IMPRS course on Space Instrumentation: IR/UV spectroscopy

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Lindau, 6.12.2006

Infrared spectroscopy

Def. from Google:

Infrared spectroscopy is an instrumental method of analysis that can be used to identify and quantify samples ranging from pharmaceuticals to diesel emissions.

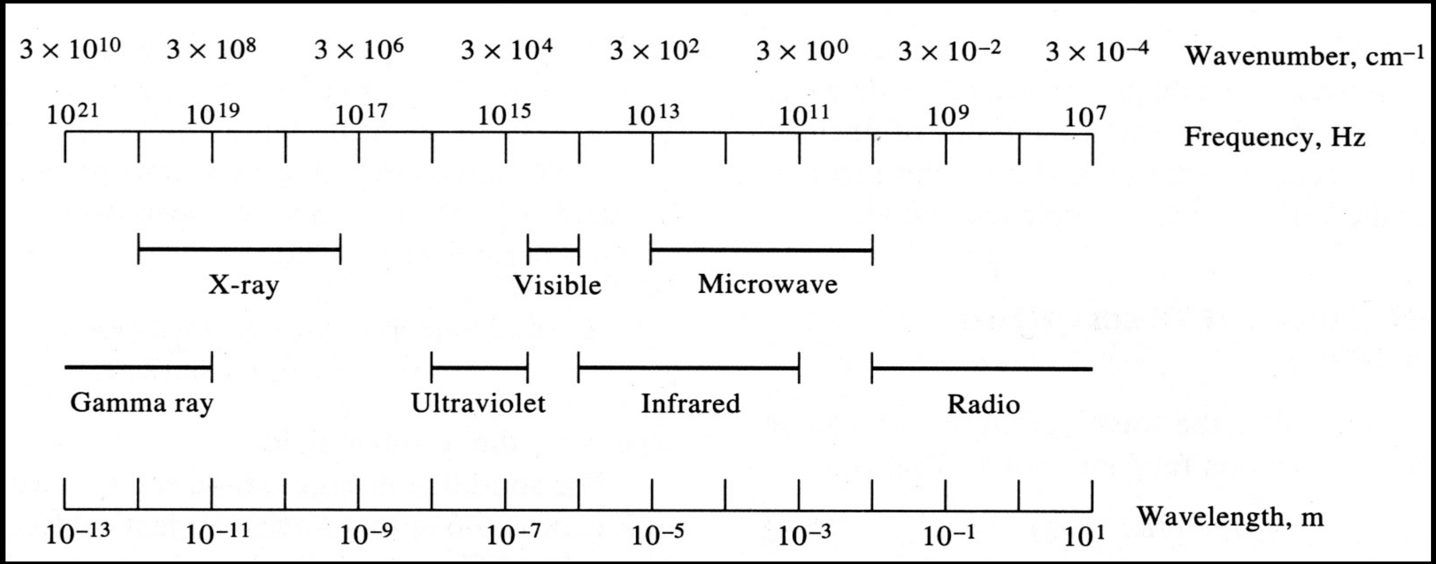
What is spectroscopy?

Def. Not from Google:

Originally, the study of the dispersion of visible light into its component colors (visible spectrum). Now it means the study of electromagnetic (EM) and other spectra including mass, electron and acoustic spectroscopy's.

The Electromagnetic Spectrum

- The electromagnetic spectrum covers a wide range of wavelengths.



- The divisions are based on the methods used to produce and observe the various types of radiation.
- Overlapping: The wavelength range for gamma rays and x-rays overlap. If the source is man-made, the radiation is usually considered x-rays. If the radiation is naturally occurring, the radiation is usually considered gamma rays.

Types of spectrometry Interaction of ER and Molecules

Phenomenon	Spectral Region	Wavelength
Inner electrons - ionization	X-rays	0.1-1.0 nm
Valency electrons	Ultraviolet	0-200 nm
Molecular vibrations, bond stretching or rotation	Infrared	200 nm-800 nm
Rotation & electron spin orientation in magnetic field	Microwaves	400 mm – 30 cm
Nuclear spin orientation in magnetic field	Radio waves	>100 cm

Property of EM radiation

- Light (EM radiation) has a dual nature.
- Light exhibits properties of waves and particles (called *photons* or *quanta)*.

Transmission of Radiation

- When light waves enter a liquid or solid propagating material they slow down.
- This is because the oscillating electric field interacts with the electrons of the medium. The wave is thus slowed.
- ***Index of refraction*** (η_i) – of a medium is the measure of the degree of interaction between a substance and radiation transmitted through that substance.

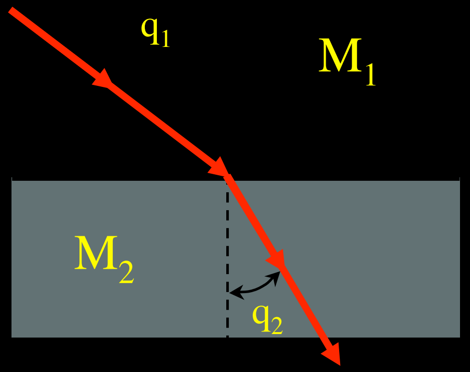
$$\eta_i = c/v_i$$

η_i = index of refraction
c = speed of light (3.00×10^8 m/s)
v_i = velocity in the medium

η_i depends on the substance.
η_i varies with wavelength (called dispersion).

Refraction of Electromagnetic Radiation

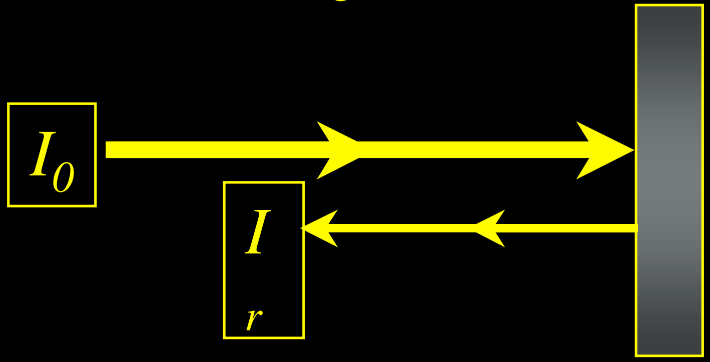
- When electromagnetic radiation passes at an angle from one medium to another of differing refractive index (h_i) the beam changes direction due to a change in velocity.



- The amount of refraction is determined by <u>Snell’s Law</u>: $$\frac{\sin q_1}{\sin q_2} = \frac{h_2}{h_1} = \frac{v_1}{v_2}$$
- This is the principle upon which optical lenses and prisms work.
- If h_1 is in vacuum it is equal to 1.0, so: $$\frac{\sin q_1}{\sin q_2} = h_2$$
- Also works well when h_1 is air because $h_{vac} = 1.00027h_{air}$

Reflection of Radiation

- Occurs when electromagnetic radiation crosses at 90° an interface between two media with different refractive indicies some of the light is reflected.

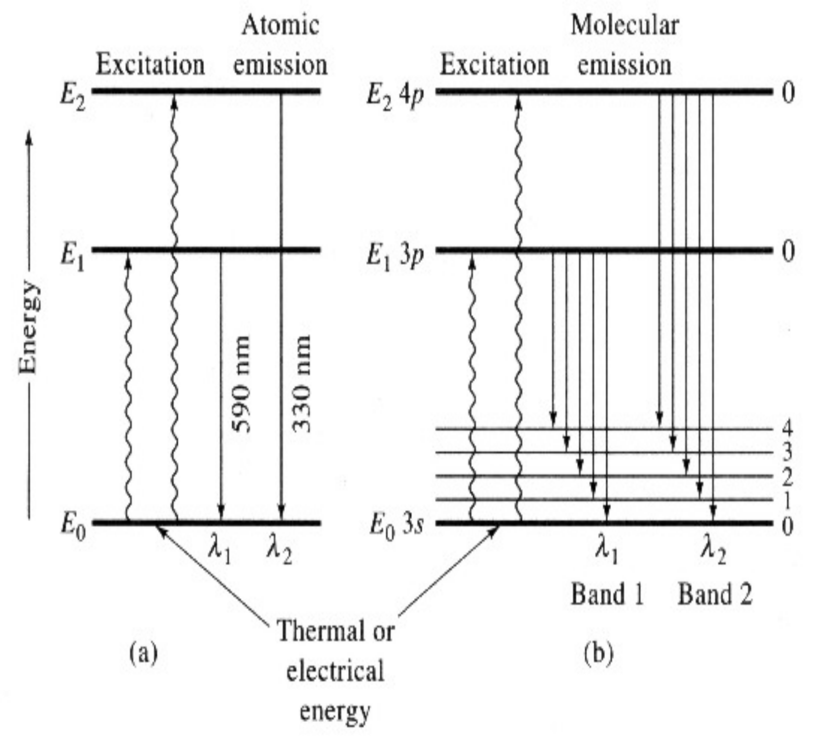


$$\frac{I_r}{I_0} = \frac{(h_2-h_1)^2}{(h_2+h_1)^2}$$

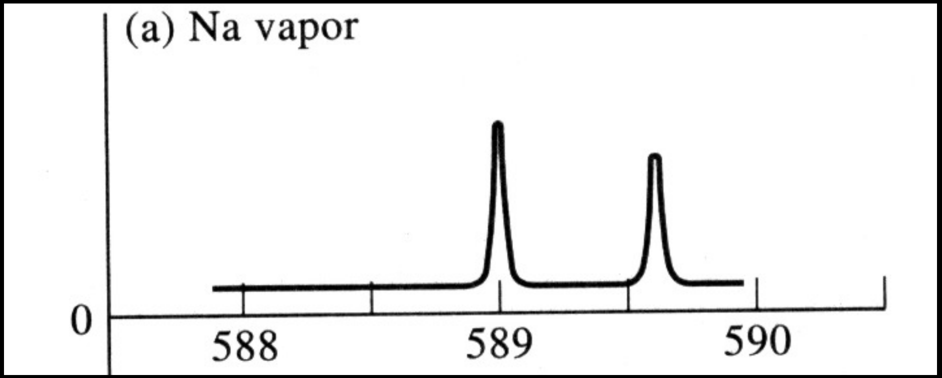
I_0 = intensity of incident radiation
I_r = intensity of reflected radiation

Emission and Absorption of Radiation

Atomic & Molecular Emission



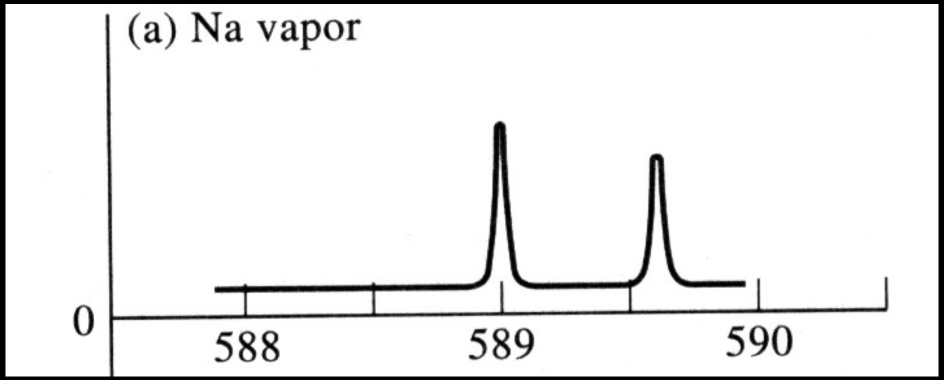
The atoms, ions, and molecules have only a limited number of discrete energy (quantum) levels, so for absorption to occur the energy of the exciting photon must <u>*exactly*</u> match the energy difference between the ground state and the excited state.



