

Department of Chemistry Cumulative Examinations December 13, 2008

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.

- 1) Analytical Cumulative Examination, Page 1
- 2) Biochemistry Cumulative Examination, Pages 2-5
- 3) Inorganic Cumulative Examination, Pages 6-10
- 4) Organic Cumulative Examination, Pages 11-12
- 5) Physical Cumulative Examination, Pages 13-15

On your examination booklet:

- 1) Print your student ID number.
- 2) Print the 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
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Analytical Cumulative Examination

December 13, 2008

Analytical chemistry is a quantitative science in which phenomena, measurements and instrumentation are best understood if they can be expressed in the form of an equation. This exam asks (i) that you write equations which apply to and/or describe the topics indicated below, including definitions of all terms in the equations, and (ii) that you then comment in the space of a page or less, on the significance and implications of each equation in analytical chemistry.

Half credit is for the equation and half for the comment. Give units wherever possible.

YOU SHOULD ANSWER ONLY 10 OF THE 17 QUESTIONS

1. Mass analysis equation for a time-of-flight mass spectrometer
2. Number of theoretical plates in a thin layer chromatogram
3. Height equivalent of a theoretical plate
4. Capacity factor
5. Unimolecular rate constant for dissociation of isolated gas phase ions
6. Nernst equation
7. Electron binding energy in XPS (ESCA)
8. Diffusion equation
9. Relationship between wavelength and wavenumber
10. Vibrational energy spacing in molecules
11. Relationship of half-life to rate constant for unimolecular reaction rate constant
12. Gyromagnetic ratio
13. Time constant for pure RC circuit
14. Time-frequency Fourier transform
15. Beer's Law expressed in terms of detected intensities
16. Relationship between bandwidth and acquisition time
17. Faraday's laws of electrolysis

December 13, 2008

Biochemistry Cumulative Examination

5 questions 20 points each

Techniques in Molecular Biology

1. (a) What is a DNA chip (a DNA microarray)? Describe in some detail (but ≤ 1 pg in blue book).

How might it be used to

- (b) Assess changes in gene expression levels between normal cells and cancer cells?
- (c) Identify (most or) all of the species of bacteria present in an infection
- (d) Screen for a genetic predisposition to breast cancer (mutation in the BCRA gene, where a point mutation almost anywhere in the gene is associated with cancer).
- (e) Screen for alternative splicing of mRNAs

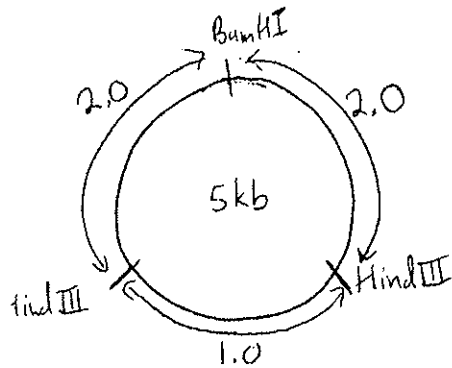
Be sure to include in your discussion what type of controls are run to correctly interpret data.

2. You have discovered a very important protein that, when present, causes cancer cells to grow and divide at 20 times the normal rate. Further study reveals that the protein is regulated by the retinoic acid receptor (RXR), which binds DNA upstream of the gene encoding this protein and acts as a transcriptional regulator. You also discover that a derivative of retinoic acid slows tumor growth (\$\$\$). Your drug candidate (retino-125) binds to the RXR protein and induces a conformational change that may alter the ability of RXR to bind to DNA with the same affinity as the RXR:retinoic acid complex. Alternatively it may still bind with similar affinity but not allow transcriptional activation. Outline strategies to test these two hypotheses.

