

CHEM 372 Rybolt Spring 2009 Exam 2 NAME KEY

Draw a CIRCLE around your final answer if math or derivation done. Clearly identify the quantity you are reporting and include the units if it is a numerical answer. Present your work neatly and in order beneath each question. Staple the requested homework sheets (in order) to the back of this exam in the extreme left hand corner. Be sure to answer only the specific question that is asked.

$R = 8.31 \text{ (J/ K mol)}$      $R = 0.08206 \text{ (L atm/ K mol)}$      $N_A = 6.02 \times 10^{23}$      $h = 6.63 \times 10^{-34} \text{ J s}$      $c = 3.0 \times 10^8 \text{ m/s}$   
 $k = 1.38 \times 10^{-23}$      $1 \text{ atm} = 760 \text{ torr} = 1.01 \times 10^5 \text{ (N/ m}^2\text{)} = 1.01 \text{ bar} = 101 \text{ kPa}$

---

1) Identify the point group for  $\text{PCl}_3\text{F}_2$

$D_{3h}$

2) Identify the point group for CO

$C_{\infty v}$

3) Identify the point group for ozone  $\text{O}_3$  (bent molecule like water)

$C_{2v}$

4) NASA is developing a space probe that will land on the surface Venus and wants to know if you would recommend the use of infrared or Raman spectroscopy to determine the possible presence of  $\text{Cl}_2$  gas on the surface. Give your answer and explain your choice.

Raman because  $\text{Cl}_2$  is not active in IR

5) How many vibrational modes would you expect for benzene  $\text{C}_6\text{H}_6$ ?

$$3N - 6 = 3(12) - 6 = 30$$

6) Draw lines from left to right to match the following types of energy with typical transition energies

electronic	<del>3000 <math>\text{cm}^{-1}</math></del>
vibrational	<del>6 <math>\text{cm}^{-1}</math></del>
rotational	<del>30,000 <math>\text{cm}^{-1}</math></del>

7) Indicate for each of the changes below whether it would have the affect of broadening or narrowing a spectral line

decrease temperature -- narrow

decrease pressure -- narrow

8) Recall  $E_J = J(J+1) \frac{h^2}{8\pi^2 I} = J(J+1)hcB$ . If the following lines were observed for a microwave rotational spectrum:  $12 \text{ cm}^{-1}$   $24 \text{ cm}^{-1}$   $36 \text{ cm}^{-1}$ , then  $B = \underline{\quad} \text{ cm}^{-1}$ .

$$12 \text{ cm}^{-1} = 2B$$

$$\boxed{6 \text{ cm}^{-1} = B}$$

9) Based on the above information find the moment of inertia,  $I$ , for the molecule studied in question 8.

$$hcB = \frac{h^2}{8\pi^2 I}$$

$$I = \frac{h^2}{hcB 8\pi^2}$$

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

$$6 \text{ cm}^{-1} \left( \frac{100 \text{ cm}}{\text{m}} \right)$$

$$I = \frac{6.63 \times 10^{-34} \text{ Js}}{(78.95) \left( 3.0 \times 10^8 \frac{\text{m}}{\text{s}} \right) (600 \text{ m}^{-1})}$$

$$= \boxed{4.66 \times 10^{-47} \text{ Js}^2}$$

10) Explain the difference between vibrational energy spacing in the Morse potential and the simple harmonic oscillator SHO. Explain in words with no graph and no equations.

SHO spacing remains constant as you go to higher energy levels, whereas Morse potential spacing between adjacent levels decreases as you go to higher levels.

11) If the vibrational frequency of HCl is  $9 \times 10^{13} \text{ s}^{-1}$  then the vibrational frequency of TCl is  $\underline{\quad} \text{ s}^{-1}$ . Assume the reduced mass is simply the mass of the lighter atom (H 1.0 and tritium T 3.0 amu/atom) and derive the simplest symbolic solution first to save time and avoid complicated calculations.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$\frac{\nu_T}{\nu_H} = \sqrt{\frac{m_H}{m_T}}$$

$$\frac{\nu_T}{\nu_H} = \frac{\frac{1}{2\pi} \sqrt{\frac{k}{m_T}}}{\frac{1}{2\pi} \sqrt{\frac{k}{m_H}}}$$

$$\nu_T = \nu_H \sqrt{\frac{1}{3}}$$

$$\nu_T = (9 \times 10^{13} \text{ s}^{-1}) (.577)$$

$$\boxed{\nu_T = 5.2 \times 10^{13} \text{ s}^{-1}}$$

12) Draw a diagram which illustrates a population inversion necessary in the operation of a laser.

