Technical Memorandum

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S. A. GEARHART and M. E. THOMAS
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S. A. GEARHART and M. E. THOMAS

THE JOHNS HOPKINS UNIVERSITY • APPLIED PHYSICS LABORATORY
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ABSTRACT

A noninvasive technique for measuring temperature in hot gases is evaluated as an alternative to conventional mechanical probing techniques. The technique uses a diode laser spectrometer to measure the line-center absorption coefficient ratio of two absorption lines that originate from different vibrational energy levels of the same absorbing species. The temperature is calculated without knowledge of the pressure, absorber concentration, or optical path length. A previous study demonstrated temperature measurements at about 2000 K at atmospheric pressure. The results of this evaluation suggest that the technique is also applicable for temperatures as low as 400 K and at pressures well below 1 atm.
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1.0 INTRODUCTION

Astrophysicists have long relied on measurements of electromagnetic spectra to determine remotely many properties of celestial bodies, such as their temperature, pressure, and chemical composition. With recent advances in optics and quantum electronics, similar spectroscopic techniques are now being employed for other applications that require a remote, noninvasive measurement. For example, Reid et al. used a tunable diode laser spectroscopic technique to identify and monitor air pollutants remotely. A similar technique has been proposed by Cassidy et al. to measure the pressure of trace gases in the atmosphere. In addition, Raman spectroscopy and coherent Raman anti-Stokes spectroscopy (CARS) techniques have been investigated to measure temperature and molecular concentration for flow and combustion diagnostics.  

This study examines a spectroscopic remote sensing technique that was first proposed by Wang to measure temperatures of hot gases noninvasively. The technique uses a tunable laser to probe the gas and measure the line-center transmittances of two absorption lines that originate from different vibration-rotation transitions of the same molecular species. The ratio of the line-center absorption coefficients, calculated from the measured transmittances, determines the temperature of the gas. Hanson et al. demonstrated this technique, using a tunable diode laser and two carbon monoxide absorption lines to measure temperatures in a flame. The temperature uncertainty at 2100 K is quoted to be better than ±2%.  

The dual-line ratio technique has two major advantages over the Raman spectroscopic and CARS techniques mentioned above. First, a relatively strong laser signal is measured as opposed to conventional Raman spectroscopy, which requires the measurement of relatively weak fluorescence. Consequently, the detection signal-to-noise ratio is significantly greater. Although the signal-to-noise ratio in the CARS technique is typically good, high powered tunable lasers are required. Furthermore, the decoupling of temperature from absorber concentration in the measured CARS signal is difficult and requires extensive calibration and data processing. By comparison, the dual-line ratio technique uses low power, relatively low cost diode lasers, and requires minimal knowledge of other gas parameters (i.e., pressure, path length, and absorber concentration). The disadvantage of the dual-line ratio technique is that it does not measure temperature at a point, but along a homogeneous path. However, Wang has proposed extending the technique to measure a cross section of gas by taking many line measurements along different paths and extracting point data via computer-aided tomographic techniques. With future advances in diode laser technology, for example the development of single-mode lasers that do not require cooling from a closed-cycle cryogenic refrigerator, a diode laser system may soon be compact enough to make temperature tomography possible for many practical applications. Indeed, such a system may be significantly simpler to implement than the rival techniques mentioned above.  

The intent of this study is to examine both analytically and experimentally the dual-line ratio technique and identify the parameters that are critical in practical applications. Since previous studies have demonstrated the basic feasibility for high temperature measurements (at about 2000 K), the applicability for temperature measurements below 1000 K is emphasized. Various total pressure regimes are also examined, as well as absorption line selection criteria. One potential use for the technique is to monitor temperature in a supersonic aerodynamic test facility such as the one at The Johns Hopkins University Applied Physics Laboratory.

---

2.0 CONCEPT

Figure 1 is a block diagram of the remote sensing concept. The beam from a tunable laser is passed through the gaseous test medium to a radiation detector. The frequency of the beam is tuned through two absorption lines of the gas. The temperature of the gas is then determined from the measured transmittance profiles. The equations for determining the temperature from transmittance measurements are developed below. The criteria for selecting the absorption lines are also presented.

![Figure 1](Image)

2.1 AN OVERVIEW OF ABSORPTION THEORY

When molecules are irradiated with a continuous spectrum of photons, the transmitted spectrum contains dark lines that correspond to absorption at discrete frequencies. The frequency at which an "absorption line" appears is proportional to the energy required to excite each absorbing molecule from a lower to higher energy configuration. The distribution of absorption lines is characteristic of the structure of the absorbing molecule.

Consider a laser beam of intensity $I_0$ passing through a gaseous medium as shown in Fig. 2. If the energy of the laser beam (i.e., the frequency) is approximately equal to the energy difference between two quantum energy levels of the gas molecules and if the transition from one energy level to the other is allowed (given quantum mechanical constraints), then the laser energy is absorbed, causing a sharp reduction in transmittance. The change in intensity of the beam after passing an infinitesimal distance into the gas is $-dl$, where

$$dl(v) = -k(v)dl.$$  (1)

Equation 1 is Lambert's law for the absorption of radiation. Solving the differential equation gives the transmittance of the beam through a thickness, or path length, $l$; thus,

$$T(v) = \frac{I(v)}{I_0} = e^{-k(v)l}.$$  (2)

The transmittance of the laser as a function of frequency defines the shape of the absorption line. The absorption coefficient, $k$, can be expressed as the product of two terms: $S$, the linestrength, and $g(r,v_0)$, the lineshape function

$$k(v) = Sg(r,v_0)$$  (3)

where $v_0$ is the line-center wavenumber.

