Department of Chemistry
Cumulative Examinations
December 10, 2005

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% *would not* yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains ***five*** examinations.

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: ____________________
3) Print the question number you are answering.
4) Print the Exam Date.

Do not write your name anywhere on the examination booklet. Each exam will be scored anonymously. If you attempt more than one exam, *you must use a separate examination booklet for each examination*.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

PURDUE
UNIVERSITY

BioNanotechnology

1. Small molecules, DNA, RNA, and proteins all are potential building blocks for construction of nanostructures. Please compare these molecular systems for nanoconstruction in terms of their structure, specificity, synthesis, diversity, and stability. (30 points)

2. In your opinion, what molecular system is the most convenient system for assembly of sophisticated nanostructures? Please give your reason, and describe an example of sophisticated nanostructures assembled from this system. (20 points)

3. Mechanically active nanostructures/nanodevices are of particular interest of current nanotechnology. Please describe one rationally designed active nanostructure: structure, mechanism, and preparation. (30 points)

4. In many cases, self-assembled molecular nanostructures themselves do not have technologically useful functions. Please describe two potential strategies to introduce functions into such nanostructures? For each approach, please give one detailed example. (20 points)

Cumulative Examination in Biochemistry
December 10, 2005

Instructions. There are three questions, and the point totals are given by each question.

1. (40 pts)

(A) Both mass spectrometry and ^{13}C NMR spectroscopy show that the oxygen of hexanal undergoes rapid oxygen exchange when dissolved in ^{18}O-H_2O, particularly in dilute base. In contrast, the rate of ^{18}O exchange undergone by the aldohexose D-mannose in solution is orders of magnitude slower. Explain why.

(B) Chitin consists largely of β-1→4-linked N-acetylglucosamine and is one of the most abundant polysaccharides. Where does it most commonly occur in nature? Draw a clear Haworth representation of its structure.

(C) With the aid of appropriate structures, describe the distinctive structural features of glycogen that make it particularly suited to the rapid supply of energy in glycolysis.

(D) Several different lines of evidence reveal that the carbohydrates on N- and O-linked glycoproteins are very mobile. Describe several specific lines of evidence and briefly explain how they support such a conclusion.

2. (25 pts)

A purified oligosaccharide did not react in Tollen's or Fehling's tests. Among other spectral data, a ^{13}C resonance peak similar to that found for the C-1 of amylose was observed. Exhaustive methylation followed by acid hydrolysis yielded equivalent amounts of 2,3,4-tri-O-methylglucose, 1,3,4,6-tetra-O-methylfructose, and 2,3,4,6-tri-O-methylgalactose. Based on these data, propose a possible structure for the sugar. Give the name of the carbohydrate whose structure you have drawn. Does any structural ambiguity remain? Explain.

3. (35 pts)

You have the possibility of being put in charge of an important project at the NIH. New research has just identified a human leukemia-specific glycan motif. It is known that this motif binds specifically to a lectin that is reportedly obtainable from a fungus *Agrocybe cylindracea*. Write a detailed proposal in which you **set priorities** and **describe specific experimental procedures** that are designed to identify any and all human proteins that contain this motif.

Inorganic Cumulative Exam
December, 2005

A table of bond energies is attached.

A. Write the three most reasonable resonance structures for the thiocyanate ion, SCN^-.

B. Qualitatively evaluate the contribution of each resonance structure to the description of the bonding in SCN^- based on the information in the table below. Explain.

	S-C bond lengths (pm)	C-N bond lengths (pm)
SCN^-	165	117
single bond	181	147
double bond	155	128
triple bond		116

C. i Calculate the formal charges in each of your three resonance structures.

ii. Qualitatively evaluate the contribution of each resonance structure to the description of the bonding in SCN^- using these formal charges. Explain.

