the burner (HABs), showing no systematic increase in decay time with height, consistent with nucleation-flame behaviour.

### Effects of hydrogen addition on soot in nucleation flames

By identifying the nucleation flame, we can investigate shifts in the onset of soot formation at C/O ratios slightly higher than that of the nucleation flame while incorporating hydrogen into the mixture. Time-resolved measurements were taken at 16 mm HAB, and in flames slightly richer than the nucleation condition, 40% H<sub>2</sub> was added. Figure 3.8 shows that the corresponding nucleation condition with 40% H<sub>2</sub> is C/O=0.60.

In the H<sub>2</sub>-doped nucleation flame at C/O = 0.60, Figure 3.8(b) shows time-resolved profiles recorded at different HABs where no increase in decay time is observed, hence no growth in soot size, consistent with the hydrogen-free nucleation flame. The decay times at the different heights were similar to those of the H<sub>2</sub>-free case (C/O = 0.59), ranging from 19-22 ns (FWHM). It is striking that a substantial addition of hydrogen has such a modest influence on the C/O ratio at which nucleation occurs. As shown in panel (a), nucleation behaviour was observed up to C/O=0.60 but absent at C/O=0.61; just beyond this point, a rapid increase in decay time is evident in flame conditions only slightly richer than the nucleation condition.

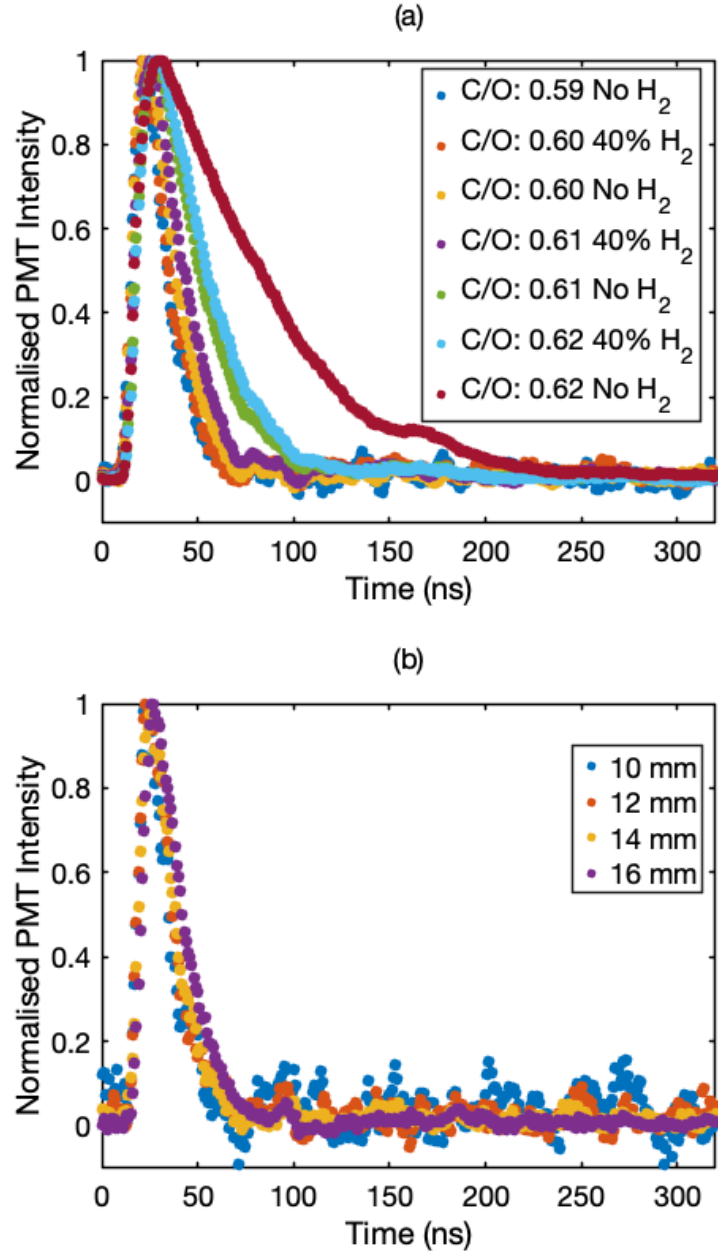


Figure 3.8: (a) Comparison of normalised time-resolved LII profiles for H<sub>2</sub>-free and 40% H<sub>2</sub>-doped flames near the nucleation condition, measured at 16 mm HAB, and (b) normalised time-resolved LII profiles for a 40% H<sub>2</sub>-doped nucleation flame with a C/O ratio of 0.60 at different HABs, showing no systematic increase in decay time with height, indicating an absence of soot growth and behaviour consistent with a nucleation flame.

### Fluence curve of hydrogen-free and hydrogen-doped nucleation flame

Figure 3.9 shows fluence curves measured at 16 mm HAB for the two nucleation flames: the hydrogen-free nucleation flame ( $C/O = 0.59$ ) and 40% hydrogen-doped nucleation flame ( $C/O = 0.60$ ). Panel (a) shows the peak of the PMT time-resolved LII measurements, with higher peaks observed in the hydrogen-doped case, consistent with a slightly higher soot nuclei concentration at the higher  $C/O$ . The signal intensities continue to rise with fluence in both cases. This is different from what is observed in richer flames, which typically plateau at fluences of 200–220  $\text{mJ cm}^{-2}$ .

This behaviour, which has been reported previously for nucleation flames [16, 91], arises due to the higher laser fluence required to approach sublimation temperature for smaller particle sizes in nucleation flames. Panel (b) shows the same data normalised to 270  $\text{mJ cm}^{-2}$ . Interestingly, the fluence curves of the  $\text{H}_2$ -free and the 40%  $\text{H}_2$ -doped nucleation flames show an almost identical response, indicating that  $\text{H}_2$  addition may not significantly alter soot characteristics under nucleation-flame conditions. This corroborates what was observed from the time-resolved measurements in Figures 3.7, and 3.8, where both nucleation flames showed very similar decay times. Since the fluence response and signal decay are both linked to the conductive cooling of laser-heated particles, their agreement suggests that the soot properties may be similar in the two flames. These properties include particle size, as well as other parameters influencing the LII response, such as heat capacity, thermal accommodation coefficient and density [11].



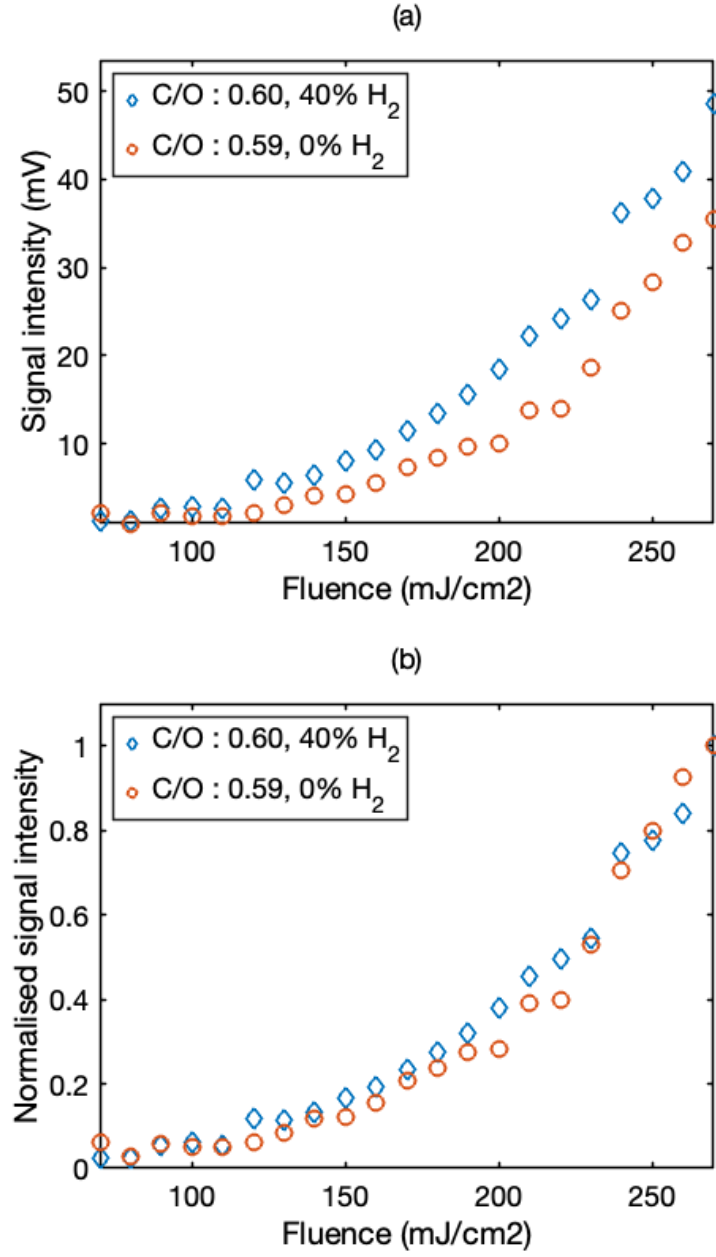


Figure 3.9: (a) Peak PMT TiRe-LII signals and (b) the corresponding normalised peak LII signals versus laser fluence for  $H_2$ -free ( $C/O = 0.59$ ) and 40%  $H_2$ -doped ( $C/O = 0.60$ ) nucleation flames at 16 mm HAB. Panel (b) shows the data from panel (a) normalised to 270 mJ cm<sup>-2</sup>. The nearly identical response in the normalised fluence curves indicates that  $H_2$  addition may not significantly alter soot characteristics under nucleation-flame conditions.

### **Studying the changes in soot concentration over a range of C/O ratios with Hydrogen addition**

Figure 3.10 shows the peak LII time-resolved profiles, calibrated to soot volume fraction, across a range of C/O ratios with and without 40% H<sub>2</sub> addition. Flow rates for each C/O ratio under H<sub>2</sub>-free and H<sub>2</sub>-doped conditions are listed in Table 2.2 in Chapter 2. Each data point represents the mean of three repeated measurements. The sensitivity of the detector was varied, including the use of ND filters and adjusting the PMT gain, to enable recording of LII signals over a large dynamic range, whilst avoiding saturation on the DC and transient signal levels. This was explained in Chapter 2 (Section 2.5.2).

To clearly illustrate the changes in soot concentration over this range, spanning nearly five orders of magnitude (a factor of 75,000) from the leanest to the richest conditions, the data were plotted on a log-log scale. Power-law relationships have been fitted to the data.

Two distinct regimes were identified: one between C/O ratios of 0.60 and 0.63, and another between 0.71 and 0.79, with a transitional stage between C/O ratios of about 0.63 and 0.71. The first regime exhibits a steeper gradient, indicating a sharper increase in soot concentration near the nucleation condition, whereas the second regime shows a more gradual increase as the flame becomes richer. Some comparison data is available from previous research exploring more limited ranges of C/O ratio for hydrogen-free flames only. It is noteworthy that the relationship observed in the second regime without H<sub>2</sub> addition closely aligns with the data from Hadeef et al. [14], who also observed a power-law relationship. Our results for H<sub>2</sub>-free flames are in close agreement with those of Desgroux et al. [75] under similar flame conditions and for the lower range of C/O ratios. Results from a limited number of other studies [64,116] are also consistent with the progressively shallower gradient leading up to Regime 2 with increasing C/O ratio.

From the power law fits, it can be observed that the effect of hydrogen is dependent on the regime. In Regime 1, the gradient decreases from around 110 in the hydrogen-free case to 85 with 40% hydrogen addition, indicating that hydrogen weakens the sharp rise in  $f_v$  close to the soot-inception region. In Regime 2, however, the gradient is slightly

steeper with 40%  $H_2$  addition, increasing from around 11 to 13. This indicates that although the hydrogen-doped flame still has a lower soot concentration in the second regime,  $f_v$  rises slightly more rapidly with C/O.

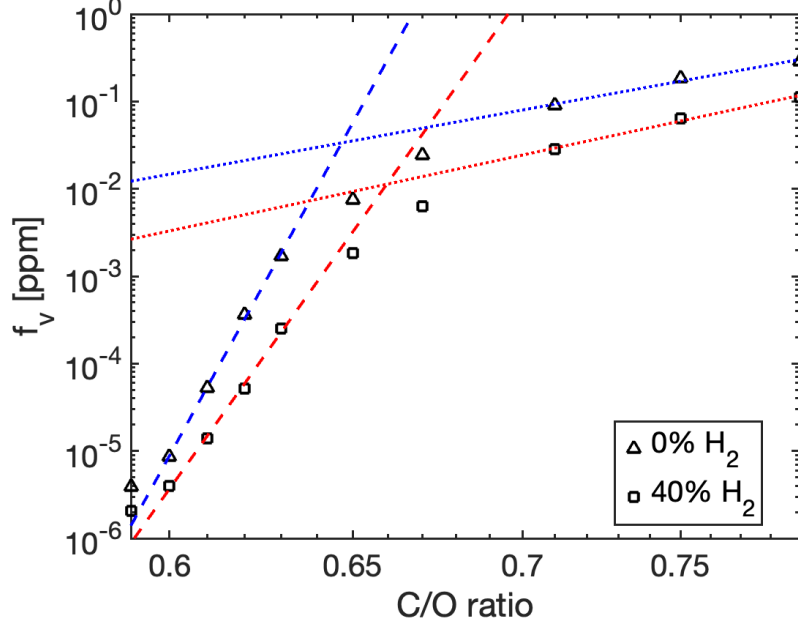


Figure 3.10:  $f_v$  [ppm] versus C/O ratio on a log-log scale for 0% and 40%  $H_2$  addition at 16 mm HAB. Symbols:  $\triangle$  = 0%  $H_2$ ,  $\square$  = 40%  $H_2$ . Power-law fits are shown for two regimes: ---  $\log(f_v) = 109.63 \log(C/O) + 19.26$  (0%  $H_2$ , Reg. 1); .....  $\log(f_v) = 10.99 \log(C/O) + 0.60$  (0%  $H_2$ , Reg. 2); ---  $\log(f_v) = 84.67 \log(C/O) + 13.35$  (40%  $H_2$ , Reg. 1); .....  $\log(f_v) = 12.98 \log(C/O) + 0.40$  (40%  $H_2$ , Reg. 2). Error bars are omitted here, as they appear negligible on the logarithmic scale spanning over five orders of magnitude.

Exponential decay times evaluated from TiRe-LII profiles are shown in Figure 3.11. The time constants increase sharply at lower C/O ratios, followed by a more gradual rise at higher C/O ratios. The increase in decay times with C/O ratio aligns with the expectation that as the flame becomes richer, soot primary particle size increases. At lower C/O ratios, near nucleation conditions, the decay times for flames with and without  $H_2$  addition are almost identical. This is in keeping with the TiRe-LII profiles for nucleation flames presented in Figures 3.7 and 3.8. There is a divergence in the results from a C/O ratio of 0.62. From this point, the increase in decay time with C/O ratio is steeper for the  $H_2$ -free flames, seeming indicative of faster soot growth in the

absence of hydrogen addition. At still richer conditions ( $C/O \gtrsim 0.71$ ) the rise in decay time becomes slightly more gradual for both mixtures.

In general, increases in soot volume fraction can result both from particle nucleation and from particle mass increase via surface growth [117]. A similar trend in  $f_v$  to the one shown in Figure 3.10 was reported by Maricq et al. [116] for  $H_2$ -free ethylene-air flat-flames. Through extractive sampling and measurement of particle electrical mobility diameter, the authors [116] identified a sharp increase in particle number at  $C/O = 0.60$  ( $\phi=1.79$ ), followed by a plateau at higher  $C/O$  ratios, beyond which surface growth became the dominant contributor to further increases in soot concentration.

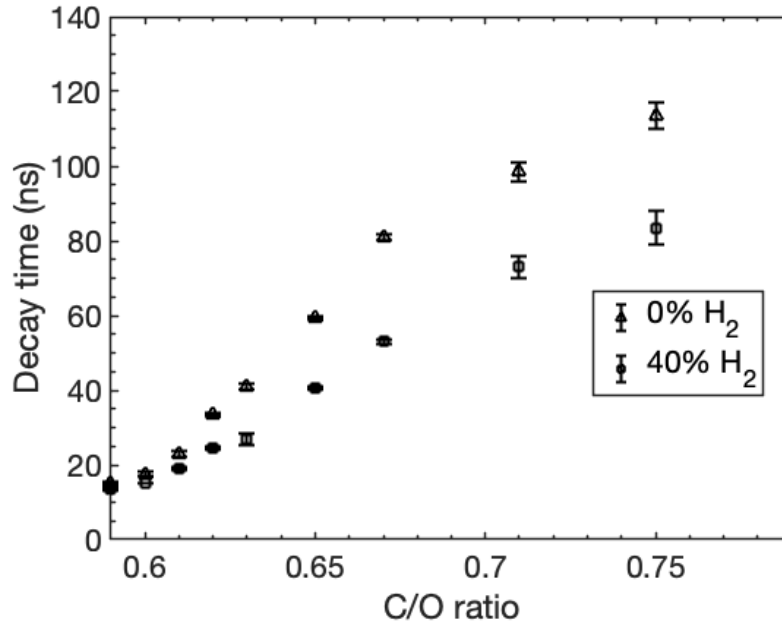


Figure 3.11: Decay times vs.  $C/O$  ratio at 0% and 40%  $H_2$  addition at 16 mm HAB. Error bars represent the standard error calculated from three independent repetitions.

The effect of  $H_2$  addition is further illustrated in Figure 3.12, in which decay time and soot concentration are plotted for the flame with 40%  $H_2$  addition as a fraction of their values for the equivalent flames without added  $H_2$ . This is therefore an alternative way of presenting the data already shown in Figures 3.10 and 3.11. Near the nucleation condition, the addition of  $H_2$  has the least effect on soot volume fraction and LII signal decay time. With increasing  $C/O$  ratio from the nucleation condition, the relative effect

of 40%  $H_2$  addition increases sharply, peaking at  $C/O = 0.62$ – $0.63$ . Beyond this point, a gradually reducing influence of  $H_2$  is observed as the flame becomes richer. This underlines that  $H_2$  addition influences both soot volume fraction and primary particle size, though its relative effect on soot volume fraction is more pronounced (indicated by the smaller ratios).

The intriguing trends observed in Figure 3.12 indicate that the influence of  $H_2$  varies considerably across flame conditions. The underlying reasons are not fully understood and involve simultaneous effects of  $H_2$  on rates of soot nucleation, surface growth and oxidation. These interactions are, however, complex and remain an active area of research.

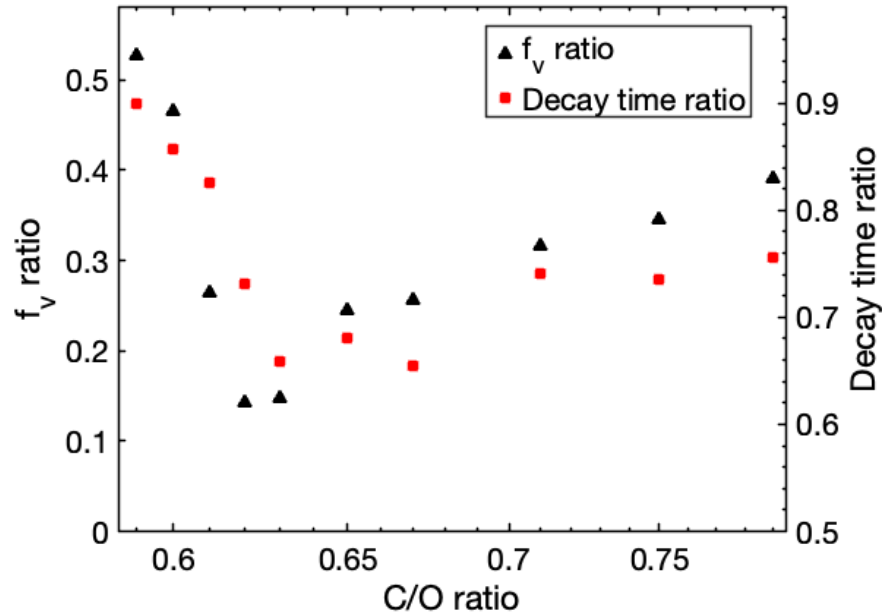


Figure 3.12: Ratio of soot concentration  $f_v$  [ppm] and decay times vs C/O ratios between 0% and 40% Hydrogen addition taken at 16 mm HAB

### 3.4 Chapter conclusion

This study investigated the effects of hydrogen addition on soot formation in atmospheric sooting and nucleation ethylene-air premixed flat-flames. To this purpose, laser-induced incandescence (LII) experiments were conducted to examine changes in soot

concentration across a range of flame conditions. In the rich flame condition, 20% and 40% hydrogen, by molar comparison to  $\text{C}_2\text{H}_4$  fuel, was added at  $\text{C/O} = 0.79$  and  $\text{C/O} = 0.69$ . It was observed that hydrogen addition resulted in a significant reduction in soot concentration at all heights, with the reduction becoming more pronounced at higher levels of hydrogen doping and at the lowest height, where nucleation is more dominant. 40% hydrogen addition causes similar reductions in  $f_v$  for both the rich and sparingly sooting flame at different heights. Regarding the effect of  $\text{H}_2$  addition on LII decay times, which serve here as a proxy for soot particle size, a clear reduction is observed across both flame conditions. The influence of  $\text{H}_2$  becomes stronger at lower heights above the burner, where soot particles are smaller and still undergoing early growth, and diminishes with increasing height as surface growth progresses and soot becomes more mature. It was observed that the effect of hydrogen on decay times, irrespective of the doping level, was greater at all heights in the richer flame. However, the decay-time ratios for the two  $\text{C/O}$  ratios converge towards similar values at higher HAB, showing that the relative reduction in particle size became less sensitive to flame richness. Overall, these observations demonstrate that  $\text{H}_2$  addition is most effective in suppressing soot growth at the lower heights (where soot particles are smaller), with its influence decreasing with height, as surface growth increases.

To study the effects of hydrogen addition on soot nucleation, a nucleation flame was first identified at a  $\text{C/O}$  ratio of 0.59. With 40%  $\text{H}_2$  addition, the nucleation condition shifted only slightly, to a  $\text{C/O}$  ratio of 0.60, perhaps suggesting that nucleation is not significantly influenced by hydrogen addition. The near-identical fluence responses of the two nucleation flames further suggest that  $\text{H}_2$  addition may not be altering the properties of the nascent soot particles. TiRe-LII measurements were subsequently conducted over a range of  $\text{C/O}$  ratios at 16 mm HAB, starting from the nucleation condition of  $\text{C/O} = 0.59$  up to the defined strongly sooting flame of  $\text{C/O} = 0.79$ . Across this range, the soot volume fraction was found to follow a power-law dependence on  $\text{C/O}$  ratio both with and without  $\text{H}_2$  addition, with two distinct regimes identified from fitting to the data. It was observed that the relative effects of  $\text{H}_2$  on both soot volume fraction and LII signal decay time depended strongly on  $\text{C/O}$  ratio: the influence

### Chapter 3. Results: Studying the effects of hydrogen addition on soot formation using laser-induced incandescence

was weakest for nucleation flames, but sharply increased up to a C/O ratio of about 0.63, after which it reduced gradually. The extent of that effect was higher on soot concentration than on the decay times at each C/O ratio.

Previous studies have reported that H<sub>2</sub> substitution can suppress key soot precursors, partly because enhanced OH levels promote their oxidation and partly because the availability of H atoms for PAH growth via HACA is reduced [18, 50]. As discussed in Chapter 1, laser-induced fluorescence (LIF) has been shown to be a useful approach for detecting different PAHs and related aromatic structures that may be linked to soot nucleation. The next chapter therefore establishes the LIF methodology used in this work, including the experimental setup and radiometric calibration process for the different excitation wavelengths used. This methodology is then applied in Chapter 5 to study the effect of hydrogen addition on fluorescence associated with PAHs and related structures under the same flame conditions studied here.

## Chapter 4

# Laser-induced fluorescence experimental set-up, radiometric calibration and data processing

### 4.1 Introduction to experimental methodology for LIF measurements

As observed in Chapter 3, the LII measurements showed that hydrogen addition reduced both the soot concentration and the LII decay times, the latter being indicative of primary particle size, with the effect of reduction being highly dependent on the carbon-to-oxygen ratio (C/O). It is therefore natural to examine how fluorescence associated with potential soot-precursor species is affected under the same conditions. As discussed previously, despite the strong interest in soot nucleation, the underlying mechanisms remain poorly understood. Nevertheless, some recent studies have identified classes of gaseous precursors that may be linked to soot nucleation, although these assignments remain uncertain. Among these, PAHs are of particular relevance because proposed nucleation routes, as discussed in Chapter 1, including PAH dimerisation [18, 22, 30] and radical-driven crosslinking [20, 23], involve PAHs as key intermediates.

As discussed in Chapter 1, LIF provides a useful approach for investigating PAHs



and related species under flame conditions, and it provides the benefit of being an in situ, non-intrusive technique. PAHs generally possess large absorption cross-sections and relatively high fluorescence quantum yields [83], making them ideal for LIF detection. However, PAH-LIF measurements in flames are not species-specific. The detected signal generally represents an unknown superposition of fluorescence from a complex mixture of molecular structures [84]. Furthermore, the absorption and emission spectra of PAHs are generally broad and overlapping, particularly at flame temperatures, meaning that a given excitation wavelength may excite contributions from multiple PAH-related structures. In general, the absorption and emission spectra of PAHs tend to shift towards longer wavelengths as molecular size increases [76]. Consequently, increasing the excitation wavelength can increase the relative contribution of larger PAH structures to the measured LIF signal [22, 80], although this should be interpreted as a gradual trend rather than a sharp separation between PAH size classes. Furthermore, the measured LIF signal may contain contributions from related species, such as resonance-stabilised radicals and aliphatic-bridged dimers, which have recently been linked to soot nucleation [23, 88].

Therefore, in this work, LIF measurements were performed using excitation wavelengths of 266, 355 and 532 nm. The aim is to determine whether hydrogen produces trends in laser-induced fluorescence signals that are consistent with the changes in soot concentration and LII decay time, which may provide further insight into the soot nucleation process. Using multiple excitation wavelengths and spectrally resolved detection, distinct features in the fluorescence data may be isolated. On this basis, the extracted features may be tentatively associated with the different classes of PAH-related precursor structures mentioned in the literature. It can then be examined how these features respond to changes in flame conditions, including C/O ratio, height above burner (HAB) and hydrogen addition.

The measured spectra were also radiometrically calibrated, allowing the fluorescence signals to be expressed as a spectral radiant energy density and, following normalisation by the incident laser fluence, in units of  $\text{m}^{-1} \text{nm}^{-1}$ . This is therefore a quantity that should be reproducible by others. When spectrally integrated, the units are  $\text{m}^{-1}$ , thus

photons emitted per photons incident per sheet propagation distance. Radiometric calibration is rarely performed in PAH-LIF experiments; LIF spectra are more typically reported as raw detector signals, uncorrected for the wavelength-dependent response of the detection system [22, 76, 82]. The presentation of signals in absolute, spectrally calibrated units is therefore a distinctive feature of the present methodology, and the calibration procedure is discussed in detail later in this chapter.

## 4.2 Flame experimental conditions

LIF measurements were performed at 16 mm HAB across a range of C/O ratios, progressing from the rich flame condition ( $C/O = 0.79$ , corresponding to  $\phi = 2.36$  in the  $H_2$ -free case) towards leaner mixtures. The lowest C/O ratio at which LIF was measured was  $C/O=0.53$  (corresponding to  $\phi = 1.60$  in the  $H_2$ -free case), thereby extending the range studied beyond that covered in the previous LII measurements, which ended at  $C/O = 0.59$ . Notably,  $C/O = 0.53$  represented a common lower limit at which LIF signal could be detected across all three excitation wavelengths while using a fluence within the linear LIF regime. Height-dependent LIF measurements were also taken in two flame conditions, namely the nucleation flame ( $C/O = 0.59$ , corresponding to  $\phi = 1.77$  in the  $H_2$ -free case) and the rich flame ( $C/O = 0.79$ ). The flame conditions are shown in Table 4.1, together with a subset of the flow conditions already used in the previous LII measurements ( $C/O = 0.59 - 0.79$ , as listed in Chapter 2).

