Fundamentals of Microscopic Chemical Analysis (CHEM 318)
Last Updated: February 12, 2013

Topics	Class period(s)

• **E-M wave radiation and properties**
  ○ Amplitude
  ○ Wavelength
  ○ Frequency
  ○ $\lambda\nu$ = Speed (in vacuum, all radiation travels at speed of light c)
  ○ Regions of EM radiation (UV, x-ray, vis, etc..)
  ○ Constructive/ Destructive interference
  ○ Diffraction and refraction
	1

• **Blackbody radiation**
  ○ Theory of blackbody radiation and energy density
  ○ Failure of classical prediction (UV catastrophe)
  ○ Planck's constant (Energy of EM wave is dependent on frequency, and energy density depends on the quantity of particular wave w/ frequency, ν)
	1

• **Photoelectric effect and applications**
  ○ Light has particle characteristic that can interact with other particles (one light particle in, one electron ejected)
  ○ $h\nu$= <u>metal specific</u> binding energy + kinetic E of <u>free</u> photoelectron
  ○ Light energy doesn't always remove electrons (it heats material instead, if ν is not high enough)
  ○ Solar cells
	2

• **Electron particles as waves**
  ○ Diffraction pattern from energized electron beam(Davisson-Germer or Thomson experiment)
  ○ Electron particle has wavelength (De Broglie wavelength is momentum-Energy- dependent)
	1

• **Hydrogen atom emission spectrum and applications**
  ○ Discreet wavelength, not continuum
  ○ Rydberg formula (infinitely many quantum state, n, that can lead to continuum at higher n)
  ○ Bohr model of atom (infinitely many fixed n electron orbitals—not necessarily occupied by electrons, Z dependent orbital energy spacing)
    ▪ Electron absorbs photon (momentum transfer), absorbs <u>kinetic</u> energy, raise total energy
	2

• **ESCA/ XPS** o Describe the experimental set-up, procedure o What information is obtained?	1
• **Atomic absorption and applications** o Atom specific wavelength signature/ response o Phototubes and photodetectors	2
• **Heisenberg uncertainty principle** o If electron is moving (has momentum/ energy), uncertain of where its location exactly is o Use a wave to describe probabilistic location of electron ▪ Use a function to describe the wave	1
• **1-D waves** o Solve 1-D wave functions given boundary and initial conditions ▪ Possibly infinitely many solutions (i.e. states) to same boundary and initial conditions o What information do you obtain knowing the wave? (Probability density) o Using probability density to obtain probability of particular observable ▪ Expectation value for a particular observable o Using linear operators for classical observable analog ▪ Hamiltonian operator and the total energy ▪ Eigenfunctions and eigenvalues	2
• **Particle (electron) in a 1-D box of length, l** o Using a wavefunction to calculate probable observables o Eigenvalues (in particular using the Schrodinger equation to obtain total E) o Vector space	1
• **Harmonic oscillator (atom in a molecule moving in 1-D space) and applications** o Quantized energy of vibration o Vibrational modes o Same frequency at higher energy, but larger displacements, same equilibrium length o Limits of H.O. (dissociation energy) o Spherical coordinates o IR detectors	2

• **Rigid rotator**
  ○ Angular momentum, angular frequency
  ○ Analog of linear motion to angular motion
  ○ Spherical coordinates and the wave function
  ○ Bond length
  ○ Non-rigid rotator
	2

• **Hydrogen atom**
  ○ Electron in 3-D motion associated with a particular wave function with a particular energy
  ○ Atomic orbitals
  ○ Spin
  ○ Spin-orbit coupling (Zeeman effect)
  ○ Relate energy of associated wave function to emission lines
	2

• **Multi-electron atom**
  ○ Matrices and determinants
  ○ Quantum numbers
  ○ Selection rules (Allowed transitions, term symbols?)
  ○ Transition dipoles
  ○ Population of states (Density, Population inversion etc…)
  ○ Absorptivity
  ○ Pauli exclusion, Aufbau, Hund's rule
	3

• **Absorption spec/ Spectral interpretations**
  A) What factors must be taken into consideration when evaluating linewidth, intensity, position, shape, etc…when looking at a spectrum?
  B) **Atomic spectroscopy**
    ○ Emission spectroscopy
      • Overview
      • Atomization sources: flames, furnaces, plasmas
      • Interferences
    ○ Absorption spectroscopy
      • Overview
      • Radiation sources: hollow cathode lamps
      • Spectral vs chemical interference
	3

C) **Molecular spectroscopy**
  ○ Absorption spectroscopy (UV-Vis)
    • -derivation of Beer's law
    • -Beer's law for chemical analysis (single analyte)
    • -Analysis of mixtures with Beer's law
	2

• -Limitations of Beer’s law	
○ Fluorescence spectroscopy • Non-radiative relaxation • Intersystem crossing • Excited state lifetime • Quantum yield and molecular structure • Fluorescence intensity and experimental parameters (solvent, temp, pH) • Fluorescence quenching (static vs. dynamic) • Fluorophore design (particle in the box)	2
D) **Instrument designs for spectroscopy** ○ Light sources: lamps, laser ○ Wavelength selectors: monochromators, filters ○ Sample holders: cuvette and cells ○ Detectors: Phototube, PMT, photodiode array, CCD devices ○ Instrumental designs: UV-Vis spectrophotometer, fluorometer • Single vs. double beam instruments	3