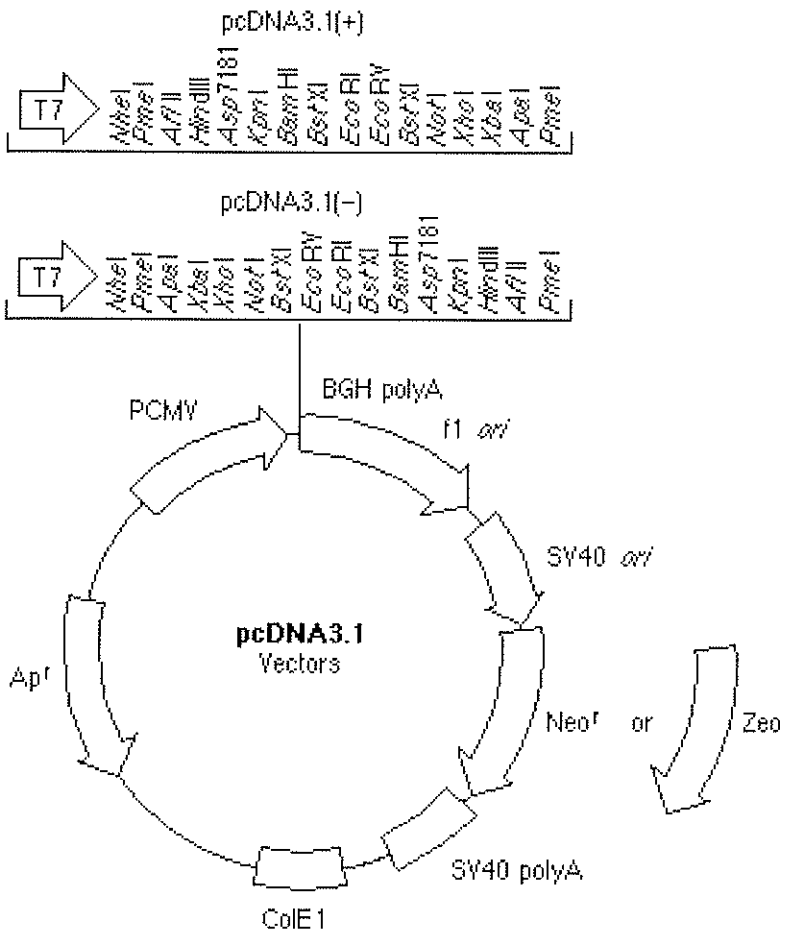
3. Most site-directed mutagenesis kits use polymerases that replicate the entire plasmid using mutagenic primers. After doing a reaction, you note that your protein is no longer expressed from the mutated plasmid and begin your trouble-shooting by doing a restriction digest of the plasmids with the enzyme EcoRI, which cuts just once. While the fragment size of the starting plasmid was 5.4 kb, as expected, the new plasmid is smaller, only 5.0 kb. Next, you do a more in depth series of restriction digests (single and double digests), of both the original plasmid and the new plasmid, to construct a restriction map and see how they differ. The following data is obtained:

Enzyme	Original plasmid Fragment sizes (kb)	New plasmid Fragment sizes (kb)
EcoRI	5.4	5.0
HindIII	2.1, 1.9, 1.4	2.1, 1.5, 1.4
Sal I	5.4	5.0
EcoRI and HindIII	2.1, 1.4, 1.3, 0.6	2.1, 1.4, 1.3, 0.2
Sal I and HindIII	1.9, 1.4, 1.2, 0.9	1.5, 1.4, 1.2, 0.9

Draw circular restriction maps for both plasmids based on this data. (Don't worry about drawing to scale just label distance between sites, as shown in example of restriction map below). Where is the difference between them?

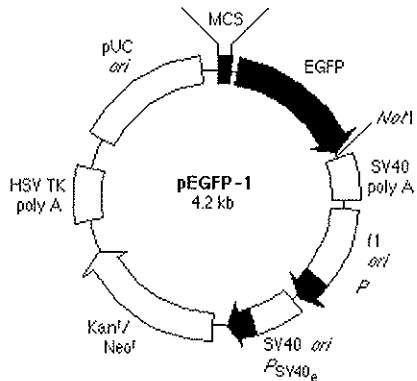
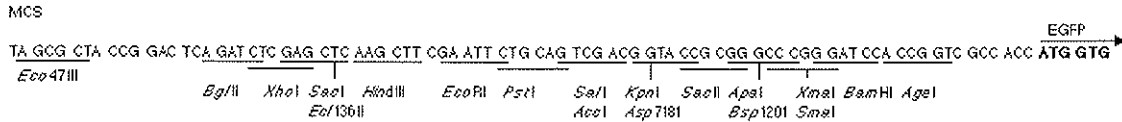


4. Identify each of the elements labeled in the plasmid below and explain the *purpose* for their presence on a cloning vector. Based on the elements that are present, what could this plasmid be used for?



5. The following vector is designed to simplify the process of making a fusion between a protein of interest and an engineered green fluorescent protein (EGFP). Design two PCR primers to amplify the gene shown below and clone it into the multiple cloning site (MCS) of the vector, in order to generate a protein fusion. STRATEGY: Incorporate restriction sites into your primers so that you can amplify the gene and clone it into the vector using restriction enzyme digestion and ligation reactions. For the purpose of this exercise, we will assume that none of the enzymes listed in the MCS cut within your gene. (Recognition sites for enzymes are underlined...all are 6 bp long).

Your grade will reflect both your ability to design PCR primers correctly (indicate 5' end!), and the success of your strategy to make the fusion protein.



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1/1          31/11          61/21
ATG GCG AGC GTA CAG CTG CAA AAT GTA ACG AAA GCC TGG GCG CAG GTC GTG GTA TCG AAR GAT ATC AAT CTC GAT ATC CAT CAA GGT GAR
H A S V Q L Q N V T K A R H H G E V V V V S K D I N L B I H E G E

91/31       121/41       151/51
TTC GTG GTG TTT GTC GGA CCG TCT GGC TGC GGT AAR TCG ACT TTA CTG CCG ATG ATT GCC GGG CTT GAG ACG ATC ACC AGC GGC GAC CTG
F V V F V G P S G C G K S T L L R H I A G L E T I T S G D L

181/61     211/71     241/81
TTC ATC GGT GAG AAA CCG ATG AAT GAC ACT CCG CCA GCA GAR CCG GGC GTT GGT ATG GTG TTT CAG TCT TAC GCG CTC TAT CCC CAC CTG
F I G E K R R N D T P P A E R G V G R V L Q L R H L L D R K P K A L

