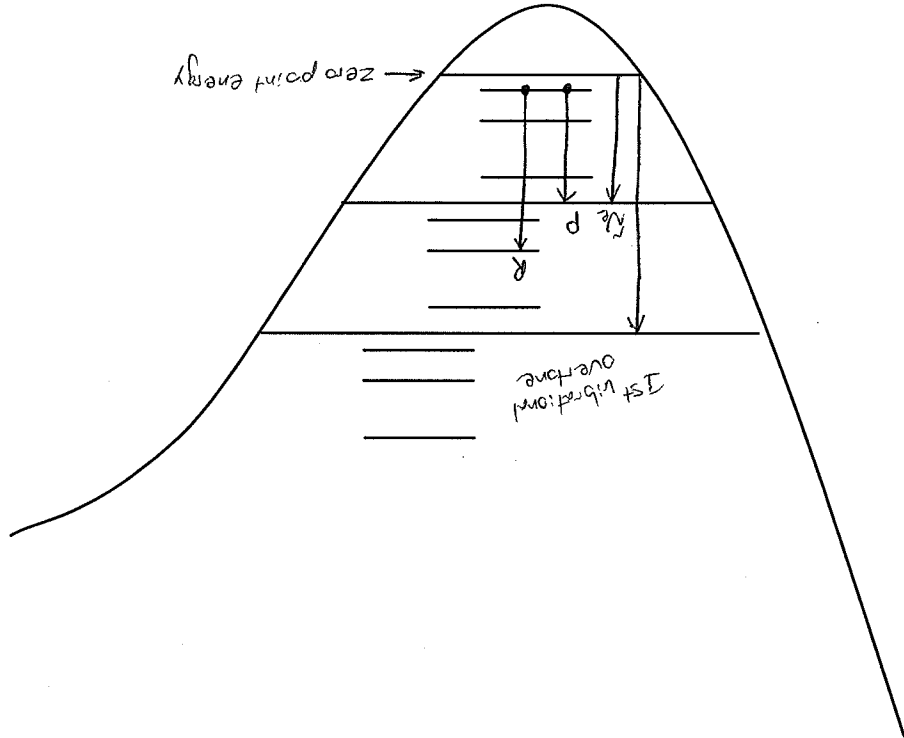


Instructions: You have fifty minutes to complete this exam. Please place your name on all pages of this exam. Exams submitted without a name will not be graded. Show all work when calculating answers. You are allowed to use a calculator for the exam.

1. (20 points) A subset of vibrational and rotational energy levels for a generic diatomic molecule are shown below. On the diagram clearly draw and label the following quantities.
- The P branch transition originating from the $v=0, j=1$ level.
 - The R branch transition which originates from the $v=0, j=1$ level.
 - The first vibrational overtone (assume $\Delta l = 0$ for this portion of the problem).
 - The fundamental vibrational frequency, $\tilde{\nu}_e$, (assume $\Delta l = 0$ for this portion of the problem).
 - The zero point energy.



2. (10 points) In a simple two-level system the probability of a transition between the two states, P_{12} , is:

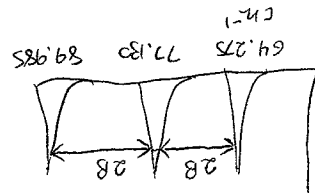
$$P_{12} \propto |\langle \mu_{12} | \langle \mu_{12} | \delta(E_2 - E_1 - \hbar\nu) | \mu_{12} \rangle|^2$$

a. What is the physical significance of the first term, $|\langle \mu_{12} | \mu_{12} \rangle|^2$?

Transition dipole moment between states one and two
 $\mu_{12} = \int \psi_2^* \mu \psi_1 dx$
 Evaluation of integral leads to the selection rules

b. What is the physical significance of the second term, $\delta(E_2 - E_1 - \hbar\nu)$?
 Bohr frequency condition - the energy of the applied radiation $\hbar\nu$ must be equal to the energy difference between E_2 and E_1 .

3. (15 points) The microwave spectrum (pure rotational spectrum) of ^{127}I shows a series of lines at 64.275 cm^{-1} , 77.130 cm^{-1} , and 89.985 cm^{-1} . Using the rigid rotator approximation determine the equilibrium bond length of the molecule. The molecular weight of ^{127}I is 127 g/mol (remember $N_A = 6.022 \times 10^{23}$ atoms/mol). Clearly state any assumptions made.



$$2B = 12.855 \text{ cm}^{-1}$$

$$B = 6.4275 \text{ cm}^{-1}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1 \text{ g/mol})(127 \text{ g/mol})}{1 \text{ g/mol} + 127 \text{ g/mol}} = 0.992 \text{ g/mol}$$

$$\tilde{B} = \frac{8\pi^2 c \mu R^2}{h}$$

$$R^2 = \frac{8\pi^2 c \mu B}{h}$$

$$R^2 = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{8\pi^2 (3.10^{10} \text{ cm/s})(0.992 \text{ g/mol}) \cdot \frac{1 \text{ kg}}{1000 \text{ g}} \cdot \frac{1}{6.022 \times 10^{23}} (6.4275 \text{ cm}^{-1})} = 2.64 \times 10^{-20} \text{ m}^2$$

