

Molecular Spectroscopy

PROBLEMS AND SOLUTIONS

13-1. The spacing between the lines in the microwave spectrum of H^{35}Cl is 6.350×10^{11} Hz. Calculate the bond length of H^{35}Cl .

Using Equation 13.6 for E_J , we find

$$\begin{aligned}\Delta E = E_{J+1} - E_J &= \frac{\hbar^2}{2I}(J+1)(J+2) - \frac{\hbar^2}{2I}J(J+1) \\ &= \frac{\hbar^2}{2I}[(J+1)(J+2) - J(J+1)] \\ &= \frac{\hbar^2}{I}(J+1)\end{aligned}$$

Substituting the last result into Equation 13.1 gives

$$\nu = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I}(J+1) \quad (1)$$

The spectrum consists of lines of frequencies ν , separated from each other by $h/4\pi^2 I$. Then

$$\begin{aligned}6.350 \times 10^{11} \text{ s}^{-1} &= \frac{h}{4\pi^2 I} \\ I &= \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{4\pi^2 (6.350 \times 10^{11} \text{ s}^{-1})} = 2.643 \times 10^{-47} \text{ kg}\cdot\text{m}^2\end{aligned}$$

The reduced mass of H^{35}Cl is

$$\mu = \frac{(1.0079)(34.969)}{(34.969 + 1.0079)} \text{ amu} = 0.97966 \text{ amu}$$

For a diatomic molecule,

$$\begin{aligned}I &= \mu R_e^2 \\ R_e &= \left(\frac{I}{\mu}\right)^{1/2} \\ &= \left[\frac{2.643 \times 10^{-47} \text{ kg}\cdot\text{m}^2}{(0.97966 \text{ amu})(1.661 \times 10^{-27} \text{ kg}\cdot\text{amu}^{-1})}\right]^{1/2} \\ &= 1.275 \times 10^{-10} \text{ m} = 127.5 \text{ pm}\end{aligned}$$

- 13-2. The microwave spectrum of $^{39}\text{K}^{127}\text{I}$ consists of a series of lines whose spacing is almost constant at 3634 MHz. Calculate the bond length of $^{39}\text{K}^{127}\text{I}$.

We use the same method as in Problem 13-1. From Equation 1 of Problem 13-1,

$$3\,634 \times 10^6 \text{ s}^{-1} = \frac{h}{4\pi^2 I}$$

$$I = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{4\pi^2 (3.634 \times 10^9 \text{ s}^{-1})} = 4.619 \times 10^{-45} \text{ kg}\cdot\text{m}^2$$

The reduced mass of $^{39}\text{K}^{127}\text{I}$ is

$$\mu = \frac{(38.964)(126.90)}{(38.964 + 126.90)} \text{ amu} = 29.811 \text{ amu}$$

From the definition of I ,

$$I = \mu R_e^2$$

$$R_e = \left(\frac{I}{\mu}\right)^{1/2}$$

$$= \left(\frac{4.619 \times 10^{-45} \text{ kg}\cdot\text{m}^2}{(29.811 \text{ amu})(1.661 \times 10^{-27} \text{ kg}\cdot\text{amu}^{-1})}\right)^{1/2}$$

$$= 3.055 \times 10^{-10} \text{ m} = 305.5 \text{ pm}$$

- 13-3. The equilibrium internuclear distance of H^{127}I is 160.4 pm. Calculate the value of B in wave numbers and megahertz.

The reduced mass of H^{127}I is

$$\mu = \frac{(1.0079)(126.90)}{(1.0079 + 126.90)} \text{ amu} = 0.99996 \text{ amu}$$

The moment of inertia for H^{127}I is

$$I = \mu r^2$$

$$= (0.99996 \text{ amu})(1.661 \times 10^{-27} \text{ kg}\cdot\text{amu}^{-1})(1.604 \times 10^{-10} \text{ m})^2$$

$$= 4.272 \times 10^{-47} \text{ kg}\cdot\text{m}^2$$

We can use Equation 13.9 for B , since B and \tilde{B} are related by $c\tilde{B} = B$:

$$B = c\tilde{B} = \frac{h}{8\pi^2 I}$$

$$= \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8\pi^2 (4.272 \times 10^{-47} \text{ kg}\cdot\text{m}^2)}$$

$$= 1.964 \times 10^{11} \text{ s}^{-1} = 1.964 \times 10^5 \text{ MHz}$$

or 6.552 cm^{-1} .

- 13-4. Assuming the rotation of a diatomic molecule in the $J = 10$ state may be approximated by classical mechanics, calculate how many revolutions per second $^{23}\text{Na}^{35}\text{Cl}$ makes in the $J = 10$ rotational state. The rotational constant of $^{23}\text{Na}^{35}\text{Cl}$ is 6500 MHz.

The energy of a classical rotator is

$$K = \frac{1}{2} I \omega^2$$

The quantum-mechanical energy is given by

$$E = hBJ(J+1)$$

where $B = h/8\pi^2 I$. Equating K with E gives

$$\frac{I\omega^2}{2} = hBJ(J+1)$$

$$\omega^2 = \frac{2hBJ(J+1)}{I} = [2hBJ(J+1)] \left(\frac{h}{8\pi^2 B}\right)^{-1}$$

$$\omega = 4\pi B [J(J+1)]^{1/2} = 4\pi(6500 \times 10^6 \text{ s}^{-1})(110)^{1/2}$$

$$= 8.57 \times 10^{11} \text{ radian}\cdot\text{s}^{-1} = 1.36 \times 10^{11} \text{ revolution}\cdot\text{s}^{-1}$$

- 13-5. The results we derived for a rigid rotator apply to linear polyatomic molecules as well as to diatomic molecules. Given that the moment of inertia I for $\text{H}^{12}\text{C}^{14}\text{N}$ is $1.89 \times 10^{-46} \text{ kg}\cdot\text{m}^2$ (cf. Problem 13-6), predict the microwave spectrum of $\text{H}^{12}\text{C}^{14}\text{N}$.

The microwave spectrum of $\text{H}^{12}\text{C}^{14}\text{N}$ will be a series of equally spaced lines separated by $2\tilde{B}$ (see Equations 13.12 and 13.13). Substituting into Equation 13.9,

$$2\tilde{B} = \frac{h}{4\pi^2 cI}$$

$$= \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{4\pi^2 (2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})(1.89 \times 10^{-46} \text{ kg}\cdot\text{m}^2)}$$

$$= 296 \text{ m}^{-1} = 2.96 \text{ cm}^{-1}$$

- 13-6. This problem involves the calculation of the moment of inertia of a linear triatomic molecule such as $\text{H}^{12}\text{C}^{14}\text{N}$ (see Problem 13-5). The moment of inertia of a linear molecule is

$$I = \sum_j m_j d_j^2$$

where d_j is the distance of the j th mass from the center of mass. Thus, the moment of inertia of $\text{H}^{12}\text{C}^{14}\text{N}$ is

$$I = m_{\text{H}} d_{\text{H}}^2 + m_{\text{C}} d_{\text{C}}^2 + m_{\text{N}} d_{\text{N}}^2 \quad (1)$$

Show that Equation 1 can be written as

$$I = \frac{m_{\text{H}} m_{\text{C}} R_{\text{HC}}^2 + m_{\text{H}} m_{\text{N}} R_{\text{HN}}^2 + m_{\text{C}} m_{\text{N}} R_{\text{CN}}^2}{m_{\text{H}} + m_{\text{C}} + m_{\text{N}}}$$

where the R 's are the various internuclear distances. Given that $R_{\text{HC}} = 106.8$ pm and $R_{\text{CN}} = 115.6$ pm, calculate the value of I and compare the result with that given in Problem 13-5.

The easiest (and best) way to do this problem is to work backwards. Let $M = m_{\text{H}} + m_{\text{C}} + m_{\text{N}}$. Then the desired equation becomes

$$\begin{aligned} MI &= m_{\text{H}}m_{\text{C}}R_{\text{HC}}^2 + m_{\text{H}}m_{\text{N}}R_{\text{HN}}^2 + m_{\text{C}}m_{\text{N}}R_{\text{CN}}^2 \\ &= m_{\text{H}}m_{\text{C}}(d_{\text{H}} - d_{\text{C}})^2 + m_{\text{H}}m_{\text{N}}(d_{\text{H}} - d_{\text{N}})^2 + m_{\text{C}}m_{\text{N}}(d_{\text{C}} - d_{\text{N}})^2 \\ &= m_{\text{H}}m_{\text{C}}d_{\text{H}}^2 - 2m_{\text{H}}m_{\text{C}}d_{\text{H}}d_{\text{C}} + m_{\text{H}}m_{\text{C}}d_{\text{C}}^2 + m_{\text{H}}m_{\text{N}}d_{\text{H}}^2 - 2m_{\text{H}}m_{\text{N}}d_{\text{H}}d_{\text{N}} \\ &\quad + m_{\text{H}}m_{\text{N}}d_{\text{N}}^2 + m_{\text{C}}m_{\text{N}}d_{\text{C}}^2 - 2m_{\text{C}}m_{\text{N}}d_{\text{C}}d_{\text{N}} + m_{\text{C}}m_{\text{N}}d_{\text{N}}^2 \end{aligned}$$

Now add and subtract $m_{\text{H}}d_{\text{H}}^2 + m_{\text{C}}d_{\text{C}}^2 + m_{\text{N}}d_{\text{N}}^2$ from the right side of this equation to obtain

$$\begin{aligned} MI &= Mm_{\text{H}}d_{\text{H}}^2 + Mm_{\text{C}}d_{\text{C}}^2 + Mm_{\text{N}}d_{\text{N}}^2 \\ &\quad - (m_{\text{H}}d_{\text{H}}^2 + m_{\text{C}}d_{\text{C}}^2 + m_{\text{N}}d_{\text{N}}^2 + 2m_{\text{H}}m_{\text{C}}d_{\text{H}}d_{\text{C}} + 2m_{\text{H}}m_{\text{N}}d_{\text{H}}d_{\text{N}} + 2m_{\text{C}}m_{\text{N}}d_{\text{C}}d_{\text{N}}) \\ &= Mm_{\text{H}}d_{\text{H}}^2 + Mm_{\text{C}}d_{\text{C}}^2 + Mm_{\text{N}}d_{\text{N}}^2 - [m_{\text{H}}d_{\text{H}} + m_{\text{C}}d_{\text{C}} + m_{\text{N}}d_{\text{N}}]^2 \end{aligned}$$

The term in brackets is equal to zero by the definition of the center of mass, so we have

$$I = m_{\text{H}}d_{\text{H}}^2 + m_{\text{C}}d_{\text{C}}^2 + m_{\text{N}}d_{\text{N}}^2$$

which is Equation 1. Numerically, for $\text{H}^{12}\text{C}^{14}\text{N}$,

$$\begin{aligned} I &= \frac{(1.0079 \text{ amu})(12.000 \text{ amu})(106.8 \text{ pm})^2}{1.0079 \text{ amu} + 12.000 \text{ amu} + 14.003 \text{ amu}} \\ &\quad + \frac{(1.0079 \text{ amu})(14.003 \text{ amu})(106.8 \text{ pm} + 115.6 \text{ pm})^2}{1.0079 \text{ amu} + 12.000 \text{ amu} + 14.003 \text{ amu}} \\ &\quad + \frac{(12.000 \text{ amu})(14.003 \text{ amu})(115.6 \text{ pm})^2}{1.0079 \text{ amu} + 12.000 \text{ amu} + 14.003 \text{ amu}} \\ &= \frac{3.082 \times 10^6 \text{ amu}^2 \cdot \text{pm}^2}{27.011 \text{ amu}} = 1.141 \times 10^5 \text{ amu} \cdot \text{pm}^2 \\ &= 1.141 \times 10^5 \text{ amu} \cdot \text{pm}^2 \left(\frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}} \right) \left(\frac{10^{-12} \text{ m}}{1 \text{ pm}} \right)^2 \\ &= 1.894 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \end{aligned}$$

This is the same as the value given in Problem 13-5.

13-7. The far infrared spectrum of $^{39}\text{K}^{35}\text{Cl}$ has an intense line at 278.0 cm^{-1} . Calculate the force constant and the period of vibration of $^{39}\text{K}^{35}\text{Cl}$.

The reduced mass of $^{39}\text{K}^{35}\text{Cl}$ is

$$\mu = \frac{(38.964)(34.969)}{(38.964 + 34.969)} \text{ amu} = 18.429 \text{ amu}$$

Use Equation 13.5:

$$\begin{aligned} \tilde{\nu} &= \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \\ k &= (2\pi c\tilde{\nu})^2 \mu \end{aligned}$$

$$\begin{aligned} &= [2\pi(2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1})(278.0 \times 10^2 \text{ m}^{-1})]^2 \\ &\quad \times (18.429 \text{ amu})(1.661 \times 10^{-27} \text{ kg} \cdot \text{amu}^{-1}) \\ &= 83.92 \text{ N} \cdot \text{m}^{-1} \end{aligned}$$

The period of vibration is

$$T = \frac{1}{\nu} = \frac{1}{c\tilde{\nu}} = 1.20 \times 10^{-13} \text{ s}$$

13-8. The force constant of $^{79}\text{Br}^{79}\text{Br}$ is $240 \text{ N} \cdot \text{m}^{-1}$. Calculate the fundamental vibrational frequency and the zero-point energy of $^{79}\text{Br}_2$.

