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Laser absorption of carbon dioxide at the vibrational bandhead near 4.2 μm in high-pressure rocket combustion environments

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A novel laser absorption sensing strategy has been developed to evaluate combustion progress through quantitative measurements of carbon dioxide (CO_2) in high-pressure (> 50 atm), high-temperature (> 3000 K) hydrocarbon-fueled rocket combustion flows. The sensor enables a broad range of operability by probing rovibrational transitions in the bandhead of CO_2 near 4.2 μm, accessed with an interband cascade laser. Under extreme rocket conditions, this targeted bandhead region experiences line-mixing effects that favorably distort the molecular spectra. A preliminary spectroscopic model of line-mixing effects has been developed utilizing a high-enthalpy shock tube to achieve scalability of spectral simulations over a range of high temperatures and high pressures. The model is employed for quantitative interpretation of measured absorption signals. The mid-infrared light source was fiber-coupled for remote light delivery at propulsion test facilities. A wavelength modulation spectroscopy technique utilizing normalized-second harmonic detection was implemented for acquiring differential absorption signals in a harsh rocket combustor environment. Using this method, measurements of CO_2 concentration have been demonstrated over a range of operating conditions up to 83 bar in a single-element-injector RP-2/GOx rocket combustor at the Air Force Research Laboratory in Edwards, CA.

I. Nomenclature

T	=	temperature
P	=	pressure
X_i	=	mole fraction of species, i
v	=	lower state vibrational quantum number
J	=	lower state rotational quantum number
$R_{M\to N}$	=	population transfer rates from state M to state N
a_i	=	MEG law coefficients
E_i''	=	lower state energy level of transition, i
k	=	Boltzmann constant
WMS	=	wavelength modulation spectroscopy
$2f/1f$	=	normalized second harmonic
MR	=	mixture ratio

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II. Introduction

Evaluation of combustion performance is key in the development of liquid-propellant rocket engines. Temperature and species measurements inside a rocket combustion chamber provide insight on combustion performance by directly reflecting chemical to thermal energy conversion. Unfortunately, the extreme thermodynamic operating conditions associated with these systems (T > 3500 K, P > 50 bar) confound such measurements with most sensing methods. In order to develop diagnostic capability in such harsh environments, our research group has put sustained effort in advancing laser absorption spectroscopy (LAS) sensing techniques for high-pressure combustion flows. Our initial effort targeted the fundamental vibrational band of carbon monoxide (CO) near 4.9 μm, which enabled successful species measurements up to 70 bar. However, at higher pressures, a reduction in differential absorption signal due to collisional broadening created an inherent pressure limitation [1]. In order to extend pressure capability, a subsequent strategy involved probing the first overtone bandhead of CO near 2.3 μm, where spectral narrowing effects occur due to line mixing. The line-mixing effect causes the transfer of spectral intensity from weak absorption regions to strong absorption regions, which leads to pronounced differential absorption. This novel strategy enabled successful CO measurements up to 105 bar [2]. Here, we describe the development of a new laser absorption spectroscopy sensing strategy that exploits rovibrational transitions of nascent carbon dioxide (CO_2) near 4.2 μm for a complementary species measurement. Similar to the CO bandhead near 2.3 μm, spectral narrowing effects from line mixing are exploited at the targeted region under extreme combustion conditions, which enables a broad range of pressure operability and provides the basis for a multi-species assessment of combustion performance.

III. Spectroscopic Approach

The high-temperature, fuel-rich conditions of hydrocarbon-fueled rockets produce a large fraction of infrared active species in the equilibrium combustion product mixture, including water (H_2O), carbon monoxide (CO), and carbon dioxide (CO_2). These major species provide an indication of combustion completion that correlates to thermal efficiency. Among these species, carbon monoxide has the smallest collisional cross-section and therefore is most resilient to collisional broadening, motivating the focus of our previous work. Carbon dioxide has a larger collisional cross-section than carbon monoxide and broadens moreso with pressure, historically yielding lower pressure limits (< 20 atm) for LAS combustion diagnostics [3, 4].

