

Rice University  
Physics 332

## VIBRATION-ROTATION SPECTRUM OF CO

I. INTRODUCTION.....	2
II. THEORETICAL CONSIDERATIONS.....	3
III. MEASUREMENTS.....	8
IV. ANALYSIS.....	9

April 2011

## I. Introduction

Optical spectroscopy is one of the most valuable tools available for the study of atoms and molecules. At the simplest level, knowledge of spectral characteristics allows us to detect the presence of particular substances in stars, planets, comets, the upper atmosphere and even interstellar space. With a more detailed analysis of various spectral features it is often possible to deduce the physical conditions in these regions. The role of atomic spectra in understanding the electronic structure of atoms is well known to students of quantum mechanics. Molecular spectra can similarly be used to understand the motions of electrons in molecules, and also the vibration and rotation of the nuclei. The study of the electronic properties has led to a theoretical understanding of chemical valence and bonding. From the vibrational frequencies we can deduce the forces between atoms, while the rotational frequencies provide accurate information about bond lengths and other geometric features of molecules. Knowledge of the physical properties of individual molecules, in turn, allows us to better understand properties of molecular gases and elementary chemical reaction processes.

In the present exercise we will be concerned with the spectrum of carbon monoxide, particularly in the infrared region. We will argue that the observed groups of lines can be understood as transitions between vibration-rotation levels of the molecule. Careful measurement of the transition frequencies will let us deduce the interatomic spacing and some characteristics of the interatomic potential.

Section II presents a quantum-mechanical calculation of the energy levels of a diatomic molecule which can both vibrate and rotate in space. From the energy levels we can calculate the frequencies at which the molecule should absorb radiation, for comparison with observations. Section III discusses the mechanics of making the measurements, and Section IV presents some suggestions for analysis of the data.

## II. Theoretical Considerations

### A. Energy level calculation

The chemist's ball and stick model of a molecule suggests that we need to consider both vibration along the bond between the atoms and rotation about that bond. Because we will be concerned only with low-energy irradiation we will neglect the possibility of exciting any of the electrons to higher states. To a first approximation, then, we expect the allowed energies to be the sum of a vibrational and a rotational part

$$E = E_{\text{rot}} + E_{\text{vib}} \quad (1)$$

The rotational levels are given by

$$E_{\text{rot}} = \frac{\hbar^2}{2I} J(J+1) \quad (2)$$

where  $I$  is the moment of inertia about an axis through the center of mass and perpendicular to the bond, and  $J$  is an integer quantum number. In terms of microscopic quantities,  $I = \mu r_e^2$  where  $\mu$  is the reduced mass and  $r_e$  is the equilibrium interatomic distance. The vibrational levels are also familiar:

$$E_{\text{vib}} = \hbar \sqrt{\frac{k}{\mu}} \left( \nu + \frac{1}{2} \right) = hc \omega_e \left( \nu + \frac{1}{2} \right) \quad (3)$$

where  $k$  is the effective spring constant for the interatomic potential and  $\nu$  is the vibrational quantum number. For compactness and later use, the second equality expresses the energy in terms of the wavenumber  $\omega_e$ , a reciprocal wavelength which we will later define carefully.

The observed spectrum is determined by the selection rules which specify the transitions allowed between energy levels. In order for a potential transition to absorb light the electric dipole operator must have a non-zero matrix element between the two states. For vibrational states, this requires that  $\nu$  change by  $\pm 1$ , while for the rotational states  $J$  must also change by  $\pm 1$ . Figure 1 shows the vibration-rotation energy levels with some of the allowed transitions marked. The figure also shows the resulting idealized spectrum, labeled in a way that will become convenient later.