The two peaks arise from the promotion of a 3*s* electron to the two 3*p* states

Absorption: Atomic & Molecular

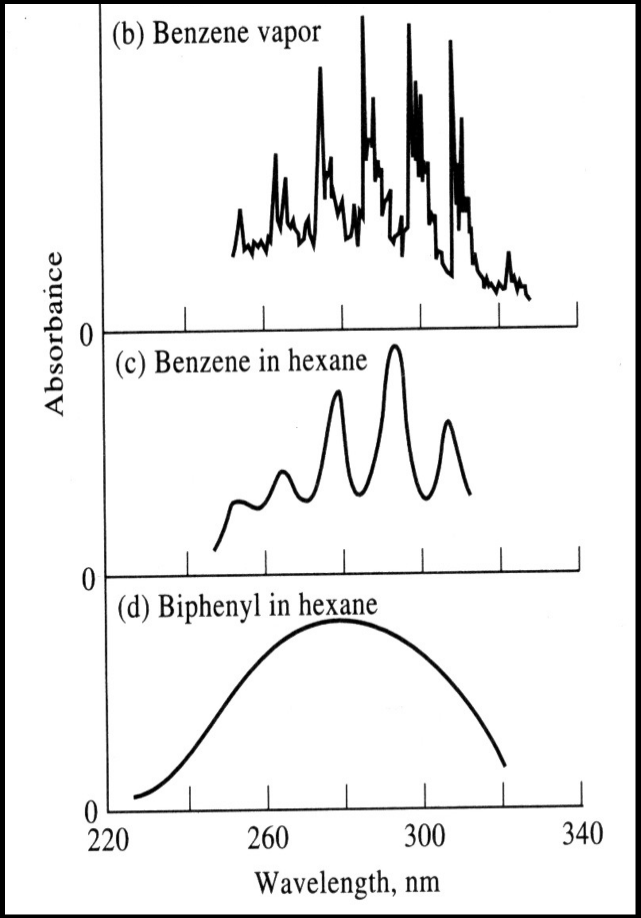
Atomic absorption



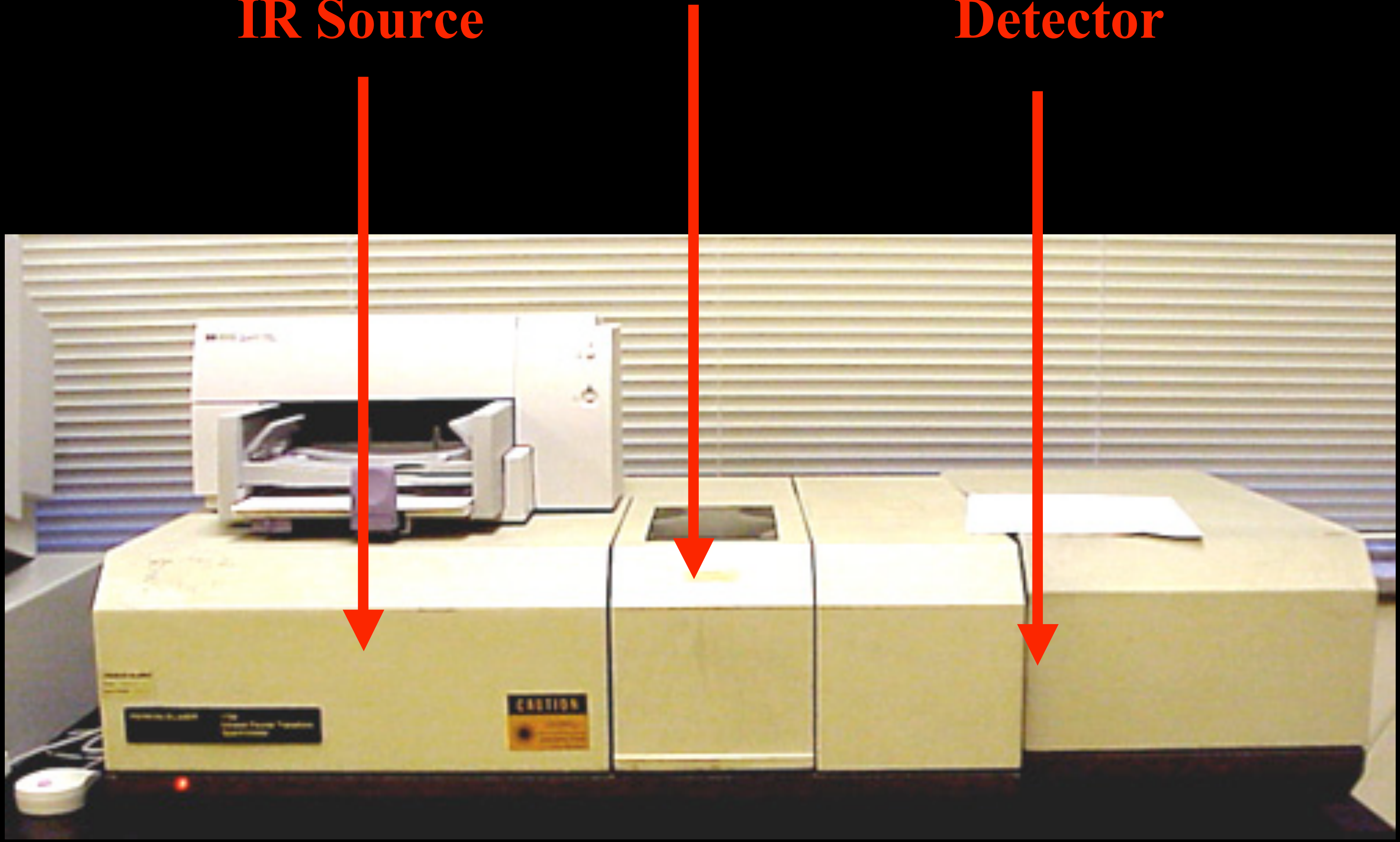
The two peaks arise from the promotion of a 3*s* electron to the two 3*p* states

The sharpness of molecular absorption spectra also depends on the state of the sample. In condensed states the spectra broaden due to molecular collisions

Molecular absorption



A typical spectrometer



Sample Compartment

IR Source

Detector

Why should we care about spectroscopy?

What is remote sensing?

Intuitive definition

- We perceive our surrounding world through our five senses
- Sight and hearing do not require close contact between sensors and externals
- **Thus, our eyes and ears are remote sensors**
- We perform remote sensing essentially all of the time.

What is Remote Sensing?

Physical definition

The acquisition of information about a target in the absence of physical contact

Measure changes in fields

- Electromagnetic fields (spectroscopy)
- Acoustic fields (sonar)
- Potential fields (gravity)

Why remote sensing?

- Spectroscopic remote sensing is one of the most powerful techniques for determining the surface composition of inaccessible targets.
- Compositional information is important for constraining the history of a target, in particular for deducing the thermal history of an object.
- Compositional information can be obtained by spectroscopic means at a number of wavelength intervals, but one the most useful is from 0.3-2.6 mm because the solar flux is high and the atmosphere is largely transparent over the range.

The Question

Most of geological remote sensing asks the following question:

- Given a reflectance curve (spectrum) taken by a spectrometer, what is the chemical composition and structure of these chemicals within the field of view of the instrument?
- Or in other words… "What kind of rock am I looking at?"

The Answer

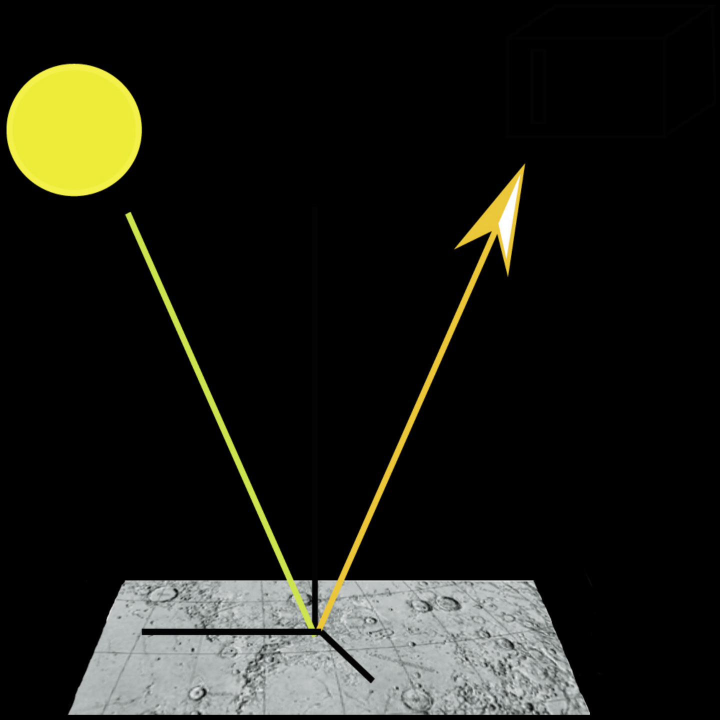
Remote Sensing of Rocks and Minerals

Clark (1999) suggests that it is possible to model the reflectance from an exposed rock consisting of several minerals or a single mineral based on Hapke's (1993) equation:

$$r_l = [[(w'/4_p)\ \ (\mu / \mu + \mu_o)]\ \ [(1+B_g(g))\ P(g) + H\ (\mu)\ H\ (\mu_o)\ -1\ ]$$

Where r_l is the reflectance at wavelength λ, μ_o is the cosine of the angle of incident light onto the rock or mineral of interest, μ is the cosine of the angle of emitted light, g is the phase angle, w' is the average single scattering albedo from the rock or mineral of interest, B_g is a back-scattering function, P_g is the average single particle phase function, and H is a function for isotropic scatterers.

What ??????

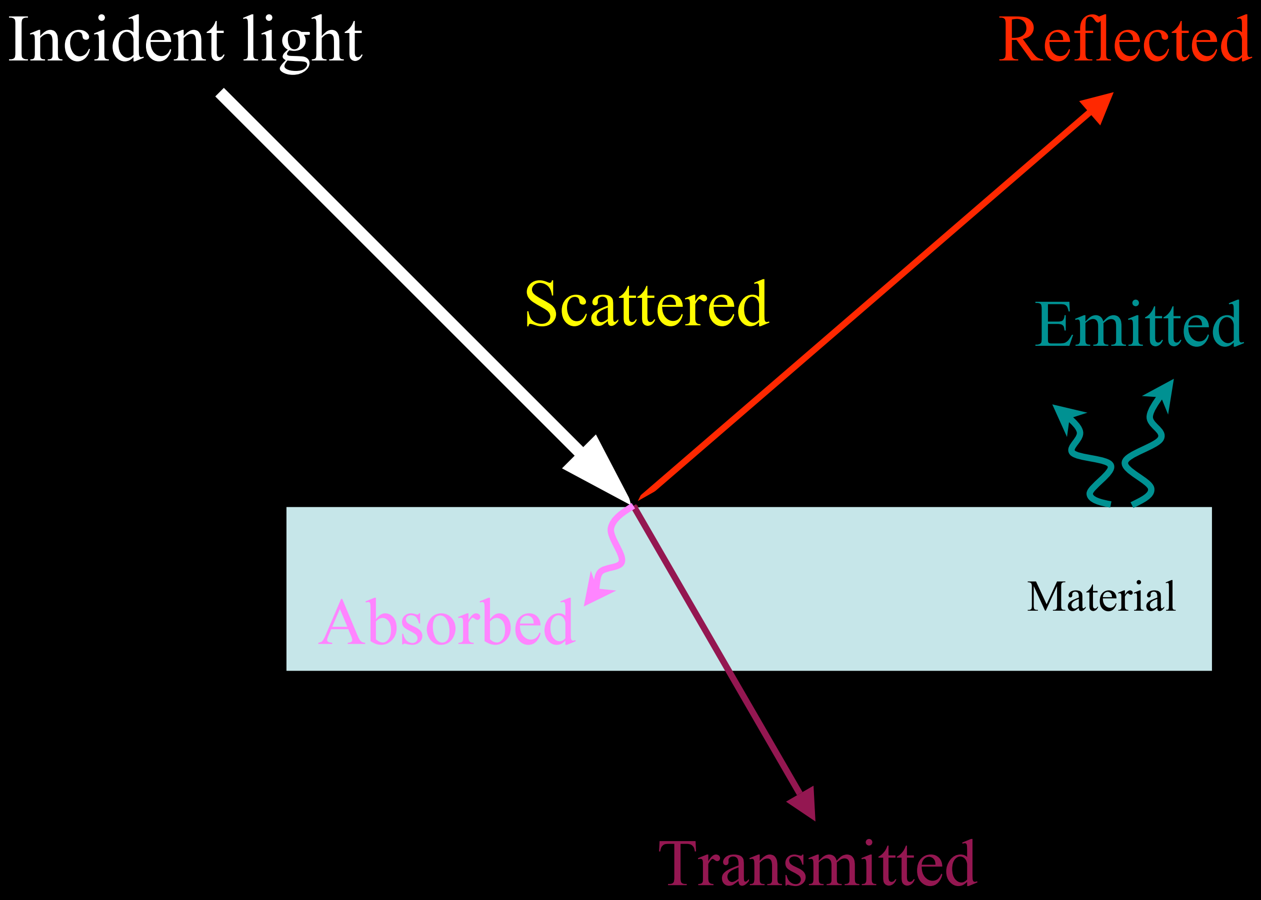


- Rock: an assemblage of minerals held together by some sort of cement (silica or calcium carbonate)

- With knowledge of
  1) known optical constants of various minerals and
  2) the angle of incident and emitted light,

- we can MODEL the reflectance of a rock with mixed grain sizes and minerals!

What happes when light hits a rock?



Interaction of EM energy (light) with material changes the energy

Reflection and Absorption

- **Beers Law**:

  $I = I_0 e^{-kx}$, I = observed light intensity,

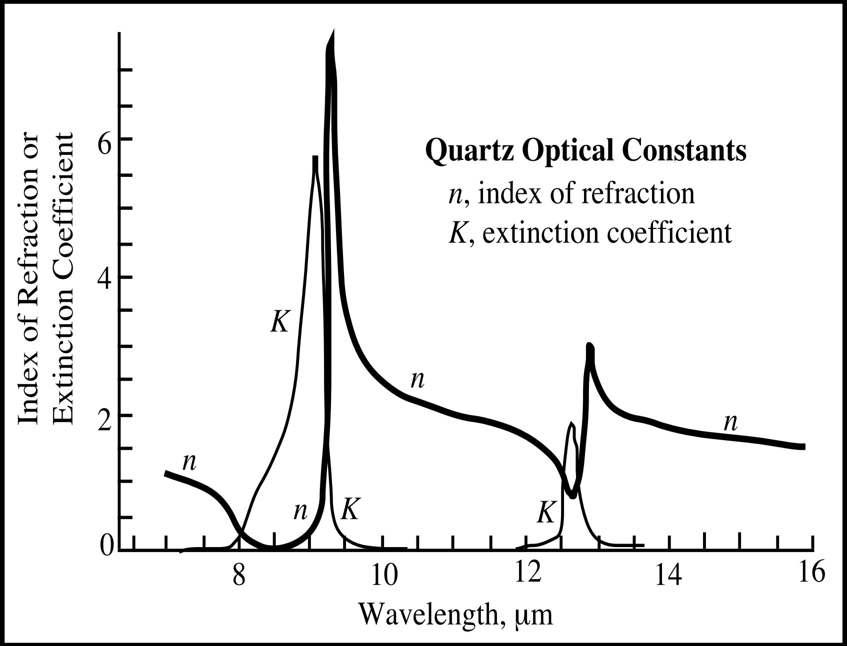
  I_0 = original light intensity, x is the distance travelled through the medium and k =absorption coefficient.

  The absorption coefficient as a function of wavelength is a fundamental parameter describing the interaction with photons with a material.

