Section 4 Exercises, Problems, and Solutions

Exercises:

1. Consider the molecules CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$.
   a. What kind of rotor are they (symmetric top, etc; do not bother with oblate, or
   near-prolate, etc.)
   b. Will they show pure rotational spectra?
   c. Assume that ammonia shows a pure rotational spectrum. If the rotational
   constants are 9.44 and 6.20 cm$^{-1}$, use the energy expression:
   \[ E = (A - B) K^2 + B J(J + 1), \]
   to calculate the energies (in cm$^{-1}$) of the first three lines (i.e., those with lowest K, J
   quantum number for the absorbing level) in the absorption spectrum (ignoring higher order
   terms in the energy expression).

2. The molecule $^{11}$B $^{16}$O has a vibrational frequency $\omega_e = 1885$ cm$^{-1}$, a rotational constant
   $B_e = 1.78$ cm$^{-1}$, and a bond energy from the bottom of the potential well of $D_0^e = 8.28$ eV.
   Use integral atomic masses in the following:
   a. In the approximation that the molecule can be represented as a Morse oscillator,
   calculate the bond length, $R_e$ in angstroms, the centrifugal distortion constant, $D_e$ in cm$^{-1}$,
   the anharmonicity constant, $\omega_e x_e$ in cm$^{-1}$, the zero-point corrected bond energy, $D_0^e$ in eV,
   the vibration rotation interaction constant, $\alpha_e$ in cm$^{-1}$, and the vibrational state specific
   rotation constants, $B_0$ and $B_1$ in cm$^{-1}$. Use the vibration-rotation energy expression for a
   Morse oscillator:
   \[ E = h \omega_e (v + 1/2) - h \omega_e x_e (v + 1/2)^2 + B_v J(J + 1) - D_e J^2(J + 1)^2, \]
   where
   \[ B_v = B_e - \alpha_e (v + 1/2), \]
   \[ \alpha_e = \frac{-6B_e^2}{h\omega_e} + \frac{6\sqrt{B_e^3 h\omega_e x_e}}{h\omega_e}, \]
   and $D_e = \frac{4B_e^3}{h\omega_e^2}$.
   b. Will this molecule show a pure rotation spectrum? A vibration-rotation
   spectrum? Assume that it does, what are the energies (in cm$^{-1}$) of the first three lines in the
   P branch ($\Delta v = +1, \Delta J = -1$) of the fundamental absorption?

3. Consider trans-C$_2$H$_2$Cl$_2$. The vibrational normal modes of this molecule are shown
   below. What is the symmetry of the molecule? Label each of the modes with the
   appropriate irreducible representation.
Problems:

1. Suppose you are given two molecules (one is CH\textsubscript{2} and the other is CH\textsubscript{2}\textsuperscript{-} but you don't know which is which). Both molecules have C\textsubscript{2v} symmetry. The CH bond length of molecule I is 1.121 Å and for molecule II it is 1.076 Å. The bond angle of molecule I is 104° and for molecule II it is 136°.

a. Using a coordinate system centered on the C nucleus as shown above (the molecule is in the YZ plane), compute the moment of inertia tensors of both species (I and II). The definitions of the components of the tensor are, for example:

\[ I_{xx} = \sum_{j} m_j (y_j^2 + z_j^2) - M(Y^2 + Z^2) \]
\[ I_{xy} = -\sum_{j} m_j x_j y_j - MXY \]
Here, \( m_j \) is the mass of the nucleus \( j \), \( M \) is the mass of the entire molecule, and \( X, Y, Z \) are the coordinates of the center of mass of the molecule. Use Å for distances and amu's for masses.

b. Find the principal moments of inertia \( I_a < I_b < I_c \) for both compounds (in amu Å\(^2\) units) and convert these values into rotational constants \( A, B, \) and \( C \) in cm\(^{-1}\) using, for example,

\[
A = \frac{\hbar}{8\pi^2 c I_a}.
\]

c. Both compounds are "nearly prolate tops" whose energy levels can be well approximated using the prolate top formula:

\[
E = (A - B) K^2 + B J(J + 1),
\]

if one uses for the \( B \) constant the average of the \( B \) and \( C \) valued determined earlier. Thus, take \( B \) and \( C \) values (for each compound) and average them to produce an effective \( B \) constant to use in the above energy formula. Write down (in cm\(^{-1}\) units) the energy formula for both species. What values are \( J \) and \( K \) allowed to assume? What is the degeneracy of the level labeled by a given \( J \) and \( K \)?