271/91     301/101    331/111
TCR GTA GCA GAA AAC ATG TCA TTT CCG GTT AAC CAG GTG CCG GAA CTG CTA CAA CTG CCG CAT TTG CTG GAT CCG AAR CCG AAR GCG CTC
S V A E N H H S F R Y N Q V R A E V L R Q L R H L L D R K P K A L

361/121    391/131    421/141
TCC GGT GGT CAG CGT CAG CGT GTG GCG ATT GCG CGT ACG CTG GTG GCC GAG CCA AGC GTA TTT TTG CTC GAT GAA CCG CTC TCC AAC CTC
S G S Q R Q R V A I G R T L V A E P S V F L L L D E P L S H L

451/151    481/161    511/171
GAT GCT GCA CTG CGT GTG CAA ATG CGT ATC GAA ATC TCC CGT CTG CAT AAA CCG CTG GCG CCG ACA ATG ATT TAC GTC ACC CAC GAT CAG
D A R A L R V Q H R I E I S R L H K R R L G G R T H I V V T H D Q

541/181    571/191    601/201
GTC GAA GCG ATG ACG CTG GCC GAC AAA ATC GTG GTG CTG GAC GCC GGT CCG GTG GCG CAG GTT GGG AAR CCG CTG GAG CTG TAC CAC TAT
V E A M T L A D K I V V L D A G R Y A Q V B K P L E L Y H Y

631/211    661/221    691/231
CCG GCA GAC CGT TTT GTC GCC GGA TTT ATC GGT TCG CCA AAG ATG AAC TTC CTG CCG GTA AAA GTG ACC GCC ACC GCA ATC GAT CAA GTG
P A D R F V A G F I G S P K M H F L P V K V T A T A I D Q V

721/241    751/251    781/261
CAG CTG GAG CTG CCG ATG CCA AAT CGT CAG CAA GTC TGG CTG CCA GTT GAA AGC CGT GAT GTC CAG GTT GGA GCC AAT ATG TCG CTG GGT
Q V E L P H P N R Q Q V M L P V E S R A D V Q V G A N H S L G

811/271    841/281    871/291
ATT GCG CCG GAA CAT CTA CTG CCG AGT GAT ATC GCT GAC GTC ATC CTT GAG GGT GAA GTT CAG GTC GTC GAG CAA CTC GGC AAC GAA ACT
I R P E H L L P S D I A D V I L E G E V Q V V E Q L G N E T

901/301    931/311    951/321
CAA ATC CAT ATC CAG ATC CCT TCC ATT CGT CAA AAC CTG GTG TAC CCG CAG AAC GAC GTG GTG TTG GTA GAA GAA GGT GCC ACA TTC GCT
Q I H I Q I P S I R Q N L V V R Q N D V V L V E E G A T F A

991/331    1021/341    1051/351
ATC GCG CTG CCG CCA GAG CGT TGC CAT CTG TTC CGT GAG GAT GCG ACT GCA TGT CGT CCA CTG CAT AAG GAG CCG GCG GTT TAA
I G L P P E R C H L F R E D G T R C R A L H K E P G V *

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- (10 points) The fundamental stretching frequency, ν_{CO} , of gaseous carbon monoxide is 2143 cm^{-1} . Using the molecular orbital bonding model for CO and the overlap of Ni and CO orbitals, explain why the infrared spectrum of $\text{Ni}(\text{CO})_4$ shows a CO stretching frequency at 2057 cm^{-1} .
- (10 points) The infrared spectra of the following compounds exhibit CO stretching frequencies as shown:

Compound	ν_{CO}
$\text{V}(\text{CO})_6^-$	1858 cm^{-1}
$\text{Cr}(\text{CO})_6$	2000 cm^{-1}
$\text{Mn}(\text{CO})_6^+$	2095 cm^{-1}

Explain the changes in these frequencies.

- (20 points)
 - Using displacement vectors co-linear with the CO bonds, derive the symmetries of the fundamental CO stretching modes in $\text{Cr}(\text{CO})_6$. (Character tables are provided.)
 - Sketch the displacements of the six CO stretching vibrations found in $\text{Cr}(\text{CO})_6$ and indicate the symmetry of each.
 - What is the symmetry of the mode giving rise to the absorption observed in the IR spectrum of $\text{Cr}(\text{CO})_6$?
 - How many lines due to CO stretching vibrations should be observed in the Raman spectrum of $\text{Cr}(\text{CO})_6$? Assign the symmetry of the mode giving rise to each.
- (20 points) $\text{BrHgMn}(\text{CO})_5$ contains a Hg-Mn metal-metal bond and a linear Br-Hg-Mn geometry.
 - Using displacement vectors co-linear with the CO bonds, derive the symmetries of the fundamental CO stretching modes in $\text{BrHgMn}(\text{CO})_5$. Indicate which of these vibrations could be observed in an IR spectrum of $\text{BrHgMn}(\text{CO})_5$ and which could be observed in the Raman spectrum. (Character tables are provided.)
 - Sketch the displacements of the five CO stretching vibrations found for $\text{BrHgMn}(\text{CO})_5$ and indicate the symmetry of each.
 - Which one of the allowed CO modes may be weak or unobserved in the IR spectrum of $\text{BrHgMn}(\text{CO})_5$. Explain the weakness.

