

**Physical Chemistry Cumulative Exam**  
**May 10, 2011**  
**Problems related to Structural aspects of Spectroscopy**  
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Focus on those problems you can answer. Some well thought out responses are better than poor attempts at all questions. READ ENTIRE EXAM FIRST.

**Answer only enough questions to total = 100 -- I stop grading at ~ 100 pts.**

**(10) 1.** We have had some interesting physically oriented seminars this previous semester, which can be designated as those hosted by a physical chemistry faculty member or having to do with the *fundamentals of chemistry reactions and structure*. For one of these, please give the speaker's name and affiliation and, more importantly, summarize his/her experimental results and conclusions. State how you think this work will affect our understanding in the future. If you are unsure of the speaker, give Pat Ratajczyk this information on Wednesday for anonymous transfer to me, so I will know whom you are writing about.

**(25) 2.** Rotational spectroscopy is sometimes said to produce the most precise measures of molecular structure (e.g. bond lengths) or any technique.

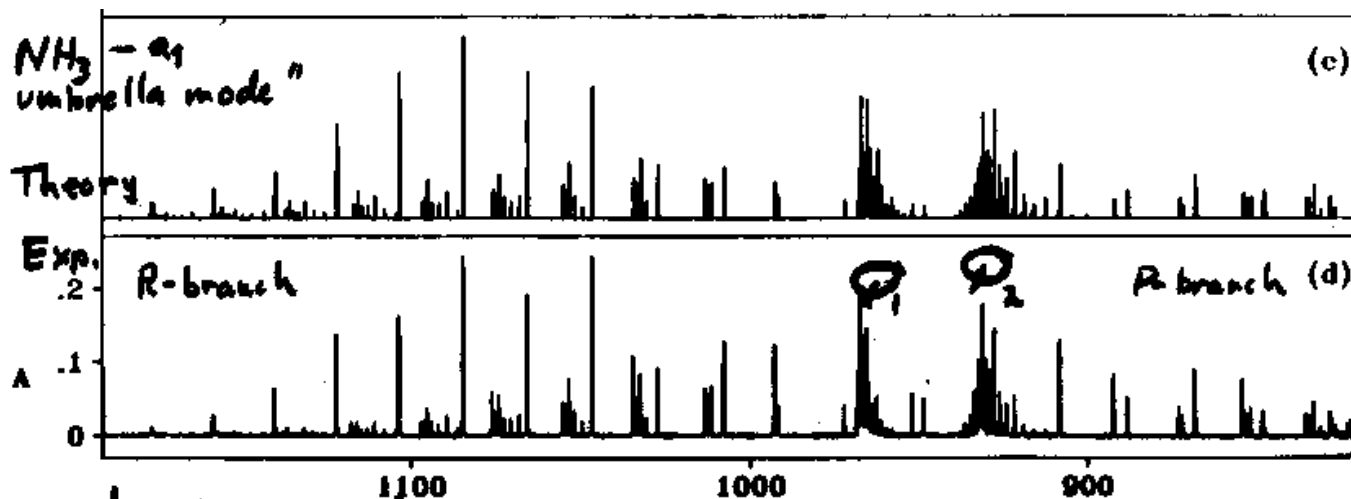
- a. What parameter is measured in rotational spectra that relates to structure and how do you relate the transition frequency to that parameter. (I am looking for a procedure that relates observables to properties of the energy levels and then to structural properties in some quantum mechanical relationship).
- b. If rotational spectra give such precise structures, why are only a few structures determined in this manner? Briefly explain the "catch".
- c. Most of us have experience in measurement of vibration-rotation spectra (rather than pure rotational spectra). Why do vibration-rotational not give as precise structural information as pure rotational spectra? (There are two reasons, one experimental, and one fundamental or intrinsic to the spectroscopy.)
- d. Briefly summarize some of the corrections that can be made to the vib-rot spectra to improve structural interpretations.

**(12) 3.** Give the ground electronic configuration and lowest energy term symbol for:

- a.  $\text{Cr}^{+3}$ ,   b.  $\text{Mn}^{+2}$ ,   c. Ag,   d. Te,   e.  $\text{B}_2$ ,   f.  $\text{O}_2$

**(12) 4.** Determine all the allowed term symbols for the  $p^3$  configuration. Be careful not to overcount. To do this the summed degeneracies of all the term symbols must equal the degeneracy of the configuration. Demonstrate your answer agrees.

