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Improvement of tunable diode laser spectrometer IRF

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Improvement of tunable diode laser spectrometer IRF

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San Jose State University, 1992

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IMPROVEMENT OF TUNABLE DIODE LASER SPECTROMETER IRF

A Thesis

Presented to

The Faculty of the Department of Physics

San Jose State University

In Partial Fulfillment

of the Requirement for the Degree

Master of Science

By

Vincent V. Dinh

December 1992

APPROVED FOR THE DEPARTMENT OF PHYSICS

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ABSTRACT

IMPROVEMENT OF TUNABLE DIODE LASER SPECTROMETER IRF

by Vincent V. Dinh

This thesis presents a method for correcting spectral line measurements using a tunable diode laser in the neighborhood of 2300 cm^{-1} . It develops an approximate mathematical model to describe a measured spectral line, then fits it to experimental data --- for subsequent extraction of the spectral line parameters, such as line width and relative line strength.

Using this method of measurement on the spectral lines proves to be beneficial --- for example, isotopic ratio differences of $\sim 5\%$, compared to the same measurements when no compensation was applied, for isotopic CO_2 were observed. The standard deviation of isotopic ratio measurements was reduced to 0.829 from 1.19. The study found, however, that there is still room for further improvements, such as in theoretical modeling and experimental approximation.

ACKNOWLEDGMENTS

Without the help and encouragement of many people this project would not have been possible. The author recalls innumerable enlightening moments spent discussing science --- and (somewhat) related thoughts --- with his mentors Dr. Joseph F. Becker and Dr. Todd B. Sauke and would like to extend many thanks them, especially for their patience, understanding, support and guidance on this project. Also, the author is much in debt to Dr. Todd B. Sauke for his help and beneficial hints on data collections. Finally, he would like to express his gratitude to Dr. K. Arya for his helpful suggestions for the thesis and his timely response to serve on the author's thesis committee.

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1 INTRODUCTION

It has been put forth by scientists that Mars had a thicker CO₂ atmosphere in the distant past.¹ Also, some surmised that if living organisms existed on Mars then variations in the martian ¹³C/¹²C ratios between organic and inorganic carbon would be similar to their terrestrial counterparts. Even though on previous Mars missions no evidence of organic material was detected at either of the landing sites, scientists speculate that the organic material was lost to surface oxidants on the planet's surface and that the information needed to establish existence of life on Mars can be obtained by taking samples beneath the martian surface.

It has also been proposed that ¹⁵N/¹⁴N ratio in the martian atmosphere has monotonically increased over time, due to the preferential escape of atmospheric ¹⁴N to space.² The ¹⁵N/¹⁴N ratio can be analyzed in a similar manner as the ¹³C/¹²C to date Martian rocks and soil.

Studies of ¹³C/¹²C ratios in organic (due to autotrophic organism) and inorganic carbon (carbonates in rocks and soil) have provided a large collection of data concerning geological and biological processes.³ Shown in Figure 1-1 is an isotopic composition of carbonate and organic carbon samples on Earth as a function of time of deposition. This figure indicates that isotopic ratios in

organic carbon are about 2 to 4 percent lower than the corresponding carbonate ratio. Principally, this difference is due to the fact that organisms preferentially fix ^{12}C at a higher rate. This 2 to 4 percent difference is indicative of the chemical and geological processes and possibly provide information about the past Earth history.⁴

Utilizing this knowledge about the Earth's $^{13}\text{C}/^{12}\text{C}$ ratios, soil samples from Mars can be brought back to Earth to be analyzed using the high accuracy and precision capabilities of the mass spectrometer. Because possible contamination can occur in the sample's return mission to Earth, NASA is interested in an instrument suitable for *in situ* measurements. Also *in situ* measurements would enable pre-screening of limited samples for the return to Earth. A mass spectrometer could do the job, except for the fact that it is bulky and requires many stages of processing to purify the samples. Recently, NASA scientists proposed that a tunable diode laser (TDL) spectrometer can be used for such mission.

The TDL has many desirable features. It can be composition tuned to operate in the IR region ($\sim 4.3\mu\text{m}$) using the advances in molecular beam epitaxy. Physically, it is light-weight and rugged. Its single mode characteristic and high spectral resolution $\sim .0003\text{ cm}^{-1}$ make it less prone to interference due to the presence of impurities in the sample --- sharp molecular lines usually do not overlap. In addition to the high resolution, the TDL consumes relatively little power (less than 3 watts), which is certainly attractive in a power limited situation. Also, the TDL spectroscopic technique requires little or no processing of samples.

Unfortunately, the present isotopic ratio accuracy of this device is only at 0.4 %, whereas a 0.1 % accuracy may be required to yield useful information about geological and biological processes (see Figure 1-1). It is believed that to improve the instrumental accuracy beyond its present value of 0.4 %, the analysis of spectral lines must include the effects of the instrument response function (IRF). Following this suggestion, this Thesis study will attempt to determine the IRF of the TDL laser spectrometer by measuring CO₂ absorption spectra in the 4.3 μm region and fitting the spectra to $\text{Voigt}_1 * \exp(-\text{Voigt}_2)$ profiles, where Voigt_1 and Voigt_2 are due to the IRF and the absorption gas, respectively, and the * denotes convolution. At low absorption pressures the model function is approximately Voigt_1 convolved with $(1 - \text{Voigt}_2)$ or effectively $\{1 - (\text{another Voigt})\}$, where the Gaussian and the Lorentzian components of the IRF are associated with the Doppler and Lorentzian components of the laser line, respectively. Since the Doppler line width is a simple function of the molecular mass and temperature, calculated widths will be compared with widths retrieved as parameters from the fitting routines to provide a difference indicative of the Gaussian width of the instrument response function. In addition, since variations in CO₂ gas pressure result in changes in the Lorentzian part of the spectral line width, a pressure series study will be done to estimate the laser's Lorentzian emission width; theoretically, CO₂ absorption width is negligible at low pressure.⁵ The spectral data obtained at the various pressures will then be used to refit to the model function which incorporates the appropriate IRF values, thereby correcting the distortion caused by the instrumental broadening.

