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RPPR Final Report

as of 03-Jan-2023

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Proposal Number: 74932WS

Agreement Number: W911NF-19-1-0238

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Report Date: 26-Dec-2022

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Final Report for Period Beginning 27-Mar-2019 and Ending 26-Sep-2022

Title: Simultaneous Velocity, Temperature, and Formaldehyde Imaging to Study Ignition in High-Pressure Turbulent Jets - Topic b.i.4

Begin Performance Period: 27-Mar-2019

End Performance Period: 26-Sep-2022

Report Term: 0-Other

Submitted By: David Rothamer

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STEM Degrees: 2

STEM Participants: 3

Major Goals: The primary scientific objectives for the work focused on development of the integrated simultaneous velocity, temperature, and formaldehyde species concentration diagnostic. The objectives for diagnostic development were:

1. Identify phosphor composition and APT approach to achieve target performance over 700 to 1150 K temperature range
2. Determine restrictions on seeding density and particle size needed to limit measurement biases for APT
3. Develop correction method to achieve the desired formaldehyde mole fraction accuracy on a single-shot basis
4. Design integrated simultaneous temperature, velocity, and formaldehyde PLIF diagnostics with limited measurement biases
5. Validate and demonstrate the simultaneous temperature, velocity, and formaldehyde PLIF diagnostic in an optical engine.

Most objectives (1-5) were successfully completed during the project period and will be discussed in Section 3. It should be noted that the project started in March of 2019 and that the COVID-19 pandemic that started in 2020 and shut-down lab operations for several months significantly impacted the project progress during 2020 and to some extent in 2021. A no-cost extension was taken to complete as much to the proposed work as possible, but even with extension it was not possible to complete objective 5 during the project period. The principal investigator intends to work towards implementation in the optical engine during 2023 through other funding.

Accomplishments: Please see attached PDF for details of accomplishments

Training Opportunities: A PhD student, Master's student, and undergraduate were involved with research during the reporting period and were mentored by the PI and trained by a research scientist on aerosol phosphor thermometry.

Results Dissemination: The results of this three year project have produced seven conference presentations, three conference papers, five journal articles, a PhD dissertation, and a Master's thesis. Conference papers, journal articles, and theses have been uploaded.

Presentations at conferences included presentations at US Central States Section of the Combustion Institute Spring Technical Meetings, the International Conference on Phosphor Thermometry (online), and a Gordon Research Conference (online).

RPPR Final Report
as of 03-Jan-2023

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Craig Worley

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Staff Scientist (doctoral level)

Participant: Dustin Witkowski

Person Months Worked: 2.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: PD/PI

Participant: David Anthony Rothamer

Person Months Worked: 1.00

Funding Support:

Project Contribution:

National Academy Member: N

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Publication Location:

Article Title: Combustion relevant aerosol phosphor thermometry imaging using Ce,Pr:LuAG, Ce:GdPO₄, and Ce:CSSO

Authors: Josh Herzog, Dustin Witkowski, David Rothamer

Keywords: aerosol phosphor thermometry (APT), thermographic phosphors, temperature measurement, particle-image velocimetry

Abstract: In this work, three phosphor compositions are investigated for application at flame relevant temperatures: Ce,Pr:LuAG, Ce:GdPO₄, and Ce:CSSO. The phosphors are characterized in a temperature-controlled furnace, and measurements of gas temperature were performed in a seeded jet after mixing with the products of an atmospheric methane-air flame. Furnace and flame measurements demonstrate that two of the phosphor compositions are capable of temperature imaging over 1000 K, with an upper temperature limit of at least 1400 K. Temperature precision estimates indicate 20-K or better single-shot precision from 500 to 1300 K for a seeding density corresponding to an added heat capacity of less than 1% of air at 1200 K, and a spatial resolution of 1.12 lp/mm. This work represents the highest reported temperature measurements made using any APT technique or composition for gas temperature measurements, and represents the highest measured quenching temperature of any phosphor exhibiting fast emiss

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Article Title: Characterization of the Ce,Pr:LuAG Phosphor for Co-doped Aerosol Phosphor Thermometry

Authors: Joshua M. Herzog, Dustin Witkowski, David A. Rothamer

Keywords: Aerosol phosphor thermometry, Thermographic phosphors, excited-state absorption, co-doped phosphor

Abstract: The Ce,Pr:LuAG phosphor is investigated for use in co-doped aerosol phosphor thermometry (APT). The phosphor was characterized by measuring the emission intensity for each ion as a function of excitation laser fluence and temperature. A simplified three-level model was used to interpret and fit the data. The phosphor was then used for co-doped APT temperature-imaging experiments performed in a heated air jet up to a maximum temperature of 694 K. The three-level model fit was used to analyze sources of bias in the imaging measurements. Both ions' emission intensities show a nonlinear dependence on excitation fluence that can potentially be explained by temperature-dependent ground- and excited-state absorption processes included in the three-level model. Single-shot temperature precision from the temperature-imaging experiments was measured to be 22, 23, and 32 K for mean temperatures of 497, 603, and 694 K, respectively, at a spatial resolution of ~1.12 lp/mm and average fluence

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Article Title: Combustion-relevant temperature imaging with scattering referenced aerosol phosphor thermometry applied to Eu:BAM

Authors: Dustin Witkowski, Joshua M. Herzog, David A. Rothamer

Keywords: Aerosol phosphor thermometry, Thermographic phosphors, Thermal quenching

Abstract: This work demonstrates precise aerosol phosphor thermometry (APT) measurements over a large temperature range by applying scattering-referenced APT (SRAPT) with the phosphor divalent Europium doped in Barium Magnesium Aluminate (Eu:BAM). Measurements were taken using Eu:BAM seeded into an air jet mixing with the products of a concentric methane-air flat flame. In-situ calibration of the SRAPT ratio versus temperature was performed from 500 to 1400 K. Peak temperature sensitivities of 1–1.5 %/K were observed, approximately 4 times higher than the spectral luminescence intensity ratio method typically used for Eu:BAM. Despite its moderate quenching temperature (700 K), the high initial signal intensities before the onset of thermal quenching for Eu:BAM allowed reliable single-shot measurements to be made continuously from 500 K to greater than 1200 K. These results highlight the importance of high signal levels for extending the measurement range of SRAPT.

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Article Title: Characterization of Ce:CSSO, Pr:CSSO, and co-doped Ce,Pr:CSSO phosphors for aerosol phosphor thermometry

Authors: Joshua M Herzog, Dustin Witkowski, David A Rothamer

Keywords: thermometry, phosphor, co-doped, CSSO, thermal quenching

Abstract: This work demonstrates precise aerosol phosphor thermometry (APT) measurements over a large temperature range by applying scattering-referenced APT (SRAPT) with the phosphor divalent Europium doped in Barium Magnesium Aluminate (Eu:BAM). Measurements were taken using Eu:BAM seeded into an air jet mixing with the products of a concentric methane-air flat flame. In-situ calibration of the SRAPT ratio versus temperature was performed from 500 to 1400 K. Peak temperature sensitivities of 1–1.5 %/K were observed, approximately 4 times higher than the spectral luminescence intensity ratio method typically used for Eu:BAM. Despite its moderate quenching temperature (700 K), the high initial signal intensities before the onset of thermal quenching for Eu:BAM allowed reliable single-shot measurements to be made continuously from 500 K to greater than 1200 K. These results highlight the importance of high signal levels for extending the measurement range of SRAPT.

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Article Title: Combined scattering-referenced and co-doped aerosol phosphor thermometry using the Ce,Pr:LuAG phosphor

Authors: Joshua M. Herzog, Dustin Witkowski, David A. Rothamer

Keywords: SRAPT, aerosol phosphor thermometry, Ce,Pr:LuAG

Abstract: This work demonstrates precise aerosol phosphor thermometry (APT) measurements over a large temperature range by applying scattering-referenced APT (SRAPT) with the phosphor divalent Europium doped in Barium Magnesium Aluminate (Eu:BAM). Measurements were taken using Eu:BAM seeded into an air jet mixing with the products of a concentric methane-air flat flame. In-situ calibration of the SRAPT ratio versus temperature was performed from 500 to 1400 K. Peak temperature sensitivities of 1–1.5 %/K were observed, approximately 4 times higher than the spectral luminescence intensity ratio method typically used for Eu:BAM. Despite its moderate quenching temperature (700 K), the high initial signal intensities before the onset of thermal quenching for Eu:BAM allowed reliable single-shot measurements to be made continuously from 500 K to greater than 1200 K. These results highlight the importance of high signal levels for extending the measurement range of SRAPT.

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Authors: Craig Worley, Dustin Witkowski, David Rothamer

Acknowledged Federal Support: Y

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Paper Title: Combustion-Relevant Temperature Imaging with Scattering Referenced Aerosol Phosphor Thermometry Applied to Eu:BAM

Authors: Dustin Witkowski, Joshua Herzog, David Rothamer

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Conference Name: Spring Technical Meeting Central States Section of The Combustion Institute

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Date Published: 17-May-2020

Conference Location: Huntsville, Alabama

Paper Title: Characterization of the Ce,Pr:CSSO phosphor for low-temperature ignition imaging in engines

Authors: Joshua Herzog, Dustin Witkowski, and David A. Rothamer

Acknowledged Federal Support: Y

RPPR Final Report
as of 03-Jan-2023

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Publication Type: Thesis or Dissertation

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Title: Quantitative Temperature & Formaldehyde Concentration Imaging for High-Pressure Turbulent Fuel Jet Ignition

Authors: Joshua M. Herzog

Acknowledged Federal Support: **Y**

Partners

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I certify that the information in the report is complete and accurate:

Signature: David Rothamer

Signature Date: 12/18/22 1:42PM

Simultaneous Velocity, Temperature, and Formaldehyde Imaging Applied to High-Pressure Turbulent Jet Ignition

Final Report Submitted to:

US Army Research Office under contract number W911NF-19-1-0238

Period of Performance: March 27, 2019 to September 26, 2022.

Project PI: David Rothamer

Institution: University of Wisconsin-Madison

1 Abstract

Ignition of high-pressure turbulent fuel jets is an area of significant research interest due to the complex coupling of turbulent transport and chemistry and its relevance to practical devices. Recent numerical simulations have led to a conceptual model for high-pressure jet ignition at diesel-engine-relevant conditions. Unfortunately, experimental measurements that can validate the proposed model are lacking. Validation and development of deeper understanding of the ignition mechanism requires simultaneous measurements of velocity, temperature, and chemical species fields. Recent work has shown the promise of aerosol phosphor thermometry (APT) to make high-precision temperature measurements at temperatures relevant for high-pressure jet ignition. Measurements of temperature using APT are readily coupled with particle image velocimetry (PIV) using the seeded particles to simultaneously measure the velocity and temperature fields. The objectives for this project focused on development of APT for measurements at conditions relevant to measurements of turbulent jet ignition in compression-ignition engines and integration of APT with particle image velocimetry and formaldehyde planar laser-induced fluorescence. The end goal of the work was focused on validation and application in an optical engine.

The first and most challenging step towards developing the desired simultaneous temperature, velocity, and species concentration measurement technique was focused on identifying suitable thermographic phosphors and APT approaches to enable temperature measurements in the appropriate temperature (700 – 1150 K) and pressure range (10 to 100 bar). Two different APT techniques were investigated: co-doped APT and scattering-referenced APT (SRAPT) (both techniques were conceptualized and demonstrated as part of an earlier grant, W911NF-18-1-0147, details are provided in previous publications [1, 2]). Three initial candidate phosphors were selected based on an analysis of their electronic structure to predict the onset of thermal quenching in the correct temperature range needed for temperature determination [3]: Ce,Pr:LuAG, Ce:GdPO₄, and Ce:CSSO. To evaluate each phosphor's performance, APT measurements were performed in an air jet heated by the products of a premixed methane flame. All three phosphor were capable of measurements at temperatures >1000 K. In particular, Ce:CSSO demonstrated reliable measurements above 1400 K with the SRAPT technique, representing a >400 K increase in maximum temperature range relative to previous APT capabilities. The results were presented at the 2020 International Combustion Symposium and were published in the biennial Proceedings of the Combustion Institute journal [4].

Based on the results of the premixed flame measurements, it was hypothesized that improving the room temperature laser-induced signal of the phosphor would enable measurements over a wide range of temperatures and that high temperature measurements would still be possible even with lower quenching temperature phosphors. To test this, measurements were performed using the strongly emitting Eu:BAM phosphor with the SRAPT technique. Eu:BAM was measured to have more than an order of magnitude higher per particle signal levels compared to the previous phosphors tested for SRAPT. As a result, even though the onset of temperature quenching began roughly 500 K earlier than Ce:CSSO (700 vs. 1200 K), Eu:BAM SRAPT single-shot measurements were demonstrate up to 1400 K, providing an additional option for the target measurements in this project. These results were published in Combustion and Flame in 2021 [5].

