A Spectroscopic Study for detection of Carbon-monoxide using Mid-Infrared Techniques for Single-pass measurement

Sandip Pal, Krikor B. Ozanyan and Hugh McCann

School of Electrical and Electronic Engineering, University of Manchester, UK.

Sandip.Pal@postgrad.manchester.ac.uk

Abstract. Tomographic imaging of minor species in combustion exhaust is an important requirement for combustion engineering. Only one group has tried carbon monoxide imaging in laminar flames in the mid-infrared region. A number of attempts have been made by different groups for single-channel multi-pass or long path-length measurement of CO. Single-pass measurement is being assessed in our work for tomographic measurement of the distribution of minor species. We report here the spectroscopic study of CO in different absorption lines of the strong fundamental bands in the mid-IR range. The criteria for selection of a light source in this context are also considered. Although strong spectral lines are available for CO in the mid-infrared region, strong water vapour and carbon dioxide interferences are also present. This addresses the choice of such useful spectral lines under interference by major species. The HITRAN 2004 database is used to predict the spectral lines of H2O and CO2 near the fundamental spectrum of CO in the mid-IR range. The exhaust condition in respect of temperature and pressure is considered in order to study the broadening of the spectral lines. The percentages of absorption for different species for different types of light sources are reported on the basis of computations. The concept can be readily extended to further species of interest in the presence of other interfering species. Different laser sources and spectroscopic methods are considered to design a strategy suitable to this application.

1. Introduction

There is great interest to develop an imaging technique for the distribution of minor combustion species for application in combustion engineering. The vast majority of gaseous chemical substances exhibit fundamental vibrational-rotational absorption bands in the mid-infrared spectrum (2.5 µm to 25 µm). Among other substances, carbon monoxide (CO) is a regulated pollutant that is produced by the incomplete combustion of carbon-based fuels. An imaging technique is proposed here to get an image of the target species in combustion exhaust gases. The combination of MIR spectroscopy and tomography offers great potential for this task.

There are emerging requirements for sensors, actuators, and control technology suitable for advanced combustors. A basic sensor requirement for closed loop control of combustors is satisfied by continuous and real-time measurement of exhaust emission of CO at bandwidths of a few Hz. CO measurement provides for on-line determination of combustion efficiency. The measurement of CO at ppm level in combustion exhaust has been tried by Wehe et al. [7]. Wondracek et al. [1] tried to image carbon monoxide in laminar frames. Over recent years high-speed imaging of hydrocarbons (a major species) inside the engine cylinder has been achieved by the Manchester group [8-10] using near-IR diode lasers. Since the concentration of combustion products like CO is very low, the focus is
now shifted towards the strong absorption band in mid-IR spectral range. But this will require
generation of new technology in mid-IR wavelength imaging. For tomographic imaging of the
combustion exhaust, single-pass measurement is considered to be most useful, even though previous
attempts at CO measurement are mostly with multi-pass techniques.

For single-pass multi-channel high-speed measurement, the main considerations are the following:
i) the optical power of the laser source should be maximum, as the absorption percentage of the overall
spectrum is small, ii) in the mid-Infra Red region low-loss 1-to-N channel splitters are not
commercially available, iii) the noise elimination technique should be such that it can eliminate both
the out-of-band as well as the in-band noise, iv) detectors and detection electronics are to be fast
enough to sense the pulsed waveform from the laser source.

This paper is structured to consider the spectral analysis of the components present in the
combustion exhaust, the choice of different light sources and the sensing techniques available to get
the best achievable low-noise signal.

2. Spectroscopic Analysis
It is necessary to know the range of wavelengths of interest to image CO in the exhaust gas. In this
paper, the temperature and pressure of the exhaust gas are set at representative values of 800 K and 1.2
atm. The method of detection of the diatomic molecule CO depends on pure absorption spectroscopy.
This absorption spectroscopy is based on the fundamental and hot-band rotational/vibrational
transitions. At the elevated temperature of 800 K, the population of the vibrational and rotational
energy levels at the hot band is more than that at room temperature [12]. At the same time combustion
exhaust has other species which will create a significant background for each measurement. Therefore,
it is of critical importance to choose the spectral line of the targeted molecule in order to avoid
significant impact of absorption by other species in nearby region.

