INTERACTIONS BETWEEN LIGHT AND MATTER

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

LIGHT AS A PARTICLE
- Photoelectric effect
- Absorption
- Emission
- Scattering

JABLONSKI DIAGRAM

- Intersystem crossing to T₁
- Intersystem crossing to S₀
- Absorption (10⁻¹⁵ s)
- Internal conversion
- Fluorescence (10⁻⁸–10⁻⁴ s)
- Phosphorescence (10⁻³–10⁵ s)

Excited vibrational and rotational levels of T₁ electronic state
**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 \( S_0 \). \( T_1 \rightarrow S_0 + \nu \)

**A SIMPLE ABSORPTION EXPERIMENT**

\[
T = \frac{P}{P_0} \quad A = \log \left( \frac{P_0}{P} \right) = -\log T
\]

**Beer’s Law**

\[
A = \varepsilon bc
\]

<table>
<thead>
<tr>
<th>Concentration relative to mixing directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.85</td>
</tr>
</tbody>
</table>

- \( T \) = transmission
- \( P_0 \) = incident power
- \( P \) = transmitted power
- \( A \) = absorbance
- \( \varepsilon \) = molar absorptivity
- \( b \) = path length
- \( C \) = analyte concentration
SOURCES OF NONLINEARITY OF BEER’S LAW

1. Solution factors
2. Non-monochromatic light
3. Not analyzing at $\lambda_{\text{max}}$
4. Stray light
5. Mismatched cuvettes
6. Instrument noise
   Too much or too little absorption

DERIVATION OF BEER’S LAW

\[ T = \frac{P}{P_0} \quad A = \log \left( \frac{P_0}{P} \right) = -\log T \]

\[ A = \varepsilon bc \]

$T$ = transmission
$P_0$ = incident power
$P$ = transmitted power
$A$ = absorbance
$\varepsilon$ = molar absorptivity
$b$ = path length
$C$ = analyte concentration
COMPONENTS OF OPTICAL INSTRUMENTS

CHEM 314
SKOOG N HOLLER CH 7

OBJECTIVES

- State the components and phenomena that can be probed with optical instruments.
- Recall the methods of wavelength isolation
- Diagram, label, describe, and compare prism- vs diffraction-based monochromators
- State and be able to perform calculations related to mono performance characteristics and $\lambda$ dispersion.
- Recall UV-Vis detectors
- Diagram, label, describe, and compare the following detectors: Vacuum phototube, PMT, silicon diode
OPTICAL INSTRUMENTATION

Phenomena probed

- Absorption
- Luminescence
- Emission
- Scattering

Components

1. Stable radiation source
2. Transparent sample holder
3. Wavelength isolation
4. Detector
5. Signal processing

BUILDING A SPECTROSCOPIC INSTRUMENT

Figure 1-1.
DU Series 600 Spectrophotometer Optical Diagram
BUILDING A SPECTROSCOPIC INSTRUMENT

Components
1. Stable radiation source
2. Wavelength isolation
3. Transparent sample holder/ optics
4. Detector
5. Signal processing

This lecture will focus on common components of instruments for atomic and molecular spectroscopies.

SOURCES

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>700</th>
<th>1000</th>
<th>2000</th>
<th>4000</th>
<th>7000</th>
<th>10,000</th>
<th>20,000</th>
<th>40,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral region</td>
<td>VAC</td>
<td>UV</td>
<td>Visible</td>
<td>Near IR</td>
<td>IR</td>
<td>Far IR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Sources</td>
<td>Ar lamp</td>
<td>Xe lamp</td>
<td>H₂ or D₂ lamp</td>
<td>Tungsten lamp</td>
<td>Nernst glower (ZrO₂ + Y₂O₃)</td>
<td>Nichrome wire (Ni + Cr)</td>
<td>Globar (SiC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Why does this chart differentiate between line and continuum sources? When would you use a line rather than continuum source?
## OPTICS

