Infrared Laser-based Method for Measuring Isotope Ratios

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Infrared Laser-based Method for Measuring Isotope Ratios

Abstract
The purpose of this research is to build an inexpensive, compact, and precise spectrometer that will measure the $^{13}\text{C}/^{12}\text{C}$ ratio in a sample of carbon dioxide gas. The infrared diode laser-based apparatus operates by modulating the laser frequency as it scans. The frequency modulation is then converted to amplitude modulation in the signal. A ratio of signal intensities for $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ can be converted to a measurement of the samples' isotope ratio. The analysis of the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio can be used for the detection of stomach ulcers and in various environmental applications.

Introduction
Isotopes of the same element have a different number of neutrons within the nucleus. The purpose of this research is to build a device that will measure an isotope ratio, which is the relative amount of two or more isotopes of the same element in a sample. The isotope ratio that we are currently focusing on is the ratio of $^{13}\text{CO}_2/^{12}\text{CO}_2$ within a sample of CO$_2$ gas. We will exploit the spectral separation of the different rotational/vibrational peaks in the infrared spectrum of these two molecules to measure the isotope ratio in a gas sample.

There are numerous applications for a device that could measure the $^{13}\text{C}/^{12}\text{C}$ isotope ratio. We seek to develop a device that could improve on previous technology that has been used to measure this ratio. The current method that is widely used to determine the isotope ratio of a sample is called mass spectroscopy. This device works by charging particles in a sample and determining the weight of the particles. The device uses an electric field that launches the charged particle. Then a magnetic field causes the particle to move in a curved path, whose curvature is determined by the mass to charge ratio. The mass spectrometer determines the mass of the particle according to the location at which the particle strikes a detector. Using the fact that most molecules possess a unique set of masses, the mass spectrometer determines molecular concentrations in a sample. To obtain very good precision, one must increase the paths of the charged particles and to do this one must use a larger magnetic and/or electric field. This has caused the development of mass spectrometers that include very bulky magnets. As a result, high-resolution mass spectroscopy is a very precise method but one that is expensive and not easily portable. We seek to develop an alternative method with lower costs and greater portability.
Isotope determination is used in numerous applications. Detection of stomach ulcers is one medical application. A person is given a C13 doped urea shake. Helicobacter pylori bacteria will digest the carbon within the shake and release two products, ammonia and 13CO2.[1] Our apparatus would be able to detect the change in the 13C/12C ratio and detect the presence of the helicobacter pylori bacteria, which has been linked to stomach ulcers. There are also numerous environmental applications. Wassenaar and Hobson have developed a stable isotope approach to delineate geographical locations of birds.[2] A tracing system was devised in order to track the different species in North America using the 13C/12C found on the birds’ feathers. By setting up migration monitoring stations across the continent, the researchers have devised a way to observe migration trends of endangered species. Another study used isotope measurements of carbon dioxide to measure the pollution off the Pakistani coast.[3] Annual wood tissue 13C/12C ratios could potentially be useful in estimating historic changes in soil water potential and basal area growth in mature forest ecosystems.[4] Finally, the 13C/12C ratio has applications in quality control. Analysis of the 13C/12C ratio has been proven as a means of characterization of the geographical origin of Pecorino Sardo cheese.[5] In addition, the 13C/12C ratio can be used to detect the authenticity of Mexican tequila.[6] Our device would be able to make the same isotope measurements with greater precision, more portability, and cheaper cost than the current standard of the mass spectrometer.

While mass spectroscopy uses charged particles and the measuring of molecular weights, our method involves absorption of infrared light. If perfected, this method could offer much to isotope ratio determination. Using spectroscopy could eliminate the sample preparation needed for mass spectroscopy. In addition, lasers are becoming both more compact and powerful, whereas magnetic fields only become more powerful with more electricity and larger magnets.

In infrared absorption spectroscopy, infrared laser light is sent through a sample. As the light passes through the sample, some of the light is absorbed. Each quantized or specific energy absorbed produces a different vibration or rotation of the molecule. CO2 exhibits three types of molecular vibrations. First is the symmetric stretch in which the oxygen molecules oscillate outward together from the central carbon atom. Next is the asymmetric stretch in which the oxygen molecules stretch out at different times. Then there are two degenerate bends in which the two oxygen molecules bend up and down or forward and backward away from the carbon atom. The specific vibration we are using for the 13CO2/12CO2 ratio is an overtone, with 3 quanta in the symmetric stretch, 0 quanta in the bend, and 1 quantum in the asymmetric stretch. Within this vibrational manifold, we are comparing two specific rotational lines in the spectrum. The light that goes into the vibration and rotation of molecules is absorbed by the sample, resulting in an intensity change that can be measured by a detector. The amount of light absorbed is proportional to the number of molecules in the sample. The central wavelength of the absorbed light indicates which molecule is absorbing the light. A comparison of the amount of light absorbed by 12CO2 and 13CO2 will give the relative amounts of these two molecules in the sample.