5. (20 points) When an excess of thallium metal is added to a solution of $\text{Co}_2(\text{CO})_8$ in toluene, a yellow solid can be isolated after 2 hours. This solid has been characterized as $\text{TlCo}(\text{CO})_4$.
- a. The IR spectra of $\text{TlCo}(\text{CO})_4$ in the CO stretching region are solvent dependent, as shown in the following table.

Solvent	ν_{CO}
Water	1914 (s,br)*
Dichloromethane	2039 (m), 1963 (m), 1931 (s)

* s, strong; m, medium; br, broad.

Explain the differences between the IR spectra of $\text{TlCo}(\text{CO})_4$ in water (1 absorption) and in dichloromethane (3 absorptions). Use the character tables to derive the symmetries of the fundamental CO stretching modes that support your discussion.

6. (20 points) $\text{TlCo}(\text{CO})_4$ is a useful reagent for the preparation of other carbonyls. Indicate the structure of the metal carbonyl produced by its reaction with each of the following:
- HCl in CH_2Cl_2
 - $\text{Co}_2(\text{CO})_8$
 - $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$
 - Addition of 1 equivalent of $\text{P}(\text{C}_6\text{H}_5)_3$ to the product of c, above.

7. The D_{nd} Groups (Continued).

D_{6d}	E	$2S_{12}$	$2C_6$	$2S_6$	$2C_3$	$2S_{12}^5$	C_2	$6C_2'$	$6\sigma_d$	
A_1	1	1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	1	1	1	1	1	1	1	R_z
B_1	1	-1	1	-1	1	-1	1	-1	1	z
B_2	1	-1	1	-1	1	-1	1	-1	1	(x, y)
E_1	2	$\sqrt{3}$	1	0	-1	$-\sqrt{3}$	-2	0	0	$(x^2 - y^2, xy)$
E_2	2	1	-1	-2	1	1	2	0	0	
E_3	2	0	-2	0	2	0	-2	0	0	
E_4	2	-1	-1	2	-1	-1	2	0	0	
E_5	2	$-\sqrt{3}$	1	0	-1	$\sqrt{3}$	-2	0	0	(R_x, R_y)

8. The S_n Groups

S_4	E	S_4	C_2	S_4^3		
A	1	1	1	1	R_z	$x^2 + y^2, z^2$
B	1	-1	1	-1	z	$x^2 - y^2, xy$
T	$\left\{ \begin{matrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{matrix} \right\}$				$(x, y); (R_x, R_y)$	(xz, yz)

S_6	E	C_3	C_3^2	i	S_6^5	S_6	
A_g	1	1	1	1	1	1	$\epsilon = \exp(2\pi i/3)$
E_g	$\left\{ \begin{matrix} 1 & \epsilon & \epsilon^* & 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon & 1 & \epsilon^* & \epsilon \end{matrix} \right\}$					R_z	$x^2 + y^2, z^2$
A_u	1	1	1	-1	-1	-1	(R_x, R_y)
E_u	$\left\{ \begin{matrix} 1 & \epsilon & \epsilon^* & -1 & -\epsilon & -\epsilon^* \\ 1 & \epsilon^* & \epsilon & -1 & -\epsilon^* & -\epsilon \end{matrix} \right\}$					z	(x, y)

S_8	E	S_8	C_4	S_8^3	C_2	S_8^5	C_4^3	S_8^7	
A	1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
B	1	-1	1	-1	1	-1	1	-1	R_z
E_1	$\left\{ \begin{matrix} 1 & \epsilon & i & -\epsilon^* & -1 & -\epsilon & -i & \epsilon^* \\ 1 & \epsilon^* & -i & -\epsilon & -1 & -\epsilon^* & i & \epsilon \end{matrix} \right\}$							$(x, y); (R_x, R_y)$	
E_2	$\left\{ \begin{matrix} 1 & i & -1 & -i & 1 & i & -1 & -i \\ 1 & -i & -1 & i & 1 & -i & -1 & i \end{matrix} \right\}$								
E_3	$\left\{ \begin{matrix} 1 & -\epsilon^* & -i & \epsilon & -1 & \epsilon^* & i & -\epsilon \\ 1 & -\epsilon & i & \epsilon^* & -1 & \epsilon & -i & -\epsilon^* \end{matrix} \right\}$								

9. The Cubic Groups

T	E	$4C_3$	$3C_2$	
A	1	1	1	$\epsilon = \exp(2\pi i/3)$
E	$\left\{ \begin{matrix} 1 & \epsilon & \epsilon^* & 1 \\ 1 & \epsilon^* & \epsilon & 1 \end{matrix} \right\}$			$x^2 + y^2 + z^2$
T	3	0	-1	$(R_x, R_y, R_z); (x, y, z)$

