Simultaneous measurements of temperature and CO mole fraction in combustion environment using TDL near 2.3 µm

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Abstract:
Simultaneous measurements of temperature and carbon monoxide (CO) mole fraction in combustion gases using Tunable Diode Laser (TDL) sensor are reported. The sensor is based on absorption transitions (ν’=2, ν”=0) and (ν’=3, ν”=1) in the first overtone band of CO near 2.3 µm (~ 4250 cm⁻¹). This band is relatively free of interference from CO₂ and H₂O, and the transitions in the first band are significantly stronger (10² times) compared to the second band near 1.5 µm (~ 6300 cm⁻¹). The measurements reported here were completed in the post flame environment of fuel rich premixed ethylene-air flames established on a water cooled McKenna burner. Co-flow of nitrogen was used to stabilize the flame. CO transitions (R 27 and R 6) were probed simultaneously using current tuning of the laser at constant temperature. Due to large difference in lower state energies, the selected line pair offered good sensitivity over the temperature range (1200 – 2200 K) of combustion products. Measurements at steady conditions were done at 100 Hz to minimize the noise and beam steering effects. The absorption due to cooler CO in the axi-symmetric mixing layer of the shroud flow was considered in the data analysis. Temperature measurements with the boundary layer correction show good agreement with N₂ vibrational CARS measurements. CO mole fraction measurements are in qualitative agreement with the equilibrium values.

1. Introduction:
Carbon monoxide (CO) is an important product species that can be used as a combustion marker. In the post combustion regime CO concentration and temperature are closely related to each other. Therefore, simultaneous measurements of these two quantities can provide insights related to the post flame gas phase chemistry. CO is an important product gas species that is generated during gasification of solid carbonaceous feedstock and is important reactant species that is converted into solid carbon structures such as carbon nanotubes (CNTs), graphene etc via condensation on catalyst particles. Both gasification and synthesis processes have applications in recycling of CO₂ to CO and for subsequent conversion into hydrocarbons. Gasification and synthesis processes can be globally represented by reversible Boudard and hydrogenation reactions (Eq. (1) and (2)). Measurements of CO concentration and temperature in the gasification and synthesis gas phase environment can be used for determination of chemical kinetics and process monitoring.

\[ C_\text{(_i)} + CO_2 \leftrightarrow 2CO \]
\[ C_\text{(_i)} + H_2O \leftrightarrow CO + H_2 \]

Tunable Diode Laser Absorption Spectroscopy (TDLAS) is a nonintrusive, path averaged, and species specific measurement technique that is commonly used for in-situ measurements in high temperature and high pressure environments. Laser absorption spectroscopy (including fixed wavelength cavity lasers and tunable diode lasers) has been used previously for CO detection in combustion gases using the near IR and mid IR transitions of CO. Line-strengths of CO transitions in the IR region are shown in Fig. 1.

The earliest measurements of CO concentration in a methane-air flame involved the use of lead salt lasers [1, 2] to probe the fundamental rovibrational band of CO near ~ 4.6 µm. Cryogenic cooling requirements render the use these lasers to be very expensive. The second overtone band of CO near ~ 1.55 µm has been utilized commonly for TDLAS measurements in combustion gases using inexpensive telecommunication type diode lasers [3, 4]. However, weak line strengths and interference by CO₂ and H₂O limit the detection in this band. The first overtone ro-vibrational band of CO
near ~ 2.3 µm is relatively free of interference from CO₂ and H₂O and can be accessed by tunable diode lasers. The transitions in this band have been previously used for CO detection [5, 6] in combustion exhausts. TDLAS has been used for diagnostics of solid combustion for measuring the gas concentration (mainly CO) inside an industrial coal fired power plant [7]. Simultaneous measurements of CO near ~1.65 µm, H₂O near ~ 1.4 µm, O₂ near ~ 0.76 µm and temperature were made in a 500 MW coal-fired boiler. Simultaneous temperature and CO concentration measurements using the two line thermometry technique on the transitions in the fundamental band have been reported in literature [8-10]. Specialty TDLs and Quantum Cascade Lasers (QCLs) have been utilized for the purpose.

