Analysis of the Rotational Structure of CO_2 by FTIR Spectroscopy

Gustavo González-Gaitano* and José Ramón Isasi

Departamento de Química y Edafología, Universidad de Navarra 31080 Pamplona, Spain, gaitano@unav.es

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Abstract: A physical chemistry experiment is described that involves the determination of some spectroscopic parameters of carbon dioxide, a molecule that obeys Bose–Einstein statistics. The main advantage of this experiment is that the spectra are easily recorded, not requiring a gas cell, because the sensitivity and resolution of conventional FTIR spectrometers is good enough to record spectra with a high signal-to-noise ratio and good resolution of the fine rotational structure. From the rotational lines of the antisymmetric stretching band, the moments of inertia and the bond lengths of CO_2 in the fundamental and the first-excited state can be accurately obtained. The particular case that carbon dioxide represents helps students understand the restrictions that symmetry and statistics impose on some molecules and the consequences that they have on the absorption of radiation.

Introduction

Among the advantages that FTIR spectrometry offers, as compared to conventional IR spectroscopy, are its high resolution and quick spectral acquisition. These advantages permit the averaging of many scans giving well-resolved spectra with high signal-to-noise ratios. Nowadays, FTIR spectrometers are widely accessible, and they are usually attached to fast computers equipped with powerful software that allows the performance of mathematical operations such as smoothing, filtering, etc. Some examples of the applications of FTIR spectrometry in the physical chemistry laboratory are the calculation of spectroscopic parameters in light, hydrogen-based gas molecules [1, 2] and the calculation of isotope ratios [3]. In this work we present a simple experiment that shows students how to measure the rotational constants of CO_2 in its fundamental and first-excited vibrational states from the fine rotational structure of the vibration bands. The experiment does not require the use of a gas cell, and the students can compare the results to the spectroscopic parameters of carbon monoxide to contrast the effect of the different statistics obeyed by these gases.

Experimental Procedure

To obtain spectral data, we have used a Nicolet Avatar FTIR spectrometer, operating at a resolution of 1 cm^{-1}. Ordinarily, FTIR instruments operate by collecting a background spectrum prior to the measurement of the sample. The background represents the intensity that reaches the detector at each wavelength and consists of a typical black-body-radiation curve on which the absorption spectra of the gases present in the air are overlapped. Air moisture and carbon dioxide traces in the optical path absorb part of the radiation but, provided their amounts remain constant between measurements, these contributions are corrected once the sample is measured. The purpose of using a purge gas (N_2, synthetic or dried air) is to minimize possible differences in the background between measurements. Thus, in order to record CO_2 spectra, the purge inlet must be open when measuring the background and closed afterwards to collect the spectrum of the environmental air. By leaving the sample compartment open, the amount of CO_2 present is considerably increased. Nevertheless, because the goal of the experiment lies in the position of the rotational lines and not in their absorbance, the recording of the intensity spectrum of the background suffices. This would also be applicable in case the instrument was not equipped with a purge system or even in the case where the purge did not eliminate CO_2.

The intensity of the lines representing the fundamental antisymmetric stretch band (ν_3) at 2349 cm^{-1} is shown in Figure 1, where the P and R branches are easily identified. Although the rotational lines are not completely resolved from the base line of the spectrum, the maxima are resolved, and their positions can be measured with fair precision.

The band shows a PR shape, in contrast to the band ν_2 at 667 cm^{-1}, having a PQR pattern (Figure 2). The differences in the shape are due to the normal mode of vibration involved; ν_3 is the result of a transition between $v = 0$ and $v = 1$ levels of the stretching modes Σ–Σ, or parallel transition, because the transition dipole moment is parallel to the molecular z axis. For these transitions, the selection rule is $\Delta J = \pm 1$, which produces the P and R branches; however, ν_2 corresponds to the transition between the $v = 0$ and $v = 1$ levels for the bending mode, that is, between Π and Σ symmetries. In this case, the transition moment is perpendicular to the z axis, and now the transitions allowed are those which meet $\Delta J = 0, \pm 1$. The transition between levels of equal J yields the Q band, much more intense due to the overlapping of the rotational lines.

If the centrifugal distortion is ignored, the wavenumber of the rovibrational lines for the stretching band satisfy the following equation [4]

$$\bar{\nu} = \bar{\nu}_0 + (B_1 + B_0)m + (B_1 - B_0)m^2 \qquad (1)$$

where $\bar{\nu}_0$ is the center of the band, B_0 and B_1 are the rotational constants in the ground and first-excited vibration states, respectively, and $m = J + 1$ for the R branch and $m = -J$ for the P branch.

