

Section 4 Exercises, Problems, and Solutions

Exercises:

- Consider the molecules CCl_4 , CHCl_3 , and CH_2Cl_2 .
 - What kind of rotor are they (symmetric top, etc; do not bother with oblate, or near-prolate, etc.)
 - Will they show pure rotational spectra?
 - 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).

- The molecule $^{11}\text{B } ^{16}\text{O}$ has a vibrational frequency $\nu_e = 1885 \text{ cm}^{-1}$, a rotational constant $B_e = 1.78 \text{ cm}^{-1}$, and a bond energy from the bottom of the potential well of $D_e^0 = 8.28 \text{ eV}$. Use integral atomic masses in the following:

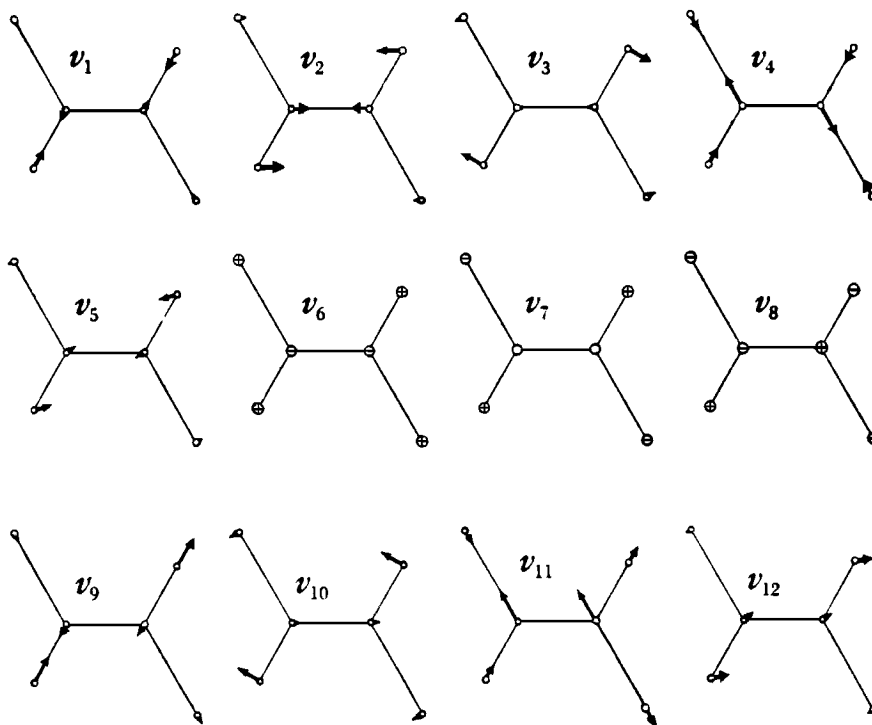
- In the approximation that the molecule can be represented as a Morse oscillator, calculate the bond length, R_e in angstroms, the centrifugal distortion constant, D_e in cm^{-1} , the anharmonicity constant, x_e in cm^{-1} , the zero-point corrected bond energy, D_0^0 in eV, the vibration rotation interaction constant, B_1 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:

$$E = \hbar \nu_e (v + 1/2) - \hbar \nu_e x_e (v + 1/2)^2 + B_v J(J + 1) - D_e J^2(J + 1)^2, \text{ where}$$

$$B_v = B_e - \nu_e (v + 1/2), \quad x_e = \frac{-6B_e^2}{\hbar \nu_e} + \frac{6\sqrt{B_e^3 \hbar \nu_e x_e}}{\hbar \nu_e}, \text{ and } D_e = \frac{4B_e^3}{\hbar \nu_e^2}.$$

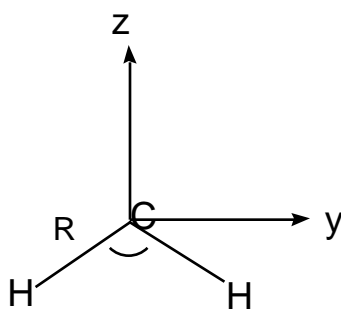
- Will this molecule show a pure rotation spectrum? A vibration-rotation spectrum? Assume that it does, what are the energies (in cm^{-1}) of the first three lines in the P branch ($v = +1$, $J = -1$) of the fundamental absorption?

