ANNOUNCEMENTS
UAF Department of Chemistry and Biochemistry

Date: 2 February 2016
Time: 4:00-5:00 PM
Place: Reichardt 201

Finding Chemistry Connecting Arctic Research: New Directions at ARCUS

Dr. Robert H. Rich, Ph.D., CAE, Director of ARCUS
The Arctic Research Consortium of the United States (ARCUS)

APPLY FOR UAF SCHOLARSHIPS!
2016-2017 academic year
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SELECTING AN ANALYTICAL METHOD

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Precision</td>
<td>Absolute standard deviation, relative standard deviation, coefficient of variation, variance</td>
</tr>
<tr>
<td>2. Bias</td>
<td>Absolute systematic error, relative systematic error</td>
</tr>
<tr>
<td>3. Sensitivity</td>
<td>Calibration sensitivity, analytical sensitivity</td>
</tr>
<tr>
<td>4. Detection limit</td>
<td>Blank plus three times standard deviation of the blank</td>
</tr>
<tr>
<td>5. Dynamic range</td>
<td>Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)</td>
</tr>
<tr>
<td>6. Selectivity</td>
<td>Coefficient of selectivity</td>
</tr>
</tbody>
</table>
TYPES OF ERRORS IN THE LABORATORY

1. Random error
   - Always present, all directions
   - Often limits precision of measurements
   - Quantify: standard deviation

2. Systematic
   - Affects all measurements in the same way—Direction and magnitude
   - Assignable cause
   - Quantify: bias

3. Gross
   - Big oops!
   - Generally clear
   - Outliers?

SOURCES OF EXPERIMENTAL NOISE

Chemical
   - Experiments are affected by uncontrollable environmental conditions affecting system

Instrumental noise
   - Affects all components of the instrument

   *Observed noise is a complex composite of all noise sources*
SOURCES OF INSTRUMENTAL NOISE

1. Thermal/ Johnson
2. Shot noise
3. Flicker noise
4. Environmental noise

To improve the signal-to-noise ratio by a factor of $n$ requires averaging $n^2$ spectra.
LIGHT- MATTER INTERACTIONS

CHEM 314

OBJECTIVES

- Review electromagnetic radiation and EM spectrum
  - Wave-particle duality
- Overview of ways light can interact with matter
  - Apply these interactions to the study of chemical systems
- Summarize excitation and relaxation within an atom or molecule using a Jablonski diagram.
Spectroscopy?
Interaction between light and matter

ELECTROMAGNETIC RADIATION

Electric field

Magnetic field

Direction of propagation
What is the frequency and energy of 500nm light?
ELECTROMAGNETIC SPECTRUM

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Frequency (Hz)</th>
<th>Wavelength (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3 \times 10^{10}$</td>
<td>$3 \times 10^{8}$</td>
<td>$3 \times 10^{6}$</td>
</tr>
<tr>
<td>$3 \times 10^{4}$</td>
<td>$3 \times 10^{2}$</td>
<td>$3 \times 10^{9}$</td>
</tr>
<tr>
<td>$3 \times 10^{-2}$</td>
<td>$3 \times 10^{-4}$</td>
<td>$3 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

- X-ray
- Visible
- Microwave
- Gamma ray
- Ultraviolet
- Infrared
- Radio

INTERACTIONS BETWEEN LIGHT AND MATTER

- Molecular vibrations
- Molecular rotations
- Core electron transitions
- Nuclear transitions
- Radiative transitions
- Radioactive decay
- Particle decay

89.9 x $10^6$ Hz
Public Radio
Molecular vibrations
Core electron transitions
Nuclear transitions

89.9
Public
Radio
INTERACTIONS BETWEEN LIGHT AND MATTER

<table>
<thead>
<tr>
<th>Type of Spectroscopy</th>
<th>Type of Quantum Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma-ray emission</td>
<td>Nuclear</td>
</tr>
<tr>
<td>X-ray absorption, emission, fluorescence, and diffraction</td>
<td>Inner electron</td>
</tr>
<tr>
<td>Vacuum ultraviolet absorption</td>
<td>Bonding electrons</td>
</tr>
<tr>
<td>Ultraviolet-visible absorption, emission, and fluorescence</td>
<td>Bonding electrons</td>
</tr>
<tr>
<td>Infrared absorption and Raman scattering</td>
<td>Rotation/vibration of molecules</td>
</tr>
<tr>
<td>Microwave absorption</td>
<td>Rotation of molecules</td>
</tr>
<tr>
<td>Electron spin resonance</td>
<td>Spin of electrons in a magnetic field</td>
</tr>
<tr>
<td>Nuclear magnetic resonance</td>
<td>Spin of nuclei in a magnetic field</td>
</tr>
</tbody>
</table>
SUPERPOSITION OF WAVES

INTERACTIONS BETWEEN LIGHT AND MATTER

LIGHT AS A WAVE
- Diffraction
- Refraction
- Transmission
- Reflection
- Scattering
- Polarization

LIGHT AS A PARTICLE
- Photoelectric effect
- Absorption
- Emission
- Scattering
DIFFRACTION - BENDING OF LIGHT AS IT PASSED THROUGH A SLIT

Wave generator

YOUNG EXPERIMENT (1800) - PROVED LIGHT IS A WAVE

Relative intensity

$X \quad \text{Distance} \quad Y$
EXAMPLE 6-1

Suppose that the screen in Figure 6-8 is 2.00 m from the plane of the slits and that the slit spacing is 0.300 mm. What is the wavelength of radiation if the fourth band is located 15.4 mm from the central band?

