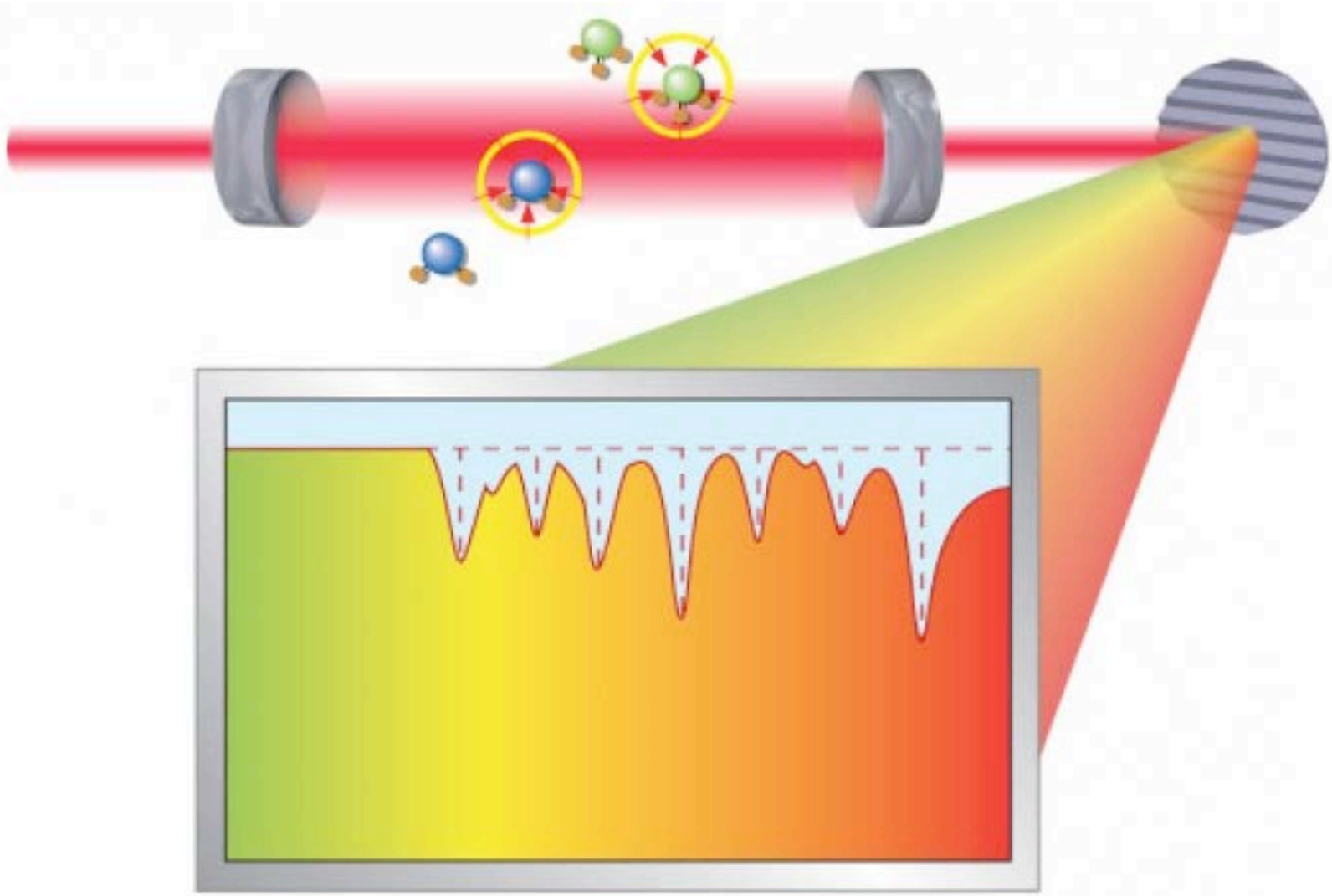
Spectroscopy: The Study of Squiggly Lines



Reflectance spectroscopy: light absorbed at specific wavelengths corresponding to energy level transitions

Interaction of Radiant Energy and Matter

What causes absorption features in visible & infrared spectra?

1) **Rotational absorption (gases)**

2) **Electronic absorption**

3) **Vibrational absorption**

Rotational Processes

Photons striking *free* molecules can cause them to rotate. The rotational states are quantized, so there are discrete photon energies that, when absorbed, cause the molecules to spin.

Rotational interactions are low-energy interactions and the absorption features are at long infrared wavelengths.

