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Towards a standard for the dynamic measurement of pressure based on laser absorption spectroscopy

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Abstract

We describe an approach for creating a standard for the dynamic measurement of pressure based on the measurement of fundamental quantum properties of molecular systems. From the linewidth and intensities of ro-vibrational transitions we plan on making an accurate determination of pressure and temperature. The goal is to achieve an absolute uncertainty for time-varying pressure of 5 % with a measurement rate of 100 kHz, which will in the future serve as a method for the traceable calibration of pressure sensors used in transient processes. To illustrate this concept we have used wavelength modulation spectroscopy (WMS), due to inherent advantages over direct absorption spectroscopy, to perform rapid measurements of carbon dioxide in order to determine the pressure. The system records the full lineshape profile of a single ro-vibrational transition of CO₂ at a repetition rate of 4 kHz and with a systematic measurement uncertainty of 12 % for the linewidth measurement. A series of pressures were measured at a rate of 400 Hz (10 averages) and from these measurements the linewidth was determined with a relative uncertainty of about 0.5 % on average. The pressures measured using WMS have an average difference of 0.6 % from the absolute pressure measured with a capacitance diaphragm sensor.

1.1. Introduction

The dynamic measurement of time-varying pressure is important for industrial processes, transportation, human health, ballistics, and the environment. For example gasoline and diesel combustion engines, ubiquitous in modern transportation, experience maximum combustion pressures of 0.1 MPa to 10 MPa [1, 2], and advanced engine concepts have been proposed for up to 50 MPa.[3] Pressure fluctuations can be up to 30 kHz if knocking occurs in the cylinder. Gas turbines, used in aircraft and for power generation, operate up to 4.5 MPa with a frequency spectrum of several hertz to 30 kHz.[4] Explosive detonation is used to launch projectiles in weapons (cannons, firearms, missiles), and the pressure is key in determining projectile range and service life of the gun barrel. Barrel pressures in center-fire rifles can be as high as 450 MPa [5], with frequencies of several hundred kilohertz.[6] Blast waves from battlefield explosions can reach 1 MPa, and the rapid change in pressure from the blast can be a major factor in traumatic brain injury for warfighters [7–9], as well as affecting the integrity of structures and equipment. Medical applications, such as blood pressure measurements, have a range of 10 kPa to 100 kPa, with a frequency content of the order of 100 Hz (a 1 % time slice of a heart beat).[10] Other applications exist for processes such as rapid cooling of high voltage circuit breakers, deployment of automotive airbags,

hydraulic fracking, hydraulic and pneumatic fluid pressure for instrument control or manufacturing (e.g., waterjet cutting), and injection molding.[6]

As in the field of steady pressure, there is a wide variety of available pressure sensors to meet frequency and pressure ranges of these applications. However, unlike steady pressure, there are no commercially available traceable calibration services for the dynamic measurement of pressure, therefore it is not known what the uncertainty is for these sensors. [6] Indeed, no National Metrology Institute lists a Calibration Measurement Capability (CMC) for time-varying pressure in the Key Comparison Database. The quoted uncertainties for sensors measuring time-varying pressure, which can be as low as 0.2 %, account for repeatability, stability, and linearity, along with traceability to steady pressure standards. An assumption is made that the sensor will respond the same to a time-varying pressure as it would to a steady pressure of the same magnitude, as long as the sensor's natural frequency far exceeds that of the generated pressure. Validating this assumption requires a time-varying pressure source of known (traceable) performance, which leads to a circularity of the argument; the only way to verify the capability of the source is through measurement with the pressure sensors, whose calibration depends on the performance of the source, and so forth. Later on in this paper we will discuss a shock tube as an aperiodic (non-cyclical) pressure source which has many desirable characteristics for calibrating time-varying pressure sensors; many of the approaches for overcoming the quandary stated above rely on calculating through physical modeling the time dependent pressure of the source (say, the shock tube) or the sensor and assigning an uncertainty to that calculation.[11] This is the approach taken in the current Euramet EMRP IND09, whose goal is the development of traceable dynamic measurement of force, torque, and pressure.[12, 13]. It is important to appreciate that in the measurement traceability concept we are proposing in this paper, *the shock tube is not the pressure standard*. The shock is simply the practical device that provides the time-varying pressure.

We propose using line-of-site absorption spectroscopy to be the standard for the dynamic measurement of pressure in a gas. This relies on the same traceability principle first proposed in [14], *i.e.*, using the unique quantum mechanical characteristics of the molecules as the standard for pressure. The approach we propose builds on the vast body of work in the gas sensing and combustion diagnostics fields pioneered by the Hanson research group.[15–18] The recent review by Hanson describes the current state-of-the-art for the laser diagnostic techniques for combustion and chemical kinetics research.[15] For example Hiller et al. demonstrated measurement of the gas velocity and pressure fields using Laser-Induced-Florescence measurements.[19] Absorption spectroscopy using narrow linewidth cw lasers in a shock tube was first demonstrated over two decades ago.[20–22] In the article by Philippe et al. the authors demonstrate the measurement of pressure, temperature, and velocity.[23] This early demonstration of measuring pressure and temperature simultaneously using wavelength-modulation spectroscopy (WMS) validates the feasibility of our proposal for a standard based on spectroscopy.

As an example, a portion of the $v = 2 \leftarrow 0$ vibrational band of carbon monoxide is shown in figure 1 which illustrates the pressure dependence of the absorption transitions at a temperature of (25 °C) and 10 % partial pressure.

Due to rapid advances in optical technology driven by the telecommunications industry over the last few decades, tunable diode lasers are now available in the infrared, along with vastly improved high speed laser current sources, photodetectors, wavelength meters, and digitizers operating in hundreds of megahertz range of frequencies. In this paper, we present our concept for a measurement system and detail the requirements for speed, sensitivity, and uncertainty in the components that will enable making a traceable dynamic measurement of pressure at an expanded uncertainty of 5 %.

The primary method we are proposing is based on measuring pressures in the gas phase, which covers a range of important applications such as automotive combustion, gas turbines, and explosive detonation. Depending on the application the relevant pressures range from 10 kPa up to several hundred megapascals, frequencies range from one hertz to hundreds of kilohertz, and fluids are both liquid and gas. As pressure is increased the measurement of the absorption lineshape profile becomes more challenging and thus the technique is most likely to be successful up to a few megapascals. A successful primary optical standard can be compared over its range to calculated pressure sources and pressure sensors; validation (or correction of) the source and sensor models against the optical standard can give more confidence in using them over extended ranges and conditions for which the optical method is not presently anticipated to be used.