The linestrength determines the intensity of the absorption line per unit path length. The linestrength depends on the difference between the number of molecules that are initially residing in each of the two energy states of the corresponding energy transition, as determined by the temperature and pressure of the absorb-
ing species and the probability that the transition will occur. The derivation of the linestrength is lengthy and not integral to this discussion; therefore, one commonly used expression is simply stated below:

\[ S = S_0 \frac{T_0}{T} \frac{P_o}{P_e} \frac{Q_{k_0}}{Q_{k_f}} \frac{Q_{t_0} Q_{t_f}}{Q_{E_0} Q_{E_f} Q_{R}} \times \exp \left[ E_i \left( \frac{T - T_0}{k_b T_0} \right) \right] \times \frac{1 - \exp (-h c v_0 / k_b T)}{1 - \exp (-h c v_0 / k_b T_0)} , \]  

where

- \( T \) is the temperature,
- \( P_o \) is the partial pressure of the absorbing species,
- \( E_i \) is the lower energy level of the transition,
- \( Q_{t_0}, Q_{t_f}, \) and \( Q_{k_f} \) are the electronic, vibration, and rotation partition functions, respectively, and
- \( k_b, h, \) and \( c \) are Boltzmann's constant, Planck's constant, and the speed of light, respectively.

The subscript "0" denotes values at a standard temperature and pressure (STP) of 296 K and 1 atm, respectively. Equation 4 expresses the linestrength as the departure from the linestrength value at STP.

The STP parameters that are relevant to this discussion, the linestrength, \( S \), the energy of the lower level of the corresponding transition, \( E_i \), and the line-center wavenumber, \( \nu_0 \), are obtained from the absorption line parameter listing prepared by the Air Force Geophysics Laboratory (AFGL) for the primary atmospheric species. A computer program that reads the AFGL data tape is provided in Appendix A. Examples of the output are included.

The lineshape function characterizes the frequency spread of the absorption line. It is normalized such that

\[ \int_{-\infty}^{\infty} g(\nu, \nu_0) \, d\nu = 1 . \]  

The lineshape function can be easily understood from a classical viewpoint by treating each absorbing molecule as an electric dipole that is excited and set into motion by the applied electromagnetic field (i.e., the laser). Using a linear systems analogy, the lineshape function then represents the frequency response of each dipole or more precisely the response of the polarization field produced by the summed fields of all the dipoles, to the applied field. This is directly analogous to the response of a damped spring-mass system to an external driving force. By evaluating the classical equations of motion for a large number of oscillating dipoles, it can be easily shown that the width of the frequency response is related to the decay rate of the resultant polarization field.

In general, at pressures above approximately 0.2 atm, the decay rate of the resultant polarization field, and hence the shape of the lineshape function, is determined by the rate of molecular collisions. This is collision broadening. The collision lineshape is a Lorentzian function given by

\[ g_c (\nu, \nu_0) = \frac{2}{\pi \Delta \nu_c} \left[ 1 + \left( \frac{2(\nu - \nu_0)}{\Delta \nu_c} \right)^2 \right] . \]  

\( \Delta \nu_c \), the collision linewidth (the fullwidth at half maximum (FWHM)), is

\[ \Delta \nu_c = 2 \alpha_0 P_{int} (T_0 T) \]  

where \( \alpha_0 \), the STP FWHM, is obtained from the AFGL compilation. Note that the use of Eq. 7 is restricted to gas mixtures having molecular composition similar to that of the atmosphere. \( \alpha_0 \) can be considered the broadening coefficient for an air mixture.

At pressures below about 0.02 atm, where atomic collisions are infrequent, the Doppler effect determines the width of the absorption line. Doppler broadening occurs when radiation at an arbitrary frequency is Doppler shifted to the line-center frequency (i.e., the resonant frequency in the moving reference frame of the molecule). Subsequently, because of the velocity distribution of the molecules in the gas, a range of incident frequencies can be absorbed. The Doppler lineshape is a Gaussian function given by

\[ g_d (\nu, \nu_i) = \frac{1}{\sqrt{\pi} \Delta \nu_d} \exp \left( -\frac{(\nu - \nu_i)^2}{\Delta \nu_d^2} \right) . \]
The Doppler linewidth (FWHM) is given by

\[ \Delta \nu_D = 2 \nu_0 \left( \frac{2k_B T \ln(2)}{MC^2} \right)^{1/2}, \]  

(9)

where \( M \) is the mass of the absorbing molecule.

At pressures from about 0.02 to 0.2 atm (for temperatures between 500 and 1000 K), both molecular collisions and the Doppler effect contribute to the absorption lineshape. This is the Voigt regime. The Voigt lineshape is expressed as a convolution of the collision and Doppler lineshapes,

\[ g \left( \nu, \nu_0 \right) = \int_{-\infty}^{\infty} g_D \left( \nu' \right) g_C \left( \nu_0 - \nu' \right) d\nu'. \]  

(10)

Figure 3 shows plots of \( \Delta \nu_C / \Delta \nu_D \) versus temperature for air-broadened carbon monoxide at a number of pressures. The calculations were performed using Eqs. 7 and 9. The three pressure regimes are marked on the figure.

