

# Ultrafast-laser-absorption spectroscopy in the mid-infrared for single-shot, calibration-free temperature and species measurements in low- and high-pressure combustion gases

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**Abstract:** This manuscript presents an ultrafast-laser-absorption-spectroscopy (ULAS) diagnostic capable of providing calibration-free, single-shot measurements of temperature and CO at 5 kHz in combustion gases at low and high pressures. Additionally, this diagnostic was extended to provide 1D, single-shot measurements of temperature and CO in a propellant flame. A detailed description of the spectral-fitting routine, data-processing procedures, and determination of the instrument response function are also presented. The accuracy of the diagnostic was validated at 1000 K and pressures up to 40 bar in a heated-gas cell before being applied to characterize the spatiotemporal evolution of temperature and CO in AP-HTPB and AP-HTPB-aluminum propellant flames at pressures between 1 and 40 bar. The results presented here demonstrate that ULAS in the mid-IR can provide high-fidelity, calibration-free measurements of gas properties with sub-nanosecond time resolution in harsh, high-pressure combustion environments representative of rocket motors.

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## 1. Introduction

Laser-absorption spectroscopy (LAS) is widely used to provide non-invasive measurements of temperature, chemical species, pressure, and velocity. The demand for LAS measurements in high pressure and highly transient combustion and propulsion environments (e.g., detonation engines, rocket motors) continues to propel innovations in LAS diagnostics [1–5] and data-processing techniques [6–8]. Several of these innovations have focused on increasing the usable spectral bandwidth of LAS diagnostics while maintaining or improving temporal resolution.

LAS diagnostics utilizing large spectral bandwidth benefit from the greater diversity of spectral information collected. This helps mitigate some challenges associated with determining the non-absorbing baseline and reduced levels of differential absorption at elevated pressures [6,9,10], as well as improve the dynamic-range of thermometry [11]. Broadband LAS diagnostics must, however, achieve fast temporal resolution in order to characterize highly transient processes such as chemical or internal non-equilibrium and to avoid time-varying, non-absorbing transmission losses such as those from beam steering or particle scattering. To date, broadband LAS diagnostics with fast time resolution can be grouped into two classes: (1) those employing broadly tunable CW light and (2) those employing ultrashort pulses. Regarding the former, vertical cavity surface-emitting lasers (VCSELs) [12,13] and rapidly tunable external-cavity quantum-cascade lasers (EC-QCLs) [14] have been utilized in the near-IR and mid-IR, respectively, to provide broadband (10s to 100s of  $\text{cm}^{-1}$ ) measurements of atomic and molecular absorbance spectra in combustion environments; however, such light sources are currently available at only a few central wavelengths. As a result, here we will focus on diagnostics employing broadband pulses within various architectures, namely, supercontinuum lasers (SCLs) [15,16], dual-frequency-comb

spectrometers (DFCS) [5,4], optical-parametric oscillators (OPOs), [3] and optical-parametric amplifiers (OPAs) [2,17–19].

Regarding SCLs, Sanders [15] utilized a femtosecond-laser-pumped SCL producing  $1000\text{ cm}^{-1}$  of bandwidth near  $1.56\text{ }\mu\text{m}$  to acquire temperature and species measurements at 50 kHz in gases at 10 bar. Similarly, Werblinski et al. [16] used an SCL with  $500\text{ cm}^{-1}$  of bandwidth near  $1.4\text{ }\mu\text{m}$  to acquire 10 kHz measurements of temperature, pressure and  $\text{H}_2\text{O}$  in a rapid compression machine (RCM) at pressures up to 65 bar. While the large bandwidth and repetition rate of such diagnostics are extremely attractive, SCL-based diagnostics are often limited by pronounced shot-to-shot intensity variations (requiring multi-shot averaging) and complexities associated with accurately modeling various instrument-broadening sources [20], particularly when dispersing fibers are used. More recently, DFCS has emerged as an effective tool for providing high-fidelity, broadband measurements of absorbance spectra with unprecedented spectral resolution. For example, Draper et al. [4] utilized a DFCS with  $160\text{ cm}^{-1}$  of bandwidth near 1660 nm to acquire 1.4 kHz measurements of temperature and  $\text{CH}_4$  at up to 30 bar inside of an RCM. However, DFCS also typically requires time-averaging to achieve high signal-to-noise ratio (SNR) and such diagnostics in the mid-IR are still emerging [5,21].

Last, the recent advent of high-speed, cryogenically cooled, mid-IR cameras has, in part, enabled the first single-shot, ultrafast (i.e., sub-nanosecond) absorption measurements in the mid-IR [2], as well as broadband absorption measurements with near-microsecond time resolution at 10s of kHz [3]. Regarding the latter, Loparo et al. [3] employed a mid-IR OPO which produced ultrashort pulses at 100 MHz to provide  $476\text{ cm}^{-1}$  of bandwidth near  $3.25\text{ }\mu\text{m}$ . This enabled the authors to acquire measurements of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  at 21.5 kHz in a shock tube at pressures near 2.5 bar. To date, this technique has demonstrated a measurement time resolution of  $37\text{ }\mu\text{s}$  (set by the integration time of the camera).

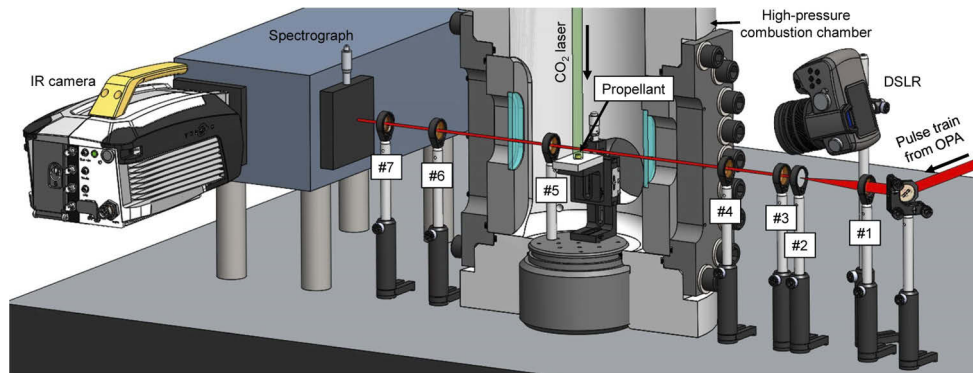
Here we build on our recent development of ultrafast laser-absorption spectroscopy (ULAS) [2] to provide the first single-shot, ultrafast, mid-IR measurements of temperature and species in high-pressure and multi-phase combustion gases. Further, we demonstrate for the first time that ULAS can provide 1D, single-shot, ultrafast measurements of temperature and species in a flame which represents a significant advancement beyond previously developed broadband LAS diagnostics. These new capabilities were made possible through advancements in the optical setups employed and several notable refinements to the spectral-modeling and -fitting procedures. This manuscript describes these advancements and the key principles of ULAS in detail. Additionally, a supplemental document discusses important practical considerations for spectral interpolation and imaging ultrashort pulses in the mid-IR.