2.1. Combustion
To estimate the spectrum of any component in the combustion products, the volumetric composition
has to be known. As a number of different hydrocarbons are present in a fossil-based fuel, iso-octane
is taken as a typical component among them. A normal combustion equation is the following, if a
complete combustion has taken place:

\[
C_8H_{18} + 12.5 \cdot (O_2 + \frac{79}{21} \cdot N_2) = 8 \cdot CO_2 + 9 \cdot H_2O + 12.5 \times \frac{79}{21} \cdot N_2
\]  

(1)

Thus, the volume percentage of different components present in the combustion exhaust is given
below:

- CO₂ : 12.5%
- H₂O : 14%
- N₂ : 73.5%

Note that, in the case of complete combustion, the CO concentration would be zero. In fact, we aim
to be sensitive to 10 ppm in the presence of interfering spectral lines of other components. The
chemical equilibrium calculation equation (1) is used to estimate the interfering effect for other major
species like CO₂, H₂O and N₂ on the spectra of CO.

2.2. Calculation Process
The JavaHAWKS program has been run to generate the spectral lines of CO in the presence of the
other combustion products. This is based on the HITRAN database 2004 [4] involving the
wavenumbers (ν), linestrengths (S), air-broadened half-width (γ_{air}), self-broadened half-width (γ_{self}),
lower state energy (E”), temperature dependence exponent for γ_{air} (n_{air}) and air pressure-induced line
shift (δ_{air}). This version of HITRAN provides the database for the temperature demanded. Accordingly
the following Beer-Lambert Law equation (2) is used to calculate the transmitted spectra.

The intensity after absorption of monochromatic light along a path of length L in a sample of gas is
given by,
\[ I = I_0 \cdot \exp\left[-\left(S(T) \cdot g(\nu - \nu_0) \cdot n_\text{a}(T) \cdot L\right)\right] \]  \tag{2}

Where,
- \( I_0 = \) initial intensity,
- \( S(T) = \) the line strength of different line of transition in molecule\(^{-1} \text{ cm}^2 \) at temperature \( T \),
- \( g(\nu - \nu_0) = \) the line shape function around the centre wavenumber \( \nu_0 \),
- \( n_\text{a}(T) = \) number of absorbing molecules \( \text{ cm}^{-3} \) at temperature \( T \),
- \( L = \) the optical path-length in cm (= 5 cm in our calculations.)

A Mathcad routine is written to evaluate the convolution of the collisional and the Doppler broadening using the Voigt profile at 800K temperature and 1.2 atm pressure. A computation result around the strong ro-vibrational region of CO is shown in fig. 1, representing the ‘P’ branch and ‘R’ branch for transitions between vibrational states \( \nu = 1 \leftarrow 0 \) and \( \nu = 2 \leftarrow 1 \) respectively. Each spectral line is designated by different numbers as specified in the HITRAN database. The absorptions by CO\(_2\) and H\(_2\)O are also shown in fig. 1. The effect of CO broadening due to the presence of CO\(_2\) and H\(_2\)O cannot be considered, because of the non-existence of the required database. N\(_2\) absorption is found negligible in this region.

![Figure 1: Absorption lines of all the exhaust components in the wavenumber range from 1970 cm\(^{-1}\) (=5.1 \(\mu\)m) to 2270 cm\(^{-1}\) (=4.4 \(\mu\)m). Blue colour represents the CO absorption spectrum in two halves of ‘P’ and ‘R’ Branch, whereas green and pink designate H\(_2\)O and CO\(_2\) respectively.](image)

When analysing absorption spectra to estimate species concentrations, line broadening effects have to be considered. These are:

- Doppler Broadening (Gaussian Broadening) being dependent on temperature and centre wavenumber, \( \nu_0 \):
  \[ g_D(\nu - \nu_0) = \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{1}{b_D(\nu_0, T)} \cdot \exp\left[-\frac{\ln 2 \cdot (\nu - \nu_0)^2}{b_D(\nu_0, T)}\right] \]  \tag{3}