The next part of the project was spent designing the experiment to ensure the APT diagnostic was able to resolve the expected low-temperature ignition phenomena accurately and precisely. Chemical kinetic and turbulent jet models were developed and used to specify temperature

precision and spatial resolution requirements for the diagnostic of 25 K and 600 μm (300 μm object pixel based on the Nyquist limit), respectively. Maximum allowable phosphor particle size and seeding densities were then determined based on models developed during the project to ensure the particle-based diagnostic could sufficiently track the gas temperature (i.e., the particle temperature is the same as the gas temperature) and that biases from multiple-scattered light in high seeding density environments were minimal.

A correction was developed to achieve the desired formaldehyde PLIF mole fraction accuracy. The method utilizes measurements from two cameras using a tunable multi-band filter to enable correction for broadband background signals. The approach relies upon knowing the temperature dependent ratio of formaldehyde emission from the two bands (in the absence of background signal) and knowing the temperature from APT measurements. The emission ratio was experimentally measured as a function of temperature, and simulations were also used to predict its temperature dependence. The minimum detectable formaldehyde mole fraction was estimated to be between 100 to 200 ppm on a single-shot basis for typical pressures in the temperature range of interest. The influence of oxygen concentration variation on diagnostic accuracy was also considered and it was estimated that this may cause up to a 50% error in formaldehyde mole fraction determination.

With the criteria for the diagnostic determined and the formaldehyde PLIF measurement approach developed, phosphor data collected from the first part of the project, along with previous data for the Ce:LuAG phosphor [1], were used to quantitatively assess the capability of each phosphor to perform the desired temperature measurements and to design an integrated temperature, velocity, formaldehyde diagnostic approach. The results of the analysis selected two promising phosphors, both of which would employ the SRAPT technique with 355-nm excitation. Ce:LuAG was found to be capable of ~ 20 K precision from 720 – 1000 K, with performance decreasing above 1000 K. Eu:BAM was found to be capable of better than 40 K precision from 750-1100 K, with better than 20 K precision from 800 – 1000 K. The Ce:LuAG phosphor was selected as being most appropriate to integrate with the velocity and formaldehyde PLIF measurements and an integrated diagnostic setup was designed including information on the cameras, filters, and collections optics to be used.

Recent work focused on developing methods to ensure accurate and unbiased temperature calibrations for the APT diagnostic prior to implementation in the optical engine. Traditional APT calibrations have been performed in heated jets using thermocouples. At temperatures near and above 1000 K, difficulties maintaining steady and uniform temperature environments and providing sufficient seeding densities for sufficient signal-to-noise ratios makes calibrations in heated jets challenging. To address this, a technique was developed to perform measurements with phosphor loadings similar to APT experiments in a tube furnace, providing a well-controlled and uniform temperature environment. Additionally, a new heated jet experimental setup was designed and built that is able to maintain center temperatures above 1100 K, approximately 200 K higher than previously achieved in our lab. Measurements in both platforms have been performed for Eu:BAM and Ce:LuAG. Due to time constraints for the project the integrated diagnostic was not able to be demonstrated in the engine.

The results of this three year project have produced seven conference presentations, three conference papers [6-8], five journal articles [4, 5, 9-11], a PhD dissertation [12], and a Master's thesis.

2 Objectives

The primary scientific objectives for the work focused on development of the integrated simultaneous velocity, temperature, and formaldehyde species concentration diagnostic. The objectives for diagnostic development were:

1. Identify phosphor composition and APT approach to achieve target performance over 700 to 1150 K temperature range
2. Determine restrictions on seeding density and particle size needed to limit measurement biases for APT
3. Develop correction method to achieve the desired formaldehyde mole fraction accuracy on a single-shot basis
4. Design integrated simultaneous temperature, velocity, and formaldehyde PLIF diagnostics with limited measurement biases
5. Validate and demonstrate the simultaneous temperature, velocity, and formaldehyde PLIF diagnostic in an optical engine.

Most objectives (1-5) were successfully completed during the project period and will be discussed in Section 3. It should be noted that the project started in March of 2019 and that the COVID-19 pandemic that started in 2020 and shut-down lab operations for several months significantly impacted the project progress during 2020 and to some extent in 2021. A no-cost extension was taken to complete as much to the proposed work as possible, but even with extension it was not possible to complete objective 5 during the project period. The principal investigator intends to work towards implementation in the optical engine during 2023 through other funding.

3 Findings

The ignition of high-pressure turbulent fuel jets is an area of significant research interest due to the complex coupling of turbulent transport and chemistry and its relevance to practical devices. Recent simulation work by Dahms et al. [13], Krisman et al. [14], and others, has led to a hypothesized mechanism for high-pressure jet ignition at compression-ignition relevant conditions. The mechanism starts with a cool flame propagation, initiated in the leaner jet periphery, followed by high-temperature ignition in richer regions, and turbulent high-temperature flame propagation through the head of the jet. Based on the proposed mechanism, ignition at these conditions appears to be a complex event involving multiple stages and multiple combustion modes [15]. Unfortunately, experimental measurements that can validate the proposed mechanism are lacking. Validation and development of deeper understanding of the ignition mechanism requires simultaneous measurements of velocity, temperature, and chemical species fields at Diesel-engine-relevant conditions. Recent previous work funded by the ARO through a previous short-term innovative research (STIR) grant (W911NF-18-1-014) has shown the promise of aerosol phosphor thermometry (APT) to make high-precision temperature measurements at temperatures relevant for jet ignition.

APT utilizes temperature-dependent emission properties of thermographic phosphors, which are often composed of rare-earth ions doped into crystalline host structures and ground or formed into particles (~ 0.1 to $10\text{ }\mu\text{m}$ in diameter). In practice, they are seeded into the flow under investigation and, following excitation by a laser, emit temperature-dependent emission that is usually insensitive to pressure and chemical environment. In the current work fast $4f^{N-1}5d \rightarrow 4f^N$ rare-

earth ion emission is used that enables freezing of flow motion for even relatively high-speed flows. The benefits of the APT approach utilized in this work, compared to other diagnostics, are readily apparent; upon seeding appropriate levels of phosphor particles into the flow of interest, minimally intrusive simultaneous planar measurements of velocity and temperature fields in high-speed flows are achievable [16, 17].

During the previous ARO-funded STIR, two new APT approaches were developed that utilize the temperature sensitivity of the phosphor signal intensity to perform measurements at higher temperatures than previously possible. The first technique, termed co-doped APT, dopes two rare-earth ions into a host material, and the ratio of luminescence emission from each ion ($R_{codoped} = S_{lum,2}/S_{lum,1}$) is measured and calibrated versus temperature. The second technique, scattering-referenced aerosol phosphor thermometry (SRAPT), uses the ratio of a temperature-insensitive reference signal from elastic laser scattering and the temperature-dependent luminescence intensity ($R_{SRAPT} = S_{Mie}/S_{lum}$) from phosphor particles to determine temperature. Using these novel approaches, the goal of this project was to develop an APT technique that can be combined with formaldehyde PLIF to enable the study of high-pressure turbulent jet ignition in internal combustion applications. Here, key findings and accomplishments from this project are highlighted, organized based on the objectives for the work, followed by conclusions from the work.

3.1 Identify phosphor compositions and APT approach to achieve target performance over 700 to 1150 K temperature range

3.1.1 Selection of phosphors based on electronic structure

Two APT techniques, co-doped APT and SRAPT, were investigated as potential approaches to achieve the proposed temperature measurements for this work. Co-doped APT was found to offer high precision measurements for temperatures ranging from 300 to ~800 K [2, 10, 11], whereas SRAPT could be applied successfully at higher temperatures ($T > 700$ K) when using appropriate phosphors. The goal of the project was to enable measurements from 700 – 1150 K, so SRAPT was determined to be the best approach to achieve the stated goals.

As mentioned earlier, SRAPT measurements are performed by taking the ratio of temperature-insensitive Mie scattering signal (S_{Mie}) to temperature-dependent luminescence signal (S_{lum}) emitted from phosphor particles. In this work, two ions were selected for investigation for SRAPT thermometry: Ce^{3+} and Eu^{2+} . Both ions are characterized by intense $4f^{N-1}5d \leftrightarrow 4f^N$ emission and absorption bands that can be accessed with commonly available harmonics of Nd:YAG lasers. The temperature-dependence of their luminescence signal magnitude comes from thermal quenching due to ionization to the host conduction band [18], and can be approximated by [18]

$$S_{lum} = \frac{S_i}{1 + C_{NR} \exp\left(-\frac{E_{dc}}{k_b T}\right)}, \quad (1)$$

where S_i is the signal intensity prior to thermal quenching, C_{NR} is a temperature-independent ratio of the electronic nonradiative and radiative transition probabilities, and E_{dc} is the energy gap between the lowest 5d level and the bottom of the host conduction band. Assuming, negligible temperature-dependence in S_i , the SRAPT ratio can be written as

$$R = \frac{S_{Mie}}{S_{lum}} = \frac{S_{Mie}}{S_i} \left(1 + C_{NR} \exp \left(-\frac{E_{dc}}{k_b T} \right) \right) \quad (2)$$

where the ratio of S_{Mie}/S_i per particle can be assumed to be a constant for the current approximations. Assuming a constant absorption cross section, as thermal quenching becomes important the SRAPT ratio increases with increasing temperature and can be used to perform temperature measurements.

Referring to equation (2), the temperature where the ration begins to increase is intimately related to the value of E_{dc} . The left side of Figure 1 displays a host-referred binding energy (HRBE) diagram for Ce^{3+} doped into different oxide hosts. The HRBE allows us to locate the position of the $Ce^{3+} 4f^1$ and $5d^1$ levels with respect to the band gap of the host material. Most importantly for SRAPT, we can use these diagrams to estimate the value of E_{dc} for each phosphor (energy between the blue line and bottom of host conduction band). The right side of Figure 1 shows the experimentally determined T_{50} quenching temperature (loosely defined as the temperature when its signal level has dropped by 50 percent) [18] as a function of E_{dc} for each phosphor shown in the HRBE. There is clearly a roughly linear relationship, showing that knowledge of a given phosphor's electronic structure allows us to predict the approximate threshold temperature above which SRAPT measurements will likely be possible.

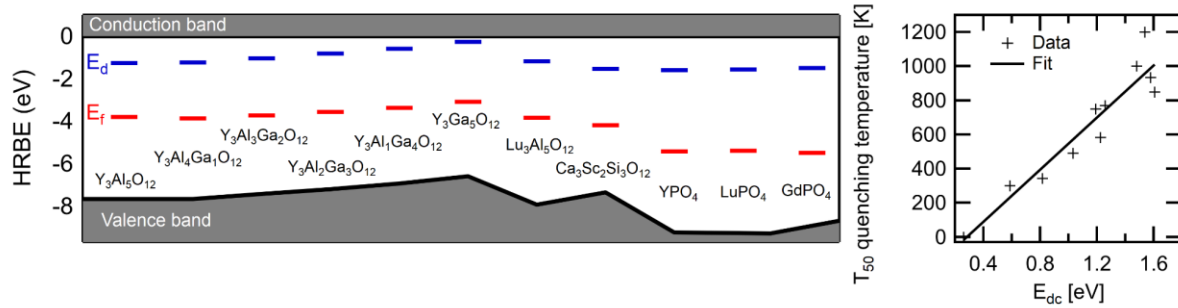


Figure 1: (Left) Host-referred binding energy diagram for different oxide hosts doped with Ce^{3+} . (Right) Experimental quenching temperature plotted vs. energy gap between lowest $5d$ level of Ce^{3+} (blue lines) and bottom of conduction band for each host.

Based on the results of the HRBE diagrams shown in Figure 1, three host materials doped with Ce^{3+} were selected as promising candidates for this work due to their large E_{dc} values: $Lu_3Al_5O_{12}$ (LuAG), $GdPO_4$, and $Ca_3Sc_2Si_3O_{12}$ (CSSO). Figure 2 displays recent measurements with these phosphors taken in a seeded jet surrounded by a concentric methane-air flat flame. Referring to the right figure, each one of these phosphors was able to measure above 1000 K using the SRAPT technique. In addition, the order of the maximum temperature for each respective phosphor (LuAG < $GdPO_4$ < CSSO) follows the same trend as their estimated E_{dc} . Finally, CSSO was able to measure as high as 1400 K, which is over a 400 K increase in the maximum temperature measured when compared to previous APT measurement. These results were published in 2020 in the Proceedings of the Combustion Institute [4].

