

Solutions

Name _____

CHM 3411, Dr. Chatfield, April 20, 2018

Exam 3

There are 5 questions; each is worth 10 points. You may use a calculator (non-graphing), but nothing else. If you need extra room, use the back of exam pages and direct the grader where to look. You may also use scratch paper, but **put all final answers on the exam itself and attach any scratch paper with work the grader should read. Read all problems carefully.** Set up problems methodically, show your work, and be neat. Partial credit will be given when it is possible for me to follow your work. If you are having trouble with a problem, go on to the next and come back.

GOOD LUCK!

Constants:

$$a_0 = 52.9 \text{ pm}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg}$$

$$amu = m_u = 1.6605 \times 10^{-27} \text{ kg}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$$

$$\hbar = \frac{h}{2\pi}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$c = 3.00 \times 10^8 \text{ m s}^{-1}$$

$$1 \text{ eV} = 8065.5 \text{ cm}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$\tilde{R}_\infty = 1.097 \times 10^5 \text{ cm}^{-1}$$

Equations (others are given directly in exam questions):

$$\lambda = \frac{h}{p}$$

$$\Delta x \Delta p \geq \frac{\hbar}{2\pi}$$

$$\lambda v = c \quad \tilde{\nu} = \frac{1}{\lambda}$$

$$\Delta E = hv = \hbar\omega$$

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V}(x)$$

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + \hat{V}(x)$$

$$E = \frac{l(l+1)\hbar^2}{2I}$$

$$E_n = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \cdot \frac{Z^2}{n^2} = -hc\tilde{R}_\infty \cdot \frac{Z^2}{n^2}$$

$$d\tau = r^2 \sin\theta dr d\theta d\phi$$

$$P(r) = 4\pi r^2 \psi^2 \quad P(r) = r^2 \mathcal{R}^2(r)$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$E_J = \frac{hc}{\lambda} B J(J+1)$$

$$E_v = \frac{hc}{\lambda} \left(v + \frac{1}{2} \right) \tilde{\nu} - x_e \tilde{\nu}$$

$$x_e = \frac{\tilde{\nu}}{4\tilde{D}_e}$$

$$\tilde{B} = \frac{h}{4\pi c I}$$

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

1. Short answer. Do brief calculations to answer the questions below.

(a) The rotation constant \tilde{B} for $^{14}\text{N}^{16}\text{O}$ is 1.67 cm^{-1} . Determine the equilibrium bond distance, R_e .

$$\tilde{B} = \frac{h}{4\pi c I} \quad I = \frac{h}{4\pi c \tilde{B}} = 1.681 \times 10^{-46} \frac{\text{J s}^2}{\text{kg m}^2}$$

$$\mu = \frac{14.16}{14+16} m_u = 1.23984 \times 10^{-26} \text{ kg}$$

$$\uparrow$$

$$1.6605 \times 10^{-27} \text{ kg}$$

$$I = \mu R_e^2$$

$$R_e = \sqrt{\frac{I}{\mu}} = 1.164 \times 10^{-10} \text{ m} = 1.164 \text{ \AA}$$

(b) The fundamental frequency $\tilde{\nu}$ for $^{14}\text{N}^{16}\text{O}$ is 1904.2 cm^{-1} . Determine the force constant, k .

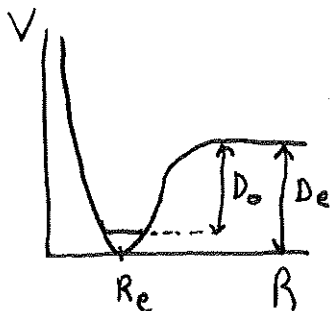
$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \Rightarrow k = 4\pi^2 c^2 \tilde{\nu}^2 \mu = 1,587 \text{ kg s}^{-2}$$

(c) The anharmonicity constant x_e for $^{14}\text{N}^{16}\text{O}$ is 0.00741. Determine the bond dissociation energy, D_0 , and the well depth, D_e , using appropriate approximations. (You may give D_0 and D_e in either units of energy or units of wavenumber, but you must be consistent.)

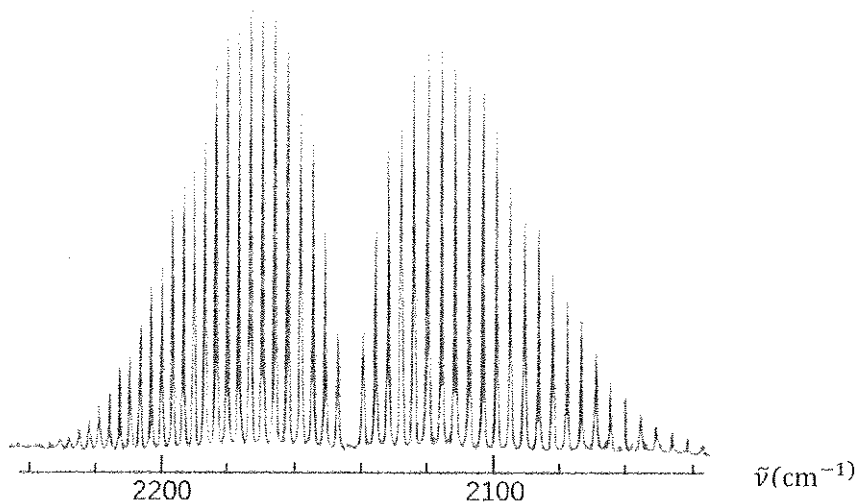
$$x_e = \frac{\tilde{\nu}}{4\tilde{D}_e} \Rightarrow \tilde{D}_e = \frac{\tilde{\nu}}{4x_e} = 64,244 \text{ cm}^{-1}$$