Applying the above correction routine to measured CO₂ spectral lines, the ratio of the isotopic carbon strength changed by more than 5 % relative to the same strength ratio due to the previous method. Even though it is not possible at this time to quantitatively determine the improved accuracy, we have confidence that this ratio change is significant because the model function properly included the IRF effects into the fit. Reflecting the IRF distortions, though, the standard deviation in the isotopic carbon strength ratio of the pressure series was smaller by 0.4 of a unit, relative to a case without the IRF correction. In addition, the percent difference of the retrieved Doppler width compared to tabulated values dropped by as much as a factor of four.

Section 2 describes in detail the apparatus used to obtain typical line spectra. We then show how a typical data scan is acquired and fit to the model function. Section 3 provides a qualitative explanation of the model used. Finally, the results of the fit, with and without the IRF correction, of the model function to a spectral line are reported and compared to accepted values in Section 4.

2 EXPERIMENTAL METHODS

2.1 Spectrometer

A simplified schematic of the spectrometer used in this project to collect IR absorption spectra is depicted in Figure 2-1. The heart of this device is the tunable diode laser (model L5621, Laser Photonics, Analytic Division, Bedford MA 01730). This buried hetero-structure diode is composition tuned to operate between $2290\text{--}2305\text{ cm}^{-1}$ using molecular beam epitaxy (MBE) techniques. In addition, this diode has a narrow lasing line width $\approx .0003\text{ cm}^{-1}$ and a single mode emission at low injection currents (above threshold). Normal operating temperature and forward current for this diode are above 77°K (which is easily obtained using liquid nitrogen) and $70\text{--}500\text{ mA}$, respectively.

The $4.3\text{ }\mu\text{m}$ coherent radiation from this light source is collected by a one-inch focal length barium fluoride lens and is then focused onto a mode-selecting Czerny-Turner type grating monochromator to pass a narrow band of the radiation frequencies. Upon emerging from this grating, the beam is then split by a pellicle beamsplitter imparting about 10 % of the total intensity on the reflected beam. This reflected signal is passed through a reference gas cell, while the other portion of the incoming beam gets transmitted through the splitter and is subsequently passed through a sample cell. With barium fluoride

windows, these cells provide the beams with a 16 *cm* path length. Finally, the beams emerging from the cells are detected by indium antimonide detectors (Infrared Associates, Cranbury, NJ 08512) cooled by LN_2 to $\sim 77^\circ \text{K}$.

When excited by the radiation, the indium antimonide detectors generate electrical currents, proportional to the incident intensities, which are dc-coupled respectively to two pre-amplifiers. These current amplifiers have similar two-stage configurations --- an inverter following a Miller integrator as illustrated in Figure 2-2. But they are individually tuned to accept different dc dark currents (no light excitation) from the individual detectors and to achieve the required signal gain of $1 \text{ V} / \text{mA}$ and $1.5 \text{ V} / \text{mA}$ at a roll-off frequency at $\approx 100 \text{ kHz}$, respectively.

These amplified signals are then monitored on an oscilloscope and at the same time fed into a high speed analog-to-digital (A/D) converter board (DAS-16F, Metrabyte Corp., Tauton, MA 02780). This A/D board has a $10 \mu\text{sec}$ conversion time and a 12-bit digital-output precision. In addition, it is configured to operate in a differential mode of $\pm 5 \text{ Volt}$ input range. The control for this board is achieved through an assembly language acquisition routine programmed to collect, co-add, display, and store data scans.

In addition to the mentioned operations, the acquisition software performs another function which allows data to be compensated at acquisition time. The function physically *tracks* slowly varying drifts (leaving the high frequency or white noise drifts in the data to be accounted for by the IRF) in the data scans. At the start of a data run, the acquisition program takes 64 trial data scans to determine the location of a strong absorption line. The line locations of subsequent scans are detected and the entire scan is shifted so

that the line location coincides with the original line location before co-adding the scan, thus correcting for slow drifts in line location.

2.2 Temperature Controller and Ramp Generator

To collect the data, it is necessary to bias the laser diode at a required operating point and cause it to emit across a specific frequency range. Figure 2-3 illustrates how this process is achieved through the use of a temperature controller and a ramp generator.

By setting the diode temperature, the temperature controller (Model SP 5820, Laser Analytics, Bedford, MA 01730) in the figure fixes the Fermi function⁷ (which predetermines a set of energy states which can be occupied) in the energy bands of the diode. Then by applying a bias across the diode, the junction barrier lowers allowing electrons and holes to diffuse toward the junction and recombine emitting radiation characteristic of the energy gap structure. Now if the current is increased by a small amount, the current density also increases filling the higher available energy states. If, instead, the temperature is increased, the Fermi distribution function smears out rendering the higher energy states to be filled by the current. Thus, by either temperature or current increase, higher energy electrons become available to participate in the recombination. In this sense, an absorption spectrum can be frequency *scanned* by linearly increasing/decreasing the current in the diode. If the power absorption spectrum is then divided by a null power spectrum corresponding to the same current sweep, a normalized transmission spectrum

is obtained. Furthermore, the magnitude of this ramping current can be used to control the frequency range of the scan.

2.3 Data Acquisition

For proper measurement of an absorption spectrum, the desired frequency range to be scanned needs to be identified. In order to identify this spectral range, one should start with a wide frequency range to observe a group of absorption line features. An unambiguous determination of the spectral range can be made by comparing these features to the HITRAN⁶ data base. Once the location of the present spectral range is identified, one can easily move the frequency range of the diode laser to the location of the lines to be studied. To increase the lasing frequencies, either the injection current or the diode's operating temperature can be increased. But to avoid the multi-moding of the laser, temperature adjustment is the preferred option. The higher temperature or current translates to a change in the Fermi function admitting higher energy states or to additional higher energy states being filled, respectively, which would subsequently lead to higher photon emission energies available in the laser beam. Similarly, decreasing the lasing frequency is achieved by lowering the temperature and/or current of the diode.

Once the desired lasing range is set, periodic pumping of the ramped current into the diode as depicted in Figure 2-3 yields a typical absorption spectrum as illustrated in Figure 2-4. At the trigger of the ramp generator, a negative-going pulse (due to the wave generator) temporarily turns off the diode establishing a zero transmission level (no light on the detector); simultaneously,

the A/D board starts the data acquisition. This corresponds to the leading pulse of the wave form illustrated in Figure 2-3.

Figure 2-4 illustrates a data scan of the P(30) and the P(33) lines of $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}^{16}\text{O}$, respectively. The spectrum represents an average of 512 data scans (containing 4504 data points each) of the two spectral lines. Each of these scans is tracked on the P(33) line.

