

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

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:

$$\langle \Psi_i | \alpha_{uv} | \Psi_0 \rangle \quad u = x, y, \text{ or } z \quad \text{and } v = x, y, \text{ or } z$$

Name _____

- (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 $a_2 = f''(a_1)/2$]

- (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 4620 cm^{-1} . Calculate the harmonic frequency ($\tilde{\nu}$) and the anharmonicity constant (x_e).

- (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.
- (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.

- (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 $\Delta J = +2$

- (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.

Prob. 4 (Cont'd)

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

Prob. 4 (Cont'd)

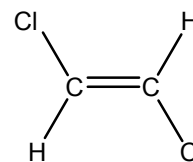
Note: For parts, (b), (c), and (d) you can use the value, $\tilde{B} = 0.14 \text{ cm}^{-1}$ if your answer to part (a) is far from this value.

- (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

- (12) 5. The vibrational force constant of the hydrogen chloride, $^1\text{H}^{35}\text{Cl}$, is 520 N/m (=520 kg/s²). The **thermodynamic** dissociation energy of the $^1\text{H}^{35}\text{Cl}$ is $D_0 = 432$ 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.

- (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:

$$\tilde{\nu}_1 = 900 \text{ cm}^{-1} (a_u) \quad \tilde{\nu}_2 = 760 \text{ cm}^{-1} (b_g) \quad \tilde{\nu}_3 = 1200 \text{ cm}^{-1} (b_u)$$

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

- (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.