d. Draw a picture of both compounds and show the directions of the three principle axes \((a,b,c)\). On these pictures show the kind of rotational motion associated with the quantum number \( K \).

e. Given that the electronic transition moment vector \( \vec{\mu} \) connecting species I and II is directed along the Y axis, what are the selection rules \( J \) and \( K \)?

f. Suppose you are given the photoelectron spectrum of \( \text{CH}_2^- \). In this spectrum \( J_j = J_i + 1 \) transitions are called R-branch absorptions and those obeying \( J_j = J_i - 1 \) are called P-branch transitions. The spacing between lines can increase or decrease as functions of \( J_i \) depending on the changes in the moment of inertia for the transition. If spacings grow closer and closer, we say that the spectrum exhibits a so-called band head formation. In the photoelectron spectrum that you are given, a rotational analysis of the vibrational lines in this spectrum is carried out and it is found that the R-branches show band head formation but the P-branches do not. Based on this information, determine which compound I or II is the \( \text{CH}_2^- \) anion. Explain you reasoning.

g. At what \( J \) value (of the absorbing species) does the band head occur and at what rotational energy difference?

2. Let us consider the vibrational motions of benzene. To consider all of the vibrational modes of benzene we should attach a set of displacement vectors in the \( x, y, \) and \( z \) directions to each atom in the molecule (giving 36 vectors in all), and evaluate how these transform under the symmetry operations of \( D_{6h} \). For this problem, however, let's only inquire about the C-H stretching vibrations.

a. Represent the C-H stretching motion on each C-H bond by an outward-directed vector on each H atom, designated \( r_i \):
These vectors form the basis for a reducible representation. Evaluate the characters for this reducible representation under the symmetry operations of the $D_{6h}$ group.

b. Decompose the reducible representation you obtained in part a. into its irreducible components. These are the symmetries of the various C-H stretching vibrational modes in benzene.

c. The vibrational state with zero quanta in each of the vibrational modes (the ground vibrational state) of any molecule always belongs to the totally symmetric representation. For benzene the ground vibrational state is therefore of $A_{1g}$ symmetry. An excited state which has one quantum of vibrational excitation in a mode which is of a given symmetry species has the same symmetry species as the mode which is excited (because the vibrational wave functions are given as Hermite polynomials in the stretching coordinate). Thus, for example, excitation (by one quantum) of a vibrational mode of $A_{2u}$ symmetry gives a wavefunction of $A_{2u}$ symmetry. To resolve the question of what vibrational modes may be excited by the absorption of infrared radiation we must examine the $x$, $y$, and $z$ components of the transition dipole integral for initial and final state wave functions $\psi_i$ and $\psi_f$, respectively:

$$|\langle \psi_f | x | \psi_i \rangle|, |\langle \psi_f | y | \psi_i \rangle|, \text{ and } |\langle \psi_f | z | \psi_i \rangle|.$$  

Using the information provided above, which of the C-H vibrational modes of benzene will be infrared-active, and how will the transitions be polarized? How many C-H vibrations will you observe in the infrared spectrum of benzene?

d. A vibrational mode will be active in Raman spectroscopy only if one of the following integrals is nonzero:

$$|\langle \psi_f | xy | \psi_i \rangle|, |\langle \psi_f | xz | \psi_i \rangle|, |\langle \psi_f | yz | \psi_i \rangle|,$$

$$|\langle \psi_f | x^2 | \psi_i \rangle|, |\langle \psi_f | y^2 | \psi_i \rangle|, \text{ and } |\langle \psi_f | z^2 | \psi_i \rangle|.$$  

Using the fact that the quadratic operators transform according to the irreducible representations:

$$(x^2 + y^2, z^2) \Rightarrow A_{1g}$$

$$(xz, yz) \Rightarrow E_{1g}$$

$$(x^2 - y^2, xy) \Rightarrow E_{2g}$$

Determine which of the C-H vibrational modes will be Raman-active.
e. Are there any of the C-H stretching vibrational motions of benzene which cannot be observed in either infrared or Raman spectroscopy? Give the irreducible representation label for these unobservable modes.