Where, the Doppler half-width at half-maximum (HWHM) \( b_0 \) is given by,
  \[ b_D(\nu_0, T) = 2 \cdot k_b \cdot T \cdot \frac{\ln 2}{M \cdot c^2 / N_A} \cdot \nu_0 \]  \tag{4}

and where,
Collisional Broadening (Lorentzian Broadening), mainly dominated by pressure but also having dependence on temperature:

\[ g_L(u - u_0) = \frac{b_N(u_0, T)}{\pi \cdot \left[ (u - u_0)^2 + b_N(u_0, T)^2 \right]} \]  

Where, the pressure broadened HWHM \( b_N \) is given by,

\[ b_N(u_0, T) = \left( \frac{T_{\text{ref}}}{T} \right)^{\gamma_{\text{air}}(u_0)} \cdot \gamma_{\text{air}} \cdot (p - p_a) + \gamma_{\text{self}} \cdot p_a \]

and where,

- \( p_a \) = Partial Pressure of the component of interest = \( v_x \times p \),
- \( v_x \) = Volumetric fraction of the component of interest in the sample gas,
- \( p \) = Total pressure of the sample (= 1.2 atm in our calculation),
- \( T_{\text{ref}} = 296 \text{ K} \).

The convolution of both effects results in a Voigt Profile with half width of \( b_R(u_0, T) \) given by the following formula,

\[ b_R = b_N / 2 + \sqrt{\left( b_N / 2 \right)^2 + \left( b_D \right)^2} \]

The Voigt Profile is approximated according to the method of Whiting [5].

Figure 2: A close look at the region of interest for choosing the optimal spectral line of CO.

Since the lasers commercially available today are costly, and tunable only over a narrow range, it is desirable to find a suitable line for choosing an appropriate laser. \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) are the main line broadening species present in the exhaust gas as determined by previous experiments on P(26) and P(29) lines [1]. Because of the presence of polychromatic light in the laser source (frequency spread around 150 MHz for pulsed QCL), the resulting line profile is influenced by the laser line function according to an overlap integral.
Since the ‘P’ band is crowded with the H2O band as evident from fig. 1, it is better to concentrate on the ‘R’ band. The problem is then the existence of the CO2 band in the highest population region of the CO band, obstructing our view as shown in fig. 1. The R(6) transition of the fundamental vibration band \( \nu = 1 \leftarrow 0 \) near 2169.196 cm\(^{-1}\) (= 4.61 \( \mu \)m) is the best choice as is evident from Fig. 2. The rest of the points are discussed in section 3.

2.3. Transmission of Polychromatic Light

The laser source is not monochromatic and it has a definite spectral width. Suppose the spectral distribution of the laser source can be designated by the function \( g_L(\nu - \nu_L) \). It has been approximated by a Lorentzian function, as given below:

\[
\int_{-\infty}^{\infty} g_L(\nu' - \nu_L) \cdot d\nu' = 1 \tag{7}
\]

\[
g_L(\nu' - \nu_L) = \frac{2 \cdot \Delta \nu_{1/2}}{\pi \cdot (\Delta \nu_{1/2})^2 + 4 \cdot (\nu' - \nu_L)^2} \tag{8}
\]

Where, \( \nu_L = \) Centre wavenumber of the laser line,

\( \Delta \nu_{1/2} = \) FWHM of the spectral distribution of the laser line.

![Figure 3: Integrated transmission signal for polychromatic laser source having line-width 0.01 cm\(^{-1}\) at absorption line R6 of CO.](image)

Therefore, the analytical treatment of the transmission due to overlapping emitter and absorption line shapes is an overlap integral of the laser line profile \( g_L(\nu - \nu_L) \) with the CO line transmission curve discussed.