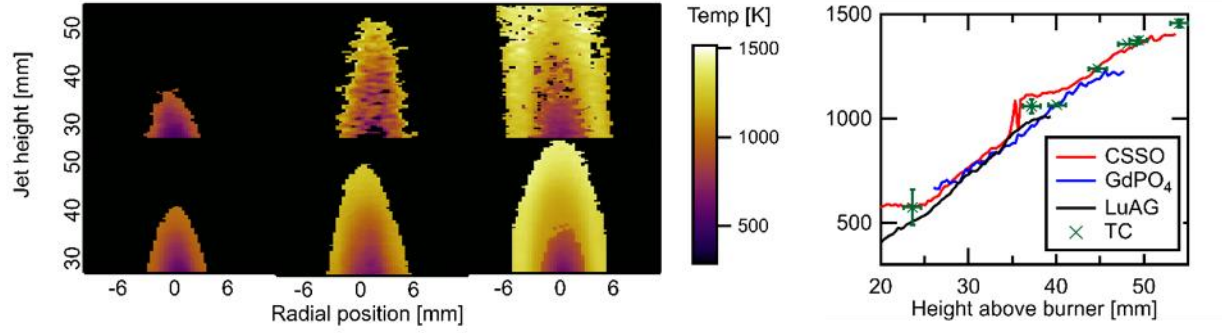


Figure 2: (Left) Single-shot (top) and average (bottom) temperature images from left to right using: Ce,Pr:LuAG, Ce:GdPO4 and Ce:CSSO. (Right) Measured average temperature profile for each phosphor along the center of the jet.

3.1.2 Selection of phosphors based on signal intensities

The results in the last section clearly demonstrate how the phosphor's electronic structure can be used to select promising phosphors for high temperature APT measurements with the SRAPT technique. Also of significant importance is the phosphor signal intensity at room temperature. To understand performance quantitatively, the temperature precision index for the technique (s_T) can be defined as a function of the fractional ratio precision index (s_R/R) and the fractional temperature sensitivity (ξ_T), i.e.,

$$s_T = \frac{\partial T}{\partial R} s_R = \frac{(s_R/R)}{\xi_T} \quad (3)$$

where

$$\xi_T = \frac{1}{R} \left(\frac{\partial R}{\partial T} \right). \quad (4)$$

To extend the temperature range of the SRAPT technique hundreds of degrees K, measurements must be able to be made over a large ratio range. We are interested in making measurements at high temperatures where $R \gg 1$. Using this criterion, and assuming the ratio precision is dominated by shot-noise, equation (3) can be re-written using equations (1) and (2) as

$$s_T \propto \frac{T^2}{E_{dc}} \frac{\exp\left(-\frac{E_{dc}}{2k_b T}\right)}{\sqrt{S_i}} \quad (R \gg 1). \quad (5)$$

Equation (5) highlights the two characteristics that can be used to optimize phosphor selection for high temperature SRAPT measurements: large nonradiative energy gaps (E_{dc}) and large initial signal levels (i.e., large absorption cross section and high quantum yield).

To investigate and demonstrate the improvements possible when employing a high luminescence intensity phosphor, the Eu^{2+} ion doped in Barium Magnesium Aluminate (Eu:BAM) was selected as the phosphor for testing. Eu:BAM has been a widely used for APT due to its high room temperature signal levels and efficient excitation with both 266 and 355 nm sources [19]. Figure 3 compares its' signal level versus temperature to the Ce^{3+} emission for the Ce,Pr:LuAG phosphor [10] with a Ce^{3+} doping of 0.5%. Figure 4 displays recent temperature measurements using Eu:BAM SRAPT in the same jet as discussed in Section 3.1.1 [6]. Eu:BAM at room temperature

has approximately 2 orders of magnitude higher signal, and still has per particle signal intensities higher than Ce,Pr:LuAG's room temperature value above 1000 K. Therefore, despite the fact that both of these phosphors quench at similar temperatures (as a result of their similar E_{dc}), measurements with Eu:BAM were able to reach as high as 1400 K, whereas Ce,Pr:LuAG was limited to approximately 1000 K when using Ce^{3+} emission. It should be noted that for these measurements the Ce^{3+} doping concentration in LuAG was not optimized and that 266 nm excitation was used which is not as efficient as 355 nm excitation for Ce^{3+} in LuAG. It is remarkable that Eu:BAM and Ce:CSSO were able to reach approximately the same temperatures despite the fact that Eu:BAM quenches approximately 450 K earlier (T_{50} of 750 K for Eu:BAM vs. 1200 K for Ce:CSSO). These results confirm Eu:BAM's potential for this work and point to the significant improvements that are still possible for the SRAPT technique if signal intensity can be increased for high quenching temperature phosphors such as Ce:CSSO.

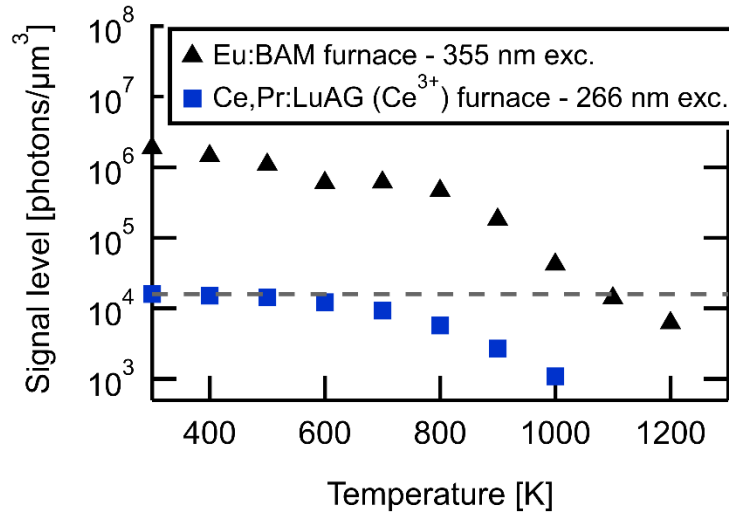


Figure 3: Comparison of signal level versus temperature for Ce,Pr:LuAG and Eu:BAM (Ce^{3+} used 266-nm excitation and Eu:BAM used 355-nm excitation).

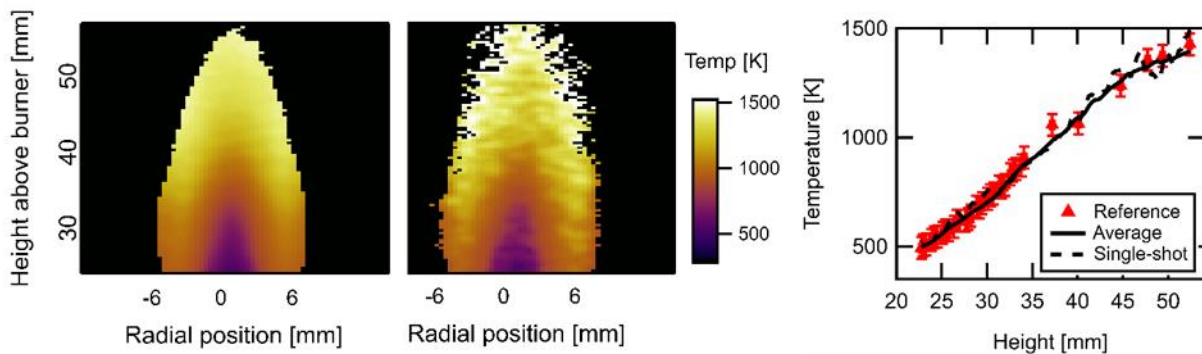


Figure 4: (Left) Average and (Middle) single-shot temperature fields for Eu:BAM. (Right) Measured temperature profile along the center of the jet.

3.1.3 Phosphors and APT approach selected for further study

Based on the findings from work focused on determination of phosphor compositions, three phosphors were selected for further study: Ce:LuAG, Ce:CSSO, and Eu:BAM. All three phosphors showed potential to be capable of single-shot measurements of temperature over most of the target temperature range from 700-1150 K when using the SRAPT approach. To determine which phosphor is most appropriate for the desired in-cylinder high-pressure turbulent jet measurements, additional factors need to be considered related to minimization of measurement biases and integration of phosphor temperature measurements with formaldehyde PLIF concentration measurements.

3.2 Determine restrictions on seeding density and particle size needed to limit measurement biases

Having identified several promising phosphors, the APT diagnostic was designed using several criteria to ensure that precise and accurate measurements would be achievable in the temperature range of interest. First, diagnostic requirements in terms of measurement precision and imaging resolution were determined from chemical kinetic and turbulent jet theory models. These requirements are needed to determine restrictions on seeding density, laser fluence, and particle size.

3.2.1 Experimental requirements to reliably identify low-temperature ignition phenomena

To successfully characterize the low-temperature ignition process, at a minimum, we must be able to determine the time and location when this occurs. Since high-pressure turbulent fuel jet ignition is believed to begin on the hot (low equivalence ratio) radial periphery, the chemistry at the initial point of low-temperature ignition was approximated using a homogeneous reactor. A series of zero-dimensional chemical kinetic calculations, using n-heptane as the model fuel with the LLNL combustion mechanism [20], were run at varied operating conditions representative of typical compression ignition operation to find the minimum expected temperature change during low-temperature ignition. The simulation results indicated that temperature increases on the order of 50 – 200 K could be expected during the low-temperature ignition process. To reliably identify this event with >95% confidence, the diagnostic must be able to achieve a single-shot temperature standard deviation (referred to as the temperature precision) of 25 K or less. Thus, a temperature precision requirement of 25 K was selected to ensure that low-temperature ignition could be observed, even for relatively small low-temperature heat release events.

Imaging resolution requirements were determined using turbulent jet theory. It has been shown previously that a diesel jet behaves similarly to a turbulent gas jet in the far field ($x/D > 30$) and, therefore, can be described using well known turbulent jet theory [21]. Pope [21] indicates that motion at the integral turbulent length scales is responsible for the bulk of transport processes in turbulent flows. Therefore, a suitable aim for this work is to have sufficient spatial resolution to measure the smallest integral length scale. From turbulent jet theory, this corresponds to the lateral scale L_{22} [21], which has a length of approximately

$$L_{22} \approx 0.3 r_{1/2} , \tag{6}$$

where $r_{1/2}$ is the radial coordinate of the jet at which the mean velocity is reduced to 50% of its peak value. A well-known characteristic of turbulent jets is that they disperse radially with constant

spreading rate [21], such that $r_{1/2}$ varies linearly with distance from the injector location (z). If we choose the imaging location to be the lift-off length (H), then the lateral scale can be re-written as

$$L_{22} \approx 0.3H\partial r_{1/2}/\partial z, \quad (7)$$

where $\partial r_{1/2}/\partial z$ is the rate of increase in $r_{1/2}$ with respect to axial position and is a constant value (i.e., constant spreading) of approximately 0.1 [21]. Lift-off length was estimated using the correlation developed by Siebers et al. [22-24]

$$H = CT^{-3.74}\rho^{-0.85}d_j^{0.34}u_jZ_{st}^{-1}, \quad (8)$$

where T is the ambient air temperature [K], ρ is the ambient air density [kg/m^3], d_j is the jet orifice diameter [μm], u_j is the jet exit velocity [m/s], and Z_{st} [-] is the stoichiometric fuel mass fraction. With these units, Pickett et al. reported the value of the proportionality constant as $C = 7.04 \times 10^8$ based on experiments using several different fuel compositions including n-heptane and #2 diesel [22].

Figure 5 displays the calculated lift-off length and corresponding lateral integral scale as a function of intake temperature and pressure for typical diesel operating conditions (details specified in caption of Fig. 5). While in the most extreme cases (i.e., highest pressures and temperatures), resolution below 0.1 mm may be required, an object-plane pixel size of 0.3 mm was specified similar in size to the expected laser sheet thickness. The actual spatial resolution for the measurements is typically on the order of two pixels resulting in a spatial resolution on the order of 0.6 mm. This should be sufficient to resolve most features at modest conditions and represents a reasonable tradeoff between imaging resolution and measurement precision.

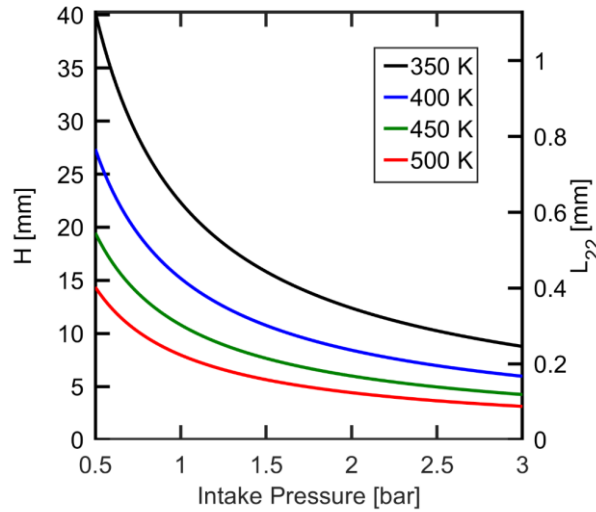


Figure 5: Calculated lift-off lengths (left axis) and smallest integral length scale (L_{22} ; right axis) for a diesel jet during engine experiments as a function of intake pressure. The stoichiometric mass fraction (Z_{st}) is 0.062 for n-heptane. Injector orifice diameter of 140 μm , and jet orifice velocity of 320 m/s (based on a 350-bar injection pressure with n-heptane) is assumed in calculations.