3. In treating the vibrational and rotational motion of a diatomic molecule having reduced mass \( \mu \), equilibrium bond length \( r_e \) and harmonic force constant \( k \), we are faced with the following radial Schrödinger equation:

\[
\frac{-\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{J(J + 1) \hbar^2}{2\mu r^2} \frac{R}{r} + \frac{1}{2} k(r - r_e)^2 R = E R
\]

a. Show that the substitution \( R = r^{-1}F \) leads to:

\[
\frac{-\hbar^2}{2\mu} F'' + \frac{J(J + 1) \hbar^2}{2\mu^2} F + \frac{1}{2} k(r - r_e)^2 F = E F
\]

b. Taking \( r = r_e + \Delta r \) and expanding \((1 + x)^{-2} = 1 - 2x + 3x^2 + ...\), show that the so-called vibration-rotation coupling term \( \frac{J(J + 1) \hbar^2}{2\mu^2} \) can be approximated (for small \( \Delta r \)) by \( \frac{J(J + 1) \hbar^2}{2\mu r_e^2} \left( 1 - \frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2} \right) \). Keep terms only through order \( \Delta r^2 \).

c. Show that, through terms of order \( \Delta r^2 \), the above equation for \( F \) can be rearranged to yield a new equation of the form:

\[
\frac{-\hbar^2}{2\mu} F'' + \frac{1}{2} k(r - r_e)^2 F = \left( E - \frac{J(J + 1) \hbar^2}{2\mu r_e^2} + \Delta \right) F
\]

Give explicit expressions for how the modified force constant \( k \), bond length \( r_e \), and energy shift \( \Delta \) depend on \( J \), \( k \), \( r_e \), and \( \mu \).

d. Given the above modified vibrational problem, we can now conclude that the modified energy levels are:

\[
E = \hbar \sqrt{\frac{k}{\mu} \left( v + \frac{1}{2} \right) + \frac{J(J + 1) \hbar^2}{2\mu r_e^2} - \Delta}
\]

Explain how the conclusion is "obvious", how for \( J = 0 \), \( k = k \), and \( \Delta = 0 \), we obtain the usual harmonic oscillator energy levels. Describe how the energy levels would be expected to vary as \( J \) increases from zero and explain how these changes arise from changes in \( k \) and \( r_e \). Explain in terms of physical forces involved in the rotating-vibrating molecule why \( r_e \) and \( k \) are changed by rotation.

**Solutions**

**Exercises:**

1. a. \( \text{CCl}_4 \) is tetrahedral and therefore is a spherical top. \( \text{CHCl}_3 \) has \( C_{3v} \) symmetry and therefore is a symmetric top. \( \text{CH}_2\text{Cl}_2 \) has \( C_{2v} \) symmetry and therefore is an asymmetric top.

   b. \( \text{CCl}_4 \) has such high symmetry that it will not exhibit pure rotational spectra. \( \text{CHCl}_3 \) and \( \text{CH}_2\text{Cl}_2 \) will both exhibit pure rotation spectra.

   c. \( \text{NH}_3 \) is a symmetric top (oblate). Use the given energy expression,
\[ E = (A - B) K^2 + B J(J + 1), \]

\[ A = 6.20 \text{ cm}^{-1}, \quad B = 9.44 \text{ cm}^{-1}, \quad \text{selection rules } \Delta J = \pm 1, \] and the fact that \( \mu_0 \) lies along the figure axis such that \( \Delta K = 0 \), to give:

\[ \Delta E = 2B (J + 1) = 2B, \quad 4B, \quad \text{and } 6B \ (J = 0, 1, \text{ and } 2). \]

So, lines are at 18.88 cm\(^{-1}\), 37.76 cm\(^{-1}\), and 56.64 cm\(^{-1}\).

2. To convert between cm\(^{-1}\) and energy, multiply by \( \hbar c = (6.62618 \times 10^{-34} \text{ J sec})(2.997925 \times 10^{10} \text{ cm sec}^{-1}) = 1.9865 \times 10^{23} \text{ J cm} \).

