

This exam consists of 5 problems on the next six pages. Please examine the booklet to make sure you have a complete examination. A periodic table and sheets containing constants, equations and conversion factors are attached to the back of the exam.

Answer each question in the space provided, continuing on the reverse side of the *same* page if more space is needed.

If a question is not clear, insufficient information is given, or there is an apparent error, please notify a member of the instructional staff immediately.

Pay attention to units and to significant figures of your numerical answers. **Show your reasoning for all problems on the exam!**

1. 20 points Nick

2. 30 points Jon

3. 20 points John

4. 10 points Nick

6. 20 points John

Name: _____

Student #: _____

Section: _____

Total (100) _____

Section 1: Tu 12:40 – 1:30 pm

Section 2: Tu 8:00 – 8:50 am

Section 3: Th 11:30 – 12:20 pm

Section 4: Th 9:10 – 10:00 am

#5 (3)

333-1800 Hagabunda

1. (20 points) The fundamental vibrational frequencies for $^{14}\text{N}^{14}\text{N}$ and $^{12}\text{C}^{16}\text{O}$ are 2330 cm^{-1} and 2170 cm^{-1} , respectively. Using these data, predict which molecule has the strongest bond? Show your reasoning!

$$\tilde{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \leftarrow \text{compare } k\text{'s}$$

$$k = \mu \cdot (2\pi c \tilde{\nu}_0)^2$$

$$\text{for } ^{14}\text{N}-^{14}\text{N}; \mu = \frac{14.14\text{ g}}{28\text{ mol}} \times \frac{1\text{ kg}}{10^3\text{ g}} \times \frac{1\text{ mole}}{6.022 \times 10^{23}} = 1.162 \times 10^{-26}\text{ kg}$$

$$k_{\text{N}_2} = (1.162 \times 10^{-26}\text{ kg}) (2\pi (3 \times 10^{10}\text{ cm/s}) 2330\text{ cm}^{-1})^2 = 2241 \frac{\text{kg}}{\text{s}^2} \text{ or } \text{N/m}$$

$$\text{for } ^{12}\text{C}-^{16}\text{O}: \mu_{\text{CO}} = \frac{12.16}{12+16} \text{ g/mol} \times \frac{1\text{ kg}}{10^3\text{ g}} \times \frac{1\text{ mole}}{6.022 \times 10^{23}} = 1.138 \times 10^{-26}\text{ kg}$$

$$k_{\text{CO}} = (1.138 \times 10^{-26}\text{ kg}) (2\pi c \tilde{\nu}_0)^2 = 1904 \frac{\text{kg}}{\text{s}^2}$$

$k_{\text{N}_2} > k_{\text{CO}}$ \Rightarrow N_2 bond is stronger.

Reasoning w/ k 's!

Circle one:

N_2

CO

b) Does N_2 have an IR spectrum? Why or why not?

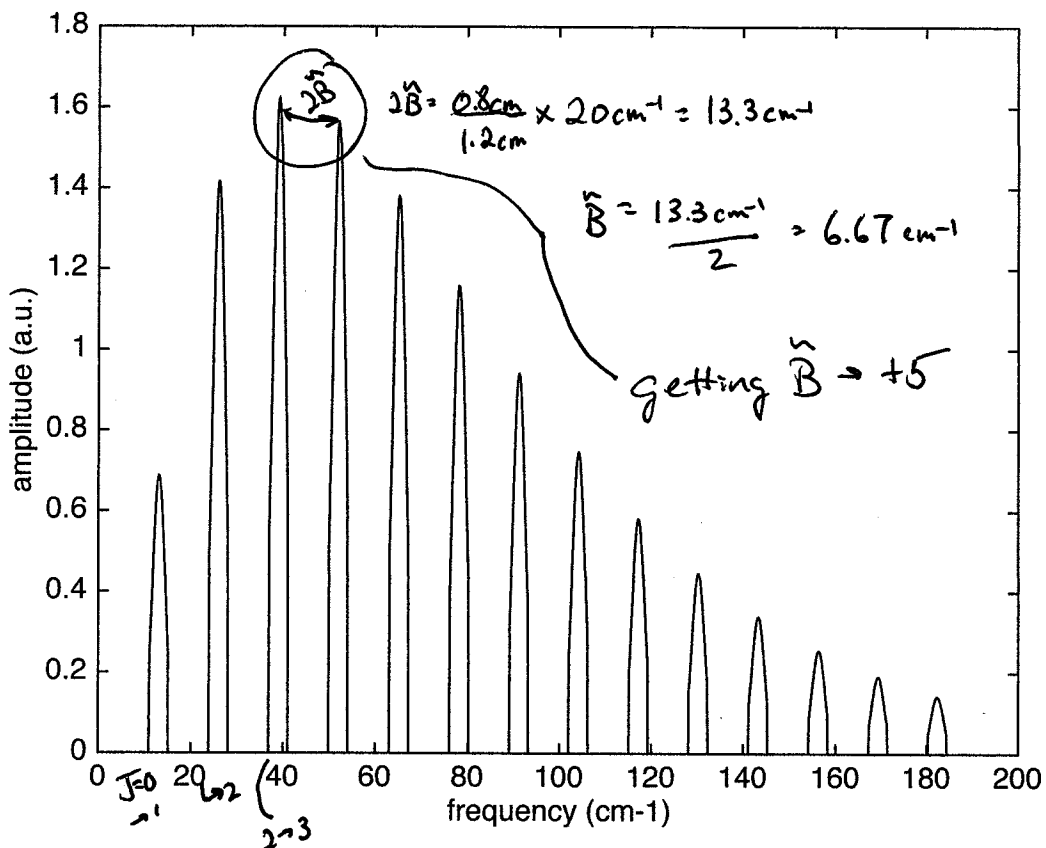
No \Rightarrow because $\left(\frac{d\mu_e}{dx}\right)_{x=0} = 0$ - N_2

