I. OFFICIAL COURSE DESCRIPTION

Mass spectrometry and applied nuclear magnetic resonance. Three lecture sessions per week. Prerequisites are either CHEM 562 or the consent of the instructor.

II. COURSE MATERIALS

Recommended Textbooks:


Course websites: The course will make extensive use of Canvas. Lecture notes, handouts, problem sets, reading assignments, and announcements will be posted to the course website regularly. You will also use Canvas to view your grades (https://canvas.wisc.edu/courses/174952).

Other websites and web sources that might be useful for extra problems and explanation are listed below; please feel free to let me know if you run across any others! If you are not comfortable with solving the types of NMR problems that you would encounter in a typical 2nd-semester undergraduate organic chemistry course, you should consider using some of these websites for additional practice.

http://www.chem.ucla.edu/~webspectra/
http://www3.nd.edu/~smithgrp/structure/workbook.html
III. LECTURE AND DISCUSSION

Reading: I’ve included background reading assignments in the accompanying list of topics that will be covered in the course. My primary goal is to give you the tools and strategies you require to elucidate structure and understand reaction behavior, not to teach you the theory or physical basis for the spectroscopic techniques discussed in class. If you are interested in obtaining a more in-depth understanding of the topics discussed in the course, I would recommend the reading assignments or taking Charlie Fry’s Chem 637 course, if it is still being offered this summer.

Grading:
Problem sets (10 x 20 points each)  200 points
Exam 1                   150 points
Exam 2 (final)             150 points
Class ‘unknown’ project    100 points
Class participation (quizzes, problem-solving sessions) 100 points

Problem Sets. There will be 10 problem sets during the course of the semester. These can be worked on in groups, but please be careful not to simply copy answers. Mastering spectroscopy requires a great deal of practice, so it is your best interest to attempt problems first on your own. Problem sets will be made available on Canvas at least a week in advance and should be turned in on the dates listed on the Tentative Agenda. I will look through the problem sets to ensure that you have made sufficient progress, assign a preliminary grade and hand the problem sets back on Friday. The class as a whole will then solve the problems—these sessions are an opportunity to rack up participation points. At the end of the class on Friday, you have the option of turning in your ‘corrected’ homework to get back 50% of the points you may have missed. You cannot get back these extra points if you opt to skip the Friday problem-solving session.

Quizzes. I will regularly pass out short ‘quizzes’ a lecture ahead of time. These are already posted on the Canvas website, but I will hand out paper copies in class, as we sometimes end up getting a bit off schedule. At the beginning of the next class period, I will ask for volunteers to solve the problems. This is another opportunity to earn participation points.

Class ‘unknown’ project. Sometime in late February, I will start assigning your unknowns. Heike has graciously agreed to collect a variety of conventional 1D and 2D NMR spectra for you, so you do not need to have taken Chem 636 or know how to operate the instruments (although we can provide you with FIDs if you wish to reprocess the data). Other data, such as a molecular weight, IR stretches or advanced 2D NMR data will be provided as needed.

You and a partner will work together to identify your unknown using both spectra and computational/modeling tools that may help you to support any tentative assignments. You are responsible for describing both the structure and the relative stereochemistry of your molecule. One week before your scheduled oral presentation to the class, you will turn in a written report describing how you analyzed your data and how you came to assign your proposed structure. This report will be made available to the class so that they have sufficient time to follow your logic prior to a final presentation you will make during the last few weeks of the course. You and your partner can split the duties of the final presentation any way you wish, but I suggest one person address functional groups present in the molecule and the 1D NMR data, while the second person discuss any 2D NMR and computational studies. More details will be forthcoming as the semester progresses.

Examinations: There will be only two exams this semester. One will be a ‘mid-term’, while the other can be given either during our scheduled Final Exam time or moved to a Saturday with agreement from the entire class. The first exam will be a take-home exam. For the second exam, you may bring any written materials you find useful to the exam. Calculators are fine, but computer devices and internet use are not allowed.
IV. LEARNING OUTCOMES

Course Learning Outcomes are included as a requirement for an upcoming audit of the university. Undergraduate and graduate learning outcomes are identical.

