

EXAM INFORMATION

Particle in Box

One Dimensional PIB Energies: $E_n = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3, \dots$

Harmonic Oscillator

Hamiltonian: $H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$

Energy Levels: $E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad n = 0, 1, 2, \dots \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

Anharmonic Oscillator

Energy Levels: $E_n = \left(n + \frac{1}{2}\right) \hbar c \tilde{\nu} - \left(n + \frac{1}{2}\right)^2 \hbar c x_e \tilde{\nu} \quad n = 0, 1, 2, \dots$

Rigid Rotor

Quantum Numbers: $J = 0, 1, 2, 3, \dots \quad M = 0, \pm 1, \pm 2, \dots, \pm J$

Energy Levels: $E_J = J(J+1) \frac{h^2}{8\pi^2 I} = J(J+1) \hbar c \tilde{B} \quad \tilde{B} = \frac{h}{8\pi^2 I c}$

Moment of Inertia: Linear Polyatomic: $I = \sum m_i r_i^2$ **Diatomic:** $I = \mu r^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

Boltzmann Distribution: $N_i \propto g_i e^{-E_i/kT}$

Constants and Conversions:

$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$

$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J}\cdot\text{s}$

$k = 1.38 \times 10^{-23} \text{ J/K}$

$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$

$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

$1 \text{ \AA} = 10^{-10} \text{ m}$

$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$

$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$

$1 \text{ N} = 1 \text{ kg}\cdot\text{m}/\text{s}^2$

$1 \text{ N/m} = 1 \text{ kg}/\text{s}^2$

C_{2h} Character Table

C_{2h}	E	C₂	i	σ_h	
A _g	1	1	1	1	x ² ,y ² ,z ² ,xy
B _g	1	-1	1	-1	xz,yz
A _u	1	1	-1	-1	z
B _u	1	-1	-1	1	x,y

Transition Moment: $M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k}$ $M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle$
 $M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle$
 $M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle$

Raman Matrix Elements: $\langle \Psi_i | \alpha_{uv} | \Psi_0 \rangle$ u = x, y, or z and v = x, y, or z

Name Solution

- (6) 1. Consider the differential equation: $\frac{df(x)}{dx} + 3x = 6f(x)$

Use the Taylor series method (e.g. $f(x) = a_0 + a_1x + a_2x^2 + \dots$) to determine the first two recursions in the solution for $f(x)$ [i.e. $a_1 = f'(a_0)$ and $a_2 = f''(a_1)/2$]

$$f(x) = a_0 + a_1x + a_2x^2 + \dots$$

$$\frac{df(x)}{dx} = 0 + a_1 + 2a_2x + \dots$$

$$\frac{df}{dx} + 3x = 6f$$

$$a_1 + 2a_2x + \dots + 3x = 6a_0 + 6a_1x + \dots$$

$$a_1 + (2a_2 + 3)x + \dots = 6a_0 + 6a_1x + \dots$$

or $\boxed{a_1 = 6a_0}$

$$2a_2 + 3 = 6a_1$$

$$\boxed{a_2 = \frac{6a_1 - 3}{2}}$$

Equate equal powers of x .

$$E_n/hc = (n + \frac{1}{2}) \bar{\nu} - (n + \frac{1}{2})^2 x_e \bar{\nu}$$

$$4620 \text{ cm}^{-1}$$

- (10) 2. The observed vibrational frequency of the **fundamental** vibration ($0 \rightarrow 1$) of O_2 is 1560 cm^{-1} . The frequency of the **second** overtone ($0 \rightarrow 3$) is at ~~7820~~ 4620 cm^{-1} . Calculate the harmonic frequency ($\bar{\nu}$) and the anharmonicity constant (x_e).

$$\frac{E_0}{hc} = \frac{1}{2} \bar{\nu} - \frac{1}{4} x_e \bar{\nu} \quad \frac{E_1}{hc} = \frac{3}{2} \bar{\nu} - \frac{9}{4} x_e \bar{\nu} \quad \frac{E_3}{hc} = \frac{7}{2} \bar{\nu} - \frac{49}{4} x_e \bar{\nu}$$

$$\bar{\nu}_{0 \rightarrow 1} = \frac{E_1}{hc} - \frac{E_0}{hc} = \left(\frac{3}{2} \bar{\nu} - \frac{9}{4} x_e \bar{\nu} \right) - \left(\frac{1}{2} \bar{\nu} - \frac{1}{4} x_e \bar{\nu} \right) = \bar{\nu} - 2 x_e \bar{\nu}$$