0000000000

higher population  
in upper energy state

00

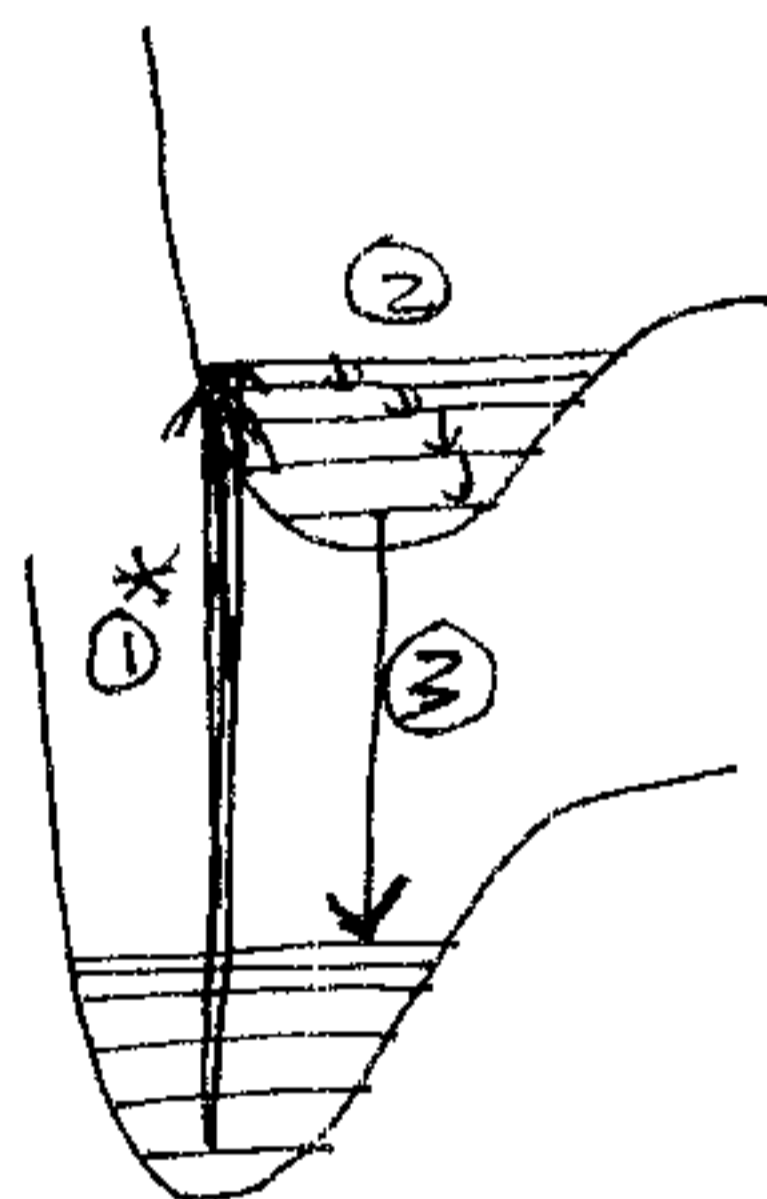
13) What is the Born-Oppenheimer Approximation?

Electronic motion is so much faster than motion of nuclei that we (B-O approx) assume nuclei are in fixed position while electron transition occurs

14) A PES experiment for Helium gives two peaks. The difference in energy value between these two peaks has what connection to the energy of  $\sigma^*$  and  $\sigma$  in the He molecular orbital diagram.

Difference in energy between peaks is equal to energy differences between  $\sigma^*$  and  $\sigma$ .  
 (Being able to do spt would require e in  $\sigma^*$  orbital)

15) Draw a diagram and label the three key steps that illustrate the transitions associated with the process of Fluorescence. Show vibrational and electronic levels.