When more than one line is contained in a data scan, even if tracking is active, the spectral frequency fluctuation can potentially broaden the other non-tracked spectral lines. For example, when two neighboring lines are arbitrarily separated, each one will experience a different amount of distortion because each line is in a different phase of the noise fluctuation. If tracking is applied to one of the lines, then the simultaneous correction will not necessarily be right for other lines because of the out-of-phase fluctuation in the spectral separation between them.

Therefore, to minimize this noise and insure reliable tracking of the spectral absorption lines, the spacing between the lines should be in phase relative to the drifting source --- if possible. (That's why the spacing of the spectral lines in Figure 2-4 is set at ≈ 16.7 msec.) Doing this synchronizes 60 Hz drifts at the line locations, which are then simultaneously corrected when the tracking shifts the data spectrum.

2.4 Fitting Method

Before the model function in the introduction can be used to correct spectral line measurements of a gas sample, experimental information about the IRF must first be estimated. As alluded to in Section 1, if the absorption is small, the model function can be approximated by

$$\begin{aligned} & Voigt_1 * (1 - Voigt_2) \\ & = k + Voigt_1 * Voigt_2 \end{aligned} \quad (1)$$

where k is the Fourier transform of $Voigt_1$ evaluated at zero with respect to the transform variable. For a normalized $Voigt_1$, $k = 1$. The convolution of two Voigts results in a Voigt where its Lorentzian width is the sum of the former Lorentzian widths and its Gaussian width is the square root of the sum of the squares of the former Gaussian widths. To simplify subsequent writings we use the definition

$$Voigt_1 \equiv L_o(\omega) * J(\omega) \quad (2)$$

where $L_o(\omega)$ and $J(\omega)$ are the laser emission spectral line and random frequency-noise density function, respectively.

To get the required lineshape information for $L_o(\omega)$ and $J(\omega)$, it is necessary to extract the information from the retrieved Lorentzian and Gaussian components of the fit. At low pressure, the Lorentzian component of the model function can be attributed to the emission line of the diode laser (because the lifetime broadening rate or the dephasing rate for an absorbing medium such as CO_2 is negligible⁵). Correspondingly, its Gaussian component can be attributed to the noise jitter in the laser and to the Doppler broadening of the absorbing gas.

In Eq. (2), $J(\omega)$ represents the random frequency-noise density function at an emission frequency of the laser. For this study, $J(\omega)$ will be approximated, however, by a density function $J(\omega)$ at all lasing frequencies. Because this density function has a complicated dependence on many uncorrelated variables, we will assume $J(\omega)$ to have roughly a Gaussian profile whose character is completely determined by a particular Gaussian width (FWHM).

To estimate this jitter noise, we merely subtract out the calculated Doppler width contribution from the retrieved Gaussian component. This *subtraction* is achieved by performing the operation

$$\Delta J = \sqrt{(\Delta G)^2 - (\Delta D)^2} \quad (3)$$

where ΔG is the measured Gaussian width of the spectral line, and ΔD is its theoretical Doppler absorption width given by

$$\Delta D = \nu_o \sqrt{\frac{8 \ln(2) kT}{mc^2}}$$

where ν_o is a transition frequency of the absorbing gas, kT is the ambient thermal energy, and mc^2 is the rest energy of the absorbing gas molecule.

In the estimation of the characteristic width for $L_o(\omega)$, a pressure series experiment will be done using the same absorption line as above. The pressure series will record the Lorentzian width of the spectral line at various absorption pressures. It is then possible from this pressure series to estimate the Lorentzian emission width as the intercept of the line width *versus* pressure curve. (Pressure broadening vanishes⁵ at the zero pressure limit.)

2.5 Iteration Algorithm

In fitting the measured spectral line data to the model function, we use a nonlinear regression technique. Written by Dr. Todd B. Sauke, NASA Ames Research Center, using Interactive Digital Language (Research Systems, Inc., Boulder, Colo. 80207), the data fitting algorithm employs a modified Levenberg-Marquardt method⁸, which is a set of criteria that moderates the convergence of the fit by switching between the inverse Hessian method and the steepest descent method. These methods hinge on the fact that any well behaved function can be approximated by a quadratic form in the vicinity of a local minimum.

The fitting algorithm first converts the channel numbers of the spectral data scan to their corresponding relative wavenumbers and then normalizes the relative transmission to 100 % transmission by analyzing an etalon data scan and an evacuated data scan belonging to that spectral data set. From the knowledge that the free spectral range of the etalon is $\approx .05 \text{ cm}^{-1}$, a relative wavenumber is assigned to each data channel where there is an etalon fringe maximum. By fitting Lagrange's formula --- Eq. (1) below --- to these ordered pairs, the other data channels can be mapped to their counterpart in wave-space using the resulting polynomial.

$$\kappa(x) = \sum_{i=1}^N \kappa_i \cdot p_i(x) \equiv \sum_{i=1}^N C_i \cdot x^{i-1} \quad (1)$$

where $p_i(x) = \prod_{j=1}^N \frac{x - x_j}{x_i - x_j} \equiv \sum_{j=1}^N P_{ji} x^{j-1}$, where $\mathbf{C} = \mathbf{P} \cdot \mathbf{K}$, where

$$\mathbf{P} \equiv \begin{bmatrix} 1 & x_1 & \dots & x_1^{N-1} \\ 1 & x_2 & \dots & x_2^{N-1} \\ \dots & \dots & \dots & \dots \\ 1 & x_N & \dots & x_N^{N-1} \end{bmatrix}, \text{ where } \mathbf{K} = \begin{bmatrix} \kappa_1 \\ \kappa_2 \\ \dots \\ \kappa_N \end{bmatrix}, \text{ and where } \kappa_i \text{ is the relative wavenumber}$$

corresponding to the data channel, x . Finally to complete the data preparation, the algorithm divides the spectral line data scan by the evacuated data scan to normalize the transmission data. (See Figure 2-5,6,7).

