CHEM 535 - Introduction to Molecular Spectroscopy

Spring 2007 Pavel Jungwirth

- The class will be held Tuesday, Thursday and Friday 9.30 – 10:50 a.m. in SSC 604

- Office hours will be held on Tuesday 12 - 1 p.m. in SSC 702. At other times, you can find me in my office. You can email me at pavel.jungwirth@uochb.cas.cz. Further details on the class, announcements and homework examples will be periodically posted at *http://www.molecular.cz/~jungwirt*.

The material is intended to be relevant to those with an interest in spectroscopy of both gas- and condensed- phase systems. The course requires a graduate level Quantum Mechanics course as prerequisite, although I will review the most relevant chapters from quantum mechanics and classical electrodynamics before proceeding to molecular spectroscopy. Mathematical background substantially beyond proficiency with matrix representations and linear algebra should not be necessary. Along with traditional methods for analyzing spectra, I will show a time dependent approach to interpretation of molecular spectra and introduce also modern femtosecond spectroscopic methods. Numerical methods to simulate spectra will be introduced in homework assignments.

There will be several homework assignments, a Midterm and a final project. My goal in this course is to have you tackle real research problems using contemporary tools in homework assignments. Programming will be kept to a minimum by exploiting "intuitive" computational environments such as Mathcad.

Course Outline:

I. *Overview of course and preview of applications of spectroscopy*

II. *Revision of relevant chapters of quantum mechanics and classical electrodynamics*
Time-independent and time-dependent Schrödinger equation.
Particle in a box, harmonic oscillator.
Approximate solutions to the Schrödinger equation – variational and perturbational methods.
Nature of electromagnetic radiation and its classical description.
Propagation of light in matter.
Quantum mechanical aspects of light.
Electrical and magnetical properties of matter.

III. *Preliminaries*
Time dependent perturbation theory.
Transition probabilities – Fermi Golden Rule.
Finite lifetime of states.

IV.*Atomic spectroscopy*
Energy levels in atoms.
E1, E2, and M1 selection rules.

Coupling diagrams and Hund's rule.
Fine structure effects.

III. *Rotational spectroscopy*
Rigid rotor.
Rotational spectra of diatomic molecules
Rotation levels of polyatomic molecules: spherical, symmetric, and asymmetric tops.
Angular momentum couplings – Hund's cases a)-d).
Hindered rotations.

IV. *Vibrational spectroscopy*
Vibration of diatomic molecules. Harmonic and anharmonic oscillator.
Vibrational-rotational couplings.
Vibration of polyatomic molecules. Normal modes and group theory.
Solvent effects on vibrational spectra.

V. *Electronic spectroscopy of molecules*
Electronic absorption spectra of diatomic molecules. Molecular orbitals and term symbols.
Dissociation and pre-dissociation in the spectra of diatomics
Electronic absorption spectra of polyatomic molecules
Fluorescence. Raman. Solvent effects.

VI. *Phenomenological treatment of absorption, emission, and scattering*
Einstein coefficients.
Light scattering.
Spectral lineshapes.
Principles of laser emission.

VII. *Introduction to non-linear spectroscopy*
Two-photon processes. Graph representations.
Higher order processes – three- and four-photon transitions.

VIII. *Introduction to the time-dependent approach to spectroscopy*
Wavepackets.
Spectra as Fourier transforms of correlation functions.

Recommended texts

No one text overlaps fully with the planned syllabus. There are a very large number of texts covering the more traditional parts of the course. I am recommending the following:

J. L. McHale – Molecular Spectroscopy (Prentice Hall, 1999).
This is the primary text. It is very readable and intuitive but not always completely rigorous. (You get extra points for finding errors in equations in the text ☺).

W. Struve - Fundamentals of Molecular Spectroscopy, (Wiley Interscience, 1987)
Covers material in a more rigorous but less intuitive framework. Good discussion of time-dependent perturbation theory. This book is no longer in print, but you'll find several copies around the department.

J. M. Hollas - High Resolution Spectroscopy, 2nd Edition (Wiley, 1998).
This is the hardcore experimentalist's choice. The book is an excellent reference for most spectroscopic techniques and briefly describes most lasers in use today.

G. C. Schatz and M. A. Ratner – Quantum mechanics in chemistry, (Prentice Hall, 1993).
This book provides in Chapter 9 an introduction to the time-dependent approach to spectroscopy.

Numerical software

Homework assignments and case studies will require use of a mathematical environment software. Most of you already have experience with the software *Mathcad,* and this will be suitable for problems assigned in this class also. But you are free to use any symbolic mathematics software or code directly in one of the programming languages (sole use of pocket calculator or abacus might be impractical ☺).