5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Problem Set #4 ANSWERS

1. The corners of a cube are numbered 1, 2, 3, 4 clockwise around the top face of the cube, and 5, 6, 7, 8 clockwise around the bottom face, corner 5 lying under corner 1, corner 6 under corner 2, and so on. A face center is denoted by the two numbers of the corners between which a face diagonal can be drawn which passes through that face center (for example, either 13 or 24 would denote the center of the top face).

   (a) The structures of several kinds of AB_4 molecules are described as follows with the above numbering system. The A–atom is placed at the center of the cube, and the A—B bond distances are given by the cube dimensions. However, the B–atoms are not necessarily all equivalent, the actual equivalence being determined by the symmetry elements remaining in the AB_4 structures.

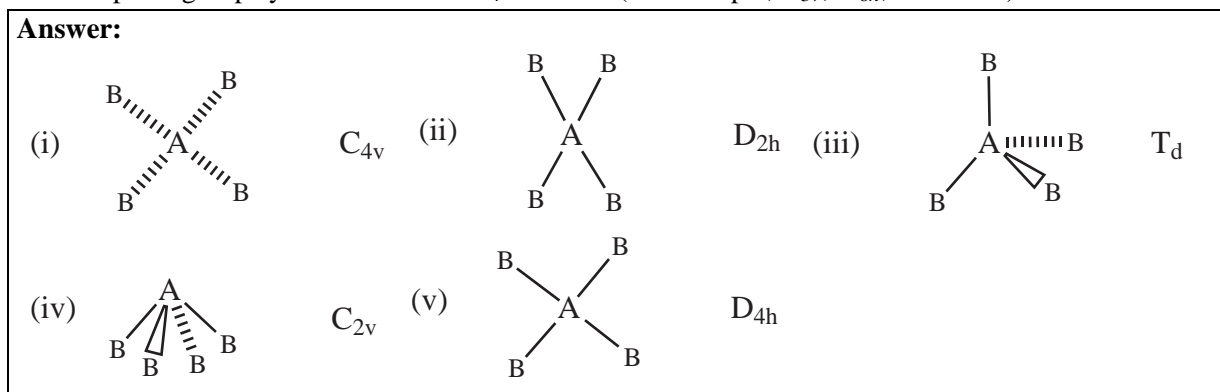   (i) $AB_4(1, 2, 3, 4)$

   (ii) $AB_4(1, 3, 5, 7)$

   (iii) $AB_4(1, 3, 6, 8)$

   (iv) $AB_4(1, 5, 16, 18)$

   (v) $AB_4(13, 36, 68, 18)$

   Give the point-group symbol for each AB_4 structure (for example, C_{3v}, D_{6h}, and so on).

   Answer:

   (b) Classify the five molecules of Part (a) as to type of molecular rotator (linear, symmetrical top, and so on).

   Answer:
   (i) Prolate Symmetric Top
   (ii) Asymmetric Top
   (iii) Spherical Top
   (iv) Asymmetric Top
   (v) Oblate Symmetric Top

(c) Which of the five molecules of Part (a) will give a pure-rotational spectrum in the far-infrared or microwave region? Which will give a pure-rotational Raman effect?

> **Answer:**
> Pure Rotation in Far IR or Microwave: (i) and (iv)
> Pure Rotational Raman: (i), (ii), (iv), and (v)

2. The harmonic oscillator (mass m) in two dimensions has a potential energy V expressed in polar coordinates r, θ, of the general form $2V = k_1 r^2 \cos^2 \theta + k_2 r^2 \sin^2 \theta$, where k_1 and k_2 are force constants. For the special case $k_1 = k_2 = k$, the oscillator has a single frequency $v = (k/m)^{1/2}/2\pi$, and its Schrödinger equation has solutions of the form

$$\psi_{v,\ell} = N_{v,\ell} \exp\left(\frac{-\alpha r^2}{2}\right) \exp(i\ell\theta) P(r)$$

where v, ℓ are quantum numbers ($v = 0, 1, 2, \ldots, \infty$; $\pm\ell = 0, 2, 4, \ldots, v$ for v even, $\pm\ell = 1, 3, 5, \ldots v$ for v odd); $N_{v,\ell}$ is a normalization constant; $\alpha = 4\pi^2 mv/h$; $P(r)$, a polynomial in r only, depends for its form on the values of v and ℓ and is an even function for even v, odd for odd v.