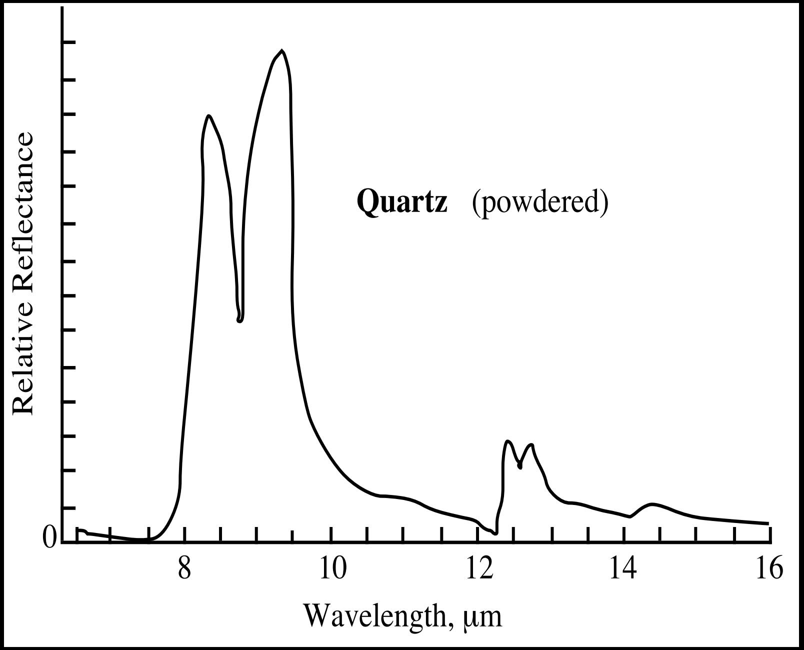
  $$k = 4\pi K/\lambda$$

- **Complex index of refraction** (m):
  m = n-jK; n is "real" part of index, $j = (-1)^{1/2}$ and K = extinction coefficient

- **Fresnel equation**:
  $R = [(n-1)^2+K^2]/[(n+1)^2+K^2]$, R=reflection of light *normally incident* onto a plane surface



Index of refraction and extinction coefficient of quartz for the wavelength interval
6-16 mm



Spectral reflectance characteristics of powdered quartz obtained using a spectroradiometer (after Clark, 1999)

What is one measuring?

Luminous intensity

Radiant flux

Radiometry

Photometry

Illuminance

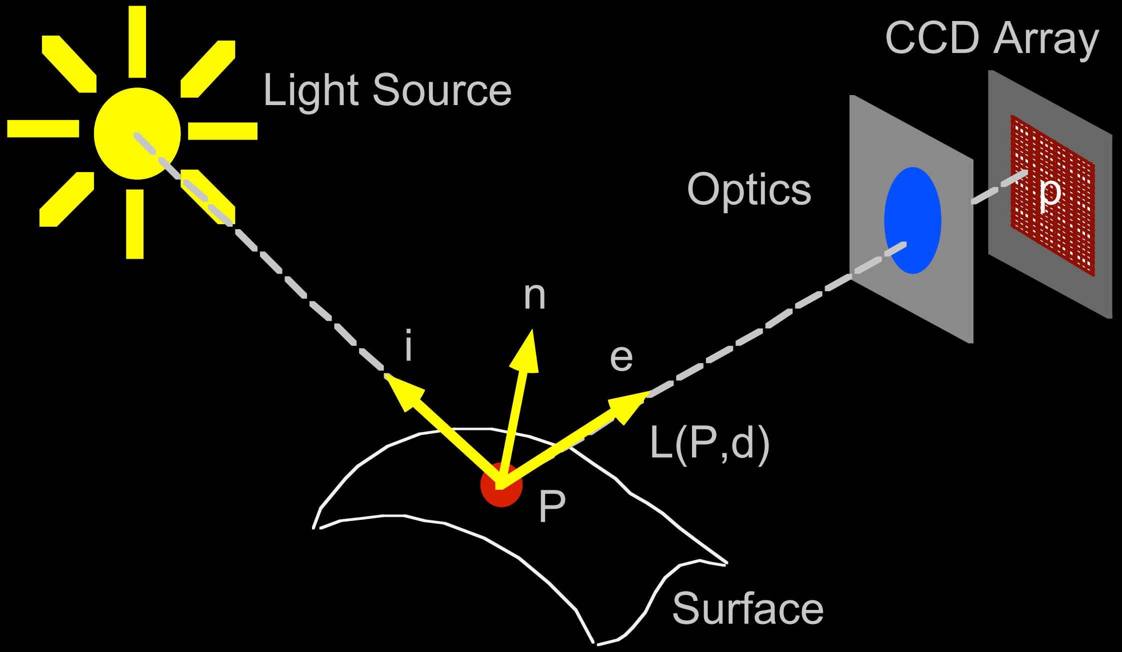
Luminance

Irradiance

It‘s all about terminology -
the big confusion is not needed

Terminology

Radiometry
Is the science of measuring or predicting how much electromagnetic energy (EM) is present, usally expressed in terms of the flow of EM energy from a source, through space or onto a detector.



There are 4 fundamental quantities of radiometry

Terminology
Radiant Flux

Power or flux Φ

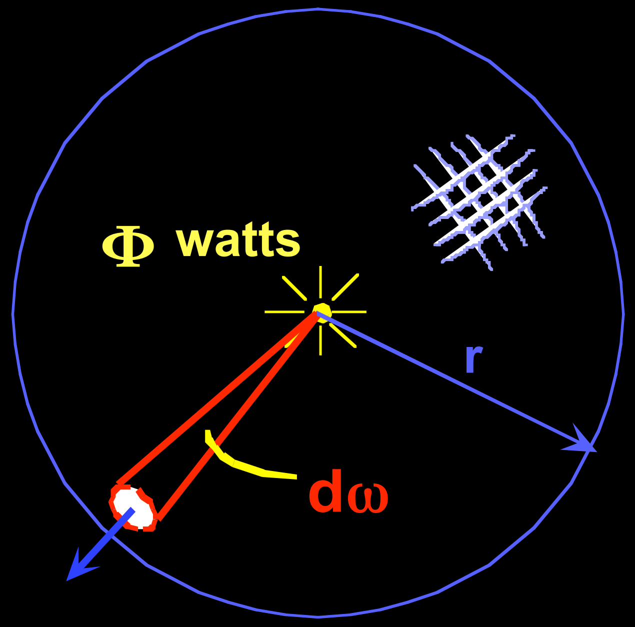
Q: Total energy

$$\boxed{\Phi = dQ/dt \quad [\mathrm{W}]}$$

Terminology

Radiant Intensity

Need a quantity to describe the energy radiating into space from a source?



$$\Phi = \int_{\text{sphere}} d\Phi$$

R = Radiant Intensity = $\frac{d\Phi}{d\omega}$ **Watts/unit solid angle (steradian)**

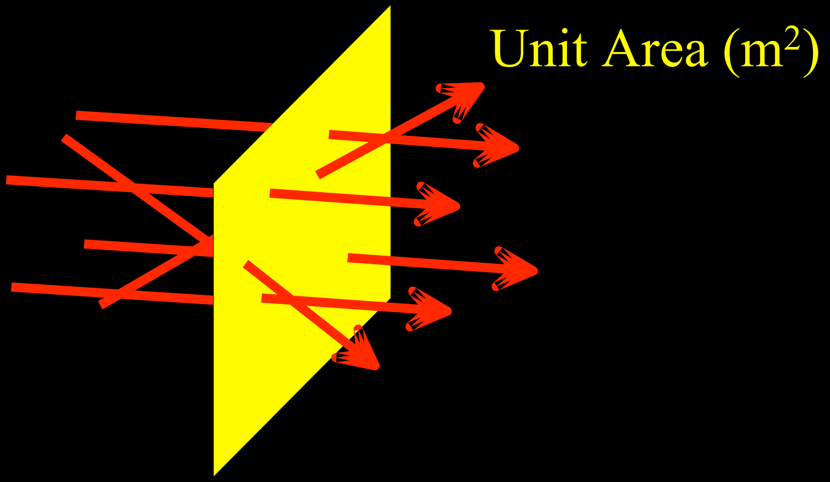
(of source)

It is a measure of the power of the source radiating into a unit solid angle.

Terminology

Irradiance (E)

- Light falling on a surface from all directions.
- How much?



Energy Flux through a surface per unit of area

- Irradiance: power per unit area falling on a surface.

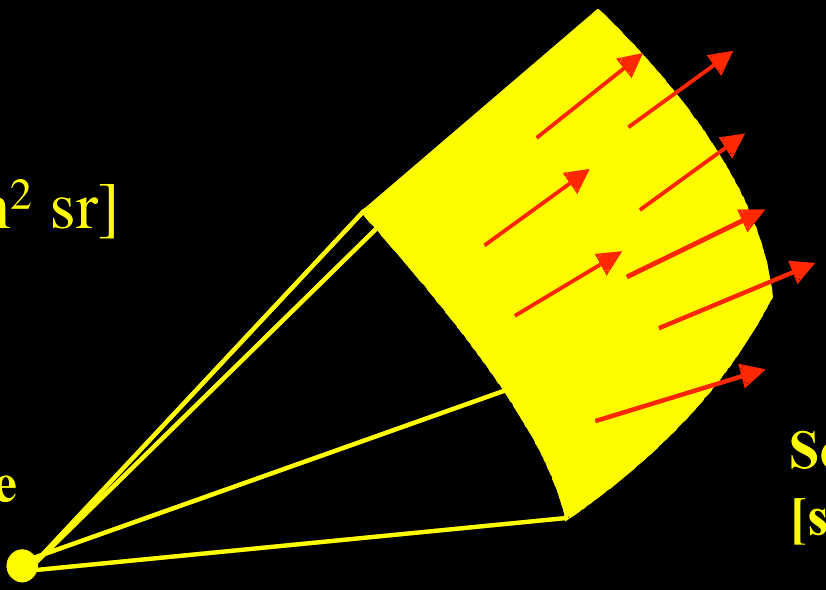
$$\text{Irradiance } E = \frac{d\Phi}{dA} \quad [\text{watts}/m^2]$$

Irradiance is defined as the rate of change in energy flux with respect to a receiver.

Terminology
Radiance (L)

Radiance is a measure of the amount of light emitted (or reflected) from a surface back into the scene as a consequence of the surface being illuminated by one or more light sources.

$$L = \frac{d^2\Phi}{dA_f\, d\omega}$$ [watts/m^2 sr]



Watts

Solid Angle [sr]

per meter square of source

Radiance is used to describe radiometric flux from sources through space onto sensors. As a result it is one of the most useful radiometric terms.

Terminology

Photometric quantities

In photometry, all the radiant quantities are modified to indicate the human eye‘s response. This response is built into the definitions.

The human eye responds only to light having wavelength between about 360 and 830 nm, known as the spectral range of the VIS spectrum.

Photometry deals only with that portion of the electromagnetic spectrum which stimulates vision in the human eye.

Terminology
radiometric-photometric quantities

Radiant quantity	***Symbol***	***Units***	***Photometric quantity***	***Symbol***	***Units***
Radiant Flux	Φ	W	Luminous flux	Φ_v	Lumen (lm)
Radiant Intensity	I_e	W/sr	Luminous Intensity	I_v	Lumen/sr= candela (cd)
Irradiance	E_e	W/m^2	Illuminance	E_v	Lm/m^2=lux (lx)
Radiance	L_e	$W/m^2\ sr^{-1}$	Luminance	L_v	$Lm/m^2\ sr^{-1}$ = cd/m2

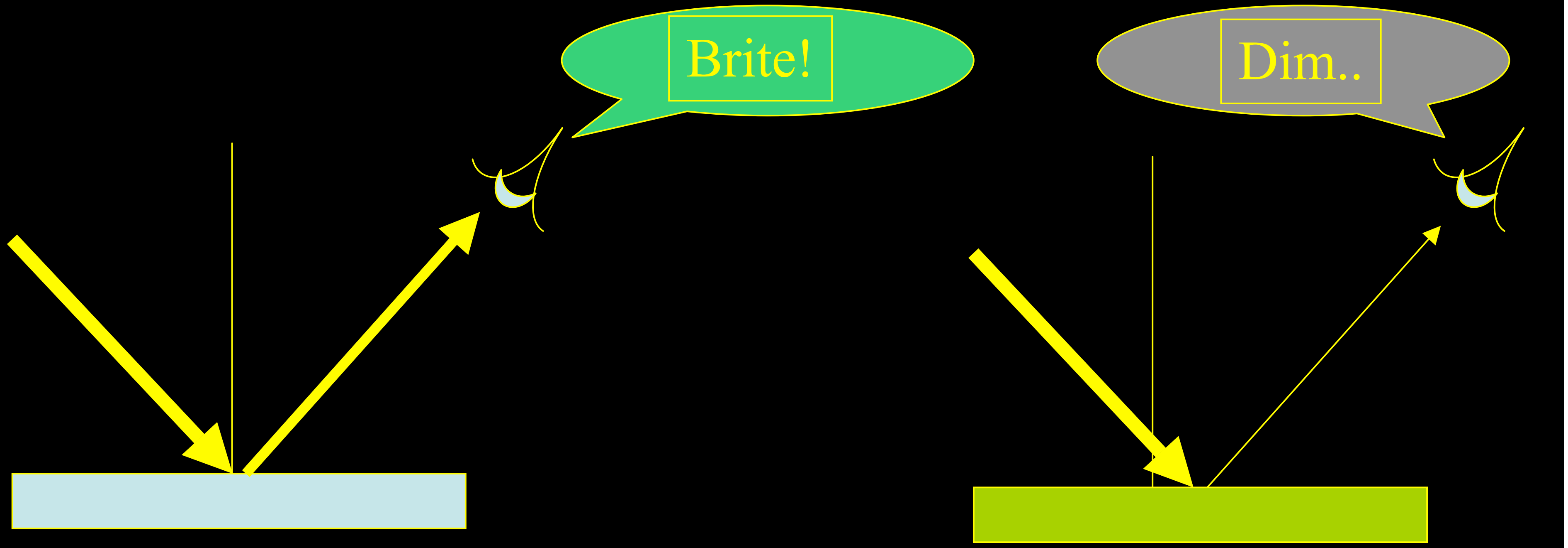
Reflectance spectroscopy

- Definition

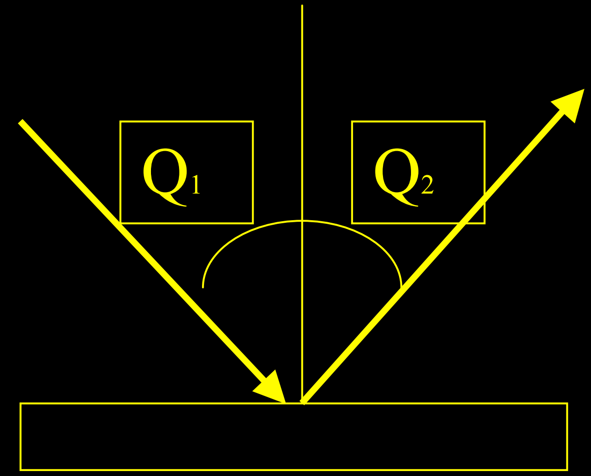
Reflection is the process by which light incident on a surface interacts with the surface such that it leaves on the incident side without change in frequency.

