
TEACHING ADVANCED SPECTROSCOPY TO UNDERGRADUATES

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INTRODUCTION

Teaching students about spectroscopy occurs at each level of the undergraduate curriculum at Missouri Western State College (MWSC). Students are introduced to various aspects of spectroscopy in general chemistry, and they get "hands-on" experience with several pieces of equipment. The goal of this practice is to expose them to some of our more "high-tech" pieces of equipment, show them what chemists really do, and get them interested in chemistry as a career option. At the sophomore level, the students receive a fairly traditional exposure to techniques like NMR and IR in organic chemistry. Here, a general overview of how the instruments work is provided along with basics of interpretation. Students gain additional exposure and experience at the junior level in courses like instrumental methods, physical chemistry, and inorganic. In order to fulfill the ACS requirement of two advanced topics courses (with physical chemistry as a prerequisite) for certification, I proposed two advanced topics courses three years ago to expand our department's offerings in this area. These courses were; advanced kinetics and applied spectroscopy. This paper will discuss the development, implementation, challenges, and evaluation of the applied spectroscopy course at MWSC.

COURSE DEVELOPMENT

The advanced spectroscopy course grew from several areas. As mentioned earlier, our department needed additional courses to fulfill an ACS requirement. I was interested in providing our students with an option for their advanced topics requirement. Previously, students had no choice in their advanced topics course. Being a physical chemist by training, the requirement of advanced organic chemistry appeared limiting to me. I was interested in giving our students a physical chemistry/spectroscopy based option. My graduate study was in NMR spectroscopy. The spectroscopy course was a natural outlet for that interest. I also taught sections of an advanced NMR course in spectral interpretation during my graduate study whenever my research advisor was off-campus. To help in the course development, I attended an NSF sponsored course entitled "Advanced 1D and Basic 2D NMR Spectroscopy" presented by Daniel Traficante. All these things contributed to my interest and dedication to this new course.

COURSE DESCRIPTION

My approach to the course is to emphasize using various spectroscopic techniques to identify compounds. Students have already been exposed to basic theory and some basic interpretation skills. One goal of this course is to reinforce these skills and expose the students to more complex spectroscopic problems. I also emphasize the mechanistic approach. Many of the current instruments have spectral libraries loaded on the computer. It is a challenge to teach students the need for interpreting spectra when they believe the "instrument will do it for them".

The instrumental techniques covered are gas chromatography-mass spectrometry (GC-MS), ultra-violet/visible spectroscopy (UV-VIS), infrared spectroscopy (IR), Raman spectroscopy, and NMR (including proton, ^{13}C , multi-nuclear, two-dimensional, and MRI). Each technique is presented in several stages. For each technique, general theory is introduced using a physical chemistry perspective. Quantum mechanical descriptions of each technique are presented and developed. The basic components of each technique are described and advantages and uses are presented. These are not presented in great detail since the students have already taken instrumental analysis.

The majority of each section is devoted to spectral interpretation. The textbook that best suits my delivery of the class is *Spectrometric Determination of Organic Compounds*¹. The students are provided with additional spectral tables and examples that illustrate the spectra of various functional groups. To exhibit their mastery of the interpretation, students are given spectral problems and calculations. The problems are given as take home assignments. This allows the students to use the resources provided in class and the time to thoroughly interpret the problems. Students must identify the structure of the compound and the rationale for the structural choice. This helps to increase their learning and to prevent "copying" answers from other students. The final consists of a problem obtained at the NSF workshop given by Dan Traficante. It involves the structural identification of Chinese parsley using NMR. I act as the "spectrometer". The students are given "money" to "buy" spectra. I only provide them with the spectra for which they ask. Using these spectra, the students must identify the structure of the compound and make the proton and ^{13}C spectral line assignments. The students work in groups of 3 or 4 and can use any resource they bring into the room.

At MWSC, we have multi-media ready classrooms. My course was scheduled for one of these rooms last spring. This allowed me to use computer simulations, computer networking to instruments, and the document camera to present the course materials. This multi-media approach improved the course delivery and allowed me to cover more material than the previous time I taught the course (in a non-multi-media ready room). Although I am sure the multi-media ready classroom was a major contributing factor, delivering the course for the second time also contributed to its improvement.