The concept for using this method as a traceable standard for the dynamic measurement of pressure involves four steps: 1) Calibrate a reference pressure sensor against a primary pressure standard operating under static conditions, such as a piston gauge or a mercury manometer. 2) Measure lineshapes of candidate gas absorbers (such as R(7) for CO) at a series of known pressures (using the calibrated reference sensor from step 1), known temperatures, and known gas concentrations under *steady* conditions. Some of this data already exists for relevant pressure and temperatures in databases such as HITRAN. Identify appropriate lineshape model for data analysis. 3) Under time-varying conditions using the spectroscopic technique proposed herein, measure the lineshape and temperature. 4) Fit the measured data to line-shape models with pressure as the fitting parameter and temperature determined from the ratio of two line intensities. In essence, traceability in this method is to a primary pressure standard at steady (time-invariant) conditions; this assumes that the molecules achieve thermal equilibrium faster than the time scales imposed by the time-varying pressure, such that the lineshapes are the same measured in transient conditions as they would be in steady conditions. The molecular lineshapes become the transfer standard between the primary pressure standard and the time-varying pressure. Although not the primary motivation for this paper, the same technique may provide a traceable time-varying temperature standard.

We should mention that an alternative spectroscopic approach was first explored nearly 25 years ago by Rosasco et. al. at NIST.[14] The main goal of that approach was to relate pressure and temperature to fundamental properties of nature, *i.e.*, the quantum mechanical behavior of molecules, rather than being tied to a physical artifact such as a mechanical sensor or a shock tube. This is similar to the approach that we are taking; however in this prior approach, molecular systems were to be interrogated optically through the use of Coherent Anti-stokes Raman Spectroscopy (CARS) on D₂ and N₂ in the gas phase. CARS is

a third order non-linear process requiring precise 2 color 3 beam alignment that requires large pulsed laser systems. The pressure dependence of the frequency shift and linewidth broadening of D₂ was proposed as the primary standard for pressure. The intensity dependence for a range of different vibrational bands of N₂ Q-branch was to be used as a measure of temperature. The proposed experiment required a resolution of about 0.001 cm⁻¹ to 0.05 cm⁻¹, which is several orders of magnitude higher resolution than even the most advanced Raman spectrographs to date (0.6 cm⁻¹).[24] The high spectral resolution would significantly reduce the intensity at a given wavelength resulting in a loss of sensitivity. The goal was to achieve a fully resolved spectrum for a single laser pulse. Another major drawback was that only a single measurement was possible per shock tube rupture due low repetition rate of the laser (10 Hz). Thus, the technique was abandoned due to these drawbacks.

1.2. Theory

The measurement of ro-vibrational line shapes and collision induced or pressure broadened linewidths has a rich history and is an area of active research.[25–27] To summarize the approach, we start with Beer's Law[28] the absorption of light is proportional to path length, L , partial pressure, P_i , the line intensity, $S_j^P(T)$, and the lineshape profile, $g(\nu, T, P, \chi)$.

$$I(\nu) = I_0(\nu) \exp[-S_j^P(T) P_i g(\nu, T, P, \chi) L] \quad (1)$$

This equation describes the transmitted intensity over a single transition. The transmission spectrum is a sum of each transition which has a characteristic line intensity and lineshape profile.

$$I(\nu) = I_0(\nu) \exp \left[- \sum_j S_j^P(T) P_i g_j(\nu, T, P, \chi) L \right] \quad (2)$$

Here, we are assuming a single absorbing species is present in a back-ground of a non-absorbing gas, at constant concentration (constant T and P) over the path length L . The pressure dependent lineshape profile of a molecular transition is determined by collisional dephasing and is described using a Lorentzian function. Collisions cause a random dephasing of the coherence between the probed energy levels of the molecule which results in a broadening of the linewidth. The average time between collisions, T_2 , is proportional to the reciprocal of the pressure. As the pressure increases, and the time between collisions decreases and the full width half max (FWHM) of the Lorentzian linewidth increases.

$$\text{FWHM} \approx \frac{1}{2\pi T_2} \approx 2\gamma P \quad (3)$$

Where P is the pressure and γ is the pressure broadening coefficient. The pressure broadening coefficient is determined experimentally by measuring the linewidth as a function of pressure.[28]

The Voigt profile is widely used over a range of pressures and is the standard lineshape used by the High-resolution TRANsmission molecular absorption (HITRAN) database.[25] The Voigt profile accounts for both pressure and Doppler broadening through a convolution of Gaussian and Lorentzian functions. The normalized Voigt profile is expressed as

$$g(P_{tot}, T, \nu) = \frac{1}{\sqrt{\pi} \Gamma_D} \int_{-\infty}^{\infty} \frac{\exp(-x^2)}{\left[\frac{(\nu - \nu_c)}{\Gamma_D} - x^2\right] + \left(\frac{\Gamma_L}{\Gamma_D}\right)^2} dx \quad (4)$$

Where Γ_L is the Lorentzian halfwidth, Γ_D is the Doppler halfwidth, and ν_c is the pressure shifted center frequency. The pressure broadened halfwidth for a gas at pressure, temperature, and mole fraction χ , is calculated as

$$\Gamma_L = [(\chi - 1) \gamma_{air} + \chi \gamma_{self}] P_{tot} \left(\frac{T_{ref}}{T}\right)^n \quad (5)$$

Where γ_{air} and γ_{self} represent the air- and self-pressure broadening coefficients and n is the temperature dependent exponent of the air-broadened halfwidth which is typically taken to be the same for both air- and self- broadening. The γ_{air} or background gas broadening coefficient is different for different chemical species and is a function of temperature. The γ_{air} coefficient is typically determined in dry nitrogen. Since we are proposing a background gas of helium the coefficient must be determined over the entire range of proposed temperatures and pressures for each transition under study. The γ_{self} coefficient must be extended to pressure and temperature ranges not previously measured. The pressure can be determined from the linewidth using (5.) with known temperature and mole fraction. The Doppler broadened halfwidth depends on frequency, temperature, and mass.

$$\Gamma_D = v \sqrt{\frac{2 \ln 2 T}{mc^2}} \quad (6)$$

At each absorption transition at fixed mole fraction, the lineshape profile is dependent only on temperature and pressure. Time-varying pressures in practical gas systems will involve time-varying temperatures, so lineshape profiles of at least two absorption transitions (with different temperature dependencies) will need to be measured to determine both pressure and temperature for the time-varying pressure measurement.