D. Pseudohalogens are produced by oxidizing pseudohalides under mild oxidizing conditions. For example, SCN^- is oxidized to $(SCN)_2$ by MnO_2 in acidic solution. However, it has not been possible to oxidize axide (N_3^-, a pseudohalide anion) to N_6.

i. Propose an electronic structure (Lewis structure) for a linear N_6 molecule.

ii. Explain why this molecule has not been isolated.

E. i. The table of bond energies contains a value for a P-P single bond but no value for a P-P triple bond. Calculate the bond energy of a phosphorus-phosphorus triple bond given

$$P_4(g) \rightarrow 2\,P_2(g) \qquad \Delta H = 217\ \text{kJ mol}^{-1}.$$

ii. Explain why this triple bond in much weaker than the triple bond in N_2.

Average Bond Energies (kJ/mol)

Bond	Energy	Bond	Energy	Bond	Energy	Bond	Energy
Single Bonds							
H—H	432	N—H	391	Si—H	323	S—H	347
H—F	565	N—N	160	Si—Si	226	S—S	266
H—Cl	427	N—P	209	Si—O	368	S—F	327
H—Br	363	N—O	201	Si—S	226	S—Cl	271
H—I	295	N—F	272	Si—F	565	S—Br	218
		N—Cl	200	Si—Cl	381	S—I	~170
C—H	413	N—Br	243	Si—Br	310		
C—C	347	N—I	159	Si—I	234	F—F	159
C—Si	301					F—Cl	193
C—N	305	O—H	467	P—H	320	F—Br	212
C—O	358	O—P	351	P—Si	213	F—I	263
C—P	264	O—O	204	P—P	200	Cl—Cl	243
C—S	259	O—S	265	P—F	490	Cl—Br	215
C—F	453	O—F	190	P—Cl	331	Cl—I	208
C—Cl	339	O—Cl	203	P—Br	272	Br—Br	193
C—Br	276	O—Br	234	P—I	184	Br—I	175
C—I	216	O—I	234			I—I	151
Multiple Bonds							
C=C	614	N=N	418	C≡C	839	N≡N	945
C=N	615	N=O	607	C≡N	891		
C=O	745	O_2	498	C≡O	1070		

ORGANIC December 10, 2005
(4 pages)

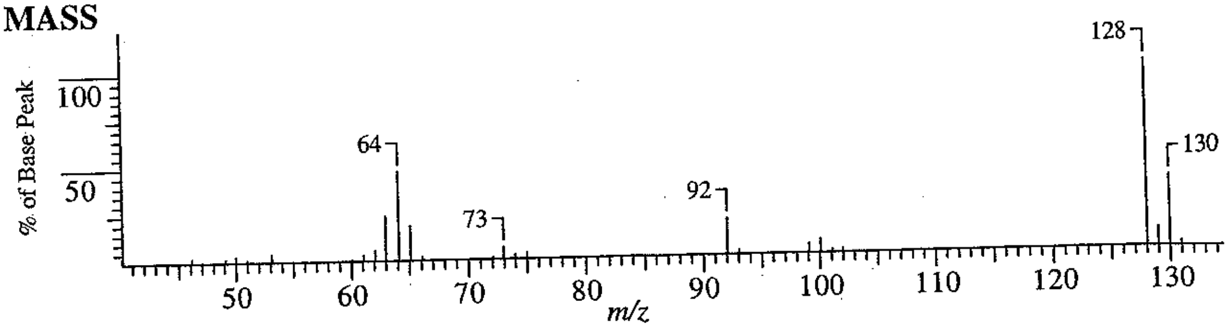
1. (30 pts) Provide the following information

(a) The C_1-C_4 distance in butadiene in its most stable conformation.
(b) The bond dissociation energy of the weakest bond in benzene.
(c) The boiling point of acetone.
(d) The ^{13}C NMR spectrum of $CDCl_3$
(e) A Newman projection of ethylene glycol.
(f) cis 1,3-dimethylcyclohexane in its most stable conformation.
(g) The structure of D-Glucose
(h) An energy diagram for the bond rotation in ethane.
(i) The pK_a values and isoelectric point of glycine
(j) An aromatic heterocycle