I also have used invited guest speakers to expose the students to current research uses of the instrumental techniques. Last spring, I invited a colleague from Arkansas State University, Scott Reeve, to give a lecture on his research. This exposure is very valuable to the students and gives them another perspective on the use of these techniques.

COURSE SPECIFICS

The course is divided into 5 main sections. These are (1) mass spectrometry, (2) UV-VIS, (3) IR, (4) Raman, and (5) NMR. For this course, my original plan was to teach MS, UV-VIS, IR and NMR. Students expressed an interest in learning about new techniques when we reached the IR

section. They felt they had seen enough IR during Organic Chemistry, Physical Chemistry and Instrumental. IR is used quite extensively in both organic lab classes. It is also used in physical chemistry (the HCl/DCI experiment) and instrumental. I added the section on Raman and shortened the coverage of IR to more novel applications. The students enjoyed and appreciated this addition.

MASS SPECTROMETRY

The section dealing with MS started with basic theory of MS separation and discussing the different components and types of each component available for this instrument. Next, we discussed the different types of ionization sources available along with advantages and disadvantages of each. Concepts such as metastable ions, isotope patterns, modes of fragmentation, mechanisms of fragmentation, and examination of correlation tables all led into spectral interpretation. This section ended with a variety of unknowns and working through the spectral interpretation and identification in class. Additional information on Stevenson's Rule and McLafferty rearrangement helped with the more complex spectra.

UV-VIS

The section on UV-VIS was next. There is some debate about this area. In the previous edition (5th) of the textbook¹, the authors state in the preface the growing concern about the usefulness of UV-VIS as a structural elucidation technique compared to the increased sophistication of NMR. The authors argue that UV-VIS is useful because it is readily accessible and it gives quick answers to questions of electron delocalization¹. The section on UV-VIS was eliminated from the 6th edition. I taught UV-VIS in my course last spring for several reasons. First, I believe it does have some use in analysis. Second, the information corresponded well with some of the experiments and lecture material the students had covered in Advanced Inorganic the previous semester. Third, it showed some uses of UV-VIS that were not analyzed using Beer's Law (the student's main experience with UV-VIS).

Concepts including electronic transitions ($n \rightarrow p^*$ and $p \rightarrow p^*$) for different functional groups and degrees of conjugation, additivity tables and rules for various conjugated and ring systems, Fieser-Kuhn Equation, and substitution effects (bathochromic and hypsochromic shifts) were all discussed. Again the majority of the section dealt with using this information in spectral interpretation.

IR AND RAMAN

The next section dealt with IR and Raman spectroscopy. For IR, I used a quantum mechanical approach for the harmonic motion approximation. We also looked at the wavefunctions for vibrational motion using Hermite polynomials². Vibrational modes and anharmonicity were also included. Interpretation was then addressed using correlation tables and discussing typical stretching and bending modes of various functional groups.

Raman spectroscopy was introduced from a historical perspective. I included the first article by Raman³, Rayleigh and Raman scattering, Stokes and Anti-Stokes lines, polarizability, depolarization ratios, and a comparison between IR and Raman activity. We also discussed the symmetry elements for molecules and the reducible and irreducible representations of various compounds. Using character tables, the IR and Raman active modes could be determined. The students had learned character tables in Advanced Inorganic. Taking that information and expanding on it helped to reinforce the information that they had already learned.

NMR

The last section dealt with NMR. Basic NMR theory from both a classical standpoint and a quantum mechanical standpoint began this section. Ideas including the Larmor equation, precession, the rotating frame of reference, the Bloch equations, relaxation (both longitudinal and transverse), chemical shift, splitting (first order, higher order, and multinuclear), and additivity tables. The calculations possible with NMR additivity tables made this section larger than the other spectroscopies. Tables found in Silverstein and Bassler in addition to others^{4,5,6} were used to calculate theoretical chemical shifts for analysis and comparison. ¹³Carbon chemical shifts were calculated using the Grant and Paul rule and the Lindeman-Adams chart. Other experiments such as decoupling, Attached Proton Test, and GASPE were examined. Two-dimensional techniques such as COSY, long range COSY, NOESY, HETCOR, HMQC, INADEQUATE, and COLOC were also introduced. Finally, a discussion of MRI concluded the semester^{7,8,9}.