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>700</th>
<th>1000</th>
<th>2000</th>
<th>4000</th>
<th>7000</th>
<th>10,000</th>
<th>20,000</th>
<th>40,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral region</td>
<td>VAC</td>
<td>UV</td>
<td>Visible</td>
<td>Near IR</td>
<td>IR</td>
<td>Far IR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Materials for cells, windows, lenses, and prisms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Lithium fluoride</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fused silica or quartz</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corex glass</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicate glass</td>
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<tr>
<td>NaCl</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td>KBr</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>TeBr or TiH</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>ZnSe</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### SAMPLE CUVETTES

**Quartz or plastic?**

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>190</td>
<td>490</td>
<td>790</td>
<td>1090</td>
<td></td>
</tr>
</tbody>
</table>

- Quartz
- Plastic
BUILDING A SPECTROSCOPIC INSTRUMENT

Components
1. Stable radiation source
2. Wavelength isolation
3. Transparent sample holder/ optics
4. Detector
5. Signal processing

WAVELENGTH SELECTION

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>700</th>
<th>1000</th>
<th>2000</th>
<th>4000</th>
<th>7000</th>
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</thead>
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<td>Spectral region</td>
<td>VAC</td>
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<td>Visible</td>
<td>Near IR</td>
<td>IR</td>
<td>Far IR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Wavelength selectors</td>
<td>Fluorite prism</td>
<td>Fused silica or quartz prism</td>
<td>Glass prism</td>
<td>NaCl prism</td>
<td>KBs prism</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Continuum</td>
<td>3000 lines/mm</td>
<td>Gratings</td>
<td>50 lines/mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discontinuous</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Signal processing
MONOCHROMATOR BANDWIDTH

Mono slit width determines spread of $\lambda$ incident on sample (bandwidth)

No such thing as a free lunch

BANDWIDTH MEASUREMENTS

Nominal wavelength

Effective bandwidth

%T maximum

$1/2$ Peak height

Wavelength

Percent transmittance

© 2007 Thermo Fisher Scientific
EFFECTIVE BANDWIDTH

EFFECT OF SLIT WIDTH ON SPECTRAL RESOLUTION
FILTERS

White radiation

Glass plate
Metal film
Dielectric layer

Narrow band of radiation

\[ \lambda = \frac{2dn}{n} \]

Effective bandwidth = 45 Å
Effective bandwidth = 45 Å
Effective bandwidth = 15 Å

Percent transmittance

Effective bandwidth = 45 Å

Effective bandwidth = 45 Å

1/2 Peak height

Wavelength, Å

© 2007 Thomson Higher Education
**MONOCHROMATORS**

1. Entrance slit - provides rectangular optical image
2. Collimating lens or mirror - makes light beams parallel
3. Dispersive element - disperses light into component wavelengths
4. Focusing element - reforms rectangular optical image focused on focal plane
5. Exit slit - on focal plane, selects desired bandwidth

---

**MONOCHROMATOR: PRISMS VS GRATINGS**

**Refraction**

- Entrance slit
- Collimating lens
- Prism
- Focusing lens
- Exit slit

**Reflection**

- Entrance slit
- Collimating lens
- Concave mirrors
- Exit slit

Consider the figures, is $\lambda_1$ or $\lambda_2$ the longer and why.
MONOCHROMATORS: PRISMS VS GRATINGS

When might a prism be better than a diffraction mono?

PRISMS WORK BY REFRACTION

Snell’s law
\[
\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} = \frac{v_2}{v_1}
\]

Refractive index
\[
n_i = \frac{c}{v_i}
\]
LEARNING CHECK

Calculate the angle of deviation of 350, 500 and 650 nm light as it passes through a prism.

$$n_{350} = 1.5392$$

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} = \frac{v_2}{v_1}$$

$$n_{500} = 1.5214$$

$$n_{650} = 1.5145$$

Blue light refracts more than red light due to the difference in wavelength. This causes blue light to deviate from its original path by a greater angle than the red light.
LEARNING CHECK

Calculate the angle of deviation of 350, 500, and 650 nm light as it passes through a prism.

\[ \frac{\sin \theta_1}{n_2} = \frac{n_1}{\sin \theta_2} \]

- \( n_{350} = 1.5392 \)
- \( n_{500} = 1.5214 \)
- \( n_{650} = 1.5145 \)

Calculate the distance between these three wavelengths of light on an exit plane placed 4 cm away from the prism.