$$\bar{\nu}_{0 \rightarrow 3} = \frac{E_3}{hc} - \frac{E_0}{hc} = \left(\frac{7}{2} \bar{\nu} - \frac{49}{4} x_e \bar{\nu} \right) - \left(\frac{1}{2} \bar{\nu} - \frac{1}{4} x_e \bar{\nu} \right) = 3 \bar{\nu} - 12 x_e \bar{\nu}$$

$$(1) 4620 = 3 \bar{\nu} - 12 x_e \bar{\nu}$$

$$(2) 1560 = \bar{\nu} - 2 x_e \bar{\nu}$$

$$(1) - 3(2) \Rightarrow 4620 - 3(1560) = [3 \bar{\nu} - 12 x_e \bar{\nu}] - [3 \bar{\nu} - 6 x_e \bar{\nu}]$$

$$\therefore -60 = -6 x_e \bar{\nu} \rightarrow$$

$$x_e \bar{\nu} = 10 \text{ cm}^{-1}$$

$$\bar{\nu} = 1560 + 2(x_e \bar{\nu}) = 1560 + 20 = 1580 \text{ cm}^{-1}$$

$$x_e = \frac{10}{1580} = 0.0063$$

(18) 3. The energies of electrons in an atom can be approximated by assuming that they are particles in a 3-Dimensional cubical box of length 'a' on each side.

(10) a) Draw a diagram with the first five (5) energy **levels** of a particle in a cubical box, including the sets of quantum numbers and degeneracies of each level
(Put your energies in units of $h^2/8ma^2$)

Note: If 2 or 3 sets of quantum numbers have the same energy, that counts as only 1 of the 5 requested levels.

$$E(n_x, n_y, n_z) = \frac{h^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2]$$

$n_x = 1, 2, \dots$
 $n_y = 1, 2, \dots$
 $n_z = 1, 2, \dots$

Energy Level	Quantum Numbers	Degeneracy (g)
1	111	1
2	211, 121, 112	3
3	221, 212, 122	3
4	311, 131, 113	3
5	222	1

(8) b) Consider a sulfur atom, which has 16 electrons. Assume that these electrons are free to move in a cubical box of length, 0.25 nm on a side. Calculate the wavelength (in nm) of the lowest energy electronic transition in a magnesium atom.

Energy Level	Occupancy
12	1 electron
11	2 electrons
9	3 electrons
6	3 electrons
3	1 electron

$$\Delta E = E_{12} - E_{11} = \frac{1}{8ma^2} h^2 - \frac{1}{8ma^2} h^2 = \frac{1}{8ma^2} h^2$$

$$= \frac{(6.63 \times 10^{-34})^2}{8(9.11 \times 10^{-31} \text{ kg})(2.5 \times 10^{-10} \text{ m})^2}$$

$$= 9.65 \times 10^{-19} \text{ J}$$

$$a = 0.25 \text{ nm} = 2.5 \times 10^{-10} \text{ m}$$

$$m = 9.11 \times 10^{-31} \text{ kg}$$

$$E_{ph} = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.0 \times 10^8 \text{ m/s})}{9.65 \times 10^{-19} \text{ J}}$$

$$= 2.06 \times 10^{-7} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = \boxed{206 \text{ nm}}$$

- (38) 4. For this problem, assume that the molecule, carbon disulfide, CS_2 , is linear, with the structure: $\text{S}=\text{C}=\text{S}$

Note: Assume that the atomic mass of C is 12 amu and the atomic mass of S is 32 amu

- (8) (a) The **third** and **fourth** lines in the rotational Raman spectrum of CS_2 have frequencies of 1.54 cm^{-1} and 1.98 cm^{-1} , respectively. Calculate the value of the rotational constant, $\tilde{B}$, in cm^{-1} .

Note: The selection rule for the rotational Raman spectrum is $\Delta J = +2$

$$\text{3rd: } \bar{\nu}_{3 \rightarrow 4} = (4/5)\bar{B} - (2/3)\bar{B} = 14\bar{B} = 1.54 \text{ cm}^{-1} \rightarrow \bar{B} = 0.11 \text{ cm}^{-1}$$

$$\text{4th: } \bar{\nu}_{3 \rightarrow 5} = (5/6)\bar{B} - (3/4)\bar{B} = 18\bar{B} = 1.98 \text{ cm}^{-1} \rightarrow \bar{B} = 0.11 \text{ cm}^{-1}$$

- (8) (b) For the Rotational Spooky spectrum, the selection rule is $\Delta J = +4$.