(a) The energy levels of this two-dimensional oscillator are $E_v = (v + 1)hv$. What is the degeneracy of the v–th level?

> **Answer:**
> What is degeneracy of vth level of 2D Harmonic Oscillator Degeneracy $\Rightarrow$ # of ℓ states!
> v odd $\Rightarrow \ell = \pm1, \pm3, \pm5, \ldots, \pm v$
> v even $\Rightarrow \ell = 0, \pm2, \pm4, \ldots, \pm v$
> $\therefore$ degeneracy $= v + 1$

(b) Find $N_{v,\ell}$ for $v = 1$, $\ell = +1$, for which $P(r) = \alpha^{1/2} r$.

> **Answer:**
> $N_{v,\ell}$ = normalization constant
> Find $N_{1,+1} = $ "N"
>
> $$\rho(r) = \sqrt{\alpha}\, r$$
>
> $$\psi_{1,+1} = N \exp\left(\frac{-\alpha r^2}{2}\right) \exp(i\theta) \sqrt{\alpha}\, r$$
>
> $$\int_0^\infty \int_0^{2\pi} \psi_{11}^* \psi_{11}\, r\, dr\, d\theta = 1 = \int_0^\infty \int_0^{2\pi} |N|^2 e^{-\alpha r^2} e^{-i\theta} e^{i\theta} (\alpha r^2)\, r\, dr\, d\theta$$
>
> $$1 = 2\pi \int_0^\infty |N|^2 e^{-\alpha r^2} \alpha r^3\, dr = \frac{2\pi |N|^2}{\alpha} \int_0^\infty e^{-x^2} x^3\, dx$$
>
> $$= \frac{2\pi}{\alpha} |N|^2 \frac{1}{2} = \frac{\pi}{\alpha} |N|^2 = 1$$
>
> $$\therefore \quad |N_{11}| = \sqrt{\frac{\alpha}{\pi}}$$

(c) Show that any two ψ's of the same v but different ℓ are orthogonal.

Answer:

$$\int_0^\infty \int_0^{2\pi} \psi_{v\ell'}\psi_{v\ell}\, r\,dr\,d\theta = N_{v\ell'}N_{v\ell}\int_0^\infty e^{-\alpha r^2}\rho^2(r)r\,dr \int_0^{2\pi} e^{i(\ell-\ell')\theta}d\theta = 0$$

Since $\ell - \ell' \neq 0$ therefore any $\psi_{v\ell} + \psi_{v\ell'}$ are orthogonal if $\ell \neq \ell'$.

(d) Find the average value of the angular momentum p_θ for any state v, ℓ.

Answer:

$$\langle p_\theta \rangle =?$$

$$\langle p_\theta \rangle_{v\ell} = \int_0^\infty \int_0^{2\pi} \psi_{v\ell}^\star p_\theta \psi\, r\,dr\,d\theta = \int_0^\infty \int_0^{2\pi} \psi_{v\ell}^\star \left(-i\hbar\frac{\partial}{\partial\theta}\right)\psi_{v\ell}\, r\,dr\,d\theta$$

$$= \hbar\ell \int_0^\infty \int_0^{2\pi} \psi_{v\ell}^\star \psi_{v\ell}\, r\,dr\,d\theta = \hbar\ell$$

(e) Find the average value of r^{-2} for the state $v = 1, \ell = +1$.

Answer:

$$\langle r^{-2}\rangle_{11} = \int_0^\infty \int_0^{2\pi} \psi_{11}^\star r^{-2}\psi_{11}\, r\,dr\,d\theta = N_{11}^2 \int_0^\infty \int_0^{2\pi} e^{-\alpha r^2}\alpha r\,dr\,d\theta = \alpha = \frac{4\pi^2 m\nu}{h} = \frac{k}{h\nu}$$

$$\langle p_\theta^2\rangle_{v\ell} = \hbar^2\ell^2 \Rightarrow \langle p_\theta^2\rangle_{11} = \hbar^2$$

$$E_{\text{rot}_{11}} = \frac{1}{2m}\frac{\langle p_\theta^2\rangle_{11}}{\langle r^2\rangle_{11}} = \frac{\hbar^2}{2m}\left(\frac{4\pi^2 m\nu}{h}\right) = \frac{h\nu}{2}$$

$E_{\text{vib}}(v = 1) = \frac{3}{2}h\nu$ $E_{\text{total}} = E_{\text{vib}} + E_{\text{rot}} = 2h\nu$

From (a) $E = (v + 1)h\nu = 2h\nu$

Substitute the results of the above in the equation for the relationship between E and p_θ in the plane rotor and find E for the state $v = 1,\ \ell = +1$. Explain the difference between this value of E and that given by the equation of Part (a).

