CHEM*2070 Test #1 Feb. 8, 2011

Name: ______________________________ Student ID:____________________

Instructions:
- only answers in boxes will be marked. Use back of each page for scrap paper.
- units are *required* for *answers* only.
- please do *not* use pencil or red pen.

h = 6.62608 H 10^{-34} Js

R = 8.31451 JK^{-1} mol^{-1}

k_B = 1.38066 H 10^{-23} JK^{-1}

c = 2.9979 H 10^8 ms^{-1} = 2.9979 H 10^{10} cm s^{-1}

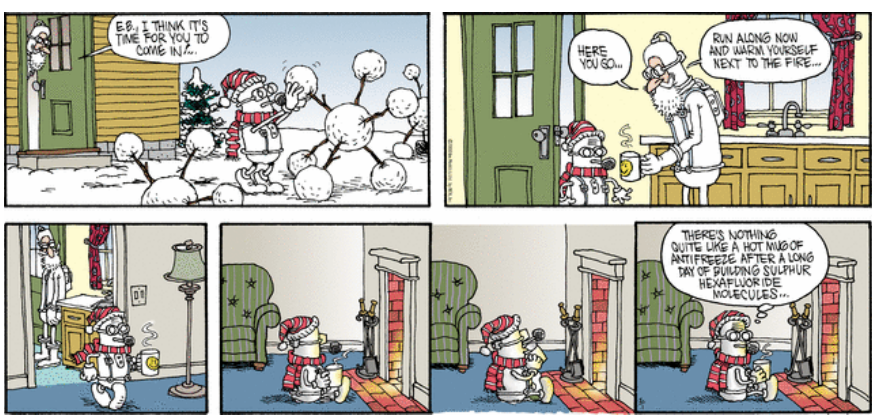
m_e = 9.10939 H 10^{-31} kg

N_A = 6.02214 H 10^{23} molecules

Q1	/5
Q2	/9
Q3	/6
Q4	/7
Q5	/6
Total	/33
	/

$$\bar{D} = \frac{h^3}{32\pi^4 m^2 r^6 k\bar{c}} \qquad \frac{n_J}{n_0} = (2J+1)\exp\left[\frac{-BhJ(J+1)}{kT}\right]$$

$$J_{\max} = \left(\frac{kT}{2hc\bar{B}}\right)^{1/2} - 1/2 \qquad \mu_{AB} = \frac{M_A M_B}{(M_A + M_B)1000 N_A}$$



Masses and natural abundances of selected nuclides

Nuclide		m/u	Abundance/%
H	^{1}H	1.0078	99.985
	^{2}H	2.0140	0.015
He	^{3}He	3.0160	0.000 13
	^{4}He	4.0026	100
Li	^{6}Li	6.0151	7.42
	^{7}Li	7.0160	92.58
B	^{10}B	10.0129	19.78
	^{11}B	11.0093	80.22
C	^{12}C	12*	98.89
	^{13}C	13.0034	1.11
N	^{14}N	14.0031	99.63
	^{15}N	15.0001	0.37
O	^{16}O	15.9949	99.76
	^{17}O	16.9991	0.037
	^{18}O	17.9992	0.204
F	^{19}F	18.9984	100
P	^{31}P	30.9738	100
S	^{32}S	31.9721	95.0
	^{33}S	32.9715	0.76
	^{34}S	33.9679	4.22
Cl	^{35}Cl	34.9688	75.53
	^{37}Cl	36.9651	24.4
Br	^{79}Br	78.9183	50.54
	^{81}Br	80.9163	49.46
I	^{127}I	126.9045	100

* Exact value.

1. Definitions.

Define the following terms as they apply to "Structure and Spectroscopy":
Note that an example is not a definition but can be used to illustrate a definition.
(maximum 2 sentences each; any more and you lose marks)

a) anti-Stokes lines:

Raman spectral lines where molecules lose rotational energy and light gains energy

b) Light: (defined in lecture #2 on the black board)

Oscillating electric and magnetic fields which are ⊥ to each other and travel in a direction ⊥ to the fields

c) Spherical top molecule:

molecule where
i) all moments of intertia, I, are the same
ii) molecule with Td, Oh or higher symmetry

d) Anisotropically polarizable molecule:

Polarizable differently in different directions.

e) Dihedral angle:

Not explicitly defined in class. Will accept anything that makes sense.

