Rotational States of the Carbon Monoxide

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Introduction: The magnitude of the absorption coefficient or the intensity of an absorption peak in rotational spectroscopy is due to several factors. First is the relative populations of the rotational energy levels as given by the Boltzmann constant. Second is the degeneracy of each of the rotational energy levels. Third is the contribution of the partition function and finally the transition moment for that transition. This activity permits you to examine each of these contributions individually and then all together.

Prerequisites: You should be able to:
1. compute the degeneracy of rotational energy levels and then the relative population of energy levels using the Boltzmann distribution,
2. compute the frequencies of allowed rotational transitions,
3. use transition moments to improve the quality of the intensity of rotational spectrum peaks,
4. use centrifugal distortion as a correction to the calculation of the frequency of a rotational transition,
5. Use Mathcad with skill to create new functions and plots of those functions.

Learning Objectives
1. Demonstrate that the spacing between spectral lines is nearly equal. Compute the percent difference between the space between the first two spectral lines and the last two spectral lines.
2. Describe the effect of the Boltzmann distribution on the shape of the rotation spectrum of a diatomic molecule.
3. Distinguish between the effects of degeneracy of states and transition moments with respect to the amplitude of a peak in the rotational spectrum.
4. Justify the need to consider centrifugal distortion and the partition function in generating a spectrum for a rotating molecule.

Performance Criteria
1. High quality demonstration of mastery of the learning objectives.
2. High quality responses to the questions, exercises, and problems below.
3. High quality definitions of the terms transition moment and centrifugal distortion.
4. Success in analyzing other spectra using the principles of Quantum Mechanics derived for the rigid rotor.
Background Information for the Activity

The fraction of the microwave power transmitted through a cell, \( P/P_0 \), which is called the transmittance, \( T \), decays exponentially with the length of the cell, \( d \), and the magnitude of the absorption coefficient, \( \gamma \), which varies with the frequency of the radiation, \( \nu \). SI units are used in this analysis so the absorption coefficient has units of m\(^{-1}\).

\[
T = \frac{P}{P_0} = e^{-\gamma d}
\]

An absorption spectrum consists of a plot of the absorption coefficient as a function of the microwave frequency, \( \gamma(v) \). Such a spectrum usually is obtained experimentally as the absorbance vs frequency since the absorbance is \( \log(P_0/P) \), which equals \( \gamma d/2.303 \).

The absorption coefficient, \( \gamma(v) \), is a sum of the absorption coefficients, \( \gamma_J(v) \), associated with the transition from each initial rotational energy level \( J \) to the final level \( J+1 \). Each \( \gamma_J(v) \) can be written as a product of several factors that are defined below.

\( C = \) all the constants that appear at various steps in the derivation.

\( N = \) the number of molecules per m\(^3\) in the absorption cell.

\( D_J = \) the square of the transition dipole moment for the transition between energy levels, depends on the permanent dipole moment of the molecule \( \mu \) and the rotational quantum number \( J \) of the initial level.

\( P_J = \) a factor accounting for the population difference between the initial and final energy levels.

\( F_n = \) the fraction of molecules in vibrational state \( n \).

\( F_J = \) the fraction of molecules in rotational energy level \( J \). Note that \( F_n F_J \) is the fraction of molecules in vibrational level \( n \) and rotational level \( J \).

\( L(v,J) = \) a lineshape function that describes how the absorption coefficient \( \gamma_J(v) \) associated with a transition from level \( J \) to \( J+1 \) depends on the microwave frequency.

Review of concepts

For a molecule in the \( n \)th vibrational state, the rotational energy of the \( J \) rotational level is given by:

\[
\frac{E_J}{\hbar} = J(J + 1) \cdot Bn - J^2(J + 1)^2 \cdot Dc
\]

(1)
where $B_n$ is the rotational constant for a molecule in the $n^{th}$ vibrational state and $D_c$ is the centrifugal stretching constant.

$$B_n = B_e - \left( n + \frac{1}{2} \right) \cdot \alpha$$  \hspace{1cm} (2)

where $B_e$ is the rotational constant and $\alpha$ is the rotation-vibration interaction constant.

We will construct the rotation spectrum for CO with a function known as a Lorentian. The Lorentian function is a standard function used to model spectral peaks.

$$L(v, J) := \frac{\Delta v}{(v - v_J)^2 + \Delta v^2} \cdot E_{\text{max}}$$  \hspace{1cm} \text{A Lorentian Function} \hspace{1cm} (3)

Notice the structure of the function. $E_{\text{max}}$ is the amplitude maximum for a peak in a spectrum. This peak is centered at $v_J$ in a spectrum that has a range $v$. $\Delta v$ is the width of the peak at half height.

Each peak in a spectrum has a function like this to describe it. The full spectrum is obtained by plotting the Lorentian function as a function of $v$ and $J$ where $J$ is the quantum number for the origin of the rotational transition giving rise to the peak.

**Exercise 1.** Using only equation 3 sketch a Lorentian function from the information given here. Label all parts of the sketch.