- The measure

The measure
What is “reflectance”



What is “reflectance”

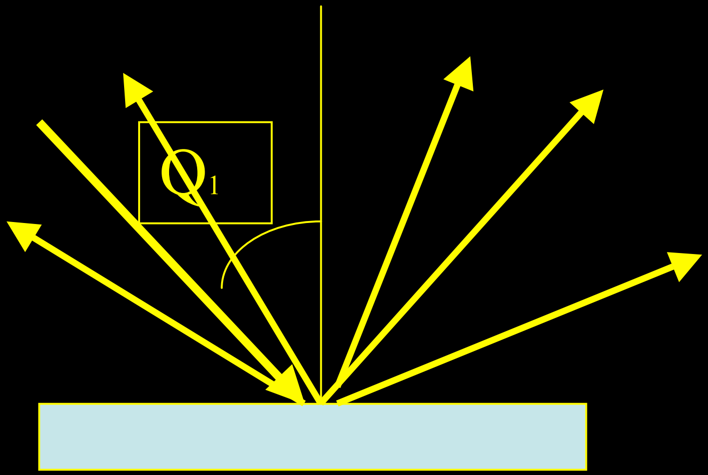


Mirror

$Q_1 = Q_2$

Perfect mirror:

Intensity of light incident equals intensity of light exiting



Perfect Diffuse Reflector:

Intensity of reflected light equal in all directions (diffuse part)

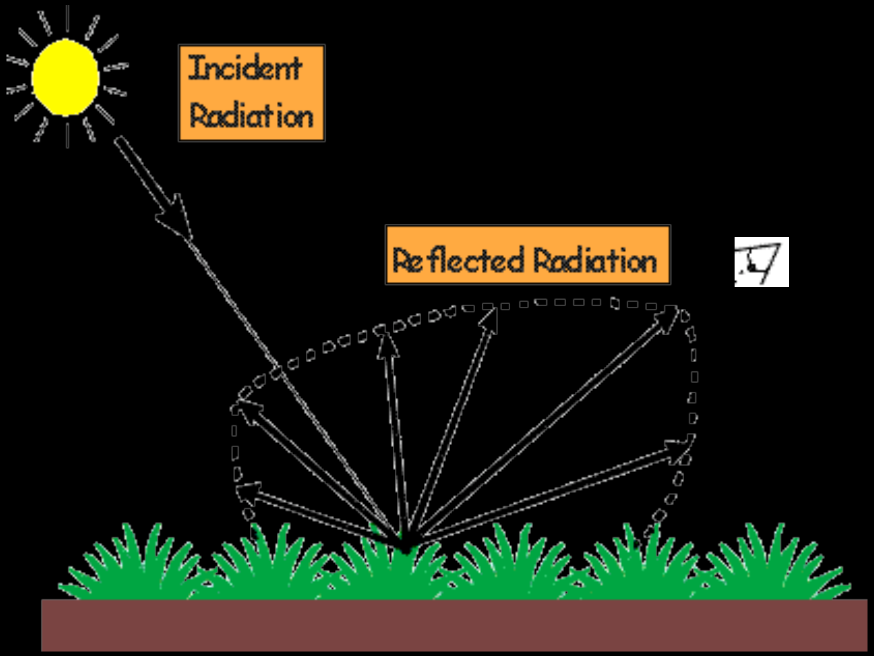
Sum of reflected light equals incident light (perfect part)

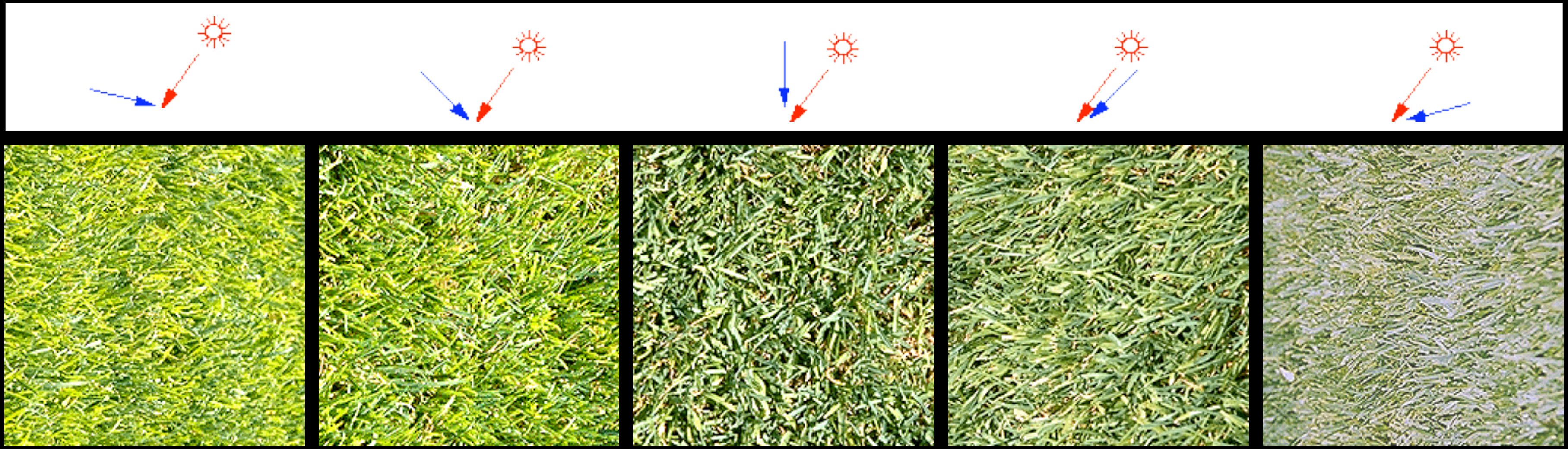
What is “reflectance”

- Ratio of the observed amount of light, (“observed” “amount” and “light” later) to a perfect diffuse reflector identically illuminated and observed.

A perfect diffuse reflector does not reflect like a mirror, but rather incident light has an equal probability of scattering in any direction

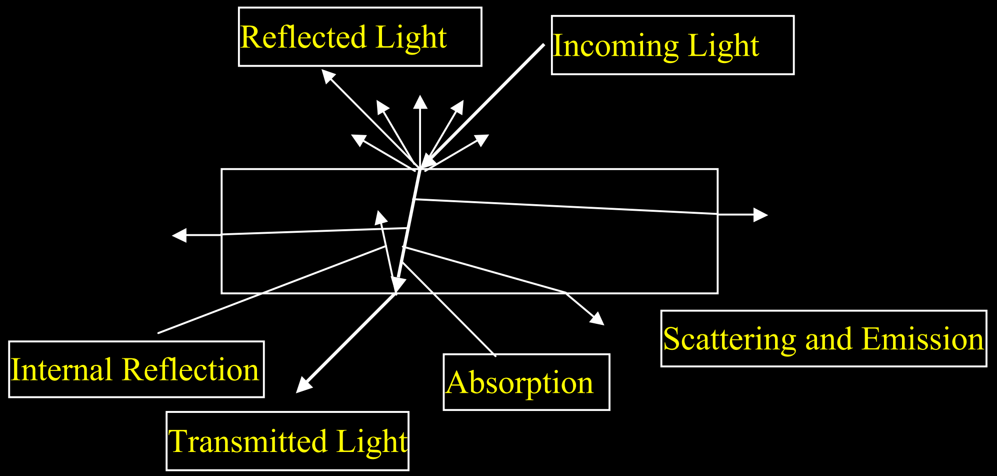
Reflectance = Dim/Brite


Incident Radiation
Reflected Radiation



What is a BRDF?

Typical light-matter interaction scenario:



Reflected Light

Incoming Light

Internal Reflection

Transmitted Light

Absorption

Scattering and Emission

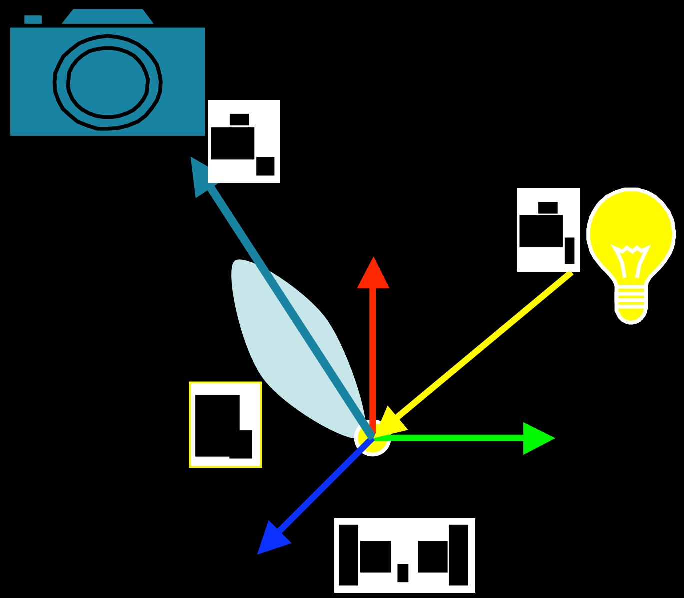
- Dependent on characteristics of the light and the matter
- Example, sandpaper vs. a mirror

BRDF describes how much light is *reflected*

The BRDF

Assuming that

- **surfaces don’t fluoresce**
- **surfaces don’t emit light (i.e. are cool)**
- **all the light leaving a point is due to that arriving at that point**



$$\mathrm{BRDF}_{\lambda}\left(\theta_i,\phi_i,\theta_o,\phi_o,u,v\right)$$

Can model this situation with the Bidirectional Reflectance Distribution Function (BRDF)

BRDF is the ratio of radiance and irradiance:

- Units: inverse steradians (sr$_{-1}$)
- BRDF is a very general notion

Why BRDF‘s matter


RENDERED BY HENRIK WANN JENSEN - 2001


RENDERED BY HENRIK WANN JENSEN - 2001

The amount of light returned from a surface is a function of the illumination and the reflective properties of the surface.

The reflective properties of the surface are captured in the bi-directional reflectance distribution function.

What is a spectrum?

- Variation in a quantity as a function of wavelength or frequency

- “Spectral reflectance” is the reflectance measured in a narrow band of wavelength as a function of wavelength or frequency

Spectral Ranges and their different names (Aerospace Industry)

UV: 200-400nm

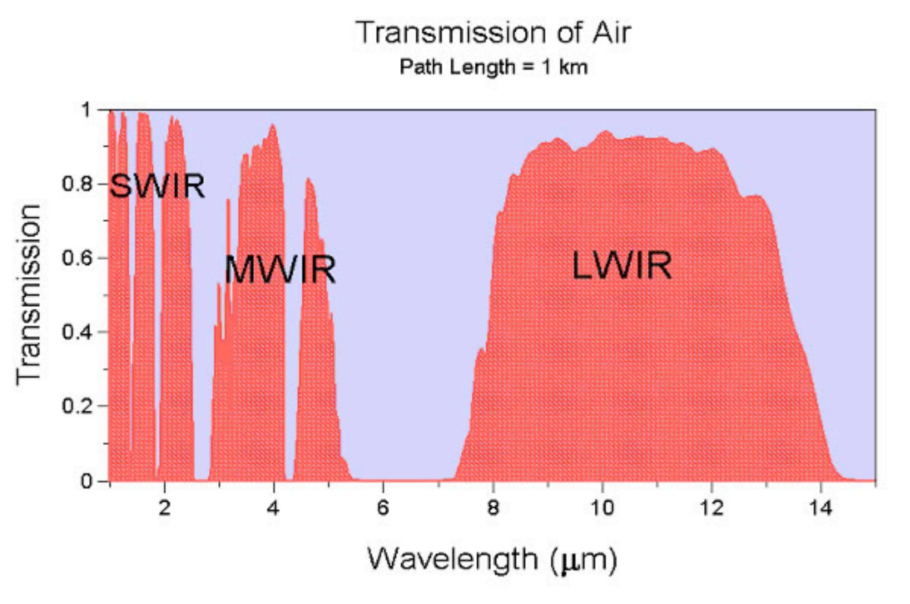
VIS: 400-800nm

NIR (near infrared) 800-1000nm (1-micron)

SWIR(short wave infrared) 1-2.5 microns

MWIR (midwave infrared): 3-5 microns

LWIR (long wave infrared) 8-14 microns



Named spectral range are historical (e.g. UV,visible), or dictated by atmospheric windows