## 4.3 LIF experimental setup

The general experimental setup for laser-induced fluorescence (LIF) is shown in Figure 4.1. Excitation was provided using the 2nd, 3rd and 4th harmonics of an Nd:YAG laser at 532, 355 and 266 nm, respectively. This required the appropriate harmonic generation modules to be installed in the laser system. The sheet-forming configuration was the horizontally oriented laser sheet of  $2 \times 10$  mm, as used in the LII measurements described in Chapter 2. This proved beneficial here for collecting fluorescence signals over a broader range of flame conditions due to the improved sensitivity afforded by the

| C/O  | Flowrates with<br>0% H <sub>2</sub><br>(NLPM) |       | Flowrates with<br>40% H <sub>2</sub><br>(NLPM) |      |                |
|------|-----------------------------------------------|-------|------------------------------------------------|------|----------------|
|      | C <sub>2</sub> H <sub>4</sub>                 | Air   | C <sub>2</sub> H <sub>4</sub>                  | Air  | H <sub>2</sub> |
| 0.53 | 1.15                                          | 10.24 | 1.10                                           | 9.85 | 0.44           |
| 0.54 | 1.17                                          | 10.22 | 1.12                                           | 9.82 | 0.45           |
| 0.55 | 1.18                                          | 10.21 | 1.13                                           | 9.80 | 0.45           |
| 0.56 | 1.21                                          | 10.18 | 1.16                                           | 9.77 | 0.46           |
| 0.57 | 1.22                                          | 10.17 | 1.17                                           | 9.75 | 0.47           |
| 0.58 | 1.24                                          | 10.15 | 1.19                                           | 9.72 | 0.48           |
| 0.59 | 1.26                                          | 10.13 | 1.20                                           | 9.71 | 0.48           |
| 0.60 | 1.27                                          | 10.12 | 1.21                                           | 9.67 | 0.49           |
| 0.61 | 1.29                                          | 10.10 | 1.23                                           | 9.67 | 0.49           |
| 0.62 | 1.31                                          | 10.08 | 1.26                                           | 9.63 | 0.50           |
| 0.63 | 1.33                                          | 10.06 | 1.27                                           | 9.62 | 0.51           |
| 0.65 | 1.36                                          | 10.03 | 1.30                                           | 9.57 | 0.52           |
| 0.67 | 1.40                                          | 9.99  | 1.33                                           | 9.52 | 0.53           |
| 0.71 | 1.47                                          | 9.92  | 1.40                                           | 9.43 | 0.56           |
| 0.75 | 1.54                                          | 9.85  | 1.46                                           | 9.34 | 0.59           |
| 0.79 | 1.62                                          | 9.77  | 1.53                                           | 9.25 | 0.61           |

Table 4.1: Flowrates for LIF measurements, established for C<sub>2</sub>H<sub>4</sub>, air, and H<sub>2</sub> for different C/O ratios under 0% and 40% H<sub>2</sub> conditions; flows are quoted in normal litres per minute (NLPM), i.e. reference conditions of 293 K and 1 atm.

horizontal sheet. The laser beam was first expanded into a collimated sheet. For 266 and 355 nm excitation, the sheet-forming telescope consisted of a UV concave lens (Thorlabs LK4166), with focal length  $f = -30.0$  mm, followed by a UV plano-convex lens (Thorlabs LA4874-UV), with focal length  $f = 150.0$  mm. To direct the beam towards the centre of the burner, two UV-enhanced aluminium mirrors (Thorlabs PF10-03-F01) were used. For 532 nm excitation, the telescope consisted of a concave lens (Thorlabs LK1743L1-A), with focal length  $f = -100$  mm, followed by a convex cylindrical lens (Thorlabs LJ4377RM-A), with focal length  $f = 400$  mm, together with two Nd:YAG laser line mirrors (Thorlabs NB1-K13). The resulting laser sheet then passed through a horizontally oriented  $2 \times 10$  mm slit before reaching the flame. To minimise contributions from scattered laser light, suitable rejection filters were used for each excitation

wavelength: a 532 nm notch filter (Thorlabs NF533-17) for 532 nm LIF, a 355 nm notch filter (Edmund Optics 39-387) for 355 nm LIF, and a 305 nm long-pass filter (Schott WG305) for 266 nm LIF. Additional laser shielding was also used to minimise stray light reaching the spectrometer, such that the residual scattering remained negligible relative to the LIF signal. The resulting fluorescence was detected at right angles to the laser propagation direction. The emission was focused onto the entrance slit of a Jobin Yvon CP200 spectrograph using a pair of 150 mm focal-length lenses. The spectrograph was coupled to the same 16-bit intensified PCO Dicam CMOS camera used for the LII experiments, thereby forming a custom-built spectrometer. The fluorescence spectra were recorded with the intensifier gate width fixed at 50 ns, since it comfortably exceeds the duration of any expected fluorescence emission [118], which is also consistent with previously reported studies [3,22]. The numerical aperture of the spectrograph was also carefully matched to the collection optics by adequately filling the diffraction grating while avoiding overfilling. Doing so ensures efficient signal throughput and prevents light clipping and unwanted stray light within the spectrograph. The core instruments used for the LIF measurements and the associated calibration procedures are described next.

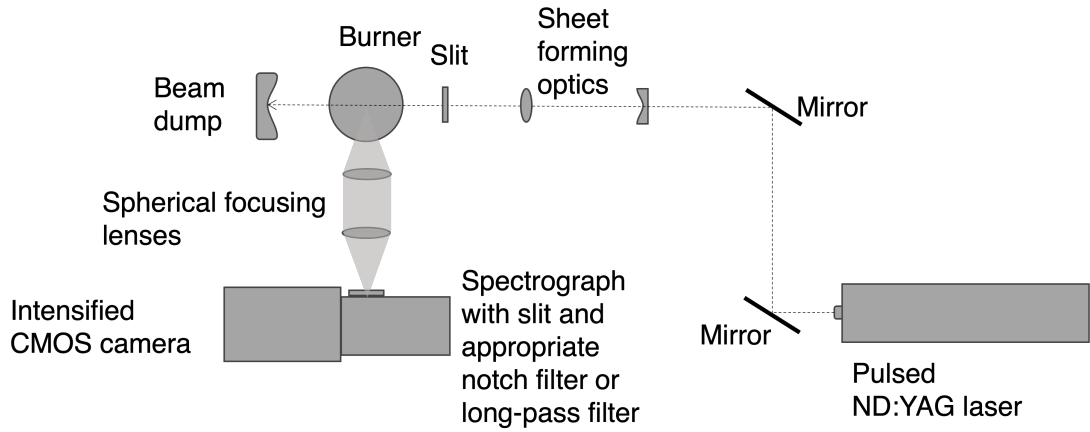


Figure 4.1: Schematic of the experimental LIF set-up including the pulsed Nd:YAG laser with appropriate harmonic generation modules, mirrors, sheet-forming optics and burner assembly, together with the collection optics, spectrograph (with slit and notch or long-pass filter) coupled to the intensified CMOS camera for spectrally resolved fluorescence measurements.

## 4.4 Core equipment for LIF measurements and detector calibration

The same intensified CMOS camera and burner used previously for LII were also employed for the LIF measurements, and are therefore not described again here.

### 4.4.1 Laser system

A Litron Nd:YAG laser was used, operating at 10 Hz, with the appropriate harmonic generation modules installed to provide access to the UV and green harmonics, which were 532, 355 and 266 nm. The 1064 nm fundamental was frequency-doubled to 532 nm by second-harmonic generation (SHG). The third harmonic, 355 nm, was produced by sum-frequency generation (SFG) mixing 1064 and 532 nm light (i.e.  $\omega_{355} = \omega_{1064} + \omega_{532} = 3\omega$ ). The fourth harmonic, 266 nm, was obtained by frequency-doubling the 532 nm beam in a second SHG stage (i.e.  $4\omega$ ). During LIF measurements, care was taken to check pulse energies with a power meter (Coherent PM10V1) before and after each experimental run to confirm stability.

### 4.4.2 Spectrometer

A custom-built spectrometer was used for this project, comprising a CP200 spectrograph (Jobin Yvon) coupled to the intensified CMOS camera previously used for the LII measurements. The spectrograph comprised an entrance slit, a small turning mirror, and a concave diffraction grating. Light entering the slit was reflected by the turning mirror towards the concave grating, where it was dispersed by wavelength and focused towards the spectrograph exit plane. The camera photocathode was positioned directly at this exit plane, allowing intensity to be recorded as a function of wavelength. Diffraction from the grating is governed by

$$m\lambda = d(\sin \alpha + \sin \beta),$$

where  $m$  is the diffraction order,  $\lambda$  is the wavelength,  $d$  is the groove spacing,  $\alpha$  is the incident angle, and  $\beta$  is the diffracted angle. The case  $m = 0$  corresponds to the 0th-order reflection, while  $m = 1$  corresponds to the 1st-order diffracted spectrum. This is illustrated in Figure 4.2, which also shows the 0th-order reflection and 1st-order diffraction recorded when broadband visible light from a fibre-coupled LED (Thorlabs MBB1F1) was passed through the entrance slit (not shown in Figure 4.2). To obtain the best spectral resolution, the camera sensor had to be positioned at the spectrograph focal plane. This was determined by inserting a 700 nm band-pass filter at the entrance slit to transmit a narrow spectral band, making focus assessment straightforward. The camera-spectrograph spacing was then varied in 1 mm increments, and focus was quantified from the recorded line profile using its full width at half maximum (FWHM), with optimum focus corresponding to the minimum FWHM and highest peak intensity. The optimum spacing was thus found to be 10 mm from the spectrograph body. A 3D-printed spacer was subsequently fabricated to set this offset while maintaining a light-tight seal to prevent stray light from reaching the camera.

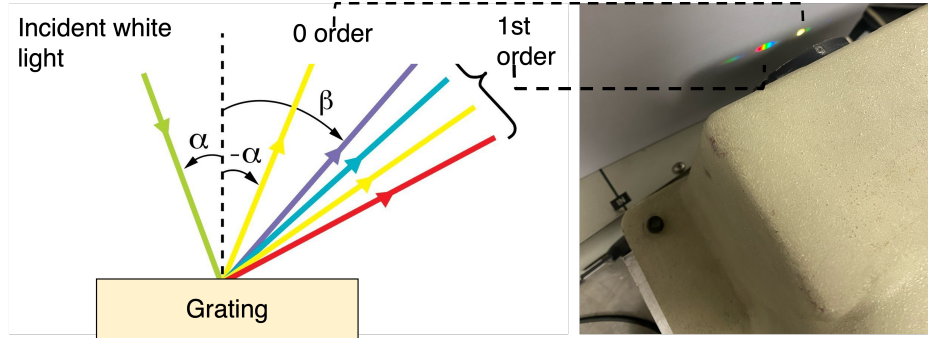


Figure 4.2: Diffraction grating: (left) schematic illustrating the 0th-order reflection and 1st diffraction order, defined by the incidence and diffraction angles  $\alpha$  and  $\beta$ . (right) Photograph showing the corresponding 0th-order reflection and 1st-order spectrum produced in the spectrograph (Jobin Yvon CP200) used in this work.

#### 4.4.3 Monochromator

The monochromator (Oriel Cornerstone 130) was not used during the LIF measurements themselves; instead, it was used in the wavelength and intensity calibrations of the spectrometer as a tuneable spectral filter. In this work, the monochromator operated

in a grating configuration: light from a broadband source entered through the entrance slit, was collimated by a mirror, and was dispersed by a diffraction grating into its constituent wavelengths. By rotating the grating, the diffracted angle changed such that a selected wavelength band was directed through the exit slit. A schematic of the monochromator is shown in Figure 4.3.

The monochromator's function is closely related to that of the spectrograph, which naturally raises the question of whether it could also have been used to record fluorescence spectra. Although this would in principle be possible, it was not suited to the present application. Even with the exit slit removed, the aperture in the wall of the monochromator provided a maximum usable spectral span of only  $\sim 40$  nm, whereas the LIF measurements in this work required a spectral window of up to  $\sim 500$  nm. A spectrograph coupled to a detector was therefore used instead. The following section describes the wavelength and intensity calibrations of the spectrometer system.

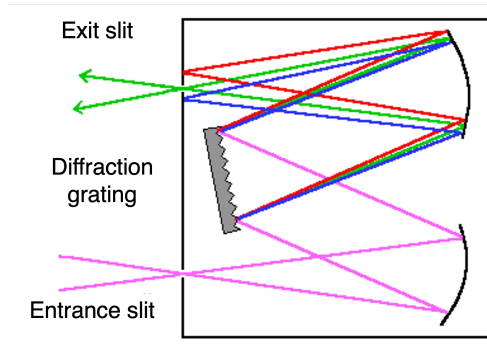


Figure 4.3: Schematic of the monochromator showing light entering through the entrance slit, being collimated and dispersed by the diffraction grating, and the selected wavelength band exiting through the exit slit.

## 4.5 Spectrometer calibration procedures

In this section, two calibration procedures are described in detail: the pixel-to-wavelength calibration and the intensity calibration. The former defines the wavelength axis of the recorded spectra, while the latter corrects for the wavelength-dependent response of the spectrometer to convert raw detector counts to radiometrically calibrated quantities, which are later expressed as spectral radiant energy density per unit laser fluence. Ra-

diometric calibration is a distinctive feature of the present work, since, as previously noted, PAH-LIF spectra in flames are often interpreted from uncorrected detector signals. By placing the spectra on a radiometrically corrected basis, changes in the spectra associated with hydrogen addition, C/O ratio and excitation wavelength could be compared with reduced bias from the detection system. The calibrated LIF spectra were subsequently normalised by the incident laser fluence and the collection volume, defined by the slit width and the height and depth of the laser sheet, providing a quantity that should therefore be reproducible by others. This is explained in detail in this section.

#### 4.5.1 Pixel-to-wavelength calibration

The wavelength calibration was performed using two broadband light sources to cover the UV to visible range. Therefore, a fibre-coupled LED source (Thorlabs MBB1F1) for the visible range and a UV-enhanced broadband source (Thorlabs SLS20) for the UV range. This section focuses on the visible-range wavelength calibration. This comprised the broadband source, the monochromator (Oriel Cornerstone 130), the detection system (CP200 spectrograph coupled to the PCO intensified CMOS camera), and appropriate spherical lenses. The LED output was focused into the monochromator, wavelength-selected at the exit slit, and then focused onto the spectrograph entrance slit. The spherical lens focal lengths and object/image distances used to couple the source to the monochromator and the monochromator to the spectrograph are indicated in Figure 4.4. These distances were selected to maintain focus at the respective slits while approximately matching the numerical apertures of the monochromator and spectrograph, thereby ensuring efficient light throughput without overfilling the grating. The monochromator input f-number of  $f/3.7$  corresponds to an acceptance numerical aperture of approximately 0.135 (or a half-angle of about  $7.8^\circ$ ). The numerical aperture of the spectrograph was estimated from its internal grating geometry, and a 1-inch spherical lens with  $f = 40$  mm was used to focus the monochromator output onto the spectrograph entrance slit.



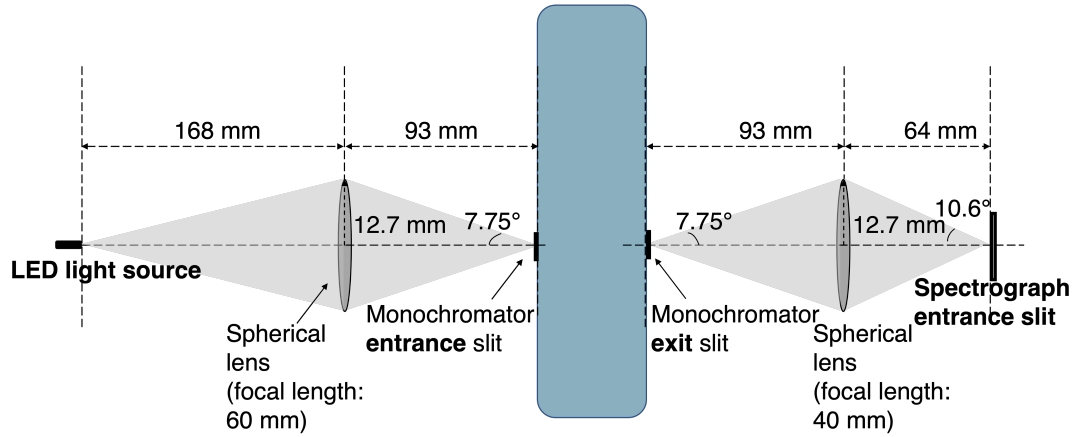


Figure 4.4: Wavelength calibration arrangement used to map detector pixel position to wavelength. Light from a fibre-coupled LED (Thorlabs MBB1F1) was wavelength-selected using the monochromator (entrance/exit slits:  $280\text{ }\mu\text{m}$ ) and imaged onto the spectrograph entrance slit ( $280\text{ }\mu\text{m}$ ) using the lenses shown. The dispersed spectrum was recorded on the intensified CMOS camera.

The size of the monochromator's entrance and exit slits and the spectrograph's entrance slit was  $280\text{ }\mu\text{m}$ . The slit size plays a significant role in determining throughput and spectral resolution. A wide entrance slit allows more light to enter the spectrometer, which is beneficial for measuring less intense sources but at the expense of spectral resolution. In contrast, a narrow entrance slit improves spectral resolution, though it reduces the signal intensity. The monochromator was stepped through a series of discrete wavelength setpoints; at each setpoint, an image was recorded separately. Figure 4.5 shows the resulting images superimposed.

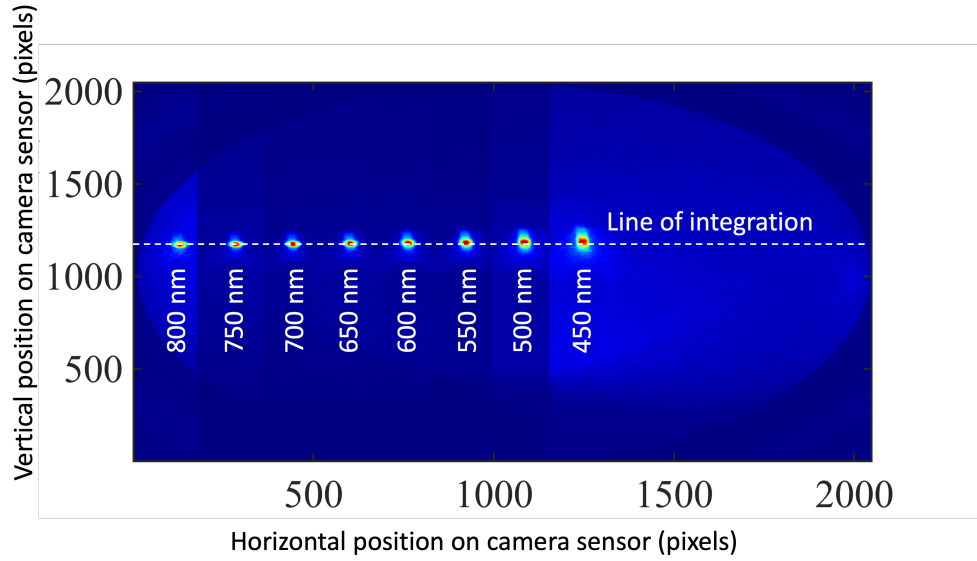


Figure 4.5: Superimposed monochromator-line images recorded at discrete wavelength setpoints, with each wavelength acquired separately. Images are shown without a common colour scale.

From each image, a 1D line profile was obtained by integrating over the full monochromator line spot at each horizontal pixel at the line of integration shown in Figure 4.5. For each monochromator setting, a Gaussian function was fitted to the resulting line profile; the peak pixel position was taken from the fitted Gaussian, and the FWHM was extracted from the fit. The spacing between adjacent 50 nm monochromator peaks was  $159 \pm 2$  pixels, giving a dispersion of approximately  $3.23 \text{ pixels nm}^{-1}$ . The measured peak widths from the monochromator-line images were  $28 \pm 1$  pixels, corresponding to a spectral resolution of  $\Delta\lambda \approx 28/3.23 \approx 8.7 \text{ nm}$ . This value, however, represents a worst-case estimate of the spectral resolution, since the measured width also includes the finite bandwidth of the monochromator output. A second estimate was therefore obtained using a Newport 78812 HgAr pen-ray calibration lamp, which provides narrower emission lines at known wavelengths. Gaussian fits to these HgAr lines gave an effective spectral resolution of 6 nm. This resolution was sufficient for the relatively broad LIF emission range considered in this work. The  $280 \mu\text{m}$  entrance slit was therefore considered a suitable compromise between spectral resolution and signal level,

particularly under flame conditions where the fluorescence signal was expected to be weak. A near-linear relationship between wavelength and horizontal pixel number was also observed from the fitted peak positions of the monochromator line profiles. This indicates a consistent change in wavelength per pixel across the measured range, as shown in Figure 4.6. An equivalent calibration procedure was also performed in the UV region using the Thorlabs SLS204 broadband source, as shown in Figure A.1 in the appendix. The resulting peak positions showed the same linear pixel–wavelength relationship down to approximately 300 nm.

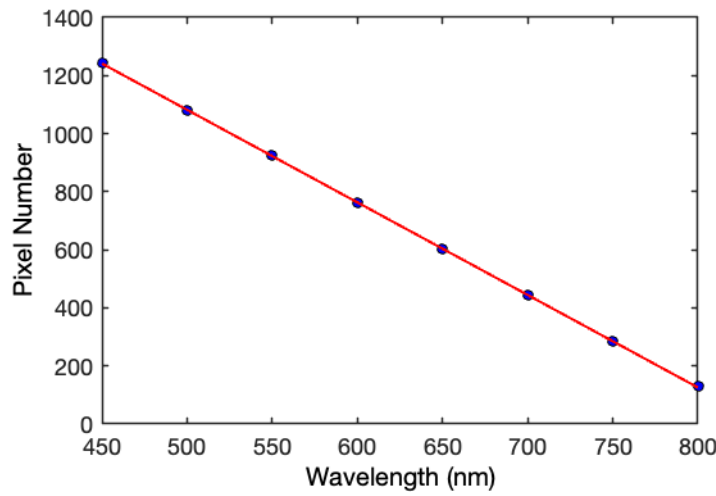


Figure 4.6: Centre (peak) horizontal pixel position extracted from Gaussian fits to the monochromator line profiles as a function of monochromator set wavelength. The near-linear trend was used for the pixel-to-wavelength calibration.

#### 4.5.2 Radiometric calibration: pixel counts to spectral radiance

As the final step in the LIF data-processing, a radiometric calibration was performed to correct for the wavelength-dependent sensitivity of the spectrometer used for LIF measurements in this work. Since a typical LIF measurement in this work spans from the UV to the near-infrared, two calibrated light sources were used to cover the required range: a stabilised deuterium source (Thorlabs SLS204) for the UV and a fibre-coupled LED (Thorlabs MBB1F1) for the visible. This was necessary due to the emission limits of each source. The resulting response curves were combined to provide radiometric cor-

rections for each LIF setup. For clarity, only the UV calibration procedure is described in detail below.

Intensity calibration can be described using a four-step framework. The first three steps were required to characterise the integrating sphere as a calibrated spectral-radiance source. In principle, these steps could be performed using a separate spectrometer, as they are independent of the LIF collection geometry. In the present work, it just happens that the same spectrometer used for LIF measurement was used to calibrate the integrating sphere. Step 1 was only a relative calibration of the spectrometer's wavelength-dependent response. The absolute calibration of the spectrometer, together with the collection optics, is what necessitates placing an integrating sphere at the LIF collection volume. However, before doing the absolute calibration, the integrating sphere first had to be characterised as a calibrated light source. Steps 2 and 3 were therefore used to correct for the spectral shape (using the detector response from step 1), and determine the absolute spectral radiance emitted by the light source through the integrating sphere. In step 4, the calibrated integrating sphere was then imaged through the same detector configuration used for LIF measurements.

The four steps were therefore:

1. Relative intensity calibration of the spectrometer.
2. Spectral calibration of the emission from the integrating sphere.
3. Absolute calibration of the spectral radiance emitted from the integrating sphere.
4. Absolute radiometric calibration of the spectrometer used for LIF measurements.

**Step 1: Relative intensity calibration of the spectrometer:** The wavelength-dependent response of the reference spectrometer was obtained by comparing the detector signal with the optical power incident at each monochromator wavelength. Assuming a linear response, the wavelength-dependent spectrometer response can be obtained. The optical arrangement was similar to that used for the pixel-wavelength calibration in section 4.5.1 (Figure 4.4), where the light from the broadband source was focused onto the monochromator entrance slit, wavelength-selected, and then focused onto the

spectrometer entrance slit. For the present intensity calibration, a UV light source was used. The monochromator was scanned over the spectral range of the lamp (acquired at 5 nm intervals), with spectra recorded using the spectrometer and corresponding power measurements made using a Thorlabs S120VC photodiode power sensor. Source stability was checked by repeating measurements at selected wavelengths after completion of the full scan. The exposure time used for each measurement was 100  $\mu$ s. To minimise second-order diffraction, in which shorter-wavelength light overlaps with first-order light at approximately twice its wavelength, the UV calibration range was limited to below a factor of two. Appropriate long-pass and short-pass filters were therefore used (WG305 long-pass filter and a 525 nm short-pass (Edmund Optics: #84-707)). Focal lengths of UV spherical lenses used were selected to match the numerical apertures of the light source, monochromator and spectrometer.

For each monochromator wavelength, a 1D line profile was extracted by vertically integrating over the full recorded spot, to avoid truncating the wings. The area under each spectral peak was determined by fitting a Gaussian function to the measured profiles, as shown in Figure A.2 in the Appendix. These integrated intensities were then divided by the corresponding power measurements (also corrected for detector sensitivity at each wavelength), to obtain the spectrometer response. Figure 4.7(a) shows the integrated spectral intensities together with the corresponding measured optical power at each wavelength. The spectrometer response is shown in Figure 4.7(b), which was smoothed and interpolated to cover a range from 285 nm to 525 nm, corresponding to the portion of the source spectrum transmitted through the optical filters. A local peak is observed at 485 nm in Figure 4.7(a), which is a feature of the light source itself. It is therefore also reflected in the corresponding optical-power measurements. When the integrated spectral intensity is divided by the measured power, the feature is largely removed, resulting in the comparatively smooth spectrometer-response curve shown in Figure 4.7(b).

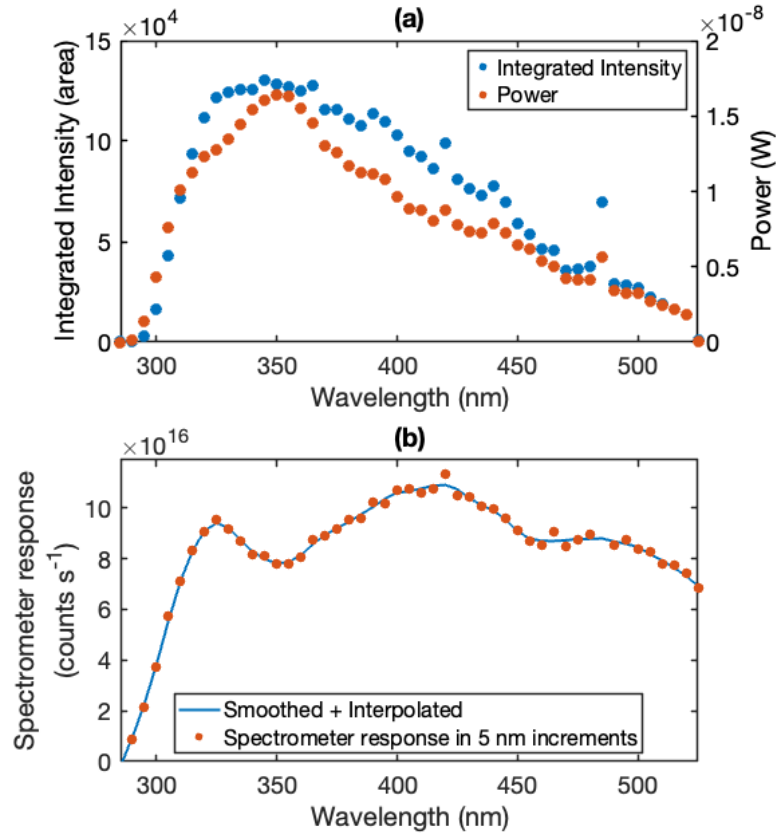


Figure 4.7: (a) Integrated spectral intensity obtained from Gaussian fits to each monochromator wavelength together with the corresponding measured optical power. (b) Relative spectral response obtained by dividing the integrated intensity by the measured optical power at each wavelength. The response values, shown in 5 nm increments, were subsequently smoothed and interpolated to obtain a continuous response curve used for radiometric correction.

## Step 2: Spectral calibration of the emission from the integrating sphere

Now that a relative wavelength-dependent response curve of the spectrometer has been obtained, it can be used to characterise the spectrum of an integrating sphere. The integrating sphere, when coupled with a broadband source, provides a light source that is of uniform radiance across its one-inch aperture. Once characterised, the integrating sphere would then be placed at the LIF collection volume to calibrate the detection system.

Two UV lenses were used to image the exit aperture of the integrating sphere onto

the entrance slit of the Jobin-Yvon spectrometer, while matching the numerical aperture of the spectrometer. The same long-pass and short-pass filtering approach as in Step 1 was used to limit the wavelength range reaching the spectrometer, and prevent second order diffraction. Unlike Step 1, no monochromator was used for this step; the full emission of the integrating sphere was recorded directly.

Figure 4.8 shows the background-subtracted spectrum obtained from the integrating sphere. The camera exposure used for these measurements was 30 ms. Figure 4.8(a) shows the uncorrected spectrum, while Figure 4.8(b) shows the spectrum after applying the spectrometer sensitivity correction (obtained from step 1). The corrected spectrum represents the relative shape of the source emission, independent of the wavelength-dependent detector sensitivity.

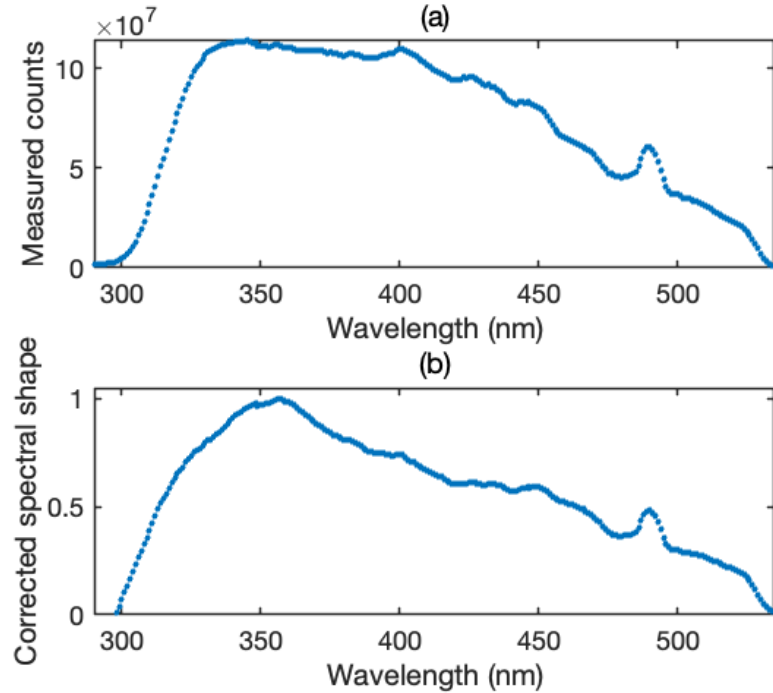


Figure 4.8: (a) Background-subtracted spectrum recorded from the integrating sphere. (b) Spectrum after correction for the wavelength-dependent sensitivity of the spectrometer using the response curve determined in the previous calibration step. The corrected spectrum therefore represents the relative spectral radiance shape of the integrating sphere light source.

