Chemistry 606: Physical Methods for Structure Determination

3 Credits

General Education

Chemistry Building 2373, MWF 11:00 AM-11:50 AM

Classroom Instruction

This class meets for three 50-minute class period each week over the spring semester and carries the expectation that students will work on course learning activities (reading, writing, problem sets, studying, and performing computations) for about 2 hours out of classroom for every class period.

INSTRUCTORS

Professor Thomas C Brunold
Office hours: MF 12:00 – 12:50 PM
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Professor Judith Burstyn
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OFFICIAL COURSE DESCRIPTION

A survey of spectroscopic methods for inorganic structure determination. This course will introduce the major non-crystallographic techniques with an emphasis on the application to structural analysis. The basic theory and methodology of each form of spectroscopy will be presented. Topics covered include: ligand field theory, electronic absorption, IR/Raman, Mossbauer and EPR spectroscopies, and magnetic susceptibility.

Pre-requisites: Chemistry 511 & 562 or cons inst. Chemistry 608 or equiv recommended

LEARNING OUTCOMES

By the end of this course:

- You will be able to apply group theory to a variety of problems dealing with molecular vibrations and chemical bonding;
- You will be able to carry out quantitative analyses of experimental data obtained using a wide range of spectroscopic techniques;
- You will be able to perform density functional theory calculations on transition metal complexes and to validate your computational results on the basis of structural and spectroscopic data;
- You will demonstrate knowledge about spectroscopy and computations by writing a paper that is based on your analysis of spectroscopic data presented in a recent publication and computations performed by you to complement your spectral analysis.

GRADING

Grades will be based on a total of five take-home problem sets (65%) and a paper written at the end of the semester (35%).

RECOMMENDED TEXTBOOK, SOFTWARE & OTHER COURSE MATERIALS

- Que, L., Jr. Physical Methods in Bioinorganic Chemistry, University Science Books (2000);
- ORCA computational software package: https://orcaforum.cec.mpg.de/;
- ORCA manual: https://cec.mpg.de/fileadmin/media/Forschung/ORCA/orca_manual_4_0_1.pdf.
- PyMol software: https://software.wisc.edu/cgi-bin/ssl/csl_download.cgi.

FINAL PAPER

1. Choose an inorganic metal-containing complex for which X-ray crystallographic and spectroscopic data have been reported in the literature or obtained by yourself (or another research group member). Although you are free to pick whatever complex you like, particularly good choices would include species with S = ½ spin ground states (e.g., Ni(I), Cu(II), low-spin Co(II), etc.) as in this case the interpretation and calculation of the corresponding EPR parameters is relatively straightforward.

2. Perform a geometry optimization of your complex (use a truncated model if necessary) and compare key metric parameters for your optimized model and the crystallographically determined structure. Discuss the origin of possible discrepancies.

3. Compute and plot an MO energy-level diagram for your complex. Remember that for complexes with S > 0, your MO diagram will have spin-up and spin-down orbitals at different energies. Label MOs according to their principal contributors (e.g. “Cu 3dxy”). Discuss your MO diagram. To facilitate this task, it is highly recommended that you generate isosurface plots of key MOs using the PyMol program.

4. Take advantage of the fact that ORCA allows you to compute a library of spectroscopic observables for your model, such as vibrational frequencies, EPR parameters, electronic transition energies and intensities (using the TD-DFT implementation), etc. Note that by using the "orca_mapspc" program, you can generate computed absorption and IR spectra that can be compared directly with the corresponding experimental spectra.

5. Now it is time to share your results with the inorganic chemistry community by writing a paper in JACS or Inorganic Chemistry format that summarizes the results and insights gained in your study. Your paper should include the following: title, abstract, introduction, experimental section (i.e., computational details), results and analysis, discussion (particularly important), and references. Avoid presenting unnecessary details – quality is much more important than quantity!

HOMEWORK ASSIGNMENTS

- You will be given at least one week to complete each homework assignment.
- You are strongly encouraged to work on homework assignments in small groups, but you must turn in individually prepared answer sheets.

RULES, RIGHTS & RESPONSIBILITIES

- See the Guide's Rules, Rights and Responsibilities.

ACADEMIC INTEGRITY

By enrolling in this course, each student assumes the responsibilities of an active participant in UW-Madison's community of scholars in which everyone's academic work and behavior are held to the highest academic integrity standards. Academic misconduct compromises the integrity of the university. Cheating, fabrication, plagiarism, unauthorized collaboration, and helping others commit these acts are examples of academic misconduct, which can result in disciplinary action. This includes but is not limited to failure on the assignment/course, disciplinary probation, or suspension. Substantial or repeated cases of misconduct will be forwarded to the Office of Student Conduct & Community Standards for additional review. For more information, refer to studentconduct.wiscweb.wisc.edu/academic-integrity/.

ACCOMMODATIONS FOR STUDENTS WITH DISABILITIES

McBurney Disability Resource Center syllabus statement: "The University of Wisconsin-Madison supports the right of all enrolled students to a full and equal educational opportunity. The Americans with Disabilities Act (ADA), Wisconsin State Statute (36.12), and UW-Madison policy (Faculty Document 1071) require that students with disabilities be reasonably accommodated in instruction and campus life. Reasonable accommodations for students with disabilities is a shared faculty and student responsibility. Students are expected to inform faculty [me] of their need for instructional accommodations by the end of the third week of the semester, or as soon as possible after a disability has been incurred or recognized. Faculty [I],

will work either directly with the student [you] or in coordination with the McBurney Center to identify and provide reasonable instructional accommodations. Disability information, including instructional accommodations as part of a student's educational record, is confidential and protected under FERPA." http://mcburney.wisc.edu/facstaffother/faculty/syllabus.php

DIVERSITY & INCLUSION

Institutional statement on diversity: "Diversity is a source of strength, creativity, and innovation for UW-Madison. We value the contributions of each person and respect the profound ways their identity, culture, background, experience, status, abilities, and opinion enrich the university community. We commit ourselves to the pursuit of excellence in teaching, research, outreach, and diversity as inextricably linked goals.

The University of Wisconsin-Madison fulfills its public mission by creating a welcoming and inclusive community for people from every background – people who as students, faculty, and staff serve Wisconsin and the world." https://diversity.wisc.edu/