- ① absorption of light
- ② radiationless decay
- ③ emission of light

\* note Born-Oppenheimer approximation in that nuclei are same distance apart

16) The absorbance of light is 3.3 for 1cm path length of a compound with an extinction coefficient of 250 (L/mol cm). What is the %transmittance (%T)?

$$A = -\log(T)$$

$$A = 2 - \log(\%T)$$

$$A = \epsilon l c$$

$$T = 10^{-A}$$

$$= 10^{-3.3}$$

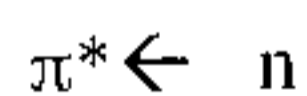
$$T = 0.0050$$

Fraction

$$\%T = 0.050\%$$

percent

17) The transition responsible for uv/vis absorbance associated with a double bond C=C is



18) Which of the following molecules has 3 different moments of inertia  $I_x$ ,  $I_y$ , and  $I_z$

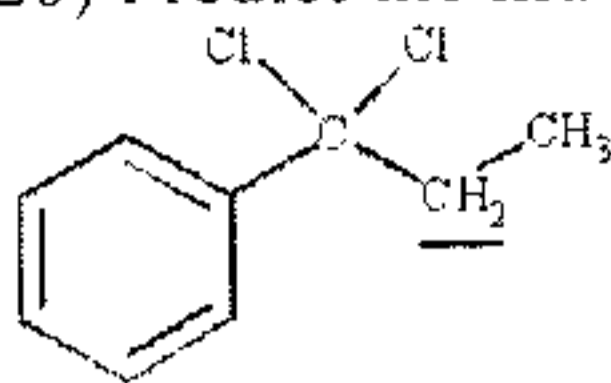
ammonia

carbon monoxide

water

19) Symbolically we can think of a FID as a plot of:  $S(t)$   $I(\nu)$   $S(\lambda)$   $I(E)$

20) Predict the multiplicity of the proton NMR signal for the hydrogens underlined in the compound below



singlet doublet triplet quartet quintet

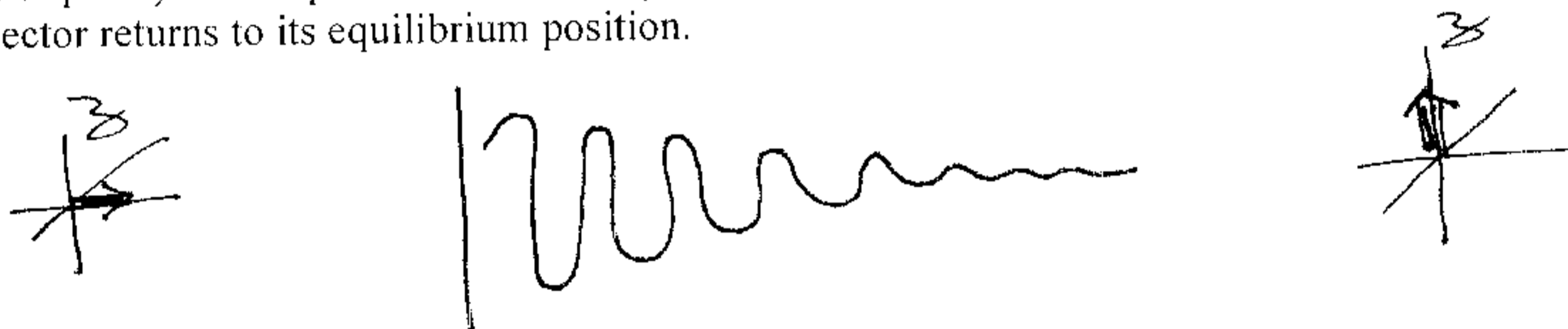
And draw the relative heights of lines that you would observe for the lines for these CH<sub>2</sub> hydrogens.



21) Why are NMR spectra reported relative to reference like TMS instead of just giving absolute resonance frequency or wavelength as is done in uv/vis spectroscopy.

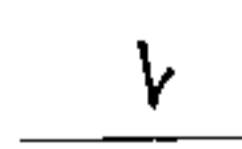
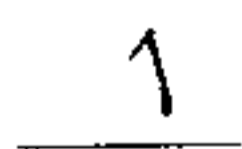
The resonance frequency is proportional to magnetic field strength so to create instrument independent spectra it is necessary to use a reference transition and calculate ppm shift.

22) In NMR if a radio frequency pulse is applied that causes the magnetization vector of to go onto the xy plane (90° pulse) draw a plot of how the magnitude of this vector along the y axis changes with time as this composite vector returns to its equilibrium position.

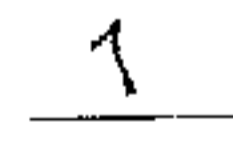
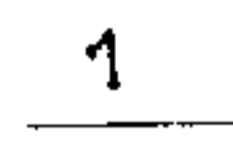


23) Phosphorescence involves intersystem crossing from singlet to triplet state. Draw below using arrows below to represent one electron in each of two different orbitals to give a

singlet



and triplet state



24) Attach Homework 13-

25) Attach Homework 14-

26) Attach Homework 15-

Attach seminar or paper summary after homework if you are doing