There has been much work and progress over the past decade to evaluate and determine the most accurate and robust lineshape profile that takes into account speed dependence of collision rates, Dicke narrowing, and collision time asymmetry while at the same time reducing to a simple profile in limiting cases. The current state-of-the-art model which will

likely be supported in future versions of the HITRAN database is the Hartman-Tran profile. [29] Additionally effects such as line mixing, which is the collisional transfer of energy from one state to another, also plays an important role as pressure increases to the relevant range of most applications, *e.g.*, above 10 kPa.[30, 31]. Although there are many high resolution spectroscopic measurements of the $v = 2 \leftarrow 0$ band of CO, see [32] and references therein, the data set is limited above 100 kPa and 300 K and with He as the collider gas (with a few exceptions). There is a high temperature study by Choa et al. [16] and a previous study of CO with a series of different collider molecules including He.[33] As such we will need to measure lineshape profiles and line intensities under time-invariant conditions from 100 kPa to 7 MPa and 300 K to 800 K, with a frequency uncertainty of ($<0.001 \text{ cm}^{-1}$) with pure CO and in a dilute mixture with He. Such an uncertainty will allow fitting models to determine lineshape coefficients, for which pressure can be determined to a fraction of a percent.

2.1. Methods

The essence of our method is that the pressure and temperature of the gas are determined on a time scale faster than the gas conditions are changing using spectroscopic measurements. By fitting the absorption line shape the pressure can be computed from the linewidth parameter. The temperature will be determined from the ratio of peak intensities using two or more ro-vibrational transitions. [17, 18, 34] The steady pressure measurement to determine mole fraction will set the uncertainty floor for the measurement of time-varying pressure. Steady pressure measurements can typically be made to 0.01 % or better.

Any adiabatic change of conditions in a gas (at the time scales of milliseconds or faster, heat exchange will be minimal) will experience both temperature and pressure changes. Hence the high speed spectroscopic system must be able to resolve both pressure and temperature changes. A shock tube will be used as a source for time-varying pressure, for which there is a well-developed theory for pressure as a function time based on geometry and initial conditions.[19–21, 35–38] This theory relies on simplifying assumptions, however it does predict that gas densities can be changed on the order of microseconds, and that any rapid change in pressure will be accompanied by a rapid change in temperature. The shock tube is currently under construction, and the spectroscopic measurement concept will be adapted to it in the near future. The tube diameter (and absorption path length) will be about 5 cm and the total tube length will be few meters. Carbon monoxide at concentrations of few percent will be seeded in the gas, and pressure changes of up to 7 MPa (total pressure) will be generated. It is anticipated that the experimental shock tube could exhibit non-ideal gas behavior, such as attenuation of the shock speed due viscous effects and heat transfer along the tube wall.[39] Non-uniform rupture of the shock-generating membrane may also occur, affecting the shock wave-front.[11] These and other non-ideal effects will produce pressure and temperature changes that differ from theory. It is important to remember that the shock tube is not the pressure standard (we are not relying on shock tube theory to determine the pressure); we are relying on it only to provide a reproducible and characteristic time-varying pressure that can be interrogated by the spectroscopic system.

A key simplifying assumption is that the molecules of the system achieve thermal equilibrium; if that occurs, then light absorption measured at time-varying gas conditions

will exhibit the same line shape and absorption strength (*i.e.*, eqn. (1)) as in a time-invariant gas which means the populations of the energy levels will follow Boltzmann statistics. The time scale to return to rotational equilibrium is fast (submicrosecond for many conditions). Vibrational equilibrium is slower, but scales with the number of collisions so at high pressures there is a more rapid return to equilibrium. For example, for a 90 % He/10 % CO mixture undergoing a shock that produces a peak pressure and temperature of 140 kPa and 340 K, the vibrational relaxation time is predicted to be about half a millisecond using (7.) and constants A and C from the literature.[40–43] These conditions represents a lower bound on reaching equilibrium because as pressure and temperature increase the relaxation rate will increase.

$$t_v \approx C \frac{\exp\left(A T^{-\frac{1}{3}}\right)}{P} \quad (7)$$

The return to local thermodynamic equilibrium time scale sets a lower bound on the speed with which the pressure rise time can be determined using our technique. The step-function type pressure increase characteristic of a shock tube typically has a duration of several milliseconds depending on the geometry of the tube. It is over this time period that our spectroscopic determination of pressure and temperature will be applied similar to previous approaches.[44, 45] A detailed approach to the spectroscopic determination of temperature will be the topic of a future paper.

We plan to develop a high-speed absorption spectroscopy system that can measure absorption profiles on the timescale of microseconds. Our goal is to achieve a traceable time-varying pressure measurement at a rate on the order of 100 kHz. The required uncertainty is estimated using the Voigt profile; in order to achieve 5 % total combined uncertainty in gas pressure we will need to measure Lorentzian halfwidths to an uncertainty of less than 2 % and temperature better than 2 %. This requires measuring relative frequency to 0.001 cm^{-1} (roughly 1 part in 10^7). As mentioned above taking into account line mixing and using more complex line shapes will likely be required.

We propose to use high-speed high sensitivity wavelength modulation spectroscopy (WMS) to probe the linewidth and intensity of molecular transitions on a timescale of microseconds. [46, 47] This method has been used for many years in the combustion diagnostics community to determine species concentrations, pressure, and temperature.[15, 16, 19, 22, 23, 44, 45, 48–50] However, our work has the goal of using the method as a pressure standard, rather than a method for pressure sensing. Experimental conditions and spectroscopic methods will be optimized to reduce the uncertainty of the measured linewidth and hence pressure. This method was chosen over direct absorption approaches due to a variety of advantages; namely, the WMS is applicable to measuring signals at high pressures because the spectra still have well resolved features. There is additional sensitivity because detection occurs at the modulation frequency far from DC where there is lower $1/f$ noise, self-normalization cancels common mode noise, and the signals are measured with a near zero background which provides high sensitivity for small signal detection.[45, 51, 52] We plan to use carbon monoxide (CO) as an absorbing molecule seeded in a background gas of

dry helium, because of the large absorption cross section, large energy level spacing between ro-vibrational transitions, and the lack of interference from neighboring transitions. Helium is chosen because of its fast vibrational relaxation rate.[41] As shown above, figure 1 illustrates the absorption spectrum of CO at various pressures. By interrogating at wavelengths of 2330 nm we can utilize commercially available distributed feedback lasers and extended range high-speed InGaAs detectors.