## 2. Experimental setup

### 2.1. Optical setup

Figure 1 shows a schematic of the optical setup used for this work. Special attention is given to the new additions and modifications to the basic ULAS optical setup (described by Tancin et al. [2]) which enabled high-pressure and 1D measurements. The ultrafast-laser system (described in previous work [2,9,10,22]) consists of a Ti:sapphire oscillator which produces 55 femtosecond pulses centered near 800 nm at 80 MHz. The pulses were selectively amplified at 5 kHz to a pulse energy of 2 mJ and subsequently converted into the mid-IR using optical parametric amplification (OPA) and non-collinear difference-frequency generation (NDFG) to achieve a center wavelength near  $4.9\text{ }\mu\text{m}$  with a pulse energy of  $\approx 5\text{ }\mu\text{J}$ .

After wavelength conversion, a  $\text{MgF}_2$  Rochon-prism polarizer was used to attenuate the pulse energy to  $\approx 2\text{ }\mu\text{J}$ . Next, a spatial filter (optics #1, #2, and #3 in Fig. 1) was used to improve beam quality and reduce the  $1/e^2$  beam diameter to  $\approx 2\text{ mm}$ . The improved beam quality provided by the spatial filter improved the spectral resolution and SNR of the diagnostic. The latter of which ultimately enabled 1D measurements through eliminating the need for spatial (i.e., intrapulse)

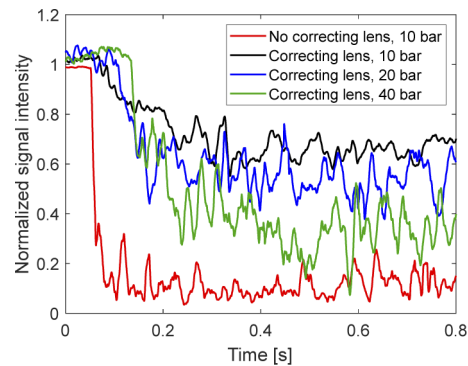


**Fig. 1.** Schematic illustrating the optical setup used to characterize propellant flames with ULAS.

averaging. The laser beam was then directed through the test gas within either a heated-gas cell or propellant flame. The transmitted pulses were then focused onto the input slit of a spectrograph (Andor Shamrock 500i) using a  $\text{CaF}_2$ , plano-convex, cylindrical lens with a focal length of 75 mm. The spectrograph employed a reflective diffraction grating to disperse the light onto the InSb FPA of a high-speed, infrared camera (Telops FAST-IR 2K). The IR camera can acquire at nearly 2 kHz at full-frame resolution (320 x 256) and faster when the resolution is reduced. A frame rate of 10 kHz can be reached at 256 x 52 resolution (what was used here) and a maximum of 90 kHz can be achieved at 64 x 4 resolution. In high-pressure propellant tests, images of single-shot spectra were averaged across the spatial dimension of the image to improve the measurement SNR. A high-resolution (300 lines/mm) diffraction grating providing  $10 \text{ cm}^{-1}$  of bandwidth (near  $5 \mu\text{m}$ ) and 0.3 nm resolution was used for propellant tests at atmospheric pressure. A low resolution (150 lines/mm) grating providing  $35 \text{ cm}^{-1}$  of bandwidth and 0.6 nm resolution was used for high-pressure propellant tests. Both gratings were used at all pressures for gas-cell tests.

Corrective optics were required in order to reduce the loss of signal from severe beam steering encountered in high-pressure propellant flames. Figure 2 illustrates that without corrective optics, complete loss of signal can occur from beam steering-induced angular deflections. These additional optics consisted of a lens telescope (optics #4 and #5 in Fig. 1) with focal lengths of  $f = 200 \text{ mm}$  and  $f = 25.4 \text{ mm}$  and a final lens (optic #6) with a focal length of 250 mm. The focal point of the lens telescope was centered at the propellant flame and acted to partially correct any angular deflections caused by beam steering, minimizing the loss of signal. The final lens aided in boosting signal counts by reducing the beam size incident on the focal plane array (FPA) of the IR camera. The improvements provided by the corrective optics are illustrated by Fig. 2, which shows the average signal counts with and without corrective optics for a variety of pressures.

For 1D, intrapulse measurements, more significant changes were required in order to improve the spatial resolution and measurement field-of-view. First, the recollimation lens used for the spatial filter (optic #3 in Fig. 1) was replaced with a 150 mm focal length lens such that the beam was expanded to over 1 cm in diameter. Next, optic #4 was replaced with a plano-convex,  $\text{CaF}_2$  cylindrical lens with a 200 mm focal length to focus the laser beam into a vertically oriented sheet on the centerline axis of the propellant flame. The beam was then recollimated using a similar cylindrical lens with a 75 mm focal length (optic #5). Finally, a plano-convex,  $\text{CaF}_2$  cylindrical lens (optic #6) with a 200 mm focal length (oriented to focus the beam in the vertical direction) was used to control the field of view of the imaging system.



**Fig. 2.** Average recorded laser intensity in AP-HTPB propellant flames both with and without corrective optics at a variety of pressures.