![Image of line-strengths of CO transitions in IR at 296 K using data in HITRAN 2008](image)

Fig. 1. Line-strengths of CO transitions in IR at 296 K using data in HITRAN 2008 [11]

In this paper an IR TDL sensor, for simultaneous measurement of CO concentration and temperature operating near 2.3 µm, is reported. The sensor provides simultaneous measurement of temperature and CO mole fraction using a two-line spectral fit technique. CO transitions were selected based on their spectroscopic properties (strength, isolation, and temperature sensitivity) and their position in the range of available laser. The sensor is demonstrated via temperature and CO mole fraction measurements in the post flame region of a water cooled McKenna flat flame burner.

2. Theory of Absorption Spectroscopy:

The fundamentals of absorption spectroscopy are well understood [12-14]. A brief background is provided in the section to facilitate the reader with various terms and units. The Beer-Lambert law (given in Eq.(3)) provides an expression for the fractional transmission \( \tau_v \) when a monochromatic light source of intensity \( I_0 \) is passed through an absorber \( i \) with mole fraction \( X_i \),

\[
\tau_v = \left( \frac{I_v}{I_0} \right) = \exp(-PX_iS(T)\phi L)
\]

\[
\alpha = PX_iS(T)\phi L
\]

where \( I_v \) is the transmitted intensity, \( S(T) \) is the line strength which is a function of temperature, \( L \) is the optical path length and \( \phi \) is the line shape function. \( \alpha \) is the spectral absorbance with absorption coefficient \( \kappa = PX_iS(T)\phi \). The temperature dependence of line strength \( S(T) \) is depicted in Eq. (4),

\[
S(T) = S(T_0)\frac{Q(T)}{Q(T_0)}\left( \frac{T_0}{T} \right) \exp\left[ \frac{hE^*}{k_B} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \left[ 1 - \exp\left( \frac{hv_o}{k_B T} \right) \right] \left[ 1 - \exp\left( \frac{hv_o}{k_B T_0} \right) \right]^{-1}
\]

where \( Q(T) \) is the partition function which is typically populated by ro-vibrational levels in the temperature regime considered, \( h \) is the Planck’s constant, \( c \) is the speed of light, \( k_B \) is the Boltzmann constant, \( E^* \) is the lower state energy for the transition (value obtained from HITRAN 2008 database [11]), and \( v_o \) is the centerline frequency for the transition.
The line shape function $\phi_\nu$ of a particular absorption transition, which represents the relative variation in the spectral absorbance with frequency, is determined by the physical mechanisms that perturb the energy levels of the transition or the way in which the absorbing molecules interact with the laser beam. The line shape function is affected by Doppler broadening and collisional broadening. The Doppler broadening results from random thermal motions of absorbing molecules. Since the random thermal motion of the molecules is governed by a Gaussian function, the Doppler broadening can be expressed as,

$$\phi_\nu (\nu) = \frac{2}{\Delta V_D} \sqrt{\frac{\ln 2}{\pi}} \exp \left[ -4 \ln 2 \left( \frac{\nu - \nu_0}{\Delta V_D} \right)^2 \right]$$  \hspace{1cm} (5)

The Doppler full-width at half maximum (FWHM) is given by,

$$\Delta V_D = v_0 \sqrt{\frac{8k_B T \ln 2}{mc^2}}$$  \hspace{1cm} (6)

Pressure broadening and shifting of spectral lines are caused by the perturbation of the energy levels due to molecular collisions. The collisions are assumed to be binary and the duration of collisions is negligibly short. In impact theory, the pressure-broadened line shape takes a Lorentzian profile, which is symmetric about the pressure-shifted line center. The line shape resulting from such broadening is given by,

$$\phi_C (\nu) = \frac{1}{\pi} \frac{\Delta V_C}{(\nu - \nu_0 - \Delta V_x)^2 + \left( \frac{\Delta V_C}{2} \right)^2}$$  \hspace{1cm} (7)

The full-width at half maximum (FWHM) for an absorber $j$ is given by,

$$\Delta V_{C,j} = \sum 2\gamma_{ji} P X_i$$  \hspace{1cm} (8)