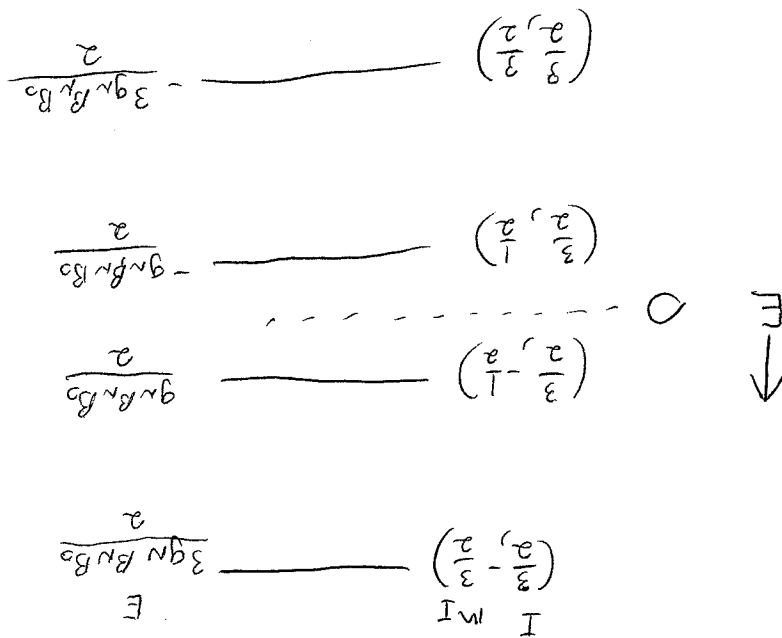
$$r = 1.62 \times 10^{-10} \text{ m} \text{ or } 162 \text{ pm}$$

4. (15 points) The isotope ^{33}S can be used in NMR spectroscopy. The nuclear spin, I , of ^{33}S is $3/2$. The nuclear spin states of ^{33}S can be described in the form of (I, m_I) . Even though there are more than two nuclear spin states for ^{33}S each individual state is still an eigenstate of the nuclear spin angular momentum operator I_z where

$$I_z(I, m_I) = m_I(I, m_I)$$

a. Construct an energy level diagram for ^{33}S in an externally applied magnetic field of strength B_0 directed along the z-axis. Label each state with its wavefunction in the form of (I, m_I) and give its energy in terms of the constants g_N , β_N , and B_0 . You may ignore the shielding constant and use the following nuclear Zeeman Hamiltonian

$$H_{NZ} = \frac{-g_N \beta_N B_0}{\hbar} I_z$$



b. What is the frequency of an ^{33}S NMR transition if the applied magnetic field is 6 T. (Some possibly useful constants: $g_N = 9.46$, $\beta_N = 5.051 \times 10^{-27} \text{ J/T}$, $\hbar = 6.626 \times 10^{-34} \text{ Js}$)

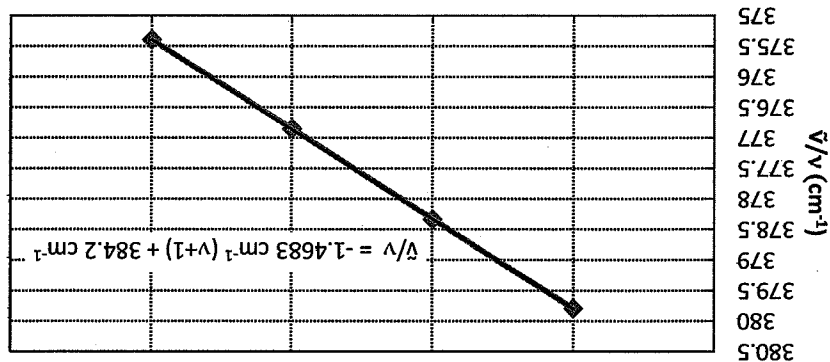
$$\Delta E = h\nu = g_N \beta_N B_0$$

$$\nu = \frac{g_N \beta_N B_0}{h} = \frac{(9.46)(5.051 \times 10^{-27} \text{ J/T})(6 \text{ T})}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}$$

$$= 4.33 \times 10^8 \text{ Hz} \Rightarrow 433 \text{ MHz}$$

5. (15 points) The fundamental vibrational frequency and overtones of $^{127}\text{I}^{35}\text{Cl}$ are located in the infrared region of the electromagnetic spectrum and are provided in the table and plotted in the chart below. You may ignore rotational transitions in this problem.