The reduced mass of $^{79}\text{Br}^{79}\text{Br}$ is

$$\mu = \frac{(78.92)(78.92)}{(78.92 + 78.92)} \text{ amu} = 39.46 \text{ amu}$$

Now we use Equation 13.5:

$$\begin{aligned} \nu &= \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \\ &= \frac{1}{2\pi} \left[\frac{240 \text{ N} \cdot \text{m}^{-1}}{(39.46 \text{ amu})(1.661 \times 10^{-27} \text{ kg} \cdot \text{amu}^{-1})} \right]^{1/2} \\ &= 9.63 \times 10^{12} \text{ s}^{-1} \\ \tilde{\nu} &= \frac{\nu}{c} = 321 \text{ cm}^{-1} \end{aligned}$$

From Equation 13.2,

$$E_0 = \frac{1}{2}h\nu = 3.19 \times 10^{-21} \text{ J}$$

13-9. Prove that

$$\langle x^2 \rangle = \frac{\hbar}{2(\mu k)^{1/2}}$$

for the ground state of a harmonic oscillator. Use this equation to calculate the root-mean-square amplitude of $^{14}\text{N}_2$ in its ground state. Compare your result to the bond length. Use $k = 2260 \text{ N} \cdot \text{m}^{-1}$ for $^{14}\text{N}_2$.

We proved this result in Problem 5-26. The reduced mass of $^{14}\text{N}_2$ is

$$\mu = \frac{(14.003)(14.003)}{(14.003 + 14.003)} \text{ amu} = 7.0015 \text{ amu}$$

For $^{14}\text{N}_2$,

$$\begin{aligned} x_{\text{rms}} &= (\langle x^2 \rangle)^{1/2} = \left[\frac{\hbar}{2(\mu k)^{1/2}} \right]^{1/2} \\ &= \left\{ \frac{1.055 \times 10^{-34} \text{ J} \cdot \text{s}}{2[(7.0015 \text{ amu})(1.661 \times 10^{-27} \text{ kg} \cdot \text{amu}^{-1}) (2260 \text{ N} \cdot \text{m}^{-1})]^{1/2}} \right\}^{1/2} \\ &= 3.21 \times 10^{-12} \text{ m} = 3.21 \text{ pm} \end{aligned}$$

The bond length of $^{14}\text{N}_2$ is 109.77 pm, so x_{rms} is 3% of the bond length.

13-10. Derive Equations 13.15 and 13.16.

We begin with the equation

$$\tilde{E}_{v,J} = \tilde{\nu} \left(v + \frac{1}{2} \right) + \tilde{B}_v J(J+1) \quad (13.14)$$

For the R branches of the $v = 0 \rightarrow 1$ transition, $\Delta J = +1$, so

$$\begin{aligned} \tilde{\nu}_R(\Delta J = +1) &= \tilde{E}_{1,J+1} - \tilde{E}_{0,J} \\ &= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1) \\ &= \tilde{\nu} + \tilde{B}_1(J^2 + 3J + 2) - \tilde{B}_0(J^2 + J) \\ &= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \end{aligned}$$

For the P branches, $\Delta J = -1$, and

$$\begin{aligned} \tilde{\nu}_P(\Delta J = -1) &= \tilde{E}_{1,J-1} - \tilde{E}_{0,J} \\ &= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J-1)(J) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1) \\ &= \tilde{\nu} + \tilde{B}_1(J^2 - J) - \tilde{B}_0(J^2 + J) \\ &= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \end{aligned}$$

13-11. Given that $B = 58\,000$ MHz and $\tilde{\nu} = 2160.0$ cm^{-1} for CO, calculate the frequencies of the first few lines of the R and P branches in the vibration-rotation spectrum of CO.

We use Equation 13.12 for the R branch and Equation 13.13 for the P branch (recall that $c\tilde{B} = B$) to obtain the general results

$$\begin{aligned} \tilde{\nu}_R &= \tilde{\nu} + 2\tilde{B}(J+1) \\ &= 2160.0 \text{ cm}^{-1} + 2 \left(\frac{58\,000 \times 10^6 \text{ s}^{-1}}{2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}} \right) (J+1) \\ &= 2160.0 \text{ cm}^{-1} + (3.87 \text{ cm}^{-1})(J+1) \end{aligned}$$

and

$$\begin{aligned} \tilde{\nu}_P &= \tilde{\nu} - 2\tilde{B}J \\ &= 2160.0 \text{ cm}^{-1} - 2 \left(\frac{58\,000 \times 10^6 \text{ s}^{-1}}{2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}} \right) J \\ &= 2160.0 \text{ cm}^{-1} - (3.87 \text{ cm}^{-1})J \end{aligned}$$

13-12. Given that $R_e = 156.0$ pm and $k = 250.0$ $\text{N} \cdot \text{m}^{-1}$ for $^7\text{Li}^{19}\text{F}$, use the rigid rotator-harmonic oscillator approximation to construct to scale an energy-level diagram for the first five rotational levels in the $v = 0$ and $v = 1$ vibrational states. Indicate the allowed transitions in an absorption experiment, and calculate the frequencies of the first few lines in the R and P branches of the vibration-rotation spectrum of $^6\text{Li}^{19}\text{F}$.

To find the lines in the R and P branches of the spectrum, we will need to find $\tilde{\nu}$ and \tilde{B} and use Equations 13.12 and 13.13. The reduced mass of ^6LiF is

$$\mu = \frac{(6.015)(18.998)}{(6.015 + 18.998)} \text{ amu} = 4.569 \text{ amu}$$

First, find the value of I :

$$\begin{aligned} I &= \mu R_e^2 \\ &= (4.569 \text{ amu})(1.661 \times 10^{-27} \text{ kg} \cdot \text{amu}^{-1})(156.0 \times 10^{-12} \text{ m})^2 \\ &= 1.846 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \end{aligned}$$

Now find \tilde{B} (Equation 13.9) and $\tilde{\nu}$ (Equation 13.5):

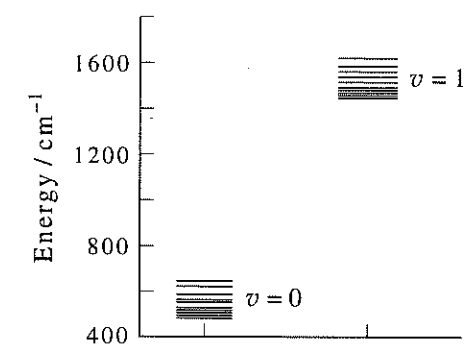
$$\begin{aligned} \tilde{B} &= \frac{h}{8\pi^2 c I} \\ &= \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{8\pi^2 (2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1})(1.846 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} \\ &= 151.6 \text{ m}^{-1} = 1.516 \text{ cm}^{-1} \\ \tilde{\nu} &= \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \\ &= \frac{1}{2\pi (2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})} \left[\frac{250.0 \text{ N} \cdot \text{m}^{-1}}{(4.569 \text{ amu})(1.661 \times 10^{-27} \text{ kg} \cdot \text{amu}^{-1})} \right]^{1/2} \\ &= 963.7 \text{ cm}^{-1} \end{aligned}$$

To construct the energy level diagram, we use Equation 13.10:

$$\begin{aligned} \tilde{E}_{v,J} &= \left(v + \frac{1}{2} \right) \tilde{\nu} + \tilde{B} J(J+1) \\ \tilde{E}_{0,J} &= 481.9 \text{ cm}^{-1} + (1.516 \text{ cm}^{-1})J(J+1) \\ \tilde{E}_{1,J} &= 1445 \text{ cm}^{-1} + (1.516 \text{ cm}^{-1})J(J+1) \end{aligned}$$

We can now construct a table of values to use in the energy-level diagram:

J	$\tilde{E}_{0,J}/\text{cm}^{-1}$	$\tilde{E}_{1,J}/\text{cm}^{-1}$
0	481.9	1445
1	484.9	1448
2	490.9	1454
3	500.0	1463
4	512.1	1475



The selection rules $\Delta v = +1$ and $\Delta J = \pm 1$ (Equations 13.11) determine the allowed transitions. The frequencies of the lines in the R and P branches are (Equations 13.12 and 13.13)

$$\begin{aligned}\tilde{\nu}_R &= \tilde{\nu} + 2\tilde{B}(J+1) \\ &= 963.7 \text{ cm}^{-1} + (1.516 \text{ cm}^{-1})(J+1) \quad J = 0, 1, 2, \dots \\ \tilde{\nu}_P &= \tilde{\nu} - 2\tilde{B}J \\ &= 963.7 \text{ cm}^{-1} - (1.516 \text{ cm}^{-1})J \quad J = 0, 1, 2, \dots\end{aligned}$$

The first few allowed transitions in the R branch are

Transition ($J'' \rightarrow J'$)	$\tilde{\nu}/\text{cm}^{-1}$
0 \rightarrow 1	966.7
1 \rightarrow 2	969.7
2 \rightarrow 3	972.8
3 \rightarrow 4	975.8

and the first few allowed transitions in the P branch are

Transition ($J'' \rightarrow J'$)	$\tilde{\nu}/\text{cm}^{-1}$
1 \rightarrow 0	960.7
2 \rightarrow 1	957.6
3 \rightarrow 2	954.6
4 \rightarrow 3	951.6

13-13. Using the values of $\tilde{\nu}_e$, $\tilde{x}_e\tilde{\nu}_e$, \tilde{B}_e , and $\tilde{\alpha}_e$ given in Table 13.2, construct to scale an energy-level diagram for the first five rotational levels in the $v = 0$ and $v = 1$ vibrational states for H^{35}Cl . Indicate the allowed transitions in an absorption experiment, and calculate the frequencies of the first few lines in the R and P branches.

From the table,

$$\tilde{\nu}_e = 2990.946 \text{ cm}^{-1} \quad \tilde{B}_e = 10.5934 \text{ cm}^{-1}$$

$$\tilde{x}_e\tilde{\nu}_e = 52.819 \text{ cm}^{-1} \quad \tilde{\alpha}_e = 0.3072 \text{ cm}^{-1}$$

Using Equations 13.10, 13.17, and 13.21, we obtain

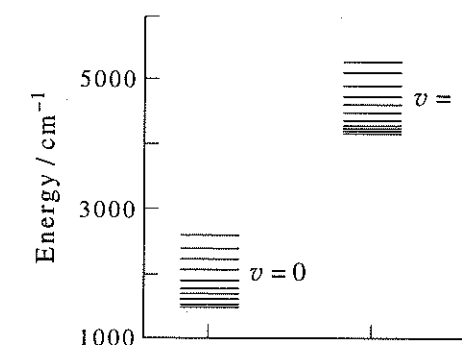
$$\begin{aligned}\tilde{E}_{v,J} &= \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}_v J(J+1) \\ &= \tilde{\nu}_e(v + \frac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v + \frac{1}{2})^2 + \left[\tilde{B}_e - \tilde{\alpha}_e(v + \frac{1}{2})\right] J(J+1)\end{aligned}$$

So

$$\begin{aligned}\tilde{E}_{0,J} &= \frac{1}{2}\tilde{\nu}_e - \frac{1}{4}\tilde{x}_e\tilde{\nu}_e + (\tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e)J(J+1) \\ &= 1482.268 \text{ cm}^{-1} + (10.4398 \text{ cm}^{-1})J(J+1) \\ \tilde{E}_{1,J} &= \frac{3}{2}\tilde{\nu}_e - \frac{9}{4}\tilde{x}_e\tilde{\nu}_e + (\tilde{B}_e - \frac{3}{2}\tilde{\alpha}_e)J(J+1) \\ &= 4367.576 \text{ cm}^{-1} + (10.1326 \text{ cm}^{-1})J(J+1)\end{aligned}$$

We can use the expressions for $\tilde{E}_{0,J}$ and $\tilde{E}_{1,J}$ to construct a table of energy values for different values of J .