The technique used in this research is called wavelength modulation spectroscopy (WMS) and is a form of absorption spectroscopy. This technique has been used by Chaux and Lavorel.[7] The main problem with absorption spectroscopy is that the amount of light that is absorbed by the gas sample is relatively small when compared to the original strength of the laser. In order to overcome the hindrance of weak signals, WMS uses a device called a lock-in amplifier. The lock-in amplifier singles out the component of the signal at a specific reference frequency then amplifies the signal. The lock-in amplifier produces an output that looks like a first derivative; however, in order to see changes in the signal more clearly, we will view the second derivative of the signal. The lock-in amplifier filters out electronic noise, allowing us to detect a very small absorbance.

Finally, after the lock-in amplifier produces the output, the areas of the two second derivative curves have to be compared to get the isotope ratio. If we were to just take the area of the 13CO2 peak and divide this by the area of 12CO2 peak, then this ratio would be proportional to the 13CO2/12CO2 ratio but not equal the exact isotope ratio. The ratio of areas does not account for the Boltzmann population distributions or the intrinsic line strengths of the two molecules. The Boltzmann distribution describes the relative populations of different states at thermal equilibrium. Intrinsic line strengths describe the strengths of the transition dipole moments for specific molecular absorptions. Previously, our method had been to calculate a weighting factor using Boltzmann’s formula[8] and the intrinsic line strengths obtained from the HITRAN Database.[9] We can multiply the peak areas by this quantity to account for these parameters. The weighting factor that we calculated was 0.2024. When using this number, our results did not agree with measurements taken by a high resolution mass spectrometer.[10] In order to obtain results that are more accurate, we attempted the use of standard addition.
In the standard addition technique, incremental amounts of an unknown sample are added to a sample whose isotope ratio is known. In our research, the known is CO$_2$ gas that has mostly $^{12}$CO$_2$ and some $^{13}$CO$_2$. The known gas has been previously analyzed by mass spectroscopy and has an $^{12}$CO$_2$/$^{13}$CO$_2$ isotope ratio of 0.010735. The unknown gas tank was prepared to have roughly double the amount of $^{13}$CO$_2$. The $^{13}$CO$_2$ doped tank is the one we want to analyze in this technique. The linear best-fit line is shown in Eq. 1.

**Eq. 1. Linear best-fit line.**

$$ S_x = aR_s + a(R_u - R_s)x_u $$

In this equation, $S_x$ is the ratio of the peak areas, $a$ is the scaling factor that accounts for Boltzmann distribution and intrinsic line strength, $x_u$ is the mole fraction of the unknown gas in the total sample, $R_u$ is the isotope ratio of the unknown gas, and $R_s$ is the isotope ratio of the standard. The intercept in this equation is $aR_s$ and the slope is $a(R_u - R_s)$. The final step is to take the slope and solve for $R_u$, the isotope ratio of the unknown.

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**Experimental Section**

We are using standard addition along with WMS. As previously stated, in a standard addition incremental amounts of unknown are added to a known. In this case, we must keep the pressure the same in all the additions in order to eliminate pressure-broadening effects. We chose to use 30 Torr as our constant pressure because of the results of a pressure broadening study that showed that this pressure is where the effects started to occur. The pressure amounts used to fill the sample cell are outlined in Table 1.

**Table 1: Pressures used in standard addition**

<table>
<thead>
<tr>
<th>Pressure Phase</th>
<th>Known Gas Tank (Torr)</th>
<th>Unknown Gas Tank (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
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<td>5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>30</td>
</tr>
</tbody>
</table>

The WMS set-up is shown in Fig. 1. The sample cell is filled with one phase of the pressures outlined in Table 1. A B. K. Precision 4011 function generator produces the scanning range that encompasses about two wavenumbers (cm$^{-1}$). The SR830 lock-in amplifier produces the modulation frequency at about 2 kHz. The two signals are combined and sent to the laser control box. This combined signal controls a piezzo electric motor, which moves a grating at different angles to change the wavelength of the photons emitted. The laser beam is emitted from the laser (Lasertechnik TEC 500 with center wavelength of 1.6 µm) and focused through the gas sample cell using ir mirrors. Irises and a neutral density filter are placed into the beam path in order to reduce the intensity of the beam.