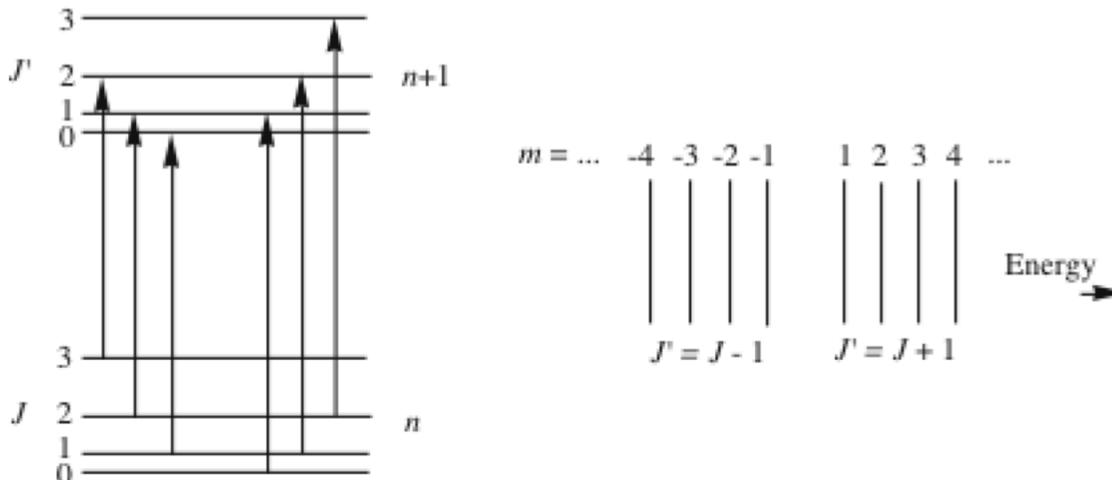


Fig 1. Energy-level diagram and resulting spectrum for ideal vibrator-rotator.

We can now combine the energy expressions with chemical data to estimate the transition energies for CO. For the vibrational transitions we need to obtain  $k$  and  $\mu$ . In our approximation the interatomic potential energy  $U = k(r-r_e)^2/2$  and we assume that the molecule is in equilibrium at the bottom of the potential well. Thermal measurements can be used to deduce the energy needed to dissociate the molecule into constituent atoms, about 11 eV for CO. As a very rough approximation, we assume that the dissociation occurs when the bond is stretched to twice its equilibrium length of about 0.1 nm, so that  $U$  is equal to the dissociation energy when  $r = 2r_e$ . This relationship is easy to solve for  $k$ , and  $\mu$  is known from the atomic masses, so we readily find a vibrational level spacing of about 0.1 eV. Radiation of this energy has a wavelength of about 10  $\mu\text{m}$ , in the far infrared region of the spectrum. The rotational energy levels can be immediately found from  $r_e$  and the atomic masses, giving  $\Delta E = 0.7$  meV for the  $J = 0 \rightarrow 1$  transition. The fact that this is much smaller than the vibrational energy indicates that the rotational levels will show up as fine structure on the vibrational transitions.

### B. Improved energy level calculation

The idealized situation considered so far leaves out some important factors. The interatomic potential is not exactly quadratic, so there should be deviations from the simple harmonic oscillator energies. If we view the connection between the atoms as a spring, it is obvious that the spring will stretch as the molecule spins, increasing the moment of inertia and decreasing the rotational level spacing. Additionally, in an anharmonic oscillator the average separation between atoms depends on the vibrational level, which in turn affects the moment of inertia and effectively couples the vibrational and rotational motions. We need to consider all these effects to get an accurate representation of the spectrum.

The deviations from a harmonic potential can be represented by expanding the interatomic potential  $U$  in a Taylor series about the equilibrium separation  $r_e$ :

$$U = f(r - r_e)^2 - g(r - r_e)^3 \quad (4)$$

Here  $g$  and  $f$  are constants, with  $g \ll f$  assumed. Applying perturbation theory to this potential yields energy eigenvalues

$$E_{vib} = hc\omega_e\left(v + \frac{1}{2}\right) - hc\omega_e x_e\left(v + \frac{1}{2}\right)^2 + \dots \quad (5)$$

where  $x_e$  is a small constant related to  $g$  and  $\omega_e$  refers to the vibration energy at the equilibrium separation. The anharmonicity has two main effects: The level spacing decreases as  $v$  increases, sometimes called a "softening of the potential"; The selection rule is relaxed so that transitions with  $\Delta v = \pm 2, \pm 3 \dots$  are also allowed, although only weakly. Both of these results, and the form of the energy, persist for other potential functions that might plausibly describe the interatomic force.