**2.2 THE TEMPERATURE DEPENDENCE OF THE LINE-CENTER ABSORPTION COEFFICIENT RATIO OF TWO ABSORPTION LINES**

Consider two absorption lines of the same species that are nearly coincident in frequency, and originate from transitions between energy states 0 and 1 and states 1 and 2, respectively, as shown in Fig. 4. As temperature increases, molecules in state 0 are thermally excited to state 1. Because of the decrease in population difference between states 0 and 1, the linestrength of the corresponding absorption line decreases. Conversely, the increase in state 1 population increases the population difference between state 1 and 2, resulting in an increase in the linestrength of the corresponding absorption line. It is the relative behavior of these two absorption lines, as predicted by Maxwell-Boltzmann statistics, that is exploited for the temperature sensing technique examined in this study. This behavior is quantified below. Using Eq. 2, the transmittance ratio of the two lines at their respective line-centers is...
Taking the natural logarithms of the numerator and the denominator gives the absorption coefficient ratio:

\[
\frac{\ln T_1(v_{01})}{\ln T_2(v_{02})} = \frac{k_1}{k_2} = \frac{S_1 g_1(v_i,v_{01})}{S_2 g_2(v_i,v_{02})}.
\]  

Using Eq. 4, this becomes

\[
\frac{\ln T_1(v_{01})}{\ln T_2(v_{02})} = \frac{S_{01}}{S_{02}} \times \exp \left[ (E_1 - E_2) \frac{T - T_0}{k_B T_0} \right] \times \frac{g_1(v_{01})}{g_2(v_{02})}
\]  

where the ratio of the factors

\[
\frac{1 - \exp(-\hbar c v_{01} k_B T)}{1 - \exp(-\hbar c v_{01} k_B T_0)} = 1
\]

\[
\frac{1 - \exp(-\hbar c v_{02} k_B T)}{1 - \exp(-\hbar c v_{02} k_B T_0)}
\]

since \( v_{01} = v_{02} \). Solving for the temperature and using Eqs. 6 through 9 yields

\[
T = \frac{T_0}{1 - \frac{k_B T_0}{E_{1\lambda} - E_{2\lambda}} \ln \left( \frac{\ln (T_1) - \alpha_1 S_{01}}{\ln (T_2) - \alpha_2 S_{02}} \right)}
\]  

for pressures in the collision broadened regime, and since \( \Delta v_{01} = \Delta v_{1\lambda} \).

The maximum absorption line spacing is limited by the continuous tuning capability of the laser. For a tunable IR diode laser, absorption line separations must be about 1 cm\(^{-1}\) or less.

The minimum spacing that can be tolerated before the lines overlap significantly is largely dependent on the test environment. For example, at pressures in the collision regime and at temperatures below 1000 K, line-center transmittances for absorption lines that are separated by less than about 0.5 cm\(^{-1}\) are subject to overlap error, because the widths of the lines are relatively large. This is evident from Eq. 17. At lower pressures and higher temperatures, however, the minimum line spacing requirements are greatly relaxed. Line overlap considerations are discussed further in later sections.
The transmittances of the absorption lines also depend on properties of the test environment: specifically, the path length, absorber concentration, temperature, and total pressure. If the test environment is such that one or both of the line-center transmittances is either very close to 100% or close to 0%, then the changes in transmittance with temperature will be small and of the same order as the measurement errors. Hence, the subsequent temperature measurement errors will be large. Although in most cases the properties of the test environment are fixed, the absorption line selection process does allow some control over transmittance values for a given environment. For example, two absorption lines whose STP line-strengths are as close as possible will yield significantly better measurement accuracy at low temperatures than that of two lines whose STP line-strengths differ by a relatively larger amount.

Carbon monoxide (CO) absorption lines were selected for this study, partly because of its abundance in most combustion processes where the dual-line ratio temperature-measuring technique might be useful. In addition, however, CO has some other attractive features. These are best described with the aid of Fig. 5, which shows an absorption spectrum of CO that was obtained with a Bomem model DA3.02 Fourier Transform Spectrometer and test cell. First, the separation between the fundamental lines (i.e., the 1-0 vibration lines) is approximately

$$\Delta v_{10} \approx 2B_1 \approx 3.8 \text{ cm}^{-1}.$$  

where $B_1$ is the rotational constant for CO ($B_1 = 1.931285$). In most test situations, these lines are far enough apart to preclude significant overlap errors. Moreover, the fundamental vibration band and the 2-1 vibration band are intermeshed; hence, it is likely that there are a number of 1-0, 2-1 line pairs that meet the spacing requirements discussed previously. Although the 2-1 vibration lines cannot be resolved on Fig. 5, the band center position, which is at 2116.80 cm$^{-1}$, can be easily calculated from other CO molecular constants. Appendix B presents the equations that determine the spectrum of CO. These equations can be used to assess the suitability of other diatomic molecules provided that the molecular constants are known.

![Figure 5 Absorption spectrum of CO measured using a Fourier transform spectrometer and test cell.](image)

3.0 EXPERIMENTAL SETUP

The dual-line ratio technique was employed to measure gas temperatures in an absorption test cell. The primary goal was to evaluate the applicability of the technique, with particular emphasis toward measurements below 1000 K. The test setup and apparatus are described below.

3.1 TEST SETUP

Figure 6 shows the test setup. The diverging beam from the diode laser is collected and collimated by a 25 mm focal length 4th Ref lens. The collimated beam is chopped at 260 Hz and focused to the
Figure 6  Experimental setup and apparatus.

monochromator input slit with a 37.5 mm fl BaF$_2$ lens. The 0.35 mm fl McPherson Model 270 monochromator serves as an optical bandpass filter to isolate a single laser mode. The monochromator wavelength dial coincides with the wavelength region of the absorption lines to be measured. The monochromator input output slit width is 300 µm. This width is large enough to pass the single laser mode over the required tuning range, but small enough to ensure secondary mode rejection.

The monochromator output, which is subsequently recollimated by a 37.5 mm fl BaF$_2$ lens, strikes a CaF$_2$ beamsplitter. The transmitted beam enters the vacuum enclosure through a BaF$_2$ window, reflects from a first surface mirror through the test cell, and exits the vacuum enclosure through a second BaF$_2$ window. The heated test cell contains various mixtures of carbon monoxide (CO) and nitrogen (N$_2$). The beam reflected by the beamsplitter strikes a germanium Fabry-Perot etalon that has a free spectral range (FSR) of 0.0060 cm$^{-1}$. By counting etalon transmission maxima, which occur when the laser wavelength is an integral multiple of twice the etalon optical thickness, the tuning rate of the laser can be monitored. The etalon was loaned from Dr. Ohio State University, Columbus, R. Bole.