[5 Marks]

3

2. Short Answer:

a) Your body emits light with a maximum intensity at around 1070 wavenumbers. In what region of the electromagnetic spectrum would you look for this light?

Infrared (IR)

b) What 3 important interactions determine the conformation of a molecule?

i) steric repulsion

ii) hydrogen bonding

iii) conjugation / electron delocalization / resonance stabilization } any one is ok.

c) What physical property is required in order to see a rotational microwave spectrum of a molecule? Give an example of such a molecule.

permanent dipole moment / many examples

d) What physical property is required in order to see a rotational Raman spectrum of a molecule? Give an example of a molecule which shows a Raman, but not a microwave spectrum.

anisotropic polarizability / any molecule with no dipole which is not Td or Oh symmetry is acceptable

e) Give an example of a molecule which will not show a microwave or Raman spectrum.

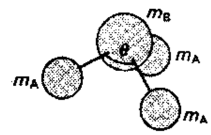
any molecule with Td or Oh symmetry is acceptable

[9 Marks]

4

3. Consider a molecule of the type BA_3. The moment of inertia for such a molecule is given as:

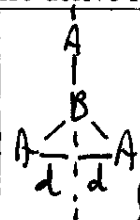
$$I_{\perp} = m_A r^2 (1 - \cos\theta) + \frac{m_A m_B}{m} r^2 (1 + 2\cos\theta)$$



a) Use this equation to obtain a simple equation for a planar BA_3 molecule. You will need this equation for part b) so if you don't know how to obtain it ask to have it given to you (you will lose 2 marks though). You can also derive $I_{\perp}$ using the method shown in class.

One way if $\theta = 120°$

$$I_{\perp} = \frac{3}{2} m_A r_{AB}^2$$



$I_{\perp} = (m_A)\, 2\, r_{AB}^2 \sin^2 60°$

or

$I_{\perp} = m_A (2)\, r_{AB}^2 \cos^2 30°$

$I_{\perp} = \frac{3}{2} m_A r_{AB}^2$

b) The rotational Raman spectrum of BF_3 is shown below. The spacing between the **R** lines is 0.6900 cm^{-1}. Calculate the B – F bond length, $\mathbf{r}_{BF}$. Hint: recall last year's midterm test.

Separation between R lines is $2\bar{B}$

$$\nu = 2\bar{B} = \frac{(2)h}{8\pi^2 c I} = \frac{(2)h(2)}{8\pi^2 c m_F r_{BF}^2} = \frac{h}{6\pi^2 c m_F r^2}$$

$$m_F = \frac{18.998 \text{ g/mol}}{(1000 \text{ g/kg})(N_A \text{ molecules/mol})}$$

$$r = \sqrt{\frac{(h)(1000)(6.02214 \times 10^{23})}{(6)(9.8296)(2.9979 \times 10^{10})(0.690)(18.998)}}$$

