
Isotope Ratio, Oscillator Strength, and Band Positions from CO₂ IR Spectra

A Physical Chemistry Experiment

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FTIR spectrometers have become readily available and can give high quality IR spectra swiftly. The most prevalent use is for routine spectra in organic chemistry. However, these instruments have other interesting possibilities and can be used to illustrate concepts that students rarely study in the laboratory. We have developed an experiment in which IR spectra of carbon dioxide gas are used to find the positions of IR bands of carbon dioxide due to some rarer isotopic species, to estimate an isotope abundance (ratio), and to find an oscillator strength. The students also see an example of the failure of Beer's law and how such a failure can be rectified using an internal standard to determine the correct area of a band.

Experimental Procedure

Any standard FTIR spectrometer capable of 4 cm⁻¹ or better resolution will serve. One necessary characteristic is an expansion or zoom feature, which is present on the majority of instruments. Also indispensable is an area function, but this may be replaced by the capability of saving spectra on diskettes and reading them into a spreadsheet program so that areas may be determined by numerical integration. Students should be familiar with a spreadsheet so that finding areas and manipulating data is well-entrenched.

Experimental data consist of a number of IR spectra of carbon dioxide, ranging from 1.0 atm down to nearly zero pressure. The spectra can be obtained using any commercial 5- or 10-cm IR gas cell with sodium chloride windows. The first spectrum obtained is the reference (background) using dry nitrogen gas.

Then the gas cell is flushed and filled with CO₂, and a spectrum is obtained at atmospheric pressure. Small amounts of dry nitrogen gas are then added, and spectra at

successively lower pressure of CO₂ are obtained until several are found with none of the strong bands saturated. A sample spectrum at relatively low pressure is shown in Figures 1 and 2. In spectra with saturated bands the tops are flat and the P and R branch division disappears.

The students are urged to minimize the introduction of water vapor (from the air) because even small amounts make the analysis less accurate. The total pressure (nitrogen plus carbon dioxide) of the gas in the cell is kept at atmospheric pressure. The temperature and barometric pressure should also be measured. Because the spectra require comparison and considerable scrutiny, they need to be stored. Most FTIR spectrometers can write data to diskettes or to a hard disk. We provide two laboratory periods for the entire experiment, including analysis.

Analysis

Positions and Branches

The students are first asked to study the spectra using the expansion or zoom feature and to identify a number of bands for two isotopic species of carbon dioxide: ¹²C¹⁶O₂ and ¹³C¹⁶O₂. Figure 2 shows some of the bands that may be identified. The positions of many of the IR bands of these species (1) are given in the table. Some have only P and R branches, whereas others have P, Q, and R branches. The properties of IR bands and the distinguishing characteristics necessary for branches are covered in lecture before the experiment is attempted (2, 3). Emphasis is on positive identification, not on detecting as many bands as possible.

The students may instead be given the positions of the stronger bands of ¹²C¹⁶O₂. They are asked to predict the positions of some of the stronger bands of ¹³C¹⁶O₂ and then

to find them on the spectra. The prediction is done using the well-known inverse dependence of the band position on the square root of the reduced mass (3, 4). We find that the oxygen atoms may be taken together as one mass, and the carbon atom as the other. For example, using the band center of 2349 cm^{-1} for the fundamental asymmetric stretch of $^{12}\text{C}^{16}\text{O}_2$ gives 2283 cm^{-1} for the band center of the same vibration for the species $^{13}\text{C}^{16}\text{O}_2$, compared to the measured value of 2284 cm^{-1} .

Isotopic Abundance

The isotopic abundance of ^{13}C is determined using the areas (from absorbance spectra and in units of cm^{-1}) of the asymmetric stretch bands of the $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ species. The ratio of their areas in unsaturated spectra should be very close to the isotope ratio (1, 2). Unfortunately, in the spectra near 1 atm where the analysis is most accurate, the very strong asymmetric stretch band of $^{12}\text{C}^{16}\text{O}_2$ is saturated, and its measured area is much too small compared to its concentration. Beer's Law is thus not valid. The procedure for correcting this area is discussed below. The area of the $^{13}\text{C}^{16}\text{O}_2$ asymmetric stretch band is determined as described in the following paragraph.

The Area of the $^{13}\text{C}^{16}\text{O}_2$ Asymmetric Stretch Band

Usually only the P branch of the $^{13}\text{C}^{16}\text{O}_2$ asymmetric stretch band is clearly visible, as shown in Figure 1. The P and R branches have nearly identical areas at room temperature (1, 2). For example, a rough estimate using the trapezoid rule gives areas for the P and R branches of the $^{12}\text{C}^{16}\text{O}_2$ asymmetric stretch band in Figure 1 of 21 and 20 cm^{-1} . In order to obtain the area of the P branch, it is necessary to subtract the tail of the P branch of the much stronger $^{12}\text{C}^{16}\text{O}_2$ asymmetric stretch band. This is accomplished by entering data covering the complete $^{13}\text{C}^{16}\text{O}_2$ band and points on either side of it into a spreadsheet. The $^{12}\text{C}^{16}\text{O}_2$ band then can be fitted roughly with a straight line or something more accurate, for example, a Maxwell-Boltzmann distribution function. Subtraction from the spectrum gives the $^{13}\text{C}^{16}\text{O}_2$ band.