J	$\tilde{E}_{0,J}/\text{cm}^{-1}$	$\tilde{E}_{1,J}/\text{cm}^{-1}$
0	1482.268	4367.576
1	1503.148	4387.841
2	1544.907	4428.372
3	1607.546	4489.167
4	1691.064	4570.228



We now subtract the appropriate energy levels subject to the selection rules $\Delta v = +1$ and $\Delta J = \pm 1$ to obtain the frequencies of the first few lines in the P and R branches of the spectrum:

$$\begin{aligned}\tilde{\nu}_R(0 \rightarrow 1) &= 2905.573 \text{ cm}^{-1} & \tilde{\nu}_P(1 \rightarrow 0) &= 2864.428 \text{ cm}^{-1} \\ \tilde{\nu}_R(1 \rightarrow 2) &= 2925.222 \text{ cm}^{-1} & \tilde{\nu}_P(2 \rightarrow 1) &= 2842.934 \text{ cm}^{-1} \\ \tilde{\nu}_R(2 \rightarrow 3) &= 2944.260 \text{ cm}^{-1} & \tilde{\nu}_P(3 \rightarrow 2) &= 2820.826 \text{ cm}^{-1} \\ \tilde{\nu}_R(3 \rightarrow 4) &= 2962.682 \text{ cm}^{-1} & \tilde{\nu}_P(4 \rightarrow 3) &= 2798.103 \text{ cm}^{-1}\end{aligned}$$

13-14. The following data are obtained for the vibration-rotation spectrum of H^{79}Br . Determine \tilde{B}_0 , \tilde{B}_1 , \tilde{B}_e , and $\tilde{\alpha}_e$ from these data.

Line	Frequency/ cm^{-1}
$R(0)$	2642.60
$R(1)$	2658.36
$P(1)$	2609.67
$P(2)$	2592.51

Following the method of Example 13.4, we substitute into Equations 13.15 and 13.16 to find

$$\begin{aligned}\tilde{R}(0) &= 2642.60 \text{ cm}^{-1} = \tilde{\nu} + 2\tilde{B}_1 \\ \tilde{R}(1) &= 2658.36 \text{ cm}^{-1} = \tilde{\nu} + 6\tilde{B}_1 - 2\tilde{B}_0 \\ \tilde{P}(1) &= 2609.67 \text{ cm}^{-1} = \tilde{\nu} - 2\tilde{B}_0 \\ \tilde{P}(2) &= 2592.51 \text{ cm}^{-1} = \tilde{\nu} - 2\tilde{B}_1 - 6\tilde{B}_0\end{aligned}$$

Subtracting $\tilde{P}(1)$ from $\tilde{R}(1)$ gives

$$\tilde{R}(1) - \tilde{P}(1) = 48.69 \text{ cm}^{-1} = 6\tilde{B}_1$$

so that $\tilde{B}_1 = 8.12 \text{ cm}^{-1}$. Likewise, subtracting $\tilde{P}(2)$ from $\tilde{R}(0)$ gives

$$\tilde{R}(0) - \tilde{P}(2) = 50.09 \text{ cm}^{-1} = 6\tilde{B}_0$$

so $\tilde{B}_0 = 8.35 \text{ cm}^{-1}$.

We now use Equation 13.17 to write \tilde{B}_0 and \tilde{B}_1 in terms of \tilde{B}_e and $\tilde{\alpha}_e$:

$$\tilde{B}_0 = \tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e = 8.35 \text{ cm}^{-1}$$

$$\tilde{B}_1 = \tilde{B}_e - \frac{3}{2}\tilde{\alpha}_e = 8.12 \text{ cm}^{-1}$$

Solving for \tilde{B}_e and $\tilde{\alpha}_e$ gives

$$\tilde{\alpha}_e = \tilde{B}_0 - \tilde{B}_1 = 0.23 \text{ cm}^{-1}$$

$$2\tilde{B}_e = 3\tilde{B}_0 - \tilde{B}_1 = 16.93 \text{ cm}^{-1}$$

$$\tilde{B}_e = 8.47 \text{ cm}^{-1}$$

13-15. The following lines were observed in the microwave absorption spectrum of H^{127}I and D^{127}I between 60 cm^{-1} and 90 cm^{-1} .

	$\tilde{\nu}/\text{cm}^{-1}$			
H^{127}I	64.275	77.130	89.985	
D^{127}I	65.070	71.577	78.084	84.591

Use the rigid-rotator approximation to determine the values of \tilde{B} , I , and R_e for each molecule. Do your results for the bond length agree with what you would expect based upon the Born-Oppenheimer approximation? Take the mass of ^{127}I to be 126.904 amu and the mass of D to be 2.014 amu.

In the rigid-rotator approximation, the spacing between the lines in a microwave absorption spectrum is $2\tilde{B}$ (Equation 13.19). The spacing between the lines given for H^{127}I is 12.855 cm^{-1} , and the spacing between the lines given for D^{127}I is 6.507 cm^{-1} . Therefore,

$$\tilde{B}_{\text{H}^{127}\text{I}} = \frac{1}{2}(12.855 \text{ cm}^{-1}) = 6.428 \text{ cm}^{-1}$$

and

$$\tilde{B}_{\text{D}^{127}\text{I}} = \frac{1}{2}(6.507 \text{ cm}^{-1}) = 3.254 \text{ cm}^{-1}$$

We now use Equation 13.9 to find I for both molecules:

$$I = \frac{h}{8\pi^2 c \tilde{B}}$$

$$I_{\text{HI}} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8\pi^2 (2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(6.428 \text{ cm}^{-1})} = 4.355 \times 10^{-47} \text{ kg}\cdot\text{m}^2$$

$$I_{\text{DI}} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8\pi^2 (2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(3.254 \text{ cm}^{-1})} = 8.604 \times 10^{-47} \text{ kg}\cdot\text{m}^2$$

Now we use the fact that $I = \mu R_e^2$ for a diatomic molecule to find R_e :

$$I = \mu R_e^2$$

$$R_e = \left(\frac{I}{\mu}\right)^{1/2}$$

$$R_{e,\text{HI}} = \left[\frac{4.355 \times 10^{-47} \text{ kg}\cdot\text{m}^2}{\left(\frac{1.008 \times 126.904}{127.912} \text{ amu}\right) (1.661 \times 10^{-27} \text{ kg}\cdot\text{amu}^{-1})} \right]^{1/2}$$

$$= 1.619 \times 10^{-10} \text{ m} = 161.9 \text{ pm}$$

$$R_{e,\text{DI}} = \left[\frac{8.604 \times 10^{-47} \text{ kg}\cdot\text{m}^2}{\left(\frac{2.014 \times 126.904}{128.917} \text{ amu}\right) (1.661 \times 10^{-27} \text{ kg}\cdot\text{amu}^{-1})} \right]^{1/2}$$

$$= 1.617 \times 10^{-10} \text{ m} = 161.7 \text{ pm}$$

These values differ by approximately 0.1%. In the Born-Oppenheimer approximation, the bond length is independent of the isotope of the atoms, in agreement with the above calculations.

13-16. The following spectroscopic constants were determined for pure samples of $^{74}\text{Ge}^{32}\text{S}$ and $^{72}\text{Ge}^{32}\text{S}$:

Molecule	B_e/MHz	α_e/MHz	D/kHz	$R_e(\nu=0)/\text{pm}$
$^{74}\text{Ge}^{32}\text{S}$	5593.08	22.44	2.349	0.201 20
$^{72}\text{Ge}^{32}\text{S}$	5640.06	22.74	2.388	0.201 20

Determine the frequency of the $J=0$ to $J=1$ transition for $^{74}\text{Ge}^{32}\text{S}$ and $^{72}\text{Ge}^{32}\text{S}$ in their ground vibrational states. The width of a microwave absorption line is on the order of 1 kHz. Could you distinguish a pure sample of $^{74}\text{Ge}^{32}\text{S}$ from a 50/50 mixture of $^{74}\text{Ge}^{32}\text{S}$ and $^{72}\text{Ge}^{32}\text{S}$ using microwave spectroscopy?

To convert the values given in the above table to wave numbers, divide by c . Then substitute into a combination of Equations 13.17 and 13.19, with $\nu=0$:

$$\tilde{\nu} = 2 \left[\tilde{B}_e - \tilde{\alpha}_e \left(\frac{1}{2}\right) \right] (J+1) - 4\tilde{D}(J+1)^3$$

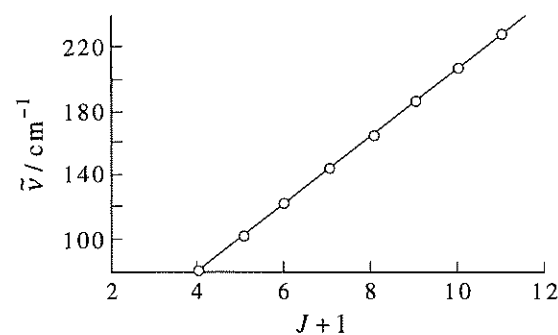
Molecule	$(\tilde{\nu}, J=0)/\text{cm}^{-1}$	$(\tilde{\nu}, J=1)/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$
$^{74}\text{Ge}^{32}\text{S}$	0.372 381	0.744 761	0.372 379
$^{72}\text{Ge}^{32}\text{S}$	0.375 505	0.751 009	0.375 504

Now, the width of the absorption line is on the order of 1000 s^{-1} , which corresponds to an energy of approximately $3 \times 10^{-8} \text{ cm}^{-1}$. This width is less than the difference between the absorption lines of $^{74}\text{Ge}^{32}\text{S}$ and $^{72}\text{Ge}^{32}\text{S}$ and so a 50/50 mixture can be distinguished from a pure sample using microwave spectroscopy.

13-17. The frequencies of the rotational transitions in the nonrigid-rotator approximation are given by Equation 13.19. Show how both \tilde{B} and \tilde{D} may be obtained by curve fitting $\tilde{\nu}$ to Equation 13.19. Use this method and the data in Table 13.3 to determine both \tilde{B} and \tilde{D} for H^{35}Cl .

$$\tilde{\nu} = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3 \quad (13.19)$$

The data from Table 13.3 are plotted in the following figure. (Compare the accuracy of this data to that in the following problem.)

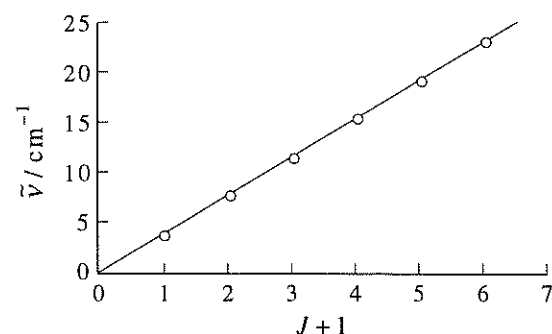


The best-fit line to this data gives $2\tilde{B} = 20.81 \text{ cm}^{-1}$ and $-4\tilde{D} = -1.772 \times 10^{-3} \text{ cm}^{-1}$. Therefore, $\tilde{B} = 10.40 \text{ cm}^{-1}$ and $\tilde{D} = 4.43 \times 10^{-4} \text{ cm}^{-1}$.

13-18. The following data are obtained in the microwave spectrum of $^{12}\text{C}^{16}\text{O}$. Use the method of Problem 13-17 to determine the values of \tilde{B} and \tilde{D} from these data.

Transitions	Frequency/ cm^{-1}
0 → 1	3.845 40
1 → 2	7.690 60
2 → 3	11.535 50
3 → 4	15.379 90
4 → 5	19.223 80
5 → 6	23.066 85

Using the method of Problem 13-17, we plot $\tilde{\nu}$ vs. $J + 1$.



The best-fit line to this data gives $2\tilde{B} = 3.8454 \text{ cm}^{-1}$ and $-4\tilde{D} = -2.5547 \times 10^{-5} \text{ cm}^{-1}$. Therefore, $\tilde{B} = 1.9227 \text{ cm}^{-1}$ and $\tilde{D} = 6.387 \times 10^{-6} \text{ cm}^{-1}$.

13-19. Using the parameters given in Table 13.2, calculate the frequencies (in cm^{-1}) of the 0 → 1, 1 → 2, 2 → 3, and 3 → 4 rotational transitions in the ground vibrational state of H^{35}Cl in the nonrigid-rotator approximation.