## 2.2. Gas-cell experiments

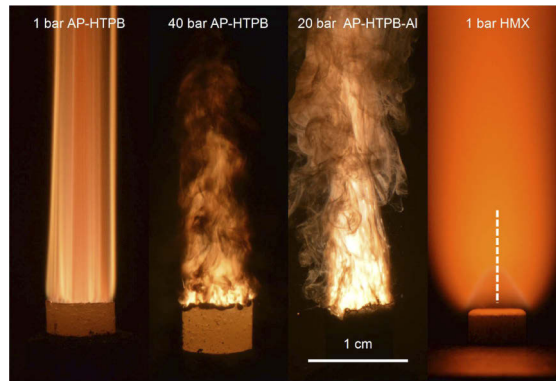
ULAS measurements were acquired in a high-uniformity, heated, static-gas cell (described by Schwarm et al. [23]) to validate the accuracy of the diagnostic at high temperature and pressure, as well as to determine the instrument response function (IRF) via a multi-spectrum fitting routine (MSFR) discussed in detail in Section 4.2. Spectra were measured in a mixture of 2% CO and 1.8% CO<sub>2</sub> by mole with a balance of nitrogen at  $1000 \pm 20$  K and pressures of 0.3, 1, 3, 10, 20, and 40 bar. The gas pressure was measured using a UNIK-5000 pressure transducer with a full-scale range of 0 to 70 bar and an accuracy of  $\pm 0.028$  bar. Temperature was measured using three type-K thermocouples with a nominal accuracy of 0.75% (at  $\geq 600$  K) fixed to the outside of the gas cell as in [23]. The gas cell was equipped with 15 cm long, wedged, CaF<sub>2</sub> rods which provided an absorbing path length of 9.4 cm at room temperature.

## 2.3. Laser-ignited propellant flames

Cylindrical propellant strands with a height of 4 to 6 mm and a diameter of 7 mm were tested. The particle size of ammonium perchlorate (AP) was distributed bimodally with mean diameters of 200  $\mu\text{m}$  and 20  $\mu\text{m}$  in a coarse-to-fine ratio of 4:1. In the aluminized propellants, Valimet H-30 aluminum with a mean particle diameter of 31  $\mu\text{m}$  was used. The AP-HTPB propellant consisted of 80% AP by mass, whereas the AP-HTPB-Al propellant was 68% AP, 15% aluminum and 17% binder by mass.

The propellant strands were ignited using a CO<sub>2</sub> laser providing an optical intensity of 38 W/cm<sup>2</sup> to the surface of the strand. The data acquisition system was triggered 100 ms prior to the CO<sub>2</sub> laser turning on to allow for the baseline laser intensity ( $I_0$ ) to be recorded. The CO<sub>2</sub> laser was turned on for 200 ms (400 ms at 1 bar) to ignite the strand. Video of each test was recorded with a Nikon D3200 DSLR camera to ensure that ignition and burning of each strand was uniform, and to provide an estimate of the absorbing path-length. The propellant flames reached a quasi-steady state approximately 100 ms after ignition. Figure 3 shows images of the propellant flames acquired using the DSLR camera.

All propellant tests were conducted in a high-pressure combustion chamber (HPCC), described in detail by Tancin et al. [24]. The ULAS beam was aligned through the centerline of the propellant for all tests. Measurements were acquired at a height of 2 mm and 1 cm relative to the initial surface location of the propellant strand for non-aluminized and aluminized propellants, respectively. Prior to each test, the chamber was evacuated using a vacuum roughing pump before being pressurized with an argon bath gas. A time history of pressure was recorded during each test enabling the data-processing routine to use an updated pressure for each subsequent laser



**Fig. 3.** DSLR images of laser-ignited AP-HTPB propellant flames at atmospheric- and high-pressure, without aluminum (left two panels) and with aluminum (middle-right panel). An image of an HMX propellant flame is shown (right) along with a dashed line representing the approximate field-of-view of the 1D ULAS measurement.

shot. The gas pressure increased by  $\approx 0.6$  bar during each test. For tests at atmospheric pressure, the HPCC vent valve was partially opened immediately prior to ignition, such that no pressure rise occurred during the test.

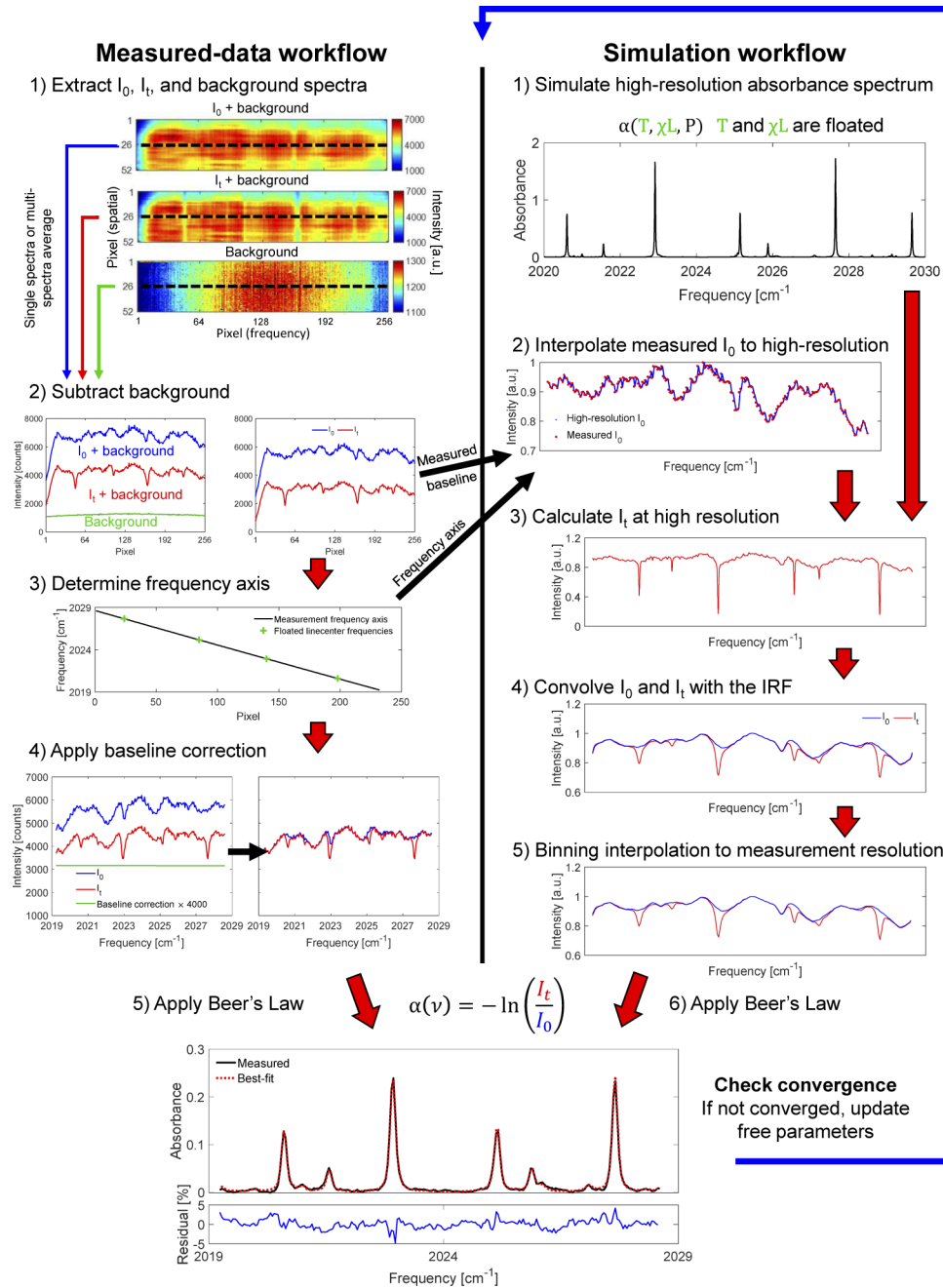
Proof-of-concept, 1D-resolved, single-shot temperature and CO measurements were acquired in an HMX (i.e., 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane) flame. The HMX was pressed into cylindrical pellets which were 6 mm in diameter and 4 to 5 mm tall. For this test, the  $\text{CO}_2$  laser was left on for the full duration of the experiment. The HMX experiment was conducted in air.