Here we describe a proof-of-concept demonstration measurement made possible by using existing equipment with measurements of carbon dioxide performed under steady conditions. The experimental methods and analysis techniques are based on previous studies.[15, 23, 45, 48, 51, 52] In contrast to previous work we use a zero-phase filter as part of the software lock-in detection scheme. An existing distributed feedback (DFB) laser system operates at 1610 nm (6211.8 cm^{-1}) and is in the vicinity of the $(30013) \leftarrow (00001)$ vibrational band of carbon dioxide. Using a one-meter path length absorption cell provides roughly 12 % absorption for CO₂ making this a reasonable candidate for demonstration. The spectroscopy of carbon dioxide is richer, more complex, and more than three hundred times weaker than the carbon monoxide band at 2330 nm and so the transition to CO should only improve our capabilities.

We will be leveraging the advances of calibration-free WMS where the current of a tunable diode laser is simultaneously modulated at a frequency (f_m) and scanned over an absorption transition and normalization is performed through ratio of the first and second harmonics of the modulation frequency which was first demonstrated by Cassidy and Reid[52] and later extended for use in harsh environments.[49, 53–63] Modulating the current produces both intensity modulation (IM) and frequency modulation (FM) and must be characterized for the particular laser and measurement scheme. The signal is detected at the n th harmonic of the modulation frequency using software lock-in detection. A critical aspect of software enabled lock-in detection is the selection of a suitable lowpass filter and for that reason we have adopted a zero-phase filter, which we describe below. The quadrature components X_{nf} and Y_{nf} of the lock-in signal at the n th harmonic can be written as the following as described by Sun et al.[51]

$$X_{nf} = [I(t) \cdot \cos(n 2\pi f_m t)] \otimes \text{Lowpass} \quad (8)$$

$$Y_{nf} = [I(t) \cdot \sin(n 2\pi f_m t)] \otimes \text{Lowpass} \quad (9)$$

The term $I(t)$, is the transmitted intensity of the laser through the absorbing medium. Recent normalization methods have been established that ratio the n^{th} harmonic to the first harmonic of the modulation signal.[45, 51] The self-normalization method removes laser intensity fluctuations and yields a quantitative spectrum. The 1-f normalized 2f-WMS spectra and background subtraction are achieved using (10).[17, 57, 64] In the analysis performed in this work a reference arm is used to provide the background signal.

$$\left(\frac{2f}{1f}\right) = \sqrt{\left(\frac{X_{2f}}{1f} - \frac{X_{2f\ bg}}{1f\ bg}\right)^2 + \left(\frac{Y_{2f}}{1f} - \frac{Y_{2f\ bg}}{1f\ bg}\right)^2} \quad (10)$$

Where X_{nf} and Y_{nf} are the sin and cos components of the lock-in signal (8.) and (9.) for both the signal and background. The $1f$ and $1f_{bg}$ are the magnitude of the X and Y components of the first harmonic for the signal and background.

In our proof-of-concept system, a distributed feedback (DFB) laser is used at 1610 nm to probe P20e transition of the (30013)←(00001) vibrational band of CO₂ centered at 6227.917 cm⁻¹. The laser was current modulated at 200 kHz and sinewave scanned at a rate of 4 kHz. A schematic of the experimental setup is shown in figure 2. The pressure is measured with a baratron capacitance manometer (MKS Model 627) which has an absolute uncertainty of 0.12 %.[65]

The modulation and scanning are performed using a current controller (SRS LDC502) driven by a waveform generator (Keysight 33522B). The modulated light is detected using a temperature controlled extended InGaAs detectors (Laser Components Inc IG26X1000T9) and amplified using high speed variable gain transimpedance amplifiers (Femto DHPCA). A small portion of the light is sent through a temperature stabilized low finesse solid silicon etalon and a reference detector. The etalon is stabilized to 30 °C and is 83 mm long (index of refraction of ≈ 3.45) giving a free spectral range of approximately 500 MHz at 1610 nm. The remaining light is directed through a 1-meter-long absorption cell. Off-axis parabolic mirrors are used to focus the light onto the detectors. The signals are digitized on a 14 bit digitizer (Picoscope 5000) at 25 megasamples per second. Lock-in detection at 1f and 2f harmonics of the modulation frequency are achieved in software using (8.) and (9.). The lowpass filter from (8.) and (9.) was a third order digital Butterworth lowpass filter with a 45 kHz cutoff frequency. The filter was applied both forward and backward to minimize boundary effects and have zero phase effects. The zero-phase filter has an effective order of six which enables a high degree of attenuation without introducing amplitude or phase distortion.[66] As described by Goldenstein et al. any distortions that are created in the filtering process are minimized since the same filtering and lock-in processing are applied to the simulated data during the fitting process.[45] Additionally, the use of two three-pole filters rather than one six-pole filter maintains a fast impulse response ($\approx 10 \mu s$). A reference detector was used to simultaneously measure modulation of the laser intensity. The raw data are shown in figure 3 and the WMS signal is shown in figure 4.

2.2. Analysis

For quantification and analysis of the lineshape parameters we follow the procedure put forth by Goldstein *et al.* and Sun *et al.* and we briefly reproduce the procedure and our results here. [45, 51] In this method the WMS spectra are fit directly after careful characterization of the modulation depth, laser intensity, IM to FM phase shift, and wavenumber versus time. Simulation and fitting are performed by using the experimentally

determined parameters of the laser tuning to generate the modulated wavenumber as a function of time.

$$v_{mod}(t) = v(t) + a \sin(2\pi f_{mod}t + \varphi) \quad (11)$$

Where wavenumber, $v(t)$, is obtained by using the unmodulated transmission through the etalon and then fitting the peak locations as a function of time using a fourth-order polynomial.