For a given laser peak frequency, the observed fractional absorption is calculated based on the convolution formula as given below:

\[
A(\nu_L) = \frac{\int g_L(\nu' - \nu_L) \cdot \exp\left[-S(T) \cdot g(\nu' - \nu_0) \cdot n(\nu) \cdot L\right] \cdot d\nu'}{\int g_L(\nu' - \nu_L) \cdot d\nu'} \tag{9}
\]

The computed result of this is illustrated in the following section. The integrated value according to the equation (9) varies with \( \nu_L \) as shown in fig. 3, if the overall scan of laser frequency is made. It makes further widening of the absorption signal from 0.033 cm\(^{-1}\) to 0.061 cm\(^{-1}\).
3. Laser absorption for the potential spectral wavenumber

Spectroscopy is dependent both on the line width of the laser source and that of the spectral line. There are two possibilities:

- the laser linewidth is greater than or equivalent to the molecular absorption linewidth
- the laser linewidth is less than the molecular absorption linewidth.

| Wavenumbers in cm\(^{-1}\) | Wavelength in nm | FWHM for Lasers \(\Delta \nu\) in cm\(^{-1}\) | Percentage absorption in gases with the following concentrations |
|----------------------------|-----------------|---------------------------------|------------------------------------------------------------|
|                            |                 |                                 | CO – 10ppm | CO\(_2\) – 12.5\% | H\(_2\)O – 14\% |
| 2169.196 (R6)              | 4610.003        | 0.005                           | 0.2544     | 0.01132   | 0.00438   |
|                            |                 | 0.01                            | 0.2202     | 0.01194   | 0.00444   |
|                            |                 | 0.05                            | 0.1138     | 0.01936   | 0.00672   |
|                            |                 | 0.1                             | 0.0712     | 0.02686   | 0.01029   |
|                            |                 | 0.5                             | 0.0183     | 0.06417   | 0.03872   |
| 2176.280 (R8)              | 4594.997        | 0.005                           | 0.3067     | 0.07985   | 0.00920   |
|                            |                 | 0.01                            | 0.2648     | 0.08105   | 0.00934   |
|                            |                 | 0.05                            | 0.1348     | 0.08243   | 0.01288   |
|                            |                 | 0.1                             | 0.0839     | 0.07503   | 0.01958   |
|                            |                 | 0.5                             | 0.0216     | 0.08804   | 0.06728   |
| 2179.773 (R9)              | 4587.634        | 0.005                           | 0.3089     | 0.06850   | 0.00472   |
|                            |                 | 0.01                            | 0.2693     | 0.06872   | 0.00502   |
|                            |                 | 0.05                            | 0.1402     | 0.06220   | 0.01049   |
|                            |                 | 0.1                             | 0.0875     | 0.06075   | 0.01706   |
|                            |                 | 0.5                             | 0.0226     | 0.08028   | 0.05235   |
| 2196.66 (R14)              | 4552.366        | 0.005                           | 0.3190     | 0.03177   | 0.00187   |
|                            |                 | 0.01                            | 0.2750     | 0.03346   | 0.00196   |
|                            |                 | 0.05                            | 0.1404     | 0.05534   | 0.00369   |
|                            |                 | 0.1                             | 0.0873     | 0.07749   | 0.00591   |
|                            |                 | 0.5                             | 0.0222     | 0.15650   | 0.02265   |

From section 2.2, the FWHM of the molecular absorption line at R6 is 0.033 cm\(^{-1}\) at 800 K and 1.2 atm. In table 1 the absorption due to different components of the exhaust gas for different FWHM of the laser source is illustrated for four different spectral lines R6 at 2169.199 cm\(^{-1}\), R8 at 2176.280 cm\(^{-1}\), R9 at 2179.773 cm\(^{-1}\), and R14 at 2196.66 cm\(^{-1}\). This novel comparative study is made to consider the effective choice of the best absorption line from the potential spectral wavenumbers.

From table 1, it is clear that as the FWHM of the laser source is increased equivalent to about or above the spectral width of the absorption line of CO, the absorption percentage is drastically reduced. The best choice of the FWHM of the laser source would be below 0.05 cm\(^{-1}\). Another important observation is that as the laser line is becoming wider, the absorption percentages due to CO\(_2\) and H\(_2\)O are comparable with that due to CO, causing difficulties in CO detection. From the relative percentage of absorption due to CO\(_2\) in relation to CO, CO\(_2\) absorption is also required to be taken care of during measurement. R6 absorption line is the best candidate in terms of ratio of absorption due to CO and that due to CO\(_2\).