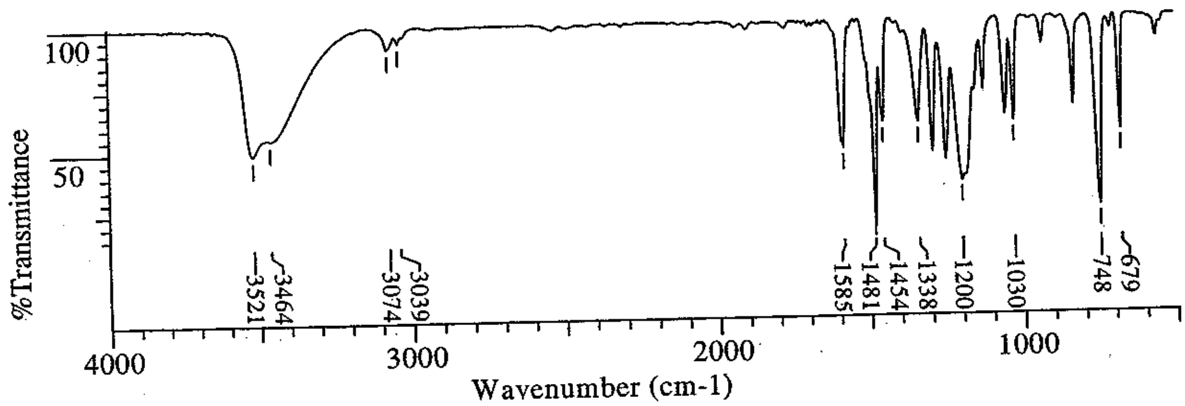
2. (20pts) The Nobel Prize in Chemistry for 2005 was awarded this week.
(a) Name the three recipients
(b) The following terms/phrases were used in the award document.
Explain by use of an example what the terms mean.
 (i) The metathesis of terminal alkenes
 (ii) Metal-alkylidene complexes
 (iii) Ru-catalyzed ROMP of cycloolefins
 (iv) What is the most common use of this chemistry in Organic Synthesis

3. (25 pts) Determine the structure of the compound whose spectra are shown below. Briefly show your reasoning. Partial credit for partial structures.