We substitute $\tilde{B} = 10.5934 \text{ cm}^{-1}$ and $\tilde{D} = 5.319 \times 10^{-4} \text{ cm}^{-1}$ (Table 13.2) into Equation 13.19 to find

$$\tilde{\nu}_{\text{calc}}/\text{cm}^{-1} = 21.1868(J + 1) - 0.002128(J + 1)^3$$

Transition	$\tilde{\nu}_{\text{calc}}/\text{cm}^{-1}$
0 → 1	21.1847
1 → 2	42.3566
2 → 3	63.5030
3 → 4	84.6110

13-20. The vibrational term of a diatomic molecule is given by

$$G(v) = (v + \frac{1}{2})\tilde{\nu}_e - (v + \frac{1}{2})^2\tilde{x}_e\tilde{\nu}_e$$

where v is the vibrational quantum number. Show that the spacing between the adjacent levels ΔG is given by

$$\Delta G = G(v + 1) - G(v) = \tilde{\nu}_e[1 - 2\tilde{x}_e(v + 1)] \quad (1)$$

The diatomic molecule dissociates in the limit that $\Delta G \rightarrow 0$. Show that the maximum vibrational quantum number, v_{max} , is given by

$$v_{\text{max}} = \frac{1}{2\tilde{x}_e} - 1$$

Use this result to show that the dissociation energy \tilde{D}_e of the diatomic molecule can be written as

$$\tilde{D}_e = \frac{\tilde{\nu}_e(1 - \tilde{x}_e^2)}{4\tilde{x}_e} \approx \frac{\tilde{\nu}_e}{4\tilde{x}_e} \quad (2)$$

Referring to Equation 1, explain how the constants $\tilde{\nu}_e$ and \tilde{x}_e can be evaluated from a plot of ΔG versus $v + 1$. This type of plot is called a *Birge-Sponer plot*. Once the values of $\tilde{\nu}_e$ and \tilde{x}_e are known, Equation 2 can be used to determine the dissociation energy of the molecule. Use the following experimental data for H_2 to calculate the dissociation energy, \tilde{D}_e .

v	$G(v)/\text{cm}^{-1}$	v	$G(v)/\text{cm}^{-1}$
0	4161.12	7	26 830.97
1	8087.11	8	29 123.93
2	11 782.35	9	31 150.19
3	15 250.36	10	32 886.85
4	18 497.92	11	34 301.83
5	21 505.65	12	35 351.01
6	24 287.83	13	35 972.97

Explain why your Birge-Sponer plot is not linear for high values of v . How does the value of \tilde{D}_e obtained from the Birge-Sponer analysis compare with the experimental value of $38 269.48 \text{ cm}^{-1}$?

Use the expression given in the problem to find Equation 1:

$$\begin{aligned} \Delta G &= G(v + 1) - G(v) \\ &= (v + \frac{3}{2})\tilde{\nu}_e - (v + \frac{3}{2})^2\tilde{x}_e\tilde{\nu}_e - (v + \frac{1}{2})\tilde{\nu}_e + (v + \frac{1}{2})^2\tilde{x}_e\tilde{\nu}_e \\ &= \tilde{\nu}_e - \tilde{x}_e\tilde{\nu}_e(2v + 2) = \tilde{\nu}_e[1 - 2\tilde{x}_e(v + 1)] \end{aligned}$$

In the limit $\Delta G \rightarrow 0$, $v \rightarrow v_{\max}$. Solving for v_{\max} gives

$$\begin{aligned} 0 &= \tilde{\nu}_e [1 - 2\tilde{x}_e(v_{\max} + 1)] \\ 2\tilde{x}_e(v_{\max} + 1) &= 1 \\ v_{\max} &= \frac{1}{2\tilde{x}_e} - 1 \end{aligned}$$

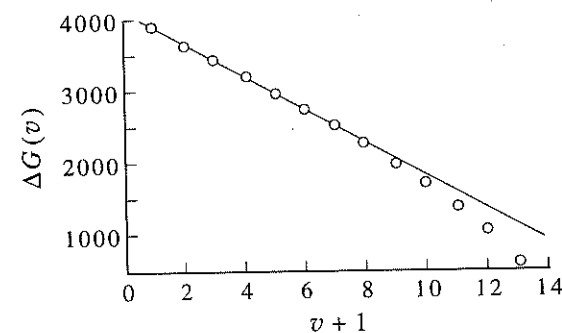
The molecule dissociates in the limit $\Delta G \rightarrow 0$, so the dissociation energy is

$$\begin{aligned} \tilde{D}_e &= G(v_{\max}) = \left(\frac{1}{2\tilde{x}_e} - \frac{1}{2}\right) \tilde{\nu}_e - \left(\frac{1}{2\tilde{x}_e} - \frac{1}{2}\right)^2 \tilde{x}_e \tilde{\nu}_e \\ &= \frac{\tilde{\nu}_e}{2\tilde{x}_e} (1 - \tilde{x}_e) - \frac{\tilde{\nu}_e}{4\tilde{x}_e} (1 - \tilde{x}_e)^2 \\ &= \frac{\tilde{\nu}_e}{4\tilde{x}_e} (2 - 2\tilde{x}_e - 1 + 2\tilde{x}_e - \tilde{x}_e^2) \\ &= \frac{\tilde{\nu}_e}{4\tilde{x}_e} (1 - \tilde{x}_e^2) \approx \frac{\tilde{\nu}_e}{4\tilde{x}_e} \end{aligned}$$

because \tilde{x}_e is very small compared to one. We can expand Equation 1 to write

$$\Delta G = \tilde{\nu}_e - 2\tilde{x}_e \tilde{\nu}_e (v + 1)$$

Therefore, a plot of ΔG vs. $(v + 1)$ will have an intercept of $\tilde{\nu}_e$ and a slope of $-2\tilde{x}_e \tilde{\nu}_e$. The experimental data points for H_2 are plotted below:



Using the best linear fit to the first eight data points gives $\tilde{\nu}_e = 4164.4 \text{ cm}^{-1}$ and $-2\tilde{x}_e \tilde{\nu}_e = -232.01 \text{ cm}^{-1}$. Then $\tilde{x}_e = 0.0279$, and so

$$\tilde{D}_e = \frac{\tilde{\nu}_e}{4\tilde{x}_e} = 37\,400 \text{ cm}^{-1}$$

The Birge-Sponer plot is not linear for large values of v because the potential curve is not well described by the anharmonic potential energy function $G(v)$ given in the statement of the problem.

13-21. An analysis of the vibrational spectrum of the ground-state homonuclear diatomic molecule C_2 gives $\tilde{\nu}_e = 1854.71 \text{ cm}^{-1}$ and $\tilde{\nu}_e \tilde{x}_e = 13.34 \text{ cm}^{-1}$. Suggest an experimental method that can be used to determine these spectroscopic parameters. Use the expression derived in Problem 13-20 to determine the number of bound vibrational levels for the ground state of C_2 .

The molecule C_2 does not have a dipole moment, and so we cannot record an infrared absorption spectrum. We can determine $\tilde{\nu}_e$ and $\tilde{\nu}_e \tilde{x}_e$ from an emission spectrum, where the lines correspond

to transitions between a specific vibrational state in the upper electronic state and the various vibrational states in the ground electronic state. The number of bound vibrational levels, v_{\max} , is given by (see Problem 13-20)

$$v_{\max} = \frac{1}{2\tilde{x}_e} - 1 = \frac{1854.71 \text{ cm}^{-1}}{2(13.34 \text{ cm}^{-1})} - 1 = 68.5$$

There are 68 bound vibrational levels for the ground state of C_2 .

13-22. A simple function that is a good representation of an internuclear potential is the Morse potential,

$$U(q) = D_e(1 - e^{-\beta q})^2$$

where q is $R - R_e$. Show that the force constant calculated for a Morse potential is given by

$$k = 2D_e\beta^2$$

Given that $D_e = 7.31 \times 10^{-19} \text{ J}\cdot\text{molecule}^{-1}$ and $\beta = 1.83 \times 10^{10} \text{ m}^{-1}$ for HCl , calculate the value of k .

We can expand $U(q)$ using a Maclaurin series:

$$\begin{aligned} U(q) &= D_e(1 - e^{-\beta q})^2 \\ &= D_e \left\{ 1 - \left[1 - \beta q + \frac{\beta^2 q^2}{2} + O(q^3) \right] \right\}^2 \\ &= D_e [\beta^2 q^2 + O(q^3)] \end{aligned}$$

Equating this result to $U(q) = kq^2/2$ (as in Equation 5.11) gives

$$k = 2D_e\beta^2$$

For HCl ,

$$k = 2(7.31 \times 10^{-19} \text{ J}\cdot\text{molecule}^{-1})(1.83 \times 10^{10} \text{ m}^{-1})^2 = 490 \text{ N}\cdot\text{m}^{-1}$$

13-23. The Morse potential is presented in Problem 13-22. Given that $D_e = 7.33 \times 10^{-19} \text{ J}\cdot\text{molecule}^{-1}$, $\tilde{\nu}_e = 1580.0 \text{ cm}^{-1}$, and $R_e = 121 \text{ pm}$ for $^{16}\text{O}_2$, plot a Morse potential for $^{16}\text{O}_2$. Plot the corresponding harmonic-oscillator potential on the same graph.

$$\tilde{\nu}_e = \frac{1}{2\pi c} \left(\frac{k}{\mu}\right)^{1/2} \quad (13.5)$$

We can find k from the parameters given in the problem. Solving for k gives

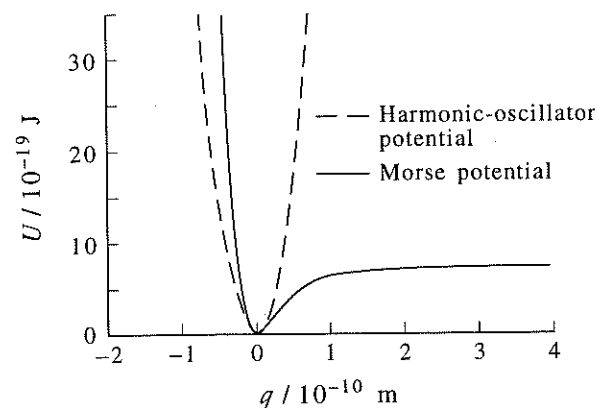
$$\begin{aligned} k &= (2\pi c \tilde{\nu}_e)^2 \mu \\ &= [2\pi(2.998 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(1580.0 \text{ cm}^{-1})]^2 (7.9975 \text{ amu})(1.661 \times 10^{-27} \text{ kg}\cdot\text{amu}^{-1}) \\ &= 1176.3 \text{ N}\cdot\text{m}^{-1} \end{aligned}$$

From Problem 13-22, we know that $k = 2D_e\beta^2$, so

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} = \left[\frac{1176.3 \text{ N}\cdot\text{m}^{-1}}{2(7.33 \times 10^{-19} \text{ J})}\right]^{1/2}$$

$$= 2.83 \times 10^{10} \text{ m}^{-1}$$

Recall (Equation 5.11) that the potential energy of a harmonic oscillator is $U(q) = kq^2/2$. Now graph the Morse potential and harmonic-oscillator potential for $^{16}\text{O}_2$:



The Morse potential is a more realistic approximation of the behavior of a molecule.

13-24. The fundamental line in the infrared spectrum of $^{12}\text{C}^{16}\text{O}$ occurs at 2143.0 cm^{-1} , and the first overtone occurs at 4260.0 cm^{-1} . Calculate the values of $\tilde{\nu}_e$ and $\tilde{x}_e\tilde{\nu}_e$ for $^{12}\text{C}^{16}\text{O}$.

We do this problem in the manner of Example 13-5, where we derived equations for the frequency of the fundamental and first overtone.

$$\text{Fundamental: } \tilde{\nu}_{\text{obs}} = \tilde{\nu}_e - 2\tilde{x}_e\tilde{\nu}_e = 2143.0 \text{ cm}^{-1}$$

$$\text{First overtone: } \tilde{\nu}_{\text{obs}} = 2\tilde{\nu}_e - 6\tilde{x}_e\tilde{\nu}_e = 4260.0 \text{ cm}^{-1}$$

Multiply the fundamental frequency by 3 and subtract the overtone to get

$$\tilde{\nu}_e = 3(2143.0 \text{ cm}^{-1}) - 4260.0 \text{ cm}^{-1} = 2169 \text{ cm}^{-1}$$

Multiply the fundamental frequency by 2 and subtract from the overtone to get

$$2\tilde{x}_e\tilde{\nu}_e = 26.0 \text{ cm}^{-1}$$

or

$$\tilde{x}_e\tilde{\nu}_e = 13.0 \text{ cm}^{-1}$$

13-25. Using the parameters given in Table 13.2, calculate the fundamental and the first three overtones of H^{79}Br .