3.2.2 APT particle size and seeding density limitations

Based on the chemical kinetic and turbulence models discussed in the previous section, temperature precision of 25 K and an object-plane pixel size of 0.3 mm is required to successfully

measure the low-temperature ignition process. Using these specifications, restrictions were placed on phosphor particle size and seeding density by considering the particles' transient response, as well as measurement biases, primarily due to multiple scattering of laser light. In the absence of biases, the performance of the SRAPT technique is optimized by maximizing both particle size and seeding density. As a result, this section discusses the process of determining the maximum allowable values for these properties to optimize performance and maintain minimal biases in temperature measurements.

To quantitatively apply particle-based diagnostics, the particle velocity and temperature need to be representative of the local flow conditions. However, since particles have mass, they must undergo acceleration and heat transfer before they equilibrate. As such, the maximum allowable particle size was determined such that the thermal and velocity equilibration times were short enough to satisfy the resolution requirement. To meet this constraint, we require that the particles equilibrate with the flow from both a thermal and momentum perspective sufficiently for equilibration to occur over a distance equal to half of the diagnostic resolution. Assuming again that imaging takes place at the lift-off length, for a 0.3 mm pixel, a minimum lift-off length of 1 cm, and a jet exit diameter and velocity of 140 μm and 320 m/s, respectively, turbulent jet theory [21] requires the time response of the particles to be on the order of 5 μs . Using this value, maximum particle diameter was calculated based on momentum and thermal relaxation using the theories for Stokes' drag [25] and lumped capacitance [26], resulting in the following expressions

$$d_v = \sqrt{\frac{18\mu\tau}{\rho_p f}}, \quad (9)$$

$$d_T = \sqrt{\frac{12k\tau}{\rho_p c_p f}}. \quad (10)$$

In equations (9) and (10), d_v and d_T are the maximum allowable particle diameters based on momentum and thermal relaxation, respectively, μ is the fluid viscosity, ρ_p and c_p are the particle's density and heat capacity, and τ is the relaxation time constant (set to 5 μs). Finally, the factor f represents the degree to which the particle's velocity has relaxed. For 95% relaxation, $f = 3$. Table 1 displays the calculated maximum allowable diameters for the three candidate phosphors selected as most promising based on the results of section 2. For all cases, d_v serves as the lower value and was therefore taken as the maximum particle size allowable.

Table 1: Calculated upper limit on particle diameter in 600 K, 30 bar air. Particle heat capacity is taken in the Dulong-Petit (high-temperature) limit.

Phosphor	d_v [nm]	d_T [nm]
Ce:LuAG	381	510
Ce:CSSO	528	540
Eu:BAM	507	520

Using the particle diameters from Table 1, maximum allowable seeding densities for each phosphor were calculated using two criteria: 1) Limiting the temperature and velocity change of

the flow by addition of particles (i.e., intrusiveness) to less than 1% , 2) Limiting induced biases in the temperature measurement from multiple-scattered light to less than 1%.

Intrusiveness was calculated using simple energy and momentum balances. The results indicated that this consideration does not place a significant restriction on the diagnostic, with maximum allowable seeding densities on the order of 50,000 – 100,000 mm⁻³ for typical engine environments. These seeding densities are much higher than typical PIV seeding densities which are on the order of 10 to 1000 mm⁻³. A much more restrictive design constraint is found by considering the effect of multiple scattering.

The effects of multiple scattering have been observed and discussed in many phosphor applications (e.g., [27-30]) and need to be considered in the experimental design to limit potential biases. From a diagnostic perspective, an important effect of multiple scattering is that it artificially changes the amount of light incident on a detector (or pixel). In the absence of multiple scattering, the luminescence intensity measured by a camera pixel is equal to the amount of light emitted from the corresponding collection volume considering the collection solid angle and filter/optic transmission, minus the fraction of emitted light that is attenuated by scattering or absorption between the source and sensor, resulting in a small reduction in signal. At high phosphor seeding densities, when multiple scattering becomes important, the light that was scattered will continue to propagate and can be collected on a nearby pixel after additional scattering events. The additional light collected on the sensor likely originates somewhere outside of the collection volume for that pixel, and thus biases the measurement. Therefore, it is necessary to identify a seeding density below which the signal bias has a negligible impact on the measurement compared to the required temperature uncertainty.

Assuming that the biases primarily are from the luminescence camera, and the measured bias at any location originates, on average, from every point inside the cylinder with similar probability, the temperature bias due to multiple scattering can be written as (see section 7.4.3 in [12] for more details)

$$\frac{b_T}{T} = \left(\frac{1}{T \cdot \xi_T} \frac{R(T)}{R(\langle T \rangle)} \right) \frac{b_{S_{lum}}(\langle T \rangle)}{S_{lum}(\langle T \rangle)}, \quad (11)$$

where b_T is the bias in the temperature measurement and $b_{S_{lum}}(\langle T \rangle)/S_{lum}(\langle T \rangle)$ is the relative bias in the luminescence signal measurement due to multiple-scattered light. Note that since the bias originates from every location in the cylinder with equal probability, this term is evaluated at the mean temperature of the environment ($\langle T \rangle$).

The expression in parentheses on the right of Equation (11) is the sensitivity of the temperature bias to multiple scattering. The term $R(T)/R(\langle T \rangle)$ shows that when the local temperature is higher than the mean temperature (i.e. $R(T) > R(\langle T \rangle)$), the sensitivity increases, whereas temperature biases due to multiple scattering become less important when the local temperature is lower than the mean. For the phosphors being considered in this work with the expected low-temperature ignition temperature increases discussed in section 3.2.1, the sensitivity can be calculated and is generally on the order of ~ 0.3 . Therefore, to keep temperature biases to 1% or lower requires a maximum multiple scattering bias of roughly $b_{S_{lum}}(\langle T \rangle)/S_{lum}(\langle T \rangle) = 0.03$.

The magnitude of $b_{S_{lum}}(\langle T \rangle)/S_{lum}(\langle T \rangle)$ was estimated by solving the radiative transfer equation using the Method of Successive Orders (see section 6.3 in [12] for detailed derivation,

implementation, and discussion on the multiple scattering theories used). For a geometry representative of the optical engine, the bias was found to only significantly depend on the optical thickness of the particles in the cylinder (see Fig. 6.10 from [12]), resulting in the following relation

$$\frac{b_{S_{lum}}(\langle T \rangle)}{S_{lum}(\langle T \rangle)} \approx 1.89\tau_0^{0.9}, \quad (12)$$

where τ_0 is the optical thickness of the particles in the cylinder, given by

$$\tau_0 = Q_{sca} \frac{\pi d_p^2}{4} L n_p. \quad (13)$$

In equation (13), Q_{sca} is the particle scattering efficiency ($Q_{sca} \sim 2$ from Mie scattering theory), d_p is the particle size for each phosphor (determined in Table 1), L is the optical engine cylinder height at TDC (estimated as 10 mm) and n_p is the phosphor seeding density. Using the criteria of $b_{S_{lum}}(\langle T \rangle)/S_{lum}(\langle T \rangle) = 0.03$, equation (12) was used to estimate a maximum allowable optical thickness $\tau_0 \approx 0.01$. Finally, equation (13) was used to calculate the maximum allowable seeding density for each phosphor considered. The final selected maximum allowable particle size and seeding density are provided in Table 2. It is notable that the resulting particle seeding densities calculated based on limiting biases due to multiple scattering to 1% or less results in a much more restrictive seeding density requirement, by over an order of magnitude, relative to intrusiveness calculations considering impacts on heat capacity and momentum alone.

Table 2: Calculated seeding density limits for each phosphor based on multiply scattered light intensity. Optical thickness is chosen as $\tau_0 = 0.01$, and particle diameters are based on d_v .

Phosphor	d_p [nm]	$n_{p,max}$ [mm ⁻³]
Ce:LuAG	381	4300
Ce:CSSO	528	2200
Eu:BAM	507	2500

Formaldehyde PLIF measureemtn

3.3 Develop correction method to achieve the desired formaldehyde mole fraction accuracy on a single-shot basis

The developed formaldehyde PLIF concentration measurement utilizes a two-camera multi-band filter imaging approach to correct for interfering signals and utilizes temperature measurements from APT and in-cylinder pressure measurements to correct for the temperature and pressure dependence of product of the absorption cross section and fluorescence quantum yield, to attempt to achieve the desired $\pm 30\%$ or better accuracy. Significant work was done in the project to model the absorption cross section, fluorescence quantum yield, and emission spectrum for formaldehyde as a function of temperature, pressure, and composition [12]. The modeling work was complemented by measurements of formaldehyde fluorescence performed in the optical engine at conditions relevant for the project and these measurements were used to partially validate the absorption cross section, fluorescence quantum yield, and emission spectrum modeling.

The two-camera approach uses two 11-band multi-bandpass filters designed specifically for formaldehyde. The bands of the filter align with the emission bands typically seen following excitation of the $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ electronic transition. By orienting the filter at different angles of incidence (AOIs) different portions of the formaldehyde fluorescence spectrum can be captured. Figure 6 shows the filter transmission bands for the two angles of incidence used in this work: 0° AOI and 15° AOI. For the 0° orientation the bands of the filter nominally line up with the peaks of the vibronic bands in the fluorescence spectrum, whereas the bands for the 15° orientation lineup with the valleys between vibronic bands.

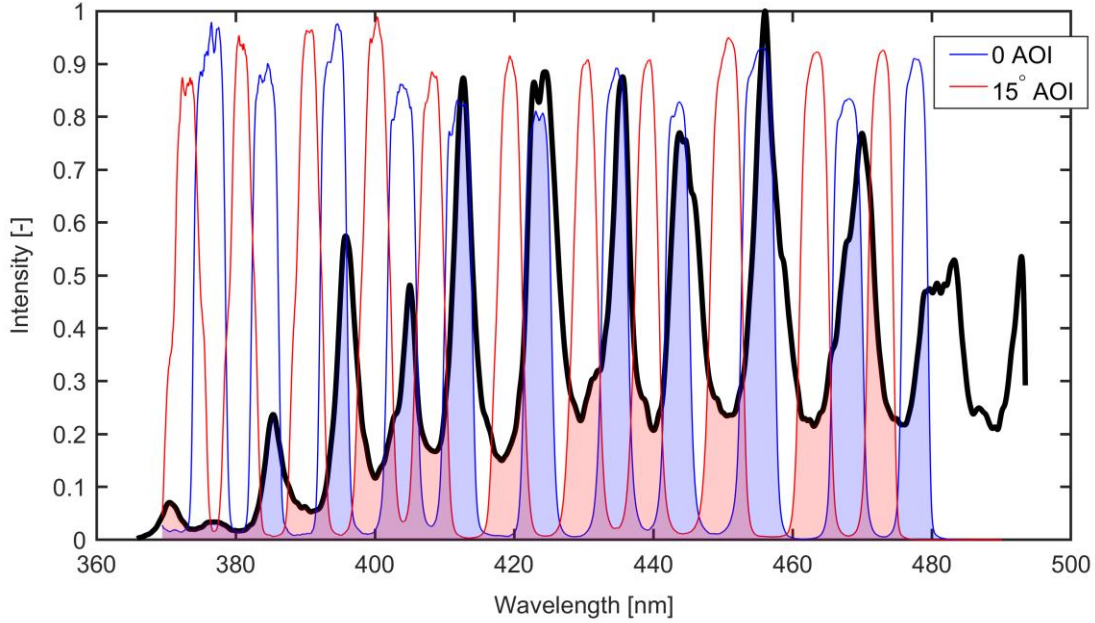


Figure 6: Filter transmission for two angles of incidence for the 11-band filter used for this work. A formaldehyde emission spectrum is also shown. Shaded regions indicate the collected portions of the spectra for the two filters orientations.

3.3.1 Formaldehyde detection limits estimation

Models were applied to estimate the detection limits for formaldehyde using the 11-band filter assuming collection using the 0° orientation filter with an ICCD camera. Performance estimates are based on the linear fluorescence equation

$$S_{LIF} = \frac{E''}{\hbar\omega_0} V n_{abs} \sigma \Phi \frac{\Omega}{4\pi} \eta$$

where E'' is the laser fluence, $\hbar$ is the reduced Planck constant ($h/2\pi$), V is the excitation volume, n_{abs} is the absorbing species number density (formaldehyde for this discussion), σ is the absorption cross section, Φ is the fluorescence quantum yield, Ω is the collection solid angle, and η is the effective optical transmission efficiency. The optical transmission (η) and the fluorescence quantum yield (FQY) are both pressure- and temperature-dependent. The absorption cross section is additionally temperature dependent, but the pressure dependence is weak above 10 bar.