### 3. High-fidelity modeling and spectral-fitting of ULAS spectra

This section provides a detailed description of the data-processing and spectroscopic modeling procedures used to infer gas properties from ULAS measurements of transmitted intensity spectra. In essence, a nonlinear least-squares fitting routine is used to fit simulated absorbance spectra to measured absorbance spectra. There are two workflows: (1) processing measured data and (2) simulating absorbance spectra which are described below and illustrated in Fig. 4.

The procedure for processing measured spectra consists of five key steps.

1. Acquire images of  $I_0$ , transmitted laser intensity ( $I_t$ ) and background emission.
2. Subtract the appropriate background from images of  $I_0$  and  $I_t$ . In propellant-flame experiments, the time-varying background was measured between successive laser-shots by acquiring images at twice the repetition rate of the laser.
3. Assign a frequency axis to the measured spectra. Spectra are extracted from images of  $I_0$  and  $I_t$  in the form of a vector. The indices corresponding to 4 or 5 prominent spectral features (e.g., the linecenter of a strong transition) are assigned frequencies which are free parameters in the spectral-fitting routine. These “control points” allow a complete frequency axis to be mapped to the measured spectrum through cubic-spline interpolation. Cubic-spline interpolation is preferred over a linear or higher-order polynomial interpolation because the former doesn’t account for slight nonlinearities in the frequency axis and the latter often leads to instability in the fitting routine.
4. Adjust the baseline laser intensity in order to account for shot-to-shot laser fluctuations and non-absorbing transmission losses. These fluctuations exhibit a weak wavelength dependence and are accounted for by multiplying  $I_0$  by a linear correction factor. Higher



**Fig. 4.** Flowchart for the spectral-fitting routine used to infer gas properties from ULAS measurements.

order corrections may yield slightly smaller residuals, but risk coupling with other free parameters and introducing error into the measurements [8].

5. Apply Beer's Law to calculate the measured absorbance spectrum ( $\alpha_{meas}$ ).

The simulation-side workflow consists of six key steps described below and in Fig. 4 (right). These steps were chosen to faithfully capture the physics which govern the optical setup and data-acquisition system. Subscripts "HR" and "conv" indicate high spectral resolution and post-convolution with the IRF, respectively.

1. Simulate an absorbance spectrum ( $\alpha_{HR}$ ) at high resolution (e.g.,  $\leq 0.001 \text{ cm}^{-1}$  for CO at 1 atm) using the methods described by Goldenstein et al. [25]. Here, the pertinent spectroscopic parameters were taken from the HITEMP 2019 database [26]. Gas properties (temperature ( $T$ ), absorbing species column density ( $\chi_{abs}L$ ), and, when relevant, pressure ( $P$ )) are free parameters in the fitting routine.  $\text{H}_2\text{O}$  was also included in the spectral simulations to account for weak interference within the interrogated wavelength band. Collisional-broadening parameters of CO lines by  $\text{H}_2\text{O}$  were taken from Hartmann et al. [27].
2. Linearly interpolate an empirically determined spectrum of  $I_0$  to the same resolution as  $\alpha_{HR}$ , yielding  $I_{0,HR}$ . Similarly, the high-resolution frequency axis is interpolated from the low-resolution frequency axis determined in step 2 on the measurement side.
3. Generate a high-resolution spectrum of transmitted intensity ( $I_{t,HR}$ ) with Beer's Law using  $\alpha_{HR}$  and  $I_{0,HR}$ .
4. Convolve  $I_{t,HR}$  and  $I_{0,HR}$  with the instrument response function to account for instrument broadening, yielding  $I_{t,HR,conv}$  and  $I_{0,HR,conv}$ , respectively. In our prior work, parameters governing the shape of the IRF were floated in the fitting routine [2,9,10,22], however, here they were determined from the multi-spectrum fitting routine (discussed in Section 4) and held fixed during spectral-fitting.
5. Interpolate  $I_{t,HR,conv}$  and  $I_{0,HR,conv}$  back to the lower spectral resolution of the data (yielding  $I_{t,conv}$  and  $I_{0,conv}$ , respectively) using the binning interpolation method (See Supplement 1).
6. Use Beer's law to calculate the simulated spectral absorbance ( $\alpha_{sim}$ ) from  $I_{t,conv}$  and  $I_{0,conv}$ .

Last,  $\alpha_{sim}$  and  $\alpha_{meas}$  are compared by the nonlinear least-squares fitting routine to determine if the fit has converged. A function tolerance of  $\leq 10^{-4}$  was used to define convergence, according to MATLAB's "lsqcurvefit" function. If the convergence criteria has not been met, the procedure is repeated with new parameters until convergence.

## 4. Determination of instrument-broadening parameters

### 4.1. Background

Accurate knowledge of line-broadening effects is crucial for correctly modeling measurements of absorption spectra, and hence, for accurate ULAS measurements of gas properties [6,28,29]. The broadening (or narrowing) of an absorption feature is due to a combination of physical (e.g., collisional broadening, Doppler broadening) and instrumental (e.g., the slit function of spectographs, spectrometers, or monochromators) broadening sources. Challenges arise when the FWHM of instrument-broadening sources are similar to, or greater than that of physical broadening sources, in which case error in one or the other can lead to inaccurate determination of gas properties.