$= 1.305 \times 10^{-10}$ m

$r_{BF} = 1.305$ Å

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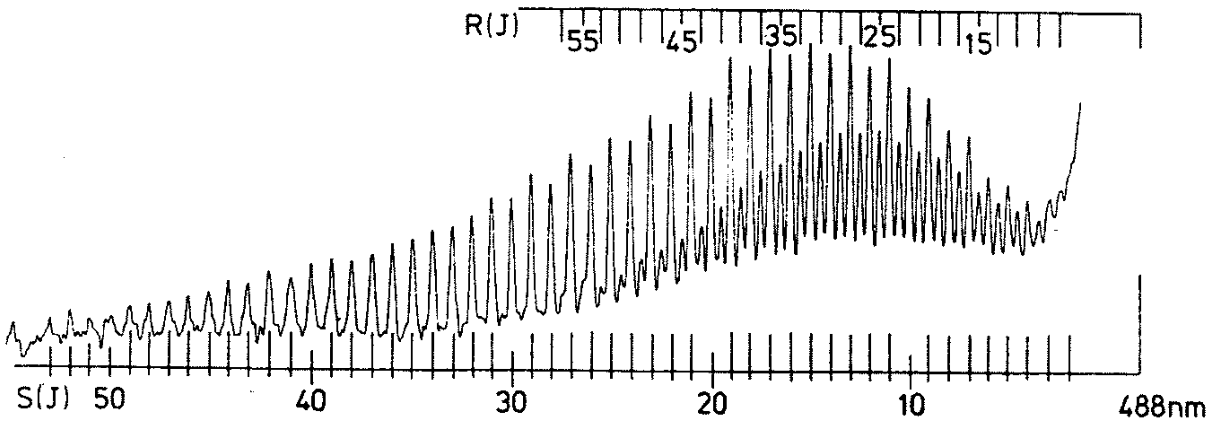
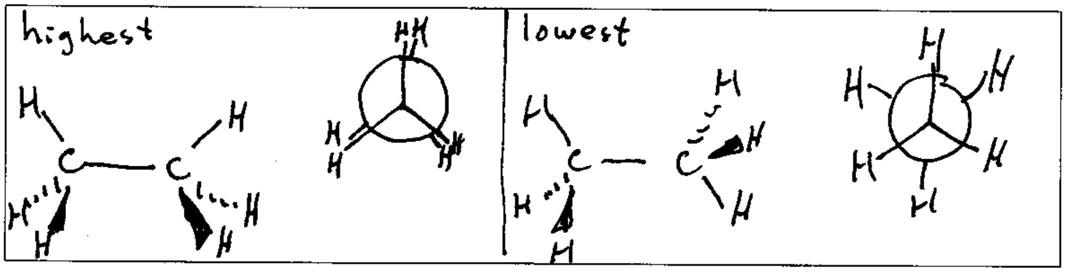


[6 Marks]

4. Consider the molecule CH_3CH_3.

a) Sketch what you think the highest and lowest energy conformations of the molecule should look like.



b) What are the geometric parameters that **completely** define the structure of this molecule? done in class for several molecules!

r_{CC}

r_{CH}

θ_{CCH}

ϕ_{HCCH}

6

c) Propose a logical set of isotopomers that one must measure in order to completely determine the structure of ethane.

$^{12}C^{1}H_3{}^{12}C^{1}H_3$
$^{12}C^{2}H_3{}^{12}C^{2}H_3$
$^{13}C^{1}H_3{}^{13}C^{1}H_3$
$^{13}C^{2}H_3{}^{13}C^{2}H_3$

- need 4 in principle
- these are the ones I did in class

- isotopic sustitution must not change the point group of the molecule (recall $CH_3C\equiv CCH_3$ example done in class)

d) What important assumption is made when determining such a structure by isotopic substitution? (Hint: recall PS#3, question #4).

isotopic substitution does not change the structure

[7 Marks]

5. a) What is the Doppler effect?

If a moving molecule emits light of a wavelength λ (frequency ν) and

i) the molecule is moving towards the detector, then the detector will measure light of smaller λ (the waves get compressed)

ii) the molecule is moving away from the detector, then the detector will measure light of longer λ (the waves get ~~compressed~~ stretched out).

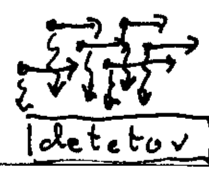
b) Explain how the Doppler Effect broadens the spectral lines in the spectrum of a gas phase sample of molecules.

In a real sample of gas phase molecules, the molecules are moving in every direction with a distribution of speeds. This will cause a spread, or distribution, of intensities, which we measure as linewidth.

c) How could one reduce the Doppler broadening?

i) cool the sample down to slow down the molecular speeds and narrow the distribution

ii) better yet, get the molecules to move in ~~one~~ the same direction and put the detetor ⊥ to this direction



[6 Marks]

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