- (14) **5.** Selection rules can lead to structural insight, at least on a qualitative basis.  $\text{CN}^-$  as a ligand in transition metal complexes has a fundamental vibration at  $\sim 2200 \text{ cm}^{-1}$ . When there are multiple equivalent ligands, the vibrations couple to form normal modes and shift in frequency.
- Pt(CN)<sub>4</sub>** has 1 band in the IR and 2 in the Raman in the range of  $2100\text{-}2300 \text{ cm}^{-1}$ , but none of these have the same frequency. What is the structure? Why?
  - Pd(CN)<sub>4</sub><sup>-2</sup>** has 1 band in the IR and 2 in the Raman in the range of  $2100\text{-}2300 \text{ cm}^{-1}$ , and one of the Raman bands has the same frequency as the IR band. Propose a structure that is consistent with this observation and explain why.
- (20) **6.** Spectra have often been used to determine structural differences for molecules related by various kinds of isomerizations. Interactions of molecules with surfaces or other species can also create an “isomerism” of orientation or type of binding. For **the following** situations describe how you would determine the isomer present, what kind of optical (fluorescence, uv absorption, IR, Raman) spectroscopy you would use (may compare multiple or two types or add some variant to one of them, such as polarization or surface reflection) and how this would distinguish the structures.
- cis*- and *trans*-stilbene ( $\text{Ph-HC=CH-Ph}$ )
  - L*- vs. *D*-Tryptophan (indol side chain) in a short tripeptide
  - $\alpha$ -helical antibiotic (based on an oligo-peptide) that is active by either penetrating in or lying on a membrane
  - “on top” vs. lying down (“side bond”)  $\text{C=O}$  on a metal surface
- (20) **7.**  $\text{NH}_3$  is very similar to  $\text{BH}_3$ , except that it is not planar.
- Propose how you would spectroscopically distinguish  $\text{BH}_3$  and  $\text{NH}_3$ .
  - Explain why the MO description of  $\text{NH}_3$  demands it be non-planar. You do not need to work this out, if you can think it through, use common chemical sense.
  - What aspect of the MO diagram makes  $\text{NH}_3$  a base? Again use your chemical sense here.
  - $\text{NH}_3$  is often termed a double well problem. What does this mean? What vibrations evidence these effects? How?
  - Below (next page) are IR spectra of  **$\text{NH}_3$  in the  $\nu_2$  state**, which is one of the two  $a_1$  modes, explain what mode is excited (which internal coordinates) and why it has two Q-branches and complex P- and R-branches.



(40) 8. Consider the  $\text{BH}_3$  molecule (planar).

- Using a valence-only basis set of the  $2s$  and  $2p_x, 2p_y, 2p_z$  orbitals on B and the  $1s$  orbitals on the 3 H atoms construct an LCAO-MO representation of the orbital energy levels. First determine and tabulate the symmetry representations of each of the basis orbitals, and symmetrize any that do not correspond to irreducible representations. Then set up the secular determinant, note any zeros that arise from symmetry or AO orthogonality. From only the form of the determinant, sketch a molecular orbital energy level diagram consistent with the AO energies and their expected interaction energies from bonding. Justify your relative energies.
- Which orbitals are bonding, non-bonding, and antibonding? Which one (if any) will be a lone pair? Which orbital is responsible for the Lewis acid character of  $\text{BH}_3$ ? Why? [Hint--orbital occupancy will help answer this.]
- Give a configuration for the **lowest energy multielectron state**. Determine its **term symbol** (spin and symmetry representation,  $2S+1\Gamma$ ).
- What are the configurations and term symbols for the **excited states** arising from the excitation of one electron (highest filled orbital) to either of the two lowest energy empty orbitals?
- Are transitions electric dipole allowed between the ground electronic state and the excited states you found? Why or why not?

- (30) **5. NiCl<sub>4</sub><sup>-2</sup>** is a tetrahedral transition metal complex that is effectively isolated in solution. To understand its spectroscopy we must be able to interpret its states in terms of its symmetry. *The usual approach to the electronic spectrum of NiCl<sub>4</sub><sup>-2</sup> is called ligand field theory, in which free ion states are perturbed by a Hamiltonian representing the ligand effects on the metal.*