Spectral Ranges (in Planetary Science)

UV: 100-400nm

VIS: 400-800nm

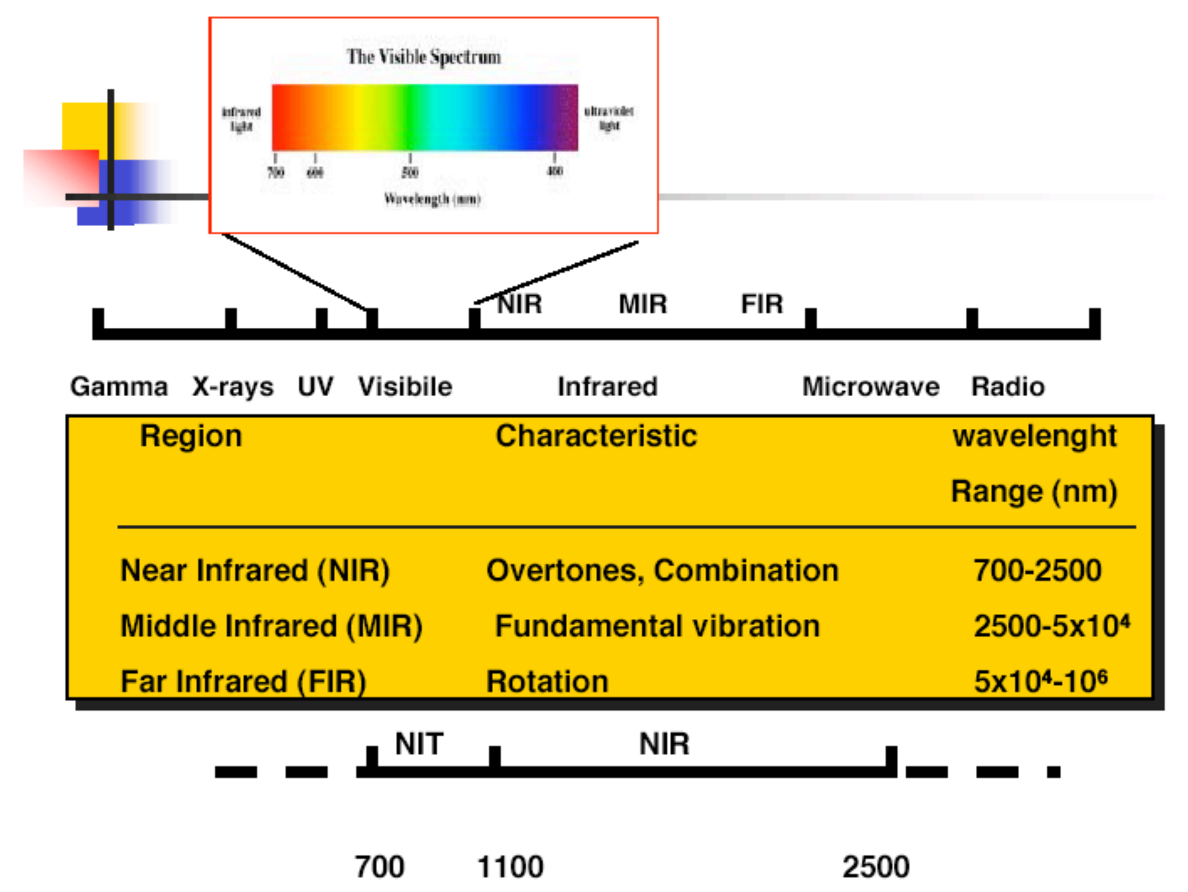
NIR (near infrared) 800-1000nm sometimes 0.8-5 microns

Mid-infrared: 3-10 microns, 7-14 microns

Thermal infrared: 4-50 microns

Real man’s infrared 10-20 microns

Infra Red (IR)



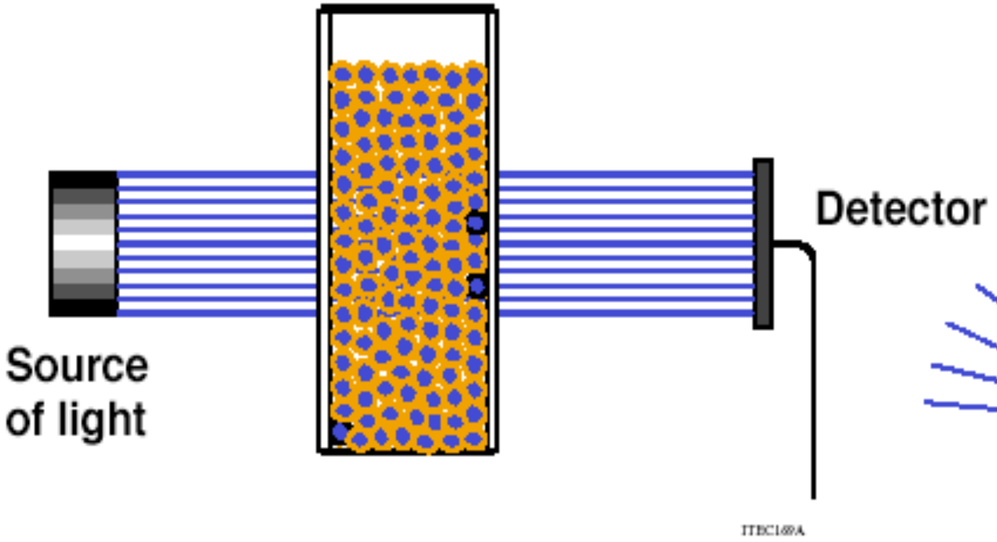
Region	Characteristic	wavelenght Range (nm)
Near Infrared (NIR)	Overtones, Combination	700-2500
Middle Infrared (MIR)	Fundamental vibration	2500-5x10^4
Far Infrared (FIR)	Rotation	5x10^4-10^6

- The NEAR INFRA RED portion of the Electromagnetic Spectrum occurs in the 0.7 µm to 1.3µm region. NIR is within the reflective portion of the spectrum and can be recorded photographically, using special false colour photographic films.
- Conventional photographic emulsions and CCD arrays will typically not able to detect reflected or radiated electromagnetic energy beyond near infra red. A specially designed thermal sensor or radiometer is required to sense energy in the mid IR and thermal bands.

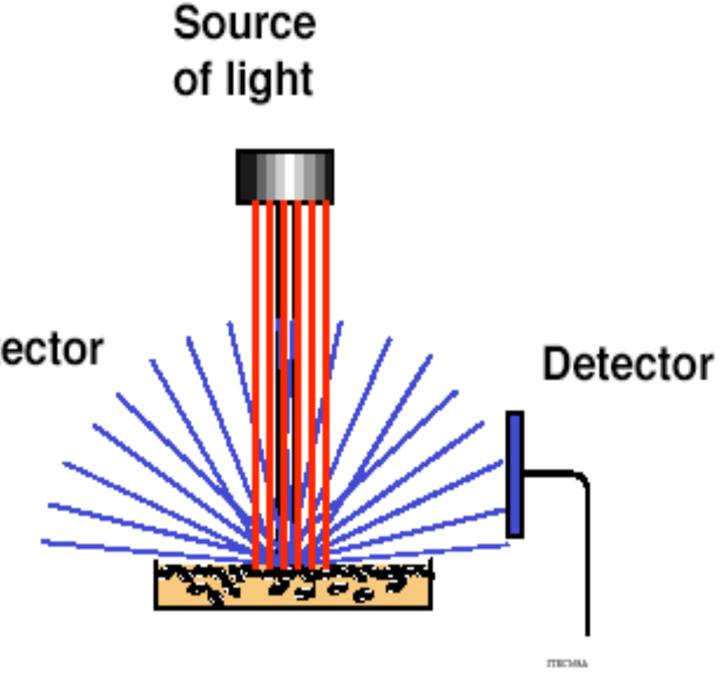
History NIR

- 1800 The First NIR Spectrum recorded (Herschel)
- 1950-1960 Potential of NIR quantitative analysis was recognized (Kaye)
- 1960s Research program at USDA (Norris) for NIR analysis of agricultural commodities
- 1971 First Generation of NIR Instruments - Reflectance
- 1975 Second Generation of NIR Instruments - More Stable Electronics and improved Optics
- 1977-1978 Third Generation of NIR Instruments - Microprocessors, Small Computers
- 1982-1983 Fourth Generation of NIR Instruments – Scanning Monochromators
- 1980s Principal components calibration techniques introduced
- 1987 Fifth Generation of NIR Instruments - Transmittance
- 1990s Nonlinear calibration methods (Local, ANN)

Reflectance – Transmission NIR Spectroscopy



Trasmission (NIT)



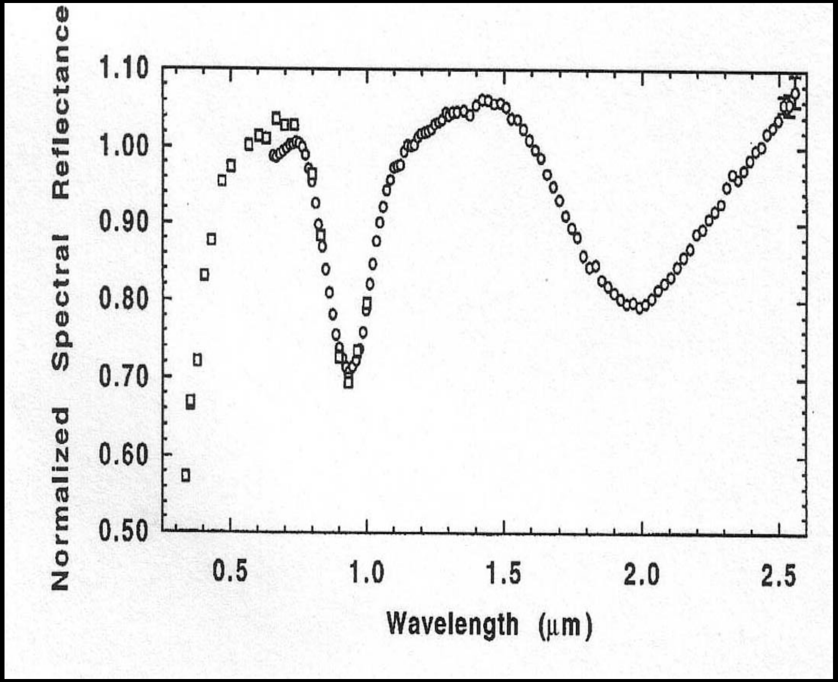
Reflectance (NIR)

Why do we get the spectra

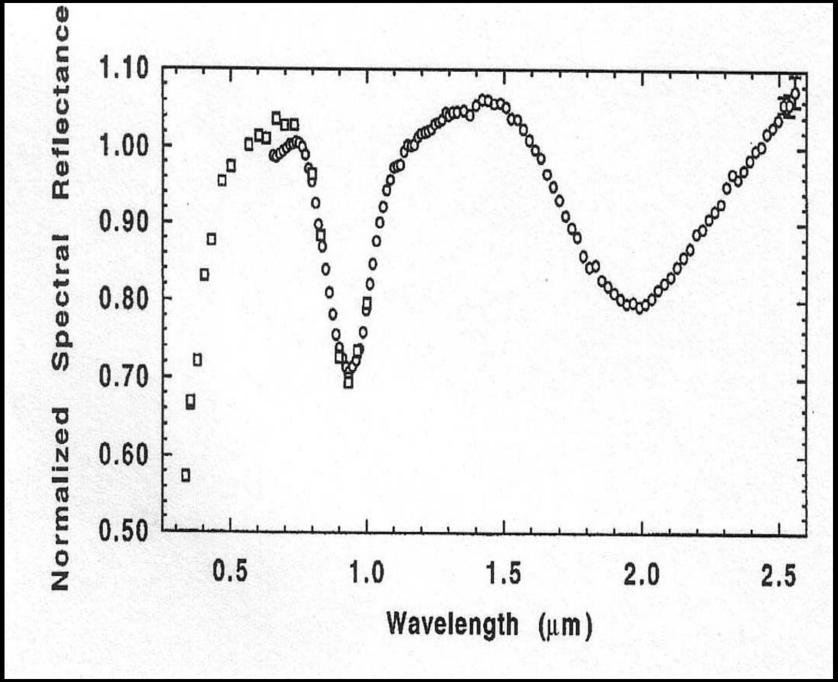
We can measure the light energy at the various frequencies = a spectrum

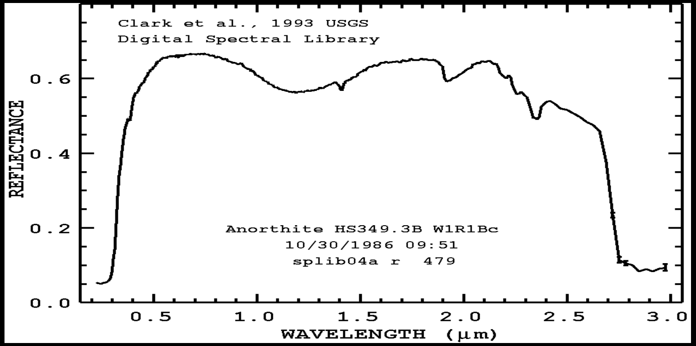
We examine the maxima and minima of spectral reflectance curves – minima are caused by molecular **absorption**, and we call these **absorption features** or **absorption bands**.

Differences in absorption and scattering for different wavelengths can be used to identify the minerals. The unique spectra are like fingerprints.