9. The Cubic Groups (Continued).

T_h	E	$4C_3$	$4C_3^2$	$3C_2$	i	$4S_6$	$4S_6^5$	$3\sigma_h$	
A_g	1	1	1	1	1	1	1	1	$\epsilon = \exp(2\pi i/3)$
A_u	1	1	1	1	-1	-1	-1	-1	$x^2 + y^2 + z^2$
E_g	$\left\{ \begin{matrix} 1 & \epsilon & \epsilon^* & 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon & 1 & \epsilon^* & \epsilon \end{matrix} \right\}$								$(2z^2 - x^2 - y^2, x^2 - y^2)$
E_u	$\left\{ \begin{matrix} 1 & \epsilon & \epsilon^* & 1 & -\epsilon & -\epsilon^* \\ 1 & \epsilon^* & \epsilon & 1 & -\epsilon^* & -\epsilon \end{matrix} \right\}$								(R_x, R_y, R_z)
T_g	3	0	0	-1	1	0	0	-1	(xz, yz, xy)
T_u	3	0	0	-1	-1	0	0	1	

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1	$(2z^2 - x^2 - y^2, x^2 - y^2)$
E	2	-1	2	0	0	(xy, xz, yz)
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_1	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	1	1	-1	-1	-1	-1	-1	$(2z^2 - x^2 - y^2, x^2 - y^2)$
E	2	0	2	0	-1	0	0	0	0	0	(xy, xz, yz)
T_1	3	1	-1	1	0	-1	0	-1	0	-1	$(R_x, R_y, R_z); (x, y, z)$
T_2	3	-1	-1	-1	0	1	0	1	0	1	(x, y, z)

I_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	1	1	1	-1	-1	-1	-1	-1	$(2z^2 - x^2 - y^2, x^2 - y^2)$
E_g	2	-1	0	0	2	0	0	0	0	0	(xy, xz, yz)
T_{1g}	3	0	-1	1	-1	0	0	-1	0	-1	(R_x, R_y, R_z)
T_{2g}	3	0	-1	-1	-1	0	0	1	0	1	(x, y, z)

10. The Groups $C_{\infty v}$ and $D_{\infty h}$ for Linear Molecules

$C_{\infty v}$	E	$2C_{\infty}^{\phi}$	\dots	$\infty\sigma_v$	
$A_1 \equiv \Sigma^+$	1	1	1	1	$x^2 + y^2, z^2$
$A_2 \equiv \Sigma^-$	1	1	1	1	z
$E_1 \equiv \Pi$	2	$2 \cos \phi$	\dots	0	$(x, y); (R_x, R_y)$
$E_2 \equiv \Delta$	2	$2 \cos 2\phi$	\dots	0	$(x^2 - y^2, xy)$
$E_3 \equiv \Phi$	2	$2 \cos 3\phi$	\dots	0	

$D_{\infty h}$	E	$2C_{\infty}^{\phi}$	\dots	$\infty\sigma_v$	i	$2S_{\infty}^{\phi}$	\dots	∞C_2	
Σ_g^+	1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
Σ_g^-	1	1	1	1	1	1	1	1	R_z
Π_g	2	$2 \cos \phi$	\dots	0	2	$-2 \cos \phi$	\dots	0	(R_x, R_y)
Δ_g	2	$2 \cos 2\phi$	\dots	0	2	$2 \cos 2\phi$	\dots	0	z
Σ_u^+	1	1	1	1	-1	-1	-1	-1	
Σ_u^-	1	1	1	1	-1	-1	-1	-1	
Π_u	2	$2 \cos \phi$	\dots	0	-2	$2 \cos \phi$	\dots	0	
Δ_u	2	$2 \cos 2\phi$	\dots	0	-2	$-2 \cos 2\phi$	\dots	0	

All the questions are from the following article (*JACS*, 2008, 130, 14891) by Professor Michael Krische, who discussed this work during the Negishi-Brown Symposium in October.