- Consider $\text{trans-C}_2\text{H}_2\text{Cl}_2$. 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_2 and the other is CH_2^- but you don't know which is which). Both molecules have C_{2v} symmetry. The CH bond length of molecule I is 1.121 \AA and for molecule II it is 1.076 \AA . 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 Å² units) and convert these values into rotational constants $A, B,$ and C in cm⁻¹ using, for example,

$$A = h(8 \pi^2 c I_a)^{-1}.$$

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 values 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 .

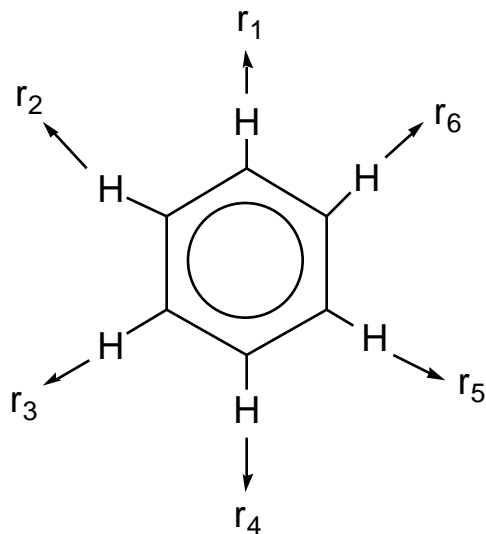
e. Given that the electronic transition moment vector μ connecting species I and II is directed along the Y axis, what are the selection rules J and K ?

f. Suppose you are given the photoelectron spectrum of 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 CH_2^- anion. Explain your 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 ψ_i and ψ_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:

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

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

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

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 μ , equilibrium bond length r_e and harmonic force constant k , we are faced with the following radial Schrödinger equation:

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

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

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

b. Taking $r = r_e + \rho$ and expanding $(1 + x)^{-2} = 1 - 2x + 3x^2 + \dots$,

show that the so-called vibration-rotation coupling term $\frac{J(J+1)\hbar^2}{2\mu r^2}$ can be approximated

(for small ρ) by $\frac{J(J+1)\hbar^2}{2\mu r_e^2} \left(1 - \frac{2\rho}{r_e} + \frac{3\rho^2}{r_e^2} \right)$. Keep terms only through order ρ^2 .

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

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

Give explicit expressions for how the modified force constant k , bond length r_e , and energy shift depend on J , k , r_e , and μ .

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

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

Explain how the conclusion is "obvious", how for $J = 0$, $k = k$, and $r_e = r_e$, 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. CCl_4 is tetrahedral and therefore is a spherical top. CHCl_3 has C_{3v} symmetry and therefore is a symmetric top. CH_2Cl_2 has C_{2v} symmetry and therefore is an asymmetric top.

b. CCl_4 has such high symmetry that it will not exhibit pure rotational spectra. CHCl_3 and CH_2Cl_2 will both exhibit pure rotation spectra.

c. NH_3 is a symmetric top (oblate). Use the given energy expression,

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

$A = 6.20 \text{ cm}^{-1}$, $B = 9.44 \text{ cm}^{-1}$, selection rules $J = \pm 1$, and the fact that μ_0 lies along the figure axis such that $K = 0$, to give:

$$E = 2B (J + 1) = 2B, 4B, \text{ and } 6B \text{ (} J = 0, 1, \text{ and } 2\text{)}.$$

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 $hc = (6.62618 \times 10^{-34} \text{ J sec})(2.997925 \times 10^{10} \text{ cm sec}^{-1}) = 1.9865 \times 10^{23} \text{ J cm}$.