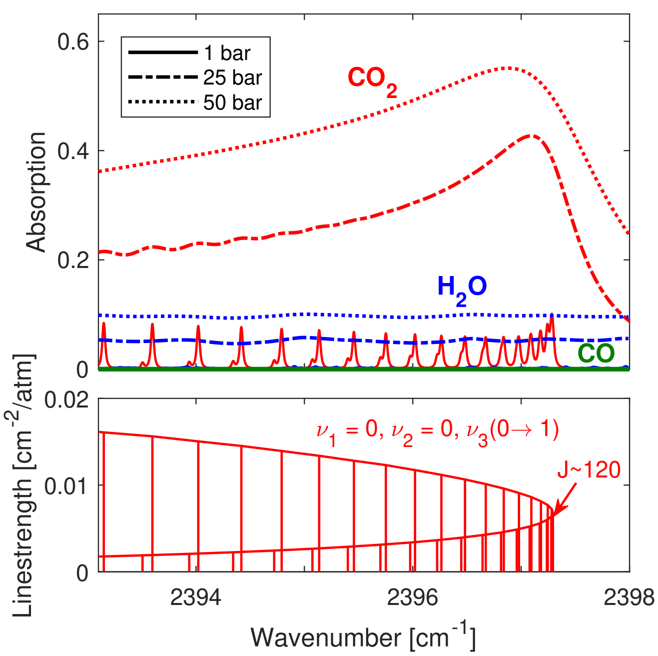

Fig. 1 Target CO_2 absorption spectra with relevant interferers and corresponding line-strengths (HITEMP: T = 3500 K, X_{CO} = 0.30, X_{CO_2} = 0.10, X_{H_2O} = 0.30)

The CO_2 fundamental vibrational bandhead near 4.2 μm has been selected for species measurements in this work by consideration of the following criteria: (1) strong differential absorption and (2) minimal interference with other combustion species. Figure 1 illustrates the simulated absorption near the targeted spectral region with other combustion species over a range of pressures. Line positions and intensities are shown below the absorption simulation and highlight the unique features of the selected region at extreme temperatures. Vibrational and rotational energy coupling distorts line spacing and causes lines within a branch to appear to 'wrap-around', resulting in a spectrally dense region known as a bandhead. Spectral line mixing occurs when intermolecular collisions are sufficiently numerous and strong (inherent to high pressures), such that absorption transitions are no longer collisionally isolated. Under these conditions, collisions induce energy level population transfers between neighboring transitions in close proximity. As a result of the diminished line spacing, line mixing acutely impacts the bandhead at extreme pressures. Generally, line mixing favors intensity transfers from weak absorption regions to strong absorption regions, causing narrowing of spectral structures [5]. The spectral narrowing effect promotes larger differential absorption countering pressure limitations associated with collisional broadening.

In order to simulate spectra with line-mixing effects, collision-induced population transfer rates between different rotational energy states must be accounted. Several empirical rate laws for modeling population transfer rates $R_{M\to N}$ have been developed. In this work, a modified-exponential-gap (MEG) law, shown in Eq. 1, has been implemented based on our analogous work with CO [2, 6, 7].

$$R_{M\to N} = a_1(T)\left[\frac{1 + a_4(E''_M/a_2kT)}{1 + a_4(E''_M/kT)}\right]^2 \times \exp\left[\frac{-a_3(E''_N - E''_M)}{kT}\right] \quad (1)$$

$E''_{M,N}$ is the lower state energy of rotational level M and N and $a_i(i = 1,2,3,4)$ are empirical MEG law coefficients. It is important to note that the MEG law coefficient $a_1(T)$, specifically, is the only free parameter that is temperature dependent, following a power law. These coefficients can be determined by implementing a least-squares fitting routine to experimental absorption data, which is outlined in Sec. 4. A more detailed discussion is provided in a previous work by our research group [8].

IV. Methodology

As mentioned in Sec. 3, the targeted spectral region near 4.2 μm is prone to line mixing at rocket combustion conditions. The initial task in sensor development was to develop an accurate line-mixing model at relevant conditions. Accordingly, studies were conducted on a high-enthalpy shock tube (HEST) facility at the University of California, Los Angeles (UCLA). Scanned-wavelength direct absorption measurements were performed at pressures and temperatures ranging from 15–60 bar and from 2000–3000 K (limiting dissociation of CO_2 into CO) in an argon bath gas.