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Figure 1: Diagram of WMS apparatus. The dotted line is the path of the laser beam. The solid lines are connections between electronic equipment.
Another device that minimizes the electronic noise is a Nirvana Detector 2017 auto-balancing detector which uses two photodiodes. One photodiode is used to collect the sample and the other is used to collect a reference beam. The reference beam is the same beam that comes from the laser but is split off before reaching the sample. The Nirvana detector takes the signal and balances it with the reference. This device isolates the section of the apparatus that occurs after the signal beam is split from the reference. Essentially, this auto-balancing eliminates etalon effects and laser instability from the signal.

The signal is then sent to the lock-in amplifier (SRS 830). The main function of the lock-in amplifier is to filter out anything that does not modulate at the same frequency as the one at which the laser is modulating. Any slow drifts in the laser or random noise are filtered out. The lock-in amplifier also has various noise filters that it uses on the signal. The signal is then amplified and the final processed signal is sent to a LeCroy 9310A digital oscilloscope, which collects the signal. The oscilloscope takes an average of 100 spectra as another filtering technique to average out random noise.

In Eq. 2, the data from the oscilloscope is fit to the second derivative of a Gaussian,

\[
\frac{d^2 G}{d\alpha^2} = \frac{A}{\alpha^3} \left[ 1 - \ln \left( \frac{\nu_0 - \nu}{\alpha} \right) \right] - \frac{2\ln 2}{\alpha^2} \left( \nu - \nu_0 \right)^2
\]

with \( A \) and \( \alpha \) as fitting parameters. \( A \) is the top-to-bottom height of the peak; \( \alpha \) is the full width at half maximum height; \( \nu_0 \) is the center frequency, or x-axis position at maximum height. \( A \) and \( \alpha \) are used as empirical fitting parameters, while \( \nu_0 \) is read from the spectral data. Next, we used the \( A \) and \( \alpha \) parameters found from the nonlinear fit in the equation of a Gaussian which is analytically integrated to obtain the area. We repeated this process of calculating the proportional areas for all the phases in the standard addition. Next we plotted the \( S_x \) for each phase against the mole fraction. This plot was then fit to the line described in Eq. 1 to find the isotope ratio in the unknown sample.

**Results**

**Pressure Broadening**

The results of a pressure broadening study show that after 30 Torr, the \(^{12}\)CO\(_2\) peak height at center does not increase linearly with the increase in pressure, as seen in Fig. 2. The graph looks linear until approximately 25 Torr, and then the change in peak height flattens out. In order to decrease the effects of pressure broadening but still have enough pressure to get good signal, we chose 30 Torr as the pressure to use in the standard additions.
Laser Diagnostics
In this research, we are very interested in finding out how our laser behaves. Unexpected factors that affect the isotope ratio have prompted some specific studies. One study investigated the effect of modulation frequency on the isotope ratio. In theory, changing the modulation frequency should not significantly affect the signal to noise ratio of the peaks. Fig. 3 shows spectra when the modulation frequency is changed from 1592 Hz to 1720 Hz. This change in modulation frequency affects the signal sizes. As seen in Fig. 3, there is a significant size change in the $^{12}\text{CO}_2$ peak. The peak heights decreased by more than a factor of eight; this caused the $^{13}\text{CO}_2$ peak to be too small to measure. One possible explanation for this behavior is that mechanical coupling in the laser’s tuning mechanism could result in a situation in which the modulation depth is unintentionally changed along with the modulation frequency. Changing the modulation depth is expected to change the peak size. Although such unintended coupling is undesirable for our purposes, correcting it is technically difficult. We have chosen to simply work at a modulation frequency that gives a good signal to noise ratio.

Time also plays a factor in the size and shape of signals that we have observed in our research. For instance, after long periods between laser use, we would notice that the read out would have interferences in the places where we recorded our spectra. These interferences would have random line shapes with some that look like first or second derivative curves. Although some looked like signals that would be produced by absorbance, these line shapes were not pressure dependent. The interferences were apparent even when there was a vacuum in the sample cell. We believe that a cause for this behavior is mode hops. A mode hop happens when the laser wavelength changes abruptly. We also believe that mode hops become more frequent after long periods without using the laser. These mod hops have become a factor that affects the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio.

In addition to infrequent use of the laser, another factor that creates interferences in the signal is the temperature of the laser. We have noticed that the signal looks different at different temperatures. At some temperatures, the peaks, which we want to analyze, are not even visible. Furthermore, we have noticed that one day a temperature setting will contain erroneous peaks and the next day it will not. We also believe that mode hops are more frequent at different laser temperatures.

**Fig. 3:** Sample spectra taken at two different modulation frequencies. The thin line spectrum at 1720 Hz and the thick line spectrum at 1592 Hz. The larger peak in each spectrum is a $^{12}\text{CO}_2$ peak at 6253.6 cm$^{-1}$ and the smaller peak is a $^{13}\text{CO}_2$ peak at 6253.9 cm$^{-1}$. The two spectra are offset for visual purposes.