At the end of this course, students should be able to:

- Analyze and interpret a variety of spectroscopic data to deduce the chemical structure of an unknown compound.
- Choose the appropriate experiment(s) in a research setting to determine the structure and/or dynamic behavior of an unknown compound.
- Utilize modern techniques, skills and tools necessary for the practice.
- Examine technical literature, resolve ambiguities and develop conclusions.
- Communicate complex scientific ideas in a clear and understandable manner through written reports, oral presentations and discussion.
- Guide, mentor and support peers to achieve excellence in practice of the discipline.
- Work in multi-disciplinary teams and provide leadership on problems that arise.
- Foster safe, ethical, and professional conduct.
<table>
<thead>
<tr>
<th>Week</th>
<th>Date</th>
<th>Reading Material</th>
<th>Reich Handouts</th>
<th>Selected Topics</th>
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</thead>
</table>
| 1    | W Jan 22 | **Pavia** Chapters 1-2  
Lambert, Chapter 1  
Lambert Ch. 8 (focus on IR) | Notes-02-IR-v23 2014 | Introduction and course outline  
Comparison of important spectroscopic methods in use  
Electromagnetic spectrum  
Vibrational spectroscopy (IR, REACT-IR)  
IR group frequencies  
Structural analysis using IR |
|      | F Jan 24 | **Pavia** Chapter 3.1-3.10  
Lambert Ch. 2, 3  
Friebolin Ch. 1.2.2, 6.2 | 05-HMR-v22-all 2014 |
|      |          |                  | 5-HMR-1   | NMR Introduction and experimental methods  
Simplified description of the NMR experiment  
¹H integration and chemical shifts  
Symmetry considerations |
|      |          |                  | 5-HMR-2   | |
| 2    | M Jan 27 | **Pavia** Chapter 3.11-3.12  
Lambert Ch. 3  
Friebolin Ch. 2.2 | 5-HMR-2, 9.5 | Quiz 1 (IR Practice)  
Factors influencing chemical shift  
Curphy-Morrison tables and exceptions  
Spin-spin splitting, why it occurs, Pascal’s triangle  
First-order multiplets, size of couplings  
Two different couplings to one proton  
Substitution patterns in aromatics  
Leaning effects  
Determining whether a multiplet exhibits a first-order pattern  
Problem Set 1 is due |
|      | W Jan 29 | **Pavia** Chapter 3.13-3.19  
Lambert Ch. 4  
Friebolin Ch. 3.1-3.3 | 5-HMR-3   | Solve Problem Set 1  
Solve Problem Set 1 |
|      | F Jan 31 | **Pavia** Chapter 5  
Lambert Ch. 4  
Friebolin Ch. 3.1-3.3, 4 | 5-HMR-3.3-3.10 | Quiz 2  
“Nutty” compounds  
More practice with ¹H-order multiplets  
Multiplets that are not ¹H-order |
|      |          |                  |          | X-ray Crystallography  
Problem Set 2 is due |
|      |          |                  |          | |
| 3    | M Feb 3  | **Pavia** Chapter 4  
Lambert Ch. 3.3-3.4  
Friebolin Ch. 2.3, 3.4, 6.3 | 6-CMR-1.1, 6-CMR-3.1-3.9, 6-CMR-3.11, 4.2 | Quiz 3  
¹³C NMR chemical shifts  
β,γ effects on chemical shift  
Ring size effects on chemical shift  
Effect of conjugation, charge effects, hydrogen bonding on ¹³C chemical shifts, parameter tables  
Introduction to Mass Spectrometry  
Presentation of data and nomenclature  
Isotopes, molecular formulas, High and low resolution techniques |
|      | W Feb 5  | **Guest Lecturer**  
Dr. Ilia Guzei | Dr. Guzei Handout |  
 |
|      | F Feb 7  | **Guest Lecturer** | Solve Problem Set 2 | Solve Problem Set 2 |
| 4    | M Feb 10 | **Pavia** Chapter 8  
Lambert Ch. 13-15  
**Guest Lecturer** | Reich Handout 3 |  
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<tr>
<th>Date</th>
<th>Day</th>
<th>Lecturer</th>
<th>Topic</th>
<th>Notes</th>
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<tbody>
<tr>
<td>Feb 14</td>
<td>F</td>
<td>Dr. Martha Vestling</td>
<td>Different ionization techniques</td>
<td>Different ionization techniques, Analysis of ions, Different types of detectors, Analyzing fragmentation patterns</td>
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<td>Feb 17</td>
<td>M</td>
<td>Solve Problem Set 3</td>
<td>Modern mass spec techniques, UW-Chemistry Mass Spec Center</td>
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<td>Feb 19</td>
<td>W</td>
<td>Pavia Chapter 4</td>
<td>Problem Set 3 is due</td>
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<td>Feb 21</td>
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<td>Pavia Chapter 5</td>
