

Name: KEY

Chemistry 61
Test 3
December 5, 2002

Instructions:

1. Write your name in the space above and on the backs of the other pages.
2. You may use as a reference both sides of an 8.5" x 11" piece of paper filled with information. No other personal references are allowed.
3. Your exam booklet should have **ten** pages total, with questions on pages 2-9, and a periodic table and other reference information on p. 10. Please check to see you have all ten pages.
4. You will have two hours and thirty minutes to work on this test.

<u>Possible Points</u>	<u>Your Score</u>
Question 1 (10)	
Question 2 (17)	
Question 3 (10)	
Question 4 (6)	
Question 5 (10)	
Question 6 (12)	
Question 7 (8)	
Question 8 (10)	
Question 9 (10)	
Question 10 (7)	
Total (100)	

mean 72.4
median 80

1. (10 points total) Circle the best answer to each of the following four questions. Your answers need not be justified, and no partial credit will be awarded.

A. Which of the following statements is false?

- (a) An electric field can exert a torque on a molecule like water.
- (b) A gyroscope would not precess in a zero-gravity environment.
- (c) Electrons in molecules have no measurable effect on the precessional frequency of ^1H nuclei present in these molecules. *Chemical shifts!!* 4
- (d) Interactions of excited nuclear spins with the lattice facilitate longitudinal relaxation.
- (e) In an FT-NMR experiment, the free induction decay is modulated down to audio frequencies before being digitized.

B. Which of the following nuclear spin states is impossible?

- (a) ^1H with $m_1 = -1/2$
- (b) ^{10}B with $m_1 = -1$
- (c) ^{13}C with $m_1 = +1/2$
- (d) ^{32}S with $m_1 = +1$ 5
- (e) ^{14}N with $m_1 = 0$.

C. Which of the following statements is true?

- (a) Radial distribution functions tell us the probability of finding an electron anywhere within a sphere of radius r .
- (b) The second transition series (Y through Cd) cannot be readily analyzed by detecting Auger electrons. *Z < 10 for Auger* 3
- (c) A LiF crystal is an effective dispersive element for visible light.
- (d) In an X-ray spectrometer, the detector remains fixed.
- (e) Statements (a), (b), (c), and (d) are all false.

D. (1 point only) Which of the following scientists do you admire the most?

- (a) Thomas "the god of noise" Coor
- (b) Charles "population inversion" Townes
- (c) Paul "ligand meister" Fischer*
- (d) Edward "I didn't expect these stupid chemical shifts" Purcell 1
- (e) Ernest "I love exploiting grad students" Rutherford 5

*a.k.a. "Paul 'I hate multiple-choice questions' Fischer"

2. Near-infrared spectroscopy is often used to determine the protein content of wheat (I am not making this up—maybe you can get a job at General Mills this summer doing this work!). The energetic IR photons are best quantified with a quantum-based detector known as a photoconductivity transducer, in which individual electrons are promoted from valence to conduction bands.

Consider a Fourier-transform near-IR experiment in which we measure the absorbance from 1.4 to 2.6 μm . We use a Nernst glower as the source, a photoconductivity transducer as the detector, and a He-Ne laser ($\lambda = 633 \text{ nm}$) to trigger data acquisition.

- (a) (9 points) Discuss whether Fellgett's advantage and Jacquinot's advantage apply to this experiment.

Fellgett: NO, since quantum detectors suffer from case I noise \leftarrow (-4 if YES)

Jacquinot: YES (no slits)

\leftarrow -1 small math error
-3 freq vs. time

- (b) (8 points) Does our experiment satisfy the Nyquist criterion? Justify your answer with a calculation.

Fastest freq in signal due to 1.4 μm radiation:

$$c = \lambda \nu \Rightarrow \nu = \frac{c}{\lambda} = \left(\frac{3.0 \times 10^8 \text{ m/s}}{\text{s}} \right) \left(\frac{1}{1.4 \times 10^{-6} \text{ m}} \right) = 2.14 \times 10^{14} \text{ Hz}$$

vs. triggering by He-Ne:

$$\nu = \frac{c}{\lambda} = \left(\frac{3.0 \times 10^8 \text{ m/s}}{\text{s}} \right) \left(\frac{1}{633 \times 10^{-9} \text{ m}} \right) = 4.7 \times 10^{14} \text{ Hz}$$

$$\begin{aligned} & \stackrel{?}{>} 2 (2.14 \times 10^{14} \text{ Hz}) \\ & \geq 4.3 \times 10^{14} \text{ Hz} \end{aligned}$$

\therefore Nyquist satisfied (barely!)