Let all quantities in cm\(^{-1}\) be designated with a bar, e.g. \( \bar{B}_e = 1.78 \text{ cm}^{-1} \).

a. \[ \bar{h} \bar{c} \bar{B}_e = \frac{\hbar^2}{2 \mu R_e^2} \]

\[ R_e = \frac{\hbar}{\sqrt{2 \mu \hbar \bar{c} \bar{B}_e}}, \]

\[ \mu = \frac{\bar{m}_B \bar{m}_O}{\bar{m}_B + \bar{m}_O} = \frac{(11)(16)}{(11 + 16)} \times 1.66056 \times 10^{-27} \text{ kg} \]

\[ = 1.0824 \times 10^{-26} \text{ kg}. \]

\[ \bar{h} \bar{c} \bar{B}_e = \bar{h} c (1.78 \text{ cm}^{-1}) = 3.5359 \times 10^{-23} \text{ J} \]

\[ \bar{R}_e = \frac{1.05459 \times 10^{-34} \text{ J sec}}{\sqrt{2(1.0824 \times 10^{-26} \text{ kg} \cdot 3.5359 \times 10^{-23} \text{ J})}} \]

\[ \bar{R}_e = 1.205 \times 10^{-10} \text{ m} = 1.205 \text{ Å} \]

\[ \bar{D}_e = \frac{4 \bar{B}_e^3}{\hbar \bar{\omega}_e^2}, \quad \bar{D}_e = \frac{4 \bar{B}_e^3}{\bar{\omega}_e^2} = \frac{(4)(1.17 \text{ cm}^{-1})^3}{(1885 \text{ cm}^{-1})^2} = 6.35 \times 10^{-6} \text{ cm}^{-1} \]

\[ \bar{\omega}_e \bar{x}_e = \frac{\hbar \bar{\omega}_e^2}{4 \bar{D}_e^0}, \quad \bar{\omega}_e \bar{x}_e = \frac{\bar{\omega}_e^2}{4 \bar{D}_e^0} = \frac{(1885 \text{ cm}^{-1})^2}{(4)(66782.2 \text{ cm}^{-1})} = 13.30 \text{ cm}^{-1}. \]

\[ \bar{D}_e^0 = \bar{D}_e^0 - \frac{\hbar \bar{\omega}_e}{2} + \frac{\hbar \bar{\omega}_e \bar{x}_e}{4}, \quad \bar{D}_e^0 = \bar{D}_e^0 - \frac{\bar{\omega}_e}{2} + \frac{\bar{\omega}_e \bar{x}_e}{4} \]

\[ = 66782.2 - \frac{1885}{2} + \frac{13.3}{4} \]

\[ = 65843.0 \text{ cm}^{-1} = 8.16 \text{ eV}. \]

\[ \alpha_e = \frac{-6 \bar{B}_e^2}{\hbar \bar{\omega}_e} + 6 \sqrt{\bar{B}_e^3 \hbar \bar{\omega}_e \bar{x}_e} \]

\[ \frac{\alpha_e}{\bar{\omega}_e} = \frac{-6 \bar{B}_e^2}{\bar{\omega}_e} + 6 \sqrt{\bar{B}_e^3 \bar{\omega}_e \bar{x}_e} \]
\[ \alpha_e = \frac{(-6)(1.78)^2}{1885} + \frac{6\sqrt{(1.78)^3(13.3)}}{1885} = 0.0175 \text{ cm}^{-1}. \]

\[ B_0 = B_e - \alpha_e(1/2), \quad \overline{B_0} = B_e - \overline{\alpha_e(1/2)} = 1.78 - 0.0175/2 \]
\[ = 1.77 \text{ cm}^{-1} \]

\[ B_1 = B_e - \alpha_e(3/2), \quad \overline{B_1} = B_e - \overline{\alpha_e(3/2)} = 1.78 - 0.0175(1.5) \]
\[ = 1.75 \text{ cm}^{-1} \]

b. The molecule has a dipole moment and so it should have a pure rotational spectrum. In addition, the dipole moment should change with R and so it should have a vibration rotation spectrum.

The first three lines correspond to J = 1 \rightarrow 0, J = 2 \rightarrow 1, J = 3 \rightarrow 2

\[ E = h \omega_e (v + 1/2) - h \omega_e x_e (v + 1/2)^2 + B_v J(J + 1) - D_e J^2 (J + 1)^2 \]

\[ \Delta E = h \omega_e - 2h \omega_e x_e - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3 \]

\[ \Delta E = \omega_e - 2\omega_e x_e - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3 \]

\[ \overline{\Delta E} = 1885 - 2(13.3) - 1.77J(J + 1) + 1.75J(J - 1) - 4(6.35 \times 10^{-6})J^3 \]

3. The C₂H₂Cl₂ molecule has a σ_h plane of symmetry (plane of molecule), a C₂ axis (⊥ to plane), and inversion symmetry, this results in C₂h symmetry. Using C₂h symmetry labels the modes can be labeled as follows: ν₁, ν₂, ν₃, ν₄, and ν₅ are aₕ, ν₆ and ν₇ are aₜ, ν₈ is bₜ, and ν₉, ν₁₀, ν₁₁, and ν₁₂ are bₜ.