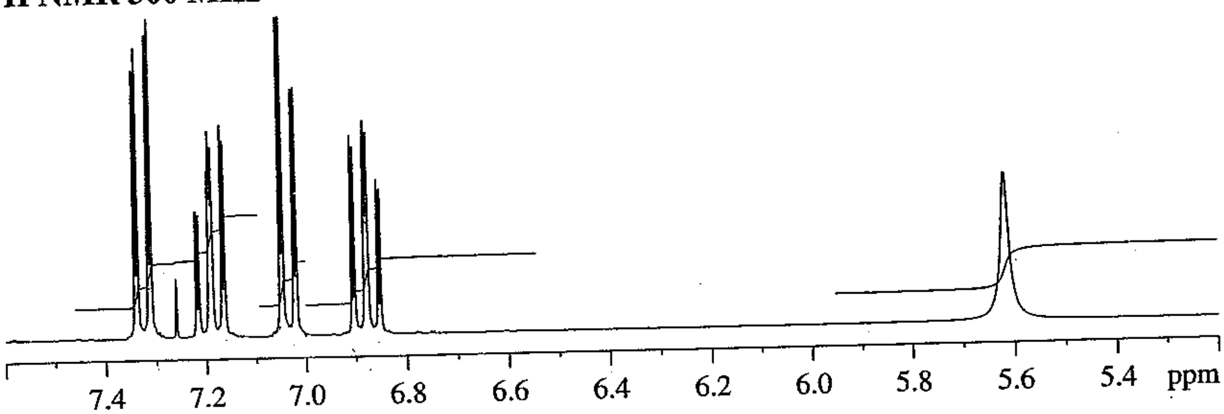
MASS



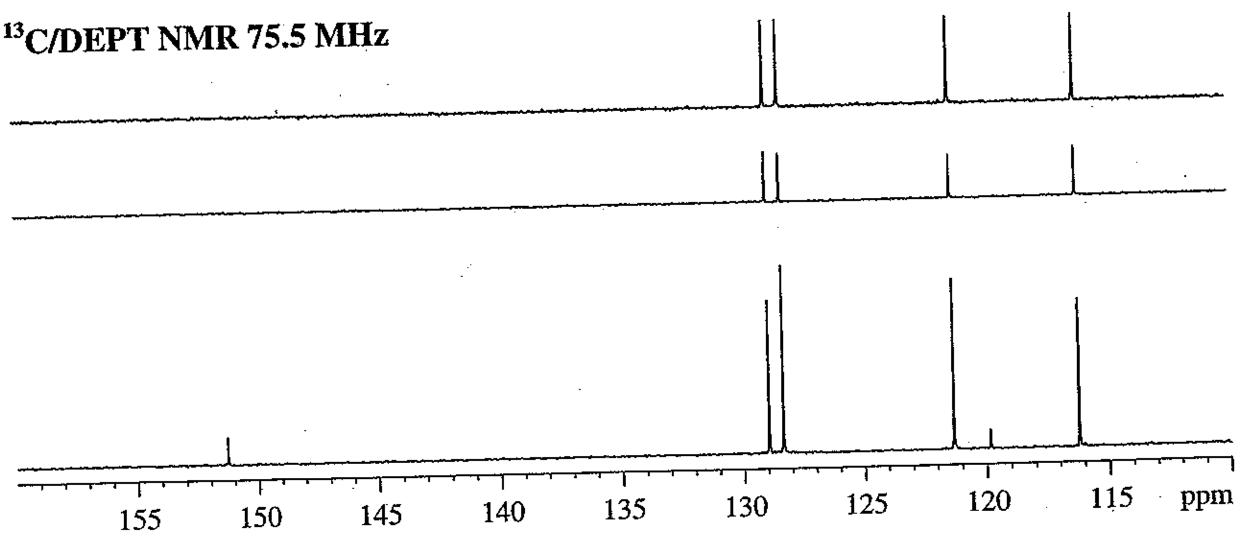
IR



^{1}H NMR 300 MHz

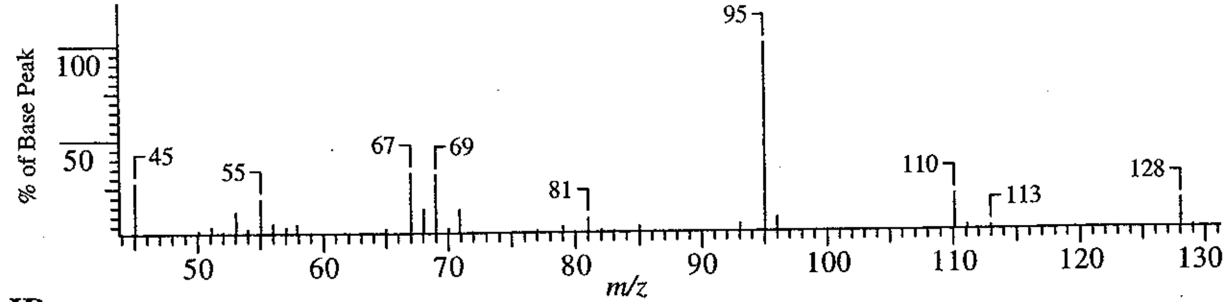


^{13}C/DEPT NMR 75.5 MHz



4. (25 pts) Determine the structure of the compound whose spectra are shown below. Briefly show your reasoning. Partial credit for partial structures.
Note: There are 2 pages of spectra for this unknown.