The first output of the etalon outputs are each focused by a 100 mm fl BaF$_2$ lens to a liquid nitrogen cooled transmission Faraday isolator. Two Lock-In Amplifiers, models 5200 and 5202, demodulate the detector outputs. A signal chromatograph read from the chopper supplies the lock in amplifier reference voltage. A variation of this voltage records the demodulated detector signal.

Proper alignment of the entire system is critical because, at best, the detector output ratio is low owing to the low laser power (approximately 1 mW) and the large attenuation through the test components. The initial alignment is performed with a helium-neon (He-Ne) beam that is aligned by laser with the diode laser beam. Fine adjustments are then made to lenses and mirrors to optimize the detected diode laser signal.

3.2 APPARATUS

The two components that are integral to this study are the diode laser system and the absorption test cell. Both components are described below.

3.2.1 The Diode Laser System

The diode laser system, manufactured by Spectra Physics, Laser Analytics Division, consists of the laser and cold head, the cryogenic refrigerator, the vacuum pump and control unit, the Model SP520 cryogenic temperature stabilizer (CTS), and the model SP5820 laser control module (LCM).

The cold head, cryogenic refrigerator, vacuum pump and theCTS form the closed-cycle cooling system that maintains the diode lasers at temperatures as low as about 13 K. Pressure lines circulate helium gas between the refrigerator and the cold head. The cold head compressor converts the helium gas to liquid. The liquid helium expands into a chamber and evaporates, cooling the cold finger where as many as four lasers are attached. The system is encapsulated in a vacuum chamber to minimize heat transfer from the ambient surroundings. The vacuum pump maintains the vacuum chamber below 10$^{-6}$ torr. The laser temperature is set by adjusting a potentiometer on the CTS. The CTS regulates the temperature via sensors and a heating coil in the cold head.

The LCM controls the laser operating current. The controls include dc amplitude adjustment, slow sweep selection at three possible rates, and square, ramp, and sawtooth modulation up to 200 Hz. The LCM also contains safety features that prevent inadvertent overheating of the individual lasers.

The diode laser used in this study is of the lead salt (PbS) variety. The output power is about 1 mW. The laser typically operates simultaneously at 3 to 5 frequency modes. The linewidth of a single laser operating mode is specified by the manufacturer to about 1 x 10$^{-7}$ rad. It is thus a narrow linewidth, combined
with tuning capability, that makes diode lasers an excellent tool for high-resolution spectroscopy. Coarse frequency tuning of the laser is performed by varying the temperature. Varying the laser temperature causes the laser modes to move discontinuously within about a 50 cm⁻¹ range. Figure 7a characterizes the frequencies of the laser used for this study as a function of temperature. The optimum operating temperature of the laser is determined by setting the monochromator dial to the frequency of a candidate absorption line pair and incrementing the laser temperature until radiation is detected at the monochromator output. This process is iterated until a match is found between a laser frequency and an absorption line pair position. For these experiments, a laser temperature of 29 K was selected.

Continuous frequency tuning of the laser is performed by sweeping the power supply current. Figure 7b shows a series of monochromator scans that were each obtained at a different laser current at a laser temperature of 29 K. The figure demonstrates continuous tuning capability of a single laser mode over a 1.4 cm⁻¹ range. This is verified by the quality of the etalon scan given in Fig. 7c.

### 3.2.2 The Test Cell

The absorption test cell was originally designed for spectroscopic studies of hot pressurized gases. Some design modifications were added in the course of this study to enhance the cell performance at higher temperatures.

Figure 8a illustrates the test cell. The cell, which is constructed of 316 stainless steel, is 12 in. long and has a center bore of 0.75 in. Optical access is provided by two sapphire windows, one at each end of the cell. Gas enters the cell through the vertical stem via a pneumatically-actuated normally-closed valve. The valve is activated by two solenoid valves and a 100 psi nitrogen supply. Pressure gauges connected to the lower stem in the right end-flange monitor the cell pressure. Although high pressures were not required for this study, the cell has been pressurized to 1000 psi in other experiments. The surface area of the cell between the end-flanges is instrumented with ceramic heating elements that are packed in ceramic insulation and radiation shielding. Two type-K thermocouples in contact with the outside wall at the center and end of the cell monitor the temperature.

Two major modifications were required to make the test cell suitable for these measurements. First, the window/end-cap assembly was redesigned to achieve higher temperatures. Second, a vacuum enclosure was constructed to capsculate the test cell and thereby improve temperature uniformity along the cell length. These modifications are discussed below.

The original window assembly incorporated two 3-in.-dia., 0.25-in.-thick sapphire windows that were each sandwiched between an end-flange and end-cap and sealed with a silicon O-ring. Because the O-rings melt above 250°C, the assembly was replaced with modified end-caps each of which contained a 1-in.-dia., 0.25-in.-thick, sapphire window. Each window was specially brazed and sealed to the stainless steel by the California based company, Ceradyne. Stainless steel O-rings were
however, because the windows fractured after a few temperature cycles of the test cell and had to be returned to Ceradyne for repair. The windows were eventually returned and successfully tested.

The temperatures between the center and end of the original version of the test cell differed by as much as 70°C. This temperature was unacceptable because experiments of the dual-line ratio technique require a reasonably homogeneous path. To improve temperature uniformity and to reduce heat loss, an aluminum vacuum enclosure was constructed to capsulate the test cell. Figure 8b shows the dimensions of the enclosure. During operation, the enclosure is evacuated to about 0.25 torr. Optical access for the laser beam is provided by two BaF$_2$ windows. Components in the vacuum enclosure are accessed from the top by removing two large plates and gaskets. The cell support platform is constructed of asbestos to minimize heat conduction to the enclosure. To preserve the seals in the pneumatically actuated valve, water-cooled copper tubing was wrapped around the valve piston housing.