Problems:

1. 

Molecule I
R_{CH} = 1.121 \, \text{Å}
\[ \angle_{HCH} = 104° \]
\[ y_H = R \sin (\theta/2) = \pm 0.8834 \]
\[ z_H = R \cos (\theta/2) = -0.6902 \]

Molecule II
R_{CH} = 1.076 \, \text{Å}
\[ \angle_{HCH} = 136° \]
\[ y_H = \pm 0.9976 \]
\[ z_H = -0.4031 \]

Center of Mass(COM):
clearly, $X = Y = 0$,
$$Z = \frac{12(0) - 2RCos(\theta/2)}{14} = -0.0986 \quad \text{or} \quad Z = -0.0576$$

a. $I_{xx} = \sum_j m_j (y_j^2 + z_j^2) - M(Y^2 + Z^2)$
$$I_{xy} = -\sum_j m_j x_j y_j - MXY$$

$$I_{xx} = 2(1.121)^2 - 14(-0.0986)^2 \quad \text{or} \quad I_{xx} = 2(1.076)^2 - 14(-0.0576)^2$$
$$= 2.377 \quad \text{or} \quad = 2.269$$
$$I_{yy} = 2(0.6902)^2 - 14(-0.0986)^2 \quad \text{or} \quad I_{yy} = 2(0.4031)^2 - 14(-0.0576)^2$$
$$= 0.8167 \quad \text{or} \quad = 0.2786$$
$$I_{zz} = 2(0.8834)^2 \quad \text{or} \quad I_{zz} = 2(0.9976)^2$$
$$= 1.561 \quad \text{or} \quad = 1.990$$
$$I_{xz} = I_{yz} = I_{xy} = 0$$

b. Since the moment of inertia tensor is already diagonal, the principal moments of inertia have already been determined to be

$I_x < I_y < I_z$:

$I_{yy} < I_{zz} < I_{xx}$

$0.8167 < 1.561 < 2.377$

$0.2786 < 1.990 < 2.269$

Using the formula:

$$A = \frac{h}{8\pi^2 c I_a} = \frac{6.626\times10^{-27}}{8\pi^2 (3\times10^{10})I_a} \times \frac{6.02\times10^{23}}{(1\times10^{-8})^2}$$

$$A = \frac{16.84}{I_a} \text{ cm}^{-1}$$

Similarly, $B = \frac{16.84}{I_b} \text{ cm}^{-1}$, and $C = \frac{16.84}{I_c} \text{ cm}^{-1}$.

So,

Molecule I

$y \Rightarrow A = 20.62$  \quad $y \Rightarrow A = 60.45$

$z \Rightarrow B = 10.79$  \quad $z \Rightarrow B = 8.46$

$x \Rightarrow C = 7.08$  \quad $x \Rightarrow C = 7.42$

c. Averaging $B + C$:

$B = (B + C)/2 = 8.94$  \quad $B = (B + C)/2 = 7.94$

$A - B = 11.68$  \quad $A - B = 52.51$

Using the prolate top formula:

$$E = (A - B) K^2 + B J(J + 1),$$

Molecule I

$E = 11.68K^2 + 8.94J(J + 1)$

Levels: $J = 0, 1, 2,...$ and $K = 0, 1, ...$ $J$

For a given level defined by $J$ and $K$, there are $M_J$ degeneracies given by:

$$\begin{cases} 1 \text{ for } K = 0 \\ 2 \text{ for } K \neq 0 \end{cases}$$

d. Molecule I  \quad Molecule II

$E = 52.51K^2 + 7.94J(J + 1)$

$E = 52.51K^2 + 7.94J(J + 1)$
e. Since $\vec{u}$ is along Y, $\Delta K = 0$ since K describes rotation about the y axis. Therefore $\Delta J = \pm 1$

f. Assume molecule I is $\text{CH}_2^-$ and molecule II is $\text{CH}_2$. Then,

$\Delta E = E_{J_i}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-)$, where:

$E(\text{CH}_2) = 52.51K^2 + 7.94J(J + 1)$, and $E(\text{CH}_2^-) = 11.68K^2 + 8.94J(J + 1)$