3. The carbon suboxide molecule C_3O_2, is believed to be linear and symmetrical.

   (a) Classify the normal vibrations of C_3O_2 according to the symmetry species of point group $D_{\infty h}$.

   Answer:

   $$O \!=\!\!=\!\! C \overset{r_1}{\underbrace{}} \!\!=\!\!=\!\! C \overset{r_2}{\underbrace{}} \!\!=\!\!=\!\! C \overset{r_3}{\underbrace{}} \!\!=\!\!=\!\! O$$

   O$=$C$=$C$=$C$=$O with r_1, r_2, r_3, r_4 over the bonds and $\theta_1, \theta_2, \theta_3$ under the atoms.

   # of modes = $3N-5 = 10$
   4 stretching modes
   3 **pairs** of bending modes
   Point Group = $D_{\infty h}$
   $\hat{i}(\delta r_1) = \delta r_4$, $\hat{i}(\delta r_2) = \delta r_3$
   $\widehat{\sigma}_v(\delta r_i) = \delta r_i \rightarrow$ no σ_g^- or σ_u^- stretching modes
   Sketches:

   $$\delta r_1 + \delta r_4 : \sigma_g^+$$
   $$\delta r_1 - \delta r_4 : \sigma_u^+$$
   $$\delta r_2 + \delta r_3 : \sigma_g^+$$
   $$\delta r_2 - \delta r_3 : \sigma_u^+$$

   Bending $\Rightarrow$ doubly degenerate $\Rightarrow \pi$ symmetry
   $\hat{i}(\delta\theta_1) = -\delta\theta_3$, $\hat{i}(\delta\theta_2) = \delta\theta_2$, $\hat{i}(\delta\theta_3) = -\delta\theta_1$
   Modes: must be orthogonal to $\delta\theta_1 - \delta\theta_3$ π_g

   $$\delta\theta_1 + \sqrt{2}\delta\theta_2 + \delta\theta_3 \quad \pi_u$$
   $$\delta\theta_1 - \sqrt{2}\delta\theta_2 + \delta\theta_3 \quad \pi_u$$

   (b) How many polarized lines should appear in the vibrational Raman spectrum? How many fundamental infrared bands should have *P*–, *Q*–, and *R*–branches?

   Answer: According to the $D_{\infty h}$ character table:

   $$\left.\begin{array}{ll} \Sigma_g^+ & x^2 + y^2, z^2 \\ \Pi_g & (xz, yz) \\ \Delta_g & (x^2 - y^2, xy) \end{array}\right\} \quad \text{Raman Active}$$

   $$\left.\begin{array}{ll} \Sigma_u^+ & z \\ \Pi_u & (x, y) \end{array}\right\} \quad \text{IR Active}$$

   Therefore σ_g^+'s ; π_g's $\Rightarrow$ 2 polarized lines will appear in Raman
   IR $\Rightarrow$ P, Q, R $\Rightarrow$ (xy) polarization $\Rightarrow \pi_u$
   $2\pi_u$'s (each degenerate) $\Rightarrow$ 2 Fundamental IR bands have P, Q, and R lines.

(c) The ground electronic state of C_3O_2 is nondegenerate. What is the degeneracy of ψ_{mol} when C_3O_2 is in its ground electronic state with $v_1 = v_2 = v_3 = v_4 = v_5 = v_6 = 0$, $v_7 = 1$, and the rotational quantum number $J = 5$? The normal coordinate Q_7 is antisymmetric with respect to simultaneous interchange of all pairs of equivalent nuclei. What is the degeneracy of ψ_{mol} for the above state with $J = 6$ instead of 5?