Let all quantities in cm^{-1} be designated with a bar,

e.g. $B_e = 1.78 \text{ cm}^{-1}$.

$$\text{a. } hcB_e = \frac{\hbar^2}{2\mu R_e^2}$$

$$R_e = \frac{\hbar}{\sqrt{2\mu hcB_e}},$$

$$\mu = \frac{m_B m_O}{m_B + m_O} = \frac{(11)(16)}{(11 + 16)} \times 1.66056 \times 10^{-27} \text{ kg} \\ = 1.0824 \times 10^{-26} \text{ kg}.$$

$$hcB_e = hc(1.78 \text{ cm}^{-1}) = 3.5359 \times 10^{-23} \text{ J}$$

$$R_e = \frac{1.05459 \times 10^{-34} \text{ J sec}}{\sqrt{(2)(1.0824 \times 10^{-26} \text{ kg})(3.5359 \times 10^{-23} \text{ J})}}$$

$$R_e = 1.205 \times 10^{-10} \text{ m} = 1.205 \text{ \AA}$$

$$D_e = \frac{4B_e^3}{\hbar^2 e^2}, D_e = \frac{4B_e^3}{e^2} = \frac{(4)(1.78 \text{ cm}^{-1})^3}{(1885 \text{ cm}^{-1})^2} = 6.35 \times 10^{-6} \text{ cm}^{-1}$$

$$e^{x_e} = \frac{\hbar^2 e^2}{4D_e^0}, e^{x_e} = \frac{e^2}{4D_e^0} = \frac{(1885 \text{ cm}^{-1})^2}{(4)(66782.2 \text{ cm}^{-1})} = 13.30 \text{ cm}^{-1}.$$

$$D_0^0 = D_e^0 - \frac{\hbar^2 e}{2} + \frac{\hbar^2 e^{x_e}}{4}, D_0^0 = D_e^0 - \frac{e}{2} + \frac{e^{x_e}}{4} \\ = 66782.2 - \frac{1885}{2} + \frac{13.3}{4} \\ = 65843.0 \text{ cm}^{-1} = 8.16 \text{ eV}.$$

$$e = \frac{-6B_e^2}{\hbar e} + \frac{6\sqrt{B_e^3 \hbar^2 e^{x_e}}}{\hbar e} \\ e = \frac{-6B_e^2}{e} + \frac{6\sqrt{B_e^3 e^{x_e}}}{e}$$

$$e = \frac{(-6)(1.78)^2}{(1885)} + \frac{6\sqrt{(1.78)^3(13.3)}}{(1885)} = 0.0175 \text{ cm}^{-1}$$

$$B_0 = B_e - e(1/2), B_0 = B_e - e(1/2) = 1.78 - 0.0175/2 = 1.77 \text{ cm}^{-1}$$

$$B_1 = B_e - e(3/2), B_1 = B_e - e(3/2) = 1.78 - 0.0175(1.5) = 1.75 \text{ cm}^{-1}$$

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 $J = 1 \rightarrow 0, J = 2 \rightarrow 1, J = 3 \rightarrow 2$

$$E = \hbar \nu_e(v + 1/2) - \hbar \nu_e x_e(v + 1/2)^2 + B_v J(J + 1) - D_e J^2(J + 1)^2$$

$$E = \hbar \nu_e - 2\hbar \nu_e x_e - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3$$

$$E = \nu_e - 2 \nu_e x_e - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3$$

