

CHEM.522

Drexel U. Winter Inorganic-II, Jan. 2016.

522Syllabus16L

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Useful Course Materials:

- 1) A. Vincent: *Molecular Symmetry & Group Theory*. 2nd Edn., Wiley, 2001.
- 2) The course notes will eventually be available on the Bb/Vista website.
- 3) Molecular model kit – Darling Models suggested.
- 4) Housecroft & Sharpe: *Inorganic Chemistry*. 4th Edn., Prentice-Hall 2012 (or 3rd Edn. 2007) or Shriver & Atkins: *Inorganic Chemistry*. 6th Edn., Freeman 2014 (or 5th Edn. 2009)

Main Web Resources:

Look for “CHEM522” after logging on at learn.drexel.edu

Kettle’s *Symmetry in Chemistry* materials are now available on the web, at:

<http://www.rsc.org/Membership/Networking/InterestGroups/EducationalTechniques/ChemistryCassettes/index.asp>

d-Orbitals & ligands: <http://www.flicksstuff.com/jsmol/ligandfield.html>

Tanabe-Sugano diagrams and Racah parameters:

http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Crystal_Field_Theory/Tanabe-Sugano_Diagrams#Racah_Parameters

Reference Materials:

- 1) F. A. Cotton: *Chemical Applications of Group Theory*. 3rd Edition, Wiley-Interscience 1990. QD461.C65.1990 (Hagerty Reserve)
- 2) M.F.C. Ladd: *Symmetry of Molecules & Crystals*, Oxford U.P., 2014: QD905.2.L33 2014.
- 3) Shriver & Atkins: : *Inorganic Chemistry*. 5th Edn., Freeman & Co., 2010.
- 4) Miessler & Tarr: *Inorganic Chemistry*, (3rd Edn.) 2003.
- 5) Huheey, Keiter & Keiter, *Inorganic Chemistry: Principles of Structure & Reactivity*. Fourth Edn., Harper-Collins 1993. (Good chapter on symmetry)
- 6) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn., Wiley-Interscience, NY, 1997 QD96.I5N33 1997 (or earlier editions): Hagerty Reserve.

Goals:

A primary goal of the GT section of the course is to be able to read and use character tables for solving molecular properties. Know the concept of a group, be able to manipulate/combine elements, using multiplication tables. Be able to use matrix representations of vectors & symmetry operations, generate simpler cases.

Understand origins of character values and representations. Be able to use character tables to find classes and subgroups and deduce and combine representations for various properties and objects (e.g., atomic orbitals). Know how to choose basis sets, generate & decompose representations from them & how to use projection operators. Apply these methods to the vibrational spectra of molecules. Use the Crystal Field Theory model to interrelate stereochemistry, symmetry, configuration, spin state, optical and (the various kinds of) common magnetic properties and crystal field stabilization energy for transition metal compounds; compute magnetic moments for *nd* [and *4f*] ions. Be able to deduce the spin & orbital multiplicity of ground and excited states. Be able to read Tanabe-Sugano diagrams and recognize *d-d*, LMCT, MLCT & π - π^* transitions. [Optional: Using symmetry methods, be able to derive normalized MO forms for diatomic, cyclic and centric molecules; deduce occupancy of MO diagrams for transition metal complexes, and molecule properties.]

Relationship to other courses and Pre-Requisite Knowledge:

The pre-requisite for CHEM.522 is CHEM.521 or good undergraduate preparation in Inorganic Chemistry. The other course in the core graduate sequence is CHEM.523 (Inorganic-III), and the other courses that may be taken include 862. Compared with 521, which has more "descriptive" content, 522 is a bit more "mathematically" (group theory) based; *e.g.* matrix algebra is alluded to.

Specific things you need to know before entering 522 are: *s,p,d,f*-atomic orbitals; symmetry elements; assignment of molecules to point groups; configurations of *nd* cations; VSEPR & geometries for 2-6-coordination; the Lewis acid/base model; from PChem., the nature of infrared and electronic (optical/UV) absorption phenomena.