Calculate (1) the frequency of the **third (3rd.)** line in the Rotational Spooky spectrum of CS_2 (in cm^{-1});

(2) the energy of the photon absorbed for this transition, $E_{\text{ph}} = \Delta E$ (in J)

Note: For parts, (b), (c), and (d) you can use the value, $\tilde{B} = 0.14 \text{ cm}^{-1}$ if your answer to part (a) is far from this value.

$$\begin{aligned} \text{3rd: } \bar{\nu}_{J=2 \rightarrow J=6} &= (6/7)\bar{B} - (2/3)\bar{B} \\ &= 36\bar{B} = 36(0.11) = \boxed{3.96 \text{ cm}^{-1}} \end{aligned}$$

$$\begin{aligned} E_{\text{ph}} &= \Delta E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \\ &= (6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^{10} \text{ cm/s})(3.96 \text{ cm}^{-1}) \\ &= 7.88 \times 10^{-23} \text{ J} \end{aligned}$$

Prob. 4 (Cont'd)

Note: For parts, (b), (c), and (d) you can use the value, $\tilde{B} = 0.14 \text{ cm}^{-1}$ if your answer to part (a) is far from this value.

(12) (c) Calculate the C=S Bond Length in CS_2 , in nm.

$$I = \frac{h}{8\pi^2 B c} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{8(3.1416)^2 (0.14 \text{ cm}^{-1})(3 \times 10^{10} \text{ cm/s})} = 2.54 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$$I = \sum m_i r_i^2 = 2 m_S R_{CS}^2 + 1 (m_C (0))^2$$

$$R_{CS}^2 = \frac{I}{2 m_S} = \frac{2.54 \times 10^{-45} \text{ kg} \cdot \text{m}^2}{2(5.31 \times 10^{-26} \text{ kg})}$$

$$= 2.39 \times 10^{-20} \text{ m}^2$$

$$S = 4 = S$$

$$\leftarrow R_{CS} \quad \leftarrow R_{CS}$$

$$m_S = 32 \text{ amu} \times 1.66 \times 10^{-27} \text{ kg}$$

$$= 5.31 \times 10^{-26} \text{ kg}$$

$$\therefore R_{CS} = (2.39 \times 10^{-20} \text{ m}^2)^{\frac{1}{2}} = 1.55 \times 10^{-10} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}}$$

$$R_{CS} = 0.155 \text{ nm}$$

$$N_J \propto (2J+1) e^{-\frac{\bar{B}hc}{kT} J(J+1)}$$

Prob. 4 (Cont'd)

Note: For parts, (b), (c), and (d) you can use the value, $\bar{B} = 0.14 \text{ cm}^{-1}$ if your answer to part (a) is far from this value.

$$T = 150^\circ\text{C} = 423 \text{ K}$$

(10) (d) Calculate the ratio of intensities of the 60th. line to that of the 20th. line in the rotational Raman spectrum of CS_2 at 150°C

$$\begin{aligned} \text{Line 60: } J=59 \rightarrow J=61 \\ \text{Line 20: } J=19 \rightarrow J=21 \end{aligned}$$

$$\frac{I_{59 \rightarrow 61}}{I_{19 \rightarrow 21}} = \frac{N_{59}}{N_{19}}$$

$$\frac{N_{59}}{N_{19}} = \frac{[2(59)+1] e^{-\frac{\bar{B}hc}{kT} (59/60)}}{[2(19)+1] e^{-\frac{\bar{B}hc}{kT} (19/20)}} = \frac{119 e^{-\frac{\bar{B}hc}{kT} 3540}}{39 e^{-\frac{\bar{B}hc}{kT} 380}}$$

$$= \frac{119}{39} e^{-\frac{\bar{B}hc}{kT} (3160)} = \frac{119}{39} e^{-(3.748 \times 10^{-4}) (3160)}$$

$$= \frac{119}{39} e^{-1.184} = (3.05)(0.306)$$

$$\boxed{= 0.93}$$

$$\frac{\bar{B}hc}{kT} = \frac{(0.11 \text{ cm}^{-1})(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^{10} \text{ cm/s})}{(1.38 \times 10^{-23} \text{ J/K})(423 \text{ K})}$$

$$= 3.748 \times 10^{-4}$$

- (12) 5. The vibrational force constant of the hydrogen chloride, $^1\text{H}^{35}\text{Cl}$, is 520 N/m ($=520 \text{ kg/s}^2$). The **thermodynamic** dissociation energy of the $^1\text{H}^{35}\text{Cl}$ is $D_0 = 432 \text{ kJ/mol}$. Calculate the **spectroscopic** dissociation energy, D_e , in kJ/mol .