With this normalized transmission data in terms of wavenumbers, the program proceeds to fit the normalized spectral data scan to Eq. (2) below using basically the following routine.

$$P(\omega; \mathbf{a}) = k + b\omega + \sum_i^n P_i(\omega; \mathbf{a}_i) \quad (2)$$

where $P_i(\omega; \mathbf{a}_i) = [L_o(\omega; \Delta L_o) * J(\omega; \Delta J)] * \exp[-L \cdot Voigt(\omega; \Delta D_i, \Delta \gamma_i)]$,

$$\text{where } \mathbf{a} = \begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \dots \\ \mathbf{a}_n \end{bmatrix}, \text{ where } \mathbf{a}_i = \begin{bmatrix} \Delta D_i \\ \Delta \gamma_i \\ \Delta L_o \\ \Delta J \end{bmatrix} \text{ which contains the characteristics of the}$$

Lorentzian and Gaussian function of an absorption line, and where n is the number of absorption lines to fit. To carry out this process, the algorithm indirectly minimizes

$$\chi^2 = \sum_{i=1}^N [P_i - P(\omega_i; \mathbf{a})]^2 \quad (3)$$

with respect to an initial parameter set $\mathbf{a}$ using a numerical iteration, where P_i is the power detected corresponding to ω_i . This is achieved by calculating

$$\mathbf{a}_{new} = \mathbf{a}_{old} + \Delta \mathbf{a}$$

then comparing the resulting χ^2 to the old χ^2 value. It can be shown that⁸

$$\Delta \mathbf{a} = \frac{\mathbf{A}^{-1} \cdot \nabla_{\mathbf{a}} \chi^2}{2}$$

moves $\mathbf{a}_{old}$ towards a better χ^2 , where

$$\mathbf{A}_{kl} = \frac{(1 + \lambda \delta_{kl})}{\sigma^2} \cdot \sum_{i=1}^N \nabla_{a_k} P(\kappa_i; \mathbf{a}) \cdot \nabla_{a_l} P(\kappa_i; \mathbf{a}), \text{ and where } \lambda \text{ is a real parameter. } \lambda$$

is increased if $\chi_{present}^2 \geq \chi_{old}^2$ --- otherwise, it is decreased. The algorithm continues by improving $\mathbf{a}_{old}$ until the maximum iteration limit is reached or until the change in χ^2 is sufficiently small to declare that $\mathbf{a}_{old}$ is a proper parameter set describing the data scan, relative to Eq. (2).

At the start of the fitting, λ is arbitrarily initialized to a small value. In addition, during the IRF estimation stage, the IRF width parameters corresponding to the laser line and the jitter noise are set to zero (to combine the effects of the laser emission width and its jitter width into the Lorentzian and Gaussian component of the absorption width).

3 RELEVANT FUNCTIONS

3.1 Gaussian Distribution

In science there are many observed quantities that can be classified as a collective result of a large number of uncorrelated processes. The Gaussian function is one of many mathematical expressions most commonly used to describe such a process. To see why this function is used, consider the process of walking forward and backward with 50/50 chance, respectively, on a straight line.

The position probability for the process looks like a set of normalized binomial expansion coefficients as illustrated in Figure 3-1. After a large number of steps, one can assign a density function, f , to the walker's position on the straight line. In Figure 3-1 the value of $f(x, t + \Delta t)$ is identical to its local average about x at t . Mathematically, the time derivative of f can be written as

$$\frac{\partial f}{\partial t} \equiv \frac{\Delta f}{\Delta t} = \frac{f(x, t + \Delta t) - f_{ave}(x, t)}{\Delta t} \quad (1)$$

For small Δt Eq. (1) can be approximated by

$$\frac{\partial f}{\partial t} \equiv \alpha \cdot \nabla^2 f(x, t) \quad (2)$$

where α is a real constant and where ∇ is the usual de/dx operator.

Eq. (2) can easily be solved by Fourier transforming the space variable x to the χ variable as follows

$$\frac{\partial F}{\partial t} = \alpha(i\chi)^2 F \quad (3)$$

where $F = \int f(x,t) \exp(-i\chi x) dx$. Solving Eq. (3) for F yields

$$F = \beta \exp(-\alpha\chi^2 t) + \xi$$

where β and ξ are constant scalars established by the initial conditions.

Reverse transforming F using the transform pair

$$\exp[-\frac{x^2}{2}] \leftrightarrow \sqrt{2\pi} \exp[-\frac{\chi^2}{2}]$$

results in

$$f = \beta \frac{\exp[-\frac{x^2}{4\alpha t}]}{\sqrt{4\pi\alpha t}} + \xi \delta(x) \quad (4)$$

If $f(x, t=0)$ is taken to be a delta distribution at $t=0$, then $\xi=0$; and if the unity character of f is to be preserved $\beta=1$.

The even form in f , with respect to x , suggests that all the odd moments are at $x=0$, and that the first even moment can be found by evaluating

$$\begin{aligned} m_2 &= \int x^2 f dx \equiv \sigma^2 \\ &= 2\alpha t \end{aligned}$$

where σ is defined as the *rms* value (or deviation) of x . Rewriting Eq. (4) in terms of the *rms* value yields

$$f = \frac{\exp[-\frac{x^2}{2\sigma^2}]}{\sqrt{2\pi} \sigma} \quad (5)$$

3.2 Maxwell-Boltzmann Distribution

The distribution function in Section 3.1 can be directly used to describe the molecular motion in a gas sample at thermal equilibrium. Here the convention is to assume that an arbitrary molecule in the sample has a 50 percent chance to gain, as well as to lose, a small amount of energy, so that the thermal equilibrium can be preserved. This poses the same situation as the random walker above. The gain/loss distribution for the molecule's kinetic energy, therefore, has a Gaussian form as derived in the previous paragraph.

But to get at the velocity distribution, one can assume $v \approx v_o$ if the thermal energy is large relative to the energies being interchanged. In which case, the energy change can be written as

$$\Delta KE \cong mv_o \Delta v$$

where ΔKE is the energy transfer, v_o is the *rms* velocity at the equilibrium temperature T , and Δv is the resulting velocity change. Since the change in velocity is approximately proportional to the change in kinetic energy, it is then reasonable to say that the distribution of Δv is Gaussian because ΔKE has a Gaussian form.

3.3 Doppler Frequency Shift

In any given sample of gas in thermal equilibrium, the molecules are all moving as described by a Gaussian velocity profile centered at an equilibrium velocity v_o . For a given transition, this means that molecules with different speeds will have to be excited at slightly different frequencies. As far as the

individual molecule is concerned, to be excited still means it must see a field oscillating with a transition wave length of λ_o .