Instrument-, Doppler-, and collisional-broadening have been the dominant sources of line-broadening in the ULAS measurements acquired to date [2,9,10,22]. The Doppler broadening FWHM ( $\Delta\nu_D$ ) has had the least uncertainty for given gas conditions, as it is only a function of molecular weight, temperature and linecenter frequency, which are either measured or relatively well known. The uncertainty in collisional-broadening FWHM ( $\Delta\nu_C$ ) was much greater, due to uncertainty in both bath gas composition (e.g., in flames) and in collisional-broadening coefficients within databases. Often, this uncertainty is accounted for in spectral-fitting routines by floating either a scalar multiplier on all  $\Delta\nu_C$  or floating  $\Delta\nu_C$  directly for a sufficiently small number of lines [6]. Initially, instrument-broadening parameters were floated during the processing of ULAS measurements. However, simultaneously floating the IRF and collisional-broadening half-widths in the nonlinear fitting routine may be unsuitable due to the similar effect they have on transition lineshapes, and the high dispersion per data point (i.e., few pixels per absorption transition) which makes measurements insensitive to subtle differences in lineshapes. Potentially, the fitting routine may converge on incorrect values for both instrument and collisional-broadening parameters and result in substantial errors in measured gas properties. Therefore, it can be necessary to determine the IRF elsewhere so it can be held fixed in the spectral-fitting routine. In our experience, this is most critical when the measured absorbance spectrum does not possess a wide variety of linewidths, as is the case for the ULAS measurements in CO's P-branch at a single temperature or pressure.

There are numerous methods for determining the IRF of a spectrograph with a given optical setup. One of the most common is to measure the IRF through fitting a model to measurements of well known spectra [30]. Another technique, is to measure the IRF directly by using a sufficiently narrowband (relative to the IRF FWHM) reference source such as a narrowband laser, low-pressure hollow-cathode lamp or a narrow, well-characterized absorption line [28]. The IRF may also be inferred in the case of a reference source with a non-negligible but well characterized linewidth [31]. That said, these methods were not deemed suitable for high-accuracy ULAS measurements. As a result, a multi-spectrum fitting routine (MSFR) was used to determine instrument-broadening parameters.

#### 4.2. Multi-spectrum fitting routine

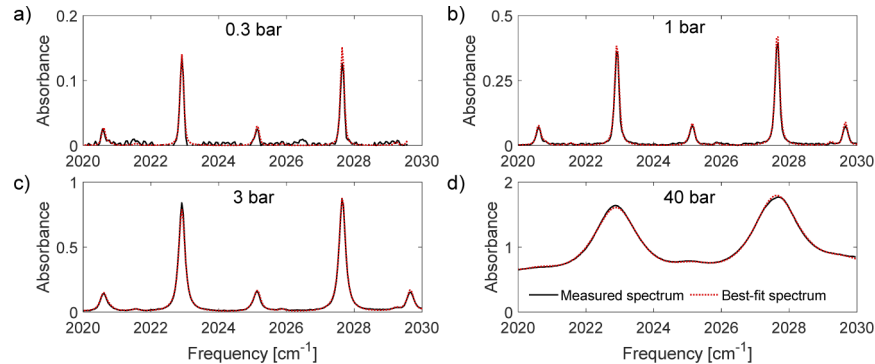
In this work, the IRF was determined by applying an MSFR to ULAS data acquired at a variety of known gas conditions. The MSFR simultaneously fit multiple simulated absorbance spectra to absorbance spectra measured at multiple pressures while floating a single set of IRF parameters and a single correction factor for all  $\Delta\nu_C$ . The latter was done to account for uncertainty in the collisional-broadening parameters. Simultaneously fitting simulated spectra to data acquired at vastly different pressures allowed for more accurate and robust determination of instrument- and collisional-broadening parameters by decreasing the total number of free parameters per spectrum [32], and by decoupling the effects of instrument- and collisional-broadening. For example, spectra acquired at sufficiently low pressure are dominated by instrument broadening and are comparatively insensitive to errors in collisional-broadening parameters, while this effect is reversed at high pressure.

In the MSFR, the IRF was modeled by Eq. (1) which represents the weighted sum of Gaussian and Lorentzian functions, with the FWHM and lineshape weighting (proportion of the lineshape which is Lorentzian vs. Gaussian) floated as free parameters.

$$\phi_{IRF}(\lambda) = w\phi_L(\lambda, FWHM) + (w - 1)\phi_G(\lambda, FWHM) \quad (1)$$

Here,  $\phi_G$  and  $\phi_L$  are Gaussian and Lorentzian lineshapes, respectively, both with integrated areas of one,  $w$  is the lineshape weighting parameter,  $\lambda$  is the wavelength and  $\phi_{IRF}$  is the IRF lineshape. Collisional-broadening coefficients for CO-CO<sub>2</sub> and CO-N<sub>2</sub> were taken from Hartmann et al. [27]. A global scaling factor for  $\Delta\nu_C$  was floated in the fitting routine as well.

The frequency axis and a linear baseline correction were floated for each spectrum according to the data-processing procedure described in Section 3, while temperature, pressure, and absorbing species concentration were held constant at their known values. Absorbance spectra measured at 0.3, 1, 3, and 40 bar within a heated-gas cell (described in Section 2.2) were used for the MSFR. The residuals of each measured spectrum and best-fit were normalized by the peak absorbance to mitigate bias towards spectra with larger absorbance values. Figure 5 shows the measured and best-fit absorbance spectra determined by the MSFR for data acquired with the 300 lines/mm grating.



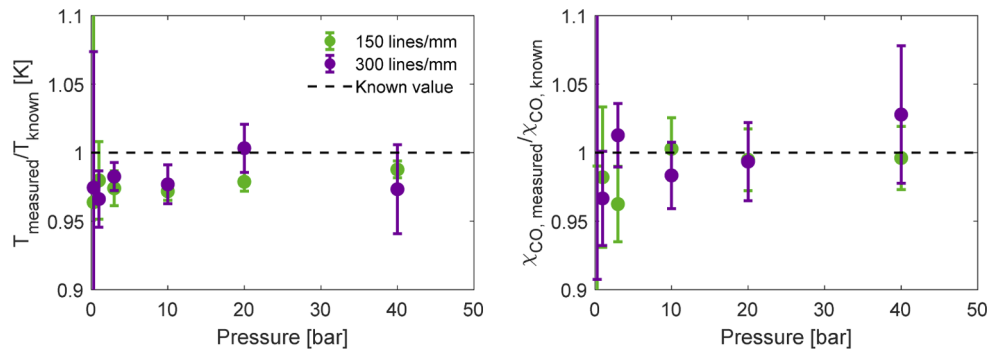
**Fig. 5.** Measured and best-fit absorbance spectra of CO acquired in a heated-gas cell at  $1000 \pm 20$  K using a 0.3 nm resolution grating. Each best-fit spectrum was determined simultaneously using the MSFR. Spectra at (a) 0.3 bar, (b) 1 bar, (c) 3 bar, and (d) 40 bar are shown.