In Eq. (8), $X_i$ is the mole fraction of the collision partner $i$, $P$ is the total pressure, and $\gamma_{ji}$ is the broadening coefficient of species $j$ with species $i$, that has a temperature dependence,

$$2\gamma_{ji} (T) = 2\gamma_{ji} (T_0) \left( \frac{T_0}{T} \right)^n$$  \hspace{1cm} (9)

The actual line shape function is calculated by convoluting the Gaussian and Lorentzian shape functions that result in a Voigt profile,

$$\phi_\nu (\nu) = \int \phi_\nu (u) \phi_C (\nu - u) du = \frac{2}{\Delta V_D} \sqrt{\frac{\ln 2}{\pi}} V (a_c, w)$$  \hspace{1cm} (10)

The normalized Voigt function is characterized by two non-dimensional parameters that characterize the relative effects of Doppler broadening and collisional broadening, and the distance from the pressure shifted line center,

$$a_v = \sqrt{\ln 2} \frac{\Delta V_C}{\Delta V_D}, w = 2\sqrt{\ln 2} \frac{\nu - \nu_0 - \Delta V_x}{\Delta V_D}$$  \hspace{1cm} (11)

Transitions with sufficiently different lower-state energies $E'$ can be used for determination of temperature due to the variation in line strength temperature dependence with lower-state energies,

$$\frac{S_i (T)}{S_j (T)} = f (T)$$  \hspace{1cm} (12)

Two-line absorbance ratio temperature determinations can be made through measurement of the ratio of integrated areas for two transitions, a direct measurement of the ratio of line strengths, or by measurement of the ratio of peak line center absorbance for two transitions, which reduces to the ratio of line strengths for transitions with the same line-shape function $\phi_\nu$ but more generally must be interpreted via spectral simulations at known pressure. In this work, the more generic spectral fit technique was used to determine the temperature using pairs of CO transitions.

3. Selection of CO transitions:

For the development of the sensor described here, CO transitions in the R branch of the first ro-vibrational band of CO near 2.3 $\mu$m were considered. Theoretical spectral simulations were performed using the HITRAN 2008 [11] database for a number of potential CO line pairs at a broad range of conditions of relevance to combustion environments. Fig. 2 shows output of one such theoretical simulation in the available laser range, for $T = 1950$ K, $P = 1$ atm, $X_{CO} = 5\%$. 

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$X_{\text{H}_2\text{O}} = 18\%$, and $L = 6$ cm. Line pairs were chosen based on absorption strength, isolation from interfering absorption ($\text{CO}_2$, and $\text{H}_2\text{O}$ absorption was considered), and temperature sensitivity. Additionally, preference was given to line pairs that could be scanned with a single laser using current tuning. The inset shows the candidate line pairs for simultaneous temperature and CO concentration measurement. The line pairs are isolated from the interference due to $\text{H}_2\text{O}$ with significant concentration ($18\%$). The interference due to $\text{CO}_2$ was found to be negligible ($\sim 10^{-5}$ that of CO). Table 1 gives the properties of the selected transitions. Each line pair contains a line from a higher vibrational band that allows for higher temperature sensitivity. Collisional broadening at different temperatures is calculated using Eq (9) and values listed in Table 1.

![Fig. 2. Theoretical simulation of absorbance using HITRAN 2008 database (T = 1950 K, P = 1 atm, $X_{\text{CO}} = 5\%$, $X_{\text{H}_2\text{O}} = 18\%$, and L = 6 cm)](image)

For thermometry in high-temperature gases containing CO, line strength ratios for both the A and B line pairs provide sufficient sensitivity at a large range of temperatures; both of these line pairs have differences in lower-state energies of greater than 3000 cm$^{-1}$ (see Table 1). In Fig. 3 (a) both the line strength ratio, $R(T) = S_1(T)/S_2(T)$, corresponding to R(27) and R(29) transitions, and the sensitivity of the ratio to temperature, $dR/R = R/T$, are plotted for both line pairs from 500 to 2000 K. Generally the sensitivity should be larger than unity for low-uncertainty temperature measurements; this is the case for all temperatures shown in Fig. 3 (a) and temperatures up to $\sim 2000$ K.