The calculated detection limits as a function of temperature for different representative pressures are shown in Figure 7 for a laser fluence of 100 mJ/cm². The results indicate that formaldehyde

mole fractions on the order of 100 ppm can be measured over much of the temperature/pressure range of interest. Typical formaldehyde concentrations formed during low temperature ignition are on the order of 1000 ppm up to ~10,000 ppm. The detection limits indicate that these concentrations should be able to be measured albeit with low to moderate single-shot SNR (~3-10).

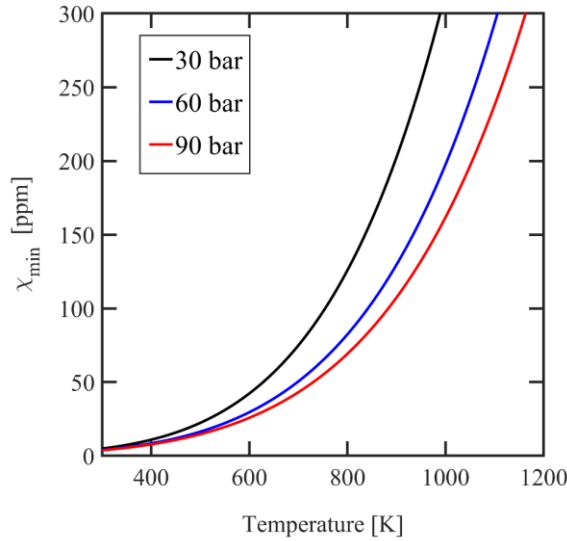


Figure 7: Calculated formaldehyde PLIF detection limits for 100 mJ/cm² laser fluence for an ideal ICCD camera. Detection limits are defined as the concentration at which the measured signal-to-noise ratio is 1.

3.3.2 Ratiometric formaldehyde PLIF background correction

Formaldehyde PLIF measurements at diesel-engine-like conditions are biased by interfering broadband fluorescence from other hydrocarbons, particularly PAH species. In addition, for the current work interfering emission from the thermographic phosphor used for temperature determination may also be an issue. To correct for these unknown broadband background signals, a novel ratiometric imaging approach was developed by collecting emission through the two 11-band filters oriented at two AOIs (0° and 15°) on two ICCD cameras.

To understand the approach, we can write the measured (biased) formaldehyde PLIF ratio R' as

$$R' = \frac{S_2 + B_2}{S_1 + B_1} = R \frac{1 + SBR_2^{-1}}{1 + SBR_2^{-1} \frac{R}{R_B}}$$

where S_i and B_i are the signal and background in band i , $R = S_2/S_1$ is the signal ratio unaffected by background, $SBR_2 = S_2/B_2$ is the signal-to-background ratio for camera 2, and $R_B = B_2/B_1$ is the ratio of background signals. The ratio of background signals R_B is assumed to be given by the ratio of the collection efficiencies for the two formaldehyde cameras, this amounts to assuming a perfectly uniform background signal within the 370 to 480 nm spectral region, which is the primary assumption used in this approach.

Solving for SBR_2^{-1} gives

$$SBR_2^{-1} = \frac{R_B}{R} \frac{R - R'}{R - R_B}$$

which enables expressions for the unbiased signals to be determined, i.e.,

$$S_2 = (S_2 + B_2) \frac{R}{R'} \frac{R' - R_B}{R - R_B}$$

and

$$S_1 = (S_1 + B_1) \frac{R' - R_B}{R - R_B}$$

since the signal plus the background is the measured signal and R_B is known, the signals can be corrected for background bias if the unbiased ratio (R) is available as a function of temperature and pressure. For this project the unbiased ratio was measured over a range of temperatures at a pressure of 32 bar and results of such a calibration are shown in Figure 8. The result demonstrates that over the temperature range from 800 to 1050 K the ratio variation is approximately linear with temperature.

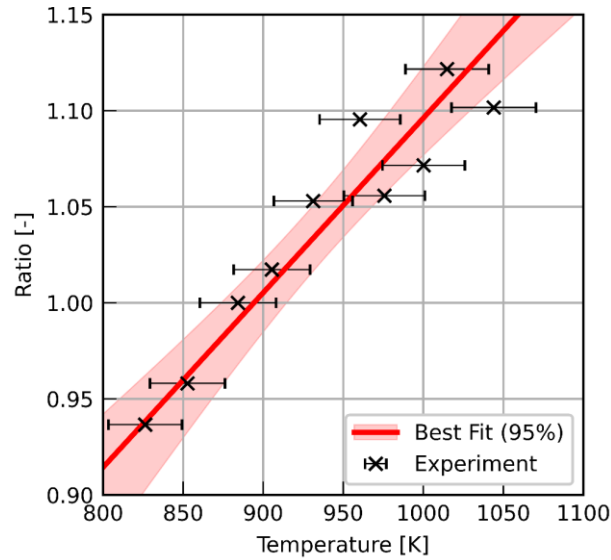


Figure 8: Formaldehyde ratio calibration measured in the optical engine normalized to the ratio at 875 K. Ratio is the S_{15°/S_0° .

Since the measured temperature from APT is used to determine the ratio used in the background correction, noise in the temperature measurement can contribute to noise in the measurement of the formaldehyde mole fraction. Assuming a single-shot temperature precision of 50 K (worst case) the temperature precision only slightly impacts the mole fraction precision, in the worst cases having a single-shot relative standard deviation of 5%, which should contribute only modestly to

the uncertainty in the formaldehyde mole fraction and not significantly degrade the single-shot precision.

3.3.3 Nonuniform oxygen concentration impact

Due to the non-uniform reacting environment of interest, oxygen concentration can vary significantly. To investigate the impact of this on the formaldehyde PLIF concentration measurements, calculations were performed to look at the magnitude of uncertainty this creates due to the differences in fluorescence quenching efficiency for molecular oxygen and nitrogen. In an approximate worst case, with oxygen concentration changing from 20% to 10% at 800 K the fluorescence quantum yield is estimated to increase by 50%, which if not corrected for would result in a 50% error in the measured formaldehyde mole fraction. During the period we are interested in O₂ mole fraction variation will generally be smaller than this and the potential bias will in most cases will be less than the $\pm 30\%$ targeted for the accuracy of the diagnostic.

3.4 Design integrated simultaneous temperature, velocity, and formaldehyde PLIF diagnostics with limited measurement biases

In section 3.2, chemical kinetic and turbulent jet models were used to determine the required temperature precision and spatial resolution of 25 K and a 0.3 mm pixel, respectively. Using these values, maximum allowable particle size and seeding density were determined for candidate phosphors by considering particle tracer response, intrusiveness, and temperature biases from multiple scattering. Considering the spatial resolution, particle size and seeding density constraints, the data from the phosphors discussed in section 2, along with previous data for the Ce:LuAG phosphor [1], were used to quantitatively assess the performance of each phosphor.

3.4.1 APT performance estimates

Single-shot precision as a function of temperature was estimated for each phosphor using equations (3) and (4), which are repeated here for convenience.

$$s_T = \frac{\partial T}{\partial R} s_R = \frac{(s_R/R)}{\xi_T} \quad (3)$$

$$\xi_T = \frac{1}{R} \left(\frac{\partial R}{\partial T} \right) \quad (4)$$

Calculation of the fractional temperature sensitivity, ξ_T , for each phosphor requires a ratio versus temperature calibration for each phosphor. This was accomplished by fitting the data acquired for each phosphor [1, 4, 5] to a three-level population model that was used to estimate the signal per particle and SRAPT ratio of each phosphor as a function of laser fluence and temperature [10]. Figure 9 shows the SRAPT ratio and corresponding fractional sensitivity for each phosphor as a function of temperature and laser fluence. The results demonstrate that the impact of laser fluence is relatively small for fluences >10 mJ/cm².

The fractional ratio precision, s_R/R , was calculated according to the following expression

$$\frac{s_R}{R} = \sqrt{\left(\frac{s_R}{R} \right)_{camera}^2 + \left(\frac{s_R}{R} \right)_{PSD}^2} . \quad (14)$$

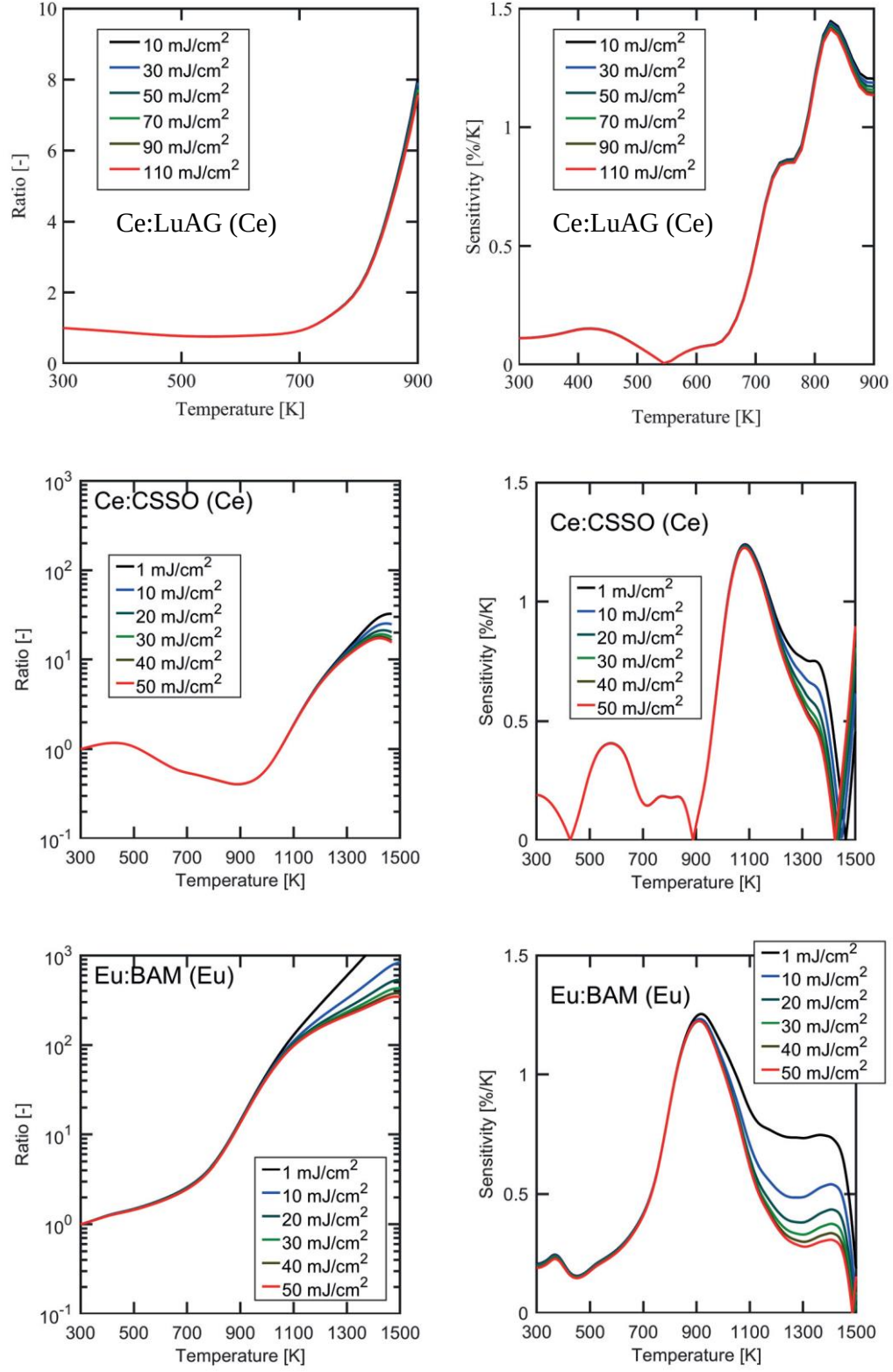


Figure 9: Ratio and temperature-sensitivity for Ce:LuAG (top), Ce:CSSO (middle), and Eu:BAM (bottom) using the SRAPT technique at several fluences.