<td>Solve Problem Set 3</td>
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<td>Feb 24</td>
<td>M</td>
<td>Guest Lecturer</td>
<td>Continue discussion of $^{13}$C NMR</td>
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<td>Feb 26</td>
<td>W</td>
<td>Pavia Chapter 5</td>
<td>$^1$H-$^{13}$C couplings, DEPT</td>
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<td>Feb 28</td>
<td>F</td>
<td>Solve Problem Set 4</td>
<td>Pople nomenclature for coupled spin systems</td>
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<td>Mar 2</td>
<td>M</td>
<td>Pavia Chapter 5</td>
<td>Symmetry and magnetic equivalence</td>
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<td>Mar 4</td>
<td>W</td>
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<td>Second-order effects in coupled systems: AX and AB patterns</td>
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<td>Mar 6</td>
<td>F</td>
<td>Solve Problem Set 4</td>
<td>Quiz 6</td>
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### Notes:
- **Problem Set 3 is due**
- **Problem Set 4 is due**
- **Quiz 4**
- **Quiz 5**
- **Quiz 6**
- **Quiz 7**
- **Quiz 8**
- **Quiz 9**
| 8 | M Mar 9 | **Pavia** Chapter 10.1-10.3, 10.9-10.10 | 8-NMR (8-Tech-1.1-2.17) | Solve Problem Set 5  
Finish coupling constant discussion  
Relaxation processes  
$T_1$ and $T_2$ in $^1$H, $^{13}$C, and other nuclei  
The Nuclear Overhauser Effect  
**Problem Set 5 is due** |
|---|---|---|---|---|
| W Mar 11 | **Pavia** Chapter 10.1-3, 10.6-7  
Schomaker basic 2D NMR | 8-NMR-9.1.1-9.3.3  
8-NMR-9.1-9.6 | In-class portion of exam | Quiz 10  
2D Multinuclear NMR (quick discussion)  
In-class portion of exam |
| F Mar 13 | **In-class portion of exam** | **In-class portion of exam** | **Solve Exam** | Solve exam and turn in Exam 1 take-home portion  
**Quiz 11**  
Isotopic labeling, isotope shifts  
Other useful nuclei: $^{19}$F, $^{31}$P, $^{10}$B, $^{15}$N, metals  
**Quiz 12**  
Continue multinuclear NMR  
The spin 1/2 nuclei, Quadrupolar nuclei, quadrupolar relaxation  
Other useful nuclei: $^{19}$F, $^{31}$P, $^{10}$B, $^{15}$N, metals  
**Problem set 6 is due** |
| 9 | M Mar 23 | **Jess Roberts** | **Solve Problem Set 6** | **Solve Problem Set 6**  
**Problem set 6 is due** |
| W Mar 25 | **Pavia** Chapter 10.8 | 8-NMR-9.1-9.6  
7-MULTI-1.1-4.8  
7-MULTI-1.1-4.8 | **Solve Problem Set 6** | **Problem set 6 is due**  
**Quiz 13**  
Finish discussion of multinuclear NMR  
Quadrupolar Nuclei  
**Quiz 14**  
Dynamic NMR: Measurement of conformational and chemical exchange rates, Line broadening - variable temperature NMR spectra  
The Forsen experiment - saturation transfer  
**Problem set 7 is due** |
| F Mar 27 | **Pavia** Chapter 10.1-3, 10.6-7  
Schomaker basic 2D NMR | 8-NMR-9.1.1-9.3.3  
8-NMR-9.1-9.6 | **Solve Problem Set 7** | **Solve Problem Set 7**  
Practical aspects of NMR kinetics, calculating thermodynamic parameters using NMR kinetics experiments, EXSY  
**Quiz 15**  
Finish NMR kinetics, $^{13}$C Kinetic Isotope Effect Measurements  
**Written Report on Unknowns is due** |
<table>
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<tr>
<th></th>
<th>Mon Apr 13</th>
<th>SCHOMAKER Notes</th>
<th>Mon Apr 15</th>
<th>Solve Problem Set 8</th>
<th>Mon Apr 17</th>
<th>SCHOMAKER Notes</th>
<th>Mon Apr 20</th>
<th>Class Presentations</th>
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<th>Final unknown report is due the day of the final exam. The Final Exam will be given at the regularly scheduled time.</th>
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|    |            |                 | Sat Apr 15 |                    | Thu Apr 17 |                 |            |                    |    |    |    | Quiz 16/17
|    |            |                 |            |                    |            |                 |            | Solve Problem Set 8 |    |    |    | Other useful NMR techniques (DOSY, trNOE, STD)
|    |            |                 |            |                    |            |                 |            | Methods to determine absolute stereochemistry by NMR, X-ray, and ECCD |    |    |    | Problem set 8 is due
|    |            |                 |            |                    |            |                 |            | Solve Problem Set 8 |    |    |    |