The fit to obtain $v(t)$ is shown in figure 5. The red line is the fit using a fourth order polynomial and the black dots are the peak locations of the etalon transmission.

The modulation depth, a from (11.), is a key parameter of the laser scanning system and must be estimated or measured because it is highly correlated to the other line shape parameters and so cannot be included in the fit. Initially, the etalon transmission of the wavelength modulated signal was analyzed by fitting the Airy function modified for wavelength modulation to the data as previous authors have shown.[67] However, we found that the fit parameters were highly correlated and required non-linear terms. This method was abandoned and the method of fitting a sinewave to the peak locations from the etalon transmission was used instead to estimate the modulation depth and IM to FM phase shift which is shown in figure 6.[16, 68] The modulation depth is estimated to be $0.061(5) \text{ cm}^{-1}$ and the phase shift was determined to be about $1.46(3) \pi$ radians. The uncertainties are shown in parenthesis and are $k=2$ type A.

With the frequency axis determined the intensity, $I_0(t)$, is determined from the wavelength modulated signal from the reference channel fit with a four term sine function (12), where the amplitude terms are the DC offset, wavelength sweep, WS , and the first and second harmonic of the modulation frequency, A and B , as shown in figure 7. All frequency terms except the DC component were fixed to their known values.

$$I_0(t) = DC \sin(2\pi v_{DC}t + \varphi_{DC}) + SW \sin(2\pi f_{SW}t + \varphi_{SW}) + A \sin(2\pi f_{mod}t + \varphi_{1f}) + B \sin(4\pi f_{mod}t + \varphi_{2f}) \quad (12)$$

A simulation is created using (11.) for the frequency axis and multiplying the fitted laser intensity, $I_0(t)$ by the simulated transmission calculated using the HITRAN parameters and the Voigt lineshape. The same lock-in and normalization procedure are applied to the WMS simulation and this generates a simulated a 1f normalized WMS 2f spectrum. This process is used to perform a non-linear least squares fit of the spectra to obtain the lineshape parameters Lorentzian linewidth, concentration, and center frequency. This method has been used for combustion diagnostic research, where the pressure is assumed to be known from commercial mechanical sensors and the temperature and concentration evolution of gas species such as CO_2 or H_2O is measured. [45] The temperature is determined by measuring the ratio of the intensity of two ro-vibrational transitions with different lower state energies.

3.1 Results

Carbon dioxide spectra of for P20e transition of the (30013) $\leftarrow$ (00001) vibrational band centered at 6227.917 cm^{-1} of CO_2 were acquired at a range of pressures from 17.1 kPa to 72.3 kPa (128 Torr to 542 Torr) and a non-linear least squares fit was performed. The Doppler broadened linewidth was fixed. All experiments were performed at room temperature and steady pressure. Figure 8 illustrates measurements and fits for each of the pressures studied. The deviation of the measured data from the fitting model grows with pressure and in this case is most likely due to line mixing. This is known to be an issue in prior measurements of CO_2 and the strength of the line mixing scales with pressure.[69] Table 1 compares the optically measured pressure and the sensor measured pressure. Figure 9 illustrates the linearity of the optically measured pressure compared to the pressure measured from a capacitance manometer. The typical uncertainty for the fit linewidth parameter is about 0.0002 cm^{-1} which translates to about 0.5 % ($k=2$ type A) for the pressure measurement on average. The agreement between the optically measured pressure and the pressure measured on the gauge is 0.6 % on average as shown in table 1.

The self-induced pressure broadening coefficient γ_{self} from (5.) can be determined by measuring the slope of linewidth versus pressure for pure CO_2 at room temperature (see left panel of figure 9). A key comparison can be made between γ_{self} determined in this paper and the γ_{self} from the HITRAN database. In our work we measure γ_{self} of the P20e line to be 0.101(1) $\text{cm}^{-1}/\text{atm}$ ($9.928(8)\times 10^{-4} \text{ cm}^{-1}/\text{kPa}$) and the HITRAN value is 0.100 $\text{cm}^{-1}/\text{atm}$. [25] The uncertainty in the slope was obtained by fitting the upper and lower 95 % bounds of the fit linewidth parameters. This extremely high level of agreement gives this method great promise for moving forward as a time-varying pressure measurement and for determination of pressure broadening coefficients.

The repeatability of the measurement is characterized by recording a series of CO_2 spectra (with no averages) and fitting each spectrum and plotting the fit Lorentzian width parameter as a function of measurement number. The repeatability is illustrated in figure 10. The total time for this measurement is about 5 seconds. The shot-to-shot fluctuations of the fit linewidth, and area parameter are currently at the 12 % ($k=2$) and 16 % level for 61.3 kPa (460 Torr) measured at a rate of 4 kHz. This translates to a pressure uncertainty of about 14 % due to the combined uncertainty of the broadening parameters, temperature, and the temperature dependent coefficient. Similarly, from the fit of the center frequency we estimate the frequency stability to be approximately 0.002 cm^{-1} .

4.1 Conclusion

Although time-varying pressure measurements and sensors have been made for decades due to their importance for societal problems, traceable primary standards are still lacking. No National Metrology Institute at present declares a calibration capability for time-varying pressure in the Key Comparison Database. Absolute uncertainties are unknown, and methods of comparison or calibration rely on “pressure scales” based on repeatability of sensing elements or pressure sources. Modern approaches taken to develop the needed standards use modeling of dynamic systems (sensors) or modeling of pressure sources

(shock tubes) which are difficult to verify without independent standards or measurements. [11, 13] We propose a fundamentally different method that relies on measuring the quantum mechanical properties of molecules to determine pressure and temperature. Our proposed technique will utilize line-of-sight absorption spectroscopy to measure time-varying pressure and temperature in a gas of known concentration, using the unique quantum mechanical characteristics of the molecules as the standard for pressure.

We have outlined a methodology for using absorption spectroscopy as a method for interrogating the pressure induced linewidth changes and hence the pressure of a gas undergoing rapid changes. We have demonstrated this technique on a proof-of-concept system of CO₂ under steady conditions, from which we can achieve uncertainties of (14 %) at a measurement rate of 4 kHz. The technique will be adapted to a shock tube, using CO as the absorbing molecule seeded in a background gas of dry helium. There has been significant work on the pressure and temperature dependent lineshapes of CO [32], however these studies are limited above atmospheric pressure and temperature. As a result, we will need to perform careful static studies of CO at temperatures up to 800 K and pressures up to several megapascals to accurately determine the lineshape parameters in a background of helium gas. This will enable accurate fitting of lineshapes at high pressure and temperature, which are characteristic of time-varying pressure applications such as advanced engine concepts and gas turbines.