The increase in separation with increasing  $J$  can be modeled by assuming that the connection between atoms is a simple spring of constant  $k$ . The rotational energy levels then become

$$E_{rot} = \frac{\hbar^2}{2I} \left[ 1 - \frac{\hbar^2}{I r_e^2 k} J(J+1) \right] J(J+1) \quad (6)$$

This is more usually written with two constants as

$$E_{rot} = hcB_e J(J+1) - hcD_e J^2(J+1)^2 \quad (7)$$

where the subscript  $e$  indicates the equilibrium value.

Since the vibrational motion is very fast compared to the rotation, the increase in average separation with increasing  $v$  can be accounted for by using  $\overline{1/r}$  in  $B$  and  $D$ , rather than  $1/r_e$ . This introduces two more constants to relate the vibrational-average quantities to the equilibrium values:

$$B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right) \quad \text{and} \quad D_v = D_e + \beta_e\left(v + \frac{1}{2}\right) \quad (8)$$

The final expression for the rotational energy is then

$$E_{\text{rot}} = hcB_v J(J+1) - hcD_v J^2(J+1)^2 \quad (9)$$

When added to  $E_{\text{vib}}$ , this specifies the coupled vibration-rotation levels of the diatomic molecule in our model.

### C. The spectrum

Given the energy levels, it is easy to compute the spectrum by finding the energy differences for all the allowed transitions. For historical reasons,\* spectroscopists express both energies and spectral positions in wavenumbers  $T = E/hc$ . In this notation, the energy levels for our diatomic are

$$T(\nu, J) = \omega_e \left(\nu + \frac{1}{2}\right) - \omega_e x_e \left(\nu + \frac{1}{2}\right)^2 + B_\nu J(J+1) - D_\nu J^2(J+1)^2 \quad (10)$$

and the spectral lines are the allowed differences of the form

$$\Delta T = T(\nu', J') - T(\nu, J) \quad (11)$$

where the primes indicate the higher-energy level in the transition.

In this exercise we are concerned with the absorption of energy by a gas at room temperature. We therefore need to consider transitions from the vibrational ground state  $\nu = 0$  to excited vibrational states  $\nu' = 1, 2, \dots$  and between rotational states  $J$  and  $J' = J \pm 1$ . With these conditions the transition energies are

$$\begin{aligned} \Delta T = \omega_e \nu' - \omega_e x_e \left[ \left(\nu' + \frac{1}{2}\right)^2 - \frac{1}{4} \right] + B_{\nu'} J'(J'+1) - B_0 J(J+1) \\ - D_{\nu'} J'^2(J'+1)^2 + D_0 J^2(J+1)^2 \end{aligned} \quad (12)$$

where  $B_0$  and  $D_0$  refer to the  $\nu = 0$  state. To proceed, we number the lines with a running index  $m$  as shown in Fig. 1. If we note that  $m = J'$  when  $J' = J + 1$  and  $m = -J$  when  $J' = J - 1$  we can combine the two cases into one expression

---

\* Wavelength is directly measured in a spectroscopic experiment. Converting to energy with  $E = hc/\lambda$  requires knowing Planck's constant and the speed of light. Since these constants were not known as well as the measured wavelengths, spectroscopists defined wavenumbers as the inverse of the wavelength in centimeters to get a quantity proportional to energy that would preserve the accuracy of their data.

$$\Delta T = \omega_e \nu' - \omega_e x_e \left[ \left( \nu' + \frac{1}{2} \right)^2 - \frac{1}{4} \right] + B_{\nu'} m(m+1) - B_0 m(m-1) - D_{\nu'} m^2 (m+1)^2 + D_0 m^2 (m-1)^2 \quad (13)$$

If, as is often true, the  $\beta_e$  correction term is negligible then  $D_{\nu'} = D_0 = D_e$  and the expression simplifies somewhat. Rewriting the simplified form as a power series in  $m$  yields the equation needed to analyze the spectra

$$\Delta T = \omega_e \nu' - \omega_e x_e [\nu'^2 + \nu'] + [2B_e - \alpha_e (\nu' + 1)]m - \alpha_e \nu' m^2 - 4D_e m^3 \quad (14)$$

Note that we can obtain values for  $B_e$ ,  $\alpha_e$  and  $D_e$  from the several rotational transitions within a given  $\nu'$ . With two or more  $\nu'$  we can also obtain  $\omega_e$  and  $\omega_e x_e$ .

