

## Topics

### Spectroscopy

- Light ↔ technique ↔ chemical information ↔ applications
- UV-vis
  - Electronic Transitions of valence electronic
  - Molecular and solvated metals (d electron transitions)
    - Absorption
      - Instrument
      - Source
        - Monochrometer
        - Sample (quartz cuvette)
        - Detector – PMT
      - Broad
      - Not qualitative
      - Quantitative
        - Beer's law
    - Fluorescence
      - Instrument
        - Two monochrometers or filters
        - 90 degree
        - PMT
      - Quantitative
        - Very sensitive
        - 90 degrees, Zero background
      - derivatization
- Atomic Spectroscopy
  - Atomic Absorption
    - Atomic emission and absorption line width are very narrow
    - Instrument
      - Flame-atomization
      - Gas-phase, ground state atoms absorb light from source
      - Source- Hollow cathode lamp, element specific
      - Appreciate the specificity of the technique; only Fe gas phase atoms can absorb light from Fe hollow cathode lamp
      - monochrometer
      - Detector PMT
    - Quantitative – Beer's law/standard addition experiment
    - Variables
      - flame characteristics effects atomization
      - Matrix effects
      -

- Atomic Emission
      - Ar torch adjusted to maximize the formation of excited gas-phase atoms
      - Emission produced is measured using expensive optics
        - Multi-element instruments
        - Can measure narrow channels in terms of wavelength to retain elemental specificity
- FT-IR
  - Vibrational and rotational transitions of molecules
  - Characterization of Functional groups; energy of vibrations are unique for different functional groups
  - Each vibrational mode has a unique transition
  - Fourier Transform
    - Analyze intensity as a function of time (time domain) and mathematically convert to frequency domain
    - Need Michelson Interferometer to slow down FID so that it can be measured
      - Advantages:
        - decreases the time it takes to acquire spectrum
        - enables signal averaging, which increases S/N
  - Instrument
    - IR source
    - Interferometer
    - Sample
    - IR detector
- FT-NMR
  - Probes nuclear spins with radio waves
    - Nuclei with spin quantum number =  $\frac{1}{2}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$
    - Splits into two states in presence of B
    - Relatively insensitive (small difference in population of spin states)
    - Sensitivity proportional to B (Boltzman's distribution)
  - Instrument
    - Large magnet, B the bigger the better
      - Spectral resolution
      - Sensitivity
    - Tuned radio receiver coil that can produce and detect radio waves
    - Super cooled magnet liquid He and liquid N<sub>2</sub>
  - Experiment
    - Sample in magnet
    - Pulse receiver coil to produce broadband burst of radio waves centered around proton (or  $^{13}\text{C}$  or  $^{19}\text{F}$ , ect.) transitions
    - Measure relaxation of excited spin states with coil

- Take FT of FID to produce NMR spectra
- NMR Spectra
  - Chemical shift
  - Spin-Spin Splittings

## Chromatography

- Need to separate complex mixtures prior to analysis
- HPLC
  - Separation of involatile compounds
    - Types of HPLC
      - Non-polar stationary phase
      - Water/meOH/acetonitrile mobile phase
      - Separation by polarity and size
    - Reversed Phase
      - Polar mobile phase
      - Non-polar stationary phase
      - Octadecyl groups attached to silica bead
      - Separation based on polarity; more polar solutes are retained less
    - Normal-phase
      - Polar stationary phase – bare silica
      - Non-polar mobile phase (ethyl acetate/hexane)
      - Separation by polarity; more polar solutes are retained more
  - Instrument
    - Mobile phases
      - Isocratic
      - Gradient elution (adv./disadv.)
    - Pumps
    - Mixer
    - Injector
      - Manual
      - Auto injector
    - Column
      - Packed with small 5µm ID particles
      - 10-30 cm long
      - 4.1 mm ID to 100 µm ID
      - Smaller ID increases sensitivity
    - Detector
      - UV/vis
      - Fluorescence
      - Electrochemical
      - Electrospray mass spectrometer