With these basic equations we can proceed to produce a rotational spectrum. First, however, we need to do some preliminary work to prepare for drawing the spectrum.

**Define some of the constants needed in this activity.**

$$c := 2.99792458 \cdot 10^8 \cdot \frac{m}{\text{sec}} \hspace{1cm} \text{Speed of light}$$

$$h := 6.6260755 \cdot 10^{-34} \cdot \text{joule} \cdot \text{sec} \hspace{1cm} \text{Plank's constant}$$

$$k_b := 1.380658 \cdot 10^{-23} \cdot \frac{\text{joule}}{K} \hspace{1cm} \text{Boltzmann's constant}$$
Compute Some Needed Values

**Reduced Mass**

<table>
<thead>
<tr>
<th>Carbon Mass</th>
<th>Oxygen Mass</th>
<th>Equilibrium Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu \coloneqq \frac{mC \cdot mO}{mC + mO}$</td>
<td>$\mu = 1.138 \times 10^{-26}$ kg</td>
<td>$Re = 1.1282 \cdot 10^{-10}$ m</td>
</tr>
</tbody>
</table>

$mC = 1.992 \times 10^{-26}$ kg \hspace{1cm} mO = $2.656 \times 10^{-26}$ kg \hspace{1cm}$\text{atomic masses}$

Moment of Inertia

$l \coloneqq \mu \cdot Re^2$

$l = 1.449 \times 10^{-46}$ kg m$^2$

Rotational Constant

$Be \coloneqq \frac{h}{8 \cdot \pi^2 \cdot l \cdot c}$

$Be = 193.198$ m$^{-1}$ \hspace{1cm}$\text{Note the Units on this constant.}$

Set the Temperature

$T \coloneqq 40 \cdot K$

**Exercise 2.** Since the temperature is very low, in which vibrational state will all of the molecules be found? What values are allowed for the vibrational quantum numbers?

Compute B0

$\alpha \coloneqq 17.48 \cdot m^{-1}$ \hspace{1cm} $n \coloneqq 0$

$B0 \coloneqq \left[ Be - \left( n + \frac{1}{2} \right) \cdot \alpha \right]$

$B0 = 184.458$ m$^{-1}$
Compute the Energy Level Energies

\[ J := 0, 1 .. 9 \]
\[ E_J := \frac{\hbar^2}{8 \cdot \pi^2 \cdot I} \cdot J \cdot (J + 1) \]

Define the range of rotational energy levels to study.

Use this equation to compute the 10 energy levels ignoring centrifugal stretching.

Exercise 3. Ask Mathcad to show these in the space to the right. What is the magnitude of the energy? What are the units?

Compute the Delta E for each transition given that the allowed transitions are J = +1 or -1. For absorption we use +1.

\[ k := 1, 2 \ldots 9 \]
\[ \Delta E_k := E_k - E_{k-1} \]
\[ \nu_J := B_0 \cdot 2 \cdot (J + 1) \]

Alternatively

Exercise 4. Display the J, E_J, Delta Ek, and \( \nu_J \). Describe your observations on the results.

What region of the electromagnetic spectrum does the data tell you to find the spectrum?

Exercise 4. Verify that \( \nu_J := B_0 \cdot 2 \cdot (J + 1) \) is the correct expression for the difference between adjacent energy levels for the CO rotor when centrifugal stretching is ignored.

Exercise 5. Verify that \( \Delta E_k \) is the same as \( \nu_J \).

Exercise 6. Convert the frequencies, \( \nu_J \), given above into Hz and MHz.

Build the Spectrum

Now we will use our knowledge about Rotational States to construct a spectrum for CO in the microwave region. Each peak in the spectrum results from one of the transitions we calculated above. In this activity you will add successive corrections to the spectrum in order to understand why the rotational spectrum has the shape we see experimentally. Specifically you will adjust the amplitude of each peak to reflect the following:

- the degeneracy of the energy levels,
- the effect of temperature,
- the effect of including rotational and vibrational partition functions,
- the population of the energy level leading to the transition,
- centrifugal stretching,
- the magnitude of the transition moment for that transition.

We will use the Lorentzian to construct the spectrum.
Define the frequency range as 100,000 to 1,200,000 MHz. This will accommodate the ten lines we will calculate each time we adjust the amplitude as we analyze the spectrum of CO.

\[ \nu := 1.00 \cdot 10^5 \text{ MHz, } 1.01 \cdot 10^5 \text{ MHz, } 1.20 \cdot 10^6 \text{ MHz} \]

Defines the width of each absorption peak.

\[ \Delta \nu := 7500 \text{ MHz} \]

\[ \nu \nu J := B_e \cdot c \cdot 2 \cdot (J + 1) \]

Rather than redefine a variable name we will use a new variable name for frequency.

\[ L(v, J) := \frac{\Delta \nu}{(v - \nu \nu J)^2 + \Delta \nu^2} \]

A Lorentian Function

\[ \Gamma J := 1 \]

For practice here we are saying that all the absorption coefficient intensities are the same. This is not true but it permits us to explore the contribution of \( \Delta \nu \) in the spectrum.

\[ \gamma(v) := \sum_J \left( \Gamma J \cdot L(v, J) \right) \]

This gives the sum of all peaks defined by the Lorentian function. When this is plotted as a function of the frequency range we get a spectrum.