Circle one: yes

no

Stretching does not yield a change in dipole moment.

2. (3 points) The pure rotational spectrum of $^1\text{H}^{127}\text{I}$ is shown below.



a) Using these data, determine the length of the HI bond.

$$\hat{B} = \frac{h}{8\pi^2 I \cdot c}$$

$$I = \frac{h}{8\pi^2 \hat{B} c} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8\pi^2 (6.67 \text{ cm}^{-1}) (3.00 \times 10^{10} \text{ cm/s})} = 4.19 \times 10^{-47} \text{ kg}\cdot\text{m}^2$$

$$\mu = \frac{1(127)}{1+127} \text{ amu} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times \frac{1 \text{ amu}}{6.022 \times 10^{23} \text{ molecules}} = 1.648 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2$$

$$r^2 = \frac{I}{\mu} = \frac{4.19 \times 10^{-47} \text{ kg}\cdot\text{m}^2}{1.648 \times 10^{-27} \text{ kg}} = 2.54 \times 10^{-20} \text{ m}^2$$

$$r = 1.59 \times 10^{-10} \text{ m}$$

Bond length = $1.59 \times 10^{-10} \text{ m}$

b) Using the HI rotational spectrum on the previous page, estimate the temperature of the sample.

x5

$$J_{\max} = 2 = \frac{1}{2} \left\{ \sqrt{\frac{2k_B T}{hc\tilde{B}}} - 1 \right\}$$

$$4 + 1 = \sqrt{\frac{2k_B T}{hc\tilde{B}}}$$

$$\frac{25 \cdot hc\tilde{B}}{2k_B} = T = \frac{25 (6.626 \times 10^{-34} \text{ J}\cdot\text{s}) (3.00 \times 10^{10} \text{ cm}^{-1}) (6.67 \text{ cm}^{-1})}{2 (1.38 \times 10^{-23} \text{ J/K})}$$

$$= 120 \text{ K}$$

+5
~~10~~

Temperature = 120 K

c) Briefly describe what happens to the HI molecules when the probing radiation excites them from the J=1 to J=2 state?