A rough sample extraction of the P branch using a straight line is shown in Figure 3. The parameters of the straight line or Maxwell-Boltzmann distribution functions must usually be adjusted until the P branch of the $^{13}\text{C}^{16}\text{O}_2$ band has the ideal shape, this judgment being left to the students. The area of the asymmetric stretch band of $^{13}\text{C}^{16}\text{O}_2$ is then obtained by numerical integration, and this area is doubled to obtain the total band area.

The isotope abundance (ratio) of ^{13}C is given by

$$\text{abundance of } ^{13}\text{C} = \frac{\text{area } ^{13}\text{C}^{16}\text{O}_2 \text{ asymmetric stretch band}}{\text{total area of } ^{12}\text{C}^{16}\text{O}_2 \text{ asymmetric stretch bands}}$$

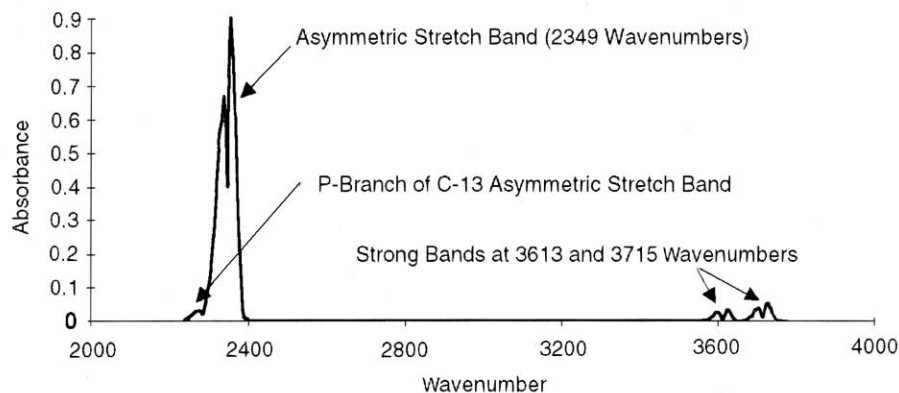


Figure 1. IR spectrum of carbon dioxide between 2000 and 4000 wavenumbers.

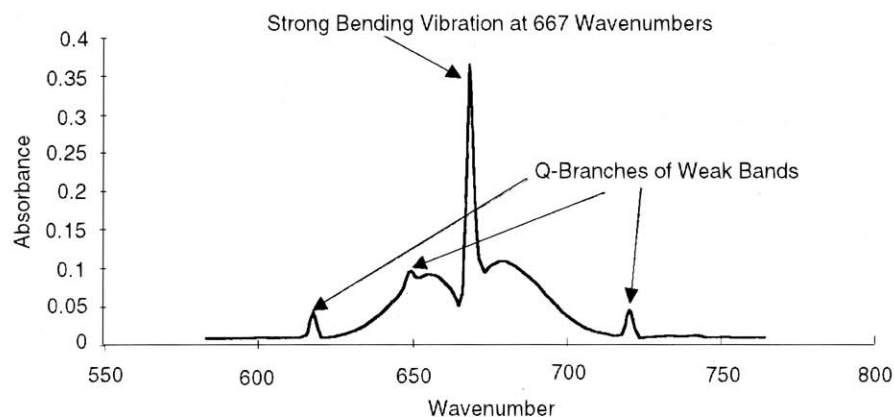


Figure 2. IR spectrum of carbon dioxide near 670 wavenumbers.

IR Bands of CO_2 between 400 and 4000 cm^{-1}

$^{12}\text{C}^{16}\text{O}_2$		
618.033	weak	$\nu_1 - \nu_2$ (difference combination)
667.379	very strong	ν_2 (fundamental bending (doubly deg.))
688.678	weak	$\nu_1 + \nu_2 - \nu_1$ (difference combination)
720.808	weak	$\nu_1 - \nu_2$ (difference comb.)
2324.148	weak	$2\nu_2 + \nu_3 - \nu_2$ (diff. comb.)
2336.637	weak	$\nu_2 + \nu_3 - \nu_2$ (diff. comb.)
2349.146	very strong	ν_3 (asymmetric stretch fundamental)
3612.844	strong	$\nu_1 + \nu_3$ (Fermi comb.)
3714.781	strong	$\nu_1 + \nu_3$ (Fermi comb.)
3723.249	weak	$\nu_1 + \nu_2 + \nu_3 - \nu_2$ (diff. comb.)
$^{13}\text{C}^{16}\text{O}_2$		
648.484		ν_2 (bending fundamental)
2283.49		ν_3 (asymmetric stretch fundamental)
3527.74		$\nu_1 + \nu_3$ (Fermi comb.)
3632.92		$\nu_1 + \nu_3$ (Fermi comb.)