MASS



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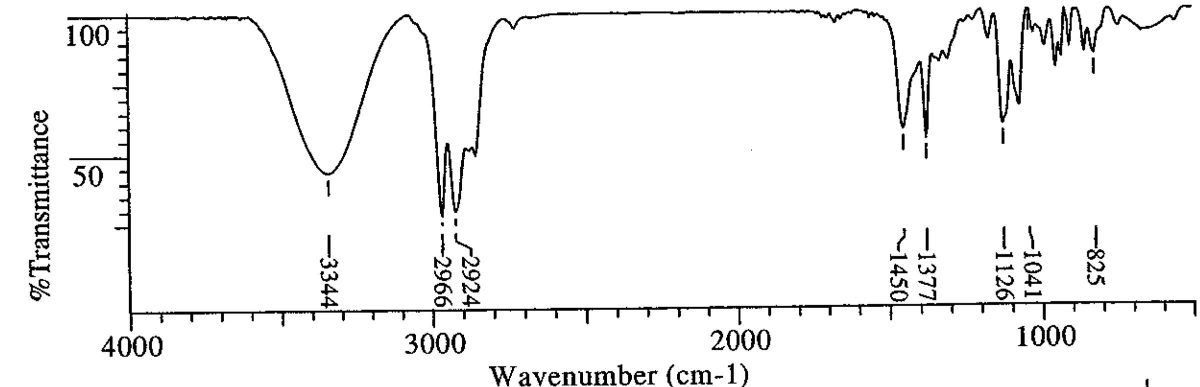