For data acquired with the 150 lines/mm grating, the MSFR returned a value of 0.520 nm for the IRF FWHM and an instrument lineshape which was 48.3% Lorentzian. For the 300 lines/mm grating, the MSFR converged on an IRF FWHM of 0.297 nm and an instrument lineshape which was 61.5% Lorentzian. These values compare relatively well to the gratings' theoretical resolutions (0.21 and 0.61 nm for the high and low resolution gratings, respectively), albeit, assuming a Gaussian IRF. The value for the scaling factor on  $\Delta\nu_C$  was 0.91 for both gratings.

The accuracy of the parameters obtained by the MSFR were validated by processing data taken at each pressure individually according to the standard one-at-a-time data-processing procedure, with instrument-broadening parameters held fixed at the values determined by the MSFR. However, the factor on  $\Delta\nu_C$  was floated for consistency with flame measurements where bath gas composition and pressure may not be known to high accuracy. Figure 6 illustrates the accuracy of the results. All measurements were either within 5% of the known value, or within the bounds of the 95% confidence intervals.

It is vital that the broadening parameters determined by the MSFR are valid outside of the dataset used in the MSFR. To test this, all heated-gas cell measurements were repeated 2 months later after the optical setup had been dismantled and rebuilt. The datasets were processed using the same instrument-broadening parameters as earlier (i.e., the MSFR was not rerun for these datasets). Gas properties were once again within 5% of the known values, with the known value falling within the 95% uncertainty bounds for most measurements.

For comparison, IRF parameters were also measured, using a quantum-cascade laser (QCL) as a reference source. The QCL emitted near  $4.8 \mu\text{m}$  and had a negligible linewidth ( $\approx 1$  MHz) compared to the IRF of the spectrograph. The laser beam was focused into the spectrograph using the same optical setup as was used for ULAS measurements in heated-gas cell and propellant-flame tests. IRF parameters were then determined by fitting Eq. (1) to the measured spectrum using a nonlinear fitting routine. The best-fit IRF FWHMs were 0.25 nm and 0.54 nm



**Fig. 6.** Temperature and CO concentration measurements normalized to their known values acquired in a heated, static-gas cell at 1000 K.

for the 300 lines/mm and 150 lines/mm gratings, respectively, which agree with values from the MSFR to within 4% and 16%. The slight disagreement compared to the MSFR can be explained by the low resolution of these QCL measurements (only 3-4 data points per spectrum) which makes them less robust.

#### 4.3. Discussion of results

The accuracy of the MSFR is supported by four key findings. (1) The broadening parameters determined through the MSFR enabled gas-cell validation measurements of temperature and absorbing species concentration which were within 5% of the known values at pressures from 0.3 to 40 bar. (2) This accuracy was shown to be repeatable after rebuilding the optical setup. (3) The scaling factor on  $\Delta\nu_C$  returned by the MSFR was the same for both of the grating resolutions which was, in turn, consistent with broadening uncertainties reported in the literature [1]. (4) Last, the IRF FWHM agrees relatively well with values which were measured directly using a QCL.

## 5. Experimental results and discussion

### 5.1. Validation tests

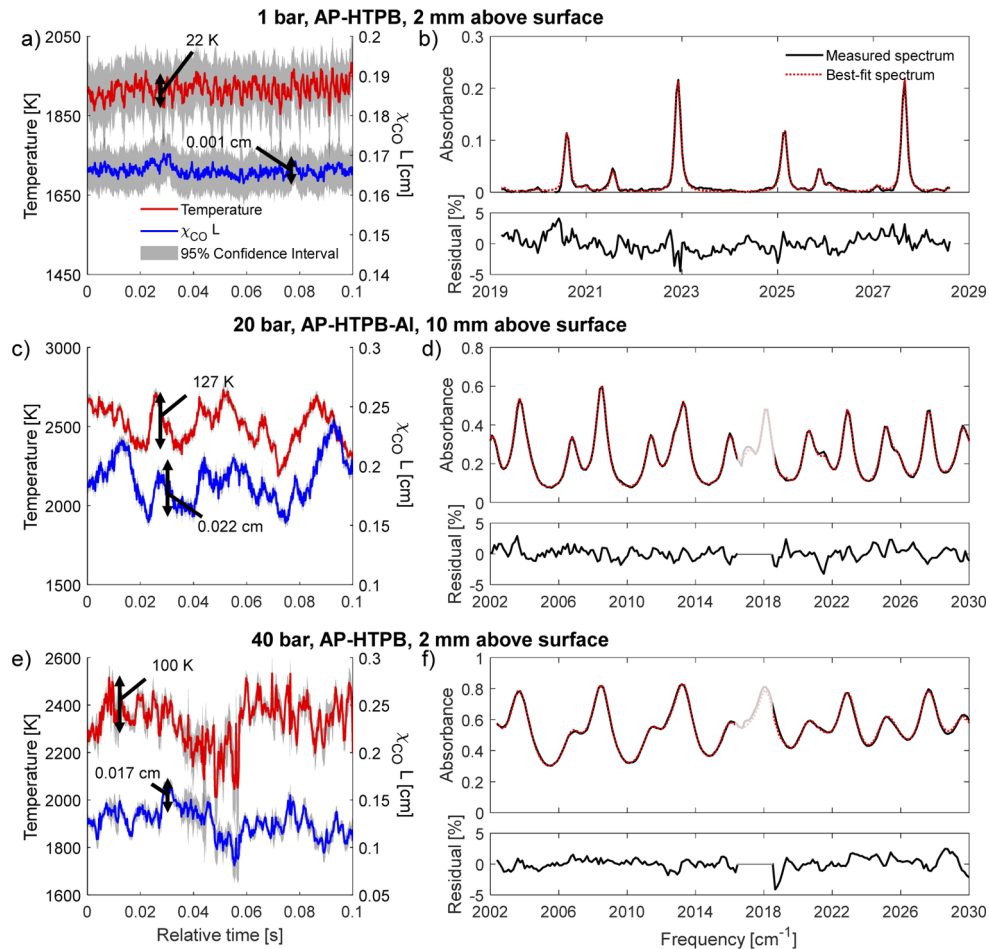
The accuracy of the ULAS diagnostic was validated at high temperature using the heated-gas cell data discussed in Section 4. Measurements of temperature and CO mole fraction were validated at  $1000 \pm 20$  K and 0.3, 1, 3, 10, 20, and 40 bar. Instrument-broadening parameters were determined from the MSFR and held fixed for consistency with flame measurements. The results normalized to the known value are shown in Fig. 6.