**Step 3: Absolute calibration of spectral radiance of the emission from the integrating sphere**

With the same optics in step 2, the exit plane of the integrating sphere is imaged onto the photodiode power sensor (S120VC). The photodiode power sensor did not directly measure spectral radiant power; instead, it generated a current proportional to the incident light. The conversion of the measured current to power requires an effective responsivity, obtained by the weighting of the photodiode responsivity over the spectrum. This is done as follows:

At a given wavelength  $\lambda$ , the current produced is proportional to the spectral radiant power  $P(\lambda)$  and the photodiode responsivity  $C(\lambda)$ , expressed in A/W:

$$dI(\lambda) = C(\lambda) \cdot P(\lambda) d\lambda \quad (4.1)$$

The total current from a broadband light source is obtained by integrating over all wavelengths:

$$I_{\text{total}} = \int P(\lambda) \cdot C(\lambda) d\lambda \quad (4.2)$$

Introducing a normalised spectral shape  $f(\lambda)$ , such that:

$$P(\lambda) = P_{\text{total}} \cdot f(\lambda), \quad \text{with} \quad \int f(\lambda) d\lambda = 1 \quad (4.3)$$

Substituting into the integral for  $I_{\text{total}}$ :

$$I_{\text{total}} = \int P_{\text{total}} \cdot f(\lambda) \cdot C(\lambda) d\lambda \quad (4.4)$$

$$= P_{\text{total}} \cdot \int f(\lambda) \cdot C(\lambda) d\lambda \quad (4.5)$$

Solving for  $P_{\text{total}}$ :

$$P_{\text{total}} = \frac{I_{\text{total}}}{\int f(\lambda) \cdot C(\lambda) d\lambda} \quad (4.6)$$

This shows that the total optical power can be recovered from the measured current,



provided the spectral shape of the source and the detector responsivity are known. The corrected normalised spectral shape of the integrating sphere output,  $f(\lambda)$ , together with the photodiode responsivity,  $C(\lambda)$ , are shown in Figure 4.9(a). The effective responsivity represents a weighted average sensitivity of the powermeter over the spectrum of the incident light. It is obtained by multiplying the normalised spectral output of the source with the photodiode responsivity at each wavelength, producing a wavelength-weighted responsivity curve. The area under this curve, calculated using numerical integration, gives the effective responsivity in units of A/W, as shown in Figure 4.9(b).

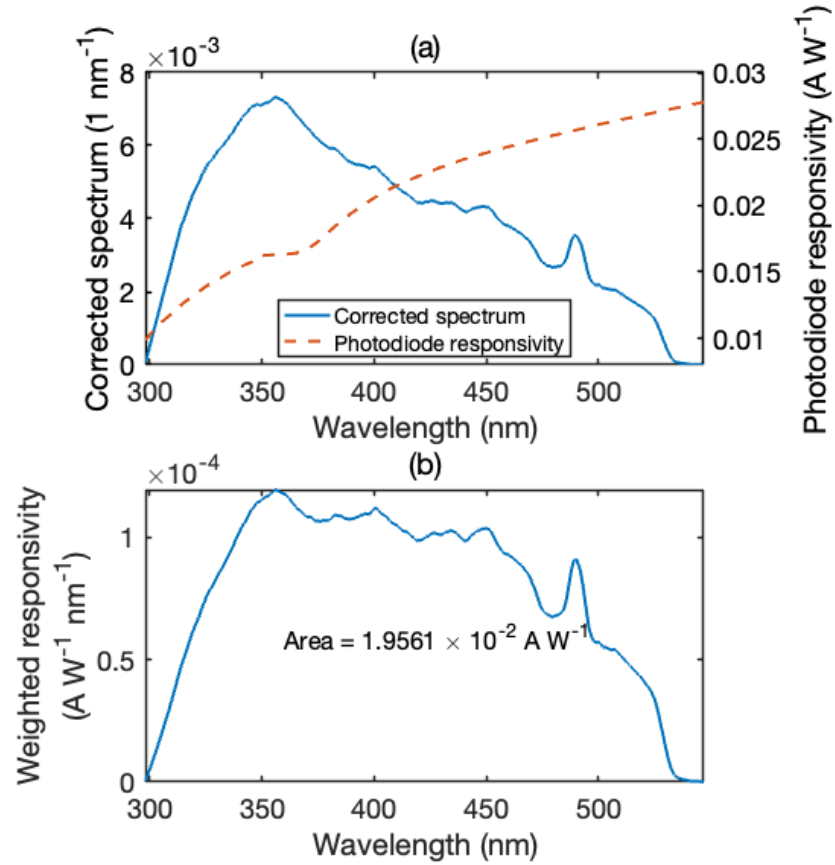


Figure 4.9: (a) Corrected normalised spectral output of the integrating sphere,  $f(\lambda)$ , together with the power meter responsivity,  $C(\lambda)$ . (b) Product of the two functions,  $f(\lambda)C(\lambda)$ , representing the wavelength-weighted responsivity of the photodiode. The area under this curve, obtained by numerical integration, gives the effective responsivity of the photodiode for the integrating sphere spectrum.

The total optical power of the broadband source can be calculated by dividing the

background-subtracted current from the photodiode by the effective responsivity. During these measurements, it was found that ambient visible light produced an appreciable photodiode response. The laboratory lights and computer monitor were therefore switched off, and the background current was measured with the broadband source blocked under otherwise identical conditions. After these precautions, the background-subtracted current was  $2.62 \times 10^{-10}$  A. The background current measured with the light source blocked was  $1.18 \times 10^{-11}$  A, corresponding to a signal-to-background ratio of approximately 22. The effective responsivity was determined to be  $1.96 \times 10^{-2}$  A/W from the weighted integration shown in the figure above. Using the relationship

$$P_{\text{total}} = \frac{I_{\text{total}}}{R_{\text{eff}}} \quad (4.7)$$

the total optical power is calculated as  $P_{\text{total}} = 1.34 \times 10^{-8}$  W. Since the spectral shape of the source,  $P(\lambda)$ , had already been normalised such that its area under the curve equals one, this shape was used to redistribute the total power across the wavelength range. The absolute spectral power distribution was obtained by scaling the normalised spectrum ( $f(\lambda)$ ) by the total broadband power:

$$P(\lambda) = P_{\text{total}} \cdot f(\lambda) \quad (4.8)$$

This yields the spectral power distribution in units of  $\text{W nm}^{-1}$ , allowing for a full reconstruction of how the source emits power as a function of wavelength, as shown in Figure 4.10.

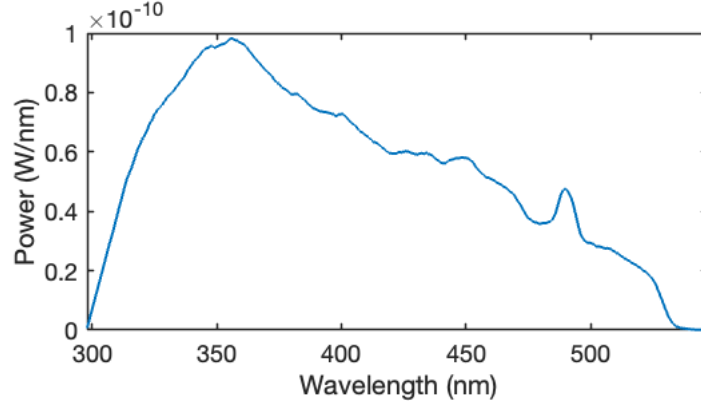


Figure 4.10: Spectral power distribution of the UV light source obtained by scaling the corrected normalised spectral shape  $f(\lambda)$  with the measured broadband optical power. The resulting curve represents the absolute spectral power emitted by the source per unit wavelength, expressed in  $\text{W nm}^{-1}$ .

To obtain the spectral radiance of the source, the calibrated spectral power distribution (in units of  $\text{W nm}^{-1}$ ) was converted by accounting for the geometry of the optical setup. Specifically, the spectral power was divided by the projected area of the integrating sphere aperture and the collection solid angle. The projected area was calculated from the aperture diameter of 5 mm. This effective aperture was defined using the iris placed at the integrating sphere exit, which was kept fixed during both the spectral-shape and absolute power measurements. The iris reduced the aperture from the original 1-inch diameter because, at approximately 1:1 imaging magnification, the full aperture would have produced an image larger than the active area of the power meter. Reducing the aperture ensured that the collected light was fully captured during the power measurement. The solid angle, given by  $\Omega = 2\pi(1 - \cos\theta)$ , was calculated from the lens collection geometry and was found to be 0.088 sr. This value quantifies the collection cone through which light exits the aperture and is captured by the lens. The resulting spectral radiance,  $R_\lambda$ , is therefore given by:

$$R_\lambda = \frac{P_\lambda}{A \cdot \Omega} \quad (4.9)$$

where  $P_\lambda$  is the spectral power in  $\text{W/nm}$ ,  $A$  is the aperture area in  $\text{m}^2$ , and  $\Omega$  is the solid angle in steradians. This yields spectral radiance in units of  $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ ,

which characterises the directional intensity of light emitted per unit area, per unit wavelength, as shown in Figure 4.11.

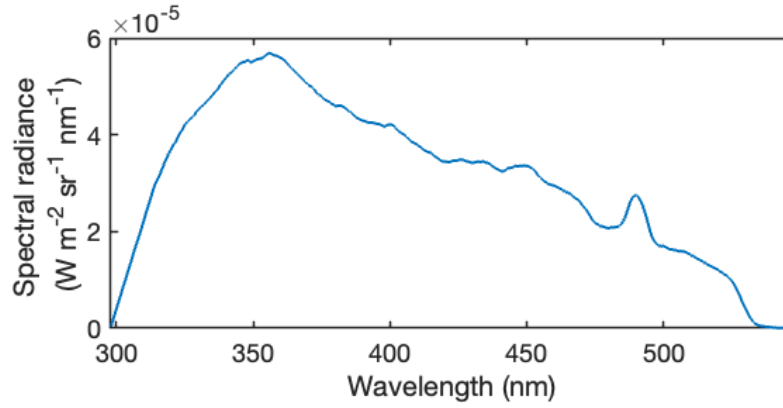


Figure 4.11: Spectral radiance (in units of  $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ ) of the UV light source, obtained by dividing the spectral power distribution by the projected area of the integrating sphere aperture and the collection solid angle.

Steps 1–3 had previously been carried out by other members of the group to calibrate a broadband light source in the visible range, using the fibre-coupled LED source (Thorlabs MBB1F1). The resulting spectral radiance of the visible integrating-sphere source is shown in Figure 4.12.

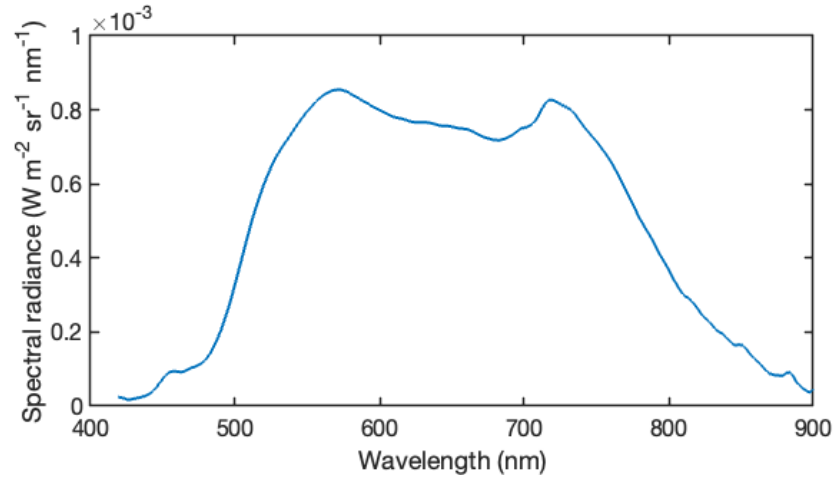


Figure 4.12: Spectral radiance of the visible integrating-sphere light source based on the fibre-coupled LED source (Thorlabs MBB1F1). The calibrated spectral radiance is expressed in units of  $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$  and was used for the visible-range calibration of the camera-spectrograph system.

**Step 4: Calibration of the spectrometer used for LIF** In this step, the calibrated integrating sphere was used to determine the wavelength-dependent response of the LIF detection system. The calibrated integrating sphere source was placed at the LIF collection volume, and the signals (denoted here by  $S_\lambda$ ) recorded by the spectrometer were related to the known spectral radiance emitted by the source. The calibration response can thus be expressed as

$$C_\lambda = \frac{S_\lambda}{4\pi R_\lambda} \quad (4.10)$$

where  $R_\lambda$  is the calibrated source spectral radiance in  $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ . The factor  $4\pi$  is used to relate the source spectral radiance to emission over a full sphere, consistent with the assumption that LIF emission is approximately isotropic.  $S_\lambda$  was initially expressed as  $\text{counts s}^{-1} \text{pix.w}^{-1} \text{pix.h}^{-1} \text{slit-width}^{-1}$ , where  $\text{pix.w}$  and  $\text{pix.h}$  denote the pixel width and height, respectively. The spectrometer entrance slit width was  $280 \mu\text{m}$ . The pixel-based units were converted to physical units of  $\text{counts s}^{-1} \text{nm}^{-1} \text{m}^{-2}$ , so that the wavelength-dependent calibration response,  $C_\lambda$ , could be expressed as  $\text{counts J}^{-1}$ . This is done as follows:

The horizontal detector pixel width,  $\text{pix.w}$  can be converted into wavelength using the previous pixel–wavelength calibration, where one horizontal pixel width corresponds to  $1/3.23 \text{ nm pix.w}^{-1}$ . In the equation below, this is written as  $\delta_w D$  ( $\text{nm pix.w}^{-1}$ ), where the horizontal pixel pitch is  $\delta_w$  ( $\text{m pix.w}^{-1}$ ), and the spectrograph linear dispersion is  $D$  ( $\text{nm m}^{-1}$ ).

The vertical detector pixel height,  $\text{pix.h}$ , was converted to a physical height at the detector plane using the known camera pixel pitch, expressed in  $\delta_h$  ( $\text{m pix.h}^{-1}$ ). However, both the magnification of the collection optics,  $M_{\text{in}}$ , and the magnification within the spectrograph/camera system,  $M_{\text{spec}}$ , had to be considered.  $M_{\text{spec}}$  accounts for the magnification from the spectrograph entrance slit to the detector plane. The image/object magnification of the spectrograph was determined to be 0.96, while the magnification associated with imaging the intensifier output onto the CMOS array was specified by the camera manufacturer as 0.53. The combined magnification,  $M_{\text{spec}}$ , was therefore calculated to be 0.51. Therefore, the detector image height was converted

back to the corresponding physical height at the spectrograph entrance slit by using the inverse factor,  $M_{\text{spec}} = 1/0.51$ . The magnification from the object plane to the spectrograph entrance slit,  $M_{\text{in}}$ , was then applied to relate the entrance-slit dimensions to the LIF collection volume. In the present setup, this magnification was unity,  $M_{\text{in}} = 1$ .

The signal counts,  $S_\lambda$ , were thus converted from counts  $\text{s}^{-1} \text{ pix.w}^{-1} \text{ pix.h}^{-1} \text{ slit-width}^{-1}$  to counts  $\text{s}^{-1} \text{ nm}^{-1} \text{ m}^{-2}$  by dividing by  $(\delta_w D)(M_{\text{in}} M_{\text{spec}} \delta_h)(M_{\text{in}} d)$ . The calibration-source image was therefore binned onto a 1 nm wavelength grid, with each bin centred at the selected wavelength and extending by  $\pm 0.5$  nm, and averaged vertically over a height where the integrating-sphere image was uniform. Placing this back into the first equation, the wavelength-dependent calibration factor becomes

$$C_\lambda = \frac{S_\lambda}{4\pi R_\lambda \delta_w D M_{\text{in}}^2 M_{\text{spec}} \delta_h d} \quad (4.11)$$

The units are therefore expressed as counts  $\text{J}^{-1}$ .

This calibration factor can thus be applied to the LIF data to calibrate the LIF signals.

In practice, a single light source did not cover the full wavelength range from LIF experiments. For example, a typical 266 nm LIF spectrum could extend from around 300 nm to 800 nm, whereas the UV calibration covered up to around 530 nm only. The fibre-coupled LED source (Thorlabs MBB1F1) was therefore used to determine the calibration response in the visible range.

Due to the time-limited availability of the different elements of the calibration equipment, both calibration branches could not be determined for each LIF detection configuration. The UV calibration measurement nevertheless closely represented the optical arrangements used for the 266 and 355 nm LIF configurations, with the exception of the filters at the spectrometer entrance slit (WG305 for 266 nm LIF and 355 nm notch filter for 355 nm LIF). The measured UV calibration response was therefore corrected for the transmission of the corresponding filter. The visible calibration measurement, which was acquired only with the 532 nm LIF configuration, was corrected for the wavelength-dependent transmission differences between the 532 nm LIF optical arrangement and

the 266 and 355 nm LIF detection paths.

For 266 and 355 nm LIF configurations, the corrected UV calibration branches were taken as reference (since it most reflected the UV LIF setups), and the respective visible branches were matched and averaged over a broad overlap region using least-squares scaling. Conversely, for the 532 nm LIF configuration, the measured visible calibration branch was taken as the reference, since it was acquired using the corresponding optical arrangement. The corrected UV calibration branch was then matched to the visible reference branch over the same overlap region.

Although the application of transmission corrections introduces an additional uncertainty into the calibration factor, this uncertainty was small over the wavelength ranges retained for analysis. In the absence of manufacturer-stated uncertainties for the relevant transmission curves, the sensitivity of the calibration constants was assessed by varying the transmission values by  $\pm 0.025$ , which is expected to be a conservative estimate, especially in the region where the transmission is mostly flat. For 266 nm and 355 nm LIF, the average induced variation in the calibration factor was found to be around 2.5% (maximum variation of 3% at most), and even less in the 532 nm LIF case. For the 266 nm LIF configuration, wavelengths below 315 nm were excluded from the calibration factor plot and subsequent analysis since the transmission of the WG305 long-pass filter fell sharply below 90%. The uncertainty introduced by the transmission correction was therefore small and did not alter the interpretation of the calibrated LIF measurements.

The resulting calibration factors specific to each detection setup for the 266, 355 and 532 nm LIF configurations are shown in Figure 4.13. A drop in the calibration factors is nevertheless observed at the lowest retained wavelengths in both UV-LIF configurations, arising from the decreasing sensitivity of the spectrograph in this spectral region.

The calibration factors were then applied to the measured LIF spectra, as explained in the next section on the LIF image processing procedure (Section 4.6). Before this procedure is described, the correction for second order diffraction is first introduced, since this correction would be applied before the radiometric calibration.

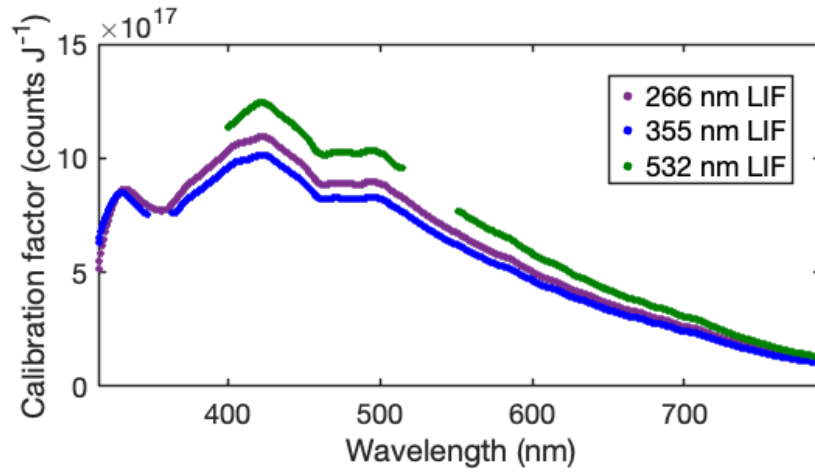


Figure 4.13: Wavelength-dependent calibration factors for the 266, 355 and 532 nm LIF configurations.

### 4.5.3 Correcting for second-order diffraction

During the calibration of the UV light source, a second-order diffraction pattern was observed in the spectrometer. This did not affect the absolute calibration of the light source, as it was separate from the first order spectrum. However, this second order diffraction would be contributing to the LIF spectra. If uncorrected, this would artificially increase the apparent LIF signal in the visible wavelength range. Figure 4.14 shows that this second-order contribution became apparent from around 600 nm and extended to approximately 850 nm, although its intensity remained much lower than the first-order signal.



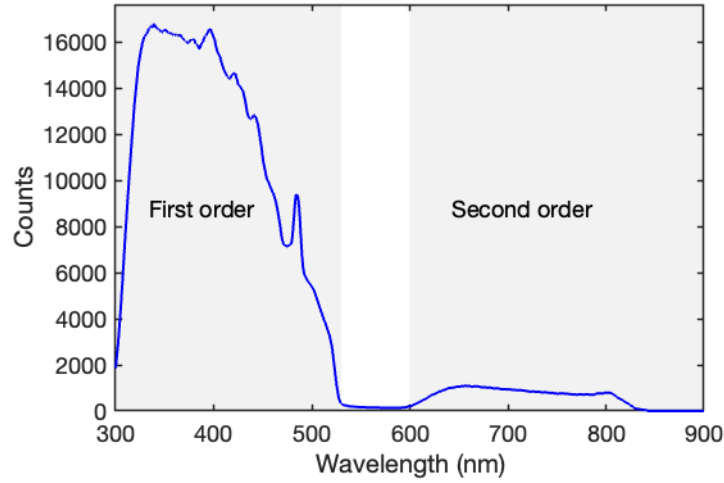


Figure 4.14: Lamp spectrum with a 525 nm short-pass: first order only below 525 nm and second order only above 600 nm; used to derive the second-order response coefficient  $\alpha(\lambda)$  for the second-order correction.

Denoting the lamp spectrum by  $S_{SP}(\lambda)$ , the wavelength-dependent second-order response coefficient was defined for  $\lambda \geq \lambda_{cut}$ , where  $\lambda_{cut} = 600$  nm, as

$$\alpha(\lambda) = \frac{S_{SP}(\lambda)}{S_{SP}(\lambda/2)}. \quad (4.12)$$

Here, the numerator represents the spectrometer signal recorded at the second-order wavelength position, while the denominator represents the corresponding first-order signal at half the wavelength,  $\lambda/2$ . Therefore,  $\alpha(\lambda)$  gives the relative second-order response of the spectrometer compared with its first-order response. The second-order response coefficient,  $\alpha(\lambda)$ , is shown in Figure 4.15.

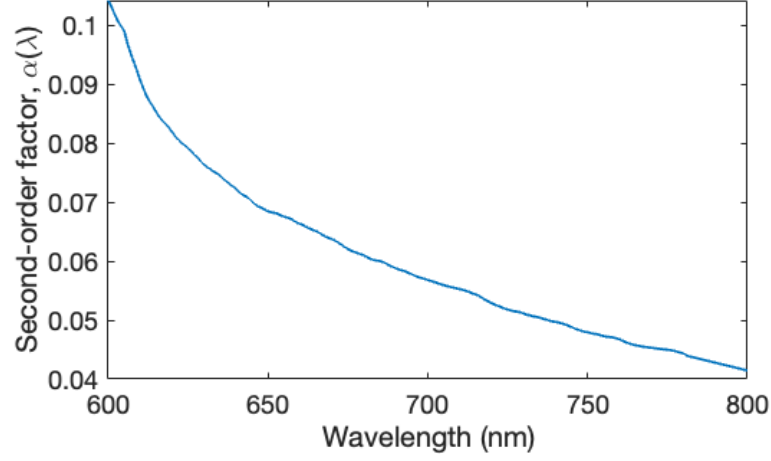


Figure 4.15: Wavelength-dependent second-order response coefficient,  $\alpha(\lambda)$ , derived from the short-pass-filtered lamp spectrum. For  $\lambda \geq 600$  nm, the measured signal at  $\lambda$  corresponds to the spectrometer response in second order and is ratioed to the corresponding first-order signal at  $\lambda/2$ . The coefficient decreases with increasing wavelength.

The second-order response coefficient was then used to correct the measured LIF spectra above 600 nm. At each wavelength in this region, the second-order contribution was estimated by multiplying the measured signal at half the wavelength by  $\alpha(\lambda)$ , and subtracting this from the measured signal:

$$I_{\text{corr}}(\lambda) = I_{\text{meas}}(\lambda) - \alpha(\lambda)I_{\text{meas}}(\lambda/2), \quad \lambda \geq 600 \text{ nm.} \quad (4.13)$$

Below 600 nm, no second-order correction was applied.

## 4.6 LIF image processing and radiometric calibration

This section describes the steps involved in processing the LIF measurements to calibrate the raw LIF measurements from pixel counts to spectral radiant energy density per unit fluence ( $\text{m}^{-1} \text{nm}^{-1}$ ) using the calibration response (Figure 4.13). This is a quantity that should be reproducible by others, as it removes dependence on laser fluence, sheet dimensions, and spectrometer gate duration.

The complete data processing workflow was done through MATLAB. A typical LIF measurement comprised 100 single-shot image acquisitions, which were ensemble-

averaged. Figure 4.16 shows an example of 266 nm LIF in a rich flame of  $C/O=0.79$  without hydrogen addition. For each condition, a corresponding background measurement (laser off, flame on) was acquired using the same number of acquisitions, averaged, and subtracted from the averaged LIF image. An example of this procedure is shown in Figure 4.16: (a) raw ensemble-averaged LIF image, (b) ensemble-averaged background image, and (c) background-subtracted LIF image.

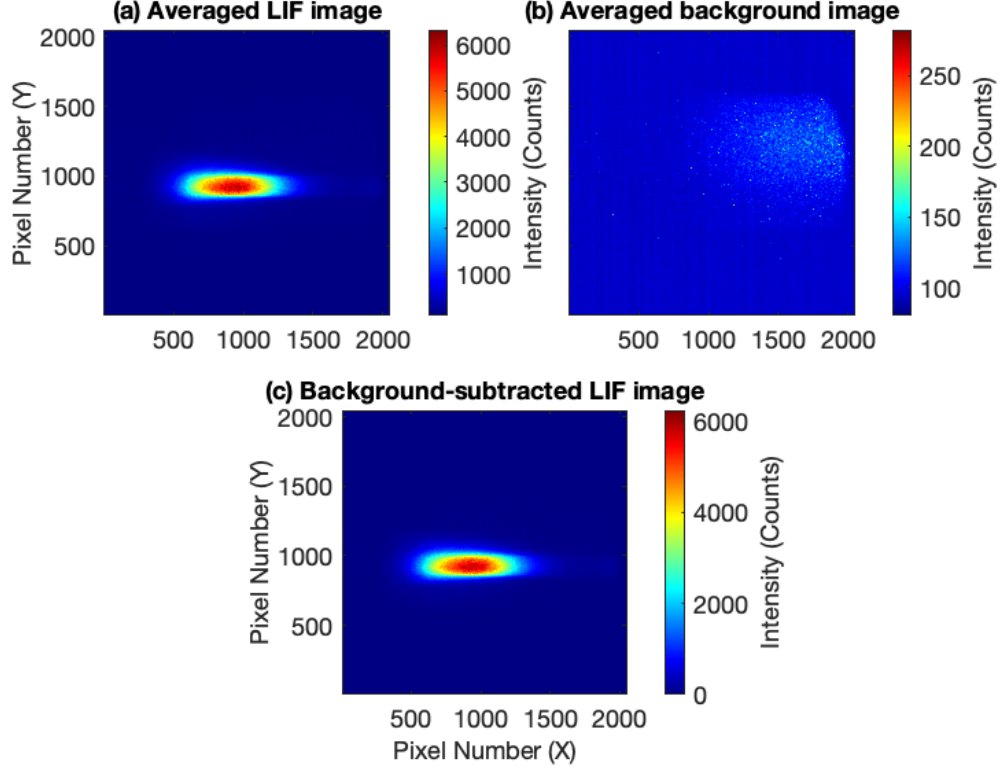


Figure 4.16: Example 266 nm LIF (in a rich flame of  $C/O=0.79$ , no  $H_2$ -addition) image processing sequence used prior to wavelength and intensity calibration: (a) ensemble-averaged raw LIF image (100 single-shot acquisitions), (b) ensemble-averaged background image recorded under identical conditions with the laser off (100 single-shot acquisitions), and (c) background-subtracted LIF image obtained by subtracting (b) from (a). Colour scales show the recorded intensity in image counts.

For each background-subtracted LIF image, the signal was integrated over the full height of the fluorescence streak, so that the complete LIF signal was retained. The resulting LIF signal is denoted here as  $L_\lambda$ , with units of counts  $\text{pix.w}^{-1} \text{sheet-height}^{-1} \text{slit-width}^{-1}$ .

The horizontal pixel-width was converted to wavelength using the pixel-to-wavelength calibration ( $\delta_w D$ ). The LIF images were binned onto a 1 nm wavelength grid, with each bin centred at the selected wavelength and extending by  $\pm 0.5$  nm. The LIF signal was then normalised by its collection volume, which was defined by the laser sheet height ( $z = 2$  mm), the laser sheet depth along the beam path ( $w = 10$  mm), and the spectrograph slit width,  $d = 280 \mu\text{m}$ , as illustrated in Figure 4.17. The LIF signal can then be expressed per unit wavelength and per unit sampled volume by dividing by  $(\delta_w D z w M_{\text{in}} d)$ , with units of  $\text{counts m}^{-3} \text{nm}^{-1}$ .

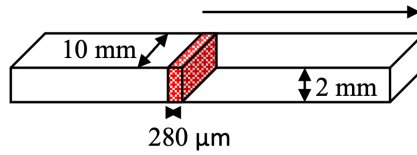


Figure 4.17: Schematic describing the LIF collection volume (red textured region) through a  $280 \mu\text{m}$  entrance slit at the spectrometer. Arrow represents direction of propagation of the 2 mm by 10 mm laser sheet.

The background-subtracted LIF spectrum had to be corrected for second-order diffraction. Figure 4.18 compares the spectrum before and after this correction. Although the change in raw counts appears small, even in the grey-boxed region, the correction is important because its effect becomes more pronounced after radiometric calibration, especially at longer wavelengths where the spectrometer sensitivity is lower. Without this correction, the calibrated spectrum could falsely suggest fluorescence at longer wavelengths where the measured signal was actually due to second-order diffraction.