The modification of the test cell window assembly and the construction of the vacuum enclosure increased the working temperature from about 250 to 500°C. Although there was some improvement in temperature uniformity across the cell, test results were still somewhat disappointing. The smallest temperature differential that could be achieved across the cell varied from about 20°C at lower temperatures to 35°C at higher temperatures. Clearly, the development of an absorption test cell with better temperature uniformity would be a primary goal of future studies.

4.0 MEASUREMENTS

Temperature measurements were conducted over a range from 385 to 840 K using two CO absorption line pairs that were selected from three absorption lines that were within the 1.4 cm$^{-1}$ tuning range of the diode laser. One line pair consisted of

$\text{C}^1\text{O}_2^1\text{H}^{2} 2-1 \text{R}(5) \text{ at } 2138.911 \text{ cm}^{-1}$

and

$\text{C}^{12}\text{O}_2^1\text{H}^{2} 1-0 \text{P}(1) \text{ at } 2139.425 \text{ cm}^{-1}$

Temperature measurements using this pair were conducted in both the Doppler and collision regimes. The second line pair consisted of
C^{12}\text{O}^{16} 2-1 R(5) at 2138.911 cm\(^{-1}\)

and

C^{12}\text{O}^{18} 1-0 R(13) at 2139.914 cm\(^{-1}\).

Two features of this line pair should be noted: first, the first absorption line is the same as that of the previous line pair, and second, the second line is of a different isotope than the first line. This combination was examined because the STP line strengths of these lines differ only by an order of magnitude. The intent was to improve temperature sensitivity at lower temperatures. (For comparison, the STP line strengths of the first line pair differ by about 10\(^4\).) The use of the second line pair was limited, however, to pressures in the Doppler regime because at the higher pressures considered, the C\(^{12}\text{O}^{18}\) line was completely overlapped by the stronger C\(^{12}\text{O}^{16}\) fundamental line. To avoid confusion later, the first line pair of the same isotopes is called the matched line pair. The second line pair, of different isotopes, is called the mixed line pair.

This chapter describes the measurement procedures, the results, and the experimental errors.

4.1 MEASUREMENT PROCEDURES

Two parameters besides the absorption line profiles are required to measure the line-center transmittances of the absorption lines:

1. The background (i.e., the 100\% transmittance level at the respective line-centers, and
2. The baseline (i.e., the 0\% transmittance level at the respective line-centers.

As illustrated in Fig. 9, once these parameters and the absorption line profiles are known, the line-center transmittance is calculated from

\[ T = \frac{\text{line minimum} - \text{baseline}}{\text{background} - \text{baseline}}. \]

Since the procedure to determine the background and baseline levels depended on the pressure regime, measurements in the two pressure regimes are described separately below.

Measurements in the collision regime were conducted using a mixture of CO and N\(_2\) at a total pressure of 1 atm. Two laser frequency scans were performed for each temperature measurement. The first scan was performed with 1 atm of N\(_2\) in the cell to record the background transmittance level. The test cell was evacuated and then both CO and N\(_2\) were injected to a total pressure of 1 atm. The CO partial pressure was about 0.026 atm. The second scan was then performed to record the CO transmittance profiles. The baseline absorption level was obtained by blocking the diode laser beam. All three transmittance levels were recorded on the same plot. The data collection time for one temperature measurement was approximately 3 minutes.

Measurements in the Doppler regime were conducted on CO alone, at pressures ranging from 0.0013 to 0.039 atm. Because of the narrow widths of the absorption lines, a separate background scan was not required. Rather, the background level at line-center was interpolated from points on the tails of the absorption lines. The baseline level was again determined by blocking the laser beam. For measurements of the mixed line pair, the baseline level was alternatively determined by injecting a large amount of CO into the test cell such that the line-center transmittance of the C\(^{12}\text{O}^{16}\) fundamental line was 0\%.

The tuning rate of the laser for each of the measurements described above was 7 × 10\(^{-3}\) cm\(^{-1}\)/s. This rate was selected to be slow enough to ensure adequate resolution of the transmittance profiles on the plotter, yet fast enough to ensure that test conditions would not change during the scan. The time constants of the lock-in amplifiers were set as long as possible (300 ms) to reject high frequency signal fluctuations.

The measured line-center transmittance values were inserted into either Eq. 15 or Eq. 16 to calculate the temperature.
4.2 RESULTS

The results are categorized according to the pressure regime in which the measurements were conducted.

4.2.1 Results of Measurements in the Doppler Regime

Figure 10 shows test results obtained with the mixed line pair at a CO pressure of 0.026 atm. The abscissa of the plot denotes the average thermocouple temperature. The extremes of the bars at each cell temperature point indicate the cell center-to-end temperatures. Note that the cell uniformity degrades with increasing temperature.

The temperature data points obtained with the dual-line ratio technique show an interesting trend. At lower temperatures, the technique predicts higher than the average thermocouple readings. Conversely, at higher temperatures, the technique predicts lower than the average thermocouple readings. The two coincide at 540 K.

The same measurements were repeated at a later date. In these tests, the time between successive temperature measurements were doubled to 90 minutes to guarantee that the temperature at the interior of the cell was stabilized. Figure 11 shows the results. The predicted temperature obtained from the mixed line pair shows the same trend as in Figure 10, except that in this case it is much better defined. The consistency between these measurements suggests that the actual averaged cell temperature is not equivalent to the average thermocouple readings. This is not unexpected since the temperature distribution across the cell varied with temperature.

Figure 11 also shows temperatures obtained with the matched line pair at a CO pressure of approximately 0.0013 atm. These measurements were performed in succession with the mixed pair measurements. Figure 12 shows one example of the transmittance profiles obtained for both line pairs. Except for one data point, the predicted temperature from the matched line pair is almost a constant factor lower than that predicted by the mixed line pair. This suggests a systematic error, perhaps due to an error in one of the AFGL parameters that was used to calculate the temperature.