$$\tilde{D}_0 = \tilde{D}_e - \frac{1}{2}\tilde{\nu} = 63,292 \text{ cm}^{-1}$$

(d) Make a sketch of the potential energy surface (PES) for NO, showing R_e , D_0 and D_e . Be as complete as possible.



2. An IR (vibrational-rotational) spectrum of $^{12}\text{C}^{16}\text{O}$ is shown below.



(a) Determine the rotational constant, \tilde{B} , and the fundamental vibrational frequency, $\tilde{\nu}$, for $^{12}\text{C}^{16}\text{O}$. The frequencies of the first several peaks of the P and R branches are given below in cm^{-1} . (Use a simple approach. You do not need to do least-squares fitting.)

$$\Delta \tilde{\nu}_P = \Delta \tilde{\nu}_R = 2\tilde{B}$$

Using the first two $\tilde{\nu}_P$ values
for simplicity:

$$\tilde{B} = \frac{1}{2} (2165.9 - 2162.1)$$

$$= 1.9 \text{ cm}^{-1}$$

$$\tilde{\nu} = \frac{1}{2} (\tilde{\nu}_P(1) + \tilde{\nu}_R(0)) = 2169.8 \text{ cm}^{-1}$$

J	P	R
0		2173.7
1	2165.9	2177.5
2	2162.1	2181.4
3	2158.2	2185.2
4	2154.4	2189.1
5	2150.5	2193.0

(b) Determine the temperature at which the spectrum was taken. Given: The population of a rotational level is proportional to $g_J e^{-E_J/kT}$ where g_J is the degeneracy.

$g_J = 2J+1$ for linear rotor (for given J , there are degenerate M_J states; $M_J = 0, \pm 1, \pm 2, \dots, \pm J$
total # = $2J+1$)

$$P(J) \propto (2J+1) e^{-hc\tilde{B}J(J+1)/kT}$$

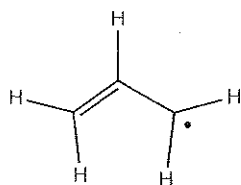
$$\text{Max is at: } 0 = \frac{dP}{dJ} = \left[2 - \frac{hc\tilde{B}}{kT} (2J+1)^2 \right] e^{-\tilde{B}J(J+1)/kT}$$

$$J_{\text{max}} = \left(\frac{kT}{2hc\tilde{B}} \right)^{1/2} - \frac{1}{2}$$

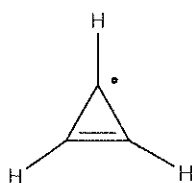
$$T = \left(J_{\text{max}} + \frac{1}{2} \right)^2 \cdot \frac{2hc\tilde{B}}{k} = 230 \text{ K}$$

$J_{\text{max}} = J$ value of
highest peak (either
branch) = 6

3. Below are Lewis structures for the cyclopropenyl radical and the allyl radical. We solved the Hückel MO equations for the allyl radical in Problem Set 10. In this problem, you will compare the energies orbitals of the π -electron systems of the two species.



allyl radical



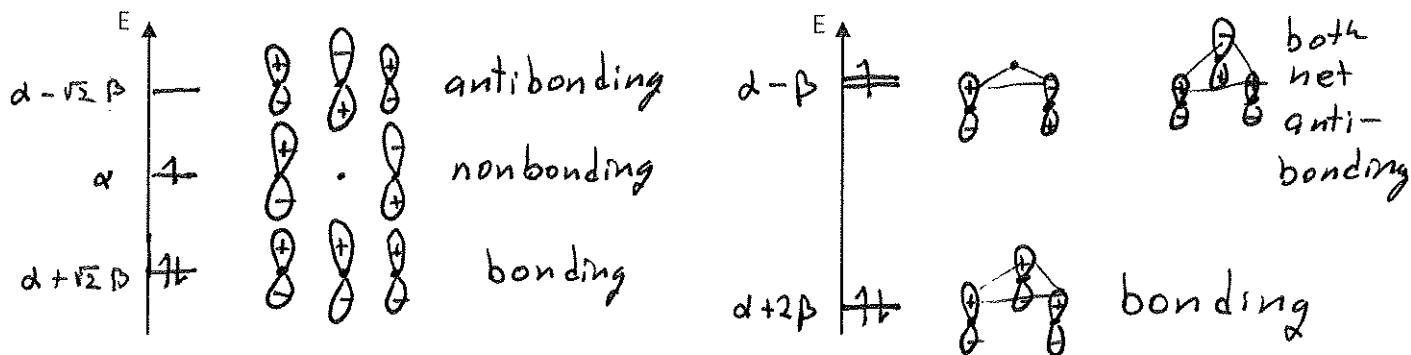
cyclopropenyl radical

- (a) Write the Hückel matrix equation the cyclopropenyl radical (do not solve it).