But to a laboratory observer this required wave length appears as⁹

$$\begin{aligned}\lambda_a &= (c - v)\tau_a \\ &= c(1 - v/c) \cdot \frac{\tau_o}{\sqrt{1 - (v/c)^2}} \\ &= \lambda_o \sqrt{\frac{1 - v/c}{1 + v/c}}\end{aligned}\quad (1)$$

where v and τ_o are the observed molecular velocity and the corresponding period of λ_o , respectively. Inverting and Taylor expanding Eq. (1), one can approximate the apparent transition frequency by

$$f_a \cong f_o + v \cdot \frac{f_o}{c}$$

or

$$f_a - f_o = \Delta f \cong v \cdot \frac{f_o}{c}$$

Since the apparent frequency shift is proportional to the velocity, the shift distribution must have a Gaussian profile centered at f_o (or a Doppler line shape) if the absorbing sample is in thermal equilibrium. (See Section 3.2.)

3.4 Absorption Line

In the approximation of fundamental absorption line shape, one assumes an electron with a point mass, m , and a charge, e , attached to a nucleus by a spring. Applying Newton's law of motion to this system yields

$$[-eE] + [-b \frac{dx}{dt}] + [-Dx] = m \frac{d^2x}{dt^2} \quad (1)$$

where $D = m\omega_0^2$ = Hook's constant,

b = decay constant,

E = applied electric field, and

x = displacement of the point mass from its equilibrium.

Taking another step by Fourier transforming the force equation yields:

$$-e\varepsilon = m(i\omega)^2\chi + b(i\omega)\chi + D\chi$$

where ε and χ are the Fourier transforms of E and x , respectively. For linear materials, the polarization density is proportional to the electron oscillator's displacement. This observation combined with the Fourier transformed force equation produces

$$\rho = N(-e)\chi = \frac{Ne^2\varepsilon}{m[\omega_0^2 - \omega^2 + i\gamma\omega]} \quad (2)$$

where ρ = the Fourier transform of the polarization density, and

N = electron oscillator density and $\gamma = \frac{b}{m}$.

In order to make use of Eq. (2), it is advantageous to invoke Maxwell's wave equation in a medium:

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 P}{\partial t^2}$$

where ε_0 is the permittivity of free space ($=8.854 \times 10^{-12}$ farad/meter),

c is the speed of light ($=2.998 \times 10^8$ meters/second), and P is the space and time representation of the polarization density. The free charge density and conduction current density are assumed to be zero. Fourier transforming this wave equation yields

$$\nabla^2 \varepsilon - \frac{(i\omega)^2}{c^2} \varepsilon = \frac{(i\omega)^2}{\varepsilon_0 c^2} \rho \quad (3)$$

With the aid of Eq. (2), (3) becomes

$$\nabla^2 \varepsilon + \frac{\omega^2}{c^2} \varepsilon = \frac{\omega^2}{\varepsilon_0 c^2} \frac{Ne^2}{m(\omega_0^2 - \omega^2 + i\gamma\omega)} \varepsilon$$

The solution for ε satisfying the wave can be immediately written as

$$\varepsilon \propto \exp[\pm kz]$$

where $k \equiv i \frac{\omega}{c} \sqrt{\frac{-Ne^2}{\varepsilon_0 m(\omega_0^2 - \omega^2 + i\gamma\omega)} + 1}$ and z is the coordinate with its unit vector

in the direction of propagation.

Now that the electric field is known, the intensity can be explicitly expressed. Since the electric intensity is proportional to the square of the electric field, one can express the intensity as

$$I(\omega) \propto \varepsilon(\omega) \varepsilon^*(\omega) = \exp[-2\text{Re}(k)z] \quad (4)$$

Only the minus exponential is used because the positive real part of k would make an increasing field. At this point one can easily identify the exponential as the absorption coefficient. For low absorption pressure, k is approximately $\frac{\omega}{c} (= \frac{2\pi}{\lambda})$, implying that the quotient in the radical is small compared to unity.

Assuming this, one can expand the radical to the first order in the quotient and taking $\omega \approx \omega_0$ to get

$$\gamma(\omega) = 2(\text{Re } k) \approx \frac{-Ne^2 \gamma / (\varepsilon_0 mc)}{(\omega_0 - \omega)^2 + (\gamma / 2)^2}$$

This result implies that the absorption coefficient is approximately a Lorentzian profile at low absorption pressures.

But in a gas sample at thermal equilibrium, the total absorption coefficient is modified by the random motions of the individual molecules to

$$\gamma_T(\omega) = \gamma(\omega) * M(\omega)$$

where $M(\omega)$ is the probability density of the center frequency shifts. (See Section 3.3.) This result comes from the fact that the beam of light actually sees a weighed average of all the individual Lorentzian profiles. Therefore, the effective absorption profile about ω_0 should be expressed as

$$\begin{aligned}\gamma_T(\omega) &= \langle \gamma(\omega) \rangle = \int \gamma(\omega - \Delta\omega) d\{\text{probability}(\Delta\omega)\} \\ &= \int \gamma(\omega - \Delta\omega) M(\Delta\omega) d\Delta\omega \\ &= \gamma(\omega) * M(\omega)\end{aligned}\tag{5}$$

As a result, the corresponding transmission for this sample can be expressed as

$$T(\omega) = \exp\{-\kappa \cdot \gamma_T(\omega)\}$$

where κ is a constant scalar. For a sample at thermal equilibrium, $\gamma_T(\omega)$ is sometimes referred to as a Voigt profile.

3.5 Laser Emission Line

In a given laser mode, the emission line shape also is approximately Lorentzian. To qualitatively see how this statement comes about, consider a rectangular cavity enclosing a gain element. Assume that the phase between the waves leaving and entering the gain element is negligible. This assumption then approximates an almost *empty* cavity. Therefore, the field in the cavity between pumping should approximately satisfy Maxwell's equation in free space:

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = 0 \quad (1)$$

Eq. (1) can be solved by assuming a plane wave solution

$$E = E(x, y, z) \exp[-i\omega t]$$

where $E(x, y, z)$ satisfies

$$\nabla^2 E(x, y, z) + \frac{\omega_n^2}{c^2} E(x, y, z) = 0$$

Since the field is bounded, it can only have discrete wavelengths ($\omega \rightarrow \omega_n$) that satisfy the boundary conditions.¹⁰

But to be useful the laser must pass a small fraction of its light to the outside world. As an approximation, one can take the power loss as the change in the field energy, U , of the cavity. If this power loss is constant at the walls¹¹, the field's energy must vary as

$$\frac{dU}{dt} = -\alpha U \quad (2)$$

or

$$U = \exp[-\alpha t] \propto \int E^2 dv \quad (3)$$

where α is a positive constant. But the solution of E as assumed by Eq. (1), when substituted in Eq. (3) will not give a decaying energy in time. To be consistent then, the form of the electric field must be adjusted to

$$E = E(x, y, z) \exp[-i\omega_n t] \exp[-\alpha t / 2] \quad (4)$$

to account for the decay specified in Eq. (2). (The equation satisfied by $E(x, y, z)$ is also changed by this adjustment.)

