

EXAM INFORMATION

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

First Order Perturbation Theory: $\Delta E = \int \psi^{(0)*} H^{(1)} \psi^{(0)} d\tau$

Quadratic Equation: $ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

INTEGRALS

$$\int \sin^2(\alpha x) dx = \frac{1}{2} x - \frac{1}{4\alpha} \sin(2\alpha x)$$

$$\int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

$$\int x^2 \sin^2(\alpha x) dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha x) - \frac{x \cos(2\alpha x)}{4\alpha^2}$$

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_{2v} Character Table

	C_{2v}	E	C₂	σ_v(xz)	σ_v'(yz)		
A ₁	1	1	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	-1	-1	R _z	xy
B ₁	1	-1	1	-1	-1	x, R _y	xz
B ₂	1	-1	-1	1	1	y, R _x	yz

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 _____

- (38) 1. For this problem, assume that the molecule, difluorodisilyne, Si_2F_2 , is linear, with the structure: $\text{F-Si}\equiv\text{Si-F}$

Note: Assume that the atomic mass of F is 19 amu and the atomic mass of Si is 28 amu

- (8) (a) The **second** and **third** lines in the rotational Raman spectrum of difluorodisilyne are found at frequencies of 0.380 cm^{-1} and 0.532 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 $\Delta J = +2$

Note: For parts, (b), (c), and (d) you can use the value, $\tilde{B} = 0.04\text{ cm}^{-1}$ if your answer to part (a) is far from this value.

- (8) (b) For the Rotational Saffy spectrum, the selection rule is $\Delta J = +3$.

Calculate (1) the frequency of the **fourth (4th.)** line in the Rotational Saffy spectrum of difluorodisilyne (in cm^{-1}); (2) the energy of the photon absorbed for this transition, $E_{\text{ph}} = \Delta E$ (in J)

Prob. 1 (Cont'd)

Note: For parts, (b), (c), and (d) you can use the value, $\tilde{B} = 0.04 \text{ cm}^{-1}$ if your answer to part (a) is far from this value.

- (10) (c) Calculate the ratio of intensities of the 150th. line to that of the 50th. line in the rotational Raman spectrum of difluorosilyne at 150 °C

Prob. 1 (Cont'd)

Note: For parts, (b), (c), and (d) you can use the value, $\tilde{B} = 0.04 \text{ cm}^{-1}$ if your answer to part (a) is far from this value.

(12) (d) The Si $\equiv$ Si bond length in difluorodisilyne is $R_{\text{SiSi}} = 2.0 \text{ \AA}$. Calculate the Si-F bond length, R_{SiF} , in $\text{\AA}$.

Hint: First calculate the moment of inertia, I , in kg m^2 , and then convert to $\text{amu \AA}^2$ before proceeding. ($1 \text{ kg m}^2 = 6.0 \times 10^{46} \text{ amu \AA}^2$)

Note: With a bit of thought, you won't need to use the quadratic equation to solve for $R_{\text{Si-H}}$. However, if you do need it, it's on the info. sheet

Additional Space for Prob. 1d on next page if needed

Prob. 1d (Cont'd) Additional Space if needed

- (10) 2. The vibrational force constant of Deuterium Fluoride, $^2\text{D}-^{19}\text{F}$, is 840 N/m (Newton/meter) = 840 kg/s². Calculate the Zero-Point vibrational energy of D-F, in **kJ/mol**.

- (10) 3. The Thermodynamic Dissociation Energy of F_2 is $D_0 = 151.$ kJ/mol, and the fundamental vibrational frequency is 890 cm^{-1} .

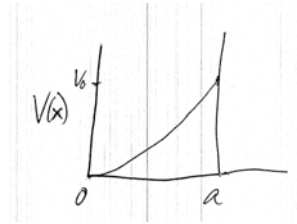
Calculate the Spectroscopic Dissociation Energy, D_e , of F_2 .

- (10) 4. The observed vibrational frequency of the **first** overtone ($0 \rightarrow 2$) Li-H radical is at 2671 cm^{-1} . The frequency of the **hot band** ($1 \rightarrow 2$) is at 1312 cm^{-1} . Calculate the harmonic frequency ($\tilde{\nu}$) and the anharmonicity constant (x_e).

- (10) 5. The ground-state wavefunction for a particle in a box is: $\psi = A \sin\left(\frac{\pi x}{a}\right) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$

Consider a particle in a box with the perturbing potential:

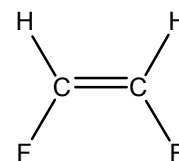
$$\begin{aligned} V(x) &\rightarrow \infty & x < 0 \\ V(x) &= \frac{V_0}{a^2} x^2 & 0 \leq x \leq a \\ V(x) &\rightarrow \infty & x > a \end{aligned}$$



Calculate the first order perturbation theory correction to the energy of a particle in the ground-state with the above perturbing potential.

Note: Your answer should be of the form of a numerical value times V_0 .

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



The vibrations (and symmetries) are:

$$\tilde{\nu}_1 = 870 \text{ cm}^{-1} (a_2) \quad \tilde{\nu}_2 = 1380 \text{ cm}^{-1} (b_1) \quad \tilde{\nu}_3 = 760 \text{ cm}^{-1} (b_2)$$

- (8) (a) Calculate frequency (1) in cm^{-1} and (2) in $\text{Hz (s}^{-1}\text{)}$ of the transition: $(2,0,1) \rightarrow (0,2,2)$.

- (6) (b) Consider the combination band $\nu_1 + 2 \nu_2$ [i.e. $(0,0,0) \rightarrow (1,2,0)$]. Determine whether or not this transition is **IR Active**.

NOTE: You MUST show your work for credit.

- (6) (c) Consider the combination mode, $\nu_1-\nu_3$ [i.e. $(0,0,1) \rightarrow (1,0,0)$]. Determine whether or not this combination mode is **IR** active.

NOTE: You MUST show your work for credit.

- (2) (d) Which, if any, of the above individual fundamental vibrations (transition from **0 to 1**) are **IR** Active (just the answers - no explanation necessary)