### III. Measurements

The goal is to measure the wavelengths of as many of the vibration-rotation lines of CO as are accessible to our instrument. We will do this by measuring the attenuation of light from a calibrated monochromator as it passes through a gaseous sample. The wavelengths of maximum absorption can then be statistically fit to determine the various constants in Eq. 14 and hence the properties of the molecule.

A sample of gaseous CO at about 30 psig (4 atmospheres) is contained in a plastic cell with glass windows. The instructor will assist you in refilling the cell if it appears that the contents have leaked out. Note that carbon monoxide is a poisonous, flammable gas. If you open the valve on the sample cell or otherwise release the gas you will, therefore, create a modest chemical hazard as well as losing your sample material.

The Cary Model 17 spectrophotometer is an integrated instrument which contains a light source, a monochromator, sample cell holder, detectors and chart recorder. It is a very flexible and somewhat fragile research device, so it is imperative that you read the manufacturer's instructions carefully and then consult with the instructor before attempting to operate it. We will be using the instrument in the infrared (IR) region, so in your reading you should concentrate on the instructions for operating the VIS-IR light source and the IR detector. Purging is not required in the wavelength range of interest here. Our instrument has the "Universal Absorbance - %T" slidewire installed, and it will usually be used in absorbance mode.

Previous workers have found absorption patterns resembling Fig. 1 at wavelengths around 4670 nm and, with rapidly decreasing intensity, 2350 nm and 1575 nm. On the basis of our previous estimates, these are presumably the  $\nu = 0 \rightarrow 1$ ,  $0 \rightarrow 2$  and  $0 \rightarrow 3$  transitions, respectively. Only the latter two transitions are within the range of our spectrophotometer, and the  $0 \rightarrow 3$  group is already too weak to observe, so you should concentrate on measuring as many lines as possible for the  $0 \rightarrow 2$  transition. Be sure also to repeat your measurement so that you can estimate errors.

## IV. Analysis

When you have good plots of the accessible vibrational transition, index the lines as shown in Fig. 1 and determine the wavenumber of each. Because the index of refraction of air is slightly greater than one, the measured wavelengths are smaller than they would be in vacuum. To correctly obtain the transition energies you must multiply the measured wavelengths by 1.000275, or divide the measured wavenumbers by the same quantity.

Fit your data to find the parameters in Eq. 14, using a multiple linear regression routine. Be sure that you obtain error estimates for each fitted parameter. (Multiple regression is a standard feature of statistics packages, or you may code the method described in Bevington, *Data Reduction and Error Analysis for the Physical Sciences*.)

You should also fit the observations for the  $0 \rightarrow 1$  transition given in Table I. The results should confirm your parameter values, and allow you to deduce a value of the anharmonicity parameter  $\omega_e x_e$ . Using these values you should be able to estimate the bond length and other molecular characteristics for CO.

Table I

Vacuum wavenumbers of the  $0 \rightarrow 1$  vibration-rotation transitions for CO. From J. Molec. Spect. 4,518 (1960). A computer-readable file containing these data can be found in the auxiliary material section of the course web page and on the lab PCs.

24	2224.694	-1	2139.432
23	2221.732	-2	2135.554
22	2218.733	-3	2131.639
21	2215.685	-5	2123.700
20	2212.600	-6	2119.677
19	2209.498	-8	2111.555
18	2206.345	-9	2107.413
17	2203.147	-10	2103.265
16	2199.929	-11	2099.096
15	2196.661	-12	2094.870
14	2193.357	-13	2090.603
13	2190.010	-14	2086.322
12	2186.636	-15	2082.009
11	2183.226	-16	2077.650
10	2179.761	-18	2068.851
9	2176.287	-20	2059.911
8	2172.759	-21	2055.391
6	2165.602	-23	2046.271
4	2158.309	-24	2041.663
3	2154.596	-25	2037.030
		-26	2032.349
		-27	2027.635
		-28	2022.899
		-32	2003.659
		-33	1998.767
		-34	1993.867
		-35	1988.910
		-36	1983.919
		-37	1978.923
		-38	1973.871
		-39	1968.805
		-42	1953.459
		-43	1948.252
		-45	1937.831
		-46	1932.555
		-47	1927.246
		-48	1921.926
		-51	1905.776]