Various system upgrades are underway to achieve the stated uncertainty goals and measurement rates. The frequency axis is currently determined by a temperature stabilized solid silicon etalon. The large thermal expansion coefficient of silicon results in drift of the of the transmission fringes even with fairly tight temperature control (0.01 °C). The current etalon will be replaced by an air-spaced confocal cavity with the length locked to a frequency stabilized He/Ne laser. The shorter free-spectral-range of the etalon will also provide a more accurate measure of the modulation depth. Errors in the modulation depth tend to cause offsets in the pressure determination. Measurement rates on the order of 25 kHz have previously been demonstrated [45] and so we believe a further increase of a factor of five should be within reach.

We have chosen the WMS method for rapid interrogation of the pressure-induced linewidth changes, due its maturity from many years of use in combustion diagnostics.[15] Ultimately, other high-speed spectroscopic methods may prove more advantageous for a standard for time-varying pressure. One of the drawbacks of modulation spectroscopy is the need to tune both wavelength and modulate wavelength using current control. At high pressures the linewidth become broader and the optimal modulation depth becomes larger and the limitations of the current input to the laser are rapidly reached. An alternative approach that has considerable advantages is to perform the wavelength tuning using temperature control which decouples the scanning from the modulation and the optimal modulation depths can be reached for high pressures. To achieve this goal, we plan on revisiting the approaches described recently by Njegovec et. al. and Sanders for rapid wavelength tuning.[70, 71] This tuning method also has the potential for scanning over many transitions rapidly (< 1 ms). The resulting spectra could be analyzed with a multi-spectrum fit [72] where each transition is fit together in order to determine the pressure and temperature. This method is routinely

performed in high resolution spectroscopy in order to determine lineshape parameters with minimal correlation between fitting variables.[32] This could be a powerful and precise method for the determination of pressure and temperature. [73]

References

1. Brunt MFJ, Pond CR, Biundo J. Gasoline Engine Knock Analysis using Cylinder Pressure Data. 1998; 1
2. Syrimis M, Assanis DN. Knocking cylinder pressure data characteristics in a spark-ignition engine. Journal of Engineering for Gas Turbines and Power-Transactions of the Asme. 2003; 125(2):494–499.
3. Hudson C, Gao X, Stone R. Knock measurement for fuel evaluation in spark ignition engines. Fuel. 2001; 80(3):395–407.
4. Paniagua G, Denos R. Digital compensation of pressure sensors in the time domain. Experiments in Fluids. 2002; 32(4):417–424.
5. Voluntary Industry Standards for Pressure and Velocity of Centerfire Rifle Sporting Ammunition for the use of commercial manufacturers.
6. Hjelmgren J. Dynamic Measurement of Pressure – A Literature Survey. SP Swedish National Testing and Research Institute. 2003; 2002:34.SP Report
7. Ortega JM. Non-lethal blast wave interactions with a human head. Computers & Fluids. 2011; 52:92–103.
8. Courtney MW, Courtney AC. Working toward exposure thresholds for blast-induced traumatic brain injury: Thoracic and acceleration mechanisms. Neuroimage. 2011; 54:S55–S61. [PubMed: 20483376]
9. Nakagawa A, et al. Mechanisms of primary blast-induced traumatic brain injury: insights from shock-wave research. J Neurotrauma. 2011; 28(6):1101–19. [PubMed: 21332411]
10. Poeggel S, et al. Optical Fibre Pressure Sensors in Medical Applications. Sensors (Basel). 2015; 15(7):17115–48. [PubMed: 26184228]
11. Downes S, Knott A, Robinson I. Towards a shock tube method for the dynamic calibration of pressure sensors. Philos Trans A Math Phys Eng Sci. 2014; 372(2023):20130299. [PubMed: 25071242]
12. Bartoli C, et al. Traceable dynamic measurement of mechanical quantities: objectives and first results of this european project. International Journal of Metrology and Quality Engineering. 2013; 3(3):127–135.
13. Matthews C, et al. Mathematical modelling to support traceable dynamic calibration of pressure sensors. Metrologia. 2014; 51(3):326–338.
14. Rosasco GJ, B VE, Hurst WS. A proposed dynamic pressure and temperature primary standard. J Res Natl Inst Stand Technol. 1990; 95(1)
15. Hanson RK. Applications of quantitative laser sensors to kinetics, propulsion and practical energy systems. Proceedings of the Combustion Institute. 2011; 33:1–40.
16. Chao X, Jeffries JB, Hanson RK. Absorption sensor for CO in combustion gases using 2.3 μm tunable diode lasers. Measurement Science and Technology. 2009; 20(11):115201.
17. Farooq A, Jeffries JB, Hanson RK. CO₂ concentration and temperature sensor for combustion gases using diode-laser absorption near 2.7 μm . Applied Physics B. 2008; 90(3–4):619–628.
18. Sane A, et al. Simultaneous CO concentration and temperature measurements using tunable diode laser absorption spectroscopy near 2.3 μm . Applied Physics B. 2014; 117(1):7–18.
19. Hiller B, Hanson RK. Simultaneous planar measurements of velocity and pressure fields in gas flows using laser-induced fluorescence. Appl Opt. 1988; 27(1):33–48. [PubMed: 20523544]
20. Mertens JD, et al. A shock tube study of the reactions of NH with NO, O₂, and O. International Journal of Chemical Kinetics. 1991; 23(2):173–196.
21. Dean AJ, Hanson RK, Bowman CT. A shock tube study of reactions of carbon atoms and methylidyne with nitric oxide including product channel measurements. The Journal of Physical Chemistry. 1991; 95(8):3180–3189.