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

$$= 1858.4 - 1.77J(J + 1) + 1.75J(J - 1) - 2.54 \times 10^{-5}J^3$$

$$E(J = 1) = 1854.9 \text{ cm}^{-1}$$

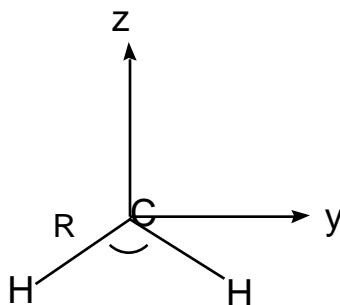
$$E(J = 2) = 1851.3 \text{ cm}^{-1}$$

$$E(J = 3) = 1847.7 \text{ cm}^{-1}$$

3. The $C_2H_2Cl_2$ molecule has a σ_h plane of symmetry (plane of molecule), a C_2 axis (to plane), and inversion symmetry, this results in C_{2h} symmetry. Using C_{2h} symmetry labels the modes can be labeled as follows: 1, 2, 3, 4, and 5 are a_g , 6 and 7 are a_u , 8 is b_g , and 9, 10, 11, and 12 are b_u .

Problems:

1.



Molecule I
 $R_{CH} = 1.121 \text{ \AA}$

$$HCH = 104^\circ$$

$$y_H = R \sin(\theta/2) = \pm 0.8834$$

$$z_H = R \cos(\theta/2) = -0.6902$$

Center of Mass(COM):

Molecule II
 $R_{CH} = 1.076 \text{ \AA}$

$$HCH = 136^\circ$$

$$y_H = \pm 0.9976$$

$$z_H = -0.4031$$

clearly, $X = Y = 0$,

$$Z = \frac{12(0) - 2RC\cos(\pi/2)}{14} = -0.0986 \qquad Z = -0.0576$$

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

$$I_{xy} = - \sum_j m_j x_j y_j - MXY$$

$$I_{xx} = 2(1.121)^2 - 14(-0.0986)^2$$

$$= 2.377$$

$$I_{xx} = 2(1.076)^2 - 14(-0.0576)^2$$

$$= 2.269$$

$$I_{yy} = 2(0.6902)^2 - 14(-0.0986)^2$$

$$= 0.8167$$

$$I_{yy} = 2(0.4031)^2 - 14(-0.0576)^2$$

$$= 0.2786$$

$$I_{zz} = 2(0.8834)^2$$

$$= 1.561$$

$$I_{zz} = 2(0.9976)^2$$

$$= 1.990$$

$$I_{xz} = I_{yz} = I_{xy} = 0$$

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

$$(I_a < I_b < I_c):$$

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

$$0.8167 < 1.561 < 2.377$$

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

$$0.2786 < 1.990 < 2.269$$

Using the formula:
$$A = \frac{h}{8 \sqrt{2cI_a}} = \frac{6.626 \times 10^{-27}}{8 \sqrt{2(3 \times 10^{10})I_a}} \times \frac{6.02 \times 10^{23}}{(1 \times 10^{-8})^2}$$

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

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

So,

Molecule I

y $A = 20.62$

z $B = 10.79$

x $C = 7.08$

Molecule II

y $A = 60.45$

z $B = 8.46$

x $C = 7.42$

c. Averaging B + C:

$$B = (B + C)/2 = 8.94$$

$$A - B = 11.68$$

$$B = (B + C)/2 = 7.94$$

$$A - B = 52.51$$

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: $J = 0, 1, 2, \dots$ and $K = 0, 1, \dots, J$

For a given level defined by J and K, there are M_J degeneracies given by: $(2J + 1) \times$

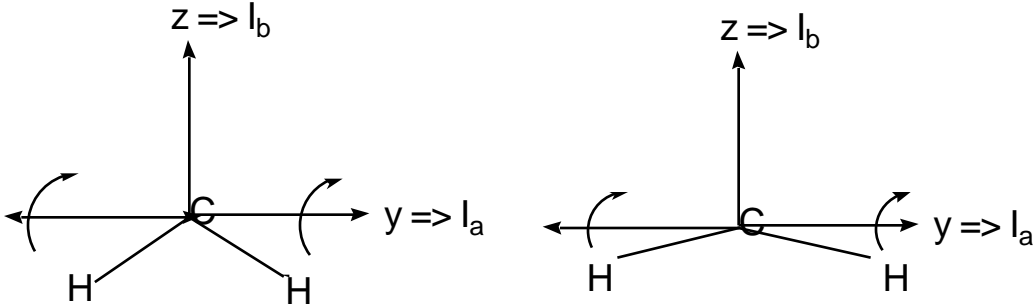
1 for $K = 0$

2 for $K = 1$

d.