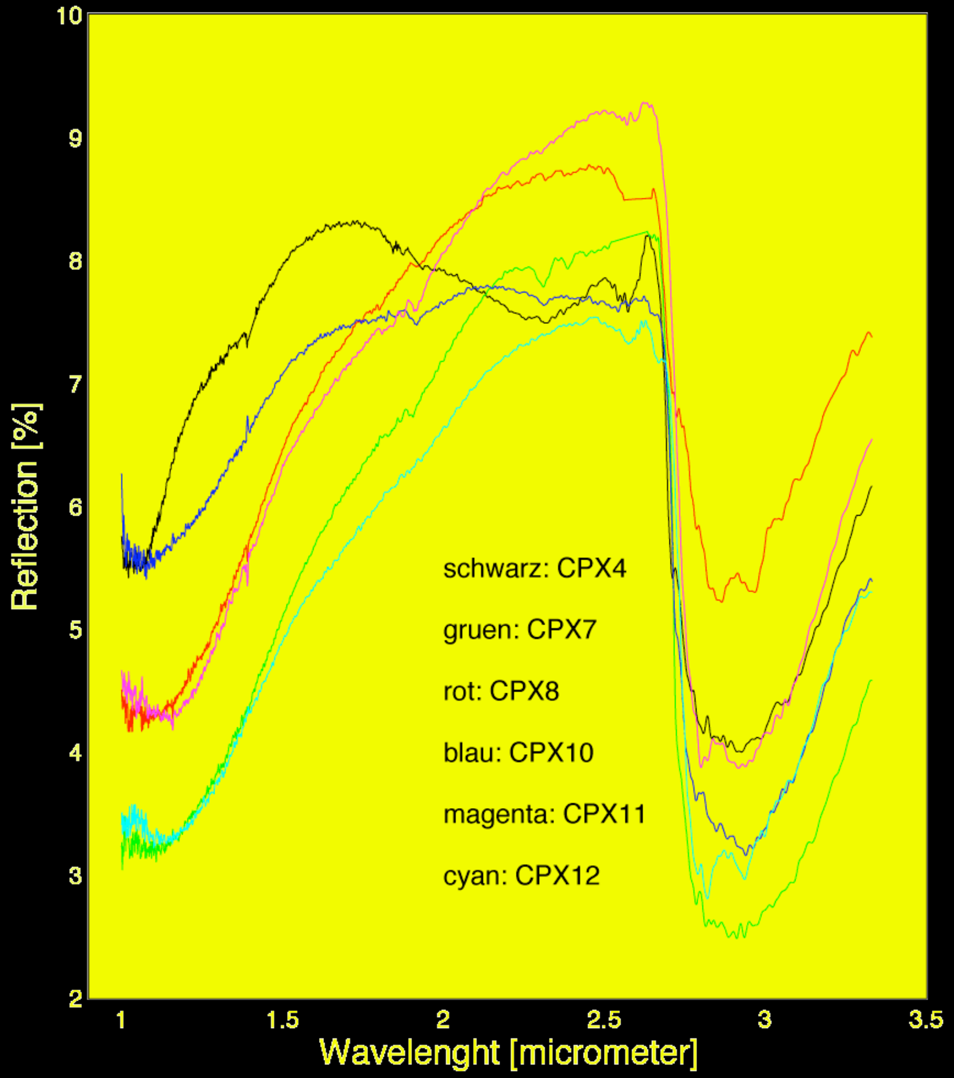
Please remember !





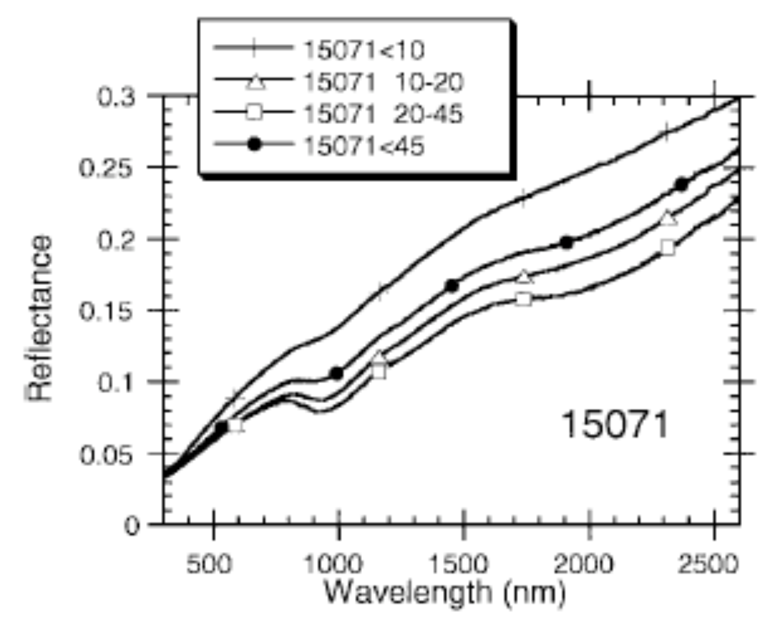
Troughs are where things are happening.
Peaks are where things are not happening
(vis and near IR only)

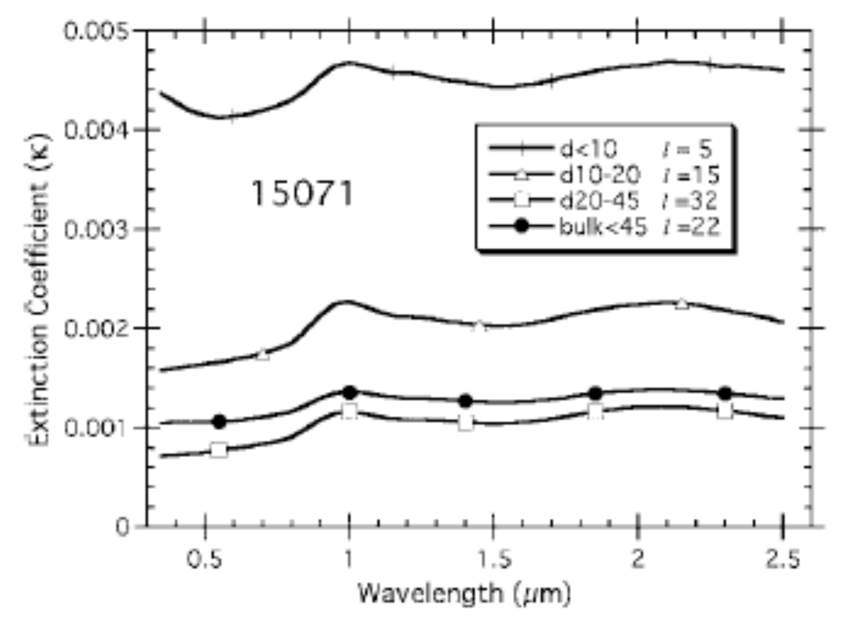
A real example from Earth



Pyroxen samples measured by Manuela Wiese

From optical to physical characterization



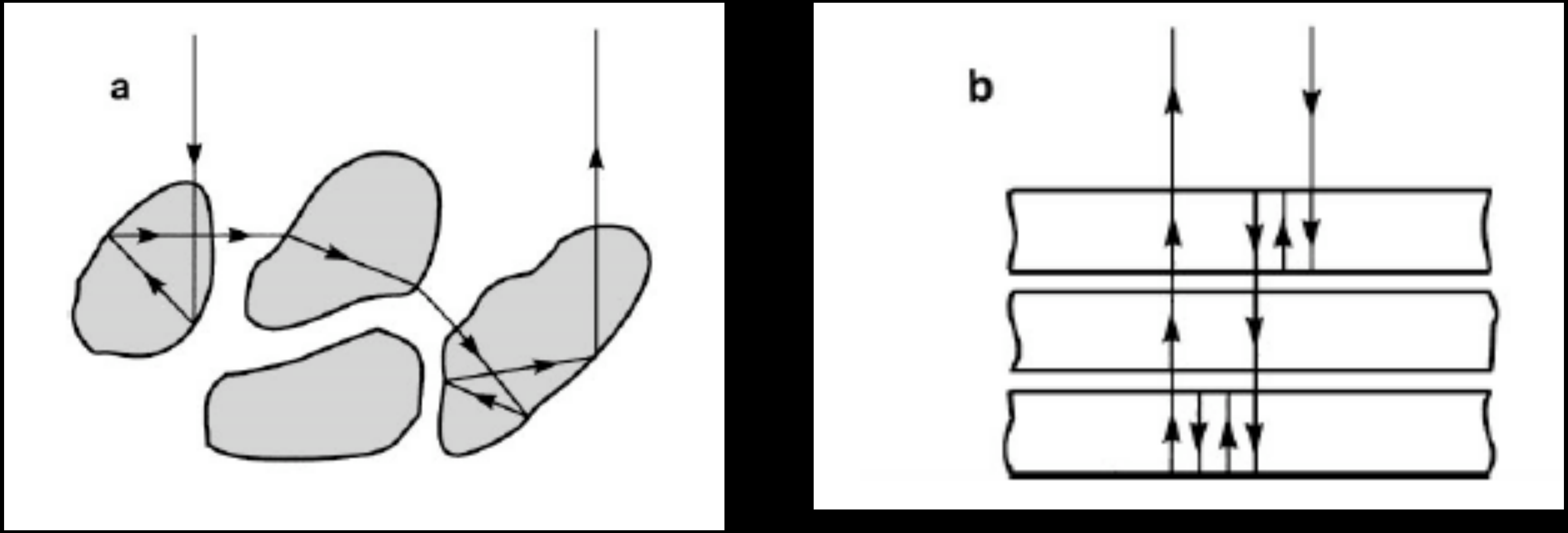


Pieters et al, Icarus 2002

Key point: the depth of an absorption feature is related to the abundance of the absorber and the grain size of the material.

From optical to physical characterization

Transform a linear measure of intensity (reflectance) into the equivalent of an absorption coefficient



$$\kappa(\lambda) = -\frac{\lambda}{4\pi l} \ln\left[\frac{b}{a} + \sqrt{\left(\frac{b}{a}\right)^2 - \frac{c}{a}}\right],$$

Shkuratov et al, Icarus 1999

What causes absorption features?

Two basic types of processes from 0.4 - 50 µm

a) Electronic (~0.4 to 1.5 µm)
  - High-energy photons absorbed by bound electrons
  - Energy states/wavelength controlled by atom and crystal
  - Primarily interactions with transition metals (e.g., Fe)
    (Not all minerals contain these)

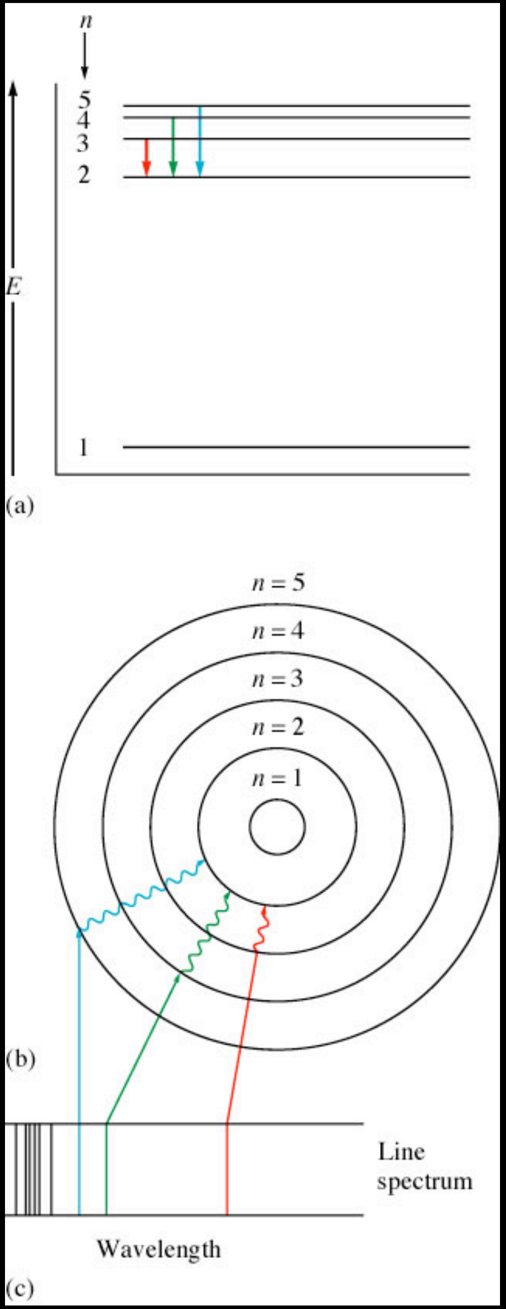
b) Vibrational (>~6 µm)
  - Excitation of fundamental vibrational motions of atoms
    - stretching and bending
    - Frequencies related to strength and length of bonds
  - ~1.5 - ~6 µm are weaker overtones and combination bands
    - Complex transitional region between reflection & emission

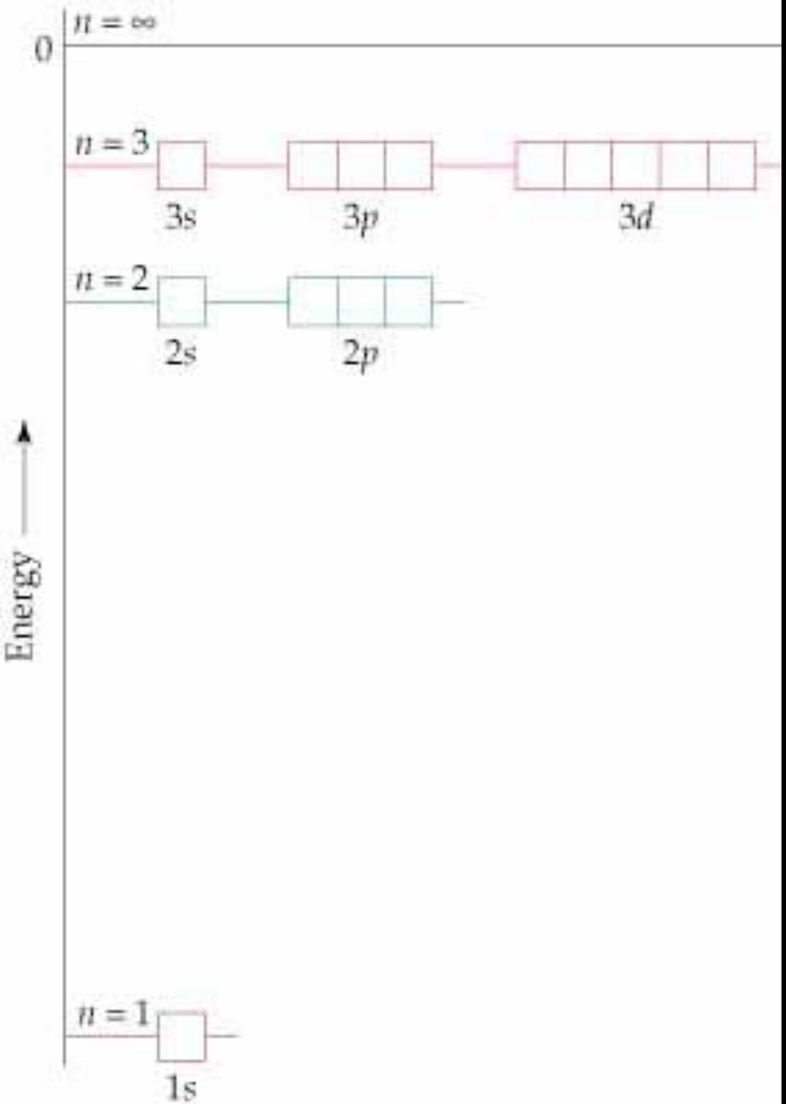
What causes absorption features?