Figure 2 shows a comparison between representative experimental data and a HITEMP-based model (that excludes line mixing) over a range of pressures. Spectral narrowing effects and amplification of the differential absorbance is clearly observed in the measurement data. The HITEMP-based spectroscopic model shows poor agreement near the spectrally dense bandhead, where most population transfer occurs. In order to account for this non-ideal phenomena, the aforementioned MEG law was implemented to model line mixing in the spectra. The MEG law coefficients, $a_i(i = 1,2,3)$, and the temperature dependence of $a_1(T)$ were obtained by implementing a least-squares fitting routine to the experimental shock tube data. a_4 describes collision duration and was set to $a_4 = 2$ based on previous works [9, 10]. To validate the model, the prescribed MEG law coefficients were then utilized to simulate the spectra over a range of conditions. Figure 2 illustrates excellent agreement between the line-mixing model and measurement data, highlighting the model's scalability with temperature and pressure. By validating the line-mixing model in high-temperature/high-pressure shock tube experiments, we can more confidently employ the model for quantitative interpretation of absorbance-based data from field testing.

For accurate interpretation of rocket combustor measurements, species-dependent collisional broadening and line-mixing coefficients have to be accounted for. In this work, species-specific broadening parameters available in literature [11, 12] were utilized to scale the CO_2-Ar broadening coefficients and population transfer rates obtained from the shock tube facility, as done in a previous study [13]. Chemical equilibrium was assumed to govern mixture composition at a given rocket combustor operating condition for the purposes of weighting the broadening and line-mixing coefficients.

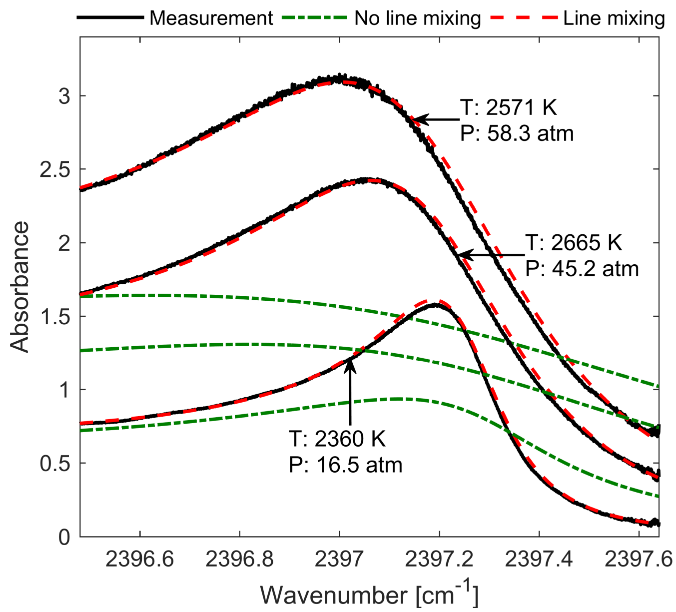

Fig. 2 CO_2 absorbance measurement of the fundamental vibrational bandhead near 4.2 μm with HITEMP simulation and modified MEG law model for line mixing shown over a range of high-pressure conditions

V. Experimental Setup

Figure 3 below shows the optical configuration for the CO_2 absorption sensor and the representative hardware

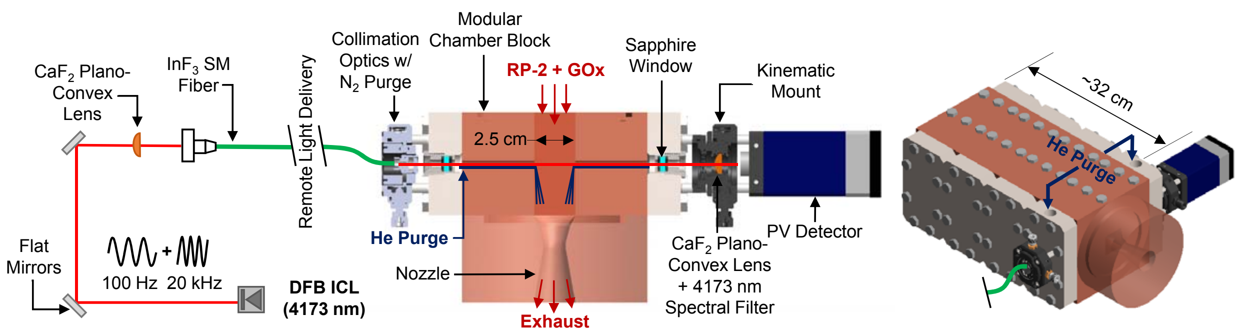

Fig. 3 Optical interface with rocket combustor for CO_2 laser absorption measurements. Graphical depiction of remote-light delivery and collection optics along with implemented He/N_2 purge systems