Using Equation 13.22, we find

$$\begin{aligned} \text{Fundamental: } \tilde{\nu}_{\text{obs}} &= \tilde{\nu}_e - 2\tilde{x}_e\tilde{\nu}_e \\ &= 2648.975 \text{ cm}^{-1} - 2(45.218 \text{ cm}^{-1}) \\ &= 2558.539 \text{ cm}^{-1} \\ \text{First overtone: } \tilde{\nu}_{\text{obs}} &= 2\tilde{\nu}_e - 6\tilde{x}_e\tilde{\nu}_e \\ &= 2(2648.975 \text{ cm}^{-1}) - 6(45.218 \text{ cm}^{-1}) \\ &= 5026.642 \text{ cm}^{-1} \\ \text{Second overtone: } \tilde{\nu}_{\text{obs}} &= 3\tilde{\nu}_e - 12\tilde{x}_e\tilde{\nu}_e \\ &= 3(2648.975 \text{ cm}^{-1}) - 12(45.218 \text{ cm}^{-1}) \\ &= 7404.309 \text{ cm}^{-1} \\ \text{Third overtone: } \tilde{\nu}_{\text{obs}} &= 4\tilde{\nu}_e - 20\tilde{x}_e\tilde{\nu}_e \\ &= 4(2648.975 \text{ cm}^{-1}) - 20(45.218 \text{ cm}^{-1}) \\ &= 9691.54 \text{ cm}^{-1} \end{aligned}$$

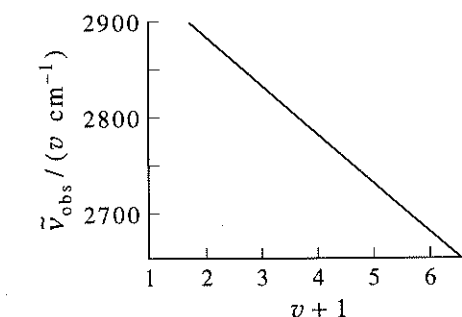
13-26. The frequencies of the vibrational transitions in the anharmonic-oscillator approximation are given by Equation 13.22. Show how the values of both $\tilde{\nu}_e$ and $\tilde{x}_e\tilde{\nu}_e$ may be obtained by plotting $\tilde{\nu}_{\text{obs}}/v$ versus $(v+1)$. Use this method and the data in Table 13.4 to determine the values $\tilde{\nu}_e$ and $\tilde{x}_e\tilde{\nu}_e$ for H^{35}Cl .

$$\tilde{\nu}_{\text{obs}} = \tilde{\nu}_e v - \tilde{x}_e\tilde{\nu}_e v(v+1) \quad (13.22)$$

Divide by v to obtain

$$\frac{\tilde{\nu}_{\text{obs}}}{v} = \tilde{\nu}_e - \tilde{x}_e\tilde{\nu}_e(v+1)$$

If we plot $\tilde{\nu}_{\text{obs}}/v$ versus $(v+1)$, the slope of the line will be $-\tilde{x}_e\tilde{\nu}_e$ and the intercept will be $\tilde{\nu}_e$. Using the data in Table 13.4, we obtain the following plot:

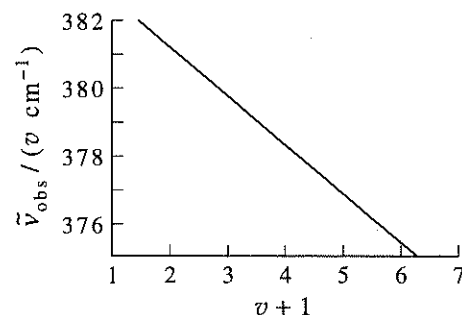


The best fit line to the data has an intercept of $\tilde{\nu}_e = 2989 \text{ cm}^{-1}$ and a slope of -51.6 cm^{-1} , so $\tilde{\nu}_e\tilde{x}_e = 51.6 \text{ cm}^{-1}$.

13-27. The following data are obtained from the infrared spectrum of $^{127}\text{I}^{35}\text{Cl}$. Using the method of Problem 13-26, determine the values of $\tilde{\nu}_e$ and $\tilde{x}_e\tilde{\nu}_e$ from these data.

Transitions	Frequency/cm $^{-1}$
0 \rightarrow 1	381.20
0 \rightarrow 2	759.60
0 \rightarrow 3	1135.00
0 \rightarrow 4	1507.40
0 \rightarrow 5	1877.00

We plot $\tilde{\nu}_{\text{obs}}/v$ vs. $(v+1)$.



The best fit line to the data has an intercept of $\tilde{\nu}_e = 384.1 \text{ cm}^{-1}$ and a slope of -1.45 cm^{-1} , so $\tilde{\nu}_e\tilde{x}_e = 1.45 \text{ cm}^{-1}$.

13-28. The values of $\tilde{\nu}_e$ and $\tilde{x}_e\tilde{\nu}_e$ of $^{12}\text{C}^{16}\text{O}$ are 2169.81 cm^{-1} and 13.29 cm^{-1} in the ground electronic state and 1514.10 cm^{-1} and 17.40 cm^{-1} in the first excited electronic state. If the $0 \rightarrow 0$ vibronic transition occurs at $6.47515 \times 10^4 \text{ cm}^{-1}$, calculate the value of $\tilde{T}_e = \tilde{\nu}'_e - \tilde{\nu}''_e$, the energy difference between the minima of the potential curves of the two electronic states.

For the $0 \rightarrow 0$ vibronic transition, $v' = v'' = 0$ in Equation 13.24 and so

$$\begin{aligned}\tilde{\nu}_{0,0} &= \tilde{T}_e + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{x}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{x}''_e\tilde{\nu}''_e\right) \\ 64\,751.5 \text{ cm}^{-1} &= \tilde{T}_e + \left[\frac{1}{2}(1514.10 \text{ cm}^{-1}) - \frac{1}{4}(17.40 \text{ cm}^{-1})\right] \\ &\quad - \left[\frac{1}{2}(2169.81 \text{ cm}^{-1}) - \frac{1}{4}(13.29 \text{ cm}^{-1})\right] \\ 65\,080.4 \text{ cm}^{-1} &= \tilde{T}_e\end{aligned}$$

13-29. Given the following parameters for $^{12}\text{C}^{16}\text{O}$: $\tilde{T}_e = 6.508\,043 \times 10^4 \text{ cm}^{-1}$, $\tilde{\nu}'_e = 1514.10 \text{ cm}^{-1}$, $\tilde{x}'_e\tilde{\nu}'_e = 17.40 \text{ cm}^{-1}$, $\tilde{\nu}''_e = 2169.81 \text{ cm}^{-1}$, and $\tilde{x}''_e\tilde{\nu}''_e = 13.29 \text{ cm}^{-1}$, construct to scale an energy-level diagram of the first two electronic states, showing the first four vibrational states in each electronic state. Indicate the allowed transitions from $v'' = 0$, and calculate the frequencies of these transitions. Also, calculate the zero-point vibrational energy in each electronic state.

Neglecting rotational energies, Equation 13.23 becomes

$$\tilde{E}_v = \tilde{\nu}_e + \tilde{\nu}_e(v + \frac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v + \frac{1}{2})^2$$

Setting the energy at the minimum of the lower electronic potential energy curve equal to zero, we have

$$\tilde{E}_v'' = 0 + \tilde{\nu}_e''(v + \frac{1}{2}) - \tilde{x}_e''\tilde{\nu}_e''(v + \frac{1}{2})^2$$

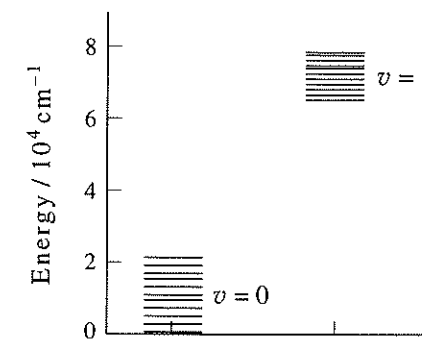
$$\tilde{E}_v' = \tilde{T}_e + \tilde{\nu}_e'(v + \frac{1}{2}) - \tilde{x}_e'\tilde{\nu}_e'(v + \frac{1}{2})^2$$

$$\tilde{E}_v'' = 2169.81 \text{ cm}^{-1}(v + \frac{1}{2}) - 13.29 \text{ cm}^{-1}(v + \frac{1}{2})^2$$

$$\tilde{E}_v' = 65\,080.43 \text{ cm}^{-1} + 1514.10 \text{ cm}^{-1}(v + \frac{1}{2}) - 17.40 \text{ cm}^{-1}(v + \frac{1}{2})^2$$

We can now make a table of the energies of the various vibrational states:

v	$\tilde{E}_v''/\text{cm}^{-1}$	$\tilde{E}_v'/\text{cm}^{-1}$
0	1081.58	65\,833.13
1	3224.81	67\,312.43
2	5341.63	68\,756.93
3	7431.53	70\,166.63



We can also create a table of allowed transitions from $v'' = 0$ and their frequencies:

$v'' \rightarrow v'$	$\Delta E/\text{cm}^{-1}$
0 \rightarrow 0	64\,751.55
0 \rightarrow 1	66\,230.85
0 \rightarrow 2	67\,675.35
0 \rightarrow 3	69\,085.05

13-30. An analysis of the rotational spectrum of $^{12}\text{C}^{32}\text{S}$ gives the following results:

v	0	1	2	3
$\tilde{B}_v/\text{cm}^{-1}$	0.81708	0.81116	0.80524	0.79932

Determine the values of \tilde{B}_e and $\tilde{\alpha}_e$ from these data.

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e(v + \frac{1}{2}) \quad (13.17)$$

If we subtract \tilde{B}_v from \tilde{B}_{v+1} , we find that

$$\tilde{B}_{v+1} - \tilde{B}_v = -\tilde{\alpha}_e$$

Using the values given in the problem, we then find

v	0	1	2
$\tilde{\alpha}_e/\text{cm}^{-1}$	0.00592	0.00592	0.00590

Take $\tilde{\alpha}_e = 0.00592 \text{ cm}^{-1}$ and substitute into Equation 13.17 to find

$$\begin{aligned}\tilde{B}_e &= \tilde{B}_v + (0.00592 \text{ cm}^{-1})(v + \frac{1}{2}) \\ &= 0.81708 \text{ cm}^{-1} + (0.00592 \text{ cm}^{-1})(\frac{1}{2}) \\ &= 0.82004 \text{ cm}^{-1}\end{aligned}$$

where we have let $v = 0$. We obtain the same value of \tilde{B}_e for $v = 1, 2$, and 3.

13-31. The frequencies of the first few vibronic transitions to an excited state of BeO are as follows:

Vibronic transitions	$0 \rightarrow 2$	$0 \rightarrow 3$	$0 \rightarrow 4$	$0 \rightarrow 5$
$\tilde{\nu}_{\text{obs}}/\text{cm}^{-1}$	12 569.95	13 648.43	14 710.85	15 757.50

Use these data to calculate the values of $\tilde{\nu}_e$ and $\tilde{x}_e \tilde{\nu}_e$ for the excited state of BeO.

We use Equation 13.24, with $v'' = 0$:

$$\tilde{\nu}_{\text{obs}} = \tilde{T}_e + (\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{x}'_e\tilde{\nu}'_e) - (\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{x}''_e\tilde{\nu}''_e) + \tilde{\nu}'_e v' - \tilde{x}'_e \tilde{\nu}'_e v'(v' + 1) \quad (1)$$

We can rewrite this equation in the form

$$\tilde{\nu}_{\text{obs}} = Av'^2 + Bv' + C$$

where $A = \tilde{x}'_e \tilde{\nu}'_e$, $B = \tilde{\nu}'_e - \tilde{x}'_e \tilde{\nu}'_e$, and C is the sum of the first three terms in Equation 1. The best fit of the quadratic equation to the experimental data gives $\tilde{\nu}_{\text{obs}} = -8.0v'^2 + 1118.2v' + 10\,365$. Therefore,

$$\begin{aligned}\tilde{\nu}'_e - \tilde{x}'_e \tilde{\nu}'_e &= 1118.2 \text{ cm}^{-1} \\ \tilde{x}'_e \tilde{\nu}'_e &= 8.0 \text{ cm}^{-1} \\ \tilde{\nu}'_e &= 1126.2 \text{ cm}^{-1}\end{aligned}$$

13-32. The frequencies of the first few vibronic transitions to an excited state of ${}^7\text{Li}_2$ are as follows:

Vibronic transitions	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$	$0 \rightarrow 3$	$0 \rightarrow 4$	$0 \rightarrow 5$
$\tilde{\nu}_{\text{obs}}/\text{cm}^{-1}$	14 020	14 279	14 541	14 805	15 074	15 345

Use these data to calculate the values of $\tilde{\nu}_e$ and $\tilde{x}_e \tilde{\nu}_e$ for the excited state of ${}^7\text{Li}_2$.

We use the same technique as in Problem 13-31. The best-fit quadratic equation to the data is $\tilde{\nu}_{\text{obs}} = -0.04v'^2 + 267.72v' + 14\,005$. Thus, we have

$$\begin{aligned}\tilde{\nu}'_e - \tilde{x}'_e \tilde{\nu}'_e &= 267.72 \text{ cm}^{-1} \\ \tilde{x}'_e \tilde{\nu}'_e &= 0.04 \text{ cm}^{-1} \\ \tilde{\nu}'_e &= 267.76 \text{ cm}^{-1}\end{aligned}$$

13-33. Determine the number of translational, rotational, and vibrational degrees of freedom in

- a. CH_3Cl b. OCS c. C_6H_6 d. H_2CO

The total number of degrees of freedom is $3N$, where N is the number of atoms in the molecule. All molecules have three translational degrees of freedom. A nonlinear molecule has three rotational degrees of freedom and a linear molecule has two rotational degrees of freedom. A linear molecule has $3N - 5$ vibrational degrees of freedom and a nonlinear molecule has $3N - 6$ vibrational degrees of freedom.