> **Answer:** Degeneracy: $(2J + 1)$(interchange term)
> # of interchanges = (# C's)×(# O's)= 6
> $\therefore$ Degeneracy = $6(2J + 1)$
> $$J = 5 \Rightarrow \text{Deg} = 66$$
> $$J = 6 \Rightarrow \text{Deg} = 78$$

4. (a) Let $\psi_a \equiv \psi_{v_1=1}(Q_1)\psi_{v_2=0}(Q_2)$ and $\psi_b \equiv \psi_{v_1=0}\psi_{v_2=2}$ be the normalized harmonic-oscillator wave functions of a polyatomic molecule corresponding to excited vibrational states of unperturbed energies E_a and E_b. If these two states are in Fermi resonance, second-order non-degenerate theory can be applied. Assume that the interaction energies H'_{aa} and H'_{bb} are zero and that H'_{ab} arises from one or more anharmonic terms in the potential function. In a certain molecule, the levels ψ_a and ψ_b are observed to be in Fermi resonance, the transitions to the *perturbed* levels being observed at 1400 and 1500 cm^{-1}, whereas the level $\psi_{v_1=0}\psi_{v_2=1}$ has an energy of 740 cm^{-1} above the zero level (see diagram). Deduce the unperturbed E_a–value from the above data (H'_{ab} is to be evaluated from the data, not by integration).
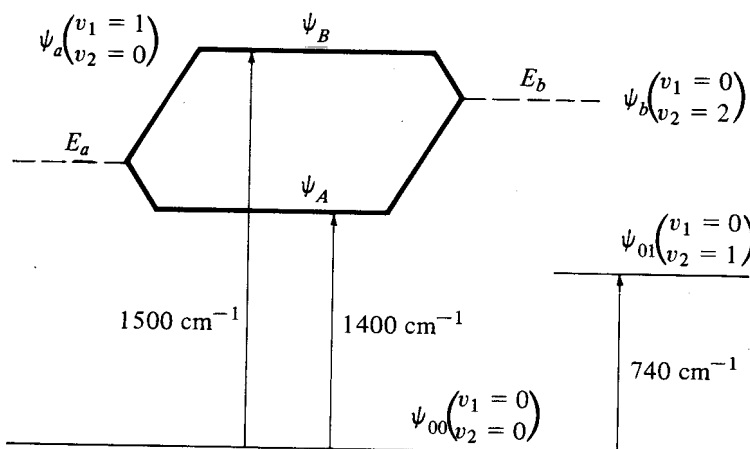
> **Answer:**
> $$\begin{vmatrix} E_a - \lambda & \mathcal{H}_{ab} \\ \mathcal{H}_{ab} & E_b - \lambda \end{vmatrix} = 0$$
>
> Find E_a
> $$(E_a - \lambda)(E_b - \lambda) - |\mathcal{H}_{ab}|^2 = 0 = \lambda^2 - (E_a + E_b)\lambda - |\mathcal{H}_{ab}|^2$$

Answer: 4(a), continued

$$\lambda = \frac{E_a + E_b}{2} \pm \frac{1}{2}\left[(E_a - E_b)^2 + 4|\mathcal{H}_{ab}|^2\right]^{1/2}$$

$$E_b = 2.740 = 1480 \text{ cm}^{-1} \text{ above } (0,0)$$

$$\frac{1}{2}(E_a + E_b) = \frac{1400 + 1500}{2} = 1450 \text{ cm}^{-1} \qquad \text{center of gravity doesn't change}$$

$$\therefore E_a = 1420 \text{ cm}^{-1} \text{ above } (0,0)$$

(b) The *intensity* of the Raman line for the transition from the ground state $\psi_{0,0}$ to the *unperturbed* state ψ_a in the absence of Fermi resonance is proportional to the square of the matrix element

$$\left\langle \psi_{0,0} \left| \frac{\partial \alpha}{\partial Q_1} Q_1 \right| \psi_a \right\rangle$$

where $\partial \alpha / \partial Q_1$ is a non-zero constant. The corresponding matrix element

$$\left\langle \psi_{0,0} \left| \frac{\partial \alpha}{\partial Q_2} Q_2 \right| \psi_b \right\rangle$$

is zero because $\Delta v_2 = 2$. Find the ratio of the intensities of the two Raman lines for the transitions from state $|\psi_{00}\rangle$ to the *perturbed* states $|\psi_A\rangle$ and $|\psi_B\rangle$.