The ULAS measurements of temperature and CO mole fraction demonstrated high accuracy across a broad range of pressures, with values all falling within 5% of the known value and most within the bounds of the 95% confidence intervals. At 0.3 bar, the accuracy was lower compared to the high-pressure cases which was due to low signal levels.

### 5.2. Characterization of AP-HTPB propellant flames

Figure 7 shows measured time histories of temperature ( $T$ ) and CO column density ( $\chi_{\text{CO}}L$ ) as well as representative examples of measured and best-fit absorbance spectra acquired in laser-ignited AP-HTPB flames at 1 and 40 bar and an AP-HTPB-Al flame at 20 bar. The spectra illustrate the high SNR of the measurements and, for all data sets, excellent agreement between the measured and simulated spectra, thereby supporting the accuracy of the spectroscopic model and fitting routine employed. The  $1-\sigma$  precision of the baseline noise level in absorbance was 0.003, 0.007

and 0.01 for the results shown in Fig. 7(b), 7(d) and 7(f), respectively. The time-averaged temperatures (1926 K at 1 bar and 2326 K at 40 bar) and CO mole fractions (0.2135 at 1 bar and 0.2138 at 40 bar) were slightly lower than constant enthalpy and pressure (HP) equilibrium calculations (i.e., 2417 K and 0.273 at 1 bar and 2483 K and 0.275 at 40 bar) [33]. Usable data was collected from every laser shot (i.e., there was no need to throw out “bad” data).

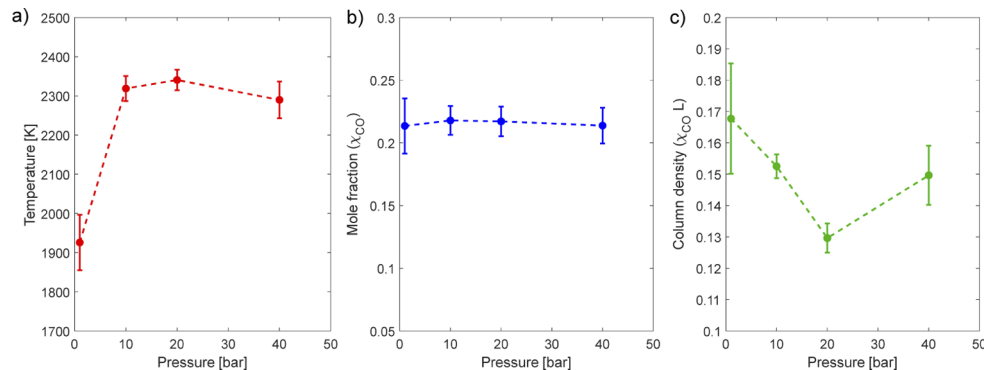


**Fig. 7.** Samples of measured time histories of temperature and  $\chi_{CO} L$  (a, c, e) as well as representative measured and best-fit absorbance spectra of CO with residuals (b, d, f) acquired in propellant tests. The shaded out portion of the spectra shown in d) and f) was ignored by the spectral-fitting routine due to interfering absorption by H<sub>2</sub>O in the ambient air outside the combustion chamber.

95% confidence intervals for temperature and  $\chi_{CO} L$  are plotted along with the measured time histories in Fig. 7(a), (c), and (e). The corresponding 95% confidence intervals for temperature and  $\chi_{CO} L$  were 150 K and 0.01 cm for AP-HTPB at 1 bar, 61 K and 0.01 cm for AP-HTPB-AI at 20 bar, and 93 K and 0.02 cm for AP-HTPB at 40 bar. Larger uncertainty was observed during the 1 and 40 bar tests. At 1 bar, this is explained by the comparatively low signal, and narrow transition FWHMs (i.e., fewer data points per transition), which increased the uncertainty in fit, even with the higher-resolution grating being used. At 40 bar, non-absorbing transmission losses were the greatest of all tests due to severe beam steering, thereby, decreasing measurement SNR and increasing measurement uncertainty.

All of the time histories (see Fig. 7(a),(c),(e)) exhibit some unstructured variation in time, consistent with mild to moderate unsteadiness in general flame structure, which is supported through visual imaging of the flames (e.g., see Fig. 3), particularly at high pressure. For example, measurements of temperature exhibited a  $1\text{-}\sigma$  variation of 22 K, 127 K, and 100 K at pressures of 1, 20, and 40 bar, respectively. Similarly, the  $1\text{-}\sigma$  variation in  $\chi_{CO}L$  was 0.0012, 0.022, and 0.017 cm for pressures of 1, 20 and 40 bar, respectively. When accounting for the time-variation in gas properties (through subtracting the data from a 10-point moving average), the  $1\text{-}\sigma$  precisions at 1, 20 and 40 bar were 0.90%, 0.91%, and 1.6%, respectively, of the measured value for temperature and 0.45%, 2.0%, and 3.7% for  $\chi_{CO}L$ . Encouragingly, the results suggest that the addition of 15% aluminum and, presumably, other metals into the propellant mixture does not significantly affect the performance of the diagnostic, thereby paving the way for future studies of metallized-propellant flames at rocket-motor-relevant pressures.

Figure 8 shows the time-averaged ( $\approx 0.1$  s average) values of temperature and  $\chi_{CO}$  at a measurement location 2 mm above the burning surface of the AP-HTPB propellant at each test condition. The measured temperature generally increased with increasing pressure, with the largest temperature rise occurring between 1 and 10 bar which is consistent with predictions from constant enthalpy and pressure (HP) equilibrium calculations. In comparison, pressure did not have a detectable impact (i.e., greater than measurement uncertainty) on CO concentration. The average value of  $\chi_{CO}$  was near 0.22 for all cases. This trend, or more accurately lack thereof, in CO concentration with pressure is also supported by HP equilibrium calculations.