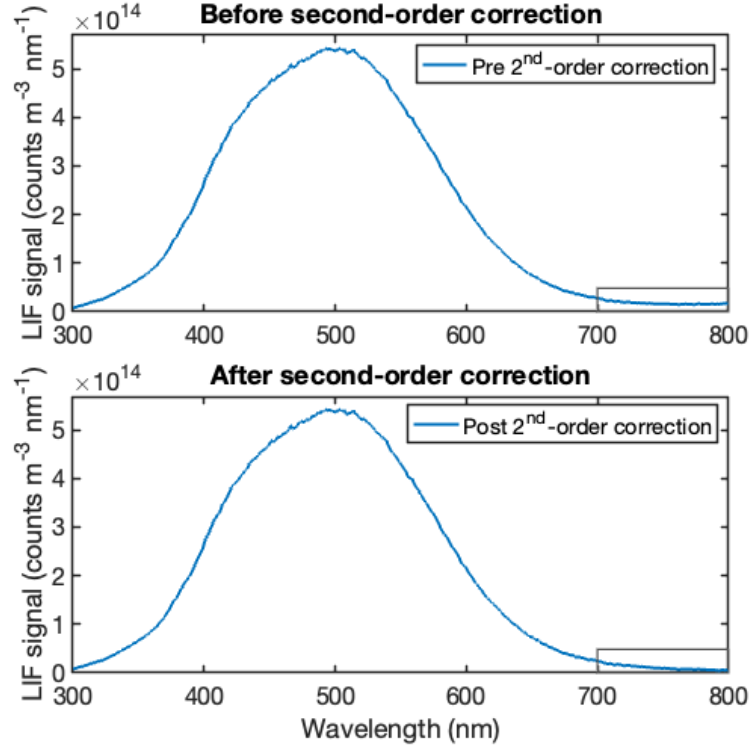


Figure 4.18: LIF spectrum, obtained from the background-subtracted image by integrating vertically over the entire LIF signal. The spectra before and after second-order diffraction correction are shown. Data correspond to a 266 nm LIF measurement at C/O= 0.79 with 0% H<sub>2</sub> addition.

By dividing the LIF signal by the calibration response,  $C_\lambda$ , it can be converted to spectral radiant energy density,  $L_\lambda/(\delta_w D z w M_{in} d C_\lambda)$ , with units of J m<sup>-3</sup> nm<sup>-1</sup>. Finally, dividing by the incident laser fluence,  $I_{laser}$  (J m<sup>-2</sup>), gives the calibrated signal, normalised by its collection volume and fluence:

$$I_{LIF}(\lambda) = \frac{L_\lambda}{\delta_w D z w M_{in} d C_\lambda I_{laser}}, \quad (4.14)$$

with units of m<sup>-1</sup> nm<sup>-1</sup>. The normalisation by the sampled volume, including the laser-sheet depth, removes the dependence on the particular collection volume used in this experiment. The resulting quantity should therefore be more directly reproducible by others, since the reported spectra are no longer tied to the exposure gate duration or laser-sheet depth used here. When spectrally integrated, the units are m<sup>-1</sup>, thus

photons emitted per photons incident per sheet propagation distance.

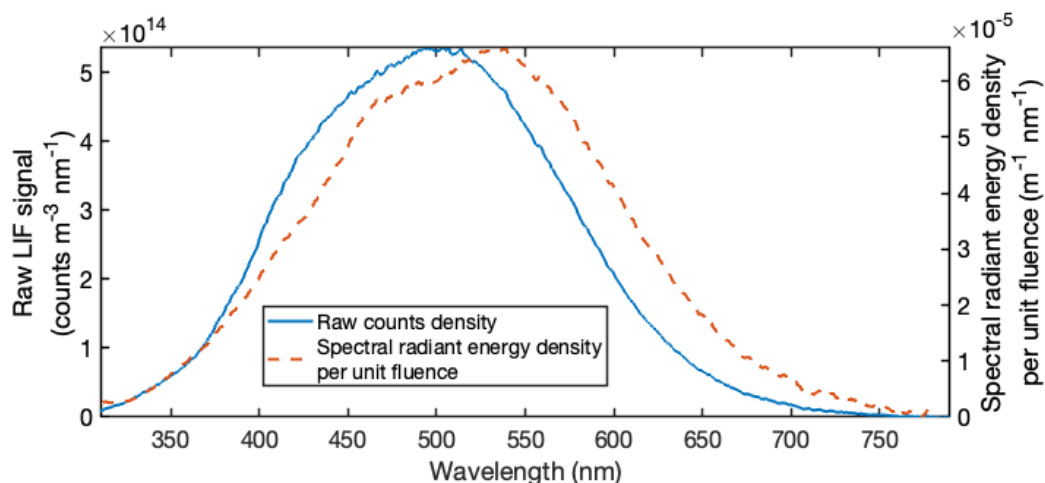


Figure 4.19: Comparison between the raw and calibrated 266 nm LIF spectra for the no-H<sub>2</sub>, C/O= 0.79 flame at 16 mm HAB.

## 4.7 Chapter conclusion

This chapter described laser-induced fluorescence (LIF), the methodology selected for examining fluorescence associated with PAHs and related species in flames. Three excitation wavelengths, 266, 355 and 532 nm, were employed to probe differently weighted fluorescence contributions from PAH-related species in the flame, including potential soot-precursor structures. By examining the LIF response to hydrogen addition under the same flame conditions previously studied using LII, these measurements enable the fluorescence trends to be compared directly with the reductions in soot concentration observed across a wide range of C/O ratios (C/O = 0.59–0.79).

Two calibration procedures were established. A pixel-to-wavelength calibration was first applied to map the horizontal pixels to nm. This calibration also allowed the spectral resolution of the spectrometer to be established, which was found to be 6 nm. This was considered sufficient for the relatively large PAH fluorescence range in this work, which extends to approximately 500 nm. Radiometric calibration was then implemented, one of the key features of this work. This is because PAH-LIF measurements in flames are often reported in relative intensity units without correction for

the wavelength-dependent response of the detection system. By placing the spectra on a radiometrically corrected basis (and thus accounting for the wavelength-dependent response), changes in the spectra associated with hydrogen addition, C/O ratio and excitation wavelength could be compared with reduced bias from the detection system. The radiometrically calibrated LIF measurements were subsequently normalised by the laser fluence and laser sheet width. The calibrated signals were therefore expressed in the units of spectral radiant energy density per unit fluence ( $\text{m}^{-1} \text{nm}^{-1}$ ). This is therefore a quantity that should be reproducible by others. When spectrally integrated, the units are  $\text{m}^{-1}$ , thus photons emitted per photons incident per sheet propagation distance. The data-processing procedure was then described, including ensemble averaging and background subtraction, correction for second-order diffraction, and application of the wavelength and radiometric calibration procedures. All processing steps were implemented in MATLAB.

With the LIF methodology established, the next chapter applies this approach to the selected flame conditions. As mentioned in Chapter 1, a measured LIF spectrum consists of contributions from all species that absorb at the excitation wavelength and fluoresce within the detection range. Since the resulting signal represents an unknown weighted superposition of overlapping fluorescence contributions, it cannot generally be resolved into concentrations of individual PAH species. Therefore, the next chapter does not attempt a species-by-species interpretation. Instead, the analysis focuses on how the overall LIF intensity and spectral shape vary with excitation wavelength, flame condition and  $\text{H}_2$  addition. Principal component analysis is then used to assess how many independent spectral variations are required to describe the measured data. The approximate spectral contributors are then extracted using a separate approach, in which the components are non-negative and smooth. These components are therefore interpreted as grouped spectral contributions, and they are tracked as a function of flame conditions (HAB, C/O and hydrogen addition). These extracted features may tentatively be associated with broad classes of PAH-related precursor structures linked with soot nucleation, including structures such as resonance-stabilised radicals and aliphatically bridged dimers, as discussed in Chapter 1.

## Chapter 5

# Results: laser-induced fluorescence measurements of the effects of hydrogen addition on soot precursor formation

In this chapter, laser-induced fluorescence (LIF) is applied at three excitation wavelengths (266, 355 and 532 nm) over flame conditions corresponding to those studied using LII in Chapter 3. The aim is to determine how hydrogen addition, which suppresses soot formation, affects fluorescence associated with PAHs and related structures under the same flame conditions. Since in situ PAH LIF is not species-specific, the use of multiple excitation wavelengths, together with spectrally resolved detection, may provide a means of separating the contributions of different classes of fluorescing species with different fluorescence properties, whose prevalence may be affected differently by flame conditions and hydrogen addition.

All measurements are performed in the linear fluorescence regime, and are radiometrically calibrated. The resulting quantity is normalised by the laser fluence and laser sheet width, which provides a quantitatively reproducible measure of fluorescence, expressed as spectral radiant energy density per unit fluence and per unit beam prop-



agation distance. When spectrally integrated, the units reduce to  $m^{-1}$ , i.e. photons emitted per photons incident per sheet propagation distance. Principal component analysis is then applied to the combined spectral dataset to investigate how many independent spectral contributions are needed to describe the measured fluorescence behaviour across the studied conditions. Approximate non-negative, smooth spectral components are subsequently extracted using a separate approach, and their fitted contributions are tracked as a function of C/O ratio, height above the burner and hydrogen addition.

## 5.1 Experimental Conditions

### 5.1.1 Fluence curves at the different excitation wavelengths

The LIF measurements were conducted at low laser fluences [22,80] in order to minimise interference from soot, particularly contamination from soot LII emission. Fluence curves at 532 nm, 355 nm, and 266 nm excitation wavelengths were recorded at a height of 16 mm above the burner (HAB) in a rich flame ( $\phi = 2.36$ , corresponding to C/O = 0.79, no H<sub>2</sub>). The linearity of the fluorescence response was assessed by plotting fluence curves (shown in Figure 5.1), by integrating the LIF spectra over wavelength at each fluence, which revealed that deviations from linearity occurred at higher fluences: above  $2.5 \text{ mJ cm}^{-2}$  for 532 nm, above  $2.0 \text{ mJ cm}^{-2}$  for 355 nm, and above  $1.5 \text{ mJ cm}^{-2}$  for 266 nm. Accordingly, the LIF measurements were performed at fluences that did not exceed these experimentally determined limits:  $1.0 \text{ mJ cm}^{-2}$  for 266 nm,  $2.0 \text{ mJ cm}^{-2}$  for 355 nm, and  $2.0 \text{ mJ cm}^{-2}$  for 532 nm. Some PAH LIF studies typically use higher fluences up to about  $20 \text{ mJ cm}^{-2}$  [22,80], which could be saturating LIF signals, although these were done in different flames (such as laminar premixed and diffusion methane-air flames).

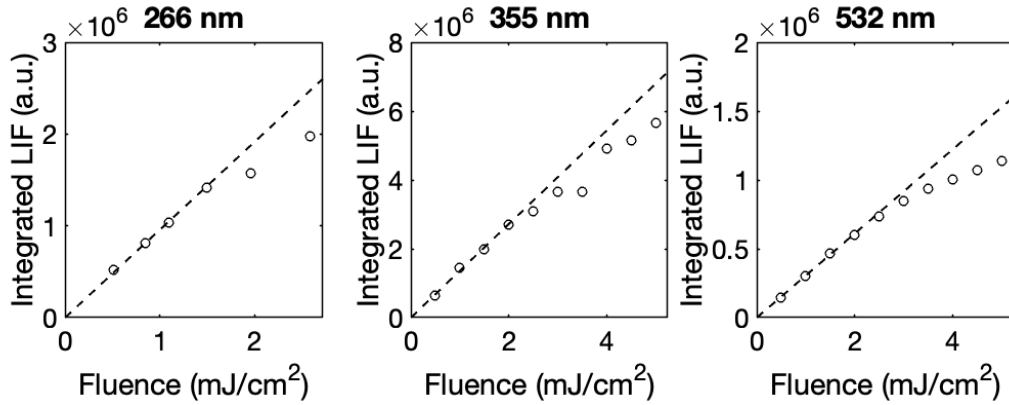


Figure 5.1: LIF fluence curves at 266 nm, 355 nm and 532 nm used to assess the linearity of the LIF signal response. Measurements were taken at 16 mm HAB in a rich flame with  $\phi = 2.36$  ( $C/O = 0.79$ , no  $H_2$ ) by integrating the LIF spectra over emission wavelength at each fluence. The curves show that deviations from linearity occurred at higher fluences, above approximately  $2.5 \text{ mJ cm}^{-2}$  for 532 nm,  $2.0 \text{ mJ cm}^{-2}$  for 355 nm, and  $1.5 \text{ mJ cm}^{-2}$  for 266 nm.

Figure 5.2 shows the normalised, uncalibrated LIF emission spectra at all investigated fluences for each excitation wavelength. The spectra are normalised to assess whether the relative distribution of fluorescence across the emission range changes with laser fluence. Over the selected fluence range, the spectral shapes remain effectively unchanged for all three excitation wavelengths, indicating no clear evidence of wavelength-dependent saturation across the emission spectra. Any fluence-dependent distortion is negligible for 266 nm and 355 nm LIF, and almost indistinguishable for 532 nm LIF.

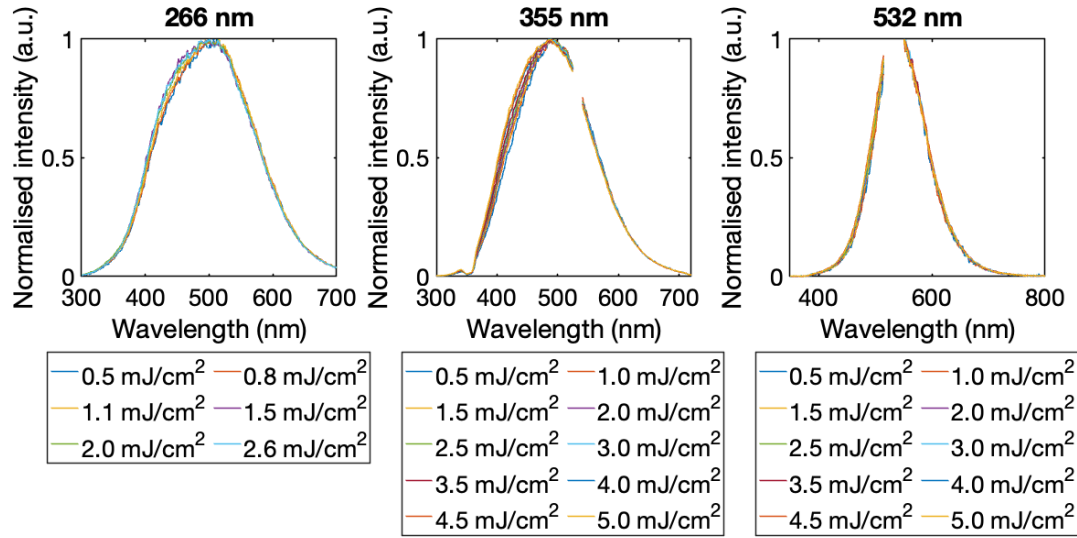


Figure 5.2: Normalised laser-induced fluorescence (LIF) emission spectra for excitation at 266, 355, and 532 nm over a range of laser fluences. Each spectrum is normalised to its own maximum intensity to highlight changes in spectral shape with fluence.

## 5.2 Laser-induced fluorescence measurements from different excitation wavelengths over a range of C/O ratios

LIF measurements at 532, 355, and 266 nm were conducted across a range of C/O ratios, spanning from sub-nucleation to very rich conditions (C/O ratio: 0.53–0.79; flow rates shown in Table 4.1), using a detection gate of 50 ns to assess the influence of H<sub>2</sub> on the emission spectra. These measurements were acquired at 16 mm HAB, corresponding to the same height at which soot concentration measurements were also performed. At this height, H<sub>2</sub> addition was previously found to reduce soot concentration, with the magnitude of this reduction depending strongly on C/O ratio (see Figure 3.12 from Chapter 3).

The fluorescence emission spectra recorded under all flame conditions are presented in Figure 5.3 as spectral radiant energy density per unit fluence ( $\text{m}^{-1} \text{nm}^{-1}$ ). For 266 nm LIF, the calibrated spectra are shown from 315 nm only, since no calibration response was available at shorter wavelengths. The corresponding raw spectra nevertheless show that the fluorescence signal starts to decrease below 315 nm, reaching approximately

zero by 295 nm. Radiometric calibration is an important feature of this work, since the spectra are corrected for the spectrometer’s response, and are reported on a quantitatively reproducible basis. Normalised spectra are also shown, which are obtained by dividing each spectrum by its respective maximum intensity, while ensuring that the normalisation is not influenced by noise. A moving-average smoothing (window size of 5 nm) is applied, consistent with the effective spectral resolution of the spectrometer, to reduce apparent oversampled features without loss of meaningful spectral information.

The sharp spectral cut-offs in the 532 nm LIF measurements arise from rejection of scattered second-harmonic laser light; a corresponding feature is also visible at 532 nm in the 355 nm LIF measurements due to residual unconverted 532 nm light leaking through from the second-harmonic stage. This is also observed at the lower C/O ratios with 266 nm excitation. Under 532 nm excitation, the fluorescence spectra exhibit both Stokes and anti-Stokes components about the laser wavelength, consistent with the literature [22,80]. This contrasts with the 355 nm-excited spectra, which are dominated by mostly red-shifted fluorescence emission [80].

Assuming that quenching and temperature effects remain approximately unchanged between conditions, variations in LIF intensity can be interpreted primarily as reflecting variations in the concentration of the fluorescing species [76]. The LIF intensity increases with increasing C/O ratio for all excitation wavelengths (see non-normalised plots in Figure 5.3), consistent with an increasing concentration of precursor-related fluorescing species as the flame becomes richer. The normalised spectra show that, for 532 nm excitation, the spectral shape remains essentially unchanged over the range of C/O ratios, with no noticeable shift in the emission peak. This suggests that the same class of visible-excited fluorophores, perhaps linked in the literature to resonance-stabilised-radical-type species (RSRs) [23], remains dominant across the conditions studied here, while its overall intensity increases with C/O ratio. In contrast, for 355 and 266 nm excitation, the peak shifts towards shorter wavelengths as the C/O ratio decreases. This effect is especially pronounced for 266 nm excitation.

This behaviour is consistent with a relatively greater contribution from smaller fluorescing PAHs under leaner conditions, whereas longer-wavelength emission from larger

aromatic species, potentially including aliphatically bridged dimers [23], becomes relatively more important as the flame becomes richer. The trend is particularly evident under 266 nm excitation because this wavelength is expected to access a broader range of PAH sizes [80]. A similar overall trend is also observed in the H<sub>2</sub>-doped cases (last two rows of Figure 5.3), shown again for the calibrated spectra and normalised spectra.

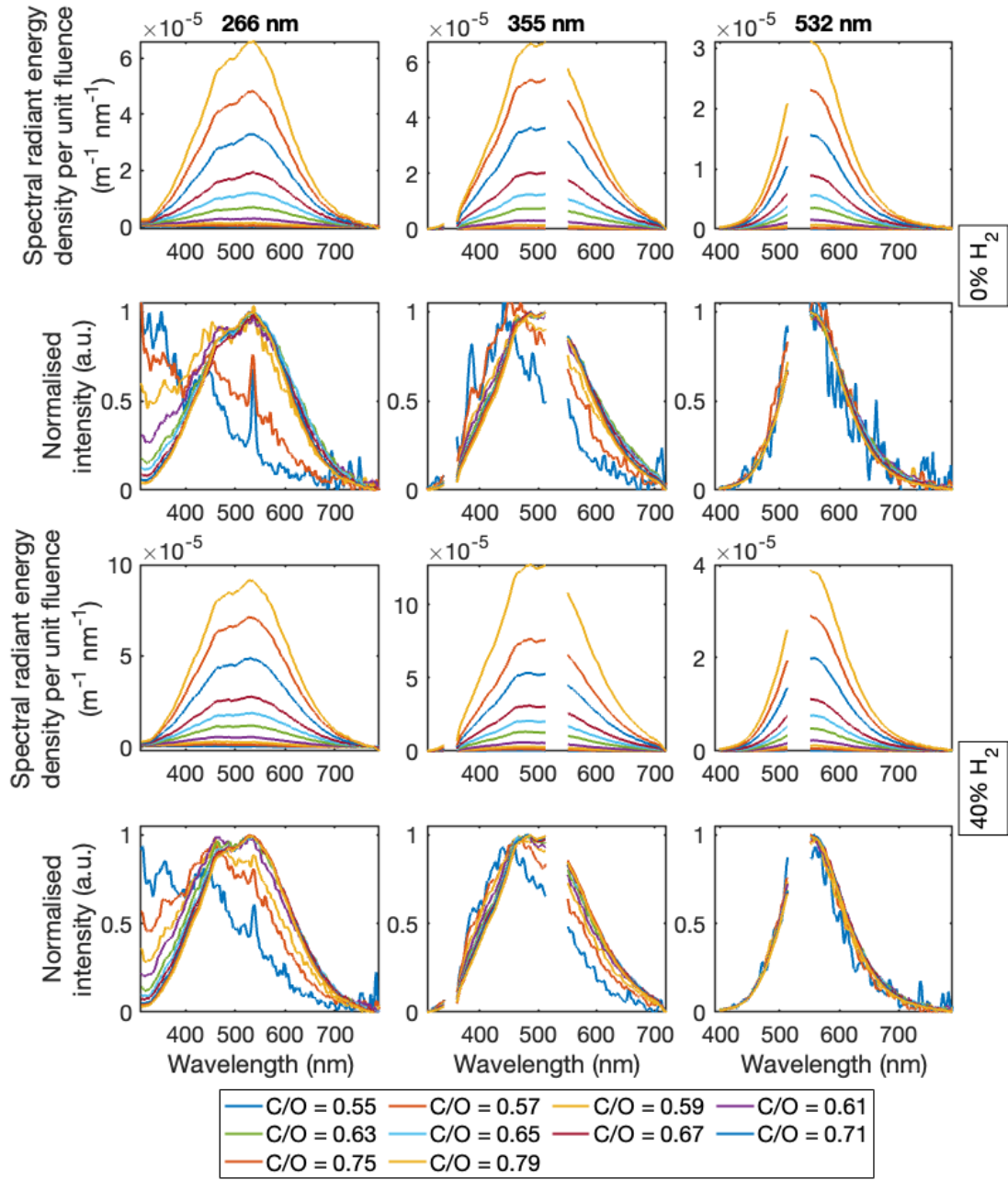


Figure 5.3: LIF emission spectra over a range of C/O ratios at a fixed height ( $HAB = 16$  mm) for three excitation wavelengths (266, 355 and 532 nm). The top two rows show the  $H_2$ -free flame: spectral radiant energy density per unit fluence [ $m^{-1} nm^{-1}$ ] (row 1), and the corresponding max-normalised spectra (row 2). The bottom two rows show the same quantities for the 40%  $H_2$  flame (rows 3–4).

Figures 5.4 and 5.5 present the same data as Figure 5.3, but reorganised to enable a

direct comparison between cases with and without  $H_2$  under each flame condition. Figure 5.4 shows the calibrated spectra (in spectral radiant energy density per unit fluence), while Figure 5.5 shows the same calibrated spectra normalised by their respective peak values. Together, these allow the influence of hydrogen on both the overall LIF intensity and the spectral shape to be assessed separately. In contrast to the corresponding LII results from Chapter 3, the LIF intensity increases with  $H_2$  addition at all C/O ratios for all three excitation wavelengths, as shown in Figure 5.4.

As shown in the subsequent normalised plots (Figure 5.5), there is no discernible change in the spectra with and without  $H_2$  addition in 532 nm LIF. This is not fully the case for 355 and 266 nm LIF measurements. From the same normalised plots, it is interesting to see that from the rich case (C/O=0.79) until a C/O ratio of 0.59, which is the C/O ratio at which soot nucleation takes place, for both 266 and 355 nm LIF, the spectral shape remains mostly unchanged with or without hydrogen addition. However, below this C/O ratio, in the  $H_2$ -free cases, the peak shifts towards shorter wavelengths, suggesting a relatively greater contribution from smaller PAHs under these leaner conditions. At these lower C/O ratios, with 355 nm LIF, the addition of hydrogen increases the fluorescence but does not change the spectral shape. An emission feature observed peaking near 387 nm with 355 nm LIF at C/O=0.53 may be associated with  $C_3$  radicals, as previously reported in a rich sooting methane diffusion flame [119]. With 266 nm LIF, at these lower C/O ratios,  $H_2$  addition increases the fluorescence across the spectrum but preferentially enhances the longer-wavelength region, producing a slight red-shift of the normalised peak and indicating a greater relative contribution from larger precursors. This is particularly evident at C/O = 0.57.

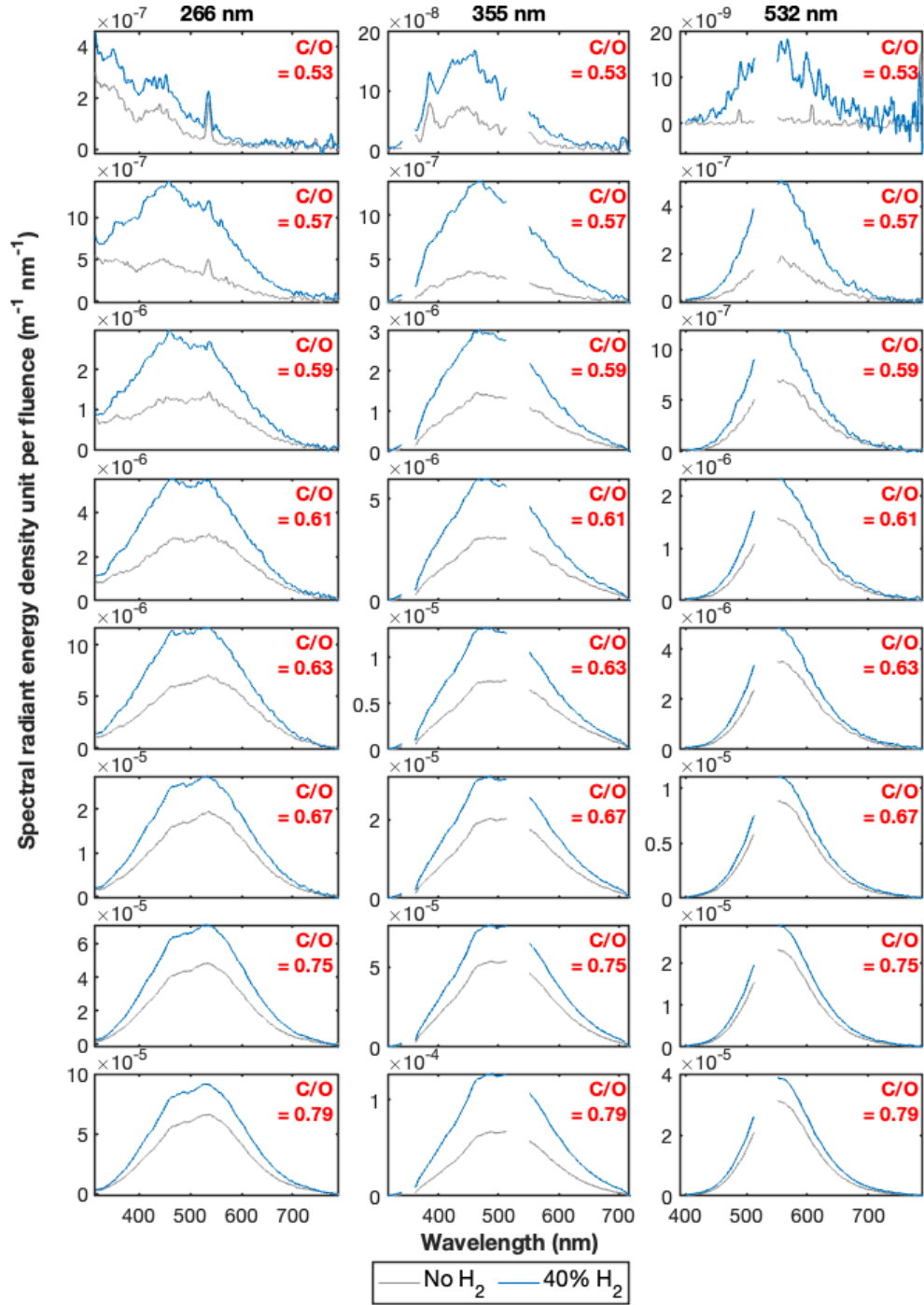


Figure 5.4: Spectral radiant energy density per unit fluence [ $\text{m}^{-1} \text{nm}^{-1}$ ], plotted as a function of wavelength for flames over a range of C/O ratios, comparing  $\text{H}_2$ -doped cases (blue) with  $\text{H}_2$ -free cases (grey). The three columns correspond to excitation at 266, 355, and 532 nm, while each row represents a different C/O ratio, labelled in red. All spectra were measured at 16 mm HAB.