Note: Note that the atomic mass of H is 1. amu and the atomic mass of Cl is 35 amu.

calculate ν

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{1 \times 35}{1 + 35} = 0.972 \text{ amu} \times \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 1.61 \times 10^{-27} \text{ kg}$$

$$\nu = \frac{1}{2\pi\mu} \sqrt{\frac{k}{\mu}} = \frac{1}{2(3.1416)} \sqrt{\frac{520 \text{ kg/s}^2}{1.61 \times 10^{-27} \text{ kg}}} = 9.03 \times 10^{13} \text{ s}^{-1}$$

calculate $E_{\text{vib}}(\text{zero point})$ in kJ/mol .

$$E_{\text{vib}} = \frac{1}{2} h \nu = \frac{1}{2} (6.63 \times 10^{-34} \text{ J}\cdot\text{s}) (9.03 \times 10^{13} \text{ s}^{-1})$$

$$= 2.99 \times 10^{-20} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$= 18.0 \text{ kJ/mol}$$

calculate D_e

$$D_e = D_0 + E_{\text{vib}} = 432 \text{ kJ/mol} + 18 \text{ kJ/mol} = \boxed{450 \text{ kJ/mol}}$$

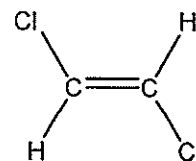
- (16) 6. Consider the three CH bending vibrations of (E)-1,2-dichloroethene, which belongs to the C_{2h} point group.

The vibrations (and symmetries) are:

$$\tilde{\nu}_1 = 900 \text{ cm}^{-1} (a_u)$$

$$\tilde{\nu}_2 = 760 \text{ cm}^{-1} (b_g)$$

$$\tilde{\nu}_3 = 1200 \text{ cm}^{-1} (b_u)$$



- (6) a) Calculate the frequency (in cm^{-1}) of the transition: $(0,1,1) \rightarrow (2,0,2)$.

$$E_{\text{init}}/hc = (0 + \frac{1}{2}) 900 + (1 + \frac{1}{2}) 760 + (1 + \frac{1}{2}) 1200 = 3390 \text{ cm}^{-1}$$

$$E_{\text{fin}}/hc = (2 + \frac{1}{2}) 900 + (0 + \frac{1}{2}) 760 + (2 + \frac{1}{2}) 1200 = 5630 \text{ cm}^{-1}$$

$$\bar{\nu} = \frac{E_{\text{fin}}}{hc} - \frac{E_{\text{init}}}{hc} = 5630 - 3390 = \boxed{2240 \text{ cm}^{-1}}$$

- (10) b) Consider the combination mode, $(0,1,0) \rightarrow (1,0,2)$. Determine whether this combination mode is (i) IR active **AND/OR** (ii) Raman active.

NOTE: You MUST show your work for credit.

$$\Gamma_{\text{init}} = a_g \times b_g \times a_g = B_g$$

$$\Gamma_{\text{fin}} = a_u \times b_g \times a_g = A_u$$

IR

$$\langle \psi_{\text{fin}} | x | \psi_{\text{init}} \rangle = A_u \times B_u \times B_g = A_g \checkmark$$

$$\langle \psi_{\text{fin}} | y | \psi_{\text{init}} \rangle = A_g \checkmark$$

$$\langle \psi_{\text{fin}} | z | \psi_{\text{init}} \rangle = A_u \times A_g \times B_g = B_g$$

IR Active

Raman

$$\langle \psi_{\text{fin}} | x^2 | \psi_{\text{init}} \rangle = A_u \times A_g \times B_g = B_u \times$$

Same for y^2, z^2, xy .

$$\langle \psi_{\text{fin}} | xz | \psi_{\text{init}} \rangle = A_u \times B_g \times B_g = A_u \times$$

Same for yz

Raman Inactive