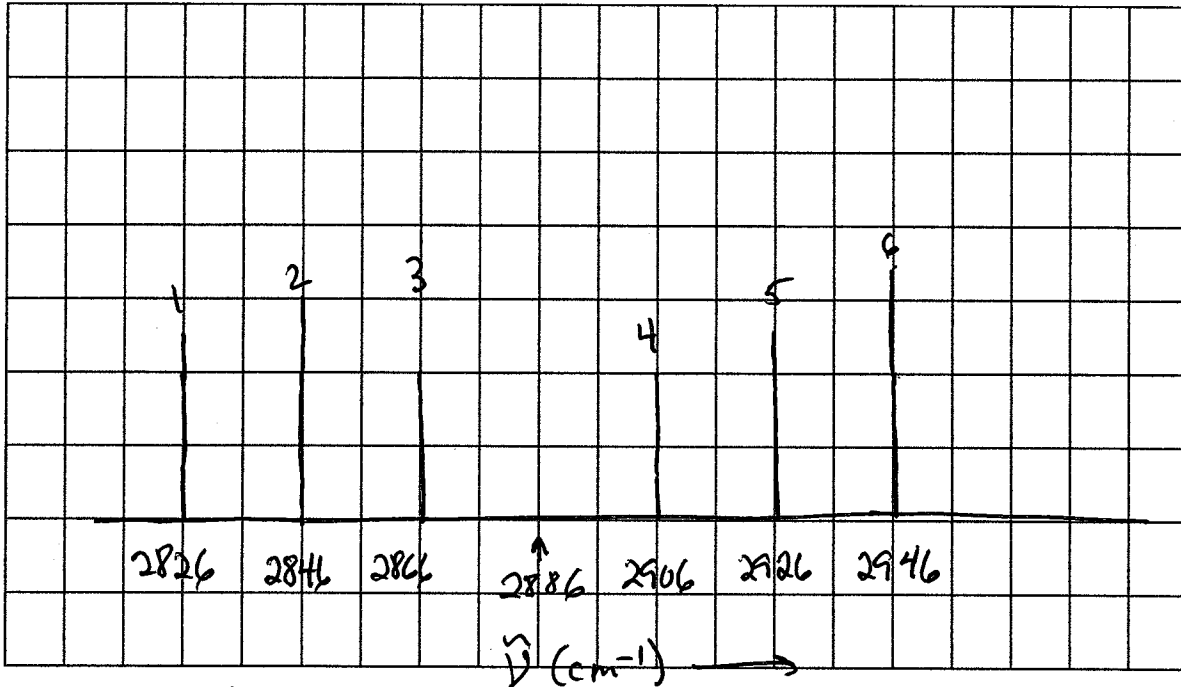
+5

→ they spin faster

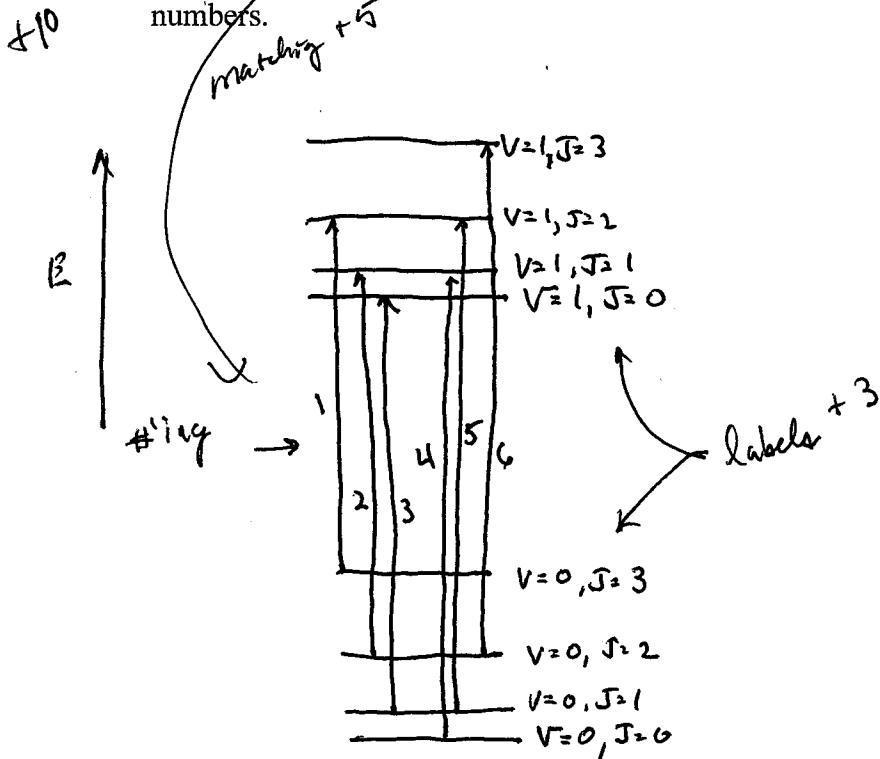
$$E_J = \frac{1}{2} I \omega^2$$

↑ ↑ ↘
const rotational frequency

3. (20 points) a) Draw the IR spectrum of $^1\text{H}-^{35}\text{Cl}$ gas taking the fundamental vibrational frequency to be 2886.0 cm^{-1} and the rotational constant to be 10.0 cm^{-1} . Label the frequency axis with the peak positions of the first 3 transitions in the P- and R-branches. You can show the absorbance lines in your drawing using "sticks" or vertical lines. For the purpose of this drawing you can make the sticks the same length.



b) Construct an energy level diagram that illustrates the six transitions shown in the above IR spectrum. Use numbers to label the transitions and their corresponding peaks in the stick spectrum that you drew for part a. Label the energy levels with the appropriate quantum numbers.