Other stuff: Be sure that I have your correct Email address for my exploder. Work on the problem sets !! Attempt to solve the homework problems as soon as we have covered the material in class. There is normally no grade given for attendance or for homework. If you do not do the homework, you will find it hard to pass the exams, and virtually impossible to get a good grade. I suggest that you form a study group with some like-minded students in the course, and collaborate in studying and problem-solving. For help with problem sets or any other concerns, I may be found in my office or lab most of the daytime during the week, though it's probably best to make an appointment. As before, your grade is based on the (usually three) exams: two midterms (20%, 30%) plus a final exam (50%). The grade ranges are: D= 43-45; D+=46-49; C-=50-53; C=54-56; C+=57-59; B-=60-64; B= 65-69; B+=70-75; A-=76-83; A=84-91; A+=92-100. You may bring our periodic table and molecular model kit to the exams (some of the assigned classrooms have no periodic table). If you are not officially registered in the course, no midterms or quizzes will be graded or returned, and you may not receive any distributed materials. Tentative mid-term dates are Jan. 27th & Feb. 24th.

Penalizable misspellings: "flourine", "valance", "assymmetric", "pyrimidal", *etc.*

Make-Up Exams ?

You don't need an excuse to take the make-up exam if you miss a midterm or final, but you *must* then attend the make-up at the designated time and place or take a zero on it - no excuses. You may make up no more than one exam. Make-up exams are never of lesser difficulty than the ones they replace. The make-up exam date is tentatively scheduled as the afternoon of Monday, March 21st.

The 10-Minute Rule: If I'm more than ten minutes late without prior notice, consider the class cancelled. If you are going to be more than ten minutes late for a class, please don't enter without prior arrangement, until the class takes a break.

Content:

There will be three major aspects in this course on (mainly transition metal) structure-properties relationships: constitution & structure, CFT, and vibrational spectroscopy. CFT is the major one, while use of group theoretical methods is an underlying theme.

- Symmetry elements and groups: combination, matrix usage, characters.
- Classes. Matrix representations of 3D vectors & of operations.
- Irreducible and reducible representations as sets of matrices. Sums. Character tables.
- Mullikan notation. Degeneracy. Representations exemplified by atomic orbitals.
- From basis set to total (motional) representation; decomposition of representations.
- Molecular vibrations; infrared & Raman selection rules.
- Group theory for orbital symmetry; representations for central atom orbitals.

- The Crystal Field model: O_h fields; d-d transitions. The spectrochemical series.
- Jørgensen's f & g ; spin states & dia/para/ferro/antiferro-magnetism of nd^x systems [spin crossover systems] dinuclear complexes.
- CFSE & stability, T_d fields, 4d- & 5d-ions; planar/ D_{4h} symmetry, Jahn-Teller "distortion".
- Products of representations: spin & symmetry UV-Vis selection rules from a simple electronic configuration viewpoint.
- Terms & states: magnetism of 4f ions.
- Products of representations: spin & symmetry selection rules.
- Sources of color for metal complexes: $d-d$, $\pi-\pi^*$ & charge-transfer transitions, optical electronegativity.
- Splitting of terms by crystal fields, Tanabe-Sugano diagrams.

[Optional coverage: likely deferred to CHEM.523.

- Diatomic MO's from a symmetry approach: from basis set to representation.
- Decomposition formula; MO's for cyclic tetraatomic (S_4^{4+} π -system): SALC's.
- Projection operators. Use of PRSG, normalisation & relative energies of MO's.
- Symmetry factoring for centric molecule: LGO's, \uparrow & \bullet MO's for BF_3 .
- MO's for octahedral complexes without and with π -bonding.]

Some University Policies we are asked to remind you about:

Academic integrity: http://www.drexel.edu/provost/policies/academic_dishonesty.asp

Disability accommodations: <http://www.drexel.edu/oed/disabilityResources/students/>

Dropping courses: http://www.drexel.edu/provost/policies/course_drop.asp

Financial Obligation: <http://drexel.edu/drexelcentral/billing/billing/policies/>