Substituting into Equation 6-10 gives

\[ 4\lambda = \frac{0.300 \text{ mm} \times 15.4 \text{ mm}}{2.00 \text{ m} \times 1000 \text{ mm/m}} = 0.00231 \text{ mm} \]

\[ \lambda = 5.78 \times 10^{-4} \text{ mm} = 578 \text{ nm} \]

TRANSMISSION - TEMPORARY POLARIZATION OF MOLECULES

Refractive index:

\[ n_i = \frac{c}{v_i} \]

At a given frequency \( i \):

- \( n_i \), refractive index
- \( v_i \), velocity of propagation
- \( c \), speed of light in a vacuum

Amplitude, \( A \)

Distance
**DISPERSION - CHANGE IN REFRACTIVE INDEX WITH FREQUENCY**

- **Normal dispersion**
  - Good for lenses
- **Anomalous dispersion**
  - Good for prisms

**REFRACTION - BENDING OF LIGHT AT INTERFACES OF MEDIA**

- Snell’s law
  \[
  \frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} = \frac{v_2}{v_1}
  \]
REFLECTION- REFLECTION OF LIGHT AT AN INTERFACE

\[ \frac{I_r}{I_0} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \]

http://maxgrace.wordpress.com/2010/07/14/the-love-chapter-one-more-time/

SCATTERING- CHANGE IN MOMENTUM OF EM RADIATION

Rayleigh- elastic scattering
Mie- large particles
Raman- inelastic scattering

Rayleigh scattering gives the atmosphere its blue color

\[ P_S \]

Stokes
Anti-Stokes

\[ v_{ex} - v_x, v_x, v_{ex} + v_y \]
POLARIZATION - SELECTION OF A SPECIFIC ORIENTATION OF EM RAD.

INTERACTIONS BETWEEN LIGHT AND MATTER

LIGHT AS A WAVE
- Diffraction
- Refraction
- Transmission
- Reflection
- Scattering
- Polarization

LIGHT AS A PARTICLE
- Photoelectric effect
- Absorption
- Emission
- Scattering
1. Light incident on the photocathode
2. Electrons liberated
3. Voltage at anode adjusted to stop current
4. Stopping voltage depends on cathode substrate and radiation energy

PHOTOELECTRIC EFFECT

Glass or quartz tube
Cathode
Emission
Vacuum
Stopping
Anode
Current meter
Voltmeter
Variable voltage source

PHOTOELECTRIC EFFECT

Graph showing a plot of $K_i$ vs. $r \times 10^{-15}$ Hz. The slope of the line is $h$.
ABSORPTION

Compare atomic and molecular absorption? Why does atomic absorption occur at discrete wavelengths while molecular absorption occur in broad peaks?
EMISSION

Thermal, electrical, or chemical energy

Emission of radiation

$P_E$

$E_{21} = h\nu_2 = h\frac{c}{\lambda_2}$

$E_2 = h\nu_2 = h\frac{c}{\lambda_2}$

$E_1 = h\nu_1 = h\frac{c}{\lambda_1}$

Energy levels:

(a) Thermal or electrical energy

(b) Band 1 and Band 2
LUMINESCENCE

JABLONSKI DIAGRAM

Excited vibrational and rotational levels of $T_1$ electronic state

Internal conversion

Intersystem crossing to $T_1$

Intersystem crossing to $S_0$

Absorption ($10^{-15}$ s)

Fluorescence ($10^{-8}$–$10^{-4}$ s)

Phosphorescence ($10^{-4}$–$10^5$ s)
**JABLONSKI DIAGRAM TRANSITIONS**

**Electronic excitation**- promotion of an electron to an excited state (electronic, vibrational, rotational). $S_0 \rightarrow S_1$

**Nonradiative decay (vibrational relaxation)**- vibrational energy transferred to other molecules through collisions. Very fast. Excited state $\rightarrow S_1$ ground vibrational state

**Fluorescence**- emission of photon to return to $S_0$. $S_1 \rightarrow S_0 + \nu$

**Internal conversion**- radiationless transition to an extremely vibrationally excited state of $S_0$ without a change in energy. $S_1 \rightarrow S_0$

**Intersystem crossing**- radiationless transition from $S_1$ to $T_1$ with no change in energy. Change of electron spin. $S_1 \rightarrow T_1$

**Phosphorescence**- emission of photon to return to $S_0$. $T_1 \rightarrow S_0 + \nu$
**Scattering Phenomena**

<table>
<thead>
<tr>
<th>Time scale</th>
<th>Phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-14}$ - $10^{-15}$ s</td>
<td>Transmission</td>
</tr>
<tr>
<td>$10^{-15}$ s</td>
<td>Nonradiative decay</td>
</tr>
<tr>
<td>$10^{-8}$ s</td>
<td>Electronic transitions</td>
</tr>
<tr>
<td>$10^{-5}$ s</td>
<td>Fluorescence</td>
</tr>
<tr>
<td>$10^{-5}$ to 100’s s</td>
<td>Phosphorescence</td>
</tr>
</tbody>
</table>

Based on these observations, can you predict which transitions might be more likely to occur (and thus more common)?
LOOKING AHEAD

Tuesday (Jan 26)- Project Overview (Due Feb 15)  
Last day for Standard Addition (Due Feb 1)

Thursday (Jan 28)- Beer’s Law (Ch 13, look through derivation on website)  
First day of Consumer Characterization Project  
Experiment 1: Metals Analysis  
Due: Prelab 1, Experiment 1