4. (10 points) Derive an expression for the classical limits of bond stretching and bond compression for a harmonic oscillator in the $v = 10$ vibrational energy state.

$$E_v = (v + \frac{1}{2}) \hbar \omega = 10.5 \hbar \omega$$

if all of the energy is potential energy; the classical value is $V = \frac{kx^2}{2}$, where x is the displacement from equilibrium.

$$10.5 \hbar \omega = \frac{1}{2} kx^2 \quad \Leftarrow \quad \pm 5$$

$$\frac{21 \hbar \omega}{k} = x^2$$

$$x^2 = \frac{21 \hbar \cdot \sqrt{\frac{k}{\mu}}}{k} = \frac{21 \hbar}{\sqrt{k\mu}} = \frac{21}{\alpha} \quad \text{when } \alpha = \frac{\sqrt{k\mu}}{\hbar}$$

$$x = \pm \sqrt{\frac{21}{\alpha}}$$

± 5 .

x =

$$\text{stretching} = +\sqrt{\frac{21}{\alpha}}$$

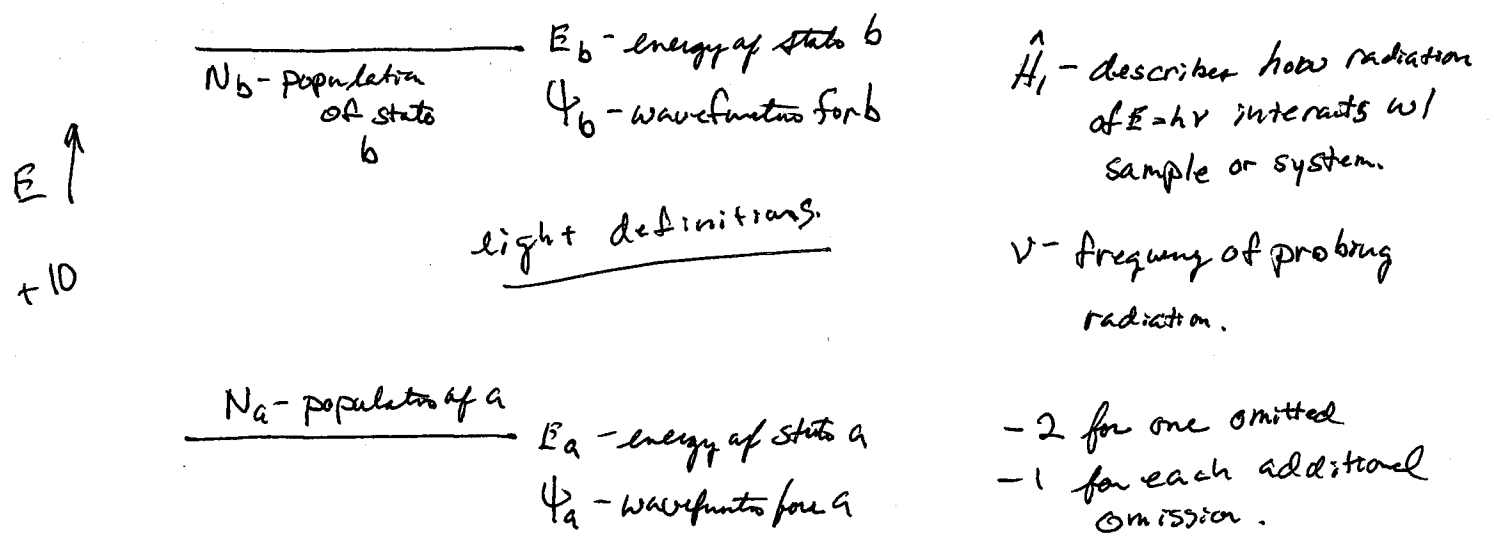
$$\text{compression} = -\sqrt{\frac{21}{\alpha}}$$

20
+5
20

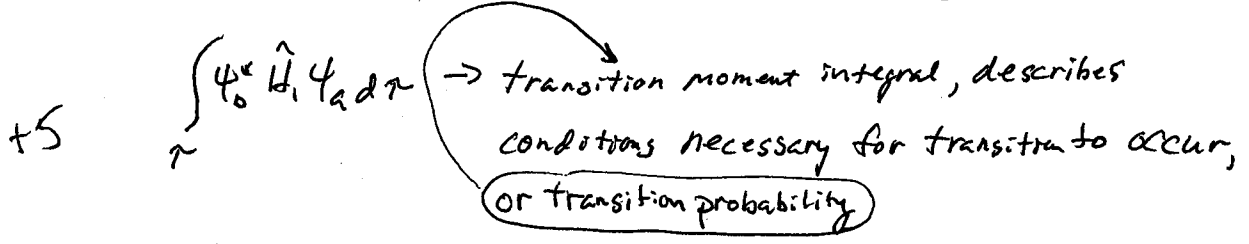
6. (15 points) In class we described the intensity of a spectroscopic transition as being proportional to

$$I(\nu) \propto (N_a - N_b) \left| \int \psi_b^* \hat{H}_1 \psi_a d\tau \right|^2 \delta(E_b - E_a - h\nu)$$

a) Define the terms in the above equation. ($N_a, N_b, \psi_a, \psi_b, \hat{H}_1, E_a, E_b, \nu$) A drawing may help you with your definitions.



b) What is the physical significance of the integral in the above expression?



c) What is the purpose of the delta function at the end of the expression?