REFRACTIVE INDEX OF GLASS AS A FUNCTION OF WAVELENGTH

Blue light refracts more than red light due to the difference in wavelength. This causes blue light to deviate from its original path by a greater angle than the red light.
OTHER PRISM GEOMETRIES

Cornu Prism

Littrow Prism

REFLECTION GRATING MONOCHROMATOR

Concave mirrors

Entrance slit

Reflection grating

\( \lambda_1 \)

\( \lambda_2 \)

Focal plane

https://encrypted-tbn0.gstatic.com/images?q=tbn:ANd9GcS53S0aT3q63kQM1QMWVO1Pbt5R-uJ1aXeFg074hL0
**ECHELLETTE - DIFFRACTION LONG EDGE**

\[ n\lambda = d\left(\sin i + \sin r\right) \]

- Diffracted beam at reflected angle \( r \)
- Grating normal
- Monochromatic beams at incident angle \( i \)

**LEARNING CHECK**

An echelle grating that contains 1450 blazes/mm was irradiated with a polychromatic beam at an incident angle 48° to the grating normal. Calculate the wavelengths of radiation that would appear at an angle of reflection of +20°, +10°, and 0° (angle \( r \), Figure 7-21).

\[
d = \frac{1 \text{ mm}}{1450 \text{ blazes/mm}} \times 10^6 \frac{\text{ nm}}{\text{ mm}} = 689.7 \frac{\text{ nm}}{\text{ blaze}}
\]

When \( r \) in Figure 7-21 equals +20°,

\[
\lambda = \frac{689.7 \text{ nm}}{n} \left(\sin 48 + \sin 20\right) = \frac{748.4 \text{ nm}}{n}
\]

<table>
<thead>
<tr>
<th>( n )</th>
<th>10</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda )</td>
<td>632</td>
<td>513</td>
</tr>
</tbody>
</table>
Calculate the angle at which the 350, 500, and 650 nm light are reflected off the surface of a diffraction grating with 1400 grooves per mm. The incident angle is 20 degrees.

Compare your results with the prism calculations.
### ECHELLE GRATING

<table>
<thead>
<tr>
<th>( \sin 20 )</th>
<th>0.342</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d \text{ (nm)} )</td>
<td>714.285714 (&lt;--\dfrac{1}{1400} \times 1000000)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \lambda \text{ (nm)} )</th>
<th>( n \times \lambda / d )</th>
<th>( \sin r )</th>
<th>( r \text{ (rad)} )</th>
<th>( r \text{ (deg)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>488</td>
<td>0.6832</td>
<td>0.3412</td>
<td>0.34819321</td>
<td>19.950014</td>
</tr>
<tr>
<td>532</td>
<td>0.7448</td>
<td>0.4028</td>
<td>0.41457394</td>
<td>23.7533371</td>
</tr>
<tr>
<td>600</td>
<td>0.84</td>
<td>0.498</td>
<td>0.52129091</td>
<td>29.867769</td>
</tr>
</tbody>
</table>

### ECHELLE MONOCHROMATOR

![Diagram of Echelle Monochromator](image)

- **Echelle grating**
- **Wavelength**
- **Diffraction order**
- **30° prism**

**Diagram Description:**
- **Wavelength:** nm
- **Grating dispersion**
- **Diffraction order**
- **Echelle grating**

- **Diagram Elements:**
  - \( \lambda_1 \), \( \lambda_2 \), \( \lambda_3 \)
  - 260, 240, 220 (wavelengths in nm)
  - 800, 780, 760, 740, 720, 700, 680, 660, 640 (wavelengths in nm)
MONOCHROMATOR PERFORMANCE CHARACTERISTICS

1. Spectral purity
2. Dispersion of grating (D)
   Reciprocal linear dispersion (D\(^{-1}\))
3. Resolving power (R = \(\lambda/\Delta\lambda\))
4. Effective bandwidth (\(\Delta\lambda_{\text{eff}}\))
5. Light gathering power (F)
   Focal length (f)