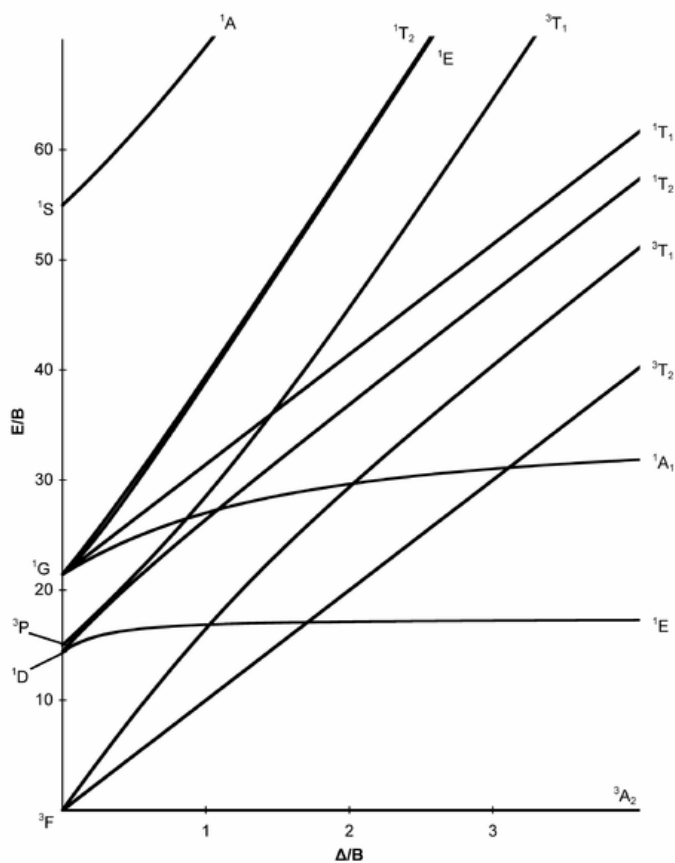
*Atomic spectra section:*

- a. To start, what are (all) the allowed term symbols ( $2S+1L_J$ ) that represent  $|\text{LSJM}\rangle$  eigenfunctions of the Ni<sup>+2</sup> ion which is in a lowest energy (3d)<sup>8</sup> configuration. (*Hint:* This is essentially a problem in the coupling of angular momenta, **L** and **S**, and in keeping track of the Pauli Principle. Since 2-electron configurations have a simple solution, you may just write down the answer and state the general rule, or take shortcuts to work it out.)
- b. Using Hund's first two rules determine the lowest energy ( $2S+1L$ ) term of Ni<sup>+2</sup>. Since Ni is in the 1<sup>st</sup> transition series, spin-orbit coupling is modest and probably can be neglected. If we were to include it, what would be the lowest  $|\text{LSJM}\rangle$  state ( $2S+1L_J$  term symbol) of the lowest term for the free ion Ni<sup>+2</sup>? (Hund's third rule)