Finally, to find the corresponding intensity distribution of the plane wave, one can take the (time) Fourier transform of Eq. (4) then square its modulus to obtain

$$I(\omega) \propto E(\omega) E^*(\omega) = E^2(x, y, z) \left(\frac{1}{i\omega - i\omega_n - \alpha} \right) \left(\frac{1}{-i\omega + i\omega_n - \alpha} \right) \\ \propto \frac{1}{(\omega - \omega_n)^2 + \alpha^2}$$

This shows that at a given laser operating mode, the emission line is approximately Lorentzian.

3.6 Instrument Response Function

An instrument response function (IRF) is conventionally defined as an operation that transforms an arbitrary input function into an output function. In this thesis the *input* function is the absorption line, whereas, the IRF contains the effects of noise in the driving sources and the emission line width of the diode laser. It is assumed here that the driving sources start the laser scanning and also introduce a *random* jitter (due to electrical noises and

temperature drifts) to the laser line. To characterize the effects of the IRF, it is then necessary to see how this jitter modifies the laser line.

At a given driving ramp current (if the diode laser is noiseless), the laser's emission line would be approximately a Lorentzian, $L(\omega)$, centered at an $\omega = \omega_n$. Noise in the driving source causes the emission line to jitter. If the emission profile is plotted many times at a given ramp current, one would expect a distribution of Lorentzians with centers clustered about ω_n and an average of

$$\begin{aligned} L_{ave}(\omega) &= \langle I_{\omega_n} \rangle = \int L(\omega - \Delta\omega) d\{\text{probability}(\Delta\omega)\} \\ &= \int L(\omega - \Delta\omega) J(\Delta\omega) d\Delta\omega \\ &= L(\omega) * J(\omega) \end{aligned} \quad (1)$$

where $J(\omega)$ is the noise-shift density function (taken to be Gaussian in this study). When this noisy laser light is passed through an absorbing medium, with a transmission profile $T(\omega)$, the resulting intensity distribution becomes

$$I_R(\omega) = L_{ave}(\omega) \cdot T(\omega)$$

which has a power of

$$\begin{aligned} P(\omega_n) &= \int I_R d\omega \\ &= \int L_{ave}(\omega) \cdot T(\omega) d\omega \end{aligned} \quad (2)$$

If $L(\omega)$ is represented by an even function, $L_o(\omega)$, shifted by ω_n and if $J(\omega)$ is also even, then $P(\omega_o)$ simplifies as follows

$$\begin{aligned} P(\omega_o) &= \iint L(\omega - \tau) J(\tau) d\tau T(\omega) d\omega \\ &= \int L_o(\omega - \omega_n) * J(\omega - \omega_n) T(\omega) d\omega \\ &= \{L_o(\omega_n) * J(\omega_n)\} * T(\omega_n) \end{aligned} \quad (3)$$

If the transmission is

$$T(\omega) = \exp[-\text{Voigt}_2]$$

the power spectrum can be written simply as

$$Voigt_1 * \exp\{-Voigt_2\}$$

Hence, if $\exp\{-Voigt_2\}$ is designated as the input function then $Voigt_1$ is the IRF.

4 DATA AND DISCUSSION

In this section, we proceed to apply the method discussed in the previous sections to an actual spectral line. The spectral lines used in the experiment will be the P(30) and P(33) of the rovibrational bands of the $^{12}\text{CO}_2$ isotopes. The particular rovibrational bands for these isotopes are similar to the bands illustrated in Figure 4-1. Even though the rovibrational lines are quite close together, using a tunable diode laser a close up of the P(33) and P(30) lines (and a neighboring line to the left) can be obtained as in Figure 4-2.

Using the two lines, we begin by experimentally estimating the laser emission width and the jitter width of the IRF. To get the laser emission width, a pressure series experiment is performed using the lines in Figure 4-2. This experiment is done with the absorption pressure of the CO_2 gas starting at 7.00 Torr, then sequentially pumped down to .0178 Torr. The normalized spectra were fit to a straight line plus a model function (as described in Section 3.6) for each of the lines with the emission line and jitter width in the IRF set identically to zero. Plots shown in Figure 4-3 indicate how the Lorentzian width of the lines vary as a function of pressure. As alluded to in Section 3.2, the y-intercepts of these plots indicate a measure of the laser emission line width.

Using linear interpolation on the retrieved data points of Figure 4-3(a) and (b), an average intercept ($\sim$ laser emission width) of $0.811 \times 10^{-4} \text{ cm}^{-1}$ is found.

To estimate the jitter width of the IRF, we again use the same absorption lines, but perform instead an experiment at a pressure of $P \approx 0.500 \text{ Torr}$ and plot the retrieved Gaussian width as a function of the relative line strength as depicted in Figure 4-4. The retrieved data points in Figure 4-4 were obtained with emission and jitter width set to zero. Figure 4-4 shows that when the spectral line was recorded with the *track* option (a drift compensation data acquisition mode) the resulting strength and Gaussian width are consistently more correlated. Now to estimate the jitter width, we take the square root of the difference of the squares of the average retrieved Gaussian width (2.18×10^{-3} and 2.16×10^{-3} wavenumbers for line #1 and line #2, respectively, in Figure 4-4) and the theoretical Doppler absorption width

$$\gamma_D = \omega_o \sqrt{\frac{8 \ln(2) k T}{m c^2}}$$

or

$$\gamma_D = 3.58 \times 10^{-7} \omega_o \sqrt{\frac{T}{M}}$$

where γ_D is the HWHM [cm^{-1}], ω_o is the line-center [cm^{-1}], M is the molecular mass [amu], and m is the former molecular mass [kg], to obtain a jitter width estimation of 3.09×10^{-4} wavenumber. (To get this value, we used $M = 44 \text{ amu}$, $\omega_o = 2307.653 \text{ cm}^{-1}$ for the P(33) line of the isotopic $^{12}\text{CO}_2$, and $T = 295.5^\circ \text{K}$.) This estimation of the jitter width provides a useful IRF-jitter width to use.