COURSE CHALLENGES

Students are provided with charts that explain each technique and provide guides for interpreting spectra. One of the challenges is the perception the students have about the necessity of learning interpretation. Many of our current instruments contain spectral libraries. In essence (in the student's mind), the computer matches the spectrum of the compound to the library and provides the student with the "correct" structure. They see little need to learn how to interpret spectra when the computer already does the work for them. Showing the students the need to learn how to deduce structures from a spectrum must be accomplished. My two main arguments are (1) Students need to understand from where the spectral matches come. Without this knowledge, they cannot interpret the information reasonably and find inconsistencies. (2) Students may encounter compounds in their work or research that are not found in the database. They still must identify these compounds using "old-fashioned" interpretation methods.

Obtaining spectra for the students to interpret is another challenge. This was made much easier by attending the NMR Concepts workshop. The handouts provided were very helpful and the permission given by Dan Traficante for our personal use back at our home institution was the beginnings for the section on NMR. Resources and opportunities like that are of a great help in developing a course at your own institution. Using in-house instruments to run spectra on compounds is another option. The availability of instruments at nearby institutions provided another avenue for spectra. Several of my research students went to KU and acquired high-field FT NMR spectra of various compounds. The willingness of other institutions to contribute is of great value. I have also had students analyze mixtures of using the techniques available at MWSC.

COURSE EVALUATION

I have taught the course twice (spring of 1997 and spring of 1999). The first time, as with any course that you develop, took a great deal of effort. I was often preparing lectures and handouts the day of class. One of the comments students made in the 1997 evaluation was the desire to have the handouts ahead of time. This was easily remedied the next time I taught the course. Overall, results have been favorable on our campus evaluation form. My course "numbers" were much better than the campus and department means. Also, this course (in 1997) was the course on which I received the best evaluation for that semester. There are several reasons I can give for this. First, the course is made up solely of chemistry majors. They have an interest in the course and/or need the course in order to graduate. This is a different population than that seen in general studies courses. I also think my enthusiasm for the course helps make the course interesting. The course deals with spectroscopy. My dissertation area is NMR. I have a great deal of enthusiasm for the material because I think it is VERY interesting. I also received some excellent material from the NSF workshop that helped begin to shape the course.

In addition to the good "numbers" on my evaluations, I received numerous positive comments from students both formally on the evaluation form and informally post-graduation. One student, who had previously taught biology at a junior college and returned to obtain his B.S. degree in chemistry, commented that "this [the advanced spectroscopy course] is the best course I have taken. It was well organized, logically presented, and interesting". Other students have commented on the value of the course after graduation. Many of these students went on to graduate school. They took a similar course during their graduate career and felt like they had an advantage having taken the course at MWSC. They felt it prepared them well for the future course they took. The coursework also helped them in their graduate research. Knowledge of spectroscopy is useful in most sub-disciplines. Several students who went to industrial positions also felt that the course prepared them for their jobs. I have not received my evaluations from the past spring course, but many comments from students to me personally have been very strong. I believe the course is still viewed favorably in the student's minds.

CONCLUSIONS

The use of spectroscopy is something all of our graduates will encounter in their future. I believe to expose them to detailed information about as many techniques as possible puts them at an advantage for graduate school and industrial positions. Combining the theory learned in the classroom with the ability to actually work on the instruments often is an advantage we have at a relatively small school. There are no TA's running the instruments for the students. Of course, a drawback of the smaller size is the availability of instruments. We are not a research-sized institution. Money is not always available for all the instruments we would like. At MWSC, we have been very fortunate to have access to funds that have allowed us to purchase several, state-of-the-art instruments. We have just received funding to purchase a high-field NMR that will complete the instrument acquisitions for this course.

Students gain a greater understanding of spectroscopy and its strength as a tool for compound identification through a course like this. It prepares them for the sort of challenges they will face in graduate school and industry. It provides them with experience that may set them apart from other applicants for jobs or admission to a graduate program. Students also enjoy the course based on evaluations I have received and comments from students post-graduation. In addition, since spectroscopy is my area of interest, I personally find teaching the course interesting and an enriching experience. I only wish I had the opportunity to teach it more than once every two years. Having the opportunity to share my excitement for NMR with my students and see them appreciate it and become excited along with me is one of the greatest rewards of teaching for me.

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