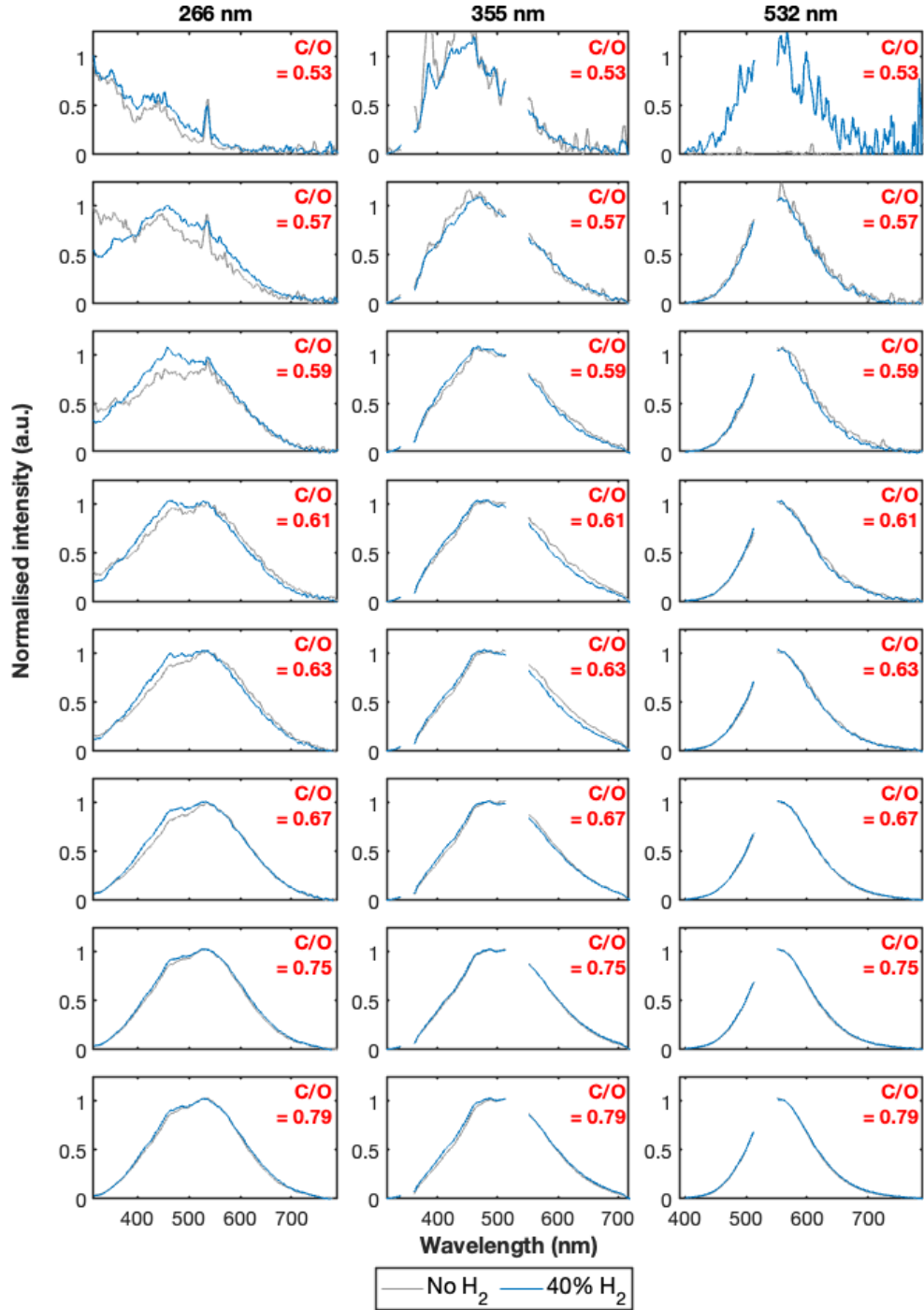


Figure 5.5: Max-normalised spectral radiance spectra as a function of wavelength for a range of C/O ratios, comparing H<sub>2</sub>-doped flames (blue) with H<sub>2</sub>-free flames (grey). Columns correspond to excitation at 266, 355, and 532 nm, and each row corresponds to a different C/O ratio, labelled in red. All spectra were measured at 16 mm HAB.

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To illustrate the effect of  $\text{H}_2$  addition on the overall LIF response across the range of C/O ratios, the area under each radiometrically calibrated LIF spectrum in Figure 5.4 was evaluated. As the spectra are expressed as spectral radiant energy density per unit fluence, integration over the detected wavelength range gives an overall fluorescence response with units of  $\text{m}^{-1}$ , representing the photons emitted per photons incident per sheet propagation distance. The resulting integrated LIF signal is shown in Figure 5.6.  $\text{H}_2$  addition increased the integrated LIF signal at all C/O ratios, and the magnitude of this increase is examined next.

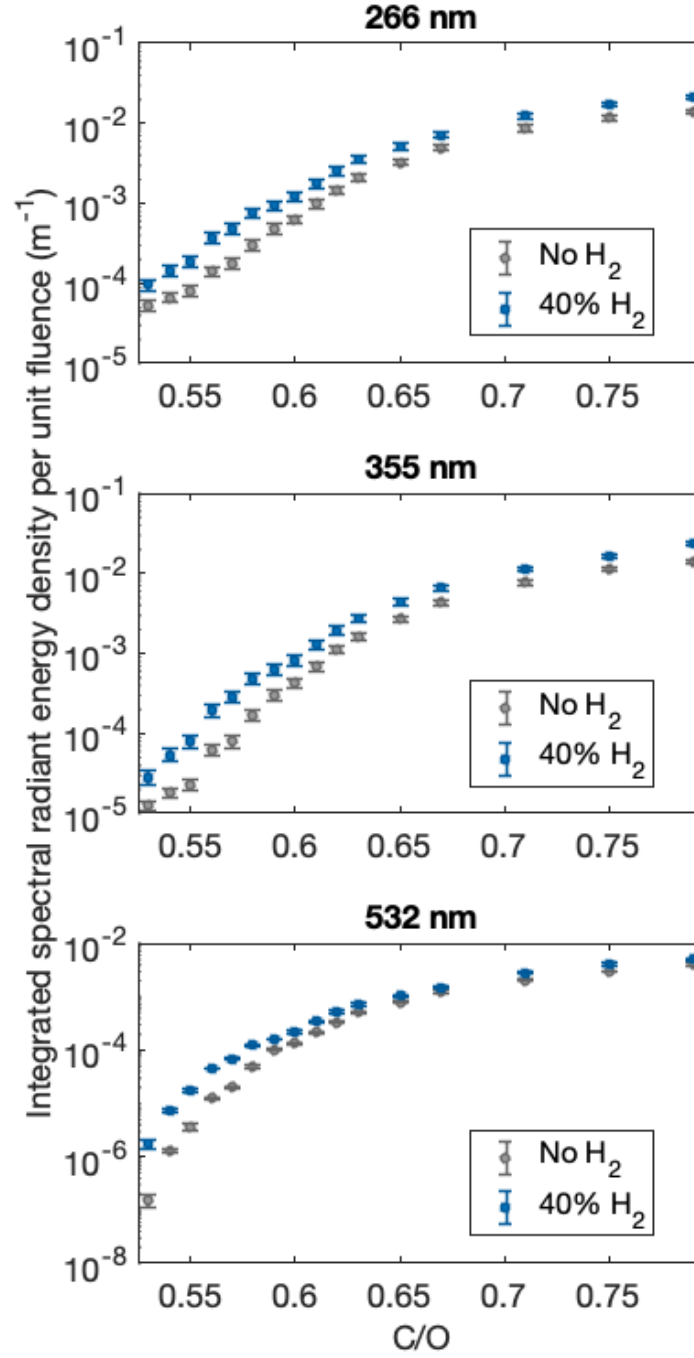


Figure 5.6: Integrated spectral radiant energy density per unit fluence, obtained from the area under the spectral radiant energy density spectra, as a function of C/O ratio for flames with and without  $\text{H}_2$  addition, measured at 16 mm HAB. Each panel corresponds to excitation at 266, 355, and 532 nm.

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The ratio of the integrated LIF signal between the 40% H<sub>2</sub> and 0% H<sub>2</sub> cases is shown in Figure 5.7, together with the previously determined ratio of soot concentration (from the same 40% H<sub>2</sub> and 0% H<sub>2</sub> cases within a smaller subset of equivalent C/O ratios) from Chapter 3. This provides an alternative representation of the trends already shown in Figure 5.6. A ratio below unity indicates a reduction in the integrated LIF signal with hydrogen addition, and the same interpretation applies to the soot volume fraction ratios. For all three excitation wavelengths, the LIF ratios remain above unity across the full C/O range, showing that H<sub>2</sub> increases the integrated LIF signal under all conditions considered. At the fixed height of 16 mm HAB, over the range of C/O ratios, where soot concentration data are available, there is therefore an inverse correspondence, with LIF increasing with H<sub>2</sub> addition as soot decreases. An additional observation is that, above the nucleation threshold (C/O = 0.59), the extent of the LIF enhancement remains relatively constant, whereas below this threshold, the increase becomes markedly larger. This suggests a stronger build-up of precursor-related fluorescence under conditions where soot may not yet be forming. At the lowest C/O ratios (less than C/O = 0.55), the enhancement in integrated LIF tends to become smaller again for the 266 and 355 nm measurements, although the ratios remain above unity throughout. Nevertheless, this fixed-height comparison does not show how H<sub>2</sub> affects precursor-related fluorescence in the lower flame region where soot nucleation occurs, which is the focus of the next section.

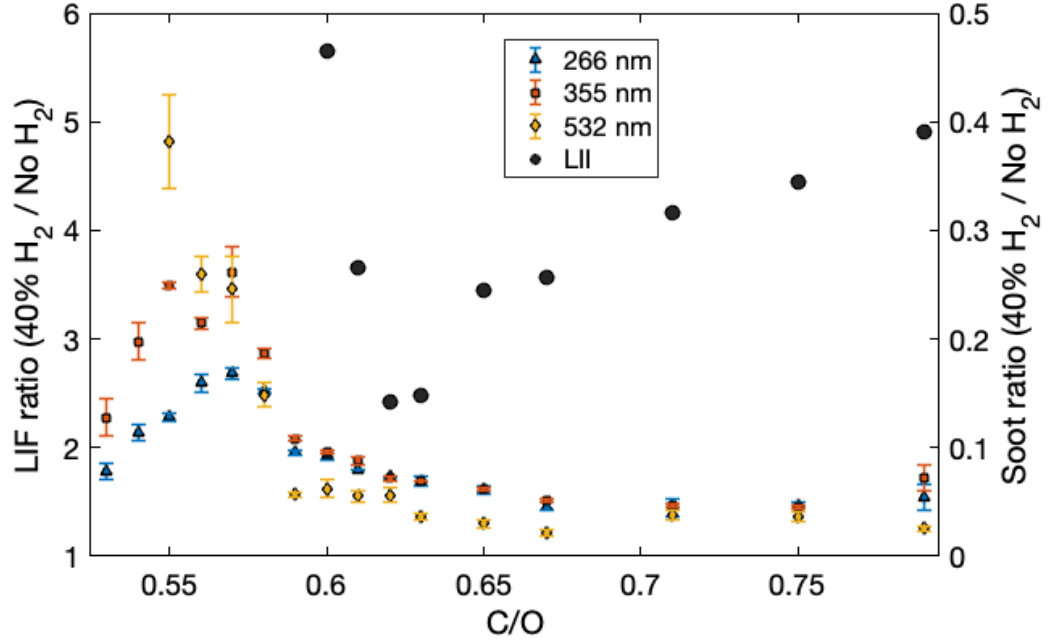


Figure 5.7: Ratio of spectral radiant energy density per unit fluence and soot concentration between flames with and without  $H_2$ , plotted as a function of C/O ratio. Error bars represent the standard error of the ratios obtained from three repetitions, with both the 0% and 40%  $H_2$  cases measured in each repetition.

### 5.3 Height-scan Laser-induced fluorescence measurements from different excitation wavelengths in a nucleation flame (C/O=0.59) and rich flame (C/O=0.79)

A height-resolved LIF scan was performed using the same gate detection as the previous C/O scan measurements (50 ns exposure) in two flames without  $H_2$ : a nucleation flame with C/O = 0.59 ( $\phi = 1.77$ ) and a rich flame with C/O = 0.79 ( $\phi = 2.36$ ) (Figure 5.8). For each excitation wavelength (266, 355, and 532 nm), measurements were acquired over heights ranging from 2.5 to 16 mm HAB in increments of 1.5 mm using the same horizontal laser sheet (2 mm  $\times$  10 mm).

In Figure 5.8, the top two rows show the calibrated spectra and corresponding normalised spectra for the nucleation flame (C/O=0.59), while the bottom two rows show the same pair of plots for the rich flame (C/O = 0.79). From Figure 5.8, for

532 nm excitation in the nucleation and rich flames, the normalised LIF spectra show no discernible evolution with height in either flame, consistent with the same trend observed with the C/O-scan 532 nm LIF measurements. In contrast, with both UV excitations, the peak moves towards shorter wavelengths at lower heights. In particular, with 266 nm excitation, the spectra in both the nucleation and rich flames show a marked shift in the dominant emission towards shorter wavelengths as the sampling location moves closer to the burner. This behaviour is consistent with a downstream evolution in the fluorescing species population, with short-wavelength-emitting species dominating closer to the burner and a progressively larger contribution from species responsible for the longer-wavelength emission further downstream. The spectral evolution is more clearly resolved in the nucleation flame ( $C/O = 0.59$ ), where the spectra develop more distinctly towards a single short-wavelength peak at low HAB. In the rich flame ( $C/O = 0.79$ ), although the same overall shift is observed, appreciable long-wavelength fluorescence remains even at 2.5 mm HAB, showing a less distinct transition. The results here show that the fixed-height spectra at 16 mm HAB reflect the downstream outcome of a substantial spectral evolution occurring earlier in the flame.

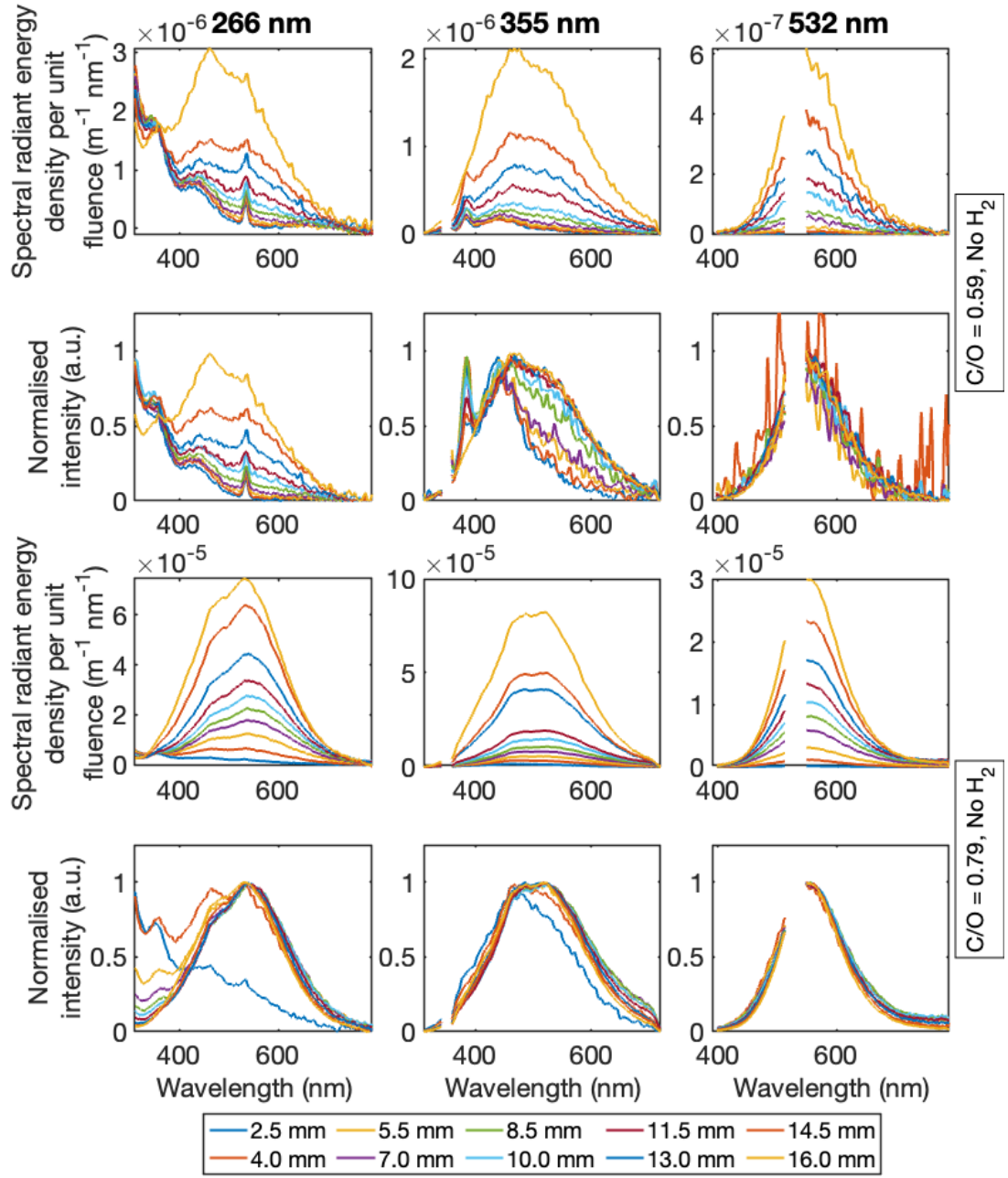


Figure 5.8: Spectral radiant energy density per unit fluence, in  $m^{-1} nm^{-1}$ , and corresponding normalised LIF spectra at different heights in  $H_2$ -free ethylene-air flames with  $C/O = 0.59$  (top two rows, nucleation flame) and  $C/O = 0.79$  (bottom two rows, rich flame) for excitation at 266, 355 and 532 nm.

Figure 5.9 compares the calibrated LIF spectra, with and without  $H_2$  addition at different heights above the burner for all three excitation wavelengths for the nucleation

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flame ( $C/O = 0.59$ ).  $H_2$  addition has little effect on LIF intensity at the lowest heights, but produces a progressively larger increase at higher positions. The corresponding normalised spectra in Figure 5.10 show no discernible spectral variation with  $H_2$  addition for 532 nm excitation. For 355 nm excitation, the previously noted shift towards shorter-wavelength emission with reducing height is observed in both the  $H_2$ -free and  $H_2$ -doped flames, with no clear change in spectral shape caused by  $H_2$  addition.

However, with 266 nm excitation, changes in spectral shape are most evident. At intermediate and higher positions (11.5 to 16 mm HAB),  $H_2$  addition increases the LIF intensity across the spectrum, with the normalised spectra in Figure 5.10 showing a stronger enhancement at longer wavelengths. This indicates a greater relative contribution from the longer-wavelength-emitting species over this height range.

Overall, in the nucleation flame, the precursor-related fluorescence detected at all three excitation wavelengths does not decrease with  $H_2$  addition, despite the reduction in soot observed at 16 mm HAB from LII. Instead, the effect of  $H_2$  is weak at the lowest heights and becomes more evident higher in the flame, with the clearest spectral changes appearing in the 266 nm measurements.



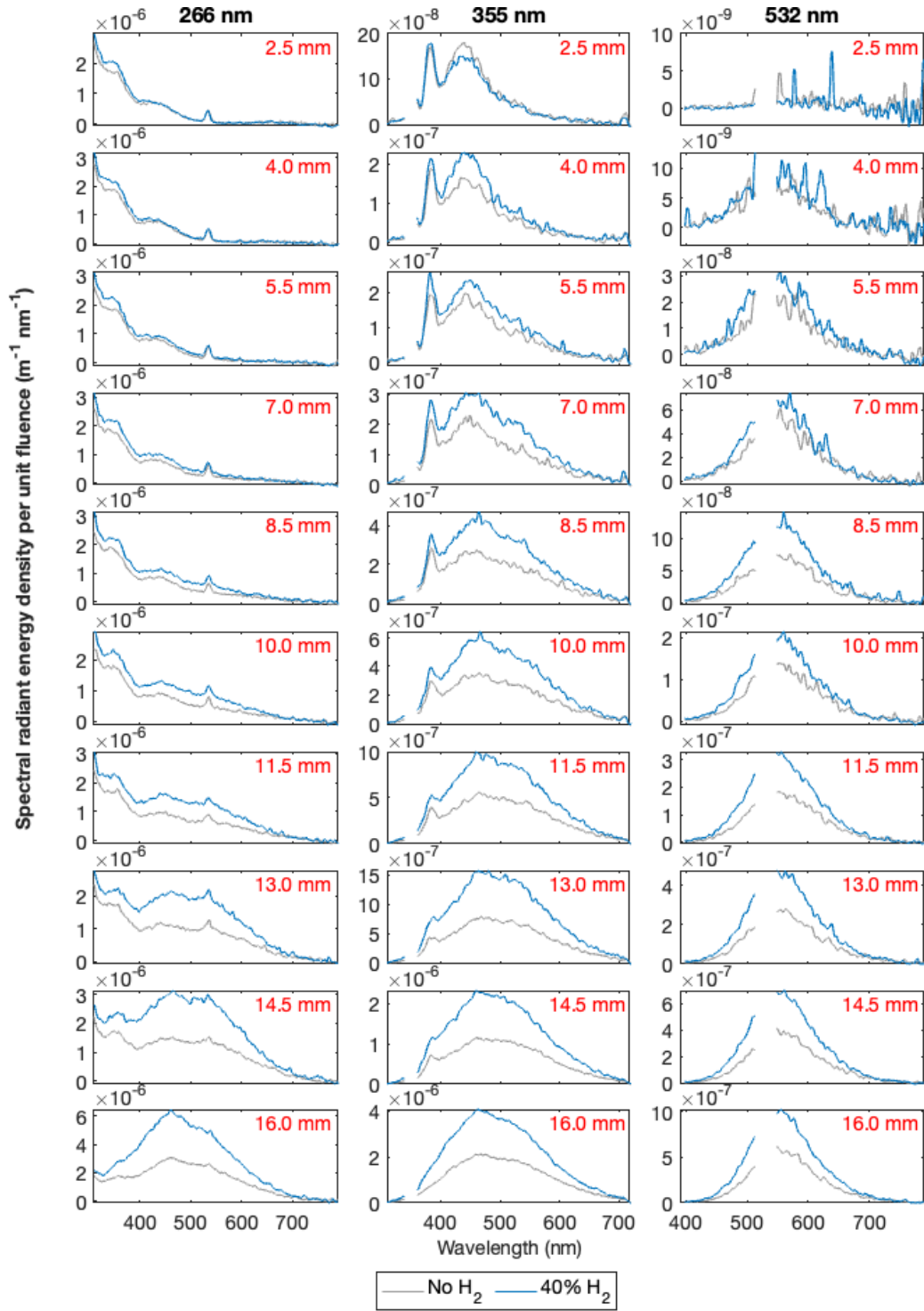


Figure 5.9: Spectral radiant energy density per unit fluence [ $\text{m}^{-1} \text{nm}^{-1}$ ], as a function of wavelength and height in a nucleation ethylene-air flame ( $C/O = 0.59$ ), with and without  $H_2$  addition. Columns correspond to excitation at 266, 355, and 532 nm, while each row represents a different height above the burner (indicated in red). Grey data points correspond to the  $H_2$ -free flame, and blue data points to the  $H_2$ -doped flame.

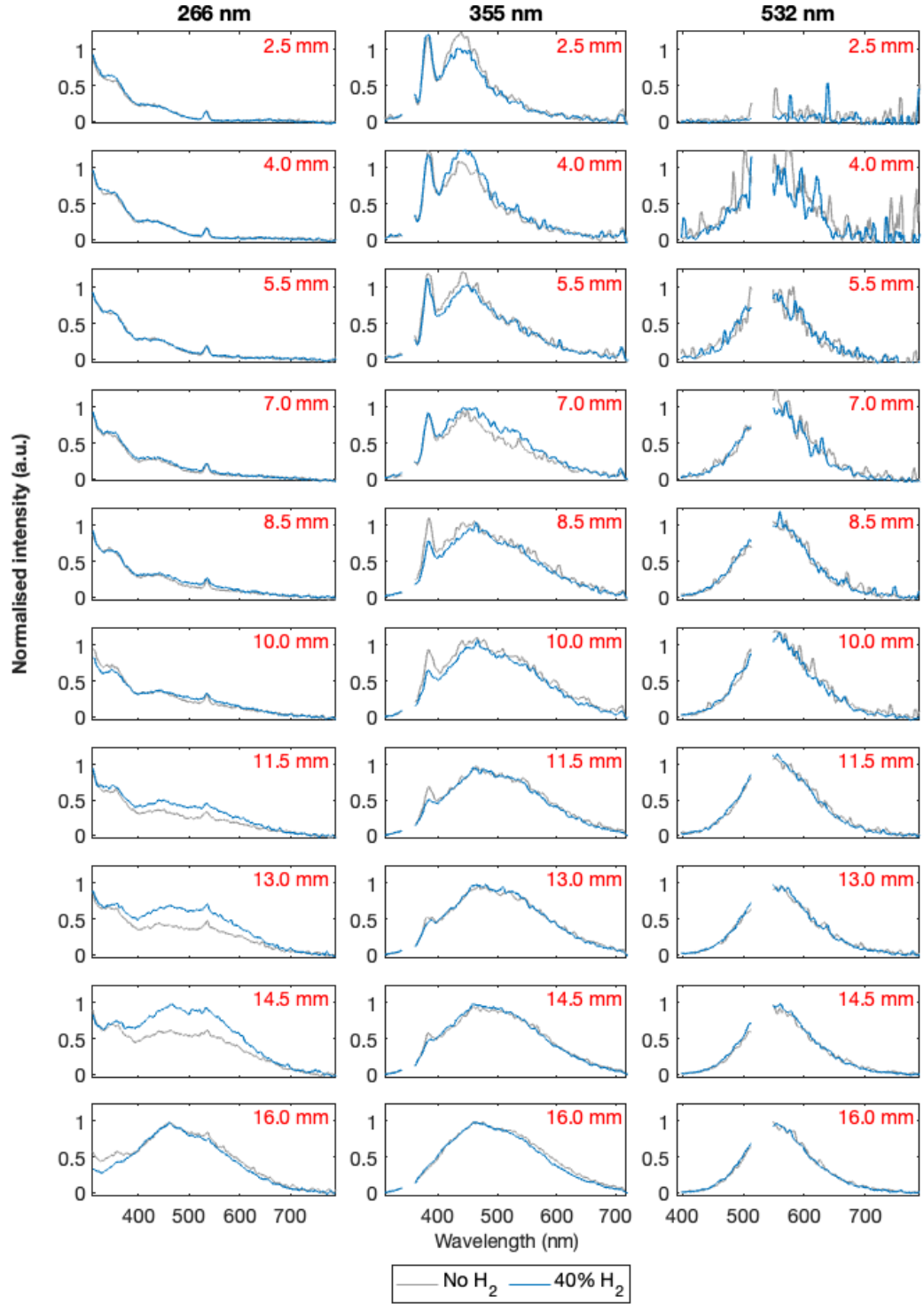


Figure 5.10: Normalised spectral radiant energy density per unit fluence in a nucleation ethylene-air flame ( $C/O = 0.59$ ) with and without  $H_2$  addition. At each height, spectra are normalised to their respective maxima. Columns correspond to excitation at 266, 355, and 532 nm, while rows represent increasing height above the burner (grey:  $H_2$ -free; blue:  $H_2$ -doped).

Figure 5.11 compares the calibrated LIF spectra measured with and without  $\text{H}_2$  addition at each height above the burner, highlighting the influence of hydrogen addition in the rich flame ( $\text{C/O} = 0.79$ ). The effect of  $\text{H}_2$  addition on LIF in the rich flame is clearly height-dependent. Unlike the nucleation flame, where the LIF intensity increased or remained nearly unchanged over the measured height range, the rich flame shows a local reduction in LIF at lower HAB, with the threshold height depending slightly on the excitation wavelength.

The normalised spectra in Figure 5.12 show no noticeable change with  $\text{H}_2$  addition for 532 nm excitation at any height, indicating that the relative spectral weighting remains broadly unchanged. By contrast, under both UV excitations, the reduction in LIF intensity at lower heights is accompanied by a shift towards shorter emission wavelengths, consistent with a reduced relative contribution from larger fluorescing species. This change becomes evident below approximately 8.5 mm HAB for both UV excitations.

Overall, in contrast to the nucleation flame, the rich flame shows a reduction in LIF intensity at lower HAB with  $\text{H}_2$  addition, together with a weaker relative contribution from the longer-wavelength emission. The fluorescence response to  $\text{H}_2$  therefore depends on both flame richness and position within the flame.

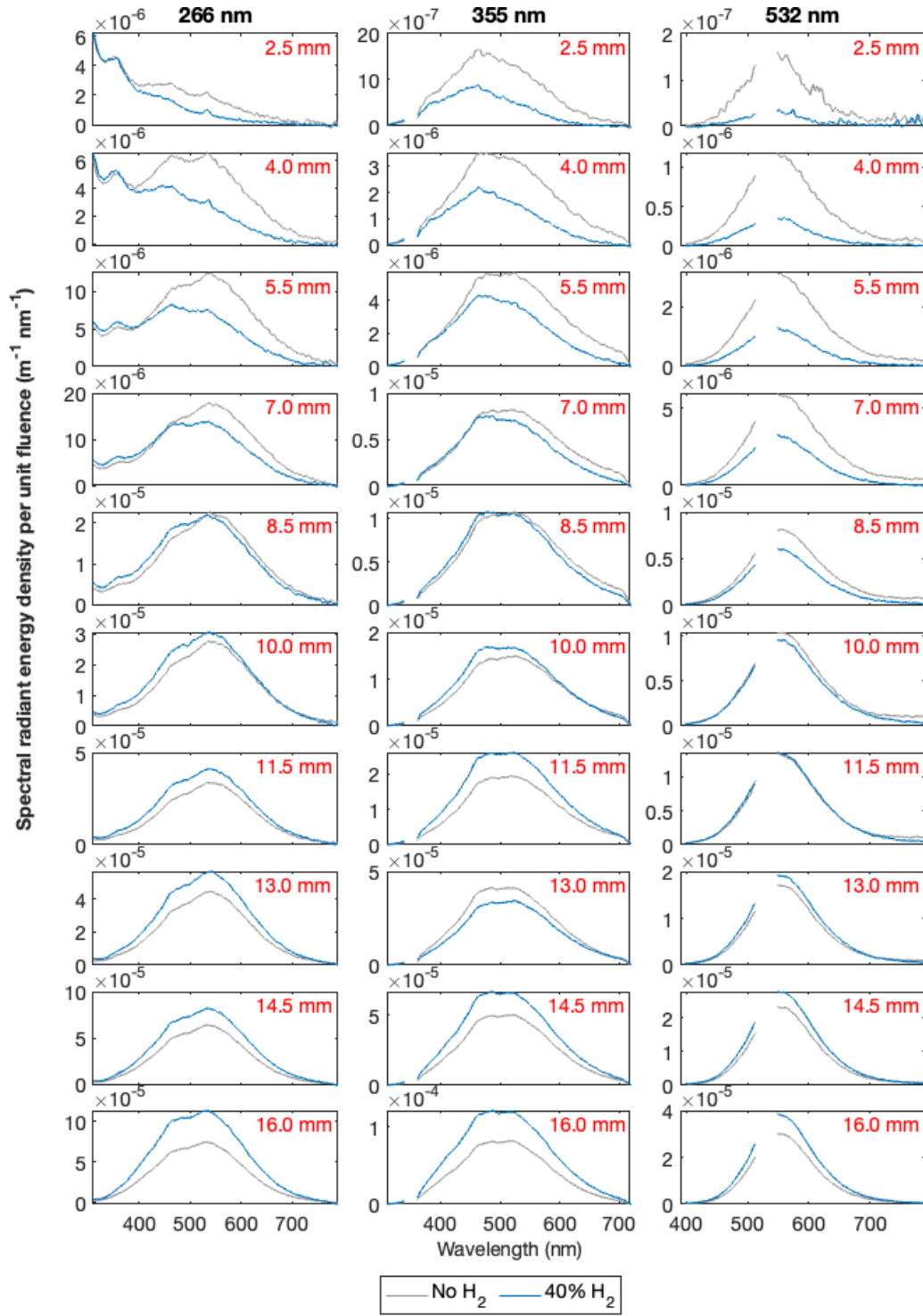


Figure 5.11: Spectral radiant energy density per unit fluence [ $\text{m}^{-1} \text{nm}^{-1}$ ], as a function of wavelength and height in a rich ethylene–air flame ( $\text{C/O} = 0.79$ ), with and without  $\text{H}_2$  addition. Columns correspond to excitation at 266, 355, and 532 nm, while each row represents a different height above the burner (indicated in red). Grey curves correspond to the  $\text{H}_2$ -free flame, and blue curves to the  $\text{H}_2$ -doped flame.