To demonstrate the effect of such an error, the following assumptions were made:

1. The temperature predicted by the mixed line pair is correct.
2. The AFGL parameters for each absorption line of the mixed line pair is correct, and
3. The STP linestrength of the fundamental line of the matched pair \( ^{12}\text{O}^{16} \text{C} \ 1-0 \ P(1) \) is in error.

Using these assumptions, the value of the STP linestrength of \( ^{12}\text{O}^{16} \text{C} \ 1-0 \ P(1) \) line, which was required for the matched and mixed line pair predictions to be equal, was determined. The procedures and results are as follows.

First, using the temperature predicted by the mixed line pair, the CO pressure for the matched line pair mea-
The previous analysis provides some evidence that the STP linestrength value listed on the AFGL listing for the C\textsuperscript{12}O\textsuperscript{16} 1-0 P(1) line might be in error. Intuitively, however, this seems unlikely, particularly for such an intense absorption line. Further study is required to resolve this issue. The goal of this exercise is to demonstrate that a systematic error, whatever the source, can explain the observed data.

4.2.2 Results of Measurements in the Collision Regime

Figure 14 shows temperature measurement results for a CO plus N\textsubscript{2} mixture at a total pressure of 1 atm as obtained for the matched line pair. Figure 15 shows a transmittance profile. For comparison, measurements were also made at the same cell temperatures using both the matched and mixed line pairs at Doppler pressures.

These data in Figs. 14 and 15 show a number of interesting features. First, the three matched line pair predictions obtained for each cell temperature are well grouped, regardless of the pressure regime over which the measurements were conducted. In addition, the matched line pair predictions are lower than the mixed line pair predictions, consistent with the results presented earlier. Most prominent, however, is that both predictions are higher than the thermocouple readings. This result was attributed to a fundamental flaw in the test setup, described next.

As shown in Fig. 8, the thermocouples are in point contact with the outer surface of the cell and restrained...
by fittings in the vacuum enclosure. A break in thermocouple contact with the cell by even 0.001 in. will result in significantly lower temperature readings. It is likely that such a break occurred in these measurements. Breaks in cell-to-thermocouple contact caused by thermal-expansion-induced movement of the test cell and vacuum enclosure have been observed in previous studies; however, this was the first occasion where apparently both thermocouples broke contact at the same time. For future measurement an alternative instrumentation technique is obviously required.

Figure 16 shows the upward shift of the matched line predictions if the modified STP line strength that was calculated previously for the C^{12}O^16 1-0 P(1) line is used in the temperature calculation. At the lower temperature the agreement between mixed and matched line pair predictions is excellent. The agreement at the higher temperature is also improved, although not quite as impressive.

Figure 15 Transmittance profiles of two collision-broadened CO absorption lines.
4.3 ERROR ANALYSIS

The experimental errors that lead to transmittance measurement inaccuracies are discussed and quantified below. The results of this discussion are used to calculate the temperature measurement uncertainty of the dual-line ratio technique.

4.3.1 Transmittance Measurement Errors

Transmittance errors arise primarily from inaccuracies in identifying the line-center minimum of each absorption line profile and the line-center background transmittance levels. The accuracy to which these can be measured depends on the level of noise in the detection system, the stability of the test cell environment and diode laser beam, and the degree of absorption line overlap. The contribution of each of these factors depends on the properties of the test environment and the measurement procedure.

For measurements in the Doppler regime, the absorption linewidths are small enough and the line separations large enough to neglect potential line overlap errors. Moreover, since a measurement is made with a single transmittance profile (i.e., no separate background scan is required), the system stability between successive scans is not a factor. Therefore, the accuracy of measuring line-center transmittances of absorption lines in the Doppler regime depends primarily on the system noise and the capability of interpolating the background transmittance level from the tails of the absorption lines. Based on test experience, it is estimated that the transmittances of Doppler broadened lines can be measured to within approximately ±0.5%.

For measurements at collision broadened pressures, however, absorption line overlap errors cannot be dismissed. Overlap error occurs when the tail of one absorption line overlaps the line-center frequency of the second absorption line. Figures 17 and 18, show transmittance profiles at various total pressures and temperatures that were calculated using Eqs. 2, 4, and 6. For the calculations, it was assumed that the line broadening characteristic of the CO, N₂ mixture was close enough to that of air to make the use of Eq. 7 (for the collision linewidth of an air-broadened absorption line) valid.

The figures indicate that absorption line overlap error will be most severe at lower temperatures and higher pressures. For example, calculations show that at 773 K and at a total pressure of 2 atm, line overlap will induce an error in the measured line-center transmittance of the C¹²O¹⁶ 2-1 R(5) line. However, the good agreement between matched line pair predictions obtained at Doppler and collision-broadened pressures, respectively, shown on Fig. 16, indicates that line overlap errors did not significantly affect the measurements at a total pressure of 1 atm.

Achieving acceptable stability between background and absorption line scans for the higher pressure measurements was a particular problem, primarily because of etalon-like effects from lenses and windows that were sensitive to even the smallest of system perturbations.
Figure 19 illustrates an etalon effect that resulted from multiple reflections between the cell windows. Etalon effects are minimized by a combination of decollimating the laser beam and skewing the beam through the system elements such that multiple reflections do not overlap. Figure 20 demonstrates the scan-to-scan repeatability that was achieved in these measurements. The estimated transmittance measurement uncertainty is higher for collision-broadened lines than for Doppler-broadened lines because of the higher background uncertainty. Specifically, the estimated transmittance uncertainty is ±1.0%.