---

**TABLE 7-1** Comparison of Performance Characteristics of a Conventional and an Echelle Monochromator

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>Echelle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focal length</td>
<td>0.5 m</td>
<td>0.5 m</td>
</tr>
<tr>
<td>Groove density</td>
<td>1200/mm</td>
<td>79/mm</td>
</tr>
<tr>
<td>Diffraction angle, (\beta)</td>
<td>10°22'</td>
<td>63°26'</td>
</tr>
<tr>
<td>Order (n) (at 300 nm)</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>Resolution (at 300 nm), (\lambda/\Delta\lambda)</td>
<td>62,400</td>
<td>763,000</td>
</tr>
<tr>
<td>Reciprocal linear dispersion, (D^{-1})</td>
<td>16 Å/mm</td>
<td>1.5 Å/mm</td>
</tr>
<tr>
<td>Light-gathering power, (F)</td>
<td>(f/9.8)</td>
<td>(f/8.8)</td>
</tr>
</tbody>
</table>
Building a Spectroscopic Instrument

Components
1. Stable radiation source
2. Wavelength isolation
3. Transparent sample holder/ optics
4. Detector
5. Signal processing

Ideal Detectors
1. High sensitivity
2. High signal to noise
3. Constant detector response as a function of $\lambda$
4. Fast response time
5. No dark current
6. Signal proportional to radiant power
7. Rugged, cheap, simple

\[ S = kP + k_d \]
DETECTORS

(b) Detectors

Phopton detectors
- Photographic plate
- Photomultiplier tube
- Phototube
- Photocell
- Silicon diode
- Charge-transfer detector

Thermal detectors
- Photoconductor
- Thermocouple (voltage) or bolometer (resistance)
- Golay pneumatic cell
- Pyroelectric cell (capacitance)

Figure 7-27

DETECTORS

![Diagram showing spectral response of various detectors](image-url)
DETECTORS

Lytle, 1974

DETECTORS

Indium gallium arsenide
Blue-enhanced silicon
Silicon
S-20 Photomultiplier
S-1 Photomultiplier
1. Photon hits cathode
to the anode
3. Generates a current
4. Converted to a measureable voltage
PHOTOMULTIPLIER TUBE (PMT)

Several electrons for each incident electron
Numerous electrons for each photon
辐射，$h$
光电阴极

Anode, $\approx 10^7$ electrons for each photon

PN JUNCTIONS

$p$ region
$n$ region

Metal contact

Wire lead

周期表: B, C, N, O, F, Ne, He, O, S, Cl, Ar, Ga, Ge, As, Se, Br, Kr, Xe, Kr, Rn

He, 4.0030

周期表: 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20
SILICON PHOTODIODE

MULTICHANNEL SI-BASED DETECTORS

Photodiode array (PDA)
Charge Injection Device (CID)
Charge Coupled Device (CCD)
MULTICHLANNEL SI-BASED DETECTORS

Photodiode array (PDA)
Charge Injection Device (CID)
Charge Coupled Device (CCD)
COMPARING DETECTOR SENSITIVITY

<table>
<thead>
<tr>
<th>detector</th>
<th>λ</th>
<th>1 s</th>
<th>10 s</th>
<th>100 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMT</td>
<td>UV</td>
<td>30</td>
<td>6.3</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Vis</td>
<td>122</td>
<td>26</td>
<td>7.3</td>
</tr>
<tr>
<td>PDA</td>
<td>UV</td>
<td>6000</td>
<td>671</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>Vis</td>
<td>3300</td>
<td>363</td>
<td>62</td>
</tr>
<tr>
<td>CCD</td>
<td>UV</td>
<td>31</td>
<td>3.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Vis</td>
<td>17</td>
<td>1.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Harris, Table 19-2

LOOKING AHEAD

Monday (Feb 1)- Instrument components (Ch 7)

Tuesday (Feb 2)- Experiment 1 Metals
   Standard Addition Calc

Thursday (Feb 4)- Experiment 1 Metals
   Atomic Spectroscopy
   Standard Addition Due
   Prelab 2, Experiment 1 Due