N.B. Actual freqs determined by speed of interferometer mirror, but proportionalities still hold (both ν 's slower by the same factor)

3. (10 points) Fourier-transform techniques involve recording signal in the time domain (or some suitable experimental surrogate for the time domain) and then evaluating the following integral for each frequency in the spectrum:

$$P(2\pi\nu) = \int_0^t P(t) \cos(2\pi\nu t) dt$$

Explain the effect of integration time on the frequency spectrum obtained. Be sure to discuss the phenomenon of beating as part of your explanation.

Some excellent answers!

-2 minor errors / incomplete thoughts

4. (6 points) Paul is responsible for keeping our NMR superconducting magnet at a chilly 4 K, periodically recharging the dewar surrounding it with liquid helium. Discuss in detail the impact of his diligence on the signal/noise ratio—that is, what effect does a large magnetic field have on the signal/noise ratio, and why?

-2 didn't explain why $\uparrow B_0 \uparrow S/N$

(ie didn't explain the relation $\frac{N_{-1/2}}{N_{+1/2}} \approx 1 - \frac{\gamma B_0 \hbar}{2\pi k T}$)

-4 no use of the relation

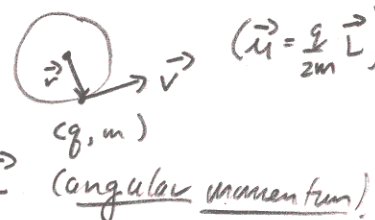


-5 no discussion of torque

-2 didn't say $\vec{\tau}$ adds to the ang mom already present in the dipole

5. (10 points) Contemporary molecular structure determinations would be impossible without the phenomenon of precession. Explain in terms of fundamental physical concepts why many nuclei precess about an external magnetic field. (You should use equations and diagrams.)

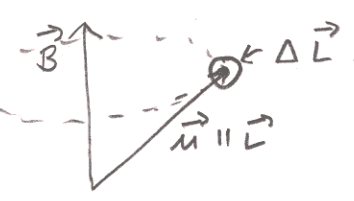
Precession in a \vec{B} field requires the presence of a magnetic dipole either by the circular orbit of a classical charge:



or the mysterious "spin" of quantum particles like nuclei: $\vec{\mu} = \gamma \vec{I}$. In both models, $\vec{\mu} \parallel \vec{L}$ (angular momentum)

A \vec{B} applies a torque on $\vec{\mu}$ (by defn). $\vec{\tau} = \vec{\mu} \times \vec{B}$.

This $\vec{\tau}$ is \perp to both $\vec{\mu}$ and \vec{B} . Moreover, a torque acting over time constitutes a 2nd ang. momentum $\Delta \vec{L} \cong \vec{\tau} \Delta t$. This $\Delta \vec{L}$, always acting \perp to the $\{\vec{B}, \vec{\mu}\}$ plane, rotates $\vec{\mu}$ about \vec{B} i.e. precession