4.3.2 Temperature Uncertainty

The temperature error caused by the transmittance measurement error is derived by expanding the absorption coefficient ratio in a Taylor’s series about a temperature $T'$,

$$ k_1(T') = k_1(T) + (T' - T) \left( \left. \frac{d}{dT} \left( \frac{k_1}{k_2} \right) \right|_t + \ldots \right).$$

Neglecting the higher order terms and solving for $(T' - T)$ gives

$$ \Delta T = T' - T = \frac{k_1(T') - k_1(T)}{\left( \left. \frac{d}{dT} \left( \frac{k_1}{k_2} \right) \right|_t \right)}.$$ 

Using Eq. 16, the temperature measurement uncertainty was calculated as follows.

The transmittance values, $k_1$, $k_2$ was calculated from

$$ k_1 = \ln(T_1 \pm \Delta \xi)$$

$$ k_2 = \ln(T_2 \pm \Delta \xi)$$

(17)

where $\Delta \xi$ is the transmittance measurement error that was estimated previously. Four curves of $k_1$, $k_2$ were generated, one for each of the four combinations of $T_1$, $T_2$ generated, one for each of the four combinations of $T_1$, $T_2$.
Matched line pair
A: C^{12}O atm 2.1 R(5)
B: C^{12}O atm 1.0 P(1)
CO pressure = 0.0013 atm
Total pressure = 0.0013 atm

(a) A
(b) k1/k2
(c) Temp error (K)

Matched line pair
A: C^{12}O atm 2.1 R(5)
B: C^{12}O atm 1.0 P(1)
CO pressure = 0.02 atm
Total pressure (CO + air) = 1 atm

(a) A
(b) k1/k2
(c) Temp error (K)

Mixed line pair
A: C^{12}O atm 1.0 R(13)
B: C^{12}O atm 2.1 R(5)
CO pressure = 0.026 atm
Total pressure = 0.026 atm

(a) A
(b) k1/k2
(c) Temp error (K)

Figure 21: Temperature uncertainty calculations for the matched line pair in the Doppler-broadened regime. (a) The calculated line-center transmittances of the two absorption lines. (b) The uncertainty envelope of the absorption coefficient ratio as determined by applying a ±0.5% transmittance error to the transmittance values calculated above. (c) The temperature error caused by the uncertainty in the absorption coefficient ratio.

Figure 22: Temperature uncertainty calculations for the matched line pair in the collision-broadened regime. (a) The calculated line-center transmittances of the two absorption lines. (b) The uncertainty envelope of the absorption coefficient ratio as determined by applying a ±1% transmittance error to the transmittance values calculated above. (c) The temperature error caused by the uncertainty in the absorption coefficient ratio.

Figure 23: Temperature uncertainty calculations for the mixed line pair in the Doppler-broadened regime. (a) The calculated line-center transmittances of the two absorption lines. (b) The uncertainty envelope of the absorption coefficient ratio as determined by applying a ±0.5% transmittance error to the transmittance values calculated above. (c) The temperature error caused by the uncertainty in the absorption coefficient ratio.
measurement error. Figure 21b shows the $k_1/k_2$ uncertainty envelope for the matched line pair in the Doppler regime. From the previous section, the transmittance error is $\pm 0.5\%$. The size of the uncertainty envelope at each temperature was used for $\Delta k_1/k_2$ in Eq. 16. Figure 21c plots the corresponding temperature uncertainty as a function of temperature for the matched line pair in the Doppler regime. Figures 22 and 23 show similar plots for the matched line pair in the collision regime (for a transmittance error of $\pm 1\%$) and the mixed line pair in the Doppler regime (for a transmittance error of $\pm 0.5\%$), respectively.

The error bars on the data points of Figs. 12 and 16 are obtained from parts c of Figs. 21 through 23. The error bars indicate that the best accuracy at low temperatures and at pressures in the Doppler regime is achieved with the mixed line pair measurement. The temperature uncertainty is better than $\pm 1\%$. However, as temperature increases to about 800 K, the uncertainty increases to higher than $\pm 2\%$. At this temperature, the matched line pair (at pressures in the Doppler regime) gives better accuracy (i.e., about 1%), demonstrating the importance of the absorption line selection process in determining measurement accuracy in a given temperature range.

5.0 CONCLUSIONS

The results of this study demonstrate the use of the dual-line absorption ratio technique for measuring temperatures below 1000 K. For pressures in the Doppler regime the measurement uncertainty is estimated to be $\pm 1\%$ at 700 K. At the same temperature at a pressure in the collision regime, the uncertainty is approximately $\pm 2\%$. The use of absorption lines of different isotopes at pressures in the Doppler regime to improve low temperature measurement accuracy was also demonstrated. This work augments a previous study by Hanson et al. that considered only temperatures above 1000 K, pressures in the collision regime, and absorption line pairs of the same isotope.

To calibrate the dual-line ratio technique accurately at temperatures below 1000 K, some improvements in the test apparatus are required. For example, a shorter path length test cell would provide significantly better temperature uniformity. In addition, an alternate technique of supporting the cell thermocouples is essential to prevent breaks in thermal contact with the test cell, caused by thermal expansion. Also, a pressure gauge that has a resolution of less than 1 torr would ensure a controlled cell environment for low pressure measurements. Lastly, replacing lenses in the optical system with off-axis aspheric mirrors and replacing plane parallel windows with wedged windows would greatly reduce etalon effects that degrade the transmittance spectra.