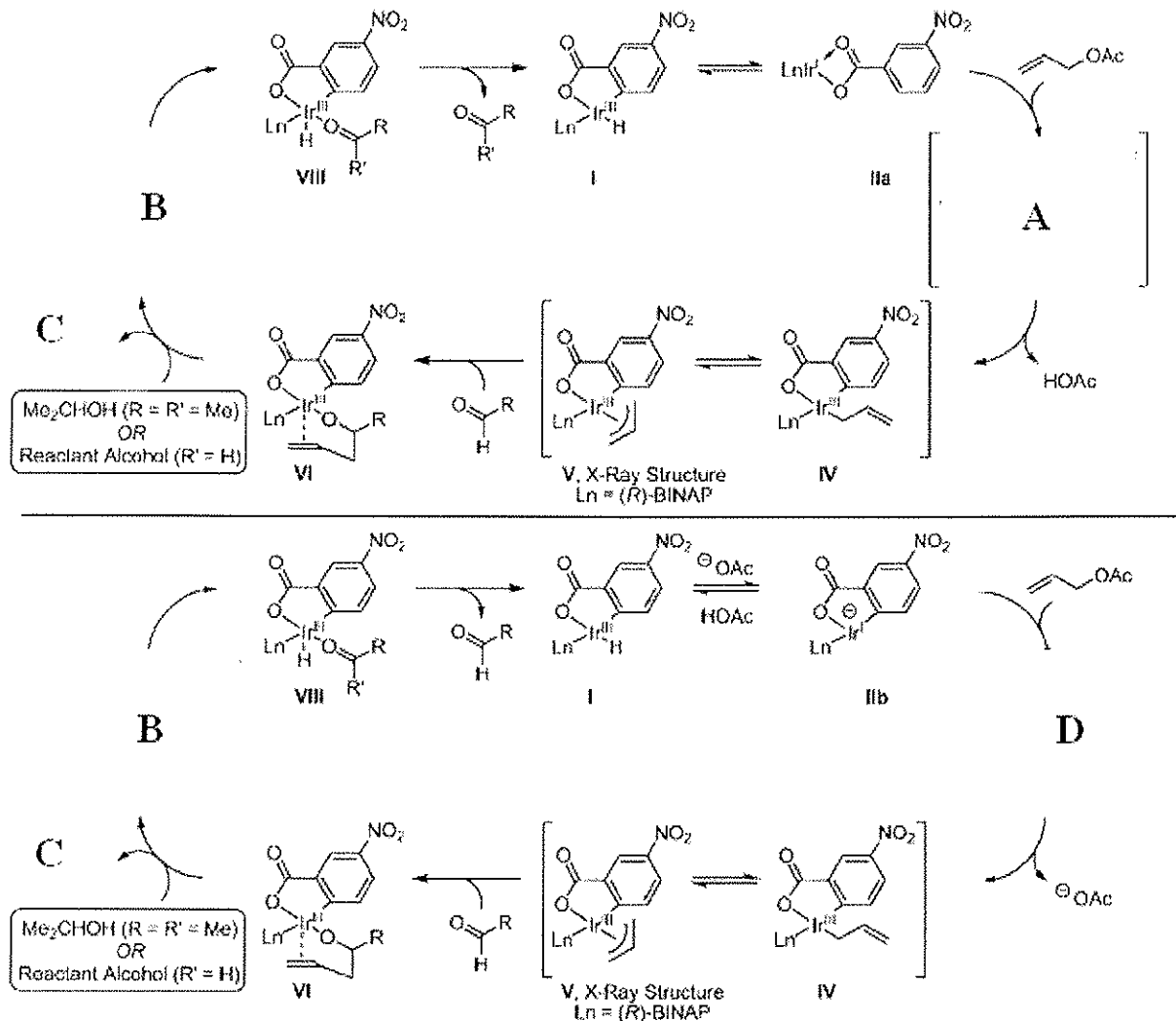
Enantioselective Iridium-Catalyzed Carbonyl Allylation from the Alcohol or Aldehyde Oxidation Level via Transfer Hydrogenative Coupling of Allyl Acetate: Departure from Chirally Modified Allyl Metal Reagents in Carbonyl Addition

In Su Kim, Ming-Yu Ngai, and Michael J. Krische*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

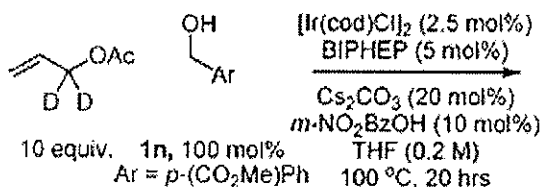
Received July 22, 2008; E-mail: mkrische@mail.utexas.edu