Transition	ν	$\tilde{\nu}$ (cm^{-1})
$\nu = 0 \rightarrow 2$	3	759.60
$\nu = 0 \rightarrow 3$	4	1135.0
$\nu = 0 \rightarrow 4$	5	1507.4
$\nu = 0 \rightarrow 5$	6	1877.0



$$\tilde{\nu}_{obs} = G(\nu) - G(0) = \tilde{\nu}_e \nu - \tilde{\nu}_e \nu_e (\nu+1)$$

$$\tilde{\nu}_{obs}/\nu = \tilde{\nu}_e - \tilde{\nu}_e \nu_e (\nu+1)/\nu$$

a. What is the fundamental frequency, $\tilde{\nu}_e$?

$$\tilde{\nu}_e = 384.2 \text{ cm}^{-1}$$

b. What is the value of the anharmonicity constant, $\tilde{\nu}_e x_e$?

$$\tilde{\nu}_e \tilde{\nu}_e x_e = 1.4683 \text{ cm}^{-1}$$

$$\tilde{\nu}_e x_e = \frac{1.4683 \text{ cm}^{-1}}{384.2 \text{ cm}^{-1}} = 0.0038$$

6. (15 points) Consider performing NMR spectroscopy on a simple system of two coupled indistinguishable protons. The wavefunctions of the states are

$$\begin{aligned} \psi_1 &= \alpha(1)\alpha(2) \\ \psi_2 &= \frac{\sqrt{2}}{2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \psi_3 &= \frac{\sqrt{2}}{2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ \psi_4 &= \beta(1)\beta(2) \end{aligned}$$

The perturbing operator for the NMR transitions is $H_1 \propto (I_1^x + I_2^x)$. Show that transitions from ψ_1 lead to ψ_2 .

$$\langle \psi_2 | H_1 | \psi_1 \rangle = \int \psi_2^* H_1 \psi_1 d\tau$$

must be non-zero for transition to occur

$$\int \frac{\sqrt{2}}{2} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] (\frac{\hbar}{2} I_1^x + \frac{\hbar}{2} I_2^x) (\alpha(1)\alpha(2)) d\tau$$

$$= \int \frac{\sqrt{2}}{2} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] (\frac{\hbar}{2} \alpha(1)\alpha(2) + \frac{\hbar}{2} \alpha(1)\beta(2)) d\tau$$

$$= \int \frac{\sqrt{2}}{2} [\psi_2] [\frac{\sqrt{2}}{2} \psi_1] d\tau$$

$$= \int \frac{\sqrt{2}}{2} \psi_2 \psi_1 d\tau = \frac{\sqrt{2}}{2}$$

non-zero, so transition occurs

7. (10 points, True/False) Determine whether each of the following statements is true or false. Write the entire word TRUE or FALSE or else no credit will be given

a. The relative energies of electronic, vibrational, rotational, and NMR transitions are – $E_{\text{NMR}} < E_{\text{vibrational}} < E_{\text{electronic}} < E_{\text{rotational}}$ FALSE

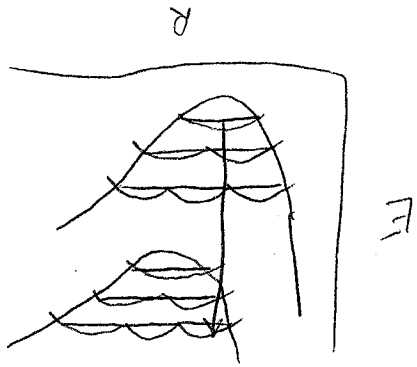
b. The zero point energy refers to the energy at the minimum of the potential well of the ground electronic state. FALSE

c. The dissociation energy of a molecule is measured between the bottom of the potential well of a given electronic state and zero energy where zero energy is defined as the energy of two widely separated atoms. FALSE

d. It is not possible to perform NMR spectroscopy on a nucleus with a nuclear spin of zero. TRUE

e. For an NMR transition to occur the applied magnetic field (B_0) must be parallel to the probing magnetic field (B_1). FALSE

8. (5 points, Extra Credit) Describe the Frank Condon principle. Use diagrams if necessary. Atomic nuclei do not move appreciably during an electronic transition.



9. (5 points, Extra Credit) MSU currently has a 900 MHz NMR. Assume the instrument operates at 21 T. The spectrum of propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) is acquired with the machine. The molecule contains two different chemical environments. One environment is experienced by the six protons at the ends of the molecule (three on each end) and another chemical environment is experienced by the two protons in the middle of the molecule. Sketch the proton NMR spectrum assuming:

- a. The multiplet of the 6 protons at the end of the molecule is centered at a chemical shift of 0.91 ppm.
- b. The difference in the transition frequency between the two chemical environments is 270 Hz.
- c. The shielding constant for the two protons is higher than that for the 6 protons.
- d. The difference between transitions within a given multiplet is roughly 0.03 ppm.