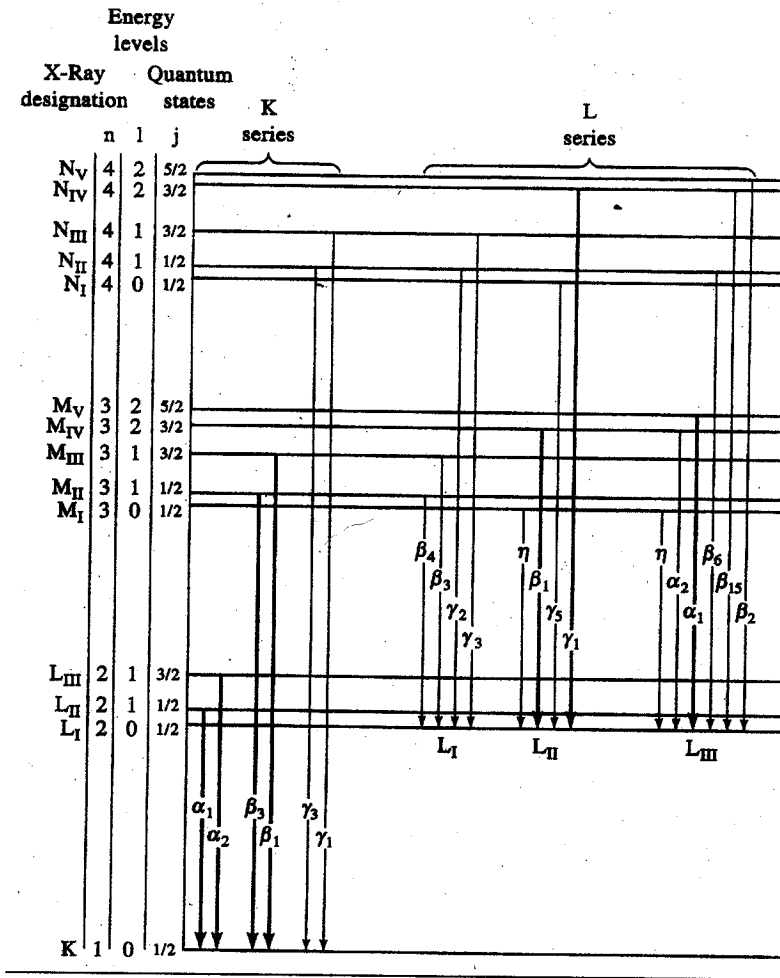


6. (12 points) In the NMR demo running right now, the ^1H nuclei in the sample are being subjected to a $\pi/2$ pulse, and then a π pulse. Explain the signals being generated in the NMR receiver coil. (Diagrams will greatly facilitate your explanation.)

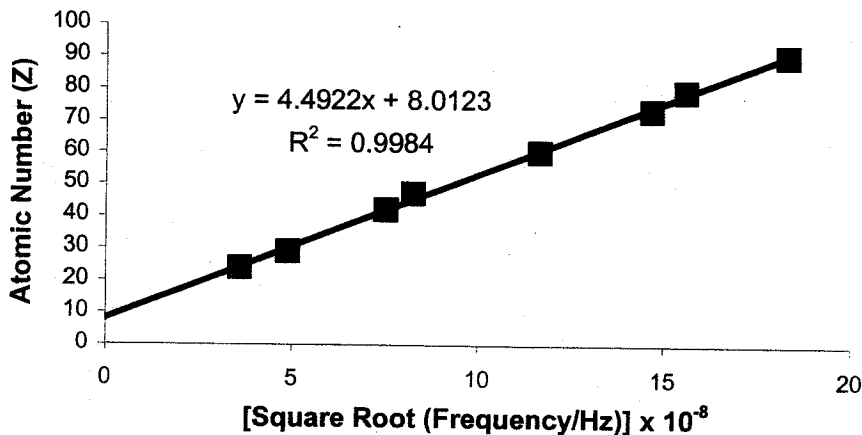
-4 no discussion of loss of spin coherence (which is why the signals decay)

-9 same thing

7. (8 points) Moseley and others measured the wavelengths of a variety of X-ray transitions:



In particular, he studied the \$L(\alpha_1)\$ transition for a series of elements, and generated the following plot:

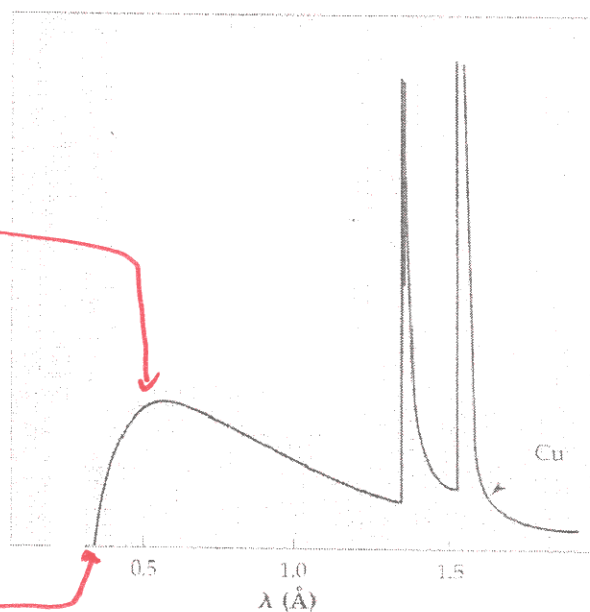


On the next page, explain in detail the physical significance of the slope and of the y-intercept of the above line.

-5 no use of Bohr model

-1 or -2 more physical insight needed

8. (10 points) The spectral output of an X-ray tube with a Cu anode is shown to the right. Explain this spectrum in detail.