I. Provide the missing structures (A-D) in the proposed mechanism of the transfer hydrogenative coupling (30 points).



ORGANIC CUME
December 2008

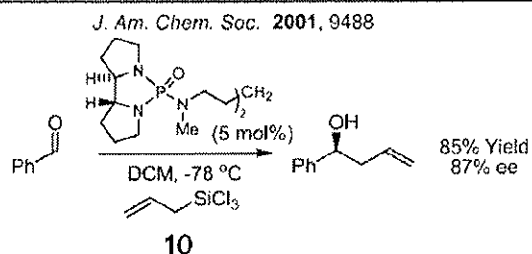
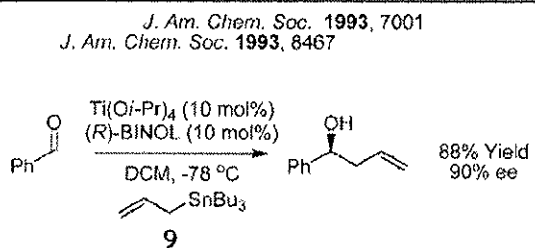
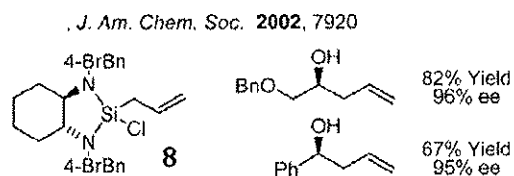
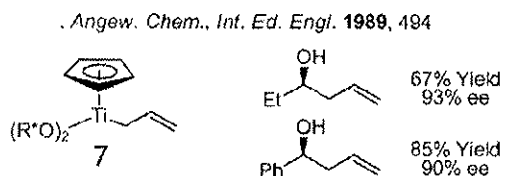
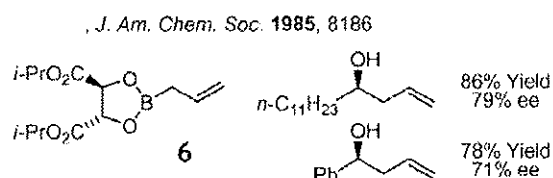
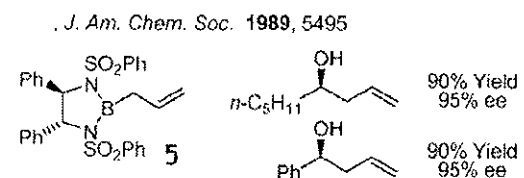
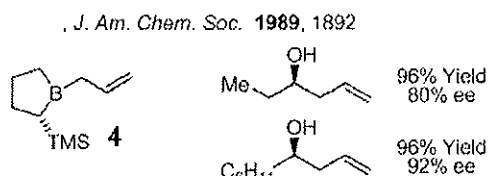
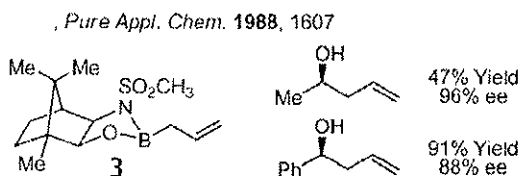
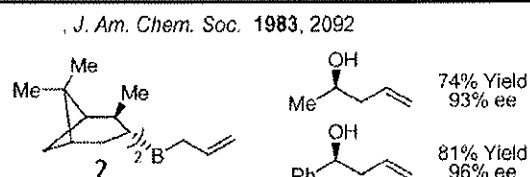
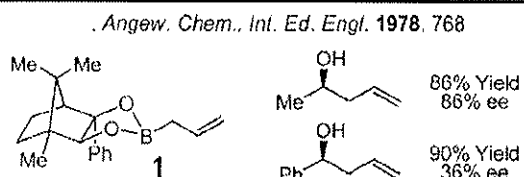
II. Provide the structure(s) of the expected product(s) from the following reaction (20 pts.)



III. Professor Krische has compared his reaction with the following reagents/reactions, which bears the name of the organic chemist who discovered them. (a) Provide the names of five of these chemists for the appropriate reagent/reaction (10 pts). (b) What is BINOL in reaction **9** (5 pts)? (c) Provide the configuration of reagent **4**. Explain (5 pts). (d) Write a plausible general mechanism for reaction **9** (30 pts).

ARTICLES

Kim et



Physical Chemistry Cumulative Exam

Part 1 (20pts): Having a firm grasp of energy conversion factors and fundamental molecular properties is important. Sometimes it is necessary to do “back of the envelope” calculations (For instance: when you’re stuck at Shoney’s with your in-laws) to get a rough idea of signal-to-noise, or to just sound intelligent at a seminar or conference. Answer each of the following questions. Please write legibly, if I can’t read it it’s wrong.

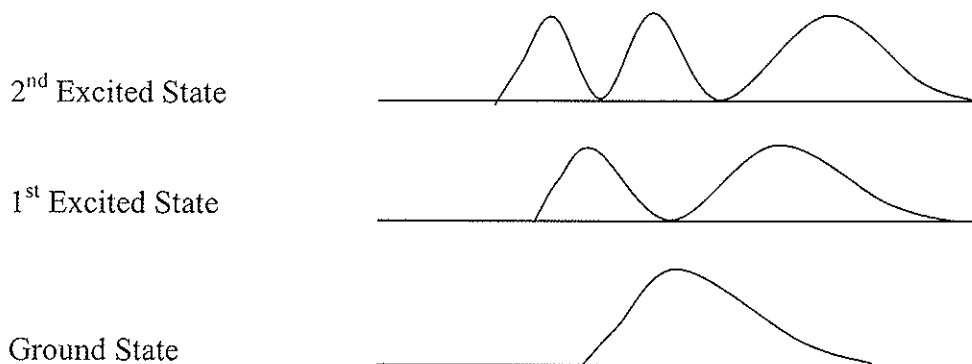
- 1.) What is kT at room temperature? cm^{-1} ?
- 2.) What is the H_2 bond energy in kJ/mol and kcal/mol ?
- 3.) How many kcal/mol in 1 eV ?
- 4.) How many cm^{-1} in 1 kJ/mol ?
- 5.) How many molecules in 1 torr?
- 6.) How many cm^{-1} in 1 THz?
- 7.) Is the absorption coefficient bigger for an IR transition or UV transition?
- 8.) What is a typical UV fluorescence lifetime? IR fluorescence lifetime?
- 9.) What is a typical rotational frequency for a diatomic? For a bigger molecule?
- 10.) What is a typical vibrational frequency for torsional motion? For stretching motion? (in either Hz or cm^{-1})

Part 2 (10pts ea., Please replicate drawings in you exam book where appropriate):