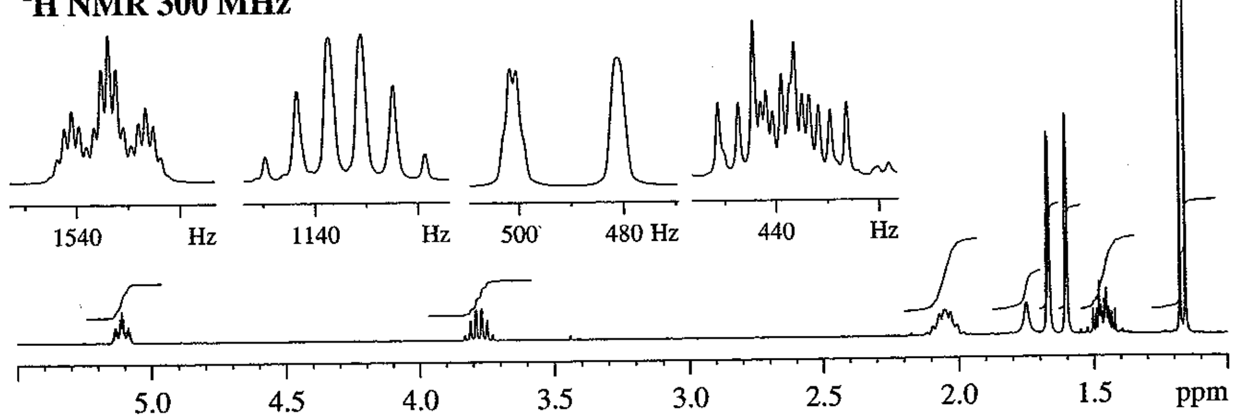
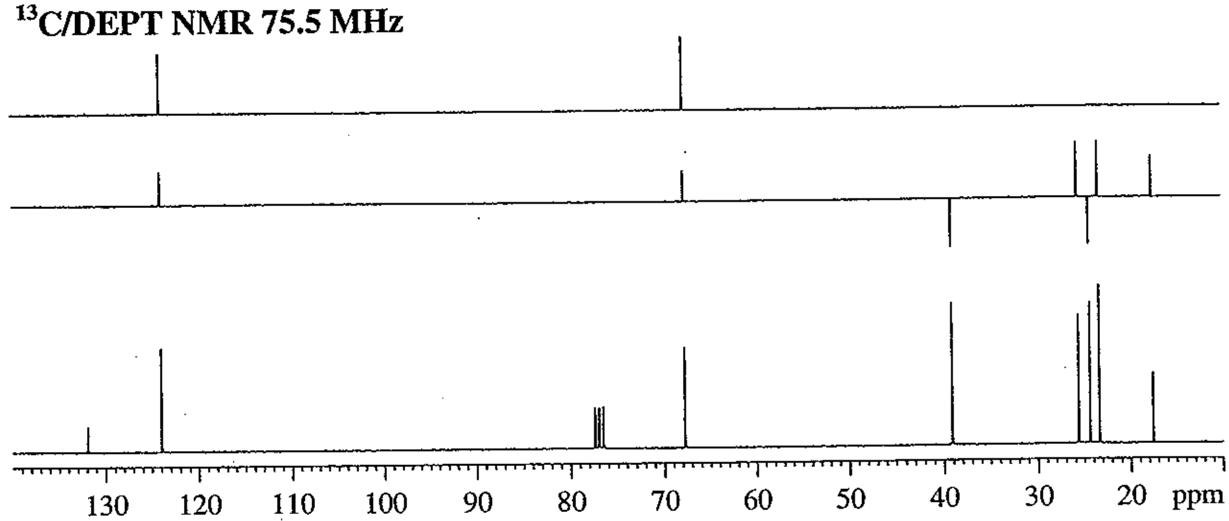
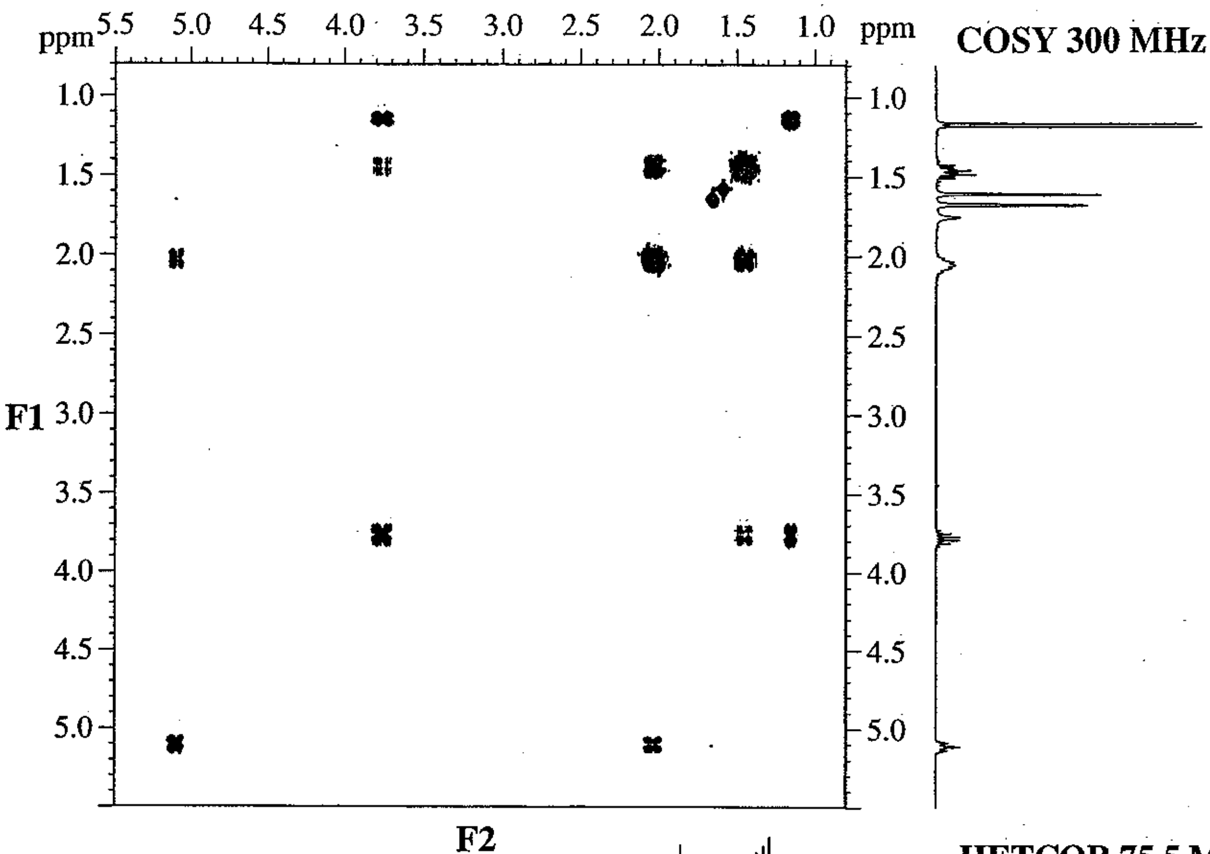