Table 1: Line strength and positions of transitions at $T_0 = 296$ K from HITRAN 2008 database [11]

<table>
<thead>
<tr>
<th>Line Pair</th>
<th>No.</th>
<th>Position (cm$^{-1}$)</th>
<th>$\Delta v_0$ (cm$^{-1}$)</th>
<th>$S_0$ (atm$^{-1}$cm$^2$)</th>
<th>$E^*$ (cm$^{-1}$)</th>
<th>$\nu^*$</th>
<th>$\nu^\prime$</th>
<th>$\gamma_{\text{CO}}(T_0)$</th>
<th>$n_{\text{air}}$</th>
<th>$n_{\text{CO}}(T_0)$</th>
<th>$n_{\text{CO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A R (27)</td>
<td>4284.8911</td>
<td>0.1178</td>
<td>5.03E-08</td>
<td>3579.975</td>
<td>1</td>
<td>3</td>
<td>0.0451</td>
<td>0.67</td>
<td>0.046</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R (6)</td>
<td>4285.0089</td>
<td>8.50E-02</td>
<td>80.7354</td>
<td>0</td>
<td>2</td>
<td>0.0612</td>
<td>0.75</td>
<td>0.069</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B R (29)</td>
<td>4288.2576</td>
<td>0.0322</td>
<td>1.91E-08</td>
<td>3796.0148</td>
<td>1</td>
<td>3</td>
<td>0.0441</td>
<td>0.67</td>
<td>0.043</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R (7)</td>
<td>4288.2898</td>
<td>8.57E-02</td>
<td>107.6424</td>
<td>0</td>
<td>2</td>
<td>0.0599</td>
<td>0.75</td>
<td>0.067</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The variation of line strength for all transitions is shown in Fig. 3 (b). Temperature measurements are limited to temperatures higher than $\sim 900$ K due to insufficient absorption strength for the high-temperature R(27) and R(29) lines at lower temperatures. Both pairs of transitions provide similar temperature dependence and sensitivity. Hence, the selection of the optimal transition pair for a particular measurement is based on desired scan rate and pressure. In the current work, results from pair A are described.
4. Experimental Arrangement:

Fuel rich premixed atmospheric pressure flames of Ethylene + air mixture at different equivalence ratios (φ) were established on the water cooled McKenna burner (60 mm diameter) with bronze porous plug. No flame stabilizer was used above the burner surface. The experimental arrangement for burner and TDLAS measurements is shown in Fig. 4. Flow rate of air was maintained at 18.5 slpm (0.369 g/s) using a choked orifice. Shroud flow of nitrogen (N₂) was used to stabilize the flame and was maintained at 46 slpm (0.9 g/s) using a choked orifice. Flow rate of cooling water was maintained at 112 sccm (1.86 g/s). Ethylene mass flow rate was varied (1.2 to 2.4 slpm) to establish the flame at different equivalence ratios. Temperature of the cooling water at the exit of the burner was measured using a K type thermocouple.

The DFB tunable diode used in the current work was provided by Sacher Lasertechnik, Germany. An InGaAs detector with 25 ns rise time (Thorlabs Inc., DET10D) was used to collect the transmitted laser output. Neutral density filter was used to avoid saturation of the detector. Diameter of the beam coming out of the laser was measured to be ~ 2 mm. Line of sight direct absorption measurements were carried out 6 mm above the burner surface.

A broadband vibrational coherent anti-Stokes Raman scattering (VCARS) system was used to obtain accurate point temperature measurements at burner center 6mm above the burner surface. Broadband VCARS is a 3rd order parametric process in which, the pump and the Stokes beam create a Raman coherence which is probed by the probe beam thereby, generating the anti-Stokes Raman signal. In our experiment, the pump, stokes and the probe beam were at 532 nm, 607 nm and 532 nm respectively.
5. Data Analysis and Correction for Shear Layer:

Rotational transitions R(6) and R(27) were probed using current tuning of the laser at a frequency of 100 Hz to eliminate any effects of beam steering and broadband scattering. A saw tooth waveform at 100 Hz generated by the function generator was fed to the controller. Data were collected for 30 seconds at each condition, at 100 kHz. Data were averaged over 100 sweeps (1 s duration) to reduce background noise. Fig. 5 (a) shows representative instantaneous scans at \( \phi = 1.6 \). Representative average scan over 100 sweeps for the same \( \phi \) is shown in Fig. 5 (b). The figure also shows the reference baseline that was obtained through polynomial fit to the wings of the absorption features. Baseline was obtained for each average scan to remove the effects of beam steering.