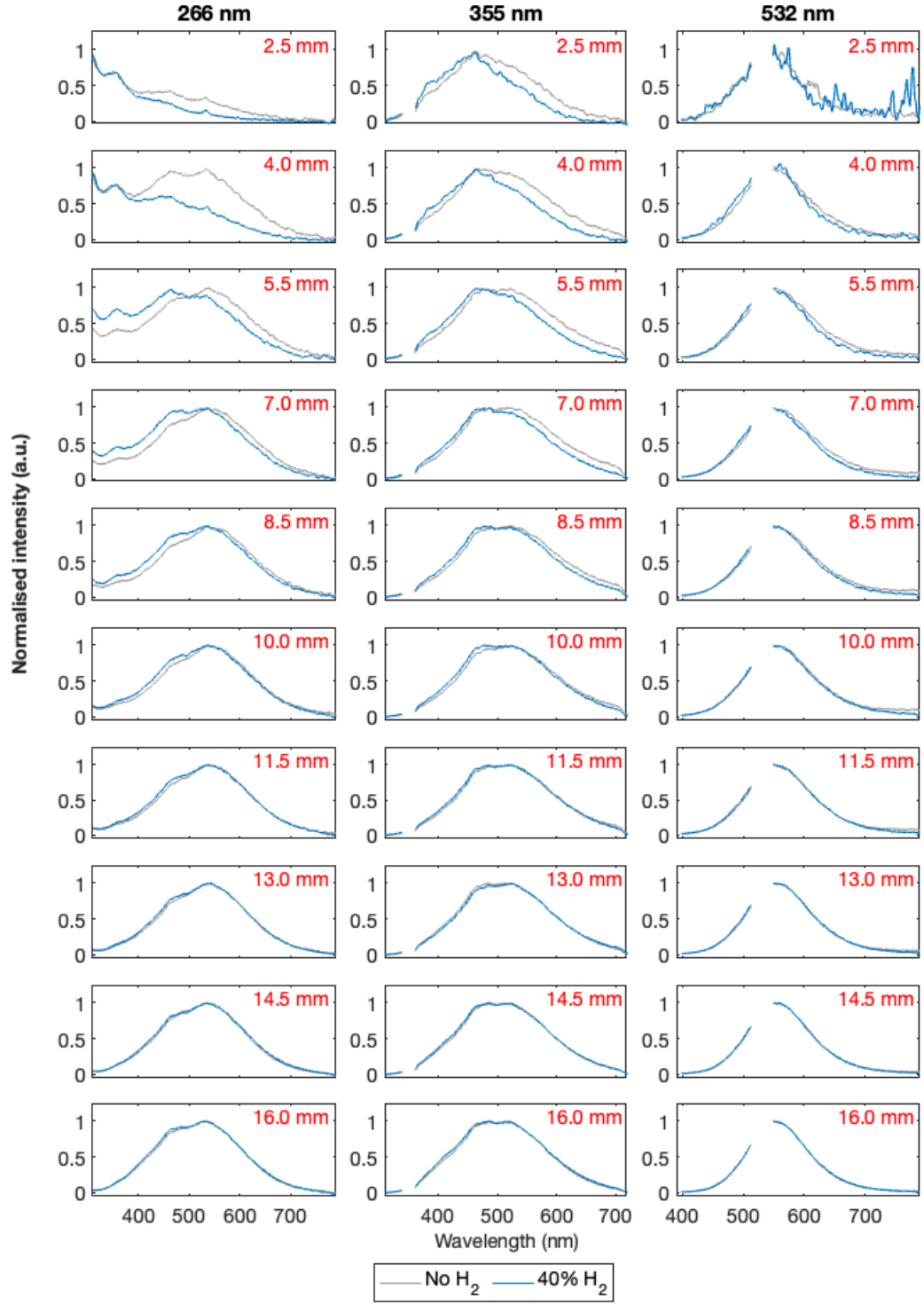


Figure 5.12: Normalised spectral radiant energy density per unit fluence in a rich ethylene-air flame ( $C/O = 0.79$ ) with and without  $H_2$  addition. At each height, spectra are normalised to their respective maxima. Columns correspond to excitation at 266, 355, and 532 nm, while rows represent increasing height above the burner (grey:  $H_2$ -free; blue:  $H_2$ -doped).

Figure 5.13 shows the wavelength-integrated spectral radiant energy density per unit fluence as a function of height for the nucleation ( $C/O = 0.59$ ) and rich ( $C/O = 0.79$ ) flames, with and without hydrogen addition, and for all three excitation wavelengths. Each point therefore represents the integrated LIF signal from the corresponding spectrum in Figures 5.11 and 5.9, showing how the LIF response to hydrogen evolves with height. The extent of these  $H_2$ -induced changes in LIF is examined next.

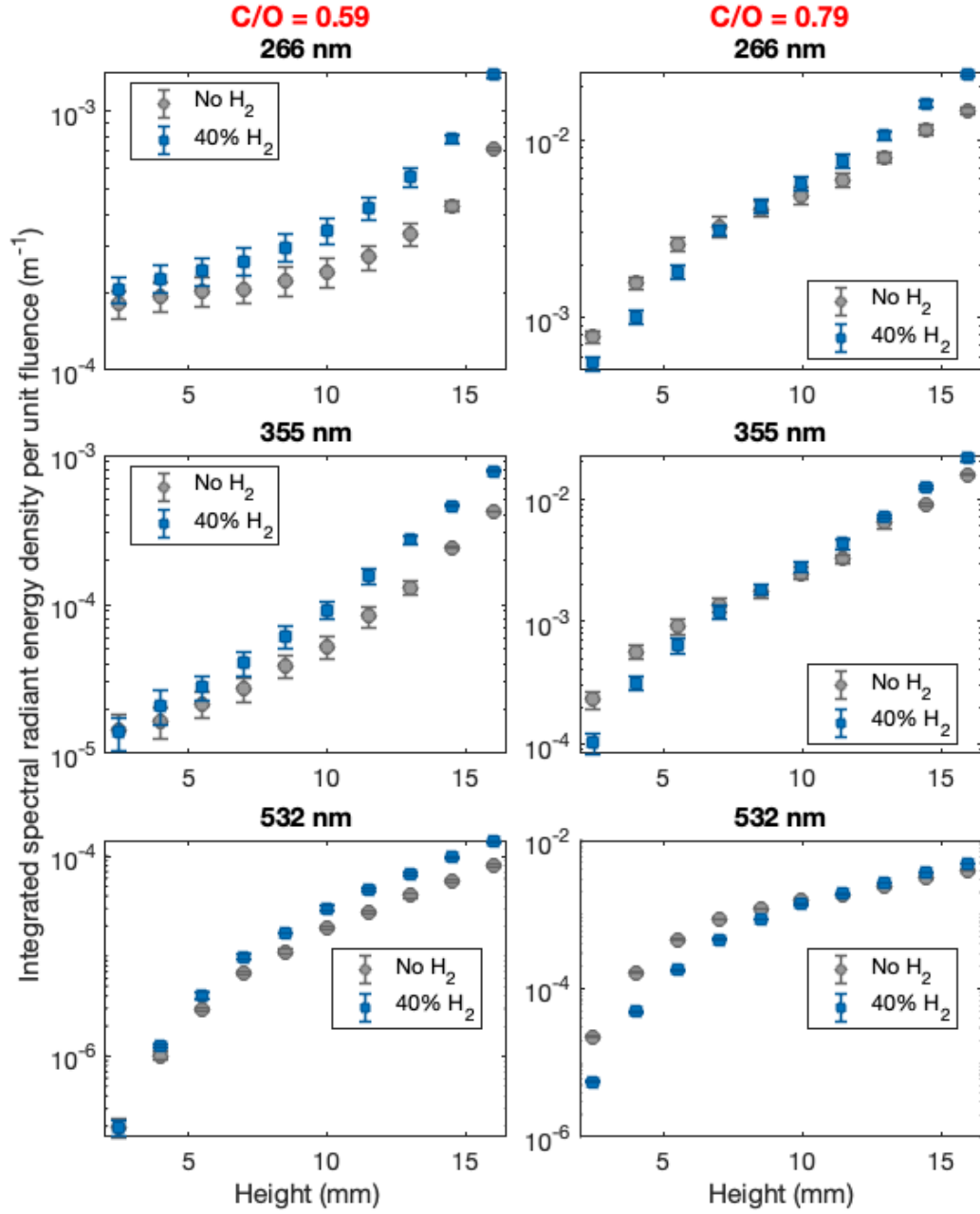


Figure 5.13: Integrated spectral radiant energy density per unit fluence ( $\text{m}^{-1}$ ), plotted on a log scale as a function of height for nucleation ( $\text{C/O} = 0.59$ , left column) and rich ( $\text{C/O} = 0.79$ , right column) ethylene-air flames. Rows correspond to excitation at 266, 355 and 532 nm. Grey and blue symbols denote the  $\text{H}_2$ -free and  $\text{H}_2$ -doped cases, respectively.

Figure 5.14 compares the effect of  $\text{H}_2$  addition on the integrated LIF signal, as a

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function of height, using the ratio between the 40% H<sub>2</sub> and 0% H<sub>2</sub> cases. The LIF ratios were determined from the values shown in Figure 5.13. Also shown are the corresponding ratios from the TiRe-LII peak signals (corresponding to soot concentration) from Chapter 3 (Figures 3.3 and 3.12).

In the nucleation flame ( $C/O = 0.59$ ), TiRe-LII measurements were only available at 16 mm HAB, where H<sub>2</sub> was found to reduce the soot volume fraction by roughly a factor of two. In contrast, the LIF ratios in Figure 5.14 are greater than unity at all heights and for all excitation wavelengths. The enhancement increases gradually with height, reaching values of about 2.1 at 16 mm HAB, while the ratios at the lowest height remain close to one. The three excitation wavelengths show similar ratios at a given height, indicating that the relative influence of H<sub>2</sub> addition is broadly consistent across the excitation conditions.

In the rich flame ( $C/O = 0.79$ ), the effect of H<sub>2</sub> on LIF is clearly height dependent. At low heights, H<sub>2</sub> suppresses the LIF signal: for UV LIF (266 and 355 nm excitation), the ratios fall below unity up to about 7 mm HAB, while for 532 nm excitation, the reduction extends to around 10 mm HAB. Above these heights, the UV LIF ratios rise above one and follow each other closely, whereas the 532 nm ratios remain lower at all heights. Thus, in the region close to the onset of soot formation, H<sub>2</sub> reduces the LIF signal at all three excitation wavelengths, with the strongest reduction observed for 532 nm excitation. Further downstream, where LIF increases with H<sub>2</sub> at all wavelengths, the 532 nm signal shows the least enhancement. In contrast, H<sub>2</sub> reduced the soot volume fraction at all heights in the rich flame, as reflected by TiRe-LII peak ratios consistently below unity (also shown in Figure 5.14).

Taken together with the LII trends, these results show that the integrated LIF signal, which represents fluorescence associated with PAHs and related structures in the flame, does not simply follow the observed changes in soot concentration. This is notable because such structures are considered to play important roles in soot nucleation and growth. At the same time, the integrated LIF results at the three excitation wavelengths lead to broadly the same overall conclusion. PCA was therefore applied to the measured LIF spectra to identify the dominant modes of spectral variation, which provided a basis



for the subsequent extraction of approximate grouped spectral components. These fitted components were tracked with respect to flame conditions (HAB, C/O, and hydrogen addition), as described in the next section.

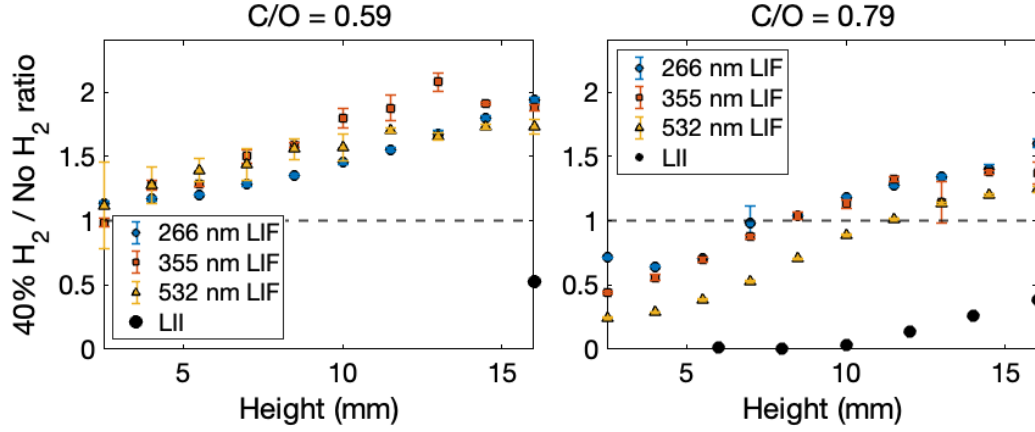


Figure 5.14: Ratio of integrated spectral radiant energy density per unit fluence versus height at different excitation wavelengths (40%  $\text{H}_2$  to 0%  $\text{H}_2$ ) for the nucleation ( $\text{C/O} = 0.59$ ) and rich ( $\text{C/O} = 0.79$ ) flames.  $f_v$  ratios from peaks of PMT LII measurements (40%  $\text{H}_2$  to 0%  $\text{H}_2$ ) at the same flame conditions and heights, as calculated in Chapter 3, are included for comparison. Ratios below unity (dashed line) indicate a reduction in LII/LIF intensity with  $\text{H}_2$  addition.

## 5.4 Identification of spectral building blocks in LIF spectra across C/O ratio, HAB, and $\text{H}_2$ addition

This section examines whether the measured LIF spectra can be described using a small number of dominant spectral patterns, and whether these can be used to define physically interpretable building blocks representing grouped fluorescence contributions across the studied flame conditions. The analysis is initially restricted to spectra recorded at 16 mm HAB across a range of C/O ratios, with and without  $\text{H}_2$  addition.

To identify the main sources of spectral variation, principal component analysis (PCA) was applied to the spectra obtained over this set of flame conditions. In practice, PCA was implemented using the singular value decomposition (SVD) of the data matrix in MATLAB. Each spectrum was mean-centred and standardised prior to decomposition so that the analysis emphasised changes in spectral shape rather than absolute signal

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For the PCA analysis, each flame condition is represented by a single stacked data array formed by concatenating the 532, 355, and 266 nm emission spectra into one column vector. Arranging these vectors side by side gives a data array  $\mathbf{X} \in \mathbb{R}^{m \times n}$ , where  $m$  is the total number of wavelength points (1 nm interval) across all three excitation wavelengths and  $n$  is the number of flame conditions in the 16 mm HAB C/O-scan dataset. Each column therefore corresponds to one flame condition, while each row corresponds to a particular emission wavelength at one of the three excitation wavelengths. After mean-centring and standardisation, PCA was performed via singular value decomposition (SVD), such that

$$\mathbf{Z} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^T, \quad (5.1)$$

where  $\mathbf{Z}$  is the mean-centred and standardised data matrix,  $\mathbf{U}$  contains the loading vectors (spectral patterns),  $\mathbf{\Sigma}$  contains the singular values, and  $\mathbf{\Sigma}\mathbf{V}^T$  defines the corresponding scores for each flame condition. The loading vectors represent the dominant modes of spectral variation across the dataset, while the corresponding scores indicate how strongly each flame condition expresses a given pattern.

In the present dataset, the first two principal components account for 82.2% and 15.5% of the total variance, respectively, so together they describe around 98% of the variability in the stacked spectra. Figure 5.15 shows the PC2–PC1 score plot and the corresponding scree plot. The percentage variance explained by principal component  $k$  was calculated as  $100 \times \sigma_k^2 / \sum_j \sigma_j^2$ , where  $\sigma_k$  is the  $k$ -th singular value. The sharp drop after the first principal component, together with the minor contribution from the third component onwards, shows that the variation in the stacked spectra is well represented by the first two principal components. In the score plot (top subplot), each point represents one flame condition. The main observation is that, especially at the lower C/O ratios,  $\text{H}_2$  addition shifts the points along the same overall trajectory as increasing C/O ratio, indicating that  $\text{H}_2$  affects the LIF spectra in broadly the same way as making the flame richer.

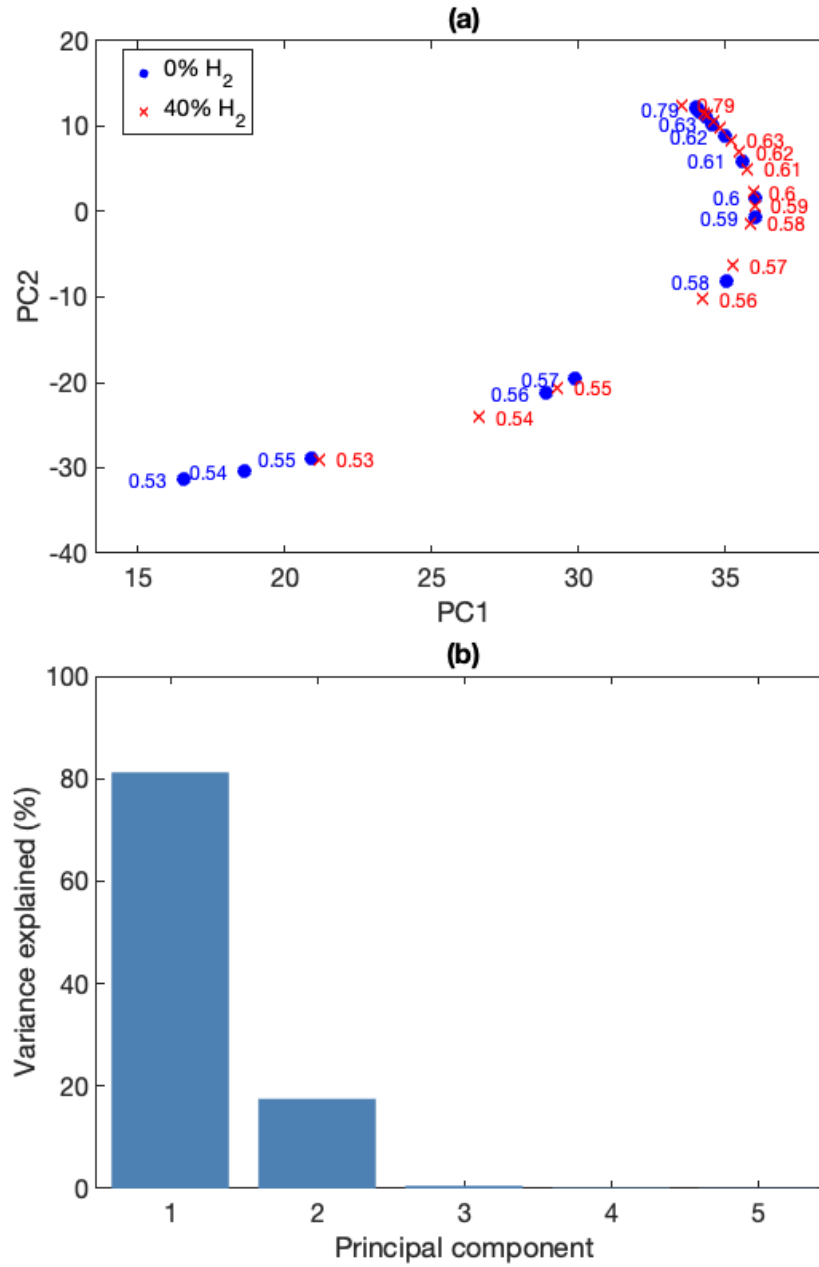


Figure 5.15: (a) PC2–PC1 score plot and corresponding (b) scree plot obtained from the PCA of the stacked LIF spectra for the 32 flame conditions at 16 mm HAB. In the score plot, each point represents one flame condition and is labelled by its C/O ratio; filled blue circles indicate 0% H<sub>2</sub> and red crosses indicate 40% H<sub>2</sub>. The scree plot shows that the first two principal components account for approximately 98% of the total variance.

Figure 5.16 shows the loading spectra for the first five principal components, sepa-

rated into their 532 nm, 355 nm and 266 nm excitation blocks. PC1 exhibits a broad, smooth loading shape across all three blocks, indicating a dominant mode of variation common to all excitation wavelengths. In contrast, the secondary variation captured by PC2, characterised by a redistribution towards shorter-wavelength emission, is most clearly apparent in the 266 nm block, with a weaker corresponding contribution in the 355 nm block, while remaining close to zero in the 532 nm block. Higher-order components (PC3–PC5) have much smaller associated variance contributions, with PC3 accounting for less than 1% of the total variance, as already shown in the scree plot (Figure 5.15 (b)), indicating that very little additional systematic spectral variation remains beyond PC2.

A separate PCA performed on each excitation wavelength gave the same overall picture: the 532 nm LIF spectra are largely described by PC1 alone, whereas the 266 nm spectra retain the largest PC2 contribution, with a smaller PC2 contribution also present at 355 nm (this is not shown here). These results motivate the subsequent building-block analysis, which seeks to represent the dominant spectral variation in a more physically interpretable form.

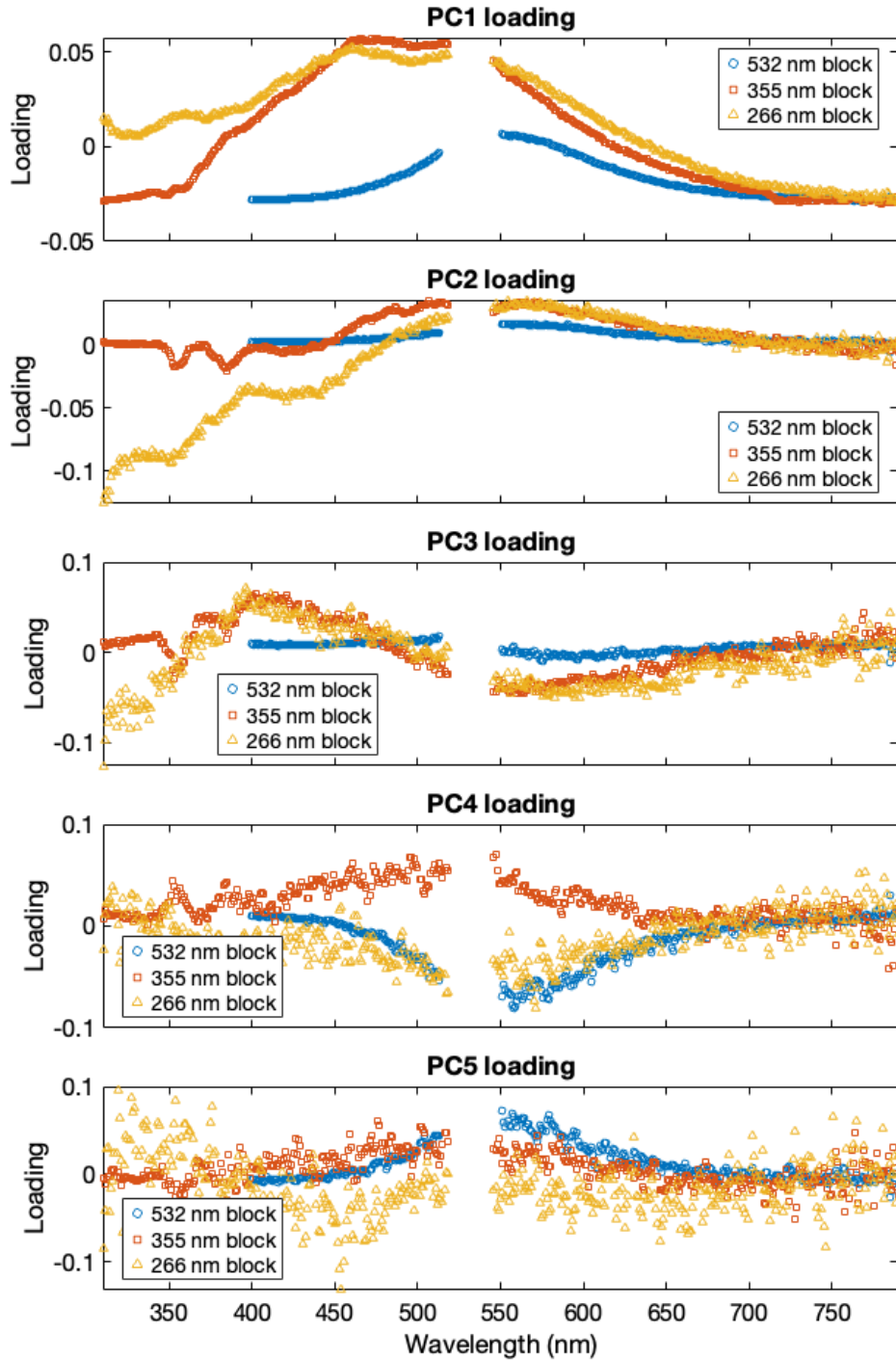


Figure 5.16: Loading spectra of the first five principal components, separated into their 532 nm, 355 nm and 266 nm emission blocks. PC1 is dominated by a broad spectral mode common to all three excitation wavelengths, whereas PC2 shows a redistribution towards shorter wavelengths that is most pronounced in the 266 nm block and weak or absent in the 355 and 532 nm blocks. Higher-order components show that little additional systematic variance remains compared to PC2.

Although PCA indicated that the dominant spectral variation could be represented using a small number of components, the loading vectors themselves were not taken here as physically meaningful spectral building blocks, since the loading vectors may not represent smooth, non-negative fluorescence spectra. To extract the dominant spectral building blocks suggested by the PCA, representative measured spectra were therefore selected from limiting flame conditions for each excitation wavelength. In the discussion that follows, the extracted building blocks are referred to as a visible component and a secondary UV–visible component. These are treated as grouped fluorescence contributions from species with overlapping emission spectra, rather than uniquely identified individual species.

As shown in Figure 5.17, for both 266 nm and 355 nm excitation, a visible-dominated base spectrum,  $B(\lambda)$ , was taken from a rich condition ( $C/O = 0.79$ ), while a UV-rich spectrum,  $U(\lambda)$ , was taken from a sub-nucleation condition ( $C/O = 0.56$ ). The visible-dominated spectrum was then scaled by a single factor  $\alpha$ , obtained by least-squares matching of  $B(\lambda)$  to  $U(\lambda)$  over a long-wavelength window  $[\lambda_{\min}, \lambda_{\max}]$  where the visible contribution was assumed to dominate. The two building blocks were then defined as

$$B_{\text{vis}}(\lambda) = \alpha B(\lambda), \quad B_{\text{UV-vis}}(\lambda) = U(\lambda) - \alpha B(\lambda), \quad (5.2)$$

and are shown in the lower panels of Figure 5.17, where each block is normalised to its own maximum. For both excitation wavelengths, the lower- $C/O$  spectrum used to derive the UV–visible component exhibited a poorer signal-to-noise ratio than the richer flame used for the visible component. A moving-average smoothing filter was therefore applied to the spectra prior to subtraction, reducing local noise while retaining the main spectral features.

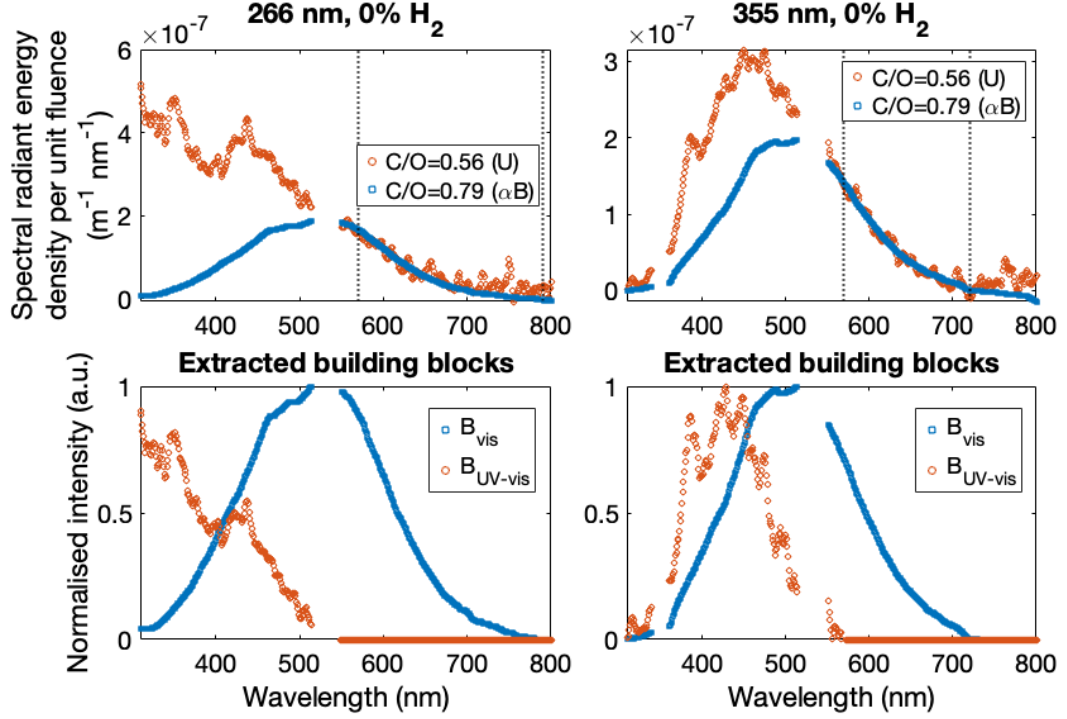


Figure 5.17: Extraction of visible and UV-visible spectral building blocks from the measured 266 nm and 355 nm spectra. For each excitation wavelength, a UV-rich spectrum,  $U(\lambda)$ , at  $\text{C/O} = 0.56$  is compared with a visible-dominated base spectrum,  $B(\lambda)$ , at  $\text{C/O} = 0.79$ , scaled over the long-wavelength region where the visible contribution is assumed to dominate (dotted vertical lines, top row). The lower row shows the resulting visible component,  $B_{\text{vis}}(\lambda) = \alpha B(\lambda)$ , and UV-visible component,  $B_{\text{UV-vis}}(\lambda) = U(\lambda) - \alpha B(\lambda)$ , both normalised.