22. Davidson DF, et al. Continuous wave laser absorption techniques for gasdynamic measurements in supersonic flows. *Appl Opt.* 1991; 30(18):2598–608. [PubMed: 20700249]
23. Philippe LC, Hanson RK. Laser diode wavelength-modulation spectroscopy for simultaneous measurement of temperature, pressure, and velocity in shock-heated oxygen flows. *Appl Opt.* 1993; 32(30):6090–103. [PubMed: 20856437]
24. Bykov SV, Sharma B, Asher SA. High-throughput, high-resolution Echelle deep-UV Raman spectrometer. *Appl Spectrosc.* 2013; 67(8):873–83. [PubMed: 23876726]
25. Rothman LS, et al. The HITRAN2012 molecular spectroscopic database. *Journal of Quantitative Spectroscopy & Radiative Transfer.* 2013; 130:4–50.
26. May AD, et al. The impact theory of spectral line shapes: a paradigm shift1. *Canadian Journal of Physics.* 2013; 91(11):879–895.
27. Lorentz HA. *Proc R Acad (Amsterdam).* 1906; 8
28. Bernath, PF. *Spectra of atoms and molecules.* 2nd. New York: Oxford University Press; 2005. p. xiv, 439
29. Ngo NH, et al. An isolated line-shape model to go beyond the Voigt profile in spectroscopic databases and radiative transfer codes. *Journal of Quantitative Spectroscopy & Radiative Transfer.* 2013; 129:89–100.
30. Brault JW, et al. Self-broadened $^{12}\text{C}^{16}\text{O}$ line shapes in the $v=2 \leftarrow 0$ band. *Journal of Molecular Spectroscopy.* 2003; 222(2):220–239.
31. Lévy A, Lacombe N, Chackerian C. Collisional Line Mixing. 1992:261–337.
32. Malathy Devi V, et al. Spectral line parameters including temperature dependences of self- and air-broadening in the $2 \leftarrow 0$ band of CO at $2.3\mu\text{m}$. *Journal of Quantitative Spectroscopy and Radiative Transfer.* 2012; 113(11):1013–1033.
33. Bouanich JP, et al. Pressure-Induced Lineshifts in the $2 \leftarrow 0$ Band of CO Self-Perturbed and Perturbed by He, Kr, O₂, and N₂. *Journal of Molecular Spectroscopy.* 1996; 179(1):22–31.
34. Hieta T, et al. High-precision diode-laser-based temperature measurement for air refractive index compensation. *Appl Opt.* 2011; 50(31):5990–8. [PubMed: 22086025]
35. Ferri, AE. *Fundamental Data Obtained from Shock Tube Experiments.* Pergamon Press; 1961.
36. Bradley, GN. *Shock Waves in Chemistry and Physics.* London: 1962.
37. Gaydon, AG.; Hurle, IR. *The Shock Tube in High Temperature Chemical Research.* London: Chapman and Hall; 1963.
38. Brun, R. *Introduction to Reactive Gas Dynamics.* Oxford University Press; 2009.
39. Petersen EL, Hanson RK. Nonideal effects behind reflected shock waves in a high-pressure shock tube. *Shock Waves.* 2001; 10(6):405–420.
40. Millikan RC, White DR. Vibrational Energy Exchange between N₂ and CO. The Vibrational Relaxation of Nitrogen. *The Journal of Chemical Physics.* 1963; 39(1):98.
41. Millikan RC, White DR. Systematics of Vibrational Relaxation. *Journal of Chemical Physics.* 1963; 39(12):3209–&.
42. White DR, Millikan RC. Vibrational Relaxation in Air. *Aiaa Journal.* 1964; 2(10):1844–1846.
43. Kalitan DM, et al. Ignition and Oxidation of Lean CO/H₂ Fuel Blends in Air. *Journal of Propulsion and Power.* 2007; 23(6):1291–1301.
44. Christopher, S.; Ronald, H. 47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit. American Institute of Aeronautics and Astronautics; 2011. Thermometry and Velocimetry in Supersonic Flows via Scanned Wavelength-Modulation Absorption Spectroscopy.
45. Goldenstein CS, et al. Fitting of calibration-free scanned-wavelength-modulation spectroscopy spectra for determination of gas properties and absorption lineshapes. *Appl Opt.* 2014; 53(3):356–67. [PubMed: 24514120]
46. Silver JA. Frequency-modulation spectroscopy for trace species detection: theory and comparison among experimental methods. *Appl Opt.* 1992; 31(6):707–17. [PubMed: 20720674]
47. Bomse DS, Stanton AC, Silver JA. Frequency modulation and wavelength modulation spectroscopies: comparison of experimental methods using a lead-salt diode laser. *Appl Opt.* 1992; 31(6):718–31. [PubMed: 20720675]