Answer: Defining λ_a, λ_b:

$$\lambda_a = \frac{E_a + E_b}{2} - \frac{1}{2}\left[(E_a - E_b)^2 + 4|\mathcal{H}_{ab}|^2\right]^{1/2}$$

$$\lambda_b = \frac{E_a + E_b}{2} + \frac{1}{2}\left[(E_a - E_b)^2 + 4|\mathcal{H}_{ab}|^2\right]^{1/2}$$

$$|\psi_A\rangle = \left[\frac{\lambda_a - E_b}{2\lambda_b - (E_a + E_b)}\right]^{1/2} |\psi_b\rangle + \left[\frac{\lambda_a - E_a}{2\lambda_b - (E_a + E_b)}\right]^{1/2} |\psi_a\rangle \qquad \text{(normalized)}$$

$$|\psi_B\rangle = \left[\frac{\lambda_b - E_a}{2\lambda_b - (E_a + E_b)}\right]^{1/2} |\psi_b\rangle - \left[\frac{\lambda_a - E_b}{2\lambda_b - (E_a + E_b)}\right]^{1/2} |\psi_a\rangle \qquad \text{(normalized)}$$

$$\frac{I_A}{I_B} = \frac{\left|\left\langle \psi_{00} \left| \frac{\partial \alpha}{\partial Q} \right| \psi_A \right\rangle\right|^2}{\left|\left\langle \psi_{00} \left| \frac{\partial \alpha}{\partial Q} \right| \psi_B \right\rangle\right|^2} = \frac{\left|\left\langle \psi_{00} \left| \frac{\partial \alpha}{\partial Q_1} \right| \psi_a \right\rangle\right|^2}{\left|\left\langle \psi_{00} \left| \frac{\partial \alpha}{\partial Q_1} \right| \psi_a \right\rangle\right|^2} \frac{\lambda_b - E_a}{\lambda_b - E_b}$$

$$= \frac{\lambda_b - E_a}{\lambda_b - E_b} = \frac{1500 - 1420}{1500 - 1480} = 4$$

$\therefore$ Ratio of intensities: $|\psi_{00}\rangle \to |\psi_A\rangle : |\psi_{00}\rangle \to |\psi_B\rangle = 4 : 1$

5. $^{16}O^{12}C^{32}S$ is a linear molecule. The bond lengths are

$r_{CO} = 1.16\text{Å}$

$r_{CS} = 1.56\text{Å}$

and the observed fundamental vibrational frequencies are

$v_1 = 858.9$ cm^{-1} stretch

$v_2 = 520.4$ cm^{-1} bend

$v_3 = 2062.2$ cm^{-1} stretch.

(a) Obtain k$_{CS}$, k$_{CO}$, and k$_\theta[r_{CO}r_{CS}]^{-1}$ in dynes/cm.

Answer:

Assume $k_{CO} > k_{CS}$.

Let $\lambda_1 = 4\pi^2 v_1^2, \qquad \lambda_3 = 4\pi^2 v_3^2$

$$\lambda_1 + \lambda_3 = k_{CS}\left(\frac{1}{m_C} + \frac{1}{m_S}\right) + k_{CO}\left(\frac{1}{m_C} + \frac{1}{m_O}\right)$$

$$\lambda_1\lambda_3 = \frac{m_C + m_S + m_O}{m_C m_S m_O}k_{CS}k_{CO}$$

$$\therefore k_{CS} = \frac{1}{2}(\lambda_1 + \lambda_3)\left(\frac{1}{m_C} + \frac{1}{m_S}\right)^{-1}\left[1 \pm \left(1 - \frac{4\left(\frac{1}{m_C} + \frac{1}{m_S}\right)\left(\frac{1}{m_C} + \frac{1}{m_O}\right)\lambda_1\lambda_3 m_C m_S m_O}{(\lambda_1 + \lambda_3)^2(m_C + m_S + m_O)}\right)^{1/2}\right]$$

$$m_C = 12 \text{ amu}$$
$$m_S = 32 \text{ amu}$$
$$m_O = 16 \text{ amu}$$

$$\therefore k_{CS} = 8.07 \times 10^5 \text{dynes/cm or } 1.76 \times 10^6 \text{dynes/cm} \qquad \text{but} \quad k_{CO} > k_{CS} \Rightarrow$$

$$k_{CS} = 8.07 \times 10^5 \text{dynes/cm}$$

$$k_{CO} = \lambda_1\lambda_3 \frac{m_C m_S m_O}{m_C + m_S + m_O}\frac{1}{k_{CS}} = 1.39 \times 10^6 \text{dynes/cm}$$

Note that this assumption is confirmed by CO_2, and CS_2 in which $k_{CO} = 1.42 \times 10^6$ dynes/cm and $k_{CS} = 8.10 \times 10^5$ dynes/cm, respectively.
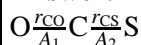
$$k_\theta[r_{CO}r_{CS}]^{-1} = \left[\frac{r_{CO}^2}{m_O} + \frac{r_{CS}^2}{m_S} + \frac{(r_{CO} + r_{CS})^2}{m_S}\right]^{-1} r_{CO}r_{CS}4\pi^2 v_2^2$$

$$\therefore k_\theta[r_{CO}r_{CS}]^{-1} = 3.72 \times 10^4 \text{dynes/cm}.$$

(b) What are the amplitudes for C-O and C-S stretch in ν_1?