![Fig. 5.Absorption signal (a) Individual scans at 100 Hz, and (b) Signal averaged over 100 scans along with reference signal](image)

Fractional transmission and absorption profiles were deduced using the absorption feature and reference baseline. Experimental absorption profiles at each equivalence ratio were fitted with simulated profiles for temperature and CO mole fractions. Differential evolution algorithm [15] was used to optimize multiple fitting parameters. Least square error minimization criterion was used to fit the simulated profile to experimental absorption. Humlicek’s algorithm [16] was used to calculate the voigt function. CO mole fraction, temperature and frequency shift parameters were calculated through the voigt fit procedure.

The axi-symmetric shear layer mixing effects due to the nitrogen shroud flow needed to be accounted for the path averaged laser absorption measurements. Photograph of the flames at different equivalence ratios are shown in Fig. 6 (a) to illustrate the shroud flow mixing effects. The conical shape of the post flame gas flow and entrainment from shroud flow is clearly visible. Due to the entrainment, the post flame sheet flow field is not one dimensional and the variation of scalars along the radius must be considered in the data analysis. Following Ouyang and Varghese [17], analysis was done to estimate the change in line strength for each transition in pair A due to the shear flow. In the shear layer the temperature decreases from its value in the core, and approaches the temperature of the shroud flow. This decrease in temperature affects the line strength of the transitions. Ouyang and Varghese calculated a theoretical energy value \( E^* \) which can be used as a basis for determining the effect of shear layer on the transitions. For the transition R(27) \( E^* = 3579.975 \text{ cm}^{-1} \), which is higher than the corresponding value of \( E(T) \) at combustion temperature. Thus, the line strength of this transition decreases significantly in the shear layer resulting in minimal change in absorption due to shear layer. However, for R(6), \( E^* = 80.7354 \) which is lower than the corresponding value of \( E(T) \) at combustion temperature. Thus the line strength for this transition increases in the shear layer and contributes significantly to the absorption. Line strength variation trends with temperature are also evident from Fig. 3 (b). The changes in the line strengths for both the transitions were accounted for in the data analysis. This was accomplished by fitting an integrated line of sight absorption profile to the experimental data. The spectral absorbance was calculated using Eq. (13),

\[
\alpha_T = \int_0^L P x_i(x) S(T(x)) \phi \, dx \tag{13}
\]

![Fig. 5.Absorption signal (a) Individual scans at 100 Hz, and (b) Signal averaged over 100 scans along with reference signal](image)
In Eq. (13), \(X_r(x)\) and \(T(x)\) correspond to the radial profiles of CO mole fraction and temperature respectively at the height above the burner (6 mm) for measurements. The spectral absorbance was calculated by numerical integration over the line of sight. The radial profiles of scalars were deduced by conducting multiple line of sight measurements at different radial locations. The measurement locations are schematically represented in Fig. 6 (b).

![Fig. 6. Deduction of shear layer effect (a) photograph of flame showing conical structure due to shroud flow, and (b) Line of sight measurements at multiple radial locations](image)

The fractional transmission profiles obtained at each radial location are shown in Fig. 7 (a). These profiles were fitted with simulated voigt profiles to obtain temperature and CO mole fraction at each radial location. Length of chord at each radial location was used as the path length for simulations. Uniform values of scalars were assumed along the line of sight. Effect of shear layer at each radial location was assumed to be the same. The measured scalars were non-dimensionalized using the value at the axis of the burner \((r=0)\) to remove the effect of shear layer. Representative non-dimensional profiles at \(\phi =1.6\) are shown in Fig. 7 (b). These non-dimensional profiles were multiplied by respective scalar values at the burner center, \(X_{\text{core}}\) and \(T_{\text{core}}\), and then were used in Eq. (13) to calculate the spectral absorbance. The values for \(X_{\text{core}}\) and \(T_{\text{core}}\) were obtained through iterative fitting procedure.