Only the strongest bands for $^{13}\text{C}^{16}\text{O}_2$ are listed. Bands for this isotopic species are only about 1% as strong as those for the more common ^{12}C -containing species, and therefore the weaker bands of the ^{13}C -containing species cannot be detected in ordinary IR spectra.

The $^{12}\text{C}^{16}\text{O}_2$ Asymmetric Stretch Band

In order to correct for the saturation of the $^{12}\text{C}^{16}\text{O}_2$ asymmetric stretch band, and thus obtain the area that would result if Beer's law were followed, we use what is essentially an internal standard. There are two strong bands of carbon dioxide (at 3613 and 3715 cm^{-1}) shown in Figure 1 that are not saturated in any of the spectra. The total area of these bands serves as the internal standard and is used to correct the area of the $^{12}\text{C}^{16}\text{O}_2$ asymmetric stretch band at higher pressures.

The total area of the two bands at 3613 and 3715 cm^{-1} and also that of the $^{12}\text{C}^{16}\text{O}_2$ asymmetric stretch band are first determined in all the spectra. The sum of the areas of the two bands at 3613 and 3715 cm^{-1} are plotted versus those of the $^{12}\text{C}^{16}\text{O}_2$ asymmetric stretch band. This plot becomes linear at low pressures where Beer's law is followed. It is extrapolated back to 1.0 atm using linear regression to get the corrected area of the saturated asymmetric stretch band for the isotope abundance analysis. The isotope abundance of ^{13}C is then calculated using the equation above, with the corrected area in the denominator. Our students usually obtain an isotope abundance on the high side of the known value of 1.1%, but within 10 to 20% of it.

The Oscillator Strength

The oscillator strength (5, 6) of a transition can be determined theoretically using quantum mechanics from transition moment calculations. It is also measurable from the areas of spectroscopic bands. It is therefore one of the direct connections between theory and experiment. We use the asymmetric stretch band of $^{12}\text{C}^{16}\text{O}_2$ for an oscillator strength determination. The pressure of CO_2 for the spectrum used is needed for the calculation. The concentration of CO_2 in mol m^{-3} for the spectrum at atmospheric pressure is calculated from the measured barometric pressure and temperature using the ideal gas equation.

Then the pressure for the spectrum used is found using the ratio calculation,

$$\frac{\text{area of 3613 and 3715 cm}^{-1} \text{ bands}}{\text{area of 3613 and 3715 cm}^{-1} \text{ bands in spectrum at atm pressure}} = \frac{P_{\text{CO}_2}}{P_{\text{atm}}}$$

The oscillator strength is proportional to the integral of the molar absorptivity over the frequency range covered by the band

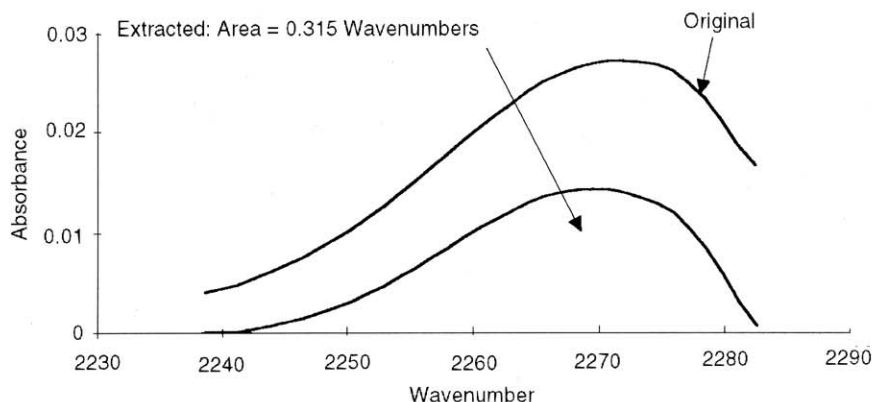


Figure 3. Original and extracted P-branch of asymmetric stretch band of carbon-13 species.

$$E_{nm} = \int \epsilon(v) dv$$

where the molar absorptivity ϵ is that in Beer's law: $A = \epsilon bc$. The equation relating the above area to the oscillator strength between two states n and m is

$$f_{nm} = (1.441 \times 10^{-18} \text{ mol s/m}^2) E_{nm}$$

where f_{nm} is the unitless quantity called the oscillator strength.

The concentration of CO_2 and the cell length are used to convert the corrected area (in cm^{-1}) to units of molar absorptivity. This area is then converted into the correct units of $\text{m}^2 \text{mol}^{-1} \text{s}^{-1}$. We find that typical oscillator strengths for strong carbon dioxide bands turn out to be near 2×10^{-5} , compared to values near 1 for very strong UV and visible electronic transitions.

Conclusion

This experiment introduces students to several novel aspects of IR spectral analysis involving both qualitative and quantitative work. Scientific integrity is tested in the identification of weak IR bands. The experiment pushes IR instruments to their limit, which is one factor that makes this our student's favorite experiment in physical chemistry.

Literature Cited

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