Answer: Amplitude change: Look at fractional bond change
$$O\frac{r_{CO}}{A_1}C\frac{r_{CS}}{A_2}S$$

$$(k_{CO} - \lambda_1\mu_{11})A_1 - \lambda_1\mu_{12}A_2 = 0$$

$$\therefore A_2 = \frac{(k_{CO} - \lambda_1\mu_{11})}{\lambda_1\mu_{12}}A_1$$

$$A_1^2 + A_2^2 = 1 \quad \text{normalizations}$$

$$\therefore \quad A_1 = \left[\left(\frac{(k_{CO} - \lambda_1\mu_{11})}{\lambda_1\mu_{12}}\right)^2 + 1\right]^{-1/2}$$

$$\mu_{11} = \frac{m_O(m_C + m_S)}{m_O + m_C + m_S} = 11.73 \text{ amu} = 1.948 \times 10^{-23}g.$$

$$\lambda_1 = 4\pi^2\nu_1^2 = 2.912 \times 10^7 \text{ cm}^{-2} = 2.621 \times 10^{28} \text{ sec}^{-2}$$

$$\mu_{12} = \frac{m_O + m_S}{m_O + m_S + m_C} = 8.53 \text{ amu} = 1.417 \times 10^{-23}g.$$

$$A_1 = \left[\left(\frac{1.39 - 0.511}{0.371}\right)^2 + 1\right]^{-1/2} = 0.389$$

$$A_2 = \sqrt{1 - A_1^2} = 0.921$$

$$\therefore \quad A_{CO} = 0.389 \cdot r_{CO} = 0.45\text{Å}$$

$$A_{CS} = 0.922 \cdot r_{CS} = 1.43\text{Å}.$$

(c) What are the vibrational frequencies for $^{18}O^{12}C^{32}S$?

Answer: For isotopically shifted $^{18}O^{12}C^{32}S$, the forces involved are the same (k_{CO}, k_{CS}, k_θ), but the masses are different, so that different frequencies are obtained.

$$\lambda_1 + \lambda_3 = (8.07 \times 10^5)\left(\frac{1}{12} + \frac{1}{32}\right)(1.66 \times 10^{-24})^{-1} + (1.39 \times 10^6)\left(\frac{1}{12} + \frac{1}{18}\right)(1.66 \times 10^{-24})^{-1}$$

$$= 1.72 \times 10^{29} \text{sec}^{-1} \quad \text{(this formula is on page 6)}$$

$$\lambda_1\lambda_3 = 3.65 \times 10^{57} \text{sec}^{-1}$$

Answer: 5(c), continued

$$\nu = \left[\frac{1.72 \times 10^{29}}{8\pi^2} \left(1 \pm \sqrt{1 - \frac{4(3.65 \times 10^{57})}{(1.72 \times 10^{24})^2}} \right) \right]^{1/2} \text{sec}^{-1} \frac{1}{3 \times 10^{10} \text{cm/sec}}$$

$$= 835 \text{ cm}^{-1}, \ 2035 \text{ cm}^{-1}$$

$$\therefore \ \nu_1 = 835 \text{ cm}^{-1} \text{ and } \nu_3 = 2035 \text{ cm}^{-1}$$

$$\nu_2 = \left[\frac{k_\theta [r_{CO} r_{CS}]^{-1}}{4\pi^2 r_{CO} r_{CS}} \left(\frac{r_{CO}^2}{m_O} + \frac{r_{CS}^2}{m_S} + \frac{(r_{CO} + r_{CS})^2}{m_C} \right) \right]^{1/2} \text{sec}^{-1} \frac{1}{3 \times 10^{10} \text{cm/sec}}$$

$$\nu_2 = 515 \text{ cm}^{-1}.$$