- a. 3 translational, 3 rotational, 9 vibrational
b. 3 translational, 2 rotational, 4 vibrational
c. 3 translational, 3 rotational, 30 vibrational
d. 3 translational, 3 rotational, 6 vibrational

13-34. Determine which of the following molecules will exhibit a microwave rotational absorption spectrum: H_2 , HCl , CH_4 , CH_3I , H_2O , and SF_6 .

The molecules HCl , CH_3I , and H_2O exhibit a microwave rotational absorption spectrum. All the other molecules do not have a permanent dipole moment and so do not have a microwave absorption spectrum.

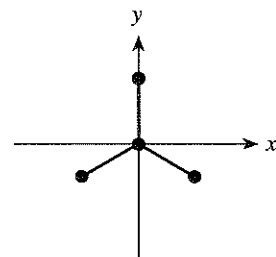
13-35. Classify each of the following molecules as a spherical, a symmetric, or an asymmetric top: CH_3Cl , CCl_4 , SO_2 , and SiH_4 .

- CH_3Cl : symmetric top
 CCl_4 : spherical top
 SO_2 : asymmetric top
 SiH_4 : spherical top

13-36. Classify each of the following molecules as either a prolate or an oblate symmetric top: FCH_3 , HCCl_3 , PF_3 , and CH_3CCH .

- FCH_3 : prolate symmetric top
 HCCl_3 : oblate symmetric top
 PF_3 : oblate symmetric top
 CH_3CCH : prolate symmetric top

- 13-37. Show that the components of the moment of inertia of the trigonal planar molecule shown below are $I_{xx} = I_{yy} = 3m/2$ and $I_{zz} = 3m$ if all the masses are m units, all the bond lengths are unit length, and all the bond angles are 120° .



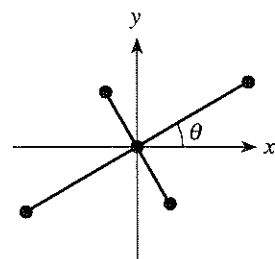
The center of mass sits at the origin, so

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(\sin^2 30^\circ) = \frac{3}{2}m$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(\cos^2 30^\circ) = \frac{3}{2}m$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m$$

- 13-38. This problem illustrates how the principal moments of inertia can be obtained as an eigenvalue problem. We will work in two dimensions for simplicity. Consider the "molecule" represented below,



where all the masses are unit masses and the long and short bond lengths are 2 and 1, respectively. Show that

$$I_{xx} = 2 \cos^2 \theta + 8 \sin^2 \theta$$

$$I_{yy} = 8 \cos^2 \theta + 2 \sin^2 \theta$$

$$I_{xy} = -6 \cos \theta \sin \theta$$

The fact that $I_{xy} \neq 0$ indicates that these I_{ij} are not the principal moments of inertia. Now solve the secular determinantal equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0$$

and compare your result with the values of I_{xx} and I_{yy} that you would obtain if you align the "molecule" and the coordinate system such that $\theta = 90^\circ$. What does this comparison tell you? What are the values of I_{xx} and I_{yy} if $\theta = 0^\circ$?

We again use trigonometric functions to find the x and y components of the direction vectors.

$$I_{xx} = \sum m_j y_j^2 = 2(1)(2 \sin \theta)^2 + 2(1) \left[\sin \left(\frac{\pi}{2} - \theta \right) \right]^2$$

$$= 8 \sin^2 \theta + 2 \cos^2 \theta$$

$$I_{yy} = \sum m_j x_j^2 = 2(1)(2 \cos \theta)^2 + 2(1) \left[\cos \left(\frac{\pi}{2} - \theta \right) \right]^2$$

$$= 8 \cos^2 \theta + 2 \sin^2 \theta$$

$$I_{xy} = - \sum m_j x_j y_j$$

$$= -(2 \cos \theta)(2 \sin \theta) - 2 [\cos(\pi + \theta)] [\sin(\pi + \theta)]$$

$$= -2 \cos \theta \sin \theta - 2 \cos \theta \sin \theta - \cos \theta \sin \theta + \cos \theta \sin \theta$$

$$= -4 \cos \theta \sin \theta - 2 \cos \theta \sin \theta - \sin \theta \cos \theta + \sin \theta \cos \theta$$

$$= -6 \cos \theta \sin \theta$$

Now the secular determinantal equation becomes

$$\begin{vmatrix} 8 \sin^2 \theta + 2 \cos^2 \theta - \lambda & -6 \cos \theta \sin \theta \\ -6 \cos \theta \sin \theta & 8 \cos^2 \theta + 2 \sin^2 \theta - \lambda \end{vmatrix} = 0$$

Expanding this determinant gives

$$0 = 64 \cos^2 \theta \sin^2 \theta + 16 \cos^4 \theta + 16 \sin^4 \theta + 4 \sin^2 \theta \cos^2 \theta$$

$$- \lambda (8 \cos^2 \theta + 2 \sin^2 \theta + 8 \sin^2 \theta + 2 \cos^2 \theta) + \lambda^2 - 36 \cos^2 \theta \sin^2 \theta$$

$$= \lambda^2 - \lambda(10)(\sin^2 \theta + \cos^2 \theta) + 16(\cos^2 \theta + \sin^2 \theta)^2$$

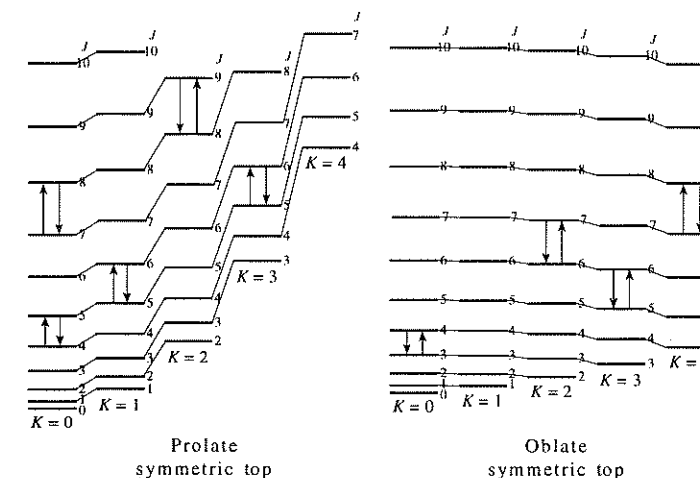
$$= \lambda^2 - 10\lambda + 16$$

$$\lambda = 5 \pm \frac{\sqrt{100 - 64}}{2} = 5 \pm 3$$

$$\lambda = 8 \text{ or } 2$$

If we align the molecule such that $\theta = 90^\circ$, then $\sin^2 \theta = 1$ and $\cos^2 \theta = 0$, so $I_{xx} = 8$, $I_{yy} = 2$, and $I_{xy} = 0$. If $\theta = 0^\circ$, $I_{xx} = 2$ and $I_{yy} = 8$ (I_{xy} will still equal zero). This tells us that the coordinate system chosen does not affect the values of the principal moments of inertia.

- 13-39. Sketch an energy-level diagram for a prolate symmetric top and an oblate symmetric top. How do they differ? Indicate some of the allowed transitions in each case.



The energies of the J levels increase as K increases for the prolate symmetric top (represented by (a) in the diagram), but decrease as K increases for the oblate symmetric top (b). Some of the allowed transitions are indicated in each diagram.

13-40. Derive Equation 13.57 from Equation 13.55.

Because $E_2 > E_1$, the second term in Equation 13.55 is dominant and so

$$\begin{aligned} a_2(t) &\propto \frac{1 - \exp[i(E_2 - E_1 - h\nu)t/\hbar]}{E_2 - E_1 - h\nu} \\ a_2^*(t) &\propto \frac{1 - \exp[-i(E_2 - E_1 - h\nu)t/\hbar]}{E_2 - E_1 - h\nu} \\ a_2(t)a_2^*(t) &\propto \frac{1 - \exp[i(E_2 - E_1 - h\nu)t/\hbar] - \exp[-i(E_2 - E_1 - h\nu)t/\hbar] + 1}{(E_2 - E_1 - h\nu)^2} \\ &\propto \frac{2 - 2\cos[(E_2 - E_1 - h\nu)t/\hbar]}{(E_2 - E_1 - h\nu)^2} \\ &\propto \frac{2\{2\sin^2[(E_2 - E_1 - h\nu)t/2\hbar]\}}{(E_2 - E_1 - h\nu)^2} \\ &\propto \frac{\sin^2[(E_2 - E_1 - h\nu)t/2\hbar]}{(E_2 - E_1 - h\nu)^2} = \frac{\sin^2[(E_2 - E_1 - \hbar\omega)t/2\hbar]}{(E_2 - E_1 - \hbar\omega)^2} \end{aligned}$$

13-41. Show that the first few associated Legendre functions satisfy the recursion formula given by Equation 13.62.

$$(2J + 1)xP_J^{|M|}(x) = (J - |M| + 1)P_{J+1}^{|M|}(x) + (J + |M|)P_{J-1}^{|M|}(x) \quad (13.62)$$

The associated Legendre functions are given in Table 6.2. For $J = 1, |M| = 0$,

$$\begin{aligned} 3xP_1^0(x) &\stackrel{?}{=} 2P_2^0(x) + P_0^0(x) \\ 3x(x) &\stackrel{?}{=} 2\left[\frac{1}{2}(3x^2 - 1)\right] + 1 \\ 3x^2 &= 3x^2 - 1 + 1 \end{aligned}$$

For $J = 1, |M| = 1$,

$$\begin{aligned} 3xP_1^1(x) &\stackrel{?}{=} P_2^1(x) + P_0^1(x) \\ 3x(1 - x^2)^{1/2} &= 3x(1 - x^2)^{1/2} \end{aligned}$$

(Remember that the superscript on P cannot be greater than the subscript.) For $J = 2, |M| = 0$,

$$\begin{aligned} 5xP_2^0(x) &\stackrel{?}{=} 3P_3^0(x) + 2P_1^0(x) \\ 5x\left[\frac{1}{2}(3x^2 - 1)\right] &\stackrel{?}{=} 3\left[\frac{1}{2}(5x^3 - 3x)\right] + 2x \\ \frac{15}{2}x^3 - \frac{5}{2}x &\stackrel{?}{=} \frac{15}{2}x^3 - \frac{9}{2}x + 2x \\ \frac{15}{2}x^3 - \frac{5}{2}x &= \frac{15}{2}x^3 - \frac{5}{2}x \end{aligned}$$

For $J = 2, |M| = 1$,

$$\begin{aligned} 5xP_2^1(x) &\stackrel{?}{=} 2P_3^1(x) + 3P_1^1(x) \\ 5x[3x(1 - x^2)^{1/2}] &\stackrel{?}{=} 2\left[\frac{3}{2}(5x^2 - 1)(1 - x^2)^{1/2}\right] + 3(1 - x^2)^{1/2} \\ 15x^2(1 - x^2)^{1/2} &\stackrel{?}{=} 15x^2(1 - x^2)^{1/2} - 3(1 - x^2)^{1/2} + 3(1 - x^2)^{1/2} \\ 15x^2(1 - x^2)^{1/2} &= 15x^2(1 - x^2)^{1/2} \end{aligned}$$

13-42. Calculate the ratio of the dipole transition moments for the $0 \rightarrow 1$ and $1 \rightarrow 2$ rotational transitions in the rigid-rotator approximation.

For the $0 \rightarrow 1$ transition (Example 13-12),

$$I_{0 \rightarrow 1} = \frac{1}{\sqrt{3}}$$

For the $1 \rightarrow 2$ transition,

$$\begin{aligned} I_{1 \rightarrow 2} &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \cos\theta Y_2^0(\theta, \phi) Y_1^0(\theta, \phi) \\ &= 2\pi \int_0^\pi d\theta \sin\theta \cos\theta \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 - 1) \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\ &= \frac{\sqrt{15}}{4} \int_{-1}^1 dx x^2 (3x^2 - 1) = \frac{2}{\sqrt{15}} \end{aligned}$$

The ratio of the dipole transition moments for these two rotational transitions is, therefore,

$$\frac{I_{0 \rightarrow 1}}{I_{1 \rightarrow 2}} = \frac{\sqrt{15}}{2\sqrt{3}} = \frac{\sqrt{5}}{2}$$

13-43. Calculate the ratio of the dipole transition moments for the $0 \rightarrow 1$ and $1 \rightarrow 2$ vibrational transitions in the harmonic-oscillator approximation.