Molecule I

Molecule II



e. Since μ is along Y, $K = 0$ since K describes rotation about the y axis.

Therefore $J = \pm 1$

f. Assume molecule I is CH_2^- and molecule II is CH_2 . Then,

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

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

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

$$\begin{aligned} E_R &= E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-) \\ &= 7.94(J_i + 1)(J_i + 1 + 1) - 8.94J_i(J_i + 1) \\ &= (J_i + 1)\{7.94(J_i + 1 + 1) - 8.94J_i\} \\ &= (J_i + 1)\{(7.94 - 8.94)J_i + 2(7.94)\} \\ &= (J_i + 1)\{-J_i + 15.88\} \end{aligned}$$

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

$$\begin{aligned} E_P &= E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-) \\ &= 7.94(J_i - 1)(J_i - 1 + 1) - 8.94J_i(J_i + 1) \\ &= J_i\{7.94(J_i - 1) - 8.94(J_i + 1)\} \\ &= J_i\{(7.94 - 8.94)J_i - 7.94 - 8.94\} \\ &= J_i\{-J_i - 16.88\} \end{aligned}$$

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 CH_2^- and molecule II is 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 CH_2^- and molecule II is CH_2 .

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

$$\begin{aligned} \frac{d(E_R)}{dJ} &= \frac{d}{dJ} [(J_i + 1)\{-J_i + 15.88\}] = 0 \\ &= \frac{d}{dJ} (-J_i^2 - J_i + 15.88J_i + 15.88) = 0 \\ &= -2J_i + 14.88 = 0 \\ J_i &= 7.44, \text{ so } J = 7 \text{ or } 8. \end{aligned}$$

At $J = 7.44$:

$$E_R = (J + 1)\{-J + 15.88\}$$

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

2. a.

D _{6h}	E	2C ₆	2C ₃	C ₂	3C ₂ '	3C ₂ "	i	2S ₃	2S ₆	h	3 d	3 v			
A _{1g}	1	1	1	1	1	1	1	1	1	1	1	1		R _z	x ² +y ² ,z ²
A _{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1			
B _{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1			
B _{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		(R _x ,R _y)	(xz,yz) (x ² -y ² ,xy)
E _{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0			
E _{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0			
A _{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		z	
A _{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1			
B _{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1			
B _{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		(x,y)	
E _{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0			
E _{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0			
C-H	6	0	0	0	0	2	0	0	0	6	2	0			

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

$$n_{\text{irrep}} = \frac{1}{g} \sum_{\text{R}} \text{red}(\text{R}) \text{ irrep}(\text{R}),$$

where g = the order of the point group (24 for D_{6h}).

$$\begin{aligned}
 n_{A_{1g}} &= \frac{1}{24} \sum_{\text{R}} \text{C-H}(\text{R}) \cdot A_{1g}(\text{R}) \\
 &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\
 &\quad + (3)(0)(1) + (3)(2)(1) + (1)(0)(1) + (2)(0)(1) \\
 &\quad + (2)(0)(1) + (1)(6)(1) + (3)(2)(1) + (3)(0)(1) \} \\
 &= 1 \\
 n_{A_{2g}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\
 &\quad + (3)(0)(-1) + (3)(2)(-1) + (1)(0)(1) + (2)(0)(1) \\
 &\quad + (2)(0)(1) + (1)(6)(1) + (3)(2)(-1) + (3)(0)(-1) \} \\
 &= 0 \\
 n_{B_{1g}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\
 &\quad + (3)(0)(1) + (3)(2)(-1) + (1)(0)(1) + (2)(0)(-1) \\
 &\quad + (2)(0)(1) + (1)(6)(-1) + (3)(2)(1) + (3)(0)(-1) \} \\
 &= 0
 \end{aligned}$$