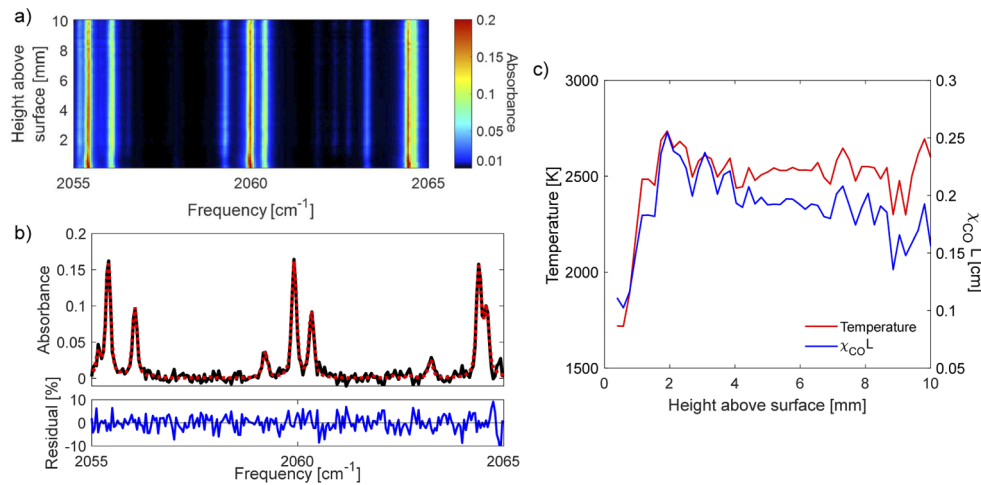
**Fig. 8.** Time-averaged temperature (a),  $\chi_{CO}$  (b), and  $\chi_{CO}L$  (c) measured 2 mm above the propellant surface in AP-HTPB flames. The uncertainty bars represent the 95% confidence intervals, which account for uncertainty in the best-fit spectra, instrument-broadening parameters, and, for  $\chi_{CO}$ , path length.

The lower than expected measured temperatures were likely due to a combination of heat loss, insufficient time and space for the product gas to fully reach equilibrium, and the path-integrated nature of the measurements [22]. The slightly lower than expected CO mole fractions were also likely affected by the product gas not fully reaching equilibrium (note the presence of large amounts of soot in Fig. 3), as well as the substantial uncertainty in the absorbing path length. Notably, the measured CO mole fractions agree well with other LAS measurements in the literature [33].

### 5.3. 1D ULAS measurements in an HMX flame

One-dimensional, intrapulse ULAS measurements were acquired in a laser-ignited HMX flame to demonstrate ULAS's ability to provide single-shot imaging of gas properties. Measurements were processed without any row (i.e., spatial) averaging, such that 52 transmitted intensity spectra were acquired with each laser pulse. The best-fit absorbance spectra from a single laser pulse

acquired during steady-state burning are plotted as a function of height in Fig. 9(a). This image showcases the stability of the measurement across the approximately 1 cm tall field-of-view (see Fig. 3). A representative measured and best-fit absorbance spectrum is shown in Fig. 9(b), which illustrates a good quality of fit despite the reduced measurement SNR from the lack of row averaging. One-dimensional profiles of temperature and  $\chi_{CO}L$  are shown in Fig. 9(c). Temperature and  $\chi_{CO}L$  measurements are lower closer to the surface of the HMX pellet where decomposition products of HMX have not yet been fully combusted. Temperature and  $\chi_{CO}L$  rise sharply until the gas reaches equilibrium conditions near 2600 K and 0.21 cm, respectively. These values, while slightly lower than the adiabatic flame temperature, are consistent with previous measurements of CO-based temperature and CO using similar wavelengths [2,24]. Notably,  $\chi_{CO}L$  is seen to decrease as a function of height further above the flame, which is likely due to the further oxidation of CO by ambient air which is entrained into the flame.



**Fig. 9.** 1D resolved, single-shot measurements acquired in a laser-ignited HMX flame burning at quasi steady-state,  $\approx 0.07$  s after ignition. a) Image of best-fit absorbance spectra as a function of height relative to the initial surface location of the HMX pellet. b) Representative measured and best-fit spectra corresponding to a height of  $\approx 6$  mm. c) Single-shot 1D temperature and  $\chi_{CO}L$  profiles.

## 6. Measurement uncertainty

Uncertainty in measured gas properties was analyzed from three sources: (1) the instrument-broadening parameters, (2) noise in the measured spectra, and (3) the absorbing path length. Uncertainty in instrument-broadening parameters was quantified by calculating the 95% confidence interval for each parameter using the covariance matrix returned by the MSFR. A Monte Carlo method was used to capture the complex and nonlinear relationship between the IRF parameters and inferred gas properties. Values for the IRF parameters were chosen as Gaussian random variables with the mean and standard deviation determined from the 95% confidence intervals. The spectral-fitting routine was then run for 100 trials at each pressure and grating resolution, resulting in distributions of inferred gas properties which were determined to be normal by the Shapiro-Wilk test with a p-value of 0.05. 95% confidence intervals from uncertainty in instrument broadening were thus determined from these distributions. For flame measurements, this was done for a single spectrum chosen soon after the flame reached steady state, and the value for uncertainty was assumed constant for the rest of the spectra acquired during steady-state burning. Uncertainty in inferred gas properties due to noise in the measured spectra for the

one-at-a-time fitting routine were similarly calculated from the covariance matrix. Uncertainty in the absorbing path-length was set at 2% for gas cell experiments based on the perceived error in the length of the CaF<sub>2</sub> rods, uncertainty in the thickness of the epoxy seal for the rods, and the uncertainty in thermal expansion of the gas cell and CaF<sub>2</sub> rods at high temperatures [23]. For flame experiments, the uncertainty in absorbing path length was determined from simultaneous visual imaging, and estimated to be 10% of the measurement. The uncertainty from all sources were added in quadrature to yield the total uncertainty for the gas properties. The calculated 95% confidence intervals are shown in Fig. 6 and Fig. 7.

## 7. Conclusions

This work presented the extension of ULAS to calibration-free, single-shot measurements of temperature and CO across a broad range of pressures, and demonstrated the first 1D, single-shot ULAS measurements of temperature and species in a flame. Numerous improvements in the optical setup and the data-processing routine made these advancements possible. Notably, an MSFR was utilized to accurately determine IRF parameters which enabled rigorous validation of the diagnostic across a wide range of pressures and a combination of spatial filtering and corrective optics improved the SNR of the measured spectra. Collectively, these results demonstrate that ULAS can be used for high-fidelity characterization of a variety of combustion environments with improved temporal and spatial resolution.

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**Disclosures.** The authors declare no conflicts of interest.

**Data availability.** Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

**Supplemental document.** See [Supplement 1](#) for supporting content.

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