For the $0 \rightarrow 1$ transition (Example 13-13),

$$\begin{aligned} I_{0 \rightarrow 1} &\propto \int_{-\infty}^{\infty} \psi_1(\xi) \xi \psi_0(\xi) d\xi \\ &\propto \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \xi^2 e^{-\xi^2} d\xi \\ &\propto \frac{\alpha^{1/2}}{\sqrt{2}} \end{aligned}$$

For the $1 \rightarrow 2$ transition,

$$\begin{aligned} I_{1 \rightarrow 2} &\propto \int_{-\infty}^{\infty} \psi_1(\xi) \xi \psi_0(\xi) d\xi \\ &\propto \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \xi^2 (2\xi^2 - 1) e^{-\xi^2} d\xi \\ &\propto \alpha^{1/2} \end{aligned}$$

The ratio of the two transitions is then

$$\frac{I_{0 \rightarrow 1}}{I_{1 \rightarrow 2}} = \frac{\alpha^{1/2}(\sqrt{2})^{-1}}{\alpha^{1/2}} = \frac{1}{\sqrt{2}}$$

- 13-44.** Use Table 13.7 to determine the 12-dimensional reducible representation for the vibrational motion of NH_3 . Use this result to determine the symmetries and the infrared activity of the normal coordinates of NH_3 .

The point group of NH_3 is C_{3v} (Table 12.2). Recall from the character table (Table 12.9) that this group has the operators \hat{E} , $2\hat{C}_3$, and $3\hat{\sigma}_v$. \hat{E} leaves all of the atoms unmoved, the \hat{C}_3 leave the nitrogen atom unmoved, and the $\hat{\sigma}_v$ planes leave the nitrogen atom and one hydrogen atom unmoved. Using Table 13.8, we find

	\hat{E}	\hat{C}_3	\hat{C}_3^2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{\sigma}''_v$
Γ	12	0	0	2	2	2

The quantity $h = 6$ for the C_{3v} point group, so Equation 12.23 becomes

$$a_{A_1} = \frac{1}{6} [12 + 0 + 6] = 3$$

$$a_{A_2} = \frac{1}{6} [12 + 0 - 6] = 1$$

$$a_E = \frac{1}{6} [24 + 0 + 0] = 4$$

where we have used Table 12.9 to determine the values of χ_i . We thus have

$$\Gamma_{3N} = 3A_1 + A_2 + 4E$$

The character table shows that x and y are jointly represented by E , that z is represented by A_1 , that R_z is represented by A_2 , and that R_x and R_y are jointly represented by E . Subtracting these translational and rotational degrees of freedom from Γ_{3N} gives us

$$\Gamma_{\text{vib}} = 2A_1 + 2E$$

Recall that we have infrared activity only if Q_i belongs to the same irreducible representation as x , y , or z , which are represented by E and A_1 . In this case, all of the vibrational modes in Γ_{vib} are infrared active.

- 13-45.** Use Table 13.7 to determine the 15-dimensional reducible representation for the vibrational motion of CH_2Cl_2 . Use this result to determine the symmetries and the infrared activity of the normal coordinates of CH_2Cl_2 .

The point group of CH_2Cl_2 is C_{2v} (Table 12.2). Recall from the character table (Table 12.7) that this group has the operators \hat{E} , \hat{C}_2 , and $2\hat{\sigma}_v$. \hat{E} leaves all of the atoms unmoved, \hat{C}_2 leaves the carbon atom unmoved, and the $\hat{\sigma}_v$ planes leave the carbon atom and two other atoms unmoved. Using Table 13.8, we find

	\hat{E}	\hat{C}_2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
Γ	15	-1	3	3

The quantity $h = 4$ for the C_{2v} point group, so Equation 12.23 becomes

$$a_{A_1} = \frac{1}{4} [15 - 1 + 3 + 3] = 5$$

$$a_{A_2} = \frac{1}{4} [15 - 1 - 3 - 3] = 2$$

$$a_{B_1} = \frac{1}{4} [15 + 1 + 3 - 3] = 4$$

$$a_{B_2} = \frac{1}{4} [15 + 1 - 3 + 3] = 4$$

where we have used Table 12.7 to determine the values of χ_i . We thus have

$$\Gamma_{3N} = 5A_1 + 2A_2 + 4B_1 + 4B_2$$

The character table shows that x transforms as B_1 , y as B_2 , z as A_1 , R_z as A_2 , R_y as B_1 , and R_x as B_2 . Subtracting these translational and rotational degrees of freedom from Γ_{3N} gives us

$$\Gamma_{\text{vib}} = 4A_1 + A_2 + 2B_1 + 2B_2$$

Recall that we have infrared activity only if the representation of the normal mode transforms as x , y , or z , which are represented by B_1 , B_2 , and A_1 . Therefore, the A_2 vibrational mode is infrared inactive, and the other vibrational modes are infrared active.

- 13-46.** Use Table 13.7 to determine the 18-dimensional reducible representation for the vibrational motion of *trans*-dichloroethene. Use this result to determine the symmetries and the infrared activity of the normal coordinates of *trans*-dichloroethene.

The point group of *trans*-dichloroethene is C_{2h} (Table 12.2). Recall from the character table (Table 12.10) that this group has the operators \hat{E} , \hat{C}_2 , \hat{i} , and $\hat{\sigma}_h$. \hat{E} leaves all of the atoms unmoved, \hat{C}_2 and \hat{i} move all the atoms, and $\hat{\sigma}_h$ leaves all the atoms unmoved. Using Table 13.8, we find

	\hat{E}	\hat{C}_2	\hat{i}	$\hat{\sigma}_h$
Γ	18	0	0	6

The quantity $h = 4$ for the C_{2h} point group, so Equation 12.23 becomes

$$a_{A_g} = \frac{1}{4} [18 + 6] = 6$$

$$a_{B_g} = \frac{1}{4} [18 - 6] = 3$$

$$a_{A_u} = \frac{1}{4} [18 - 6] = 3$$

$$a_{B_u} = \frac{1}{4} [18 + 6] = 6$$

where we have used Table 12.10 to determine the values of χ_i . We thus have

$$\Gamma_{3N} = 6A_g + 3B_g + 3A_u + 6B_u$$

The character table shows that x and y are independently represented by B_u , z by A_u , R_z by A_g , and R_x and R_y independently by B_g . Subtracting these translational and rotational degrees of freedom from Γ_{3N} gives us

$$\Gamma_{\text{vib}} = 5A_g + B_g + 2A_u + 4B_u$$

Recall that we have infrared activity only if the representation of the normal mode transforms as x , y , or z , which are represented by B_u and A_u . Therefore, the A_g and B_g vibrational modes are infrared inactive, and the other vibrational modes are infrared active.

- 13-47. Use Table 13.7 to determine the 15-dimensional reducible representation for the vibrational motion of XeF_4 (square planar). Use this result to determine the symmetries and the infrared activity of the normal coordinates of XeF_4 .

The point group of XeF_4 is D_{4h} (Table 12.2). Recall from the character table (Table 12.12) that this group has the operators \hat{E} , $2\hat{C}_4$, \hat{C}_2 , $2\hat{C}_2'$, $2\hat{C}_2''$, \hat{i} , $2\hat{S}_4$, $\hat{\sigma}_h$, $2\hat{\sigma}_v$, and $2\hat{\sigma}_d$. \hat{E} and $\hat{\sigma}_h$ leave all of the atoms unmoved, the \hat{C}_4 , \hat{C}_2 , \hat{C}_2' , \hat{i} , \hat{S}_4 , and $\hat{\sigma}_d$ leave only Xe unmoved. The \hat{C}_2' each leave Xe and two F unmoved, as do the two $\hat{\sigma}_v$. Using Table 13.8, we find

	\hat{E}	$2\hat{C}_4$	\hat{C}_2	$2\hat{C}_2'$	$2\hat{C}_2''$	\hat{i}	$2\hat{S}_4$	$\hat{\sigma}_h$	$2\hat{\sigma}_v$	$2\hat{\sigma}_d$
Γ	15	1	-1	-3	-1	-3	-1	5	3	1

The quantity $h = 16$ for the D_{4h} point group, so Equation 12.23 becomes

$$\begin{aligned}
 a_{A_{1g}} &= \frac{1}{16} [15 + 2 - 1 - 6 - 2 - 3 - 2 + 5 + 6 + 2] = 1 \\
 a_{A_{2g}} &= \frac{1}{16} [15 + 2 - 1 + 6 + 2 - 3 - 2 + 5 - 6 - 2] = 1 \\
 a_{B_{1g}} &= \frac{1}{16} [15 - 2 - 1 - 6 + 2 - 3 + 2 + 5 + 6 - 2] = 1 \\
 a_{B_{2g}} &= \frac{1}{16} [15 - 2 - 1 + 6 - 2 - 3 + 2 + 5 - 6 + 2] = 1 \\
 a_{E_g} &= \frac{1}{16} [30 + 0 + 2 + 0 + 0 - 6 + 0 - 10 + 0 + 0] = 1 \\
 a_{A_{1u}} &= \frac{1}{16} [15 + 2 - 1 - 6 - 2 + 3 + 2 - 5 - 6 - 2] = 0 \\
 a_{A_{2u}} &= \frac{1}{16} [15 + 2 - 1 + 6 + 2 + 3 + 2 - 5 + 6 + 2] = 2 \\
 a_{B_{1u}} &= \frac{1}{16} [15 - 2 - 1 - 6 + 2 + 3 - 2 - 5 - 6 + 2] = 0 \\
 a_{B_{2u}} &= \frac{1}{16} [15 - 2 - 1 + 6 - 2 + 3 - 2 - 5 + 6 - 2] = 1 \\
 a_{E_u} &= \frac{1}{16} [30 + 0 + 2 + 0 + 0 + 6 + 0 + 10 + 0 + 0] = 3
 \end{aligned}$$

where we have used Table 12.12 to determine the values of χ_i . We thus have

$$\Gamma_{3N} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

The character table shows that x and y are jointly represented by E_u , z by A_{2u} , R_x by A_{2g} , and R_y and R_z jointly by E_g . Subtracting these translational and rotational degrees of freedom from Γ_{3N} gives us

$$\Gamma_{\text{vib}} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$$

Recall that we have infrared activity only if the normal mode transforms as x , y , or z , which are represented by E_u and A_{2u} . Therefore, the A_{1g} , B_{1g} , B_{2g} , and B_{2u} vibrational modes are infrared inactive, and the other vibrational modes are infrared active.

- 13-48. Use Table 13.7 to determine the 15-dimensional reducible representation for the vibrational motion of CH_4 . Use this result to determine the symmetries and the infrared activity of the normal coordinates of CH_4 .

The point group of CH_4 is T_d (Table 12.2). Recall from the character table (Table 12.14) that this group has the operators \hat{E} , $8\hat{C}_3$, $3\hat{C}_2$, $6\hat{S}_4$, and $6\hat{\sigma}_d$. \hat{E} leaves all of the atoms unmoved, all atoms are moved by \hat{C}_3 , \hat{C}_2 and \hat{S}_4 leave only the central carbon atom unmoved, and $\hat{\sigma}_d$ leaves the central carbon atom and two of the hydrogen atoms unmoved. Using Table 13.8, we find

	\hat{E}	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_d$
Γ	15	0	-1	-1	3

The quantity $h = 24$ for the T_d point group, so Equation 12.23 becomes

$$\begin{aligned}
 a_{A_1} &= \frac{1}{24} [15 - 3 - 6 + 18] = 1 \\
 a_{A_2} &= \frac{1}{24} [15 - 3 + 6 - 18] = 0 \\
 a_E &= \frac{1}{24} [30 - 6] = 1 \\
 a_{T_1} &= \frac{1}{24} [45 + 3 - 6 - 18] = 1 \\
 a_{T_2} &= \frac{1}{24} [45 + 3 + 6 + 18] = 3
 \end{aligned}$$

where we have used Table 12.14 to determine the values of χ_i . We thus have

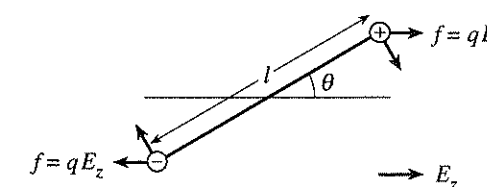
$$\Gamma_{3N} = A_1 + E + T_1 + 3T_2$$

The character table shows that x , y , and z are jointly represented by T_2 and R_x , R_y , and R_z are jointly represented by T_1 . Subtracting these translational and rotational degrees of freedom from Γ_{3N} gives us

$$\Gamma_{\text{vib}} = A_1 + E + 2T_2$$

Recall that we have infrared activity only if the normal mode transforms as x , y , or z , which are represented by T_2 . The A_1 and E vibrational modes are infrared inactive and the T_2 vibrational mode is infrared active.

- 13-49. Consider a molecule with a dipole moment μ in an electric field \mathbf{E} . We picture the dipole moment as a positive charge and a negative charge of magnitude q separated by a vector \mathbf{l} .