$$\begin{aligned}
n_{B_{2g}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\
&\quad + (3)(0)(-1) + (3)(2)(1) + (1)(0)(1) + (2)(0)(-1) \\
&\quad + (2)(0)(1) + (1)(6)(-1) + (3)(2)(-1) + (3)(0)(1) \} \\
&= 0 \\
n_{E_{1g}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(2) + (2)(0)(1) \\
&\quad + (2)(0)(-1) + (1)(6)(-2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 0 \\
n_{E_{2g}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(2) + (2)(0)(-1) \\
&\quad + (2)(0)(-1) + (1)(6)(2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 1 \\
n_{A_{1u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\
&\quad + (3)(0)(1) + (3)(2)(1) + (1)(0)(-1) + (2)(0)(-1) \\
&\quad + (2)(0)(-1) + (1)(6)(-1) + (3)(2)(-1) + (3)(0)(-1) \} \\
&= 0 \\
n_{A_{2u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\
&\quad + (3)(0)(-1) + (3)(2)(-1) + (1)(0)(-1) + (2)(0)(-1) \\
&\quad + (2)(0)(-1) + (1)(6)(-1) + (3)(2)(1) + (3)(0)(1) \} \\
&= 0 \\
n_{B_{1u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\
&\quad + (3)(0)(1) + (3)(2)(-1) + (1)(0)(-1) + (2)(0)(1) \\
&\quad + (2)(0)(-1) + (1)(6)(1) + (3)(2)(-1) + (3)(0)(1) \} \\
&= 0 \\
n_{B_{2u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\
&\quad + (3)(0)(-1) + (3)(2)(1) + (1)(0)(-1) + (2)(0)(1) \\
&\quad + (2)(0)(-1) + (1)(6)(1) + (3)(2)(1) + (3)(0)(-1) \} \\
&= 1 \\
n_{E_{1u}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(-2) + (2)(0)(-1) \\
&\quad + (2)(0)(1) + (1)(6)(2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 1 \\
n_{E_{2u}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(-2) + (2)(0)(1) \\
&\quad + (2)(0)(1) + (1)(6)(-2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 0
\end{aligned}$$

We see that $c-H = A_{1g} \ E_{2g} \ B_{2u} \ E_{1u}$

c. x and y E_{1u} , z 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 polarized.

d. $(x^2 + y^2, z^2)$ A_{1g} , (xz, yz) E_{1g} , $(x^2 - y^2, xy)$ 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.

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

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

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

So,

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

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

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

Using the above derived identity gives:

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

Cancelling out an r^{-1} :

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

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

So,

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

c. Using this substitution we now have:

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

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

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

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

Now, we must complete the square:

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

So,

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

Now, redefine the first term as $\frac{1}{2} k$, second term as $(r - \bar{r}_e)^2$, and the third term as - giving:

$$\frac{1}{2} k (r - \bar{r}_e)^2 -$$

From:

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

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

and making the above substitution results in:

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

or,

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

d. Since the above is nothing but a harmonic oscillator differential equation in x with force constant k and equilibrium bond length \bar{r}_e , we know that:

$$\frac{-\hbar^2}{2\mu} F'' + \frac{1}{2} k (r - \bar{r}_e)^2 F = E F, \text{ has energy levels:}$$

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

So,

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

tells us that:

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

As J increases, \bar{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 $\hbar\sqrt{\frac{k}{\mu}} v + \frac{1}{2}$ (which has a force constant k which increases with J) .