Including an emission width of $0.8 \times 10^{-4} \text{ cm}^{-1}$ and a jitter width of $3 \times 10^{-4} \text{ cm}^{-1}$ in the data fitting procedure yields better predictions for the

Gaussian width and the relative absorption strengths of the P(30) and P(33) lines. Using these particular IRF values for the laser emission width and the jitter width, we refit the pressure series and obtain the plots in Figure 4-5. Graphically, the difference between these plots and the ones in Figure 4-3 is slight, but the linear regression of the lines reveals marked differences. Table 4-1 (a) summarizes these differences. Under the first column, one can see that the y-intercept was reduced by more than ten times from the uncompensated y-intercept. Note that the broadening coefficients for both of the absorption line came closer (by ~1 % relative to the uncompensated coefficient) to the accepted values of the HITRAN database⁶. Also the standard deviation (~distortion) of the strength ratios of the P(33) to the P(30) lines dropped to 0.829 from 1.19 for the uncompensated case. (See Figure 4-6.)

Figure 4-7 shows a plot of the IRF compensated Gaussian width versus the relative line strength (repeatability experiment). Again, the graphical difference in this plot and that of Figure 4-4 is small, but numerically significant. Reported in Table 4-1 (b) is a summary of this difference in the retrieved line widths (of the P(30) and P(33) lines) and their relative strength ratio for both data acquisition modes, track and no-track. For example, the Gaussian absorption width of the P(33) line is closer by ~2 % to its theoretical value as compared to the uncompensated case. The relative strength ratio as indicated in Table 4-1 (b) maintains a difference of ~ 5 % compared to the uncompensated ratio. Even though, a quantitative number for this ratio improvement is not possible here, the ~5 % difference shows that there is at least an improvement because we believe that our model function is correct.

It should be noted that some initial results from our stable isotope laser spectrometer have been reported elsewhere.¹²⁻¹⁶

5 CONCLUSION

In this thesis we have presented a method for correcting measured spectral lines using a $Voigt_{IRF} * \exp[-Voigt_{Absorption}]$ profile which took into account the instrumental errors, such as the Gaussian scanning-current noise, and the Lorentzian laser line function. At low absorption pressures the model function is approximately a $Voigt$, where the Gaussian and the Lorentzian components of the IRF are associated with the Doppler and Lorentzian components of the absorption line, respectively. Since the Doppler line width is a simple function of the molecular mass and temperature, calculated widths were compared with widths retrieved as parameters from the fitting routines to provide a difference indicative of the Gaussian width of the instrument response function. In addition, since variations in CO_2 gas pressure result in linear changes in the Lorentzian part of the spectral line width, a pressure series study was performed to estimate the laser's Lorentzian emission width; theoretically, this CO_2 absorption width is negligible at low pressure.⁵ The spectral data obtained at the various pressures were then refit to the model function with the appropriate IRF values, thereby correcting the distortion caused by the instrumental broadening.

As a result of this correction, the isotopic carbon ratio distortion was lowered to 0.829 from 1.19. Likewise, the relative absorption strength ratio (of P(33) to P(30) of the isotopic $^{12}\text{CO}_2$ gas) changed by ~5 % compared to the uncompensated case. This change is significant because we have confidence in our model function. Also, the percent difference of the Doppler width of the P(33) line was lowered by as much as a factor of four.

It is not clear at this time how much the IRF correction improved the previous 0.4 % accuracy. But it is certain that the ratio accuracy is better than 0.4 %, because of the improved measurements in the Doppler widths, the Lorentzian widths (pressure broadening), and the isotopic ratio distortions.

It should be noted, however, that the model function is only an estimation of the systematic errors. An item that will testify to this is the jitter density function of the laser, which was assumed to be roughly Gaussian in form, when in fact the actual behavior was found on test runs to be a rather *complicated* function of many uncorrelated and correlated variables. Another item on this list is the laser emission line and the absorption line profile, which are only first order approximations of the full Maxwell solutions.

It is obvious, in light of these rudimentary approximations, that there are still many things which can be done to *really* improve line measurements. Probably the most effective of the improvements would have to be in fine-tuning the modeling of the IRF to account for the subtle effects, e.g., jitter distribution as a function of lasing frequencies. Another step forward can be made in improving the experimental method for approximating the IRF parameters.

Likewise, physical improvements can be made in the incorporation of noise-free band-pass filters to filter out the 60 Hz component of the signals in

both the laser's power supply and the preamplifiers at the detector's output and in shielding the low-level signal cables from noise sources. In terms of instrumental improvement, a faster computer and acquisition circuitry together with better leak-free sample cells would help minimize system drifts on the measured data scans.

Again, one should note that these are just some of the possible improvements to make for better spectral line measurements. The improvements, no doubt, will increase the isotopic ratio accuracy from the previous 0.4 % down to better than 0.1 %. Considering all the possible improvements to attain a 0.1 %-accuracy measurement, one should bear in mind that this thesis is *an initial step in that direction*.

6 REFERENCES

1. Polack, J. B. and D. C. Black (1982) "Noble Gases in Planetary Atmospheres: Implications for the Origin and Evolution of Atmospheres", *Icarus*, **51**, 169-198.
2. McElroy, T. Y. Kong, and K. L. Young (1977) "Photochemistry and Evolution of Mars' Atmosphere: A Viking Perspective", *J. Geophys. Res.* **82**, 4379-4388.
3. Gregor, C. B., R. M. Garrels, F. T. Mackenzie and J. B. Maynard (1988) "Chemical Cycles in the Evolution of the Earth", John Wiley and Sons, New York, p. 276.
4. Schidlowski, M. (1988) "A 3800-million-year Isotopic Record of Life from Carbon in Sedimentary Rocks", *Nature* **333**, 313-318.
5. A. Siegman, *Lasers*, University Science Books, Mill Valley, CA., 1986, pp. 126-134.
6. Rothman, L. S., R. R. Gamache, A. Goldman, L. R. Brown, R. A. Toth, H. M. Pickett, R. L. Poynter, J-M. Flaud, C. Camy-Peyret, A. Barbe, N. Husson, C. P. Rinsland, and M. A. H. Smith (1987), "The HITRAN database: 1986 edition," *Appl. Opt.* **26**, 4058-4097.
7. C. Kittel, *Introduction to solid States Physics*, 6th edition, John Wiley and Sons. Inc., New York, 1986, pp 200-205.
8. W. Press, B. Flannery, S. Teukolsky, and W. Vetterling, *Numerical Recipes In C*, Cambridge University Press, New York, 1990, pp. 540-545.
9. M. Schwartz, *Principles of Electrodynamics*, Dover Publications, Inc., New York, 1972, pp. 110-112.