For R-branches: $J_j = J_i + 1$, $\Delta K = 0$:

$\Delta E_R = E_{J_i}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-)$

$= 7.94(J_i + 1)(J_i + 1 + 1) - 8.94J_i(J_i + 1)$

$= (J_i + 1)\{7.94(J_i + 1 + 1) - 8.94J_i\}$

$= (J_i + 1)\{(7.94 - 8.94)J_i + 2(7.94)\}$

$= (J_i + 1)\{-J_i + 15.88\}$

For P-branches: $J_j = J_i - 1$, $\Delta K = 0$:

$\Delta E_P = E_{J_i}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-)$

$= 7.94(J_i - 1)(J_i - 1 + 1) - 8.94J_i(J_i + 1)$

$= J_i\{7.94(J_i - 1) - 8.94(J_i + 1)\}$

$= J_i\{(7.94 - 8.94)J_i - 7.94 - 8.94\}$

$= J_i\{-J_i - 16.88\}$

This indicates that the R branch lines occur at energies which grow closer and closer together as J increases (since the 15.88 - $J_i$ term will cancel). The P branch lines occur at energies which lie more and more negative (i.e. to the left of the origin). So, you can predict that if molecule I is $\text{CH}_2^-$ and molecule II is $\text{CH}_2$ then the R-branch has a band head and the P-branch does not. This is observed therefore our assumption was correct:

molecule I is $\text{CH}_2^-$ and molecule II is $\text{CH}_2$.

g. The band head occurs when $\frac{d(\Delta E_R)}{dJ} = 0$.

$\frac{d(\Delta E_R)}{dJ} = \frac{d}{dJ}[J_i + 1\{-J_i + 15.88\}] = 0$

$= \frac{d}{dJ}(-J_i^2 - J_i + 15.88J_i + 15.88) = 0$

$= -2J_i + 14.88 = 0$

$\therefore J_i = 7.44$, so $J = 7$ or 8.

At $J = 7.44$:

$\Delta E_R = (J + 1)\{-J + 15.88\}$
\[ \Delta E_R = (7.44 + 1) \{-7.44 + 15.88 \} = (8.44)(8.44) = 71.2 \text{ cm}^{-1} \text{ above the origin.} \]

2. a.

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b. The number of irreducible representations may be found by using the following formula:

\[
\left| n_{\text{irrep}} \right| = \frac{1}{g} \sum_{R} \chi_{\text{red}}(R) \chi_{\text{irrep}}(R),
\]

where \( g \) = the order of the point group (24 for \( \text{D}_{6h} \)).

\[
n_{A_{1g}} = \frac{1}{24} \sum_{R} \Gamma_{C-H}(R) A_{1g}(R) = \frac{1}{24} \{ (1)(6)(1) + (2)(2)(0)(1) + (2)(0)(1) + (1)(0)(1) \}
\]

\[
= \frac{1}{24} \{ (1)(0)(1) + (1)(0) + (0)(1) + (0)(0) \}
\]

\[
= 1
\]

\[
n_{A_{2g}} = \frac{1}{24} \Gamma_{C-H}(R) A_{2g}(R) = \frac{1}{24} \{ (1)(6)(1) + (2)(2)(0)(1) + (2)(0)(1) + (1)(0)(1) \}
\]

\[
= 0
\]

\[
n_{B_{1g}} = \frac{1}{24} \Gamma_{C-H}(R) B_{1g}(R) = \frac{1}{24} \{ (1)(6)(1) + (2)(2)(0)(1) + (2)(0)(1) + (1)(0)(1) \}
\]

\[
= 0
\]

\[ (R_x, R_y) \] (xz, yz)

\[ (x^2 - y^2, x_y) \] (xz, yz)
\[ n_{B2g} = \frac{1}{24} \{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1) + (3)(0)(-1)+(3)(2)(1)+(1)(0)(1)+(2)(0)(-1) + (2)(0)(1)+(1)(6)(-1)+(3)(2)(-1)+(3)(0)(1)\} = 0 \]

\[ n_{E1g} = \frac{1}{24} \{(1)(6)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(0)(-2) + (3)(0)(0)+(3)(2)(0)+(1)(0)(2)+(2)(0)(1) + (2)(0)(-1)+(1)(6)(-2)+(3)(2)(0)+(3)(0)(0)\} = 0 \]