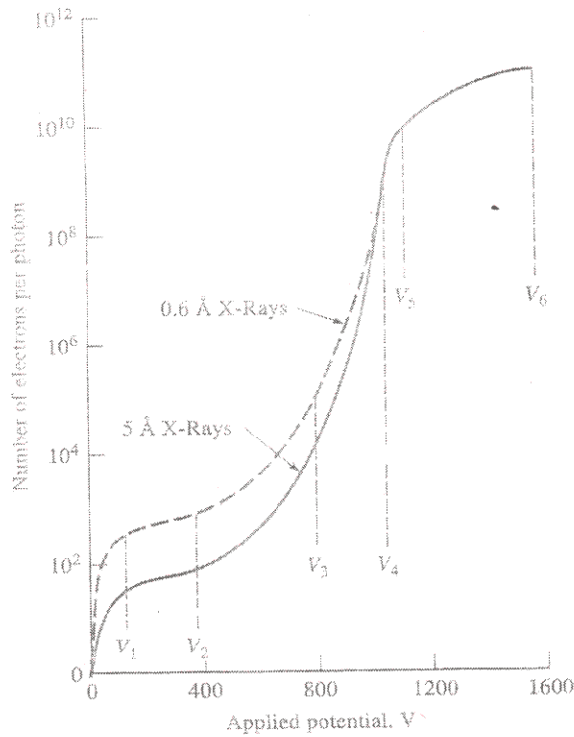
-2 no discussion of local max

-3 no discussion of short λ limit

-5 Bremsstrahlung due to transitions in Cu

-7 absorption spectrum

9. (10 points) Consider the following data for a gas-flow proportional detector:



Explain in detail all that contributes to the detector's intrinsic gain from V_3 to V_4 .

-3 no mention of avoiding re-combination
 -3 " " " 2^o ionization

10. (7 points) In an astonishing act of holiday generosity, your instructor requires you to solve only one of the following quantitative problems. The choice is yours!

- (i) The Chemistry Department's Nicolet FTIR scans from 400 to 4000 cm^{-1} . Say that we want the highest-frequency signal in the Nicolet's interferogram to be 35 kHz. What is the fastest speed (in cm s^{-1}) at which the interferometer's mirror should move?
- (ii) Paul has explored the synthesis of transition metal complexes with triphenylphosphine ligands, and wants to analyze them using our department's "300 MHz" NMR. Compute the precessional frequency (in Hz) for bare ^{31}P nuclei.
- (iii) One of the detectors in the Keck XRF instrument is a gas-flow proportional counter that uses Xe, which has an ionization energy of 12.1 eV. Neglecting the effect of anode bias, estimate the intrinsic gain in detecting a 1.0-Å photon using a Xe detector.

$$(i) f = 2 \frac{v_M}{c} \nu \quad \text{and} \quad \nu = c\bar{\nu} \Rightarrow f = 2v_M\bar{\nu} \Rightarrow v_M = \frac{f}{2\bar{\nu}}$$

The upper bound is set by the highest energy wavenumber

$$v_M = \frac{35 \times 10^3 \text{ s}^{-1}}{2(4000 \text{ cm}^{-1})} = \boxed{4.4 \text{ cm s}^{-1}}$$

$$(ii) \nu_i = \frac{\gamma_i}{2\pi} B_0 \quad \text{set up proportionality}$$

$$\frac{\nu_P}{\nu_H} = \frac{\gamma_P}{\gamma_H} \Rightarrow \nu_P = \nu_H \left(\frac{\gamma_P}{\gamma_H} \right) = 300 \text{ MHz} \left(\frac{1.0841 \times 10^8}{2.6752 \times 10^8} \right) = \boxed{122 \text{ MHz}}$$

$$(iii) n \approx \frac{hc/\lambda}{IE(\text{Xe})} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m s}^{-1})}{(1.0 \times 10^{-10} \text{ m})(12.1 \text{ eV})} \left(\frac{\text{eV}}{1.6 \times 10^{-19} \text{ J}} \right)$$

$$= 1026 \approx 1000$$

-3 1 major error

-2 math

Possibly Useful Information

1 H 1.0079																2 He 4.0026	
3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 †Ac 227.03															

Nucleus	Magnetogyric Ratio (radian T ⁻¹ s ⁻¹)
¹ H	2.6752 × 10 ⁸
¹³ C	6.7283 × 10 ⁷
¹⁹ F	2.5181 × 10 ⁸
³¹ P	1.0841 × 10 ⁸