10. P. Milonni, J. Eberly, *Lasers*, John Wiley and Sons, New York, 1988, pp. 23-25.
11. J. D. Jackson, *Classical Electrodynamics*, 2nd edition., John Wiley and Sons, New York, 1975, pp. 356-357.
12. Ramil Yaldaei, "Isotopic Ratio Measurements Using Ultra-high Resolution Infrared Tunable Diode Laser Spectroscopy", Masters Thesis, San Jose State University, December 1988, San Jose, CA.
13. Kirsten W. Hall, "Comparison of Data Analysis and Experimental Techniques for Analysis of Planetary Atmospheres", Masters Thesis, San Jose State University, August 1990, San Jose, CA.
14. Patrick J. Saldanha, "Temperature and Pressure Effects on Spectral Line Broadening of CO₂ Using Ultra-high Resolution Diode Laser Spectroscopy", Masters Thesis, San Jose State University, May 1990, San Jose, CA.
15. T. B. Sauke, J. F. Becker, T. D. Gutierrez, and V. V. Dinh, "Tunable Diode Laser Spectrometer for ¹²C/¹³C Measurements", SPIE Optical Engineering Society of Northern California Symposium, November 1990, Santa Clara, CA.
16. J. F. Becker, T. B. Sauke, M. Loewenstein, "Stable Isotope Analysis Using Tunable Diode Laser Spectroscopy", *Applied Optics*, vol. 12, pp. 1921-1927.

7. FIGURES AND CAPTIONS

Figure 1-1. Isotopic composition of carbonate, organic carbon, and a variety of extant autotrophic organism samples as a function of time of deposition. (source: J. B. Polack and D. C. Black (1982) "Noble Gases in Planetary Atmospheres: Implications for the Origin and Evolution of Atmospheres," *Icarus*, **51**, 169-198.)

Figure 2-1. Stable isotope laser spectrometer with LN_2 cooled lead-salt diode laser, grating monochromator, and LN_2 cooled InSb detectors.

Figure 2-2. A schematic of the dc-coupled pre-amplifier.

Figure 2-3. (a) Temperature controller and current ramp generator used to bias the diode laser, and (b) wave form of current ramp.

Figure 2-4. A typical absorption spectrum of two isotopic CO₂ lines of interest obtained from the diode laser spectrometer.

Figure 2-5. Typical evacuated and etalon data scans used to normalize and to correct the wave number axis for a certain absorption spectrum.

Figure 2-6. The corresponding absorption spectrum of the isotopic CO₂ lines referred to in Figure 2-5.

Figure 2-7. The normalized spectrum of the absorption spectrum in Figure 2-6.

Figure 3-1. Distribution of the first three steps of the *random walker*.

Figure 4-1. Two rovibrational bands of the isotopic $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ lines

Figure 4-2. A close-up of the P(30) and the P(33) in the isotopic $^{12}\text{CO}_2$ lines.

Figure 4-3. (a) A plot of the retrieved Lorentzian width (without the IRF correction) of the isotopic $^{12}\text{CO}_2$ P(30) absorption line versus its absorption pressure.

Figure 4-3. (b) A plot of the retrieved Lorentzian width (without the IRF correction) of the isotopic $^{12}\text{CO}_2$ P(33) absorption line versus its pressure over an extended range.

Figure 4-4. A scatter plot of the retrieved Gaussian width (without the IRF compensation) of the P(33) absorption line at ~ 0.5 Torr versus its relative line strength.

Figure 4-5. (a) A plot of the retrieved Lorentzian width (with the IRF compensation) of the isotopic $^{12}\text{CO}_2$ P(30) absorption line versus its absorption pressure.

Figure 4-5. (b) A plot of the retrieved Lorentzian width (with the IRF compensation) of the isotopic $^{12}\text{CO}_2$ P(33) absorption line versus its absorption pressure.

Figure 4-6. A plot of the isotopic strength ratio of the P(33) to P(30) absorption line (without the IRF compensation) versus the absorption pressure.

Figure 4-7. A scatter plot of the retrieved Gaussian width (with the IRF compensation) of the P(33) absorption line at ~ 0.5 Torr versus its relative line strength.

	Y-int[cm-1]	Slope[cm-1/atm] (Broadening Coefficient)		Strength Ratio(2/1)		Standard Deviation
			%Diff			
Uncompensated Line 1	7.79E-05	0.092851	-3.28021	13.65261	1.188361	
	8.43E-05	0.067758	-26.35			
IRF Compensated Line 1	3.40E-06	0.094002	-2.08125	14.34449	0.828562	
	5.88E-06	0.082812	-9.98696			
HITRAN Line 1	XXX	0.096	XXX	15.33898	XXX	
	XXX	0.092	XXX			
Line 2						

Table 4-1. (a) The summary of the pressure series results of the P(30) and P(33) lines.

	Uncompensated		IRF Compensated	
		Standard Deviation		Standard Deviation
Average Gaussian Width Line 1: Track %Difference NoTrack %Difference Line 2: Track %Difference NoTrack %Difference	2.18E-03	1.74E-05	2.15E-03	1.44E-05
	4.297994		2.531041	
	2.21E-03	3.39E-05	2.17E-03	2.67E-05
	5.587393		3.629417	
	2.16E-03	6.22E-06	2.13E-03	6.36E-06
	1.027557		-0.51378	
	2.19E-03	8.95E-06	2.15E-03	9.27E-06
	2.055114		0.513779	
	2.09E-03		2.09E-03	
	2.14E-03		2.14E-03	
Ratio of Line Strength(2/1) Track %Difference NoTrack %Difference	14.47349	0.13923	15.06226	0.141005
	-5.64242		-1.80403	
	14.3273	0.115082	14.85056	0.110469
	-6.59548		-3.18418	
Accepted Value for the Line Strength Ratio (HITRAN)	15.33898	15.33898	15.33898	15.33898

Table 4-1. (b) The summary of the repeatability results of the P(30) and P(33) lines.