\[ n_{E2g} = \frac{1}{24} \{(1)(6)(2)+(2)(0)(-1)+(2)(0)(-1)+(1)(0)(2) + (3)(0)(0)+(3)(2)(0)+(1)(0)(-2)+(2)(0)(1) + (2)(0)(1)+(1)(6)(2)+(3)(2)(0)+(3)(0)(0)\} = 1 \]

\[ n_{A1u} = \frac{1}{24} \{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1) + (3)(0)(1)+(3)(2)(1)+(1)(0)(-1)+(2)(0)(-1) + (2)(0)(-1)+(1)(6)(-1)+(3)(2)(1)+(3)(0)(1)\} = 0 \]

\[ n_{A2u} = \frac{1}{24} \{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1) + (3)(0)(-1)+(3)(2)(-1)+(1)(0)(-1)+(2)(0)(-1) + (2)(0)(-1)+(1)(6)(-1)+(3)(2)(1)+(3)(0)(1)\} = 0 \]

\[ n_{B1u} = \frac{1}{24} \{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1) + (3)(0)(1)+(3)(2)(-1)+(1)(0)(1)+(2)(0)(1) + (2)(0)(1)+(1)(6)(1)+(3)(2)(-1)+(3)(0)(1)\} = 0 \]


\[ n_{E1u} = \frac{1}{24} \{(1)(6)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(0)(-2) + (3)(0)(0)+(3)(2)(0)+(1)(0)(-2)+(2)(0)(1) + (2)(0)(1)+(1)(6)(2)+(3)(2)(0)+(3)(0)(0)\} = 1 \]

\[ n_{E2u} = \frac{1}{24} \{(1)(6)(2)+(2)(0)(-1)+(2)(0)(-1)+(1)(0)(2) + (3)(0)(0)+(3)(2)(0)+(1)(0)(-2)+(2)(0)(1) + (2)(0)(1)+(1)(6)(-2)+(3)(2)(0)+(3)(0)(0)\} = 0 \]

We see that \( \Gamma_{C-H} = A_{1g} \oplus E_{2g} \oplus B_{2u} \oplus E_{1u} \)

c. \( x \) and \( y \Rightarrow E_{1u} \), \( z \Rightarrow A_{2u} \), so, the ground state \( A_{1g} \) level can be excited to the degenerate \( E_{1u} \) level by coupling through the \( x \) or \( y \) transition dipoles. Therefore \( E_{1u} \) is infrared active and \( \perp \) polarized.

d. \( (x^2 + y^2, z^2) \Rightarrow A_{1g}, (xz, yz) \Rightarrow E_{1g}, (x^2 - y^2, xy) \Rightarrow E_{2g} \), so, the ground state \( A_{1g} \) level can be excited to the degenerate \( E_{2g} \) level by coupling through the \( x^2 - y^2 \) or \( xy \)
transitions or be excited to the degenerate $A_{1g}$ level by coupling through the $xz$ or $yz$ transitions. Therefore $A_{1g}$ and $E_{2g}$ are Raman active.

e. The $B_{2u}$ mode is not IR or Raman active.

3. a. $\frac{d}{dr} (Fr^{-1}) = F' r^{-1} - r^{-2} F$

$r^2 \frac{d}{dr} (Fr^{-1}) = r F' - F$

$\frac{d}{dr} \left( r^2 \frac{d}{dr} (Fr^{-1}) \right) = F' - F' + r F''$

So,

$$-\frac{\hbar^2}{2\mu} \frac{d}{dr} \left( r^2 \frac{d}{dr} (Fr^{-1}) \right) = \frac{-\hbar^2 F''}{2\mu r}.$$ 

Rewriting the radial Schrödinger equation with the substitution: $R = r^{-1} F$ gives:

$$\frac{-\hbar^2}{2\mu^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} (Fr^{-1}) \right) + \frac{J(J + 1)\hbar^2}{2\mu^2} (Fr^{-1}) + \frac{1}{2} k (r - r_e)^2 (Fr^{-1}) = \frac{E}{r} (Fr^{-1})$$

Using the above derived identity gives:

$$\frac{-\hbar^2 F''}{2\mu r} + \frac{J(J + 1)\hbar^2}{2\mu^2} (Fr^{-1}) + \frac{1}{2} k (r - r_e)^2 (Fr^{-1}) = \frac{E}{r} (Fr^{-1})$$