^{1}H NMR 300 MHz



^{13}C/DEPT NMR 75.5 MHz




COSY 300 MHz
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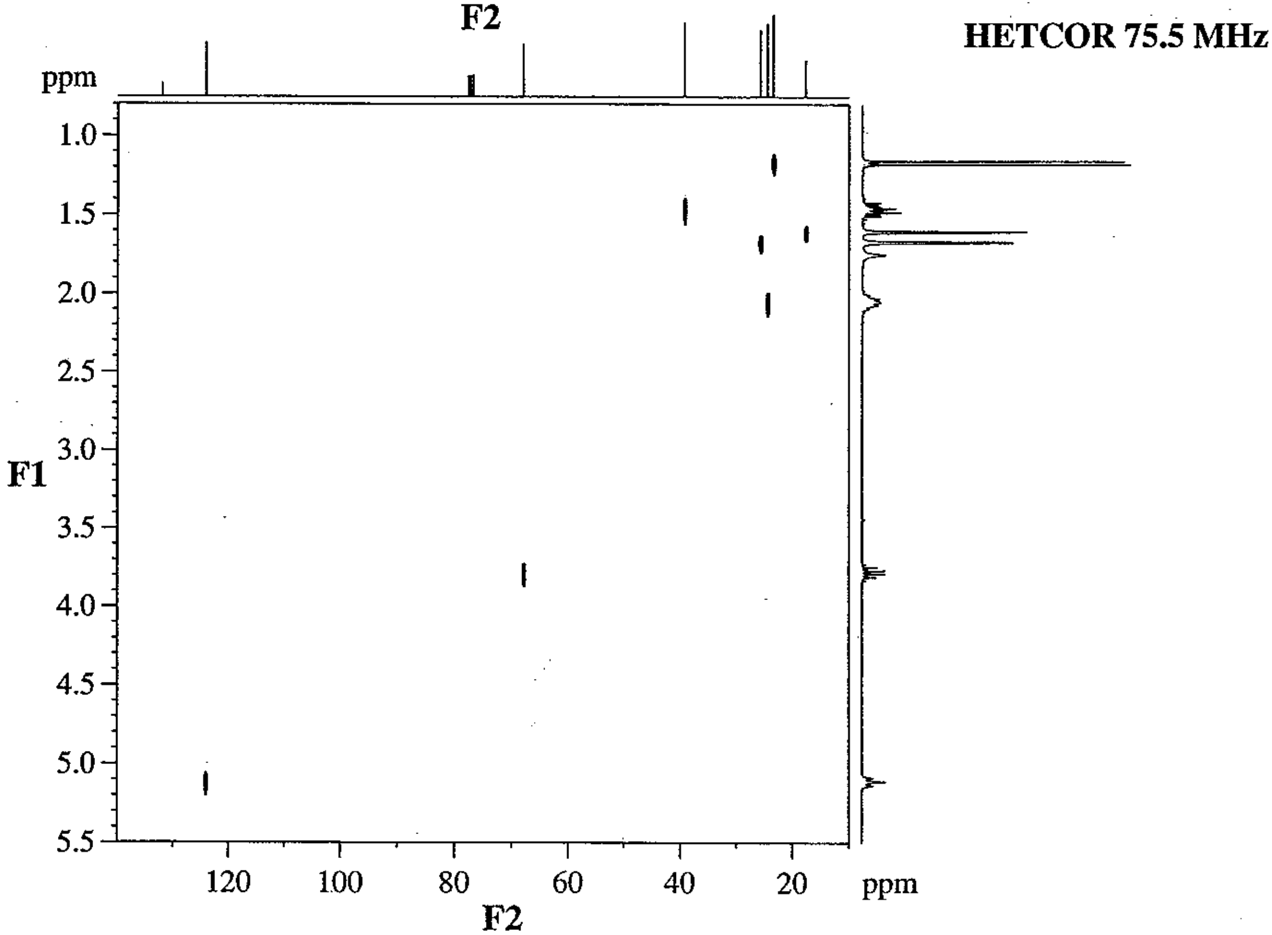
F1
F2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5.0
5.5
F1
120
100
80
60
40
20
F2