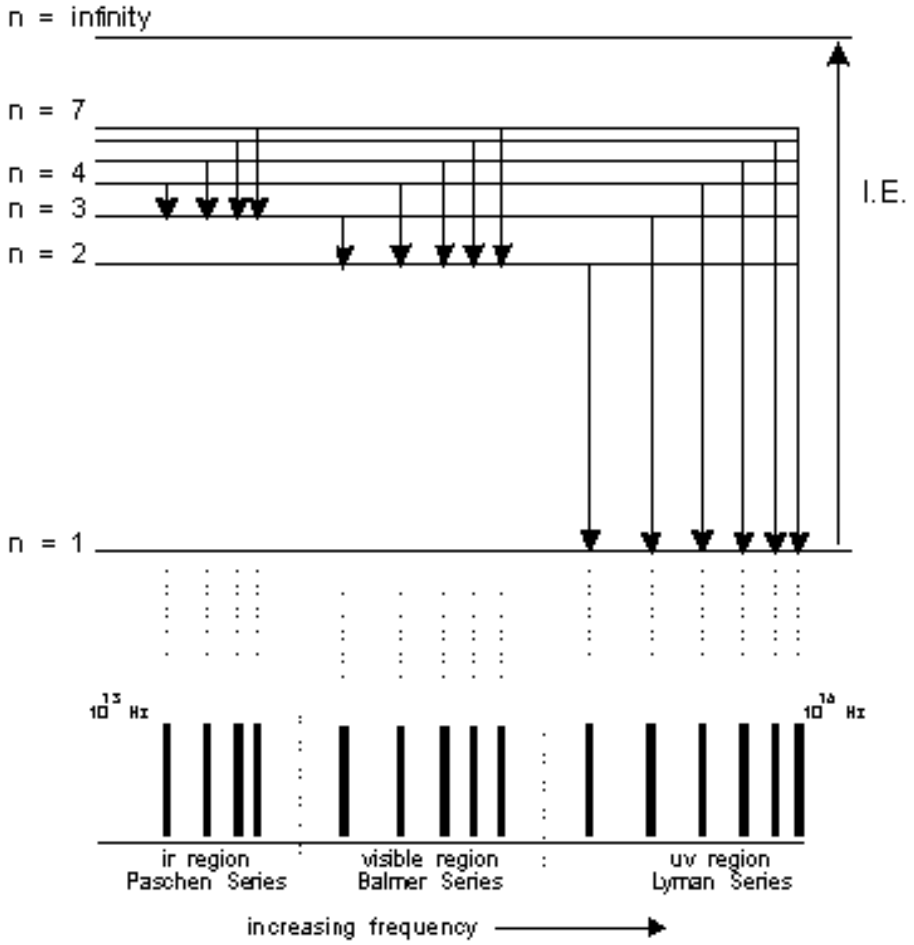
Not important in remote sensing of solid materials

Electronic Processes

Isolated atoms and ions have discrete energy states. Absorption of photons of a specific wavelength causes a change from one energy state to a higher one.

Four types:

- **Crystal Field Effects**
- **Charge Transfer Absorptions**
- **Conduction Bands**
- **Color Centers**

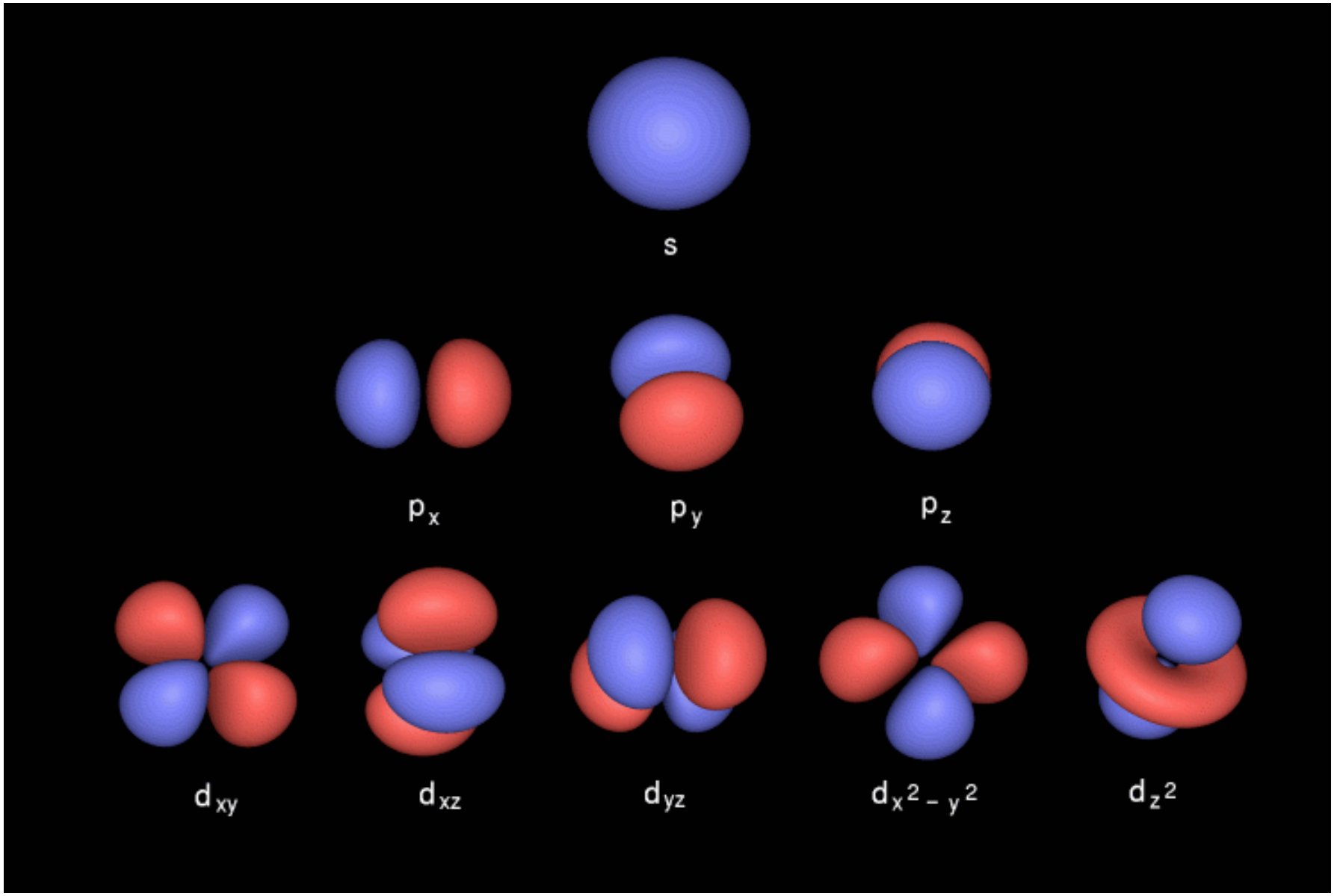


Electronic Processes