- Electronic processes
  - **Crystal field effect**
    - Roger Burns interpreted near-IR absorptions in terms of Bethe’s “crystal field theory”
    - Absorption is due to photons exciting an electron in unfilled d-shells in transition metals.
  - **Charge transfer absorptions**
  - **Conduction bands**
  - **Color centers**

Remember: Basic QM

- Solve the Schrödinger equation - get wave functions ψ and energies for the wave functions. We call wave functions orbitals.
- Each orbital is characterized by a unique set of quantum numbers:
  - principal quantum number n
  - angular momentum quantum l number is usually designated by a letter (s, p, d, f, etc) and describes the shape of the orbital.
  - Magnetic Quantum Number, m_l give the 3D orientation of each orbital
- The Pauli Exclusion Principle





- Orbitals can be ranked in terms of energy to yield an Aufbau diagram.
- Note that the following Aufbau diagram is for a single electron system.
- As *n* increases, note that the spacing between energy levels becomes smaller.

Electron configurations

Electron configurations tells us in which orbitals the electrons for an element are located.

Three rules:

- **electrons fill orbitals starting with lowest *n* and moving upwards;**
- **no two electrons can fill one orbital with the same spin (Pauli);**
- **for degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron (Hund's rule).**

How does it work?

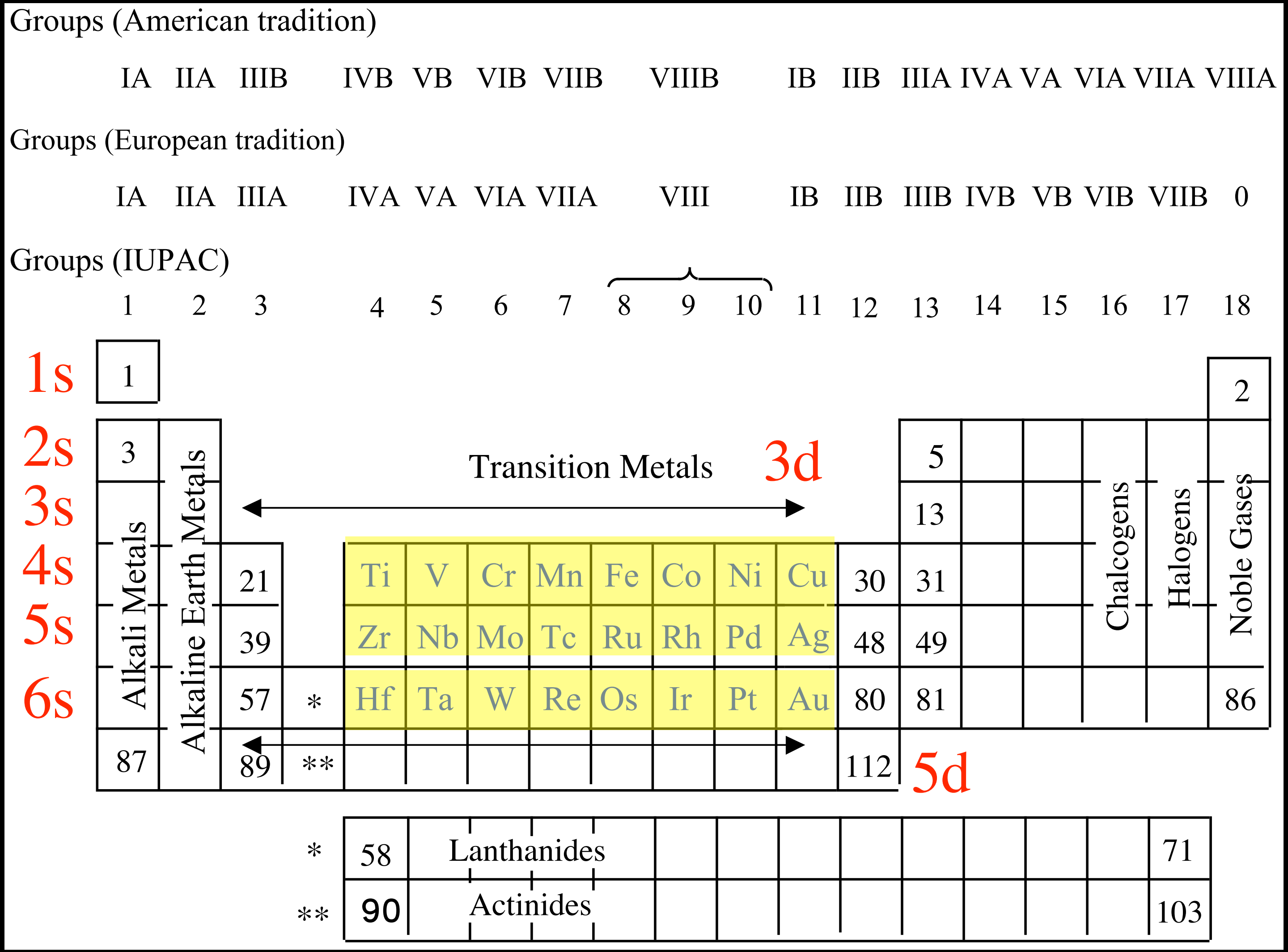
	Z	1s	2s	2p			3s	
H	1	↑						$1s^1$
He	2	↑↓						$1s^2$
Li	3	↑↓	↑					$1s^2 2s^1$
Be	4	↑↓	↑↓					$1s^2 2s^2$
B	5	↑↓	↑↓	↑				$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$

Electron Configurations and the Periodic Table

The periodic table can be used as a guide for electron configurations.

- **The period number is the value of *n*.**
- **Groups 1A and 2A have the *s*-orbital filled.**
- **Groups 3A - 8A have the *p*-orbital filled.**
- **Groups 3B - 2B have the *d*-orbital filled.**
- **The lanthanides and actinides have the *f*-orbital filled.**
- **Note that the 3*d* orbital fills after the 4*s* orbital.**
- **Similarly, the 4*f* orbital fills after the 5*d* orbital.**

Transition Metals



Groups (American tradition)

IA IIA IIIB IVB VB VIB VIIB VIIIB IB IIB IIIA IVA VA VIA VIIA VIIIA

Groups (European tradition)

IA IIA IIIA IVA VA VIA VIIA VIII IB IIB IIIB IVB VB VIB VIIB 0

Groups (IUPAC)

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

1s 2s 3s 4s 5s 6s

1 2 3 5 13 21 30 31 39 48 49 57 * 80 81 86 87 89 ** 112

Alkali Metals

Alkaline Earth Metals

Transition Metals 3d

Ti V Cr Mn Fe Co Ni Cu

Zr Nb Mo Tc Ru Rh Pd Ag

Hf Ta W Re Os Ir Pt Au

5d

Chalcogens

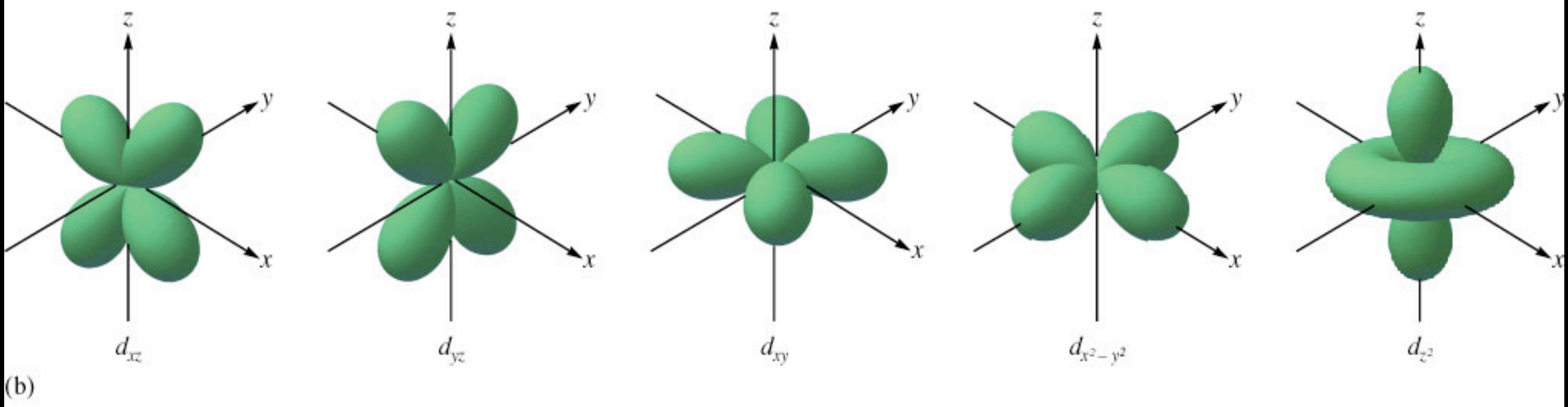
Halogens

Noble Gases

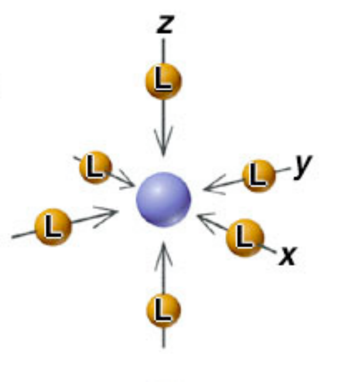
* 58 Lanthanides 71

** 90 Actinides 103

CFT



The d orbitals in a free ion (i.e. with no attached ligands), will be *degenerate*, i.e. all 5 have the same energy.

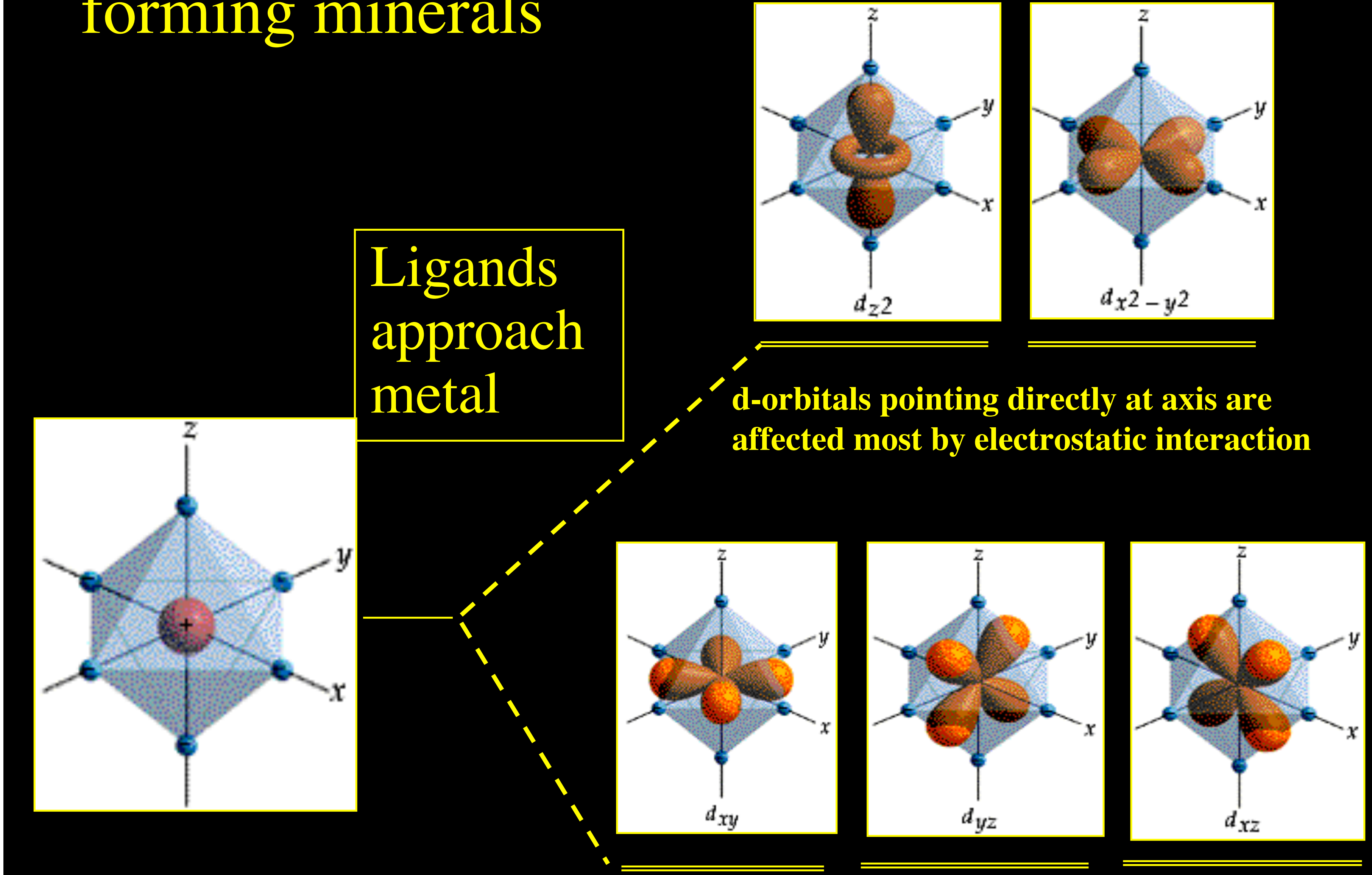


CFT presumes that the ligands may be represented by point (negative) charges lying along the bonding axes and that these will perturb the energies of any electrons which populate the d orbitals.

crystal field splitting

The removal of a degeneracy of the energy levels of molecular entities or ions due to the lower site symmetry created by a crystalline environment.