1. (25) Assuming that two protons of H_2^+ molecule are fixed at their normal separation of $1.06A^o$:
   (a) (5) Sketch the potential energy of the electron along an axis passing through the protons
   (b) (5) Sketch the electron wave functions for the two lowest states
   (c) (5) Explain the formation of the chemical bond for this system, what is ground state binding energy (just an order of magnitude! 1,10,100,1000 kcal/mol)
   (d) (5) What happens to the two lowest energy levels in the limit that the protons are moved far apart
   (e) (5) Explain the Born-Oppenheimer approximation for molecular systems, when do you think this approximation will break down, give an example

2. (25) Discuss the degeneracies of the first three energy levels of a particle in :
   (a) (5) One-dimensional box
   (b) (5) Two-dimensional box when the two sides have the same length
   (c) (5) Two-dimensional box when the two sides have different length
   (d) (5) Three-dimensional box when all three sides have the same length
   (e) (5) Three-dimensional box when all three sides have different length

The energy of a particle of mass m in a one-dimensional box with length L is given by $E = \frac{h^2}{8m}\frac{n^2}{L^2}$, where n is the quantum number.

3. (25) Determine whether the following functions are acceptable or not as wave functions over the indicated intervals, explain why

   (a) (5) $\Psi(x) = \frac{2}{3x}$ $(0, \infty)$

   (b) (5) $\Psi(x) = cox(4x)$ $(0, \infty)$

   (c) (5) $\Psi(x) = e^{-2x}$ $(0, \infty)$

   (d) (5) $\Psi(x) = e^{+3x}$ $(0, \infty)$

   (e) (5) $\Psi(x) = 5x$ $(0, \infty)$

4. (25) The wave function for an electron in a one-dimensional potential $V(x)$ at time t is given by the expression

   $\Psi(x,t) = \sqrt{\frac{2}{a}}\ Sin[\frac{\pi x}{a}]\ e^{i\gamma t/\hbar}$, for $0 \leq x \leq a$
   where a and γ are constants

   (a) (5) Is the particle bound? Explain

   (b) (5) What is the probability density for a measurement of the total energy E of the particle

   (c) (5) Sketch the potential for this wave function

   (d) (5) Find the lowest energy eigenvalue of $V(x)$ in terms of the given quantities

   (e) (5) Can we use this wave function and model potential to describe the motion of a π-electron in conjugated molecules

Periodic Classification of the Elements

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	O
1 H 1.00797																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.903	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9044	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac† (227)															

***Lanthanides**	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
†Actinides	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lw (257)

(Numbers in parentheses are the mass numbers of the most stable isotopes.)