Since the precision of the STP absorption line parameters are crucial to the dual-line ratio technique, a calibration of the technique should include accurate measurement of these parameters. Because of its narrow single-mode linewidth, the tunable diode laser is an ideal tool for this. However, such measurements require a precisely controlled environment.
The Air Force Geophysics Laboratory (AFGL) compilation lists absorption line parameters for the seven primary atmospheric species:

<table>
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<th>Molecule</th>
<th>Identification no. on AFGL listing</th>
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<td>H₂O</td>
<td>1</td>
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<tr>
<td>CO₂</td>
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<tr>
<td>O₃</td>
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<td>N₂O</td>
<td>4</td>
</tr>
<tr>
<td>CO</td>
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<td>CH₄</td>
<td>6</td>
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<tr>
<td>O₂</td>
<td>7</td>
</tr>
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</table>

The data for each absorption line includes \( n_o \), the line-center wavenumber, \( S_o \), the linestrength (molecules/cm\(^2\)), \( \Delta \), the half-width (cm/\text{atm}) , \( E_v \), the term value of the lower energy level (cm\(^{-1}\)), the transition quantum numbers, the date the data were acquired, the isotope, and the molecule identification number. An example of the AFGL listing is shown below.

A Fortran program that reads the AFGL 9-track magnetic tape is shown at the right. The program was developed on an IBM system 3033 computer.

### APPENDIX A

The AFGL Absorption Line Compilation

The data for each absorption line includes \( n_o \), the line-center wavenumber, \( S_o \), the linestrength (molecules/cm\(^2\)), \( \Delta \), the half-width (cm/\text{atm}) , \( E_v \), the term value of the lower energy level (cm\(^{-1}\)), the transition quantum numbers, the date the data were acquired, the isotope, and the molecule identification number. An example of the AFGL listing is shown below.

A Fortran program that reads the AFGL 9-track magnetic tape is shown at the right. The program was developed on an IBM system 3033 computer.

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<th>WAVENO.</th>
<th>LINE STRNGL WIDTH</th>
<th>LOWER STATE</th>
<th>TRANSITION QUANTUM NUMBERS</th>
<th>DATE</th>
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APPENDIX B

The Spectra of Diatomic Molecules

The equations that determine the spectra of diatomic molecules are discussed briefly below. A more complete development can be found in Ref. 8.

Solution of the Schrödinger equation for a vibrating-rotator gives the values of the quantized energy values of a diatomic molecule:

\[ E = G(V)hc + F(J)hc, \quad (B-1) \]

where \( V \) and \( J \) are the respective vibration and rotational quantum numbers. The first term of Eq. B-1, representing the energy of an anharmonic oscillator, is given by

\[ G(V)hc = (\omega_0 V - \omega_0 x_0 V^2 + \omega_0 y_0 V^3 + \ldots)hc, \quad (B-2) \]

where

\[
\begin{align*}
\omega_0 & = \omega_v - \omega_r x_r + 3\omega_r y_r/4 + \ldots, \\
\omega_0 x_0 & = \omega_r x_r - 3\omega_r y_r/2 + \ldots, \\
\omega_0 y_0 & = \omega_r y_r + \ldots. 
\end{align*}
\]

The first term of Eq. B-2 represents the energy of a simple harmonic oscillator. The other terms in the series are required in order to obtain the energy of an anharmonic oscillator, such as is observed in nature. (The harmonic oscillator has energy levels of equal spacing—the anharmonic oscillator has energy levels that become closer as \( V \) increases.) The second term in Eq. B-1 represents the energy of a nonrigid rotator, given by

\[ F(J)hc = \left[ B_r J(J + 1) - D_r J^2 (J + 1)^2 \right]hc. \quad (B-4) \]

The first term in Eq. B-4 contains the rotational constant \( B_r \), which is inversely proportional to the molecular moment of inertia. The second term, which is small for small \( J \), accounts for the change in the moment of inertia caused by centrifugal stretching of the molecule. Note that Eq. B-4 neglects the effect of vibration on the moment of inertia since this is small for small values of \( V \). The molecular constants, \( \omega_v, \omega_r, x_r, y_r, B_r, \) and \( D_r \), in Eqs. B-2 and B-4 are tabulated in Ref. 8 for a number of diatomic molecules. Using these constants, the energy levels can be determined, as depicted in Fig. B-1a.

Using Eqs. B-1 to B-4 and the quantum-mechanical selection rules for a diatomic molecule, which dictate that energy transitions only occur in such a way that both \( V \) and \( J \) change by \( \pm 1 \), respectively, the frequencies of the spectral lines can be determined. A change in \( J \) of 1 denotes an R transition; a change in \( J \) of \( \pm 1 \) denotes a P transition, as indicated in Fig. B-1b. Thus, for a given vibration transition, there is a host of narrowly spaced spectral lines corresponding to the changes in rotational energy. These lines are centered about the frequency (in wavenumbers)

\[ v_0 = G(V) - G(V') \quad (B-5) \]

where \( V' \) and \( V'' \) are the initial and final quantum numbers, respectively. Using Eqs. B-4 and B-5, the frequencies of the spectral lines are, therefore, given by

\[ v_R = v_0 + F(J + 1) - F(J) \]

for the R transitions, and

\[ v_P = v_0 + F(J - 1) - F(J) \]

for the P transitions. Neglecting the centrifugal force term in Eq. B-4, these equations reduce to

\[ v_R = v_0 + 2B_r + 2B_r J \quad (B-6) \]

\[ v_P = v_0 + 2B_r J \quad (B-7) \]

The rotation-vibration of HCl for the \( r = 0 \) to \( r = 1 \) transition (called the fundamental) is shown in Fig. B-1c. Note that the R branch is on the higher frequency side of \( v_0 \). In addition, there is no absorption line at \( v_0 \) because the selection rules preclude a \( J = 0 \) to \( J = 0 \) transition. The spacing between fundamental lines is approximately

\[ v_{R,J} - v_{R,J-1} = 2B_r. \quad (B-8) \]

---

(a) Energy levels of a vibrating-rotator.

(b) R and P energy transitions.

(c) Vibration-rotation spectrum for the fundamental transitions \(v = 0 \rightarrow 1\) of HCl.

**Figure B-1** Energy levels and spectrum of a diatomic molecule.
REFERENCES

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