In equation (14), $(s_R/R)_{camera}^2$ is the fractional mean squared noise in the SRAPT ratio from the detection system. To calculate this term, rigorous testing of the noise characteristics of the cameras used in this work was performed as a function of measured signal (Appendix E from [12]). Estimated phosphor signal levels were calculated as a function of temperature and fluence using the three-level population model [10], in combination with the spatial resolution, particle diameter, and seeding density design constraints, for a representative optical engine measurement geometry (Table 7.4 on [12]). $(s_R/R)_{PSD}^2$ is an additional noise term for the SRAPT technique that arises due to a particle size distribution. Since the measured signal depends on diameter-cubed for luminescence, but closer to diameter squared for scattering, the ratio has some dependence on particle diameter. To understand this further, the SRAPT ratio can be written explicitly to account for this particle size distribution as

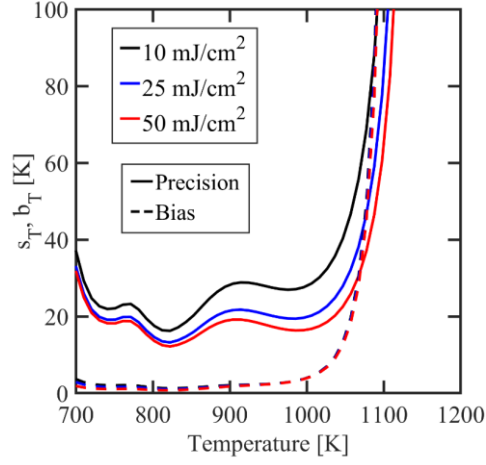
$$R_{SRAPT} \approx \frac{s_{Mie}}{s_{lum}} \frac{\sum Q_{sca} d_{p,i}^2}{\sum d_{p,i}^3} . \quad (15)$$

The right term in equation (15) shows that there is additional noise in a SRAPT measurement that arises from random sampling of a discrete number of particles in a given pixel volume. The form of this noise can be derived from equation (15) with first-order uncertainty propagation as [12]

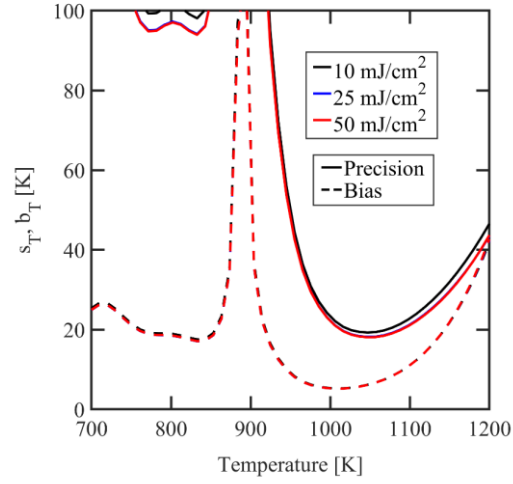
$$\left(\frac{s_R}{R}\right)_{PSD}^2 = \frac{k_Q^2}{N} , \quad (16)$$

where N is the number of particles in the collection volume and k_Q^2 is a parameter that is related to size and width of the particle size distribution. The value of k_Q^2 was calculated for each phosphor tested using their measured particle-size distributions. To provide confidence in the accuracy of this approach, it was validated for Eu:BAM by comparing direct measurements of this added uncertainty to the model results (see section 6.6 of [12] for further theoretical and experimental details).

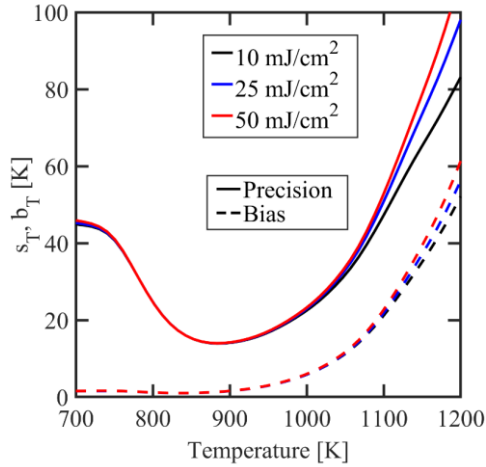
Figure 10 displays the resulting performance estimates for the three phosphors under consideration: Ce:LuAG, Ce:CSSO, and Eu:BAM. In addition to the precision estimates, shown as solid lines, the estimated measurement bias due to multiple scattering and fluctuations and drift in the laser fluence are also included as dashed lines. First, it is noted that for each phosphor the estimated bias due to laser fluence variation and multiple scattering is significantly lower than the temperature precision within the temperature range where each phosphor is usable for thermometry. Further, it is clear that Ce:LuAG and Eu:BAM are able to satisfy the precision requirements of the diagnostic over much of the temperature range where low-temperature ignition is expected to occur. Ce:LuAG is capable of ~ 20 K single-shot precision from 720 – 1000 K and is capable of better than 40 K single-shot precision from 700 to almost 1100 K, above 1100 K the predicted performance begins to degrade due to its low signal levels as a result of thermal quenching. Eu:BAM appears capable of better than 40-K single-shot precision from 750 – 1100 K, with better than 20 K from 800 – 1000 K. The Ce:CSSO phosphor shows potential for high-temperature SRAPT measurements, with estimated precision better than 40 K from 950 – 1200 K and 20 K from 1000 – 1100 K, thermal quenching with this phosphor does not begin to occur until roughly 1000 K, making its precision quite poor over much of the target temperature range for this specific application.



(a) Ce:LuAG



(b) Ce:CSSO



(c) Eu:BAM

Figure 10: Estimated performance for (a) Ce:LuAG SRAPT with 355-nm excitation, (b) Ce:CSSO SRAPT with 266-nm excitation, and (c) Eu:BAM SRAPT with 355-nm excitation in the optical engine at TDC pressure of 32 bar. Seeding densities and particle sizes for each calculation are from Table 2, and the camera pixel size is 0.3 mm.

From the perspective of integrating the technique with simultaneous formaldehyde PLIF measurements, both Ce:LuAG and Eu:BAM are advantageous in that they employ the same excitation wavelength as formaldehyde (355 nm), significantly simplifying the experimental setup. The Eu:BAM phosphor emission spectrum (ranging from ~390 – 520 nm) significantly overlaps the formaldehyde spectrum (~360 – 480 nm). To eliminate biases from background formaldehyde emission, a delayed camera gating approach would be required to wait until the formaldehyde emission is complete to begin imaging the Eu:BAM luminescence. This will have adverse effects on the SRAPT performance above 1000 K once the Eu:BAM emission becomes much faster due to increasing nonradiative transition rates. The emission spectrum of Ce:LuAG (~470 – 650 nm) does not significantly overlap the formaldehyde spectrum, and therefore the delayed gating approach should not be necessary. Based on the results provided here, the combination of adequate diagnostic performance and ease of experimental integration makes Ce:LuAG the recommended phosphor to use for optical engine measurements.

3.4.2 Integrated diagnostic design

The combined diagnostic for simultaneous temperature, velocity, and formaldehyde concentration uses aerosol phosphor thermometry (APT) with particle image velocimetry (PIV) and formaldehyde planar laser-induced fluorescence (PLIF). Phosphor particles are seeded into the air flow entering the engine, while formaldehyde is formed in-cylinder by low-temperature reactions during ignition. The third harmonic output of an Nd:YAG laser at 355 nm will be used to excite luminescence from formaldehyde and the phosphor particles; ultra-violet laser light scattered from the phosphor particles will be used for PIV and as the scattering signal for SRAPT. Four cameras will be used to image the various light sources; one camera for phosphor luminescence, one camera for particle Mie scattering (used for PIV and for SRAPT), and 2 cameras for the background corrected formaldehyde diagnostic. One of the formaldehyde imaging cameras captures the peaks of the formaldehyde emission, and another captures the valleys or local minima. Since multiple diagnostics are being performed simultaneously, the emitted or scattered light from either formaldehyde PLIF or APT can act as a background signal for the other diagnostic.

The formaldehyde measurements are expected to be biased due to broadband background radiation, either from the phosphor particles, or from other interfering species such as polycyclic aromatic hydrocarbons (PAHs). To remove this background, the ratiometric imaging approach introduced in Section 3.3.2 is used where the two cameras for formaldehyde imaging image different portions of the emission spectrum, one on-peak and one off-peak. This is accomplished using the 11-band formaldehyde imaging filters as discussed in Section 3.3. The ratio of the two images is used to correct the signals for interfering background emission. The proposed approach for background subtraction extends the approach suggested by Thering et al. [31], where emission was collected using the same two multi-band filters but a direct frame subtraction was applied. The approach used by Thering et al. is limited in that a significant portion of formaldehyde emission exists in the off-peak band, and the fraction is both temperature and pressure dependent. The proposed approach is intended to provide a quantitative measurement by accounting for the temperature and pressure dependence of the intensity ratio.

Based on the APT performance estimates and emission band considerations, Ce:LuAG SRAPT with 355-nm excitation was chosen to be used for APT with PIV to be performed using the same detector that is used for elastic scattering imaging of the SRAPT technique. The Mie scattering camera could be either a high-speed CMOS camera or an ICCD camera. The luminescence camera

will likely need to be an ICCD camera, although a high-speed CMOS camera with sufficient sensitivity and quantum efficiency may be possible as well. The formaldehyde PLIF technique can be performed using two separate ICCD cameras or possibly two high-speed CMOS cameras with sufficiently high quantum efficiency and low noise, separated by a beam splitter.

The proposed optical layout is shown in Figure 11, with optics specifications listed in Table 3. In addition to the optics explicitly listed in Table 3, each camera will additionally require a bandpass filter. The bands are listed in Table 4. Note that the specification for each ICCD camera requires a $\leq 50 \mu\text{m}$ binned pixel; since the assumed magnification is 0.165, a $50 \mu\text{m}$ binned pixel size at the photocathode is required to achieve the proposed collection volume (e.g., 4x4 binning with a $12.5 \mu\text{m}$ physical pixel size in the image plane).

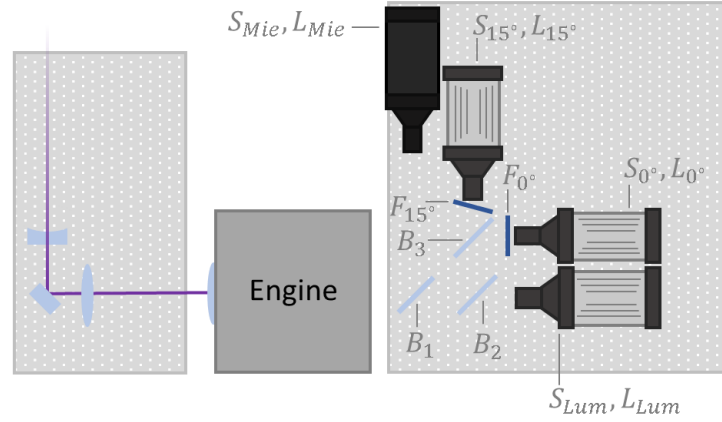


Figure 11: Optical layout of the proposed APT, formaldehyde PLIF, and PIV diagnostic. The optics specifications for each element are listed in

Table 3: Equipment for the simultaneous APT, formaldehyde PLIF, and PIV diagnostic. Note that the formaldehyde cameras are listed as S_0° and S_{15}° could be high-speed CMOS cameras if they have high quantum efficiency (QE), low read noise, and good temporal gating capability ($< 200 \text{ ns}$).

Label	Type	Specifications
S_{Mie}	ICCD camera (or high-speed CMOS)	$< 90 \mu\text{s}$ frame transfer, $\leq 50 \mu\text{m}$ binned pixel
S_{Lum}	ICCD camera (or high-speed CMOS)	$\geq 0.4 \text{ QE}$, $\leq 50 \mu\text{m}$ binned pixel
S_0°	ICCD camera	$\geq 0.4 \text{ QE}$, $\leq 50 \mu\text{m}$ binned pixel
S_{15}°	ICCD camera	$\geq 0.4 \text{ QE}$, $\leq 50 \mu\text{m}$ binned pixel
L_{Mie}	Camera lens	105-mm f.l., UV-transmissive
L_{Lum}	Camera lens	$f/1.4$, 85-mm f.l.
L_0°	Camera lens	$f/1.4$, 85-mm f.l.
L_{15}°	Camera lens	$f/1.4$, 85-mm f.l.
B_1	dichroic beamsplitter	Reflect $\leq 360 \text{ nm}$
B_2	dichroic beamsplitter	Reflect $\leq 490 \text{ nm}$
B_3	broadband beamsplitter	50% reflection, 50% transmission
F_0°	formaldehyde imaging filter, 0° AOI.	Semrock Inc., FF01-CH2O
F_{15}°	formaldehyde imaging filter, 15° AOI.	Semrock Inc., FF01-CH2O

Table 4: Imaging bands for combined APT, PIV, and formaldehyde PLIF diagnostic.

Sensor	Minimum [nm]	Maximum [nm]
S_{Mie}	350	360
S_{Lum}	490	650
S_{0°	380	480
S_{15°	380	480

The proposed approach requires the Ce:LuAG phosphor with a mean particle diameter of ~ 400 nm, and a log-normal distribution width parameter of 0.15, corresponding to a 140-nm FWHM, or typical particle diameters from 330 to 470 nm. Maximum seeding densities at TDC should be on the order of 4500 mm^{-3} . Performance predictions were made using a laser fluence of 50 mJ/cm^2 for APT and 100 mJ/cm^2 for formaldehyde PLIF. In reality, both techniques will be applied simultaneously and will, therefore, utilize the same fluence. From a practical perspective fluence tends to be limited by window damage in the optical engine. It should be noted that further APT diagnostic optimization is possible by optimizing the doping concentration of Ce^{3+} in LuAG.