![Fig. 7. Boundary layer analysis (a) Fractional transmission at different radial locations, and (b) Radial profiles of non-dimensional scalars](image)
6. Results and Discussion:

Representative fits to the experimental data at $\phi = 1.6$ are shown in Fig. 8. The residual absorbance was found to be within ± 5% of the peak absorbance for all theoretical simulations. Average value of CO concentration and temperature obtained from fits to 30 seconds of data, are reported as measured values and the precision of the measurements is based on 1 $\sigma$.

![Voigt fit to the experimental data for $\phi = 1.6$](image)

Fig. 8. Voigt fit to the experimental data for $\phi = 1.6$

Measured values of temperature as a function of equivalence ratio are shown in Fig. 9 (a). Measurements obtained from vibrational N$_2$ CARS and CO TDLAS two line thermometry with and without the effect of shear layer are shown. CARS and both TDLAS measurements show a good qualitative agreement. Temperatures measured by CO TDLAS without the shear layer effect, being averaged over the burner diameter, are consistently lower than those measured by spatially resolved CARS technique. However, temperatures measured by CO TDLAS with consideration of shear layer effect, show excellent quantitative and qualitative agreement with the temperatures measured by N$_2$ CARS.

All temperature measurements show a minima near $\phi = 1.1$. Similar observation has been made previously by Vestin et. Al [18]. This observation can be explained on the basis of flame speed and heat loss to the burner. Adiabatic equilibrium temperatures and temperature change for the cooling water across the burner are shown in Fig. 9 (b). The measured temperatures are lower than the adiabatic temperatures due to the heat loss to the burner, cooling water and the surroundings. It is noted that highest temperature change for the cooling water occurs for $\phi = 1.1$. Burning velocity reaches maxima near $\phi = 1.1$ [19] which results in stabilization of the flame closest to the burner in the range of equivalence ratios studied in this work. Consequently, the heat loss to the burner and cooling water is maximum at this $\phi$. Decrease in flame temperature at this equivalence ratio was estimated to be $\sim 500$ K based on heat loss calculations considering water and gas flow rates and heat capacities. This estimate agrees well with the difference observed between the adiabatic flame temperature and temperature measured by CARS and CO TDLAS with shear layer effect. The change in cooling water temperature across the burner decreases with increase in equivalence ratio. At higher equivalence ratio the burning velocity and the flame temperature decrease and the flame is stabilized farther from the burner. This reduces the heat loss to the burner. As a result, a relatively flat temperature profiles are observed at higher equivalence ratios with maxima occurring near $\phi = 1.7$.

Measured values of CO mole fraction as a function of equivalence ratio are shown in Fig. 10. Measured values of CO mole fraction show an increasing trend with the equivalence ratio as expected, however are quantitatively lower than the equilibrium values. This observation suggests that CO concentration comparison may be needed with detailed chemistry calculations. For $\phi > 1.5$, the rate of CO mole fraction increase with equivalence ratio becomes flatter as compared to $\phi < 1.5$. This trend is similar to that observed for equilibrium concentrations.
7. Conclusions and Future Work:

A TDL sensor based on rotational transitions of CO in first ro-vibrational band (~ 2.3 µm) for simultaneous measurement of temperature and concentration has been demonstrated. Effect of shear layer has been incorporated into the path averaged TDLAS measurements. The TDLAS temperature measurements corrected for the shear layer effect show good quantitative and qualitative agreement with the point $N_2$ CARS measurements. The measured values of CO mole fraction with TDLAS with shear layer correction are lower than the equilibrium value. Detailed chemistry calculations along with spatially resolved pure rotational CARS measurements of CO mole fraction are planned to validate the TDLAS CO concentration measurements.

Acknowledgements

The authors would like to acknowledge financial support from Air Force Office of Scientific Research (AFOSR) and John Zink Company Graduate Fellowship Fund. Assistance from Weichao Wang and Rajat Singh with the experimental arrangement is appreciated.
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