

# CHEMISTRY 546 FALL 2014 – MODULAR COURSE ON SPECTROSCOPY

LECTURES TUE & THURS 11:00 – 12:20 215 LSC

## **PART 1 Group Theory** Four weeks: Aug 26, 28, Sept 2, 4/ 9, 11/ 16, 18\*

When a molecule has symmetry, the electronic, vibrational and rotational states must correspond to one of the irreducible representations of the point group formed by the symmetry operations that leave the molecule invariant. The dimensionality of the irreducible representation of a state specifies its degeneracy. Spectroscopic transitions must be between states of defined symmetry. This leads to selection rules that permit spectral intensity prediction. Given the molecular point group, the symmetry labels are exact; selection rules are usually only exact in certain limits. However, when the standard approximations fail it is usually only a small effect. Molecules like ethane and ammonia have more than one minimum energy conformation. The spectroscopy of such molecules is best treated by use of the more general permutation-inversion symmetry. The role of symmetry in electronic structure calculations will be outlined.

This section will provide background for the use of group theory in molecular spectroscopy. You will learn to use point group character tables to make predictions. This will be illustrated in the two following modules where group theory will be used extensively and expanded to include the spectroscopy of periodic solids and cases in which the ground or excited electronic states have potential energies that span two different point groups.

## **PART 2 Vibrational Spectroscopy** Five weeks: Sept 23, 25, 30; Oct 2, 7, 9, 14, 16, 21, 23\*

In the harmonic approximation the vibrations of a molecule with  $N$  atoms are separable into  $3N-6$  individual "normal modes". These are linear combinations of the displacements of the atoms from their equilibrium position. These collective normal modes have the symmetry of the point group of the molecule. Each normal mode is treated as a harmonic oscillator. Each vibrational level of an  $N$ -atom molecule is thus defined by a string of  $3n-6$  harmonic quantum numbers.

We will discuss vibrational absorption (IR) spectroscopy and scattering (Raman) versions of vibrational spectroscopy, their selection rules and analysis by group theory and experimental methods. Vapor, solution and crystalline solids will be discussed as well as overtone and combination transitions. We will also discuss novel methods of vibrational spectroscopy as well as novel samples. Use of polarized light as a method for obtaining additional information will be discussed for both crystalline solids and stretched films.

## **PART 3 Electronic Spectroscopy** Five weeks: Oct 28, 30; Nov 4, 6/11, 13/18, 20/ Dec 2, 4\*

We will begin with a description of the use of group theory to classify molecular orbitals and molecular excited states giving rise to selection rules for one and two-photon spectroscopy. The second major topic in the electronic spectroscopy module will be the vibrational structure of electronic transitions, what this tells us about the excited state involved and about the mechanism of the absorption. The orientation of the transition with respect to the molecular frame will also be of interest. The concept of allowed and forbidden electronic transitions will be discussed and subjected to group theory analysis. In this analysis the distinction between totally symmetric and non-totally symmetric vibrations will be important. In this regard the analysis of resonance Raman spectroscopy will be presented in both its vibronic theory and as wave-packet time-dependent quantum mechanical methods.

Photophysics is the empirical (phenomenological) summary of the fate of electronic energy following electronic excitation. This includes fluorescence, phosphorescence, triplet-triplet absorption radiationless transitions and quantum yields of each. It also includes diffusional quenching, excimer formation, recombination luminescence, fluorescence anisotropy decay, ionization, recombination and resonance fluorescence energy transfer as well as photochemistry. This is the basis of many practical devices that can be used as sensors or labels or to measure distances between two points in a large biological structure.

\*The last class session of each module will be an examination on that material of that module. There will be no final overall examination.