Exercise 7. Systematically vary \( \Delta \nu \) and describe your observations for the plot above for lower and higher values of \( \Delta \nu \). Do your changes in terms of 500 MHz steps?

- How does changing the width at half height affect the spectrum?
- What is the consequence of using \( B_0 \) instead of \( B_e \)? What is the significance of using \( B_0 \) instead of \( B_e \)?
You be the Spectroscopist

Below we list the essential components that lead to a rotational spectrum for CO. Use the data here to create a spectrum that includes each of the significant factors.

\[ \varepsilon_0 := 8.854187817 \cdot 10^{-12} \text{ farad/m} \]

\[ \kappa := 4 \cdot \pi \cdot \varepsilon_0 \]

\[ \kappa = 1.113 \times 10^{-10} \text{ sec}^2 \text{ coul}^2 \text{ kg}^{-1} \text{ m}^{-3} \]

\[ C := 8 \cdot \frac{\pi^2}{3 \cdot \kappa \cdot c \cdot h} \]

\[ C = 1.191 \times 10^{36} \text{ coul}^2 \]

\[ \nu_n := 6.4252 \cdot 10^{13} \text{ sec}^{-1} \]

Zero vibrational level for Carbon Monoxide.

\[ B_0 = 184.458 \text{ m}^{-1} \]

Rotational Constant for CO in the zero vibrational level.

\[ D_{c} := 0.18358 \text{ MHz} \]

Cetrifugal stretching constant for carbon monoxide.

\[ D := 3.3564 \cdot 10^{-30} \text{ coul} \cdot \text{m} \]

The definition of a Debye unit for dipole moments

\[ D_{M} := 0.11 \cdot D \]

Dipole Moment of Carbon Monoxide in Debyes

\[ D_{M} = 3.669 \times 10^{-31} \text{ m coul} \]

\[ D_{M} := D_{M}^2 \cdot \frac{(J + 1)}{(2 \cdot J + 1)} \]

\[ F_{J} := \left( \frac{h \cdot B_0 \cdot c}{k_b \cdot T} \right) \cdot \exp \left[ -\frac{h \cdot B_0 \cdot J \cdot c \cdot (J + 1)}{k_b \cdot T} \right] \]

This is the fraction of molecules in a particular energy level. It is obtained from the rotational partition function.

\[ D_{G_{J}} := 2 \cdot J + 1 \]

This is the degeneracy of each energy level.

\[ F_{n} := 1 - \exp \left( \frac{-h \cdot \nu_n}{k_b \cdot T} \right) \]

\[ CNT_{J} := -4 \cdot D_{c} \cdot (J + 1)^3 \]

Centrifugal stretching contribution to the frequency of a peak in the spectrum.
The frequency expression that you will modify in your exploration of the intensities of the lines in the rotational spectrum of CO

\[ \nu_{vJ} := B \cdot c \cdot 2 \cdot (J + 1) + CNT_J \]

The frequency expression that you will modify in your exploration of the intensities of the lines in the rotational spectrum of CO

\[ P_J := 1 - \exp \left( \frac{-h \cdot \nu_{vJ} \cdot 10^6}{k_b \cdot T} \right) \]

\[ N := \frac{3.1 \cdot 10^{23}}{m^3} \] Number of molecules in one meter cubed of the sample.

\[ \Gamma_{J} := C \cdot N \cdot F_J \cdot F_N \cdot D_J \cdot D_G \]

\[ \Gamma_{J} \] is the factor that you will modify to include the degeneracy of the transition, the population of the origin of the transition, and the transition moment of a transition. All these factors affect the absorption intensity of peaks observed by spectroscopists.

\[ L(v, J) := \frac{\Delta \nu}{(v - \nu_{vJ})^2 + \Delta \nu^2} \cdot \frac{v^2}{\nu_{vJ}} \]

\[ \gamma_{J}(v) := \sum_{J} (\Gamma_{J} \cdot L(v, J)) \]

\[ \gamma_{J}(v) \]

Compute the difference between peaks.

\[ l := 0 \ldots 8 \]

\[ M_l := \nu_{vJ_l+1} - \nu_{vJ} \]
Exercise 8. Your job as the spectroscopist is to study the effect of each term in $\Gamma$.

- You do this by starting with $\Gamma$ equal to one.
- Then add terms in the following order: C, N, F, Fn, P, D, and DG.
- Report the consequence and significance of each factor.
- How do your results differ from the experimental peak intensities?
- What else do you need to consider in order to reproduce the experimental spectrum.

Exercise 9. Modify this document to generate the rotational spectrum for HCl.

References