4. Comparative Study of Sources and Spectroscopic Methods

A typical laser-based gas sensor consists of three key components: 1) the most appropriate radiation source for the application, 2) either a single or multi-pass cell used as an optical cavity to hold the
target gases and define the effective path length L, and 3) a sensitive IR detector and associated electronics for absorption-based sensors.

The Light Emitting Diode (LED) is one of the cheapest polychromatic light sources in the mid-infrared region. However, it cannot be used for high accuracy measurement because of the influence of other H2O absorption lines in this region due to the spectral breadth of the LED output (0.55 µm). Our calculations reveal that CO concentrations about 1% can be measured with LED sources.

The four most successful tunable CW mid-infrared sources suitable for high accuracy laser-based minor species sensing in any sample are:

- Lead-salt laser sensors based on tunable group IV-VI lead-salt diode laser,
- Difference Frequency Generation (DFG) based sources which perform optical frequency mixing of two near-IR diode lasers in a non-linear optical crystal,
- Optical Parametric Oscillators (OPOs) and
- Solid-state Quantum Cascade Lasers (QCLs).

Every source has different pros and cons to fulfil the requirement of absorption measurement in the mid-IR range. A detailed comparative study of the available sources is presented in reference [14].

From the study we have concentrated on the Quantum Cascade Lasers as a source. DFB Quantum Cascade Lasers can be of two types: Pulsed or Continuous Wave (CW).

In the spectral range of interest, CW type will be cryogen cooled. Tittel and his group [15] found that they are much more stable compared to the pulsed alternative. The laser must be operated at a reduced duty cycle (typically 10% to 25%) in order to avoid fast boil-off of liquid nitrogen and related frequency and alignment drifts. Current is supplied in pulses of 120-235 µs duration at a 0.8-1 kHz repetition rate to achieve best performance. The lasing characteristics under such long pump current pulses are essentially the same as in real CW operation, because the temperature of the laser active region reaches equilibrium on a nanosecond time scale. Each current pulse results in a wavenumber scan covering 2 cm⁻¹ [15]. In this case the total scan was performed and absorbed signal was recorded in terms of time, later calibrated with wave-numbers. The Balanced Ratio Detection (BRD) technique is used to subtract the background radiation to eliminate the other noises. The wavelength modulation technique is also adopted in one approach [16].

A solution for non-cryogenic QC-DFB laser-based spectroscopy is to apply very short (5–50 ns) pulses of the pump current at a low duty cycle, typically 1%. In pulsed operation the minimum QC-DFB laser linewidth is typically 290 MHz due to the frequency chirp related to the fast heating of the active area during the pump current pulse. With pulsed lasers one approach is just like the previous one as with CW mode. An alternative approach to data acquisition with pulsed QC-DFB lasers is to use a fast detector and measure the peak power or integrated energy of every pulse with gated electronics. In this mode of measurement, the detected signal is much higher than the detector noise and does not depend on the repetition rate. Time-gating permits suppression of the scattered light that occurs earlier or later than the informative signal. This approach was utilized in the first successful application of a pulsed QC-DFB laser to the trace gas detection in ambient air [15].

In both the cases either BRD technique or gated integrator is the method for noise elimination. Different types of filtering technique like Kalman Filter [17] can be adapted for this application for faster operation. Sinusoidal dither can be used as lock-in detection in 1st harmonics for enhanced sensitivity [13] by removing sloping background and discriminating the features not related to wavelength-absorption.