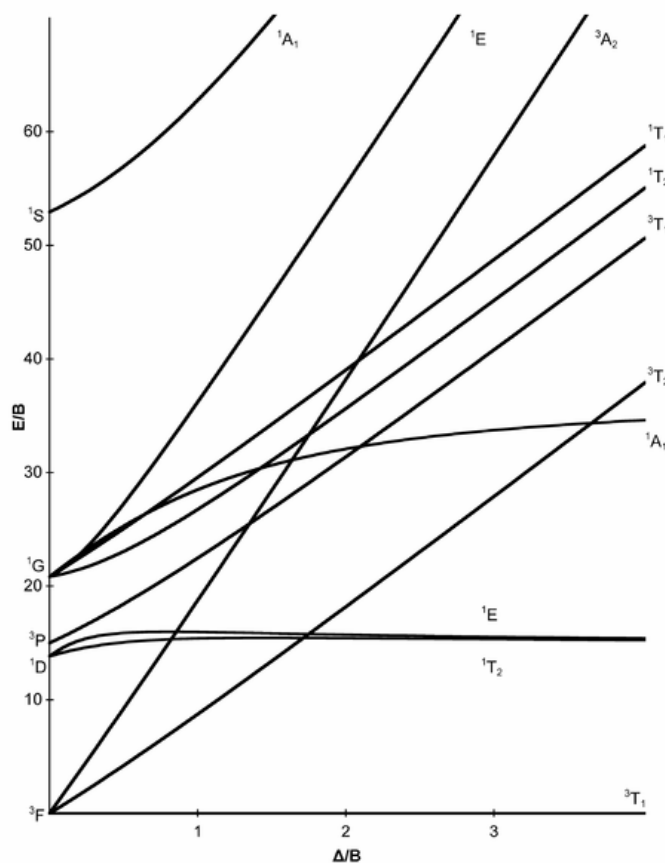
*Ligand field model section:*

- c. In the molecular ion NiCl<sub>4</sub><sup>-2</sup>, however, the ligands provide a much larger perturbation on the d-electron states than does the spin-orbit coupling. In a tetrahedral molecule the lowest L-S free ion term  $|\text{LSM}_L\text{M}_S\rangle$  is perturbed to give rise to a lowest <sup>3</sup>T<sub>1</sub> and excited <sup>3</sup>T<sub>2</sub> and <sup>3</sup>A<sub>2</sub> molecular "term symbols." This is sometimes called the weak-field limit. In a Tanabe-Sugano diagram (attached are the d<sup>2</sup> and d<sup>8</sup> diagrams) these diverge quickly with increasing ligand field strength. Explain why you should use a d<sup>2</sup> octahedral T-S diagram for this problem. The next L-S term gives rise to nearly degenerate <sup>1</sup>T<sub>2</sub> and <sup>1</sup>E molecular terms that don't change significantly in energy relative to the <sup>3</sup>T<sub>1g</sub>. To which of the above states are transitions allowed by the electric dipole mechanism? Why? For those that are forbidden, explain the cause.
- d. If you have correctly worked out the above problems, you have found that some of the transitions, ignoring spin-orbit coupling, are forbidden. However, these transitions can be observed. Explain how this can happen.
- e. All of the above transitions are from states of essentially d orbital character to other d states. Also possible are transitions from states primarily formed from products of d-orbitals with ligand orbitals to primarily d states. These are called charge transfer transitions, which are usually in the near-uv and visible,

overlapping the highest energy d states. Some of the more intense of these transitions are to  ${}^3T_2$  and  ${}^3T_1$  charge transfer (CT) states. Do you expect the CT to be more or less intense than the d $\rightarrow$ d type transitions we have discussed in parts c through d? Why? Do you expect either of these to be more intense than a transition to a state of predominantly metal p orbital character? Why? (This last transition would be interconfigurational, but metal-centered e.g.,  $(4d)^2 \rightarrow (4d)^1 (5p)^1$ .)



$d^8$  – octahedral T-S diagram



$d^2$  – octahedral T-S diagram

**Character table for  $T_d$  point group**

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

hydrogen 1 <b>H</b> 1.0079																			helium 2 <b>He</b> 4.0026
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122													boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305												aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948	
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80		
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29		
caesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	57-70 *	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]	
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	89-102 * *	lawrencium 103 <b>Lr</b> [262]	rutherfordium 104 <b>Rf</b> [261]	dubnium 105 <b>Db</b> [262]	seaborgium 106 <b>Sg</b> [266]	bohrium 107 <b>Bh</b> [264]	hassium 108 <b>Hs</b> [269]	meitnerium 109 <b>Mt</b> [268]	ununilium 110 <b>Uun</b> [271]	unununium 111 <b>Uuu</b> [272]	ununbium 112 <b>Uub</b> [277]		ununquadium 114 <b>Uuq</b> [289]					

\* Lanthanide series

\*\* Actinide series

lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium 67 <b>Ho</b> 164.93	erbium 68 <b>Er</b> 167.26	thulium 69 <b>Tm</b> 168.93	ytterbium 70 <b>Yb</b> 173.04
actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> 232.04	protactinium 91 <b>Pa</b> 231.04	uranium 92 <b>U</b> 238.03	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	einsteinium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]

### Character table for $C_{3v}$ point group

	E	$2C_3(z)$	$3\sigma_v$	linear, rotations	quadratic
$A_1$	1	1	1	z	$x^2+y^2, z^2$
$A_2$	1	1	-1	$R_z$	
$E$	2	-1	0	(x, y) ( $R_x, R_y$ )	$(x^2-y^2, xy)$ (xz, yz)

### Character table for $D_{3h}$ point group

	E	$2C_3$	$3C'_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
$A'_1$	1	1	1	1	1	1		$x^2+y^2, z^2$
$A'_2$	1	1	-1	1	1	-1	$R_z$	
$E'$	2	-1	0	2	-1	0	(x, y)	$(x^2-y^2, xy)$
$A''_1$	1	1	1	-1	-1	-1		
$A''_2$	1	1	-1	-1	-1	1	z	
$E''$	2	-1	0	-2	1	0	( $R_x, R_y$ )	(xz, yz)

**Character table for  $D_{4h}$  point group**

	E	$2C_4(z)$	$C_2$	$2C'_2$	$2C''_2$	i	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
$A_{1g}$	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	$R_z$	
$B_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1		$x^2-y^2$
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1		xy
$E_g$	2	0	-2	0	0	2	0	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	-1	-1	-1	-1	-1	1	1	z	
$B_{1u}$	1	-1	1	1	-1	-1	1	-1	-1	1		
$B_{2u}$	1	-1	1	-1	1	-1	1	-1	1	-1		
$E_u$	2	0	-2	0	0	-2	0	2	0	0	$(x, y)$	

**Character table for  $O_h$  point group**

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