A number of practical methods are implemented to mitigate signal-convoluting factors in the test environment. Specific methods include a nitrogen (N_2) purge system in the fiber-optic and pitch assembly and a recessed helium (He) purge system in front of the sapphire windows. The N_2 purge system displaces excessive water vapor and ambient CO_2 in the optical path that can cause spectral interference. The He purge system provides clear optical access to the combustion chamber by minimizing soot deposition on the sapphire windows.

A scanned-wavelength modulation spectroscopy technique was implemented for all rocket combustor measurements in order to distinguish the spectroscopic signal from non-absorbing effects and maximize signal-to-noise ratio (SNR). A scan depth of 0.63 cm^{-1} at 100 Hz and modulation depth of 0.36 cm^{-1} at 20 kHz were chosen to optimize signal quality. More details on the signal optimization strategy can be found in previous works [1, 13]. The normalized harmonic ($2f/1f$) signals were extracted from measured raw signals through a lock-in amplifier and frequency filter. The calibration-free harmonic signals are sensitive to differential absorption and relatively insensitive to low-frequency beam steering, scattering, and thermal emission [14].

VI. Results

The CO_2 sensor was deployed on a coaxial single-element-injector rocket combustor at the Air Force Research Laboratory (Edwards, CA). A series of measurements were conducted over a range of pressures and mixture ratios (MR) from 28–83 bar and 2.3–4.6, respectively, with RP-2 (kerosene) and gaseous oxygen as propellants. The combustion chamber is comprised of stackable modular sections, with optical access located at the furthest downstream axial location, where chemical equilibrium was most likely to be achieved. Chemical equilibrium was calculated using NASA CEA [15] to provide a reference point for the measurements.

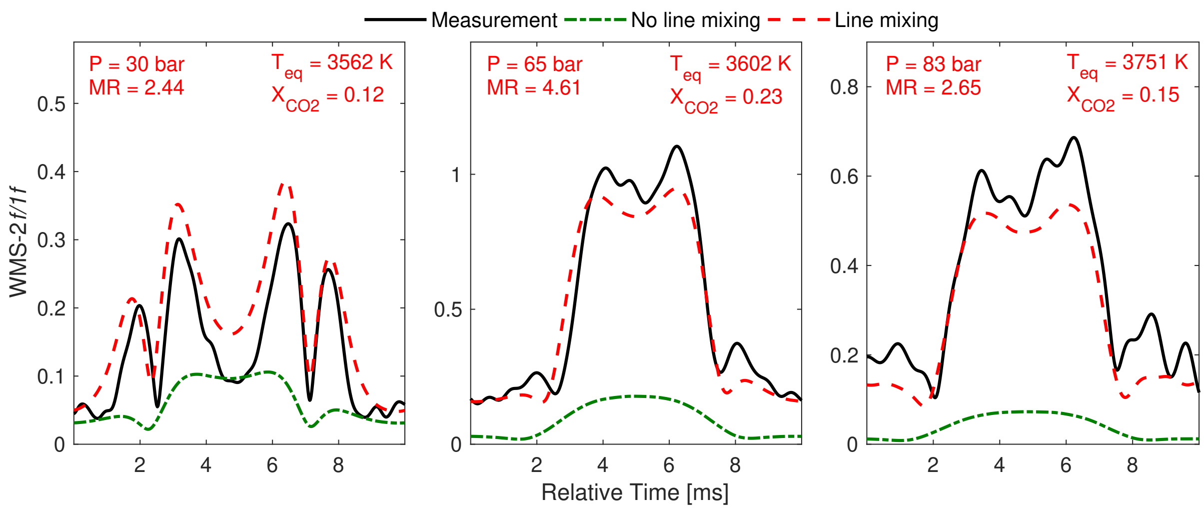

Fig. 4 Measured WMS-$2f/1f$ signals for an averaged single scan period compared to simulated signals with and without the line mixing model for three test conditions of RP-2/GOx