Performance estimates for the technique suggest that better than 30-K temperature precision is possible between 700 and 1000 K, with temperature biases less than 5 K in this range. Above 1000 K, temperature measurement performance is predicted to decrease significantly, although this temperature range is extrapolated using furnace data and may not be representative of the aerosol luminescence intensity above 1000 K. Formaldehyde PLIF detection limits are estimated to be less than 100 ppm at 800 K throughout the 30 to 100 bar pressure range but increase significantly at higher temperatures to several hundred ppm at the highest temperatures of interest for this work (1150 K).

3.5 Validate and demonstrate the simultaneous temperature, velocity, and formaldehyde PLIF diagnostic in an optical engine

With the diagnostic layout designed, a key issue to address was the calibration of the temperature measurement technique. Significant effort was devoted to developing methods for accurate high-temperature calibrations for the selected SRAPT temperature measurement approach. This was motivated by two factors; first, it is well known that furnace measurements using bulk phosphor suffer from multiple sources of measurement bias, second, calibration in the engine can be difficult for the temperature range of interest and there can be relatively significant uncertainty in the in-cylinder temperature. Due to these issues a method that shows promise for avoiding the biases associated with typical furnace calibrations was investigated, and calibrations were also performed using the more common heated jet approach. Work in these areas is describe in the following subsections.

Due to time limitations we haven't yet been able to test the combined APT, PIV, formaldehyde PLIF diagnostic in the optical engine so this is not included in the report.

3.5.1 Development of accurate high-temperature calibration methods for SRAPT

Following determination of required design criteria and a suitable APT technique, work focused on developing methods to ensure accurate and unbiased temperature calibrations for the APT diagnostic prior to implementation in the optical engine. To date, most phosphor characterization and calibration for APT have been performed in heated jets seeded with phosphor particles [9, 10, 32-34]. The temperature-dependence of the phosphor is determined by comparing its' emission to

thermocouples used to measure temperature in-situ. As temperatures begin to approach and surpass 1000 K, difficulties maintaining steady and uniform temperature environments and providing sufficient seeding densities for sufficient signal-to-noise ratios makes reliable calibrations with this method challenging. There have also been attempts to perform phosphor characterization by placing the phosphor in bulk powder form inside a furnace [35]. The use of a furnace provides a well-controlled and accurately known temperature environment. Unfortunately, the luminescence behavior of the bulk powder does not accurately convey the behavior seen in optically thin environments due to effects such as multiple scattering and radiative trapping [19]. To address this and provide reliable calibrations for phosphors in the temperature range of interest for this project, a new characterization technique was developed that mimics aerosol seeding concentrations, similar to the work of Fond [36], while also providing the capability to assess the temperature dependence of the phosphor emission properties at high temperatures.

3.5.2 Optical coating preparation and measurements

To create an optically-thin phosphor layer that is not prone to effects that have been observed in bulk powder form [37], a disperse coating of Eu:BAM particles (Phosphor Technology KEMK63/FF-P1) was prepared by diluting 1 mg of phosphor powder in distilled water. Eu:BAM was selected for validation of the setup due to its well-known photophysical properties [19]. A pipette was used to sample the solution and dispense it onto the surface of a fused silica window. The weight of the window was measured with a high-precision scale (Mettler AE 240) before and after depositing the phosphor mixture, and the net weight increase was used to estimate the total phosphor mass. The window was then placed in a furnace (CM Furnaces, Rapid Temp, Model 1720-12) until visual inspection verified the solution had dried. An image of the final prepared coating is shown in Figure 12. Based on the concentration of the phosphor solution, the optical thickness of the coating was estimated at 0.03 and this was confirmed using extinction measurements [8].



Figure 12: Fused silica substrate with optically thin Eu:BAM coating.

The prepared Eu:BAM substrate was inserted into the center of a tube furnace for phosphor characterization from room temperature to 1100 K in increments of 100 K. The experimental setup is shown in Figure 13 (see [8] for more details). A 10-Hz Nd:YAG laser outputting the 3rd harmonic at 355 nm provided phosphor excitation. Laser fluence at each temperature was varied between 6

mJ/cm^2 and $36 \text{ mJ}/\text{cm}^2$. To quantify the time-dependent luminescence behavior, a photomultiplier tube (PMT) was used to collect the phosphor luminescence. Spectral data were additionally collected using a spectrometer outfitted with an intensified charge-coupled device (ICCD) camera. As will be seen, using the results of the time-resolved and spectral data allows photophysical properties critical to design of the SRAPT experiment, such as signal per particle and estimated SRAPT ratio as a function of laser fluence over the entire temperature range of interest, can be quantitatively assessed.

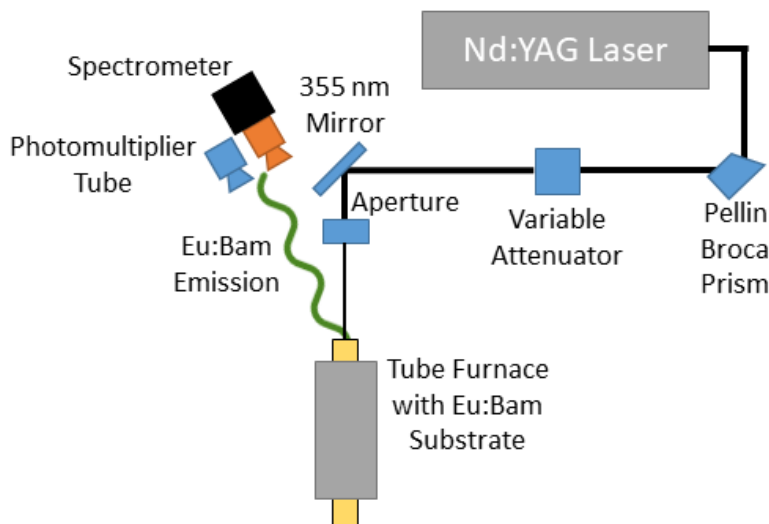


Figure 13: Tube furnace calibration experimental setup.

In addition to furnace characterization, a new heated aerosol jet was designed and built to provide a stable aerosol environment for SRAPT calibrations up to 1100 K. The experimental setup is shown in Figure 14 (see [8] for further details). Eu:BAM was seeded into the air and then heated to temperatures up to 1100 K via an inline flow heater (Kanthal KFH2-03-230). The heated aerosol exits as a 25.4-mm diameter jet, and a co-axial heated co-flow with an outer diameter of 76.2 mm surrounds the seeded jet to help maintain stable flow conditions. A 0.13-mm diameter type-K thermocouple was positioned 14 mm from the jet's exit to provide temperature measurements for calibration of the SRAPT technique. The thermocouple measurements were corrected for conduction and radiation using a method similar to that reported in [4]. The estimated correction was quite modest, with a maximum correction of 12 K at 1100 K.

The Eu:BAM phosphor was excited with the 355-nm output of an Nd:YAG laser operating at 10 Hz that was formed into a 38-mm tall by 750 μm thick sheet. Phosphor luminescence was captured with an intensified charge-coupled device (ICCD) camera (Princeton Instruments PI-Max 4 1024i with Gen. III HbF intensifier) and an f/1.4 85-mm lens (Nikon Nikkor). The scattered laser light was collected using a CCD camera (Princeton Instruments MicroMax 1300YHS-DIF) outfitted with a UV f/2.8 100-mm lens (Cercos lens). Following background subtraction and camera alignment during software processing, a SRAPT ratio was calculated and a whitefield correction was applied for each pair of luminescence and scattering images acquired. The calibration was performed using the corrected thermocouple temperature for a sub-region in each average ratio image (100 images per average) located in approximately the same location as the thermocouple measurement.

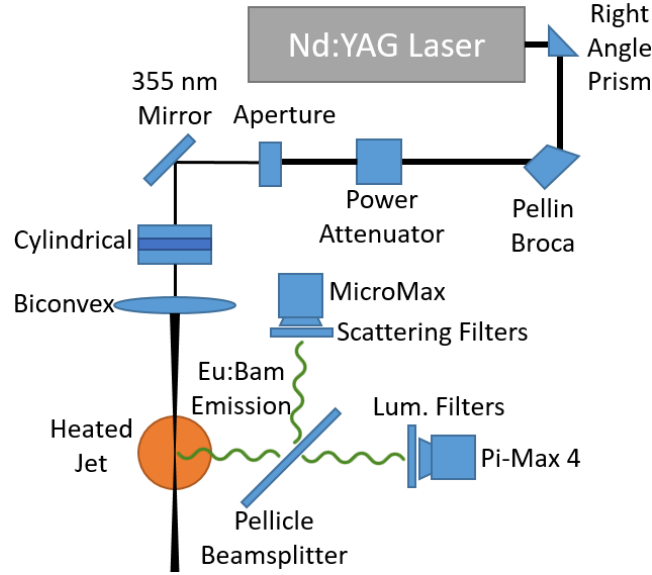


Figure 14: Tube furnace calibration experimental setup.

3.5.3 Phosphor photophysical property and SRAPT calibration results

The time-resolved PMT signal measurements performed in the furnace [8] using the coated fused silica substrate were integrated with respect to time to obtain the total number of photons emitted per mass of Eu:BAM using equation (17) and the values in Table 5.

$$n_{Eu:BAM} = \frac{S_{total}}{K \frac{\Omega}{4\pi} \eta_{opt} m_{Eu:BAM}} \quad (17)$$

Table 5: Optical parameters used in equation (17).

Symbol	Definition	Value	Units
S_{total}	Integrated PMT signal		[V-s]
K	System gain	1E-14	[V-s/photon]
$\Omega/4\pi$	Fractional collection solid angle	4E-5	[-]
η_{opt}	Collection efficiency	0.88	[-]
$m_{Eu:BAM}$	Mass of excited Eu:BAM	4E-4	[mg]

Figure 15 displays the results as a function of temperature and laser fluence. At room temperature and a fluence of 24 mJ/cm², Eu:BAM emits 1.1E+15 photons/mg. Prior to furnace testing, three independent coatings were prepared and tested at room temperature and the repeatability was estimated at 25% based on the experimental standard deviation. The value obtained here agrees with previous room temperature characterization at similar laser fluences to within a factor of 2 [36]. Considering the large uncertainties in many of the values used both in this work and in the literature, this agreement is considered satisfactory and helps validate that the coating is behaving in a way that is representative of APT applications. The characterization technique developed here is useful to help facilitate reliable experimental design for future APT experiments.

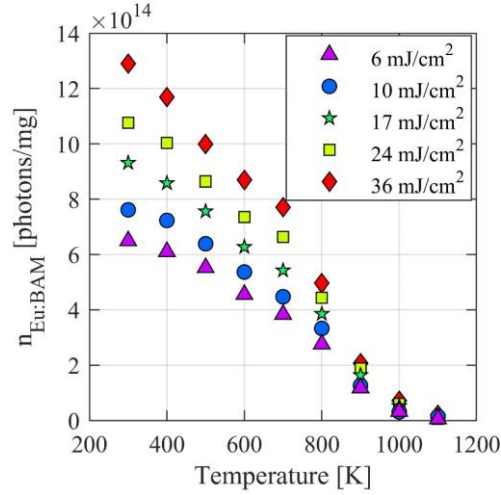


Figure 15: Photons per milligram of Eu:BAM versus temperature for a range of laser fluences.

Figure 16 displays the average SRAPT ratio images acquired in the jet from room temperature to 1100 K for Eu:BAM. Data from the ratio images used for the in-situ calibration determined for the average signal in the region from -1.5 to 1.5 mm in the horizontal direction and 14 mm to 20.5 mm in the vertical direction. This region was selected to maximize the number of pixels considered while also minimizing any temperature gradients within the region. Figure 17 compares the calibrations from the furnace (spectral and time-resolved) to the jet calibration. The temperature uncertainty bars shown on the jet data include the thermocouple corrections and heater variability, and the ratio uncertainty bars are due to the combination of statistical variation within the region of interest and the ratio uncertainty due to the temperature uncertainty. Spectral response corrections were applied to each data set to account for the differing wavelength dependent quantum efficiency of each instrument, making direction comparisons possible.

Overall, agreement between the three measurements is reasonable, especially for the spectral and jet data. The ratio extracted from the time-resolved data does not increase as rapidly during initial quenching as the other two measurements. This may be a result in differences in the response of the two detectors, as both the spectral and jet data used PI-MAX4 ICCD's for data collection while the time-resolved data was collected by a point detector. At 1100 K, both furnace calibrations diverge from the jet calibration. The reason for the disagreement is not currently known. Potential reasons for the disagreement include oxidation of Eu^{2+} to Eu^{3+} in the furnace due to the long measurement times and multiple scattering at high temperatures in the jet leading to biases in ratio measurement.