Origin of near-IR spectra features in igneous rock-forming minerals



Ligands approach metal

d-orbitals pointing directly at axis are affected most by electrostatic interaction

(Octahedral Field)

d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

Do not forget this !

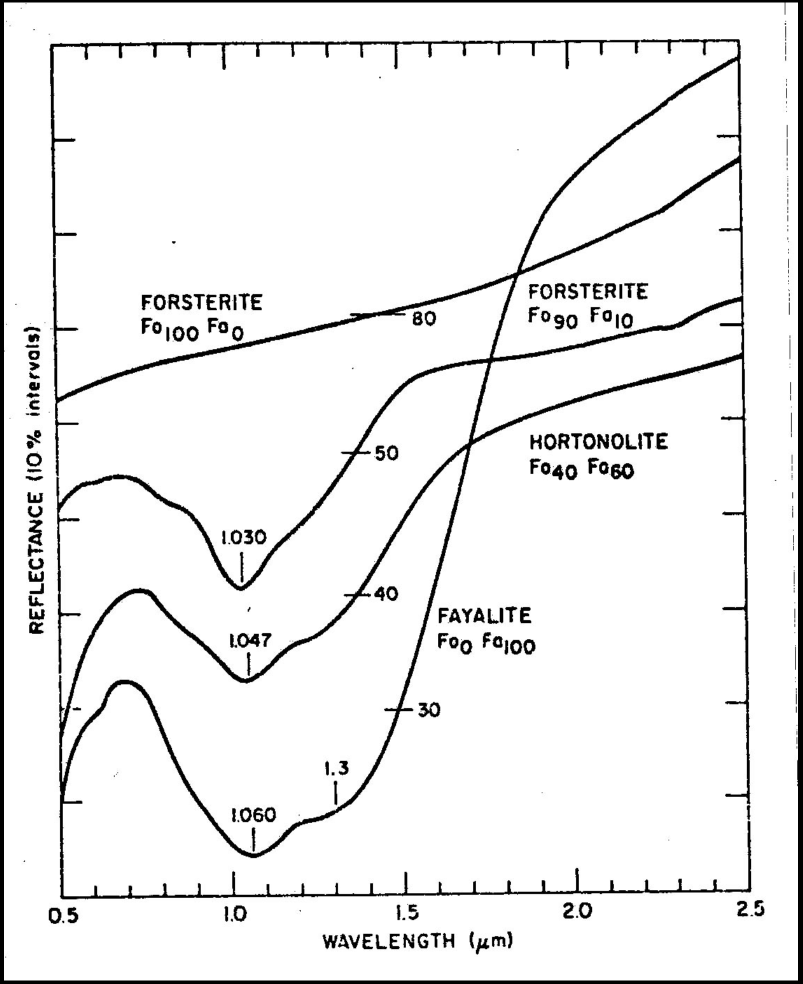
- For all transition elements, d orbitals have identical energies in an isolated ion
- but energy levels split when the atom is located in a crystal field. This splitting of the orbital energy states enables an e^- to be moved from a lower level to a higher level by photon absorption.
- Energy levels are determined by the valence state of the atom (Fe^+, Fe^{2+}), its coordination number, and the symmetry of the site it occupies.
- The crystal field varies with crystal structure from mineral to mineral changing the amount of splitting. The same ion (Fe^{2+}), produces different absoprtions, making specific mineral identification possible from spetroscopy.

Where is the evidence

Solid solution - olivine [$(Mg,Fe)_2SiO_4$]

- forsterite (Mg_2SiO_4) and
- fayalite (Fe_2SiO_4),

define a complete solid-solution series in which magnesium cations (Mg^{2+}) are replaced partially or totally by Fe^{2+}.



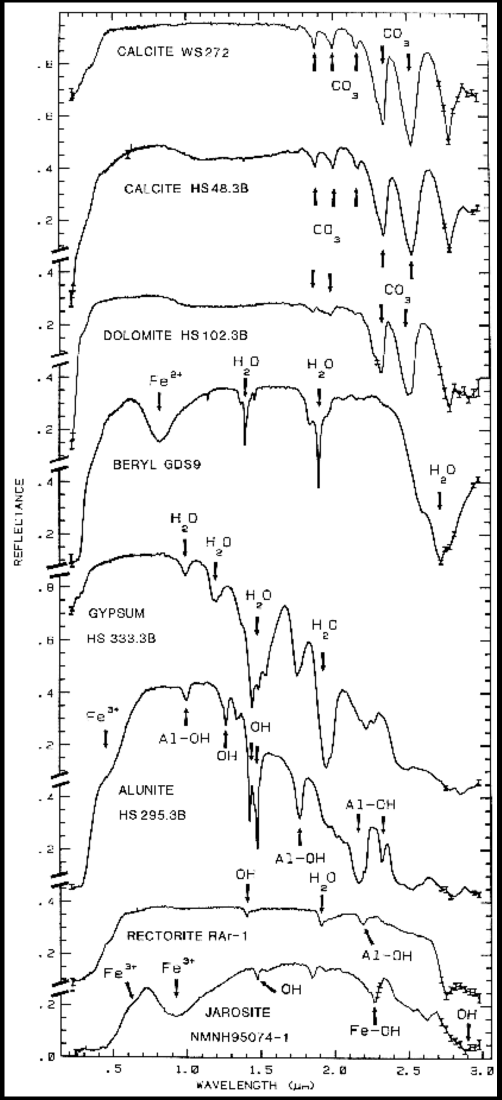
- Spectra of olivines of widely varying compositions provides an important clue:
- Iron-free olivine (forsterite) lacks an absorption feature and is bright
- Suggests absorption is due to iron

Limits of CFT

- Crystal field theory can predict the approximate position of absorptions.
- Current theory cannot predict width, or intensity
- There is hope, studies of chemical dynamics may enable a theory to be generated

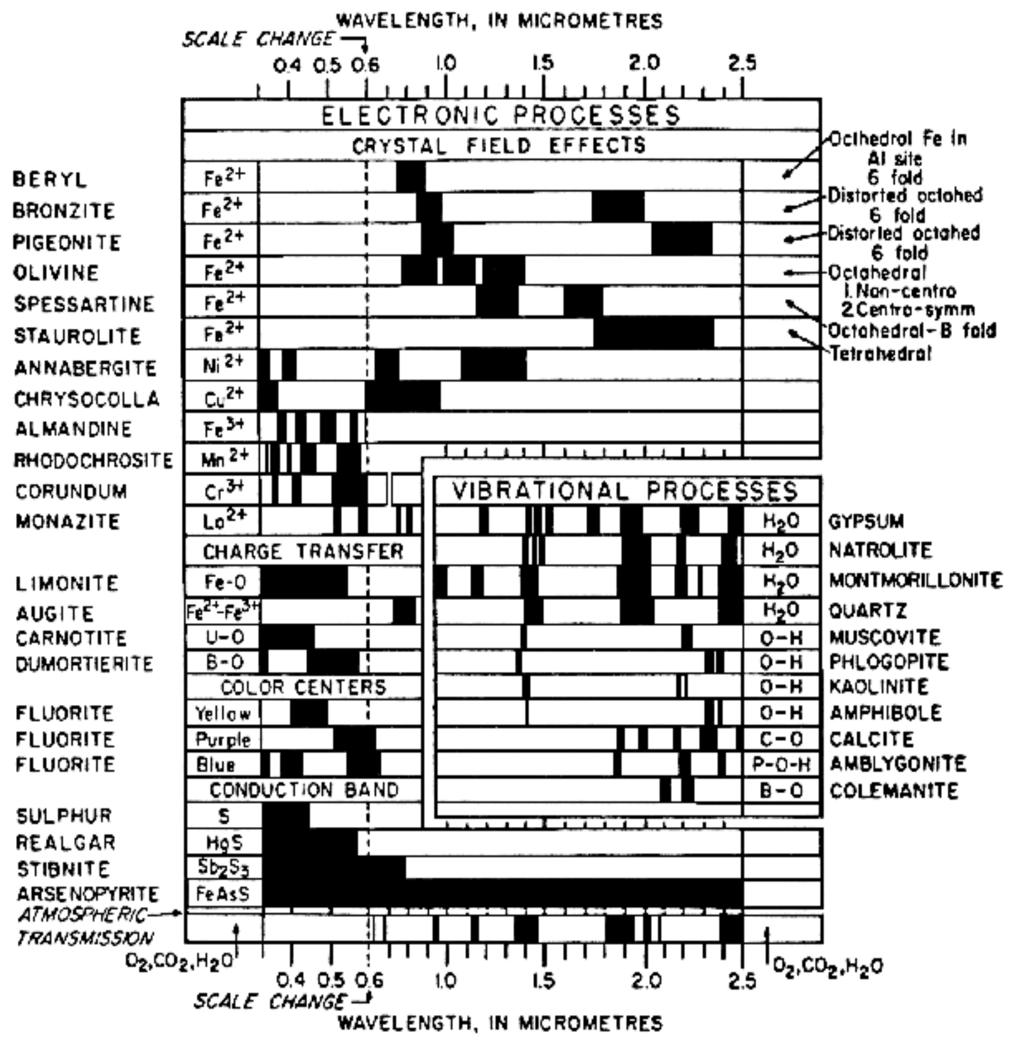
What causes absorption features?

- Vibrational processes
  - Bonds in a molecule vibrate, the frequency is dependent on the type of bond and the atom masses.
  - Certain materials have important vibrational absorption bands: water, hydroxyl, carbonates, phosphates, borates, arsenates, vanadates.



Identifying Minerals

We can use all of these absorption features to determine the chemical composition of a spectral reflectance curve.



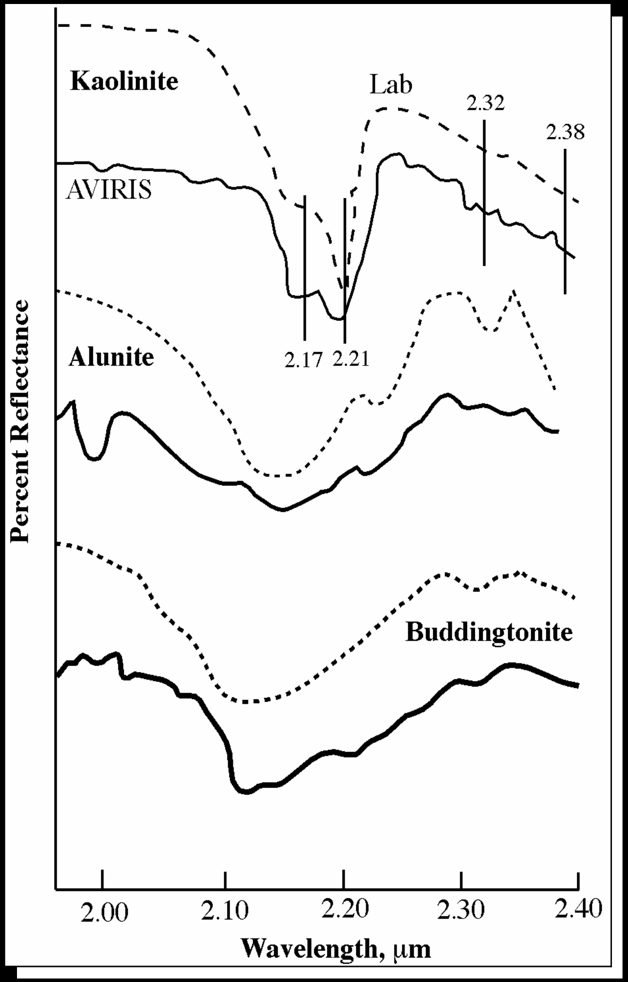
Continuum and Band Depth

- Absorption features defined by continuum and the depth of the absorption
  - Think of the continuum as the continuation of the reflectance curve if there was no absorption
  - The depth of the absorption feature is defined as:

    $D=1-R_b/R_c$, R_b is the reflectance at the bottom of the absorption feature and R_c is the reflectance of the continuum at the same wavelength.
- Key point: the depth of an absorption feature is related to the **abundance** of the absorber and the **grain size** of the material.

Spectral Libraries

- Collections of high radiometric and spectral resolution spectrum of various materials.
- Collected spectrum can be compared to these spectrum to identify them.
- Important to note: data from spectrometers is collected in radiance, but must be converted to **reflectance factor** to compare to other samples.



Spectral Resolution

- Absorption features are typically very narrow (< 20 nm), so narrow band widths are necessary.
- Many important band widths are also fairly shallow, so high radiometric resolution and SNR is also necessary.