$$\begin{pmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

- (b) The energies and AO coefficients for the MOs of each species obtained from Hückel calculations are given below. For each species, draw an MO energy level diagram (using the energy axes shown) and draw pictures of the MOs. Recall that $\alpha < 0$ and $\beta < 0$.

Allyl radical:	E	c_1	c_2	c_3	Cyclopropenyl radical:	E	c_1	c_2	c_3
	α	$\frac{1}{\sqrt{2}}$	0	$\frac{-1}{\sqrt{2}}$		$\alpha + 2\beta$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$
	$\alpha + \sqrt{2}\beta$	$\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$		$\alpha - \beta$	$\frac{1}{\sqrt{2}}$	0	$\frac{-1}{\sqrt{2}}$
	$\alpha - \sqrt{2}\beta$	$\frac{1}{2}$	$\frac{-1}{\sqrt{2}}$	$\frac{1}{2}$		$\alpha - \beta$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$



- (c) Determine the π -electron binding energy for each species. ^{2.82}

$$\text{allyl radical: } 2(\alpha + \sqrt{2}\beta) + \alpha = 3\alpha + 2\sqrt{2}\beta = E_{\pi}$$

$$\text{cyclopropenyl radical: } 2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta = E_{\pi}$$

- (d) Determine which species has the more stable π -electron system and discuss why (refer to your pictures of the MOs).

cyclopropenyl radical is more stable (smaller E_{π})

Mainly b/c the bonding orbital is more bonding than in the allyl radical (3 overlaps vs 2)

4. Short answer.

a. Order the following computational methods in order of accuracy from 1 (least accurate) to 4 (most accurate). Simply place a numeral in front of each method.

2 HF
 3 or 4 DFT
 1 Semi-empirical
 3 or 4 MP2

DFT & MP2 similar

b. Which of the following computational methods are variational, and which are ab initio (the two categories are not mutually exclusive). Place a check in the appropriate column for each.

	<u>variational</u>	<u>ab initio</u>
HF	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
DFT	<input type="checkbox"/>	<input type="checkbox"/>
Molecular Mechanics	<input type="checkbox"/>	<input type="checkbox"/>
MP2	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
Semi-empirical	<input checked="" type="checkbox"/>	<input type="checkbox"/>

c. Explain what a 6-31G* basis set is (i.e. explain the meaning of the notation). Hint: think about core vs valence electrons and about STOs and GTOs.

core electrons: 1 STO expressed as sum of 6 GTOs
 valence .. { 1 STO 3 .. (one zeta value)
 { 1 STO single GTO (different zeta ..)
 * = 1 set of polarization functions on heavy atoms (non-hydrogens)
 ↑ = 3d GTOs for 2nd-row atoms

d. State what experimental data (i) Pauling electronegativities and (ii) Mulliken electronegativities are based on.

Pauling:

based on bond lengths

Mulliken:

based on ionization energy and electron affinity

5. Short answer

- (a) State the gross selection rule for microwave spectroscopy, and circle each molecule that is microwave active.

Definition: *molecule has permanent dipole moment*

Molecules: (a) N_2 (b) CCl_4 (c) SO_2 (nonlinear) (d) HF

- (b) State the gross selection rule for rotational Raman spectroscopy, and circle each molecule that is rotational Raman active.

Definition: *molecule is anisotropically polarizable*

Molecules: (a) N_2 (b) CCl_4 (c) SO_2 (d) HF

- (c) Give the number of vibrational modes for each molecule:

CH_3CH_3 (ethane) 18 $\overset{\#atoms=8}{\downarrow} 3N-6$ (nonlinear)

HCN 4 $3N-5$ (linear)


H_2O 3 $3N-6$ (nonlinear)

- (d) (i) State the gross selection rule for IR spectroscopy (i.e. for vibrational transitions during absorption or emission of radiation); (ii) Draw the vibrational modes for CO_2 ; (iii) Identify each mode as IR active or IR inactive.

Definition: *Dipole moment must change during vibration*

Modes of CO_2 (draw):

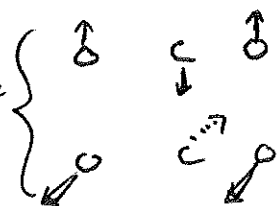
IR active or inactive (each mode)?

 sym. stretch

NO

 asym. ..

YES

degenerate {  bending

YES