Jet measurements were also performed for Ce:LuAG to create a high temperature SRAPT ratio temperature calibration. Previous measurements had been performed in a jet for Ce:LuAG, but only up to 900 K. Measurements for the current work extend this to almost 1100 K. Average ratio images in the jet are shown in Figure 18. Average ratios from the region from -3.8 mm to +3.8 mm in the horizontal direction and from 16 mm to 26 mm above the jet exit in the vertical direction are shown versus temperature in Figure 19. The results agree well with previous jet ratio measurements up to 900 K, the highest temperature where previous measurements were available. The current measurements extend the range of data up to almost 1100 K.

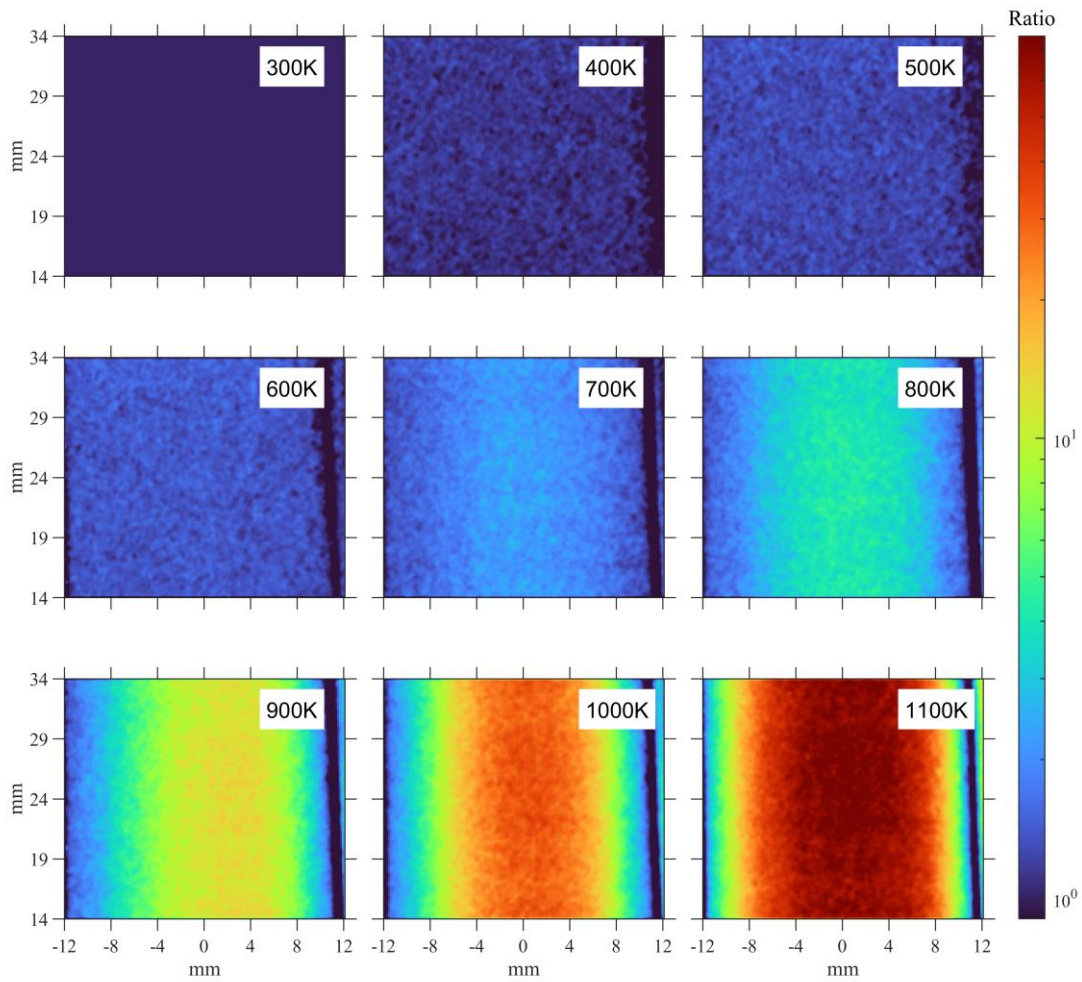


Figure 16: Average ratio images for a fluence of 17 mJ/cm^2 for Eu:BAM.

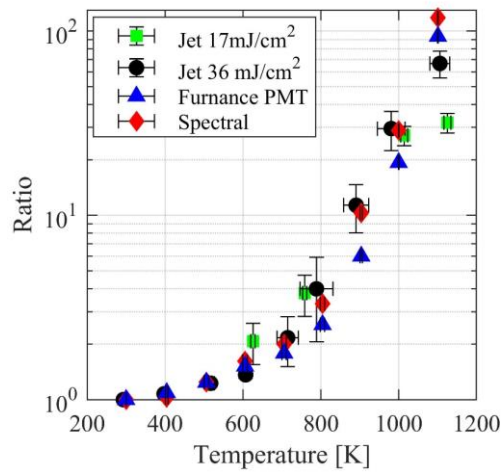


Figure 17: Jet, furnace PMT and spectral ratios. The furnace PMT ratio was collected at 17 mJ/cm^2 and the spectral calibration at 36 mJ/cm^2 . Corresponding jet data at each fluence are also plotted.

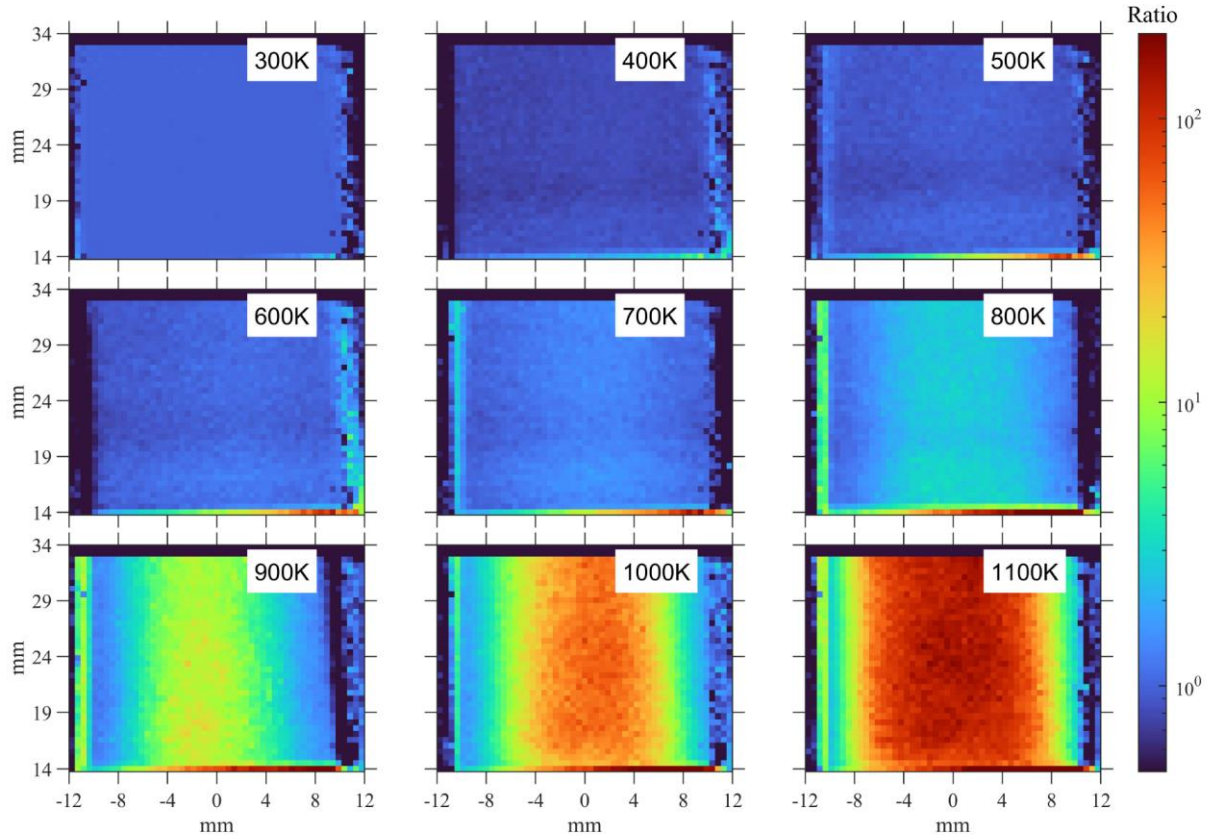


Figure 18: Average ratio images in the jet for a fluence of 65 mJ/cm^2 .

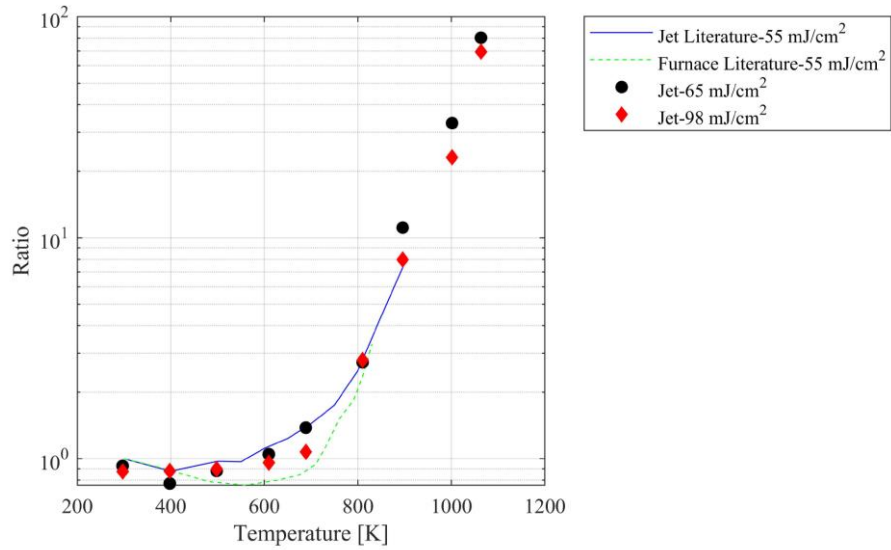


Figure 19: Ce:LuAG SRAPT ratio versus temperature measured in the heated jet compared to previous measurement results.

4 Conclusions

During the three years of work performed for this project, a combined temperature, velocity, and formaldehyde species concentration measurement approach was designed that is capable of relatively precise and accurate single-shot measurements of high-pressure turbulent ignition in an optical engine. Candidate thermographic phosphors were selected based on the phosphor electronic structure and room temperature per particle signal levels, and measurements performed in a seeded air jet heated by the products of a premixed methane flame demonstrated that reliable single-shot measurements were possible with a range of phosphors at temperatures above 1000 K. In particular, the Ce:CSSO and Eu:BAM phosphors were able to demonstrate reliable measurements up to 1400 K with the SRAPT technique, representing a greater than 400 K increase from previous APT capabilities. The results of these measurements were published in the biennial Proceedings of the Combustion Institute journal [4] and in Combustion and Flame in 2021 [5].

Following selection and demonstration of candidate phosphors, the APT diagnostic was designed to ensure it was able to resolve the expected low-temperature ignition phenomena accurately and precisely. Based on chemical kinetic and turbulent jet models, measurement criteria including a 25-K temperature precision and 300- μm spatial resolution (based on object plane pixel size) were selected. Using the determined criteria, along with models used to specify maximum allowable phosphor particle size and seeding densities, two promising phosphors were selected. Ce:LuAG was found to be capable of ~ 20 K precision from 720 – 1000 K, with performance decreasing rapidly above 1100 K. Eu:BAM, on the other hand, could achieve better than 40 K precision from 750-1100 K, with better than 20 K precision from 800 – 1000 K. Given the strong spectral overlap of Eu:BAM emission with formaldehyde PLIF emission, Ce:LuAG was selected as the phosphor for the combined APT, PIV, and formaldehyde PLIF diagnostics.

Given the high likelihood of broadband background emission biasing the formaldehyde PLIF concentration measurements, a novel ratiometric formaldehyde PLIF background correction approach was developed. Models for formaldehyde PLIF absorption cross section, fluorescence quantum yield, and emission spectrum were implemented and validated (at least partially) with experimental measurements performed in the optical engine. The models were used to estimate the detection limits for formaldehyde PLIF at the conditions of interest and results indicated an approximate detection limit of 100 to 200 ppm. The influence of oxygen concentration non-uniformity was also investigated, and models were used to estimate at maximum expected impact on the fluorescence signal of <50% uncertainty for most scenarios.

Finally, an integrated diagnostic design was presented that enables simultaneous measurements of temperature, velocity, and formaldehyde mole fraction using four cameras. Additionally, methods were developed to ensure accurate and unbiased temperature calibrations for the APT diagnostic prior to implementation in the optical engine. A technique was developed to perform calibration measurements in a tube furnace on an optically-thin phosphor coating deposited on a fused silica window. A new heated jet experimental setup was also built to maintain center temperatures above 1100 K for reliable APT calibrations. Measurements in both platforms have been performed for Eu:BAM and Ce:LuAG, and the results will be used for future optical engine experiments.

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