The field \mathbf{E} causes the dipole to rotate into a direction parallel to \mathbf{E} . Therefore, work is required to rotate the dipole to an angle θ to \mathbf{E} . The force causing the molecule to rotate is actually a torque (torque is the angular analog of force) and is given by $l/2$ times the force perpendicular to \mathbf{l} at each end of the vector \mathbf{l} . Show that this torque is equal to $\mu E \sin \theta$ and that the energy required to rotate the dipole from some initial angle θ_0 to some arbitrary angle θ is

$$V = \int_{\theta_0}^{\theta} \mu E \sin \theta' d\theta'$$

Given that θ_0 is customarily taken to be $\pi/2$, show that

$$V = -\mu E \cos \theta = -\boldsymbol{\mu} \cdot \mathbf{E}$$

The magnetic analog of this result will be given by Equation 14.10.

The component of the force perpendicular to \mathbf{l} is $qE \sin \theta$, so the torque at each end of the dipole is given by $lqE \sin \theta/2$. The total torque is twice this amount, and so the total torque is $lqE \sin \theta$ or $\mu E \sin \theta$ (recall that $\mu = lq$). To find the energy required to rotate the dipole, we must integrate over the torque:

$$\begin{aligned} V &= \int_{\theta_0}^{\theta} \mu E \sin \theta' d\theta' \\ &= \mu E \int_{\pi/2}^{\theta} \sin \theta' d\theta' \\ &= \mu E (-\cos \theta') \Big|_{\pi/2}^{\theta} = -\mu E \cos \theta \\ &= -\boldsymbol{\mu} \cdot \mathbf{E} \end{aligned}$$

(This last equality is from the definition of dot product in MathChapter C.)

13-50. The observed vibrational-rotational lines for the $v = 0$ to $v = 1$ transition of $^{12}\text{C}^{16}\text{O}(\text{g})$ are listed below. Determine \tilde{B}_0 , \tilde{B}_1 , \tilde{B}_e , $\tilde{\alpha}_e$, \tilde{I}_e , and r_e .

2238.89	2215.66	2189.84	2161.83	2127.61	2094.69	2059.79
2236.06	2212.46	2186.47	2158.13	2123.62	2090.56	2055.31
2233.34	2209.31	2183.14	2154.44	2119.64	2086.27	2050.72
2230.49	2206.19	2179.57	2150.83	2115.56	2081.95	2046.14
2227.55	2202.96	2176.12	2147.05	2111.48	2077.57	
2224.63	2199.77	2172.63	2139.32	2107.33	2073.19	
2221.56	2196.53	2169.05	2135.48	2103.12	2068.69	
2218.67	2193.19	2165.44	2131.49	2099.01	2064.34	

[Hint: Recall that the transition ($v'' = 0, J'' = 0$) \rightarrow ($v'' = 1, J'' = 0$) is forbidden.]

We must first establish where the R and P branches are in this spectrum. The ($v'' = 0, J'' = 0$) \rightarrow ($v'' = 1, J'' = 0$) transition is forbidden and so we expect the energy difference between $R(0)$ and $P(1)$ to be approximately twice the difference between successive lines in the R and P branches. Examining the data in the table, we find that the gap between the lines at 2147.05 cm^{-1} and 2139.32 cm^{-1} is approximately twice as large as the gap between any other neighboring pair of lines. So the first line in the R branch (for $J = 0$) occurs at 2147.05 cm^{-1} , and the first line in the P branch (for $J = 1$) occurs at 2139.32 cm^{-1} .

We now combine Equations 13.15 and 13.16

$$\tilde{\nu}_R(J \rightarrow J+1) = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \quad (13.15)$$

$$\tilde{\nu}_P(J \rightarrow J-1) = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \quad (13.16)$$

to find the following equations for \tilde{B}_1 and \tilde{B}_0 :

$$\Delta\tilde{\nu}_1 = \tilde{\nu}_R(J \rightarrow J+1) - \tilde{\nu}_P(J \rightarrow J-1)$$

$$= 2\tilde{B}_1 + (4\tilde{B}_1)J$$

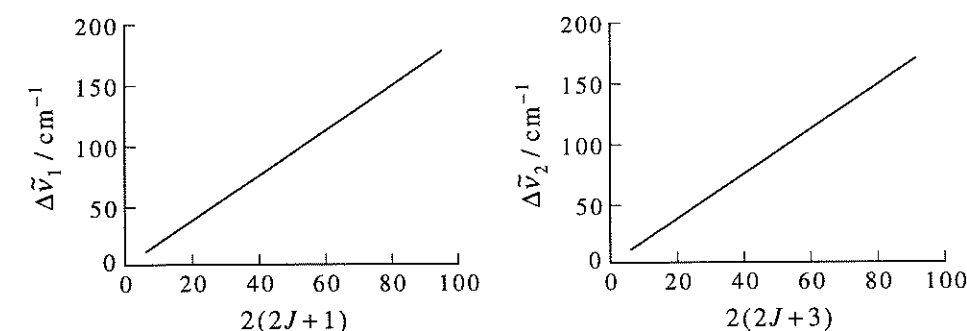
$$= 2\tilde{B}_1(2J+1)$$

$$\Delta\tilde{\nu}_2 = \tilde{\nu}_R(J \rightarrow J+1) - \tilde{\nu}_P(J+2 \rightarrow J+1)$$

$$= 2\tilde{B}_1(2J+1) + 2(\tilde{B}_1 + \tilde{B}_0) - 4J(\tilde{B}_1 - \tilde{B}_0) - 4(\tilde{B}_1 - \tilde{B}_0)$$

$$= 2\tilde{B}_0(3+2J)$$

These equations show that a plot of $\Delta\tilde{\nu}_1$ versus $2(2J+1)$ has a slope of \tilde{B}_1 , and a plot of $\Delta\tilde{\nu}_2$ versus $2(2J+3)$ has a slope of \tilde{B}_0 . These two plots are shown below.



From the slopes of the best fit lines to the data, we find that $\tilde{B}_0 = 1.9163 \text{ cm}^{-1}$ and $\tilde{B}_1 = 1.8986 \text{ cm}^{-1}$. To find \tilde{B}_e and $\tilde{\alpha}_e$, we use Equation 13.17:

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e(v + \frac{1}{2})$$

$$\tilde{B}_0 = \tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e$$

$$\tilde{B}_1 = \tilde{B}_e - \frac{3}{2}\tilde{\alpha}_e$$

$$\tilde{B}_0 - \tilde{B}_1 = \tilde{\alpha}_e$$

$$1.9163 \text{ cm}^{-1} - 1.8986 \text{ cm}^{-1} = 0.0177 \text{ cm}^{-1} = \tilde{\alpha}_e$$

$$1.9163 \text{ cm}^{-1} = \tilde{B}_e - \frac{1}{2}(0.0177 \text{ cm}^{-1})$$

$$1.92515 \text{ cm}^{-1} = \tilde{B}_e$$

We can now use Equation 13.9 to find cI and then use the definition of the moment of the inertia to find R_e .

$$\mu = \frac{(12.00 \text{ amu})(15.99 \text{ amu})}{27.99 \text{ amu}} (1.661 \times 10^{-27} \text{ kg} \cdot \text{amu}^{-1}) = 1.139 \times 10^{-26} \text{ kg}$$

$$\tilde{B}_e = \frac{h}{8\pi^2 c I}$$

$$I = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8\pi^2 (2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})(192.515 \text{ m}^{-1})} = 1.454 \times 10^{-46} \text{ kg}\cdot\text{m}^2$$

$$I = \mu R_e^2$$

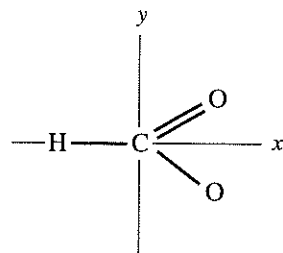
$$R_e = \left(\frac{I}{\mu}\right)^{1/2} = 113.0 \text{ pm}$$

13-51. This problem is a three-dimensional version of Problem 13-41. The rotational spectrum of a polyatomic molecule can be predicted once the values of \tilde{A} , \tilde{B} , and \tilde{C} are known. These, in turn, can be calculated from the principal moments of inertia I_A , I_B , and I_C . In this problem, we show how I_A , I_B , and I_C can be determined from the molecular geometry. We set up an arbitrarily oriented coordinate system, whose origin sits at the center-of-mass of the molecule, and determine the moments of inertia I_{xx} , I_{yy} , I_{zz} , I_{xy} , I_{yz} , and I_{zx} . The principal moments of inertia are the solution to the secular determinantal equation

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} - \lambda & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} - \lambda \end{vmatrix} = 0$$

The assignment for the subscripts A, B, and C to the three roots of this determinant are done according to the convention $I_A \leq I_B \leq I_C$. Use this approach to find the principal moments of inertia for the planar formate radical, HCO_2 , given the following geometry: The H-C bond length is 109.7 pm, the C=O bond length is 120.2 pm, and the C-O bond length is 134.3 pm.

Take the origin to sit on the carbon atom and the molecule to sit in the xy -plane, as shown below:



We can use straightforward trigonometry to find the following Cartesian coordinates for the atoms given the geometry in the problem.

	C	H	O (carbonyl)	O
x	0.0	-109.7 pm	43.1 pm	75.5 pm
y	0.0	0.0	112.2 pm	-111.1 pm
z	0.0	0.0	0.0	0.0

The center of mass is then located at

$$x_{\text{cm}} = \frac{1}{M} \sum_i m_i x_i = \frac{1}{45.0 \text{ amu}} [(1.008)(-109.7) + (15.999)(43.1 + 75.5)] \text{ amu}\cdot\text{pm}$$

$$= 39.7 \text{ pm}$$

$$y_{\text{cm}} = \frac{1}{45.0 \text{ amu}} [(15.999)(112.2 - 111.1)] \text{ amu}\cdot\text{pm}$$

$$= 0.39 \text{ pm}$$

$$z_{\text{cm}} = \frac{1}{45.0 \text{ amu}} (0) = 0 \text{ pm}$$

The coordinates of the atoms relative to the center of mass are then

	C	H	O (carbonyl)	O
x	-39.7 pm	-149.4 pm	3.4 pm	40.2 pm
y	-0.4 pm	-0.4 pm	111.8 pm	-111.5 pm
z	0.0	0.0	0.0	0.0

We now find the components of the moment of inertia.

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2)$$

$$= \{(12.01)(-0.4)^2 + (1.008)(-0.4)^2 + 15.99[(111.8)^2 + (-111.5)^2]\} \text{ amu}\cdot\text{pm}^2$$

$$= 3.97 \times 10^5 \text{ pm}^2\cdot\text{g}\cdot\text{mol}^{-1}$$

$$I_{yy} = \sum_i m_i (x_i^2 + z_i^2)$$

$$= \{(12.01)(-39.7)^2 + (1.008)(-149.4)^2 + 15.99[(3.4)^2 + (40.2)^2]\} \text{ amu}\cdot\text{pm}^2$$

$$= 6.74 \times 10^4 \text{ pm}^2\cdot\text{g}\cdot\text{mol}^{-1}$$

$$I_{zz} = I_{xx} + I_{yy} = 4.64 \times 10^5 \text{ pm}^2\cdot\text{g}\cdot\text{mol}^{-1}$$

$$I_{xz} = I_{zx} = I_{yz} = I_{zy} = 0$$

$$I_{xy} = I_{yx} = -\sum_i m_i x_i y_i$$

$$= -\{(12.01)(-39.7)(-0.4) + (1.008)(-149.4)(-0.4) + 15.99[(3.4)(111.8) + (40.2)(-111.5)]\} \text{ amu}\cdot\text{pm}^2$$

$$= 6.53 \times 10^4 \text{ pm}^2\cdot\text{g}\cdot\text{mol}^{-1}$$

We then have the determinantal equation

$$\begin{vmatrix} 3.97 \times 10^5 - \lambda & 6.53 \times 10^4 & 0 \\ 6.53 \times 10^4 & 6.74 \times 10^4 - \lambda & 0 \\ 0 & 0 & 4.64 \times 10^5 \end{vmatrix} = 0$$

One of the principal moments of inertia is $4.64 \times 10^5 \text{ pm}^2\cdot\text{g}\cdot\text{mol}^{-1}$. To find the other two we need to solve the 2×2 determinantal equation

$$\begin{vmatrix} 3.97 \times 10^5 - \lambda & 6.53 \times 10^4 \\ 6.53 \times 10^4 & 6.74 \times 10^4 - \lambda \end{vmatrix} = 0$$

Expanding this determinant gives

$$\lambda^2 - 4.64 \times 10^5 \lambda + 2.25 \times 10^{10} = 0$$

or

$$\lambda = \frac{4.64 \times 10^5 \pm \sqrt{(4.64 \times 10^5)^2 - 4(2.25 \times 10^{10})}}{2} = \frac{4.64 \times 10^5 \pm 3.54 \times 10^5}{2}$$

The other two moments of inertia are $5.50 \times 10^4 \text{ pm}^2\cdot\text{g}\cdot\text{mol}^{-1}$ and $4.09 \times 10^5 \text{ pm}^2\cdot\text{g}\cdot\text{mol}^{-1}$.