As illustrated for selected  $\text{C/O}$  ratios in Figures 5.18 and 5.19, the two-block decomposition reproduces the measured 266 nm and 355 nm LIF spectra closely, with small residuals, for both 0% and 40%  $\text{H}_2$ . This agreement indicates that the dominant features of the UV-excited emission for the  $\text{C/O}$ -scan measurements can be represented using a visible component together with an additional UV-visible component. The 532 nm LIF spectra were adequately represented by a single visible building block, taken from the  $\text{H}_2$ -free rich flame at  $\text{C/O} = 0.79$  and 16 mm HAB (see Figure A.3 in Appendix A). Each spectrum was represented as a linear combination of the two extracted building blocks,

$$x_i(\lambda) \approx a_i B_{\text{vis}}(\lambda) + b_i B_{\text{UV-vis}}(\lambda), \quad (5.3)$$

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where  $a_i$  and  $b_i$  are fitted coefficients representing the visible and UV-visible components, respectively, obtained using the MATLAB solver `lsqlin`.



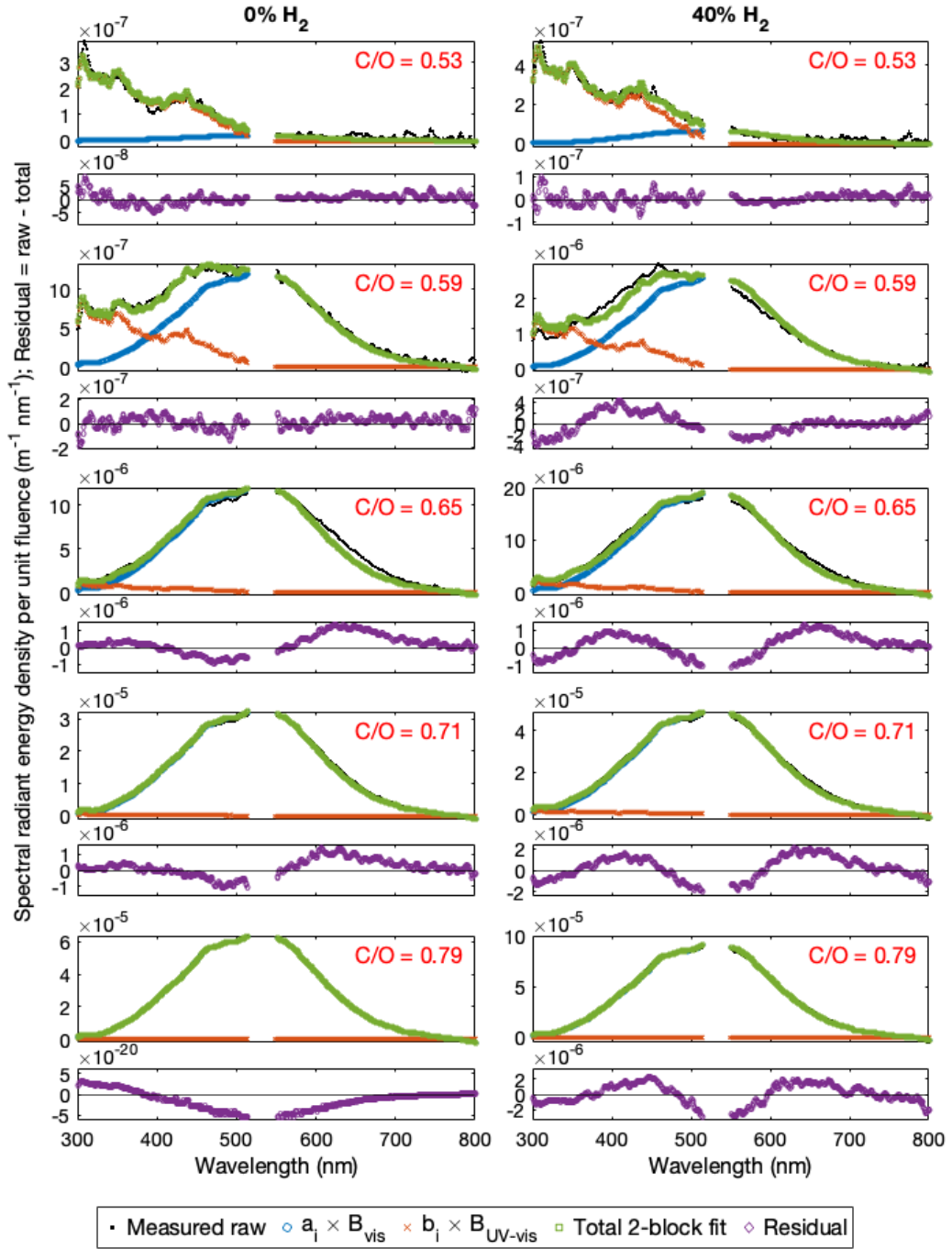


Figure 5.18: Two-block decomposition of 266 nm LIF spectra across the C/O scan for flames without  $H_2$  (left column) and with 40%  $H_2$  (right column). The total two-block fit closely follows the measured signal over the full wavelength range, while the residual (raw – total fit) remains small across all C/O ratios. These results indicate that the two-block model captures the dominant spectral features consistently for both hydrogen-free and hydrogen-doped flames.

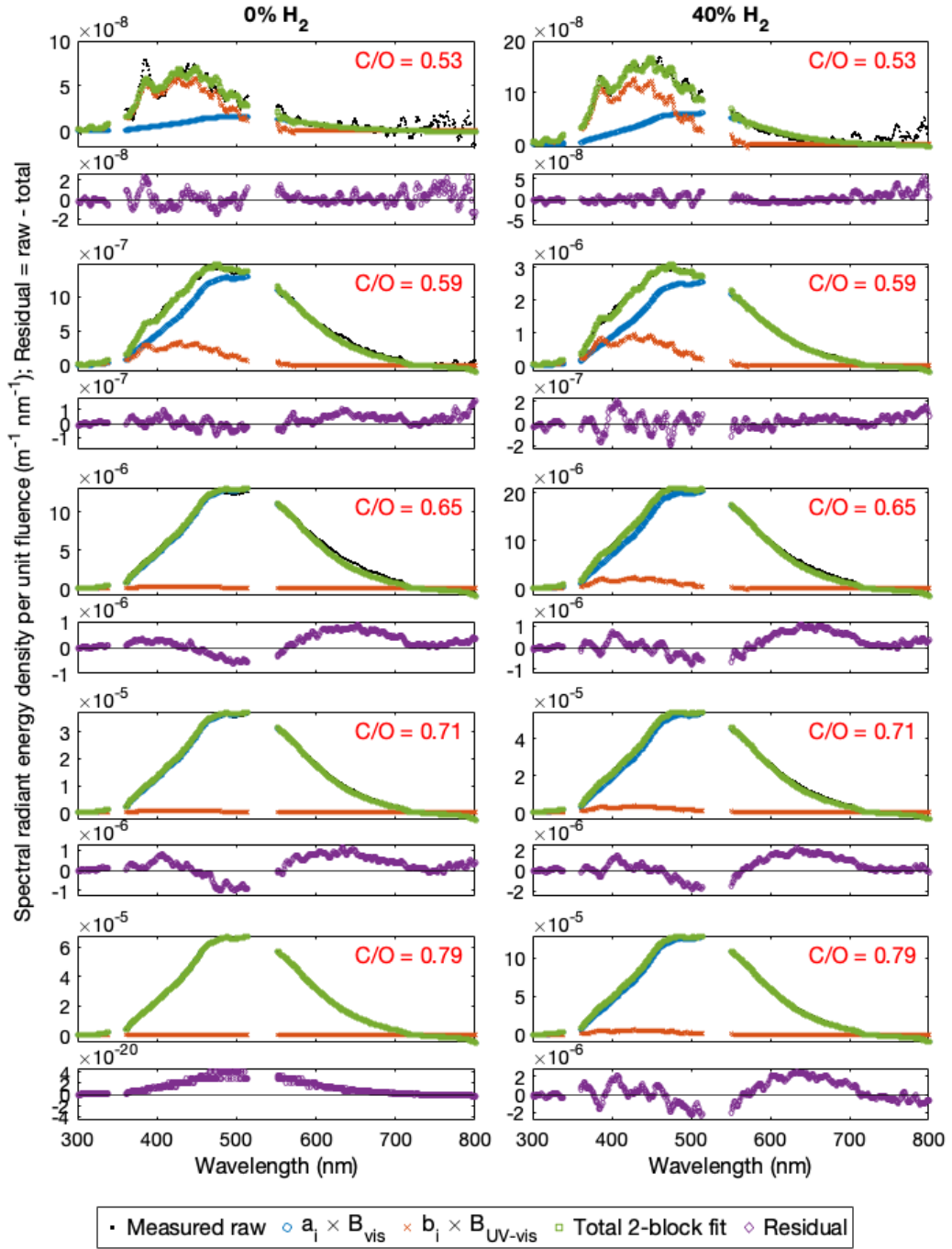


Figure 5.19: Two-block decomposition of 355 nm LIF spectra across the C/O scan for flames without H<sub>2</sub> (left column) and with 40% H<sub>2</sub> (right column). The total two-block fit closely follows the measured signal over the full wavelength range, while the residual (raw – total fit) remains small across all C/O ratios. These results indicate that the two-block model captures the dominant spectral features consistently for both hydrogen-free and hydrogen-doped flames.

Figure 5.20 shows how the integrated fitted-component area varies with C/O ratio, based on the visible and UV–visible components obtained from the two-block decomposition of the raw 266 nm and 355 nm spectra. For both 0% and 40% H<sub>2</sub>, the integrated area of the visible component increases strongly with C/O, showing that this component becomes progressively stronger as the flame becomes richer. The same overall trend is observed for both H<sub>2</sub> conditions, with the 40% H<sub>2</sub> flames giving slightly larger visible-component values at the lower and intermediate C/O conditions, although the two cases become closer at the richest conditions.

The integrated UV–visible component remains relatively weak compared to the visible component across the full C/O range examined. Its associated uncertainty increases substantially towards the richest conditions, consistent with the fitted spectra in Figures 5.18 and 5.19, where the UV–Vis component becomes increasingly difficult to distinguish from the baseline. For this reason, the integrated UV–visible areas shown in Figure 5.20 are restricted to  $C/O \leq 0.65$ , where it remained sufficiently appreciable to be interpreted with greater confidence.

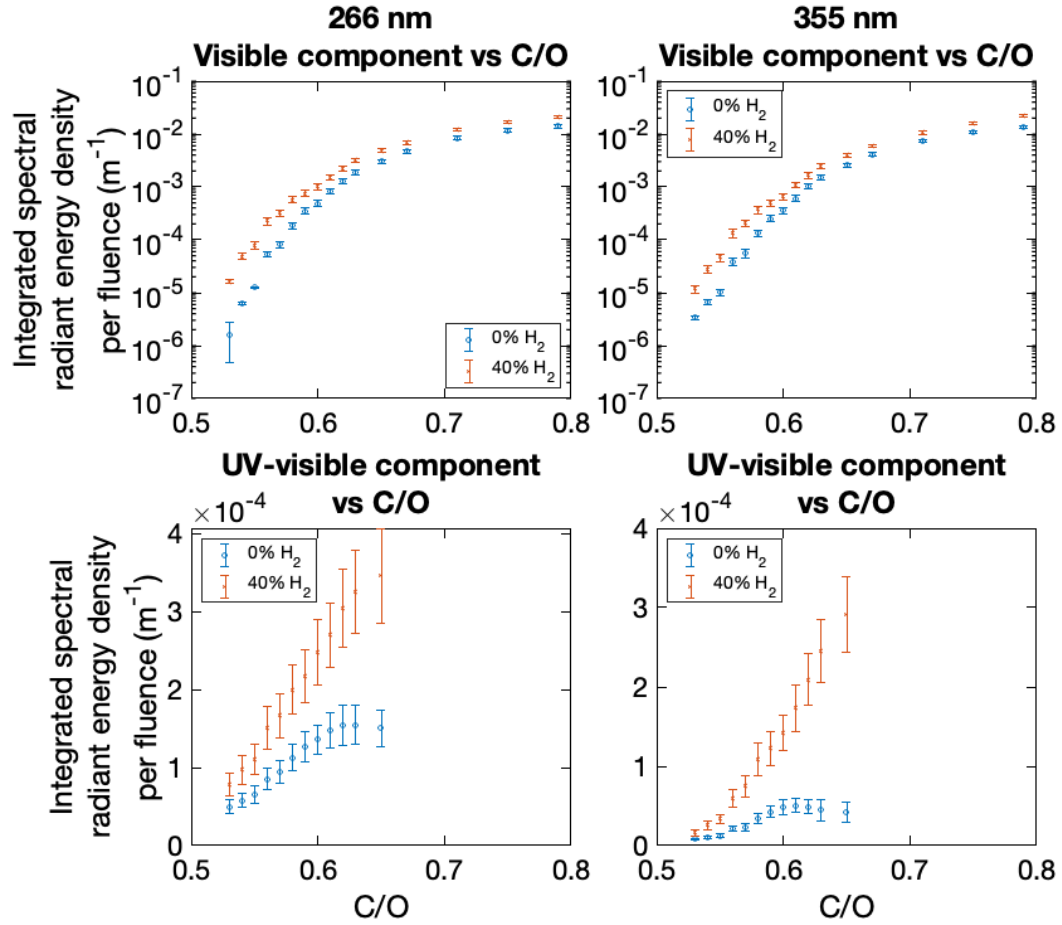


Figure 5.20: Integrated areas of the fitted visible and UV-visible components from the two-block decomposition of the calibrated 266 nm and 355 nm LIF spectra, shown as a function of C/O for 0% and 40%  $\text{H}_2$ . The left column shows the 266 nm results and the right column the 355 nm results. In each case, the upper panel shows the visible component on a logarithmic scale, while the lower panel shows the UV-visible component on a linear scale. Values are given as integrated spectral radiant energy density per unit fluence and represent the mean of three repetitions with error bars. The decomposition was performed using building blocks constructed from the first-repetition reference spectra, which were then used for fitting all three repetitions.

A particularly interesting result is shown in Figure 5.21(a). For each excitation wavelength, the fitted visible-component areas for the 0%  $\text{H}_2$  cases were normalised to their value at the highest C/O ratio (C/O = 0.79). The fitted visible-component areas for the corresponding 40%  $\text{H}_2$  cases were then normalised using the same 0%  $\text{H}_2$ , C/O = 0.79 reference value. On this common reference basis, the normalised

visible-component areas collapse very closely across all three excitation wavelengths. For the 266 nm and 355 nm LIF measurements, these fitted areas were obtained from Figure 5.20. For the 532 nm LIF measurements, the fitted visible-component areas shown here were obtained using the single visible building block defined from the H<sub>2</sub>-free rich-flame spectrum at C/O = 0.79 and 16 mm HAB, as previously described.

This close agreement is particularly notable in the context of PAH-related structures proposed to contribute to soot nucleation. Previous studies have suggested that visible emission observed under UV excitation may be associated with aliphatically bridged PAH dimers, whereas visible emission observed under visible excitation may be associated with resonance-stabilised radicals [22, 23, 88]. The very similar trends across the different excitation wavelengths therefore suggest that the visible fluorescence contributions could arise either from the same underlying emitting population or from different species contributions that track each other very closely. To the author’s knowledge, this degree of agreement across all three excitation wavelengths has not been highlighted previously in the literature.

Figure 5.21(b) shows the effect of H<sub>2</sub> addition on the fitted visible-component area as a function of C/O ratio, expressed as the H<sub>2</sub>/no-H<sub>2</sub> ratio. These ratios are broadly similar at each C/O ratio, irrespective of excitation wavelength. It is interesting that hydrogen increases the fitted visible-component areas, given their potential link with PAH-related structures associated with soot nucleation. Notably, at sub-nucleation C/O ratios (C/O < 0.59), the H<sub>2</sub>/no-H<sub>2</sub> ratios of the visible component increase more strongly. This is consistent with the possibility that, below the nucleation threshold, H<sub>2</sub> addition promotes a greater build-up of species contributing to the visible component under conditions where they are not yet being consumed into soot.

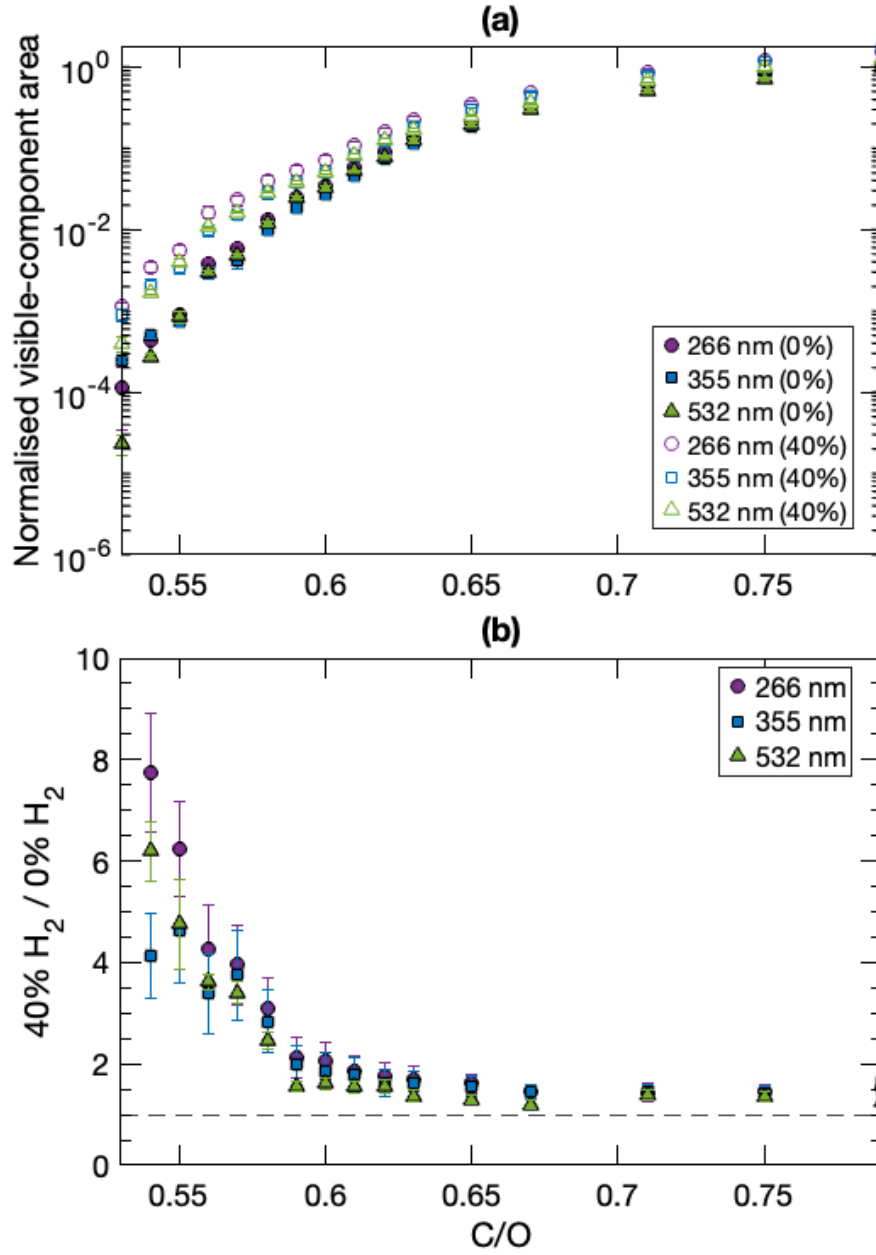


Figure 5.21: (a) Integrated area of the fitted visible component for the 0% and 40%  $H_2$  cases, normalised using the corresponding 0%  $H_2$  value at  $C/O = 0.79$  for each excitation wavelength. Normalisation to a common hydrogen-free reference preserves the relative effect of  $H_2$  addition and enables comparison of the component trends across excitation wavelengths. (b) Ratio of the fitted visible-component area with 40%  $H_2$  addition to that without  $H_2$  addition as a function of  $C/O$  ratio. Ratios greater than one (dashed line) indicate increased fluorescence from hydrogen addition.

Figure 5.22 shows the effect of  $H_2$  addition on the UV-visible component contributions as a function of C/O ratio. Based on its shorter-wavelength emission range, the UV-visible component is tentatively associated with fluorescence consistent with PAH-like fluorescence [3, 23, 76, 82]. Unlike the visible component, at sub-nucleation C/O ratios especially ( $C/O < 0.59$ ), the  $H_2$ /no- $H_2$  ratio of the UV-visible component remains comparatively flat. The ratios obtained with 355 nm excitation are generally slightly larger than those obtained with 266 nm excitation. At the highest C/O ratios, the fitted component ratios are associated with significantly increased uncertainty. These points are therefore omitted.

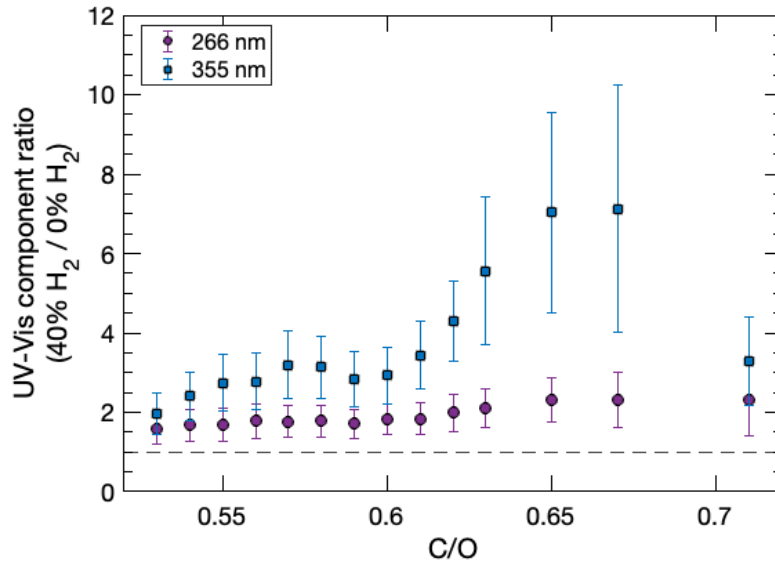


Figure 5.22: Effect of  $H_2$  addition on the fitted UV-visible component contributions as a function of C/O ratio, shown as the ratio between the 40%  $H_2$  and 0%  $H_2$  cases, for 266 and 355 nm excitation. Error bars represent the standard error from three repetitions.

It was then assessed whether the same spectral building blocks used for the C/O-scan reconstruction could also reproduce the height-scan spectra in the rich flame ( $C/O = 0.79$ , 0% and 40%  $H_2$ ). Figure 5.23 shows the corresponding 266 nm reconstructions, while Figure 5.24 shows the 355 nm reconstructions. Overall, the same two-block model reproduces the measured spectra well across the full height range for both 0% and 40%  $H_2$  conditions. The residuals are generally small relative to the measured signal, although some structured deviations remain at the lower and intermediate heights.

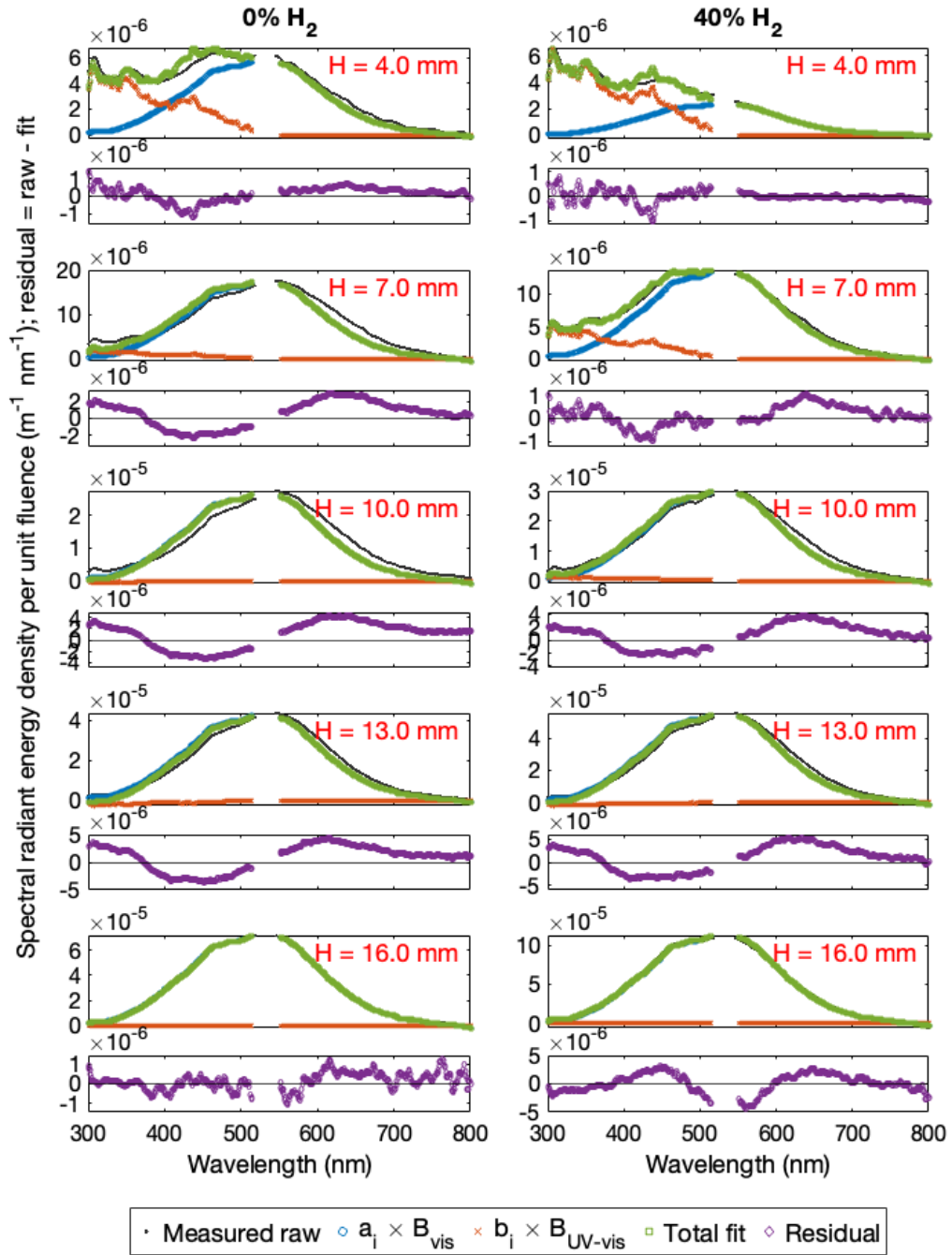


Figure 5.23: Two-block decomposition of 266 nm LIF spectra across the height-scan for flames without  $\text{H}_2$  (left column) and with 40%  $\text{H}_2$  (right column). The total two-block fit closely follows the measured signal over the full wavelength range, while the residual (raw – total fit) remains small across all C/O ratios. These results indicate that the two-block model captures the dominant spectral features consistently for both hydrogen-free and hydrogen-doped flames.



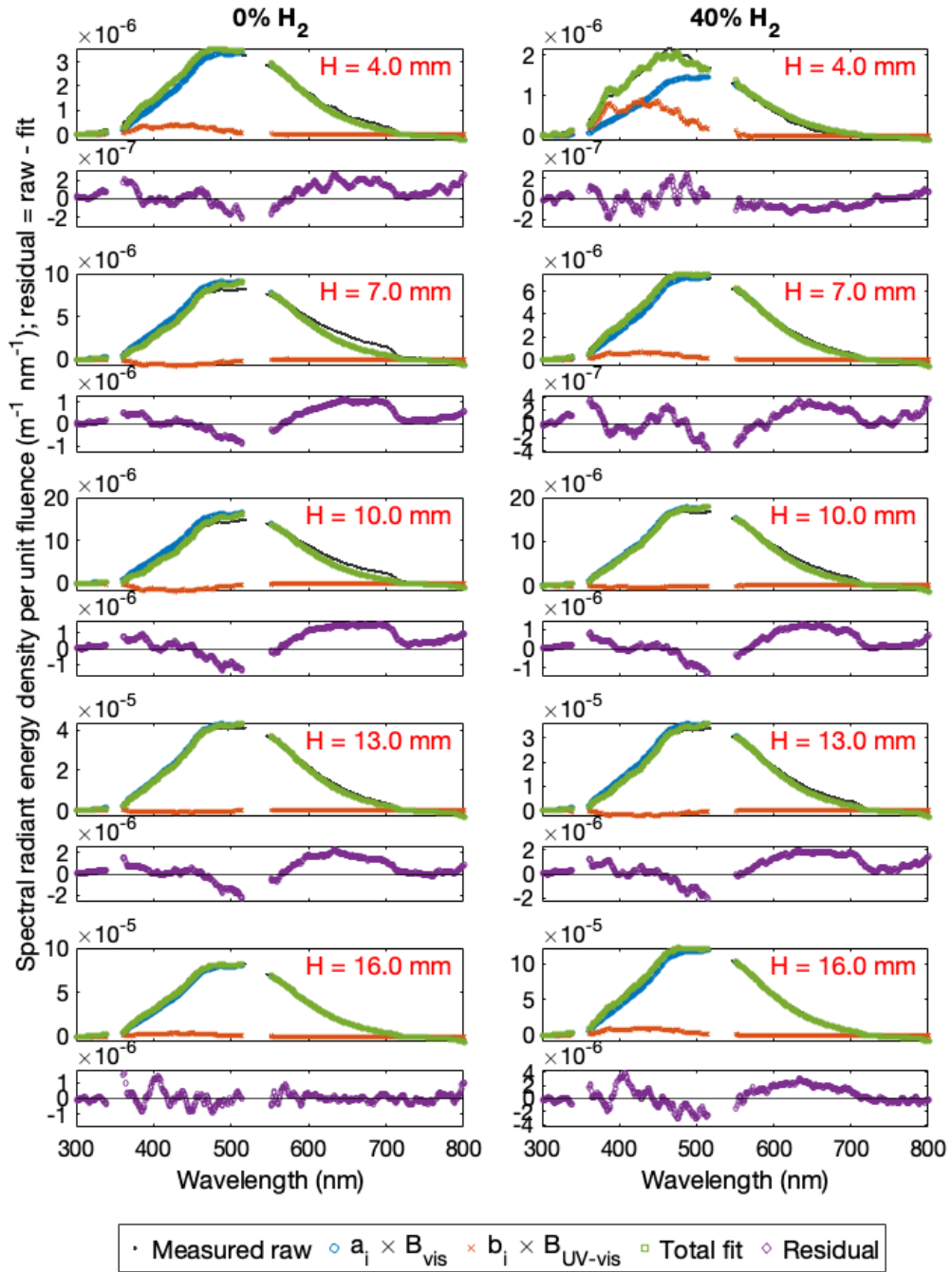


Figure 5.24: Two-block decomposition of 355 nm LIF spectra across the height-scan for flames without  $H_2$  (left column) and with 40%  $H_2$  (right column). The total two-block fit closely follows the measured signal over the full wavelength range, while the residual (raw – total fit) remains small across all C/O ratios. These results indicate that the two-block model captures the dominant spectral features consistently for both hydrogen-free and hydrogen-doped flames.