The value of B_0 is always greater than B_1, because the amplitude of the vibration increases with v. This alters the mean value of the internuclear distance and, even for $v = 1$, this effect can be detected. Thus, a different moment of inertia (and, therefore, a different CO bond length) must be found for each vibrational state. These quantities are related by

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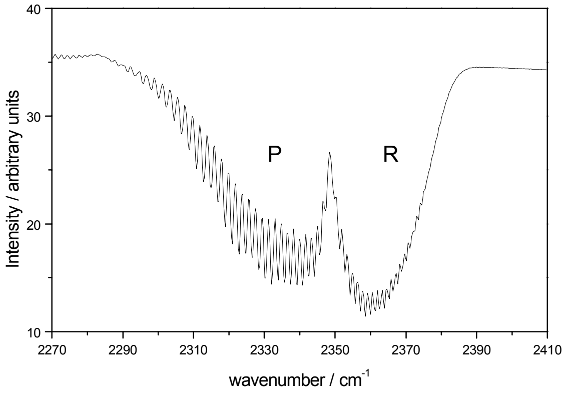

Figure 1. FTIR spectrum of the antisymmetric stretching fundamental band of CO_2.

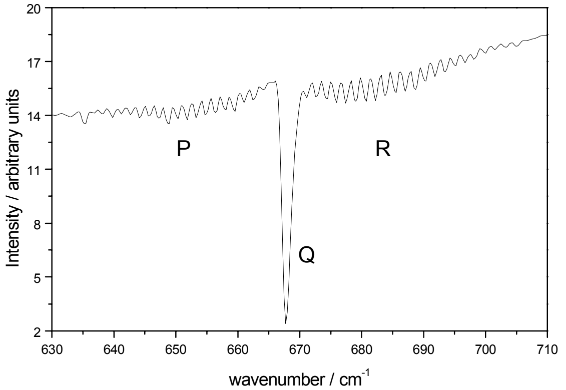

Figure 2. FTIR spectrum of the bending fundamental band of CO_2.

$$B_v = \frac{h}{8\pi^2 c I_v} \text{ and } I_v = 2m_\mathrm{O} r_v^2 \qquad (2)$$

where v is the vibrational level (0, 1) and m_O is the mass of an ^{16}O atom. To a high degree of approximation, B_v for a vibrational level v can be related to the value it has at equilibrium, B_e, and a constant, α.

$$B_v = B_\mathrm{e} - \alpha(v + \frac{1}{2}) \qquad (3)$$

from which the equilibrium bond length, r_e, can be estimated and is the value usually tabulated in the literature. The approximation used in eq 3 neglects the interaction between rotation and vibration for all the modes of vibration. Otherwise, a more general expression should include three values of α [4], but they cannot be obtained from a sole vibrational band.

CO_2 represents the simplest case that shows the effect of nuclear spin on the molecular structure. This molecule belongs to the $D_{\infty h}$ point group with a center of symmetry that makes both ^{16}O atoms equivalent. The electronic wave function in this molecule is $^1\Sigma_g^+$, which remains unchanged on nuclear exchange. For the stretching mode with $v = 0$, the vibrational function is Σ_g^+, which is also symmetric. In contrast, the rotational wave function is altered by nuclear exchange, being symmetric with even J and antisymmetric with odd J. The Bose–Einstein statistics require the total molecular wave function to be symmetric, and this happens only if the rotational quantum number in the ground vibrational state is even. This means that rotational levels with odd J are absent, so transitions to or from these cannot be reflected in the spectrum. When $v = 1$, however, the vibrational function is antisymmetric, Σ_u^+, which implies that allowed rotational states must have odd J to obey the Pauli exclusion principle. The consequence of these symmetry constraints is evidenced in the spectrum as a line spacing of about $4B$, instead of the typical spacing of $2B$. The allowed transitions, according to these explanations, are shown schematically in Figure 3. Thus, in eq 1, m will take the values –2, –4, etc. for the P branch, and 1, 3, 5, etc. for the R branch, different from other linear molecules such as CO, HCN, etc. that have no restrictions in their rotational quantum numbers.

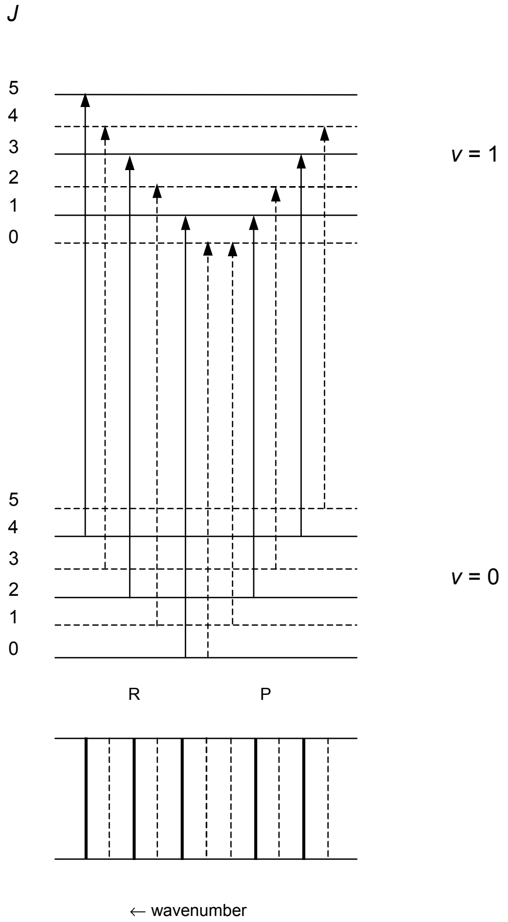

Figure 3. Rotation–vibration energy-level diagram and transitions in CO_2.