In order to improve SNR, the raw optical signal was averaged over the steady-state region of approximately 1 second and post-processed though a digital lock-in amplifier to extract WMS harmonics. Figure 4 compares the averaged WMS-$2f/1f$ measurements to simulated WMS-$2f/1f$ signals with and without the developed line-mixing model at different pressures and mixture ratios. Notably, the CO_2 measurements exhibit high SNR at pressures up to 83 bar, indicating a potential to conduct measurements at even higher pressures. The line-mixing model shows reasonable agreement with the measurements regarding the spectral structure for all three test conditions shown. In contrast, simulations not accounting for line-mixing effects demonstrate large disagreement with the measurement data in both magnitude and spectral shape. The updated model enables quantitative inference of species concentration from the measured WMS signals

Figure 5 compares inferred mole fraction to chemical equilibrium expectations for RP-2/GOx. The CEA results are bounded by the highest and lowest pressures measured, 83 bar and 28 bar, respectively, and shown for reference. Previous measurements on the rocket combustor with RP-2/GOx demonstrated generally 100–300 K lower temperature than equilibrium temperature, potentially due to poor mixing, heat losses, or a cold boundary layer [13]. Species uncertainties (as shown by error bars) were calculated with an assumed temperature uncertainty of 200 K, yielding a typical uncertainty of 9%. Notably, the inferred CO_2 mole fraction from all tests followed the expected trends and agreed well with equilibrium expectations.

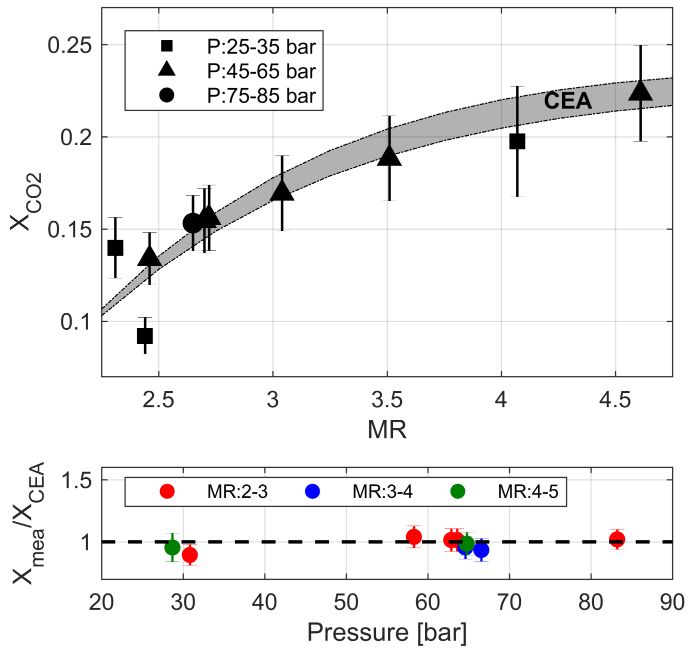

Fig. 5 CO_2 mole fraction measurements with representative error bars at steady-state combustor conditions compared to CEA over a range of mixture ratios and pressures for RP-2/GOx

VII. Conclusion

A novel laser absorption sensing strategy targeting the CO_2 fundamental vibrational bandhead near 4.2 μm was employed to measure species concentration in situ on a single-element rocket combustor at the Air Force Research Laboratory in Edwards, CA. Quantitative species measurements were performed by collecting and interpreting WMS-$2f/1f$ signals over a range of pressures and mixture ratios for RP-2/GOx propellant combinations. Signal interpretation required an underlying spectroscopic model to account for spectral distortation at high gas pressures. Spectroscopic studies were conducted utilizing a high-enthalpy shock tube facility to characterize the temperature and pressure dependence of line-mixing effects at rocket conditions. Line-mixing effects on the molecular spectra were modeled using a modified-exponential-gap rate law to account for collision-induced changes in rotational energy. Line mixing was shown to be favorable for amplifying differential absorption at the bandhead. The refined WMS-$2f/1f$ signals simulated using the line-mixing model enabled quantitative inference of species concentration in the liquid propellant rocket combustor, showing good agreement with chemical equilibrium within measurement uncertainty. The range of pressures studied (28 bar to 83 bar) highlights the advanced pressure capability of the novel sensing strategy, which can provide a basis for evaluating combustion efficiency/performance at practical high-pressure rocket combustion conditions.

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