Figure 5.25 shows the integrated visible and UV–visible components obtained from the two-block decomposition of the 266 nm and 355 nm height-scan spectra for the rich flame ( $C/O = 0.79$ ). The visible component shows a clear height dependence. For both excitation wavelengths, its fitted contribution was lower in the 40%  $H_2$  flames at the lower heights, before becoming comparable to and then larger than the  $H_2$ -free case higher in the flame. A similar reduction was observed in the integrated 532 nm LIF signal (shown in lower right panel of Figure 5.13), which can be adequately represented using a single visible building block. Over this same lower-height region, the fitted UV–visible contribution was larger in the  $H_2$ -doped flames. The UV–visible component remained small compared to the visible component across the full height range, but generally decreased with height up to around 10–12 mm HAB.

At the highest HAB, an increase in the fitted UV–visible contribution was observed in both cases, which nevertheless represented only a very small fraction of the total signal and was associated with relatively large uncertainties. This behaviour was therefore attributed to the sensitivity of the two-block fitting procedure when extracting a weak component, and was therefore forced to zero. Nevertheless, the 266 nm and 355 nm UV–visible components showed similar trends at the lower heights, including a larger contribution in the 40%  $H_2$  case.

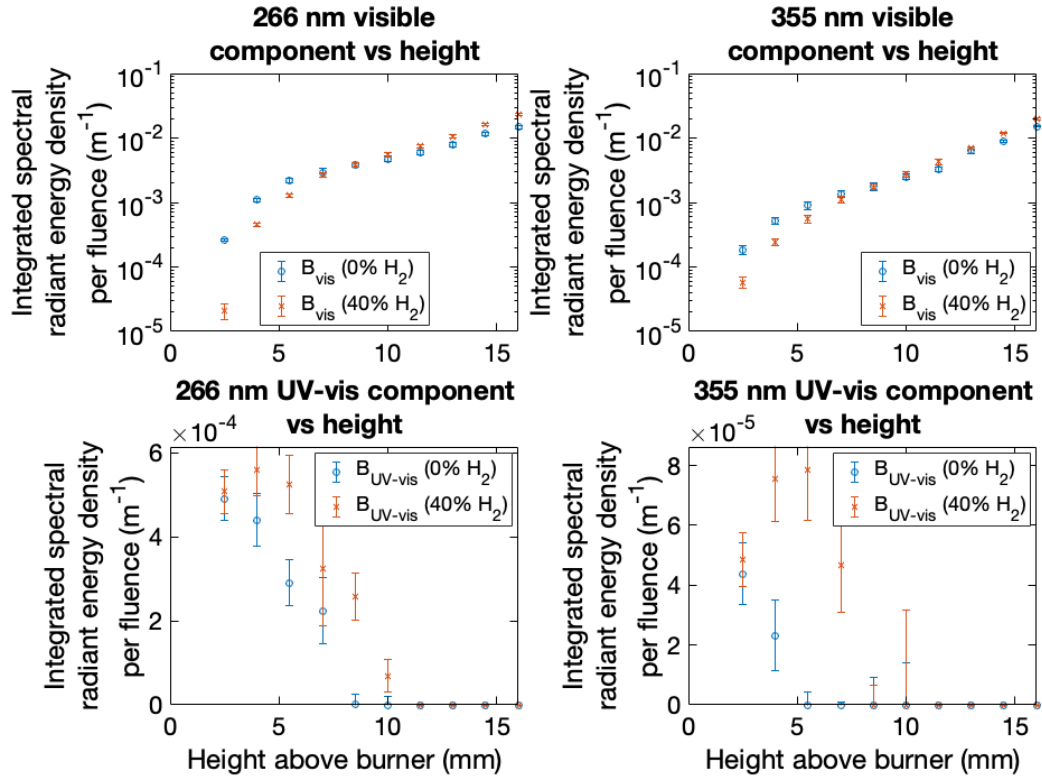


Figure 5.25: Integrated fitted-component areas obtained from the two-block decomposition of the calibrated 266 nm and 355 nm height-scan spectra for the rich flame condition ( $C/O = 0.79$ ), shown as a function of height above the burner for 0% and 40% H<sub>2</sub>. The upper row shows the visible component on a logarithmic scale, while the lower row shows the UV-visible component on a linear scale. Values are expressed as integrated spectral radiant energy density per unit fluence and represent the mean of three repetitions, with error bars showing the associated uncertainty. The decomposition was performed using building blocks constructed from the first-repetition C/O-scan reference spectra at  $C/O = 0.56$  and  $0.79$ , recorded at 16 mm HAB without H<sub>2</sub> addition.

Figure 5.26 shows the corresponding normalised visible-component comparison for the height-scan measurements. In contrast to the C/O-scan case (Figure 5.21), where the normalised visible-component areas collapsed very closely across all three excitation wavelengths, the collapse here is less complete. In particular, the 266 nm and 532 nm excitation cases remain in close agreement, whereas the 355 nm excitation case shows a slight deviation. Nevertheless, the same overall height-dependent trend is retained: for both H<sub>2</sub> conditions, the normalised visible-component area increases with height towards its maximum at 16 mm HAB.

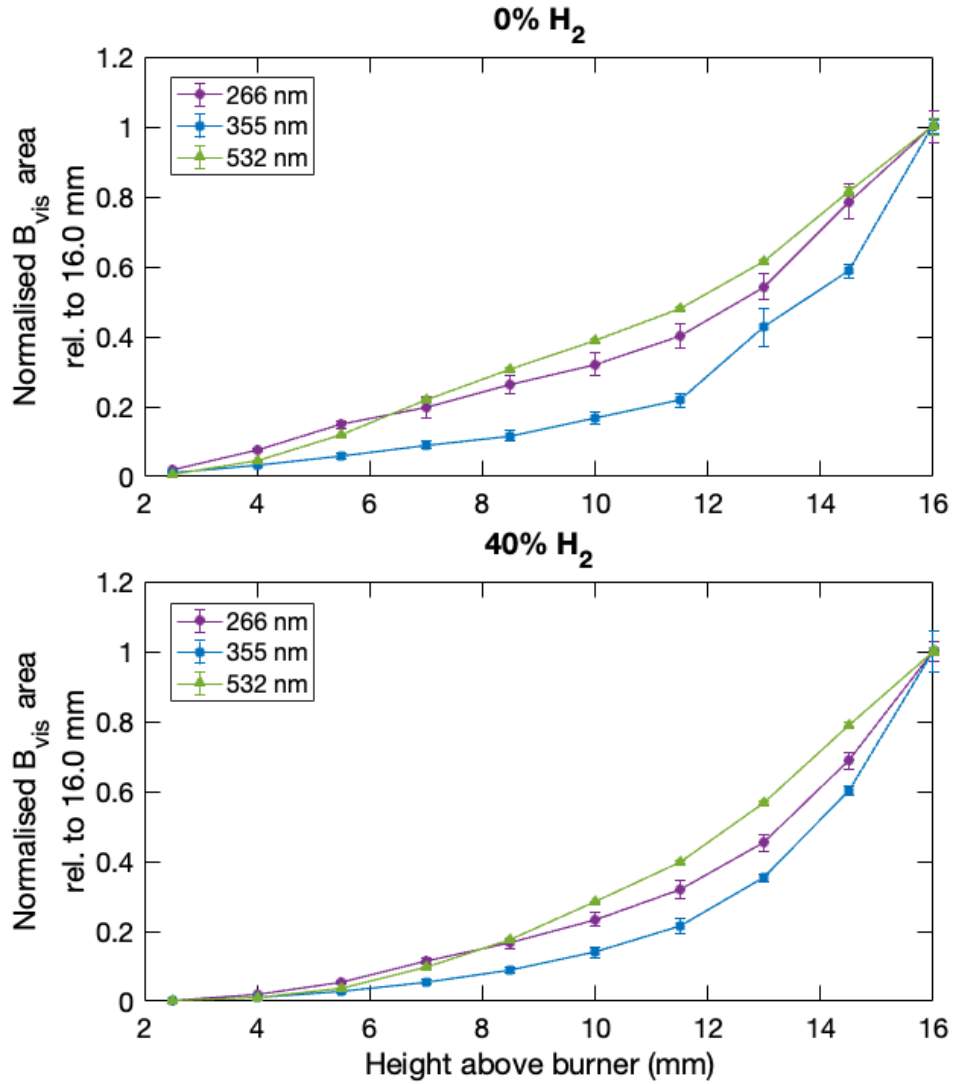


Figure 5.26: Normalised integrated visible component as a function of height above the burner for 266, 355, and 532 nm excitation, shown for 0% (top) and 40%  $H_2$  (bottom) at  $C/O = 0.79$ . In each case, the visible component is normalised to its value at the maximum height. A generally consistent trend is observed across excitation wavelengths, with close agreement between the 266 nm and 532 nm cases. The 355 nm excitation exhibits a systematic deviation from this behaviour, indicating a weaker collapse compared to the C/O-scan case. Error bars represent the standard error from three repetitions.

The two-block basis derived from the C/O-scan measurements provided good reconstructions of the 16 mm HAB spectra across the full C/O range and also reproduced the rich-flame height-scan spectra (0% and 40%  $H_2$ ) reasonably well. However, when applied to the nucleation-flame height scan, larger residual mismatches remained, par-

ticularly at the lower heights. This suggested that the two-block basis did not fully capture the spectral variability in that regime. Although not shown here, they indicated that an additional, more localised UV component may be required to represent the remaining variation in the nucleation flame height scan spectra. It is likely that the UV-visible component used in the present two-block analysis may itself contain more than one constituent with narrower spectral structure. Resolving this additional structure could improve the fitting in the nucleation-flame spectra, but this was not investigated further here.

## 5.5 Chapter conclusion

Laser-induced fluorescence (LIF) measurements were performed using 266, 355 and 532 nm excitation to examine fluorescence associated with PAHs and related structures in ethylene–air premixed flat flames, with and without  $H_2$  addition. Some of these structures may be linked to soot nucleation. The aim was to determine whether the effect of  $H_2$  addition on the fluorescence signal reflects the corresponding reduction in soot concentration, as observed in Chapter 3. Using the three excitation wavelengths, LIF measurements were therefore acquired at a fixed height of 16 mm HAB across a range of C/O ratios, from C/O=0.53 to 0.79, thereby slightly extending the range covered by LII. The LIF spectra were radiometrically calibrated to account for the wavelength-dependent response of the detection system, allowing the fluorescence trends to be compared on a quantitatively reproducible basis.

Contrary to the reduction observed in soot concentration, hydrogen addition increased the LIF signal at all C/O ratios irrespective of the excitation wavelengths. Height-scan measurements were also done in both a nucleation flame (C/O = 0.59) and a rich flame (C/O = 0.79). In the height-scan measurements, hydrogen addition increased the LIF signal at all heights in the nucleation flame (C/O=0.59), whereas the response in the rich flame (C/O=0.79) was height-dependent, with reductions in LIF signal observed only at lower HABs. Since PAH-related structures are considered to play a significant role in soot nucleation and growth, it is therefore surprising that they should be more abundant in the hydrogen-doped flames in which soot concentration is

suppressed. Across all three excitation wavelengths, the same overall conclusion was therefore reached, which showed that the measured fluorescence signal does not simply follow the changes in soot concentration observed using LII.

Principal component analysis (PCA) was therefore applied to extract further information from the data, which showed that the first two principal components account for almost all of the spectral variation in the C/O-scan dataset. This provided a basis for extracting approximate spectral components separately for each excitation wavelength. Using two limiting flame conditions ( $C/O = 0.56$  and  $0.79$ ) at each excitation wavelength, the UV-excited spectra were therefore represented using two approximate spectral building blocks: a visible component and a secondary UV-visible component. Fluorescence contributions in the visible emission region have recently been discussed in relation to PAH-related structures potentially involved in soot nucleation, such as resonance-stabilised radicals and aliphatically bridged dimers of PAHs.

The 266 nm and 355 nm spectra were reconstructed well using the two building blocks, whilst the 532 nm spectra were reconstructed using only a single visible component. A particularly notable result is that, when normalised to the highest C/O ratio ( $0.79$ ), the fitted visible-component areas followed a similar trend at all three excitation wavelengths in the C/O scan, for both 0% and 40%  $H_2$ . This suggests that the visible fluorescence contributions observed under 266, 355 and 532 nm excitation may arise either from the same underlying emitting population or from different contributions that track each other very closely. The effect of  $H_2$  addition on this visible component was also very similar across excitation wavelengths. Below the nucleation threshold, LIF signals, as a result of hydrogen addition, increased more strongly. This raises the possibility that  $H_2$  addition promotes a greater build-up of fluorescing contributions represented by the visible component under sub-nucleation conditions, where soot formation has not yet occurred.

The same building-block analysis was also applied to the rich-flame height scans. Good agreement was obtained for both 266 nm and 355 nm spectra, with small residuals over most of the measured height range. Across the height scan, when normalised to 16 mm HAB, the 266 nm and 532 nm visible components agreed more closely with each

other, whereas the 355 nm height scan exhibited a slight deviation from that trend. A consistent reduction in the fitted visible-component area was also observed at the lower heights for the 40% H<sub>2</sub> case across all three excitation wavelengths, before the H<sub>2</sub>-doped signal became larger further downstream. The two components used for the C/O scan measurements and the rich-flame height scan measurements did not reproduce the nucleation flame height-scan spectra reasonably well, especially at the lower heights, where a narrower UV component may be required.

## Chapter 6

# Conclusions and future work

### 6.1 Overview of this study

This study demonstrated that hydrogen addition substantially reduces soot volume fraction and LII decay time while increasing PAH-related fluorescence under the same flame conditions. By combining LII and multi-wavelength LIF measurements, it was therefore possible to reveal an apparent decoupling between soot formation and precursor-related fluorescence across the C/O ratio range studied.

The effects of hydrogen addition were investigated in atmospheric premixed ethylene–air flat flames across conditions ranging from soot nucleation to rich, sooting flames. At 16 mm HAB, LII measurements covered C/O ratios from 0.59 to 0.79, while LIF measurements covered the wider range from C/O = 0.53 to 0.79. Additional measurements were performed as a function of height above the burner for selected flame conditions.

By using a horizontal laser sheet to increase the collection volume, it was possible to obtain LII and LIF measurements across these broad ranges of conditions, including under nucleation conditions where the signals were particularly weak. The LII measurements quantified changes in soot volume fraction and LII decay time, the latter being used as a proxy for soot particle size. LIF measurements using 266, 355 and 532 nm excitation quantified changes in fluorescence intensity and spectral shape, with increasing excitation wavelength generally increasing the relative contribution of larger PAH structures to the measured signal.



A further distinctive feature of this work was the radiometric calibration of the LIF spectra, which is rarely performed in flame LIF studies. Such spectra are typically reported as measured detector signals without correction for the wavelength-dependent response of the detector and collection optics. By applying this correction and normalising by the incident laser fluence, the spectra were instead reported in absolute units of spectral radiant energy density per unit fluence ( $\text{m}^{-1} \text{nm}^{-1}$ ), a quantity that should be reproducible by others.

## 6.2 Main findings and overall conclusion

LII measurements, taken at 16 mm HAB, demonstrated that hydrogen addition significantly reduced soot volume fraction across all flame conditions studied. In a rich and sparingly sooting flame, the reduction was observed at all heights above the burner and became more pronounced with increasing hydrogen addition. Hydrogen addition also reduced the LII decay time, used here as a proxy for primary particle size. Across the C/O scan measurements, the extent of soot reduction was weakest at the nucleation threshold, increased sharply up to  $\text{C/O} \approx 0.62\text{--}0.63$ , and then diminished gradually at higher C/O ratios. The nucleation threshold itself shifted only marginally with 40% hydrogen addition (from  $\text{C/O} = 0.59$  to  $0.60$ ), and the near-identical fluence responses of the two nucleation flames suggest that hydrogen does not substantially alter the properties of nascent soot particles at nucleation.

In contrast, hydrogen addition increased LIF signals across all C/O ratios and excitation wavelengths. Height-scan measurements in a nucleation flame ( $\text{C/O} = 0.59$ ) showed that hydrogen increased LIF at all heights, whereas in the rich flame ( $\text{C/O} = 0.79$ ) the response was height-dependent: reductions were observed at lower heights, with an increase further downstream. Since fluorescence from these PAH-related structures has been linked with soot nucleation, it was therefore surprising that they would be more abundant in hydrogen-doped flames, despite the corresponding reduction in soot concentration, as observed with LII.

PCA showed that two principal components accounted for around 98% of spectral variation in the data. Guided by this result, two approximate spectral components

(UV-Vis and visible) were extracted and fitted to the dataset. A notable finding was that the fitted visible components closely followed consistent trends across all three excitation wavelengths, both with and without hydrogen. Depending on the excitation wavelength, fluorescence in the visible emission region has recently been associated with PAH-related structures potentially involved in soot nucleation, such as resonance-stabilised radicals and aliphatically bridged dimers of PAHs. Our results indicate that the visible fluorescence contributions at 266, 355 and 532 nm excitation may either arise from the same underlying emitting population, or from different species contributions that track each other closely.

Taken together, these results suggest that hydrogen may not suppress soot simply by depleting the PAH-related structures probed here, and the mechanism behind this decoupling remains an open question. The findings of this thesis open several directions for further investigation, which are discussed in the next section.

### 6.3 Recommendations for future work

**Extended sensitivity and excitation wavelength range.** Bidirectional signal collection could further increase LII and LIF sensitivity, enabling measurements at lower C/O ratios. For LIF, dye-laser excitation could be used to determine whether the trends observed at 266, 355 and 532 nm persist at intermediate wavelengths.

**Flame temperature measurements.** The effect of hydrogen addition on flame temperature was not quantified. Although the expected temperature changes may be small [15], OH-LIF thermometry [120] across the same C/O-ratio and height-scan conditions could establish whether temperature contributes to the observed soot reduction.

**Species-resolved measurements.** Species-resolved techniques under the same conditions would allow specific precursor populations to be identified and tracked as a function of hydrogen addition. Electron paramagnetic resonance (EPR), which is sensitive to unpaired electrons, could be used for the detection of RSRs [43]. Sampling-based mass spectrometry could similarly be used to identify aliphatically bridged dimers [41].

Applying these techniques may establish whether the increased fluorescence signal is driven by RSRs, aliphatically bridged dimers, or both.

**Computational modelling.** The apparent decoupling between the PAH-LIF and soot trends raises the possibility that hydrogen addition increases the concentration of soot-inception precursors while inhibiting their conversion into soot. Detailed kinetic modelling could therefore be used to identify the reaction pathways responsible for these opposing trends across the C/O-ratio range studied here.

**Extension to other flames and fuels.** Extending these measurements to diffusion flames and other fuels, such as methane and propane, could establish whether the observed LIF/soot decoupling is specific to premixed ethylene–air flames or is a general feature of hydrogen-enriched combustion. Hydrogen addition to the existing total mass flux, rather than substituting part of the hydrocarbon fuel, as done here, could also be examined to determine the influence of the addition strategy.

**Uncertainty in the soot absorption function,  $E(m)$ .** A constant  $E(m)$  of 0.36 was assumed, although lower values have been reported near nucleation conditions [75]. The soot volume fractions at low C/O ratios may therefore be underestimated. Determining  $E(m)$  across the C/O range using LII and modelling approaches [75,104] would improve the accuracy of these measurements.

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# Appendices

## A.1 Verification of the pixel–wavelength dispersion in the UV

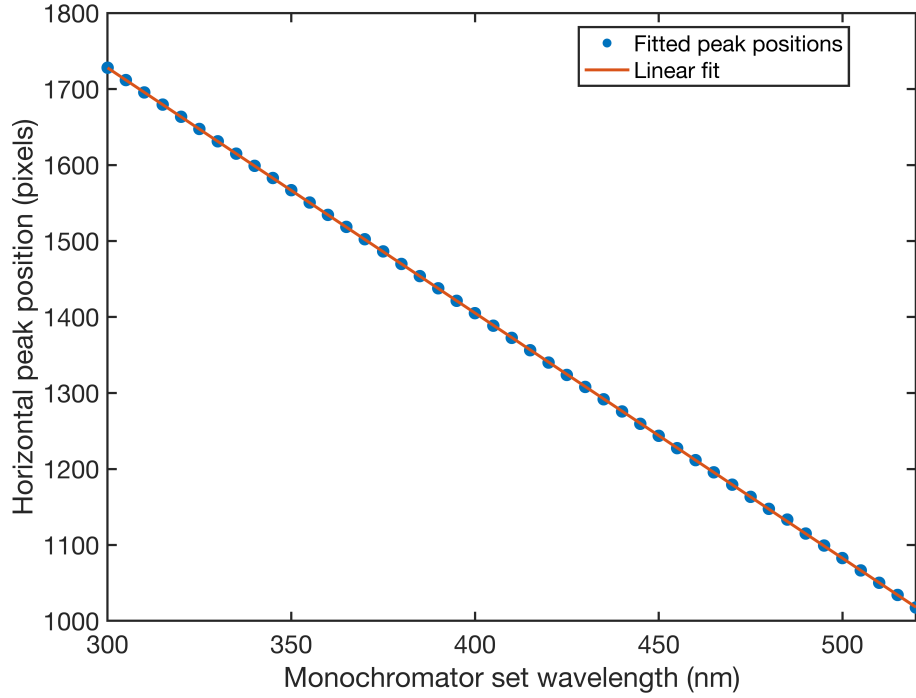


Figure A.1: Centre horizontal pixel positions obtained from Gaussian fits to the integrated monochromator line profiles over the UV calibration range. The fitted peak positions show a linear dependence on the monochromator set wavelength, confirming that the pixel–wavelength dispersion remains consistent in the UV region, with a value of approximately  $3.23 \text{ pixels nm}^{-1}$ .

## A.2 Gaussian fitting of the monochromator line profiles

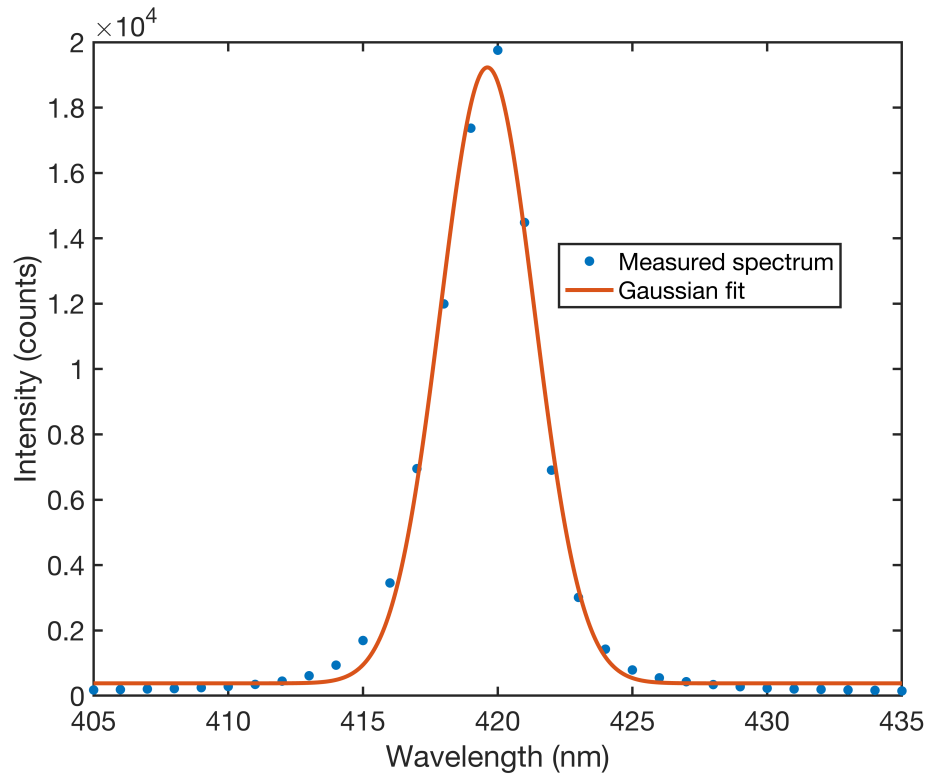


Figure A.2: Measured monochromator line profile at a wavelength setpoint of 450 nm, together with the corresponding Gaussian fit. The area under the fitted Gaussian was divided by the exposure time and the corresponding sensitivity-corrected optical power to obtain a relative spectrometer response at 450 nm, as shown in Figure 4.7(b).

### A.3 Single-component fits to the 532 nm LIF spectra across the C/O scan

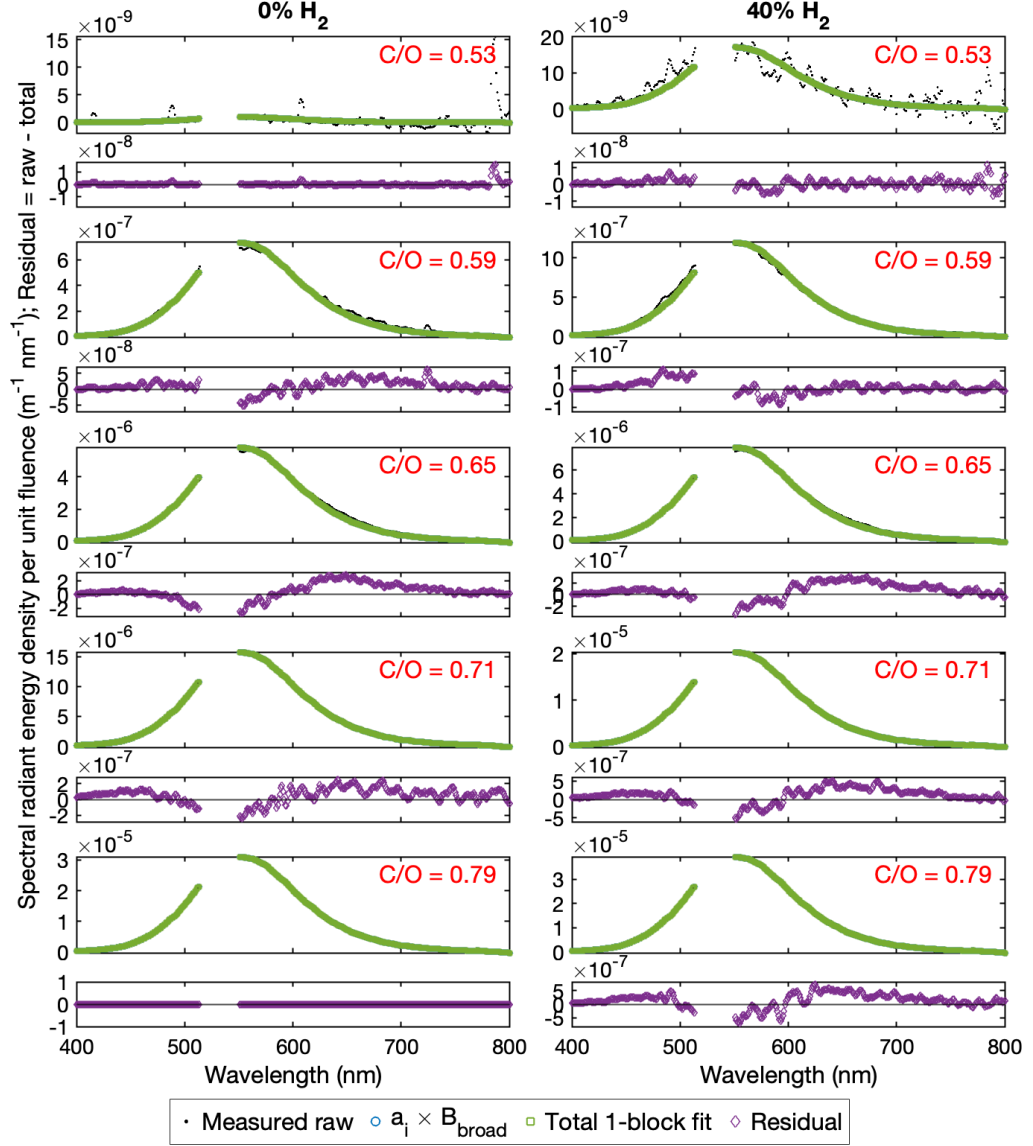


Figure A.3: Single-component fits to the 532 nm LIF spectra across the C/O scan for flames without H<sub>2</sub> (left column) and with 40% H<sub>2</sub> (right column). The fitted visible component closely follows the measured spectra over the analysed wavelength range. Residuals are shown as the difference between the measured spectrum and the single-component fit.

## Appendices