We have obtained the spectroscopic parameters with eq 1, using the positions of the lines of both branches. The positions of the lines have been fitted to a second-order polynomial, which can be done using any data processing program (Figure 4). We have used the Microcal Origin software [5], which, in addition to the fitting parameters, yields their standard deviation. (We have included, as supplementary material, a program written for the Matlab software, which performs polynomial fitting and gives the standard deviations in the parameters). The results are collected in Table 1.

The band at 667 cm^{-1} results from the fundamental transition of the bending mode (double degeneracy), $\Sigma_g^+ \rightarrow \Pi_u$. The explanation above concerning the symmetry requisites for the total wave function also apply to this case: levels with odd J will be depopulated in $v = 0$, whereas even levels will be depopulated in $v = 1$. Although the treatment described could be performed on this band in the same manner, the weak intensity of the rotational lines makes the assignment of the J values for each line difficult, precluding any quantitative studies.

Table 1. Rotational Constants and Internuclear Distances for CO_2 in $v = 0$ and $v = 1$

$\bar{\nu}_0 \pm_0$ / cm^{-1}	2348.97 ± 0.02
B_0 / cm^{-1}	0.3899 ± 0.0005
r_0 / Å	1.1625 ± 0.0008
B_1 / cm^{-1}	0.3868 ± 0.0005
r_1 / Å	1.1671 ± 0.0008

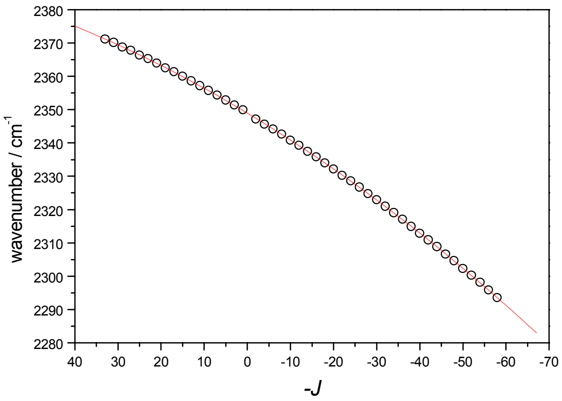

Figure 4. Fit of the lines of the P and R branches to eq 1.

From the results of the fit, the calculation of B_e and α from eq 3 yields 0.3915 ± 0.0008 cm^{-1} and (3.1 ± 0.5) × 10^{-3} cm^{-1}, respectively. With these constants, the CO bond distance at the minimum of the potential energy well is r_e = 1.1602 ± 0.0012 Å. The value found in the literature is 1.1615 Å [6, 7], which represents a relative error of 0.11 %.

The absorbances of the rotational lines in the IR spectrum give information on the population of the energy levels. It is instructive for the student to verify that the Boltzmann distribution for the rotational levels

$$\frac{N_J}{N_0} = (2J+1)\mathrm{e}^{-J(J+1)h^2/8\pi^2 IkT} \tag{4}$$

is satisfied with the moment of inertia calculated, which is in accordance with the shape of the bands, justifying that the most intense lines are not those with low J values.

Summary

The experiment described herein shows students how rotational constants can be deduced from FTIR rovibrational spectra with good accuracy as well as the effect that the vibrational state has on the internuclear distance. The specific case of CO_2 points out the constraints that symmetry and statistics impose on some molecules and the consequences of these factors on the absorption of radiation. Other topics, such as bandshape and the population of energy levels, are also considered. The experimental procedure for the recording of the spectra makes the experiment easy because neither a gas cell nor reactants are required.

Suporting Materials. Spectrum of CO_2 antisymmetric stretching band in ASCII format (file: CO2str.dat) (http://dx.doi.org/ 10.1007/s00897000521b), Rotational lines versus m (eq 1) in ASCII format (file: CO2fit.dat) (http://dx.doi.org/10.1007/s00897000521c) and Matlab function for the fitting of a data set (x, y) to a polynomial of degree n, together with the standard deviations of the parameters

```
% Errfit(x,y,n) performs a least-squares fit
to a polynomial
% y = ax^n + bx^(n-1) +cx^(n-2) +...together
with the standard deviations
function [coef,delta]=errfit(x,y,n)
[p,S]=polyfit(x,y,n);
V(:,1) = ones(length(x),1);
for j = 2:1:n+1
V(:,j) = x'.*V(:,j-1);
end
dispersion=diag((inv(V'*V)).^.5);
delta=(flipud(dispersion.*S(n+3,1)/(length(x
)-n-1)^.5))';
R=1-sum((y-polyval(p,x)).^2)/sum((y-
mean(y)).^2);
COEFFICIENTS = p
DEVIATIONS= delta
CORRCOEF = R^.5
plot(x,y,'yo',x,polyval(p,x),'c-');
```

References and Notes

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