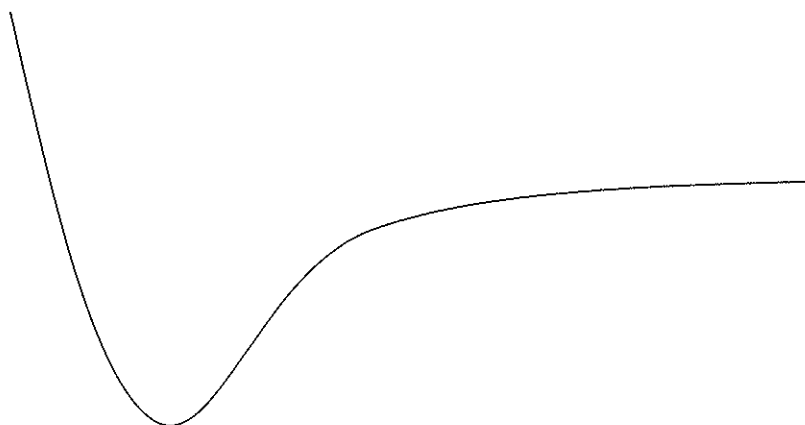
1. If the following figure represents the two nuclei in H_2^+ , draw the probability density of the electron in the ground electronic state.



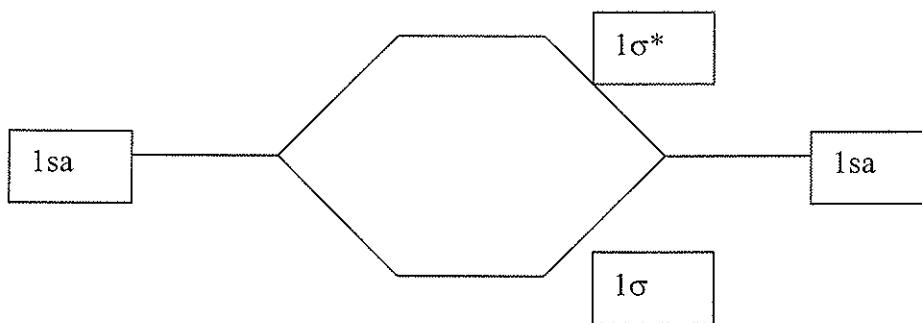
2. Given the following probability densities (assume these represent the ground and first two excited states), draw the potential curve that would give rise to them and explain why you chose that shape for the potential.



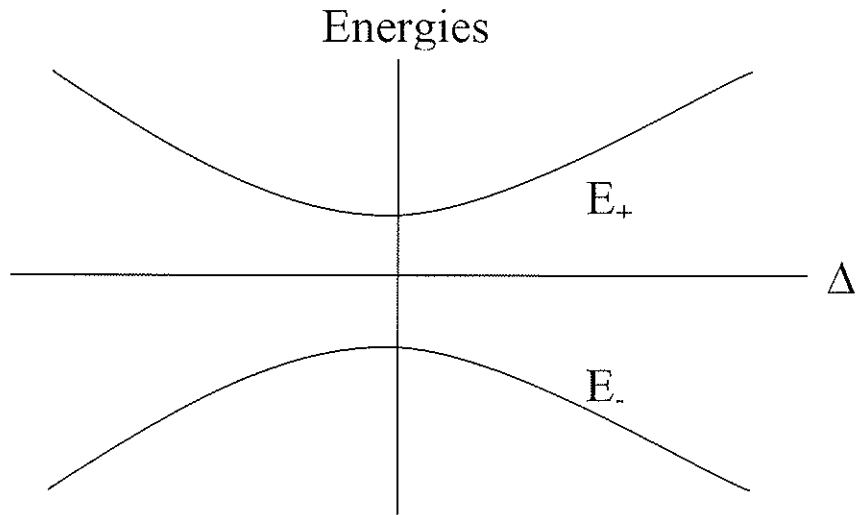
3. A Morse potential is frequently used as a better approximation (that can be solved analytically) than the Harmonic Oscillator potential for determining vibrational frequencies. What new information is obtained from solution of Schrodinger equation when the vibrational and rotational wavefunctions are used to solve the equation and why?
4. The molecule H_2^+ can be solved exactly under the Born-Oppenheimer approximation using the LCAO-MO method. The solution to the positive linear combination ($1s_a+1s_b$) leads to two types of integrals commonly denoted $\frac{J}{1+S}$ and $\frac{K}{1+S}$. Graph both of these terms as a function of energy vs. internuclear distance. Discuss the classical origins of these integrals and the implications toward the chemical bond.
5. In your exam booklet draw the following potential and fill in the energy levels. Explain why you drew the energy levels the way you did.:



6. Discuss the quantum mechanical origin of the following MO diagram for H_2 . (What is the origin of the shape of the graph, what are $1s_a$, 1σ , etc.):



7. The perturbative treatment of a two-level interaction leads to the following graphical solution:



Where:
$$E_+ = E_M + \sqrt{\Delta^2 + |W_{12}|^2}$$

$$E_- = E_M - \sqrt{\Delta^2 + |W_{12}|^2},$$

And W_{12} is the magnitude of the interaction between the two levels. Discuss this graph in the limiting cases when $W_{12} = 0$ and when $W_{12} > 0$ (the above graph).

8. Explain the Variational Method and the Variational Theorem.