Cancelling out an $r^1$:

$$\frac{-\hbar^2 F''}{2\mu} + \frac{J(J + 1)\hbar^2}{2\mu^2} F + \frac{1}{2} k (r - r_e)^2 F = E F$$

b. $\frac{1}{r^2} = \frac{1}{(r_e + \Delta r)^2} = \frac{1}{r_e^2 \left( 1 + \frac{\Delta r}{r_e} \right)^2} \approx \frac{1}{r_e^2} \left( 1 - 2 \frac{\Delta r}{r_e} + \frac{3 \Delta r^2}{r_e^2} \right)$

So,

$$\frac{J(J + 1)\hbar^2}{2\mu^2} \approx \frac{J(J + 1)\hbar^2}{2\mu e^2} \left( 1 - 2 \frac{\Delta r}{r_e} + \frac{3 \Delta r^2}{r_e^2} \right)$$

c. Using this substitution we now have:

$$\frac{-\hbar^2 F''}{2\mu} + \frac{J(J + 1)\hbar^2}{2\mu e^2} \left( 1 - 2 \frac{\Delta r}{r_e} + \frac{3 \Delta r^2}{r_e^2} \right) F + \frac{1}{2} k (r - r_e)^2 F = E F$$

Now, regroup the terms which are linear and quadratic in $\Delta r = r - r_e$:

$$\frac{1}{2} k \Delta r^2 + \frac{J(J + 1)\hbar^2}{2\mu e^2} \frac{3}{r_e^2} \Delta r^2 - \frac{J(J + 1)\hbar^2}{2\mu e^2} \frac{2}{r_e} \Delta r$$

$$= \left( \frac{1}{2} k + \frac{J(J + 1)\hbar^2}{2\mu e^2} \frac{3}{r_e^2} \right) \Delta r^2 - \left( \frac{J(J + 1)\hbar^2}{2\mu e^2} \frac{2}{r_e} \right) \Delta r$$

Now, we must complete the square:

$$a \Delta r^2 - b \Delta r = a \left( \Delta r - \frac{b}{2a} \right)^2 - \frac{b^2}{4a}.$$ 

So,
Now, redefine the first term as $\frac{1}{2}k\left(r - r_e\right)^2$, second term as $(r - r_e)^2$, and the third term as $-\Delta g$ giving:

$$\frac{1}{2}k\left(r - r_e\right)^2 - \Delta$$

From:

$$-\frac{\hbar^2}{2\mu} F'' + \frac{J(J + 1)\hbar^2}{2\mu r_e^2} \left(1 - \frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2}\right) F + \frac{1}{2} k (r - r_e)^2 F = E F,$$

and making the above substitution results in:

$$-\frac{\hbar^2}{2\mu} F'' + \frac{J(J + 1)\hbar^2}{2\mu r_e^2} F + \left(\frac{J(J + 1)\hbar^2}{2\mu r_e^2} \left(- \frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2}\right) + \frac{1}{2} k \Delta r^2\right) F = E F,$$

or,

$$-\frac{\hbar^2}{2\mu} F'' + \frac{1}{2} k (r - r_e)^2 F = E F,$$

and this is nothing but a harmonic oscillator differential equation in $x$ with force constant $k$ and equilibrium bond length $r_e$, we know that:

$$-\frac{\hbar^2}{2\mu} F'' + \frac{1}{2} k (r - r_e)^2 F = \varepsilon F,$$

has energy levels:

$$\varepsilon = \hbar \sqrt{\frac{k}{\mu} \left(\nu + \frac{1}{2}\right)}, \quad \nu = 0, 1, 2, ...$$

So,

$$E + \Delta - \frac{J(J + 1)\hbar^2}{2\mu r_e^2} = \varepsilon$$

tells us that:

$$E = \hbar \sqrt{\frac{k}{\mu} \left(\nu + \frac{1}{2}\right)} + \frac{J(J + 1)\hbar^2}{2\mu r_e^2} - \Delta.$$

As $J$ increases, $r_e$ increases because of the centrifugal force pushing the two atoms apart. On the other hand $k$ increases which indicates that the molecule finds it more difficult to
stretch against both the centrifugal and Hooke's law (spring) Harmonic force field. The total energy level (labeled by \( J \) and \( v \)) will equal a rigid rotor component \( \frac{J(J + 1)\hbar^2}{2\mu r_e^2} \) plus a Harmonic oscillator part \( \hbar \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right) \) (which has a force constant \( k \) which increases with \( J \)).