For working in industrial environment, cryogenic application will introduce different operational hazards. Therefore, the pulsed laser source is the best choice. There should be a trade-off for the pulse duration between heating-related laser frequency chirp for longer pulses and Fourier transform limitation for shorter pulses. It is found by the previous researchers [22, 23] that 7-20 ns pulse duration is the best choice to achieve the desired result using Quantum Cascade Laser. The detector to be used should be fast enough (response time < 3 ns) to gather signal of about 10 ns pulse. This will incorporate a frequency chirp of around 0.0095 cm⁻¹. From the spectroscopic study it is evident that the best choice of spectral width for the laser source is less than 0.05 cm⁻¹.
We are targeting the formation of the tomographic images at the rate of 1000 frames per second. To achieve this we have to gather signals at the 2 kHz rate according to Nyquist criteria. If we consider the pulse repetition rate of 20 kHz or more, it is possible to adopt current modulation of the laser source both at the centre of the absorption line of interest and at another line showing only background absorption. Current modulation will affect both the wavelength and the intensity of the laser source. If we incorporate the lock-in detection technique as demodulation method [18], we can recover the resultant component of intensity due to absorption. Subtraction of these two signals will eliminate the absorption due to the presence of interfering species in the sample gas. Another channel will be required as a baseline detection to adopt BRD technique for elimination of the floor-level noise due to laser source and optoelectronics. Initial involvement of this technique in analog form will enhance the dynamic range of the analog to digital converter. An equivalent technique was adopted by a group [19] for simultaneous detection of CO and CO\textsubscript{2} with commercial DFB diode lasers in the near-IR region.

![Figure 4. Schematic Detection System to be followed for single-pass measurement](image-url)

5. Conclusion

We are now trying to adapt the spectroscopic techniques mentioned earlier. To incorporate both the BRD as well as second harmonic lock-in detection technique as in Ref [20], hybrid electronic circuits will be most suitable. Detectors should be around 3 ns rise time to respond quickly at the fast pulse and integrator transimpedance amplifier electronics will be provided to acquire each sample. Analog subtractor circuits are considered to be followed. The gain of the reference signal is adjusted depending on the signals available at the edges of the spectral region where we can eliminate the presence of the other interfering species. As we shall follow the integration method for sensing the overlap integral, the ADC required will not be very fast. 473 kSamples/s ADC circuits with FPGA as developed by the Manchester group [21] may be adequate. The total scheme as illustrated in Figure 4 is under development.

References

[1] Lothar Wondraczek et al, Combustion and Flame 138 (2004) 30-39.
[2] Kosterev et al, Applied Optics, 41 (2002), 1169-1173.
[3] Wehe et al, Sensors, 2003, Proceedings of IEEE, 795-800.
[4] L.S.Rothman et al, J. of Quan. Spec., 96 (2005) 139-204.
[5] Whiting E.E., J. Quant.Spectrosc. Radiat. Transfer, 8 (1968) 1379-1384.
[6] Clausen S et al, Meas. Sci. Technol., 13 (2002) 1223-1229.
[7] Wehe S et al, Sensors, 2003. Proceedings of IEEE, 2003, 795-800.
[8] Hindle FP et al, J. Elec. Imaging, 10(3) (2001), 593-600.
[9] Wright P. at al, App. Optics, 44(31) (2005), 6578-6592.
[10] Wright P. at al, Proceedings of Photon06, http://www.photon06.org/OPD%20P2.15.doc
[11] Sonnenfroh D M et al, App. Optics, 40(6) (2001), 812-820.
[12] Herzberg G., Molecular Spectra and Molecular Structure : Volume I, Florida, 1989.
[13] Namjou K et al, Optical Letters, 23(3) (1998), 219-221.
[14] Tittel F.K. et al, Applied Physics, 89, (2003), 445-516.
[15] Anatoliy A. Kosterev and Frank K. Tittel, IEEE Journal Of Quantum Electronics, 38, 6, June 2002.
[16] Weidmann D et al, App. Phy. B 79, (2004), 907-913.
[17] Leleux DP, et al, App. Phy. B, 74, (2002), 85-93.
[18] Schilt S et al, Applied Optics, 42(33) (2003), 6728-6738.
[19] Rainer E et al, 6. Conference on Infrared Sensors and Systems, Erfurt, Germany, 9-11.5.2000.
[20] Zhu X et al, Applied Optics, 34(36) (1995), 8303-8308.
[21] Garcia-Stewart CA et al, 4th World Conf. on Industrial Process Tomography, Aizu, Japan, 2005.
[22] Kosterev AA et al, Applied Optics, 39 (36) (2000), 6866-6872.
[23] So SG et al, accepted to IEEE Sensors Journal, January 17, 2006, http://www2.ece.rice.edu/lasersci/IEEE_So_DSP.pdf