**Fig. 4:** Neutral density filter study results of the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio. $^{13}\text{CO}_2$ is at 6253.9 cm$^{-1}$ and $^{12}\text{CO}_2$ is at 6253.6 cm$^{-1}$. Diamonds are individual trials run. Square is the average ratio for that filter.
Another unforeseen factor that plays a part in ratio modification is the effect of the optical devices that are in the path of our laser beam. We use neutral density, iris, mirrors and beam splitters. We performed a study in which we took spectra with different neutral density filters using only the standard gas tank. We found a subtle change in the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio. The filters seemed to affect the size of the $^{13}\text{CO}_2$ peak as seen in Fig. 4.

**Standard Addition**

The $^{13}\text{CO}_2$ gas tank has not been analyzed yet by an outside source, therefore we cannot comment on the accuracy of our technique. Nevertheless, our efforts to analyze the $^{13}\text{CO}_2$ doped gas tank have not been reproducible. Fig. 5 shows four standard additions performed. Each gave a different slope and intercept. Fig. 6 shows an expanded view of one of the trials shown in Fig. 5. In the four standard additions already performed, we can see some trends in the data. Fig. 7 and Fig. 8 show Gaussian fits to $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ peaks in the most recent standard addition. These fits make up the third data point in Fig. 6. These two Gaussian fits do not match up perfectly. The $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio calculated from the fit line found from all the data points shown in Fig. 6 was 0.219541. We assume that the ratio should be roughly double that of the known, which was 0.010735. The ratio that we calculated yields a 20-fold increase. This could be caused because the Gaussian fits are not as accurate for the $^{13}\text{CO}_2$ peaks.

Another trend that we see in all the data is one that appears in all the standard additions so far. The first three data points in Fig. 6 show no change in the isotope ratio. This is a concern because there should be a linear increase of the isotope ratio. With the first points showing no change in the isotope ratio, our linear fit has been false. Therefore, the overall ratio of the gas tank is undeterminable. The equipment is not sufficiently sensitive to detect the small changes in the first two steps of the standard addition which causes little to no change in the ratio. If these points do not fall into the linear fit, then our ratio cannot be accurate. The rest of the data points in the other trials all show a linear relationship. Without the first points, the slope is similar, as shown in Fig. 9. Unfortunately, the intercept also governs what the ratio is; if the intercept is too high or too low, then the ratio of the unknown will be inaccurate.
As shown in Fig. 5, the intercept is a different value in every standard addition. According to Eq. 1, the intercept in every standard addition should be constant and equal to the ratio of the standard. Excluding the first two points in the performed standard additions shows a similar slope in all three trials. All the standard additions were taken under the same conditions and the intercept should not change to this degree. In using the standard addition technique, the only thing that must be accurate is the ratio of the standard. Everything else, if held constant, would be factored into the constants given in the intercept and slope.

Discussion
The pressure broadening study tells us that we have to work at low pressures so we do not get skewed results. This means that we cannot, in our current setup, take a ratio of CO2 in air because there is less than 1% of carbon dioxide in air. This means that our sample tank would have to be at much higher pressure than what our pressure study allows. We are currently examining ways to measure the ratio at higher pressures so that our final apparatus would not need a high-powered vacuum attached to get pressures low enough for precise measurements.

The next step is to better understand the laser and incorporate our findings into the apparatus. Methods have been refined to create a more stable diode laser. Use of these methods will probably be the next step in our pursuit to perfect the apparatus. There are many aspects of the laser that must be explored. Diode lasers are prone to have frequent mode hops. Is there anything that we can manufacture or that has already been created that we can put to use in our experiment to get better results while still maintaining our goal to create a compact inexpensive device that measures isotope ratios? We need to explore whether our specific laser has

![Fig. 7: $^{12}$CO$_2$ peak at 6253.6 cm$^{-1}$ fit to 2nd derivative of Gaussian.](image)

![Fig. 8: $^{13}$CO$_2$ peak at 6253.9 cm$^{-1}$ fit to 2nd derivative of Gaussian.](image)

![Fig. 9: Comparison of previous standard additions performed with the first three data points removed.](image)
technology built into it that suppresses mode hops. If so, would a different laser have the ability to better stabilize itself? We would also like to decrease power jumps that occur during our experiment. We are also exploring whether our laser’s power output is constant with input voltage. If our laser’s intensity changes drastically between absorption peaks, problems could result. Since absorption does depend on input light intensity, a drastic change in light intensity between peaks would affect the peak ratio. We are currently working on normalizing the spectra to input light intensity.
References