48. Farooq A, Jeffries JB, Hanson RK. Sensitive detection of temperature behind reflected shock waves using wavelength modulation spectroscopy of CO₂ near 2.7 μm . *Applied Physics B*. 2009; 96(1):161–173.
49. Rieker GB, Jeffries JB, Hanson RK. Calibration-free wavelength-modulation spectroscopy for measurements of gas temperature and concentration in harsh environments. *Appl Opt*. 2009; 48(29):5546–60. [PubMed: 19823239]
50. Sun K, et al. Wavelength modulation diode laser absorption spectroscopy for high-pressure gas sensing. *Applied Physics B*. 2012; 110(4):497–508.
51. Sun K, et al. Analysis of calibration-free wavelength-scanned wavelength modulation spectroscopy for practical gas sensing using tunable diode lasers. *Measurement Science and Technology*. 2013; 24(12):125203.
52. Cassidy DT, Reid J. Atmospheric-Pressure Monitoring of Trace Gases Using Tunable Diode-Lasers. *Applied Optics*. 1982; 21(7):1185–1190. [PubMed: 20389829]
53. Fernholz T, Teichert H, Ebert V. Digital, phase-sensitive detection for in situ diode-laser spectroscopy under rapidly changing transmission conditions. *Applied Physics B-Lasers and Optics*. 2002; 75:2–3. 229–236.
54. Liu JTC, Jeffries JB, Hanson RK. Wavelength modulation absorption spectroscopy with 2 f detection using multiplexed diode lasers for rapid temperature measurements in gaseous flows. *Applied Physics B: Lasers and Optics*. 2004; 78:3–4. 503–511.
55. Liu JT, Jeffries JB, Hanson RK. Large-modulation-depth 2f spectroscopy with diode lasers for rapid temperature and species measurements in gases with blended and broadened spectra. *Appl Opt*. 2004; 43(35):6500–9. [PubMed: 15617289]
56. Iseki T, Tai H, Kimura K. A portable remote methane sensor using a tunable diode laser. *Measurement Science and Technology*. 2000; 11(6):594–602.
57. Li H, et al. Extension of wavelength-modulation spectroscopy to large modulation depth for diode laser absorption measurements in high-pressure gases. *Applied Optics*. 2006; 45(5):1052. [PubMed: 16512549]
58. Gustafsson J, Chekalin N, Axner O. Improved detectability of wavelength modulation diode laser absorption spectrometry applied to window-equipped graphite furnaces by 4th and 6th harmonic detection. *Spectrochimica Acta Part B-Atomic Spectroscopy*. 2003; 58(1):111–122.
59. Wainner RT, et al. Handheld, battery-powered near-IR TDL sensor for stand-off detection of gas and vapor plumes. *Applied Physics B-Lasers and Optics*. 2002; 75:2–3. 249–254.
60. Silver JA, Kane DJ. Diode laser measurements of concentration and temperature in microgravity combustion. *Measurement Science & Technology*. 1999; 10(10):845–852.
61. Duffin K, et al. Tunable Diode-Laser Spectroscopy With Wavelength Modulation: A Calibration-Free Approach to the Recovery of Absolute Gas Absorption Line Shapes. *Journal of Lightwave Technology*. 2007; 25(10):3114–3125.
62. Reid J, Labrie D. Second-harmonic detection with tunable diode lasers: Comparison of experiment and theory. *Applied Physics B Photophysics and Laser Chemistry*. 1981; 26(3):203–210.
63. Aizawa T. Diode-Laser Wavelength-Modulation Absorption Spectroscopy for Quantitative in situ Measurements of Temperature and OH Radical Concentration in Combustion Gases. *Appl Opt*. 2001; 40(27):4894–903. [PubMed: 18360532]
64. Kluczynski P, Axner O. Theoretical description based on Fourier analysis of wavelength-modulation spectrometry in terms of analytical and background signals. *Appl Opt*. 1999; 38(27): 5803–15. [PubMed: 18324097]
65. Certain commercial products are identified in this paper in order to specify adequately the experimental or theoretical procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.
66. Walter, PL. Guidance for the Filtering of Dynamic Force, Pressure, Acceleration (and Other) Signals. *PCB Piezotronics*; p. 1-11. Technical Note 29
67. Tao L, et al. Current and frequency modulation characteristics for continuous-wave quantum cascade lasers at 9.06 μm . *Optics Letters*. 2012; 37(8):1358–1360. [PubMed: 22513685]

68. Engelbrecht R. A compact NIR fiber-optic diode laser spectrometer for CO and CO(2): analysis of observed 2f wavelength modulation spectroscopy line shapes. *Spectrochim Acta A Mol Biomol Spectrosc.* 2004; 60(14):3291–8. [PubMed: 15561611]
69. Long DA, et al. Frequency-agile, rapid scanning cavity ring-down spectroscopy (FARS-CRDS) measurements of the (30012)←(00001) near-infrared carbon dioxide band. *Journal of Quantitative Spectroscopy and Radiative Transfer.* 2015; 161:35–40.
70. Njegovec M, Donlagic D. Rapid and broad wavelength sweeping of standard telecommunication distributed feedback laser diode. *Optics Letters.* 2013; 38(11):1999–2001. [PubMed: 23722816]
71. Sanders ST, et al. Rapid temperature tuning of a 1.4- μ m diode laser with application to high-pressure H₂O absorption spectroscopy. *Optics Letters.* 2001; 26(20):1568–1570. [PubMed: 18049665]
72. Benner DC, et al. A Multispectrum Nonlinear Least-Squares Fitting Technique. *Journal of Quantitative Spectroscopy & Radiative Transfer.* 1995; 53(6):705–721.
73. manuscript in preparation.

Figure 1.

The plot shows simulated spectrum of the R branch of the $2 \leftarrow 0$ vibrational band of carbon monoxide at various pressures in a 5 cm path length and 10 % partial pressure. The panel on the right is a zoom on R(7).

Figure 2.
Schematic of WMS setup

Figure 3.

The black line is the WMS signal and the red line is the transmitted signal through the optical cell in the presence of 26.7 kPa (200 Torr) CO_2 . The grey and light red traces are the corresponding signals from the reference detector. The bottom panel is the transmitted laser intensity through the etalon detector with no modulation.

Figure 4.
The 2f/1f normalized WMS spectrum for 26.7 kPa (200 Torr) CO₂ at 6210.9736 cm⁻¹.

Figure 5.

The top panel is the unmodulated laser transmission through the etalon. The peak locations (dots lower panel) are fit with a 4th order polynomial (red).

Figure 6. Sinewave fit (gray dashes) to determine the modulation depth and IM to FM phase shift using the peak locations of the etalon transmission (black dots).

Figure 7.
The fit (red) to obtain the wavelength modulated intensity vs time (black).

Figure 8.

The plots illustrate the pressure dependent changes to the wavelength modulated spectra for P20e of the (30013) $\leftarrow$ (00001) vibrational band of CO₂ centered at 6210.9736 cm⁻¹. Each spectrum is a result of 10 averages for a total measurement time of 2.5 ms.

Figure 9.

The panel on the left illustrates the measurement of the linewidth of the P20e transition of CO₂ at 6210.9736 cm⁻¹ at various sensor measured pressures. The panel on the right is the pressure calculated using the fit linewidth parameter from (5.).

Figure 10.

The plot illustrates the fit linewidth and fit uncertainty for a series of measurements of CO₂ at 61.3 kPa (460 Torr). The dashed gray line is the average linewidth and the solid black lines are the two sigma standard deviation. Although we have the capability to stream the data directly that mode was not chosen for this measurement in order to capture longer term drift.

Table 1

Comparison of optical and sensor measured pressures

Optical (kPa)	Sensor (kPa)	% difference
17.6(2)^a	17.12(2) ^b	3.1
29.7(2)	29.84(4)	−0.5
43.0(1)	42.88(5)	0.3
55.9(1)	56.72(7)	−1.4
73.9(2)	72.34(9)	1.6
average		0.6

^a uncertainties are shown in parenthesis and are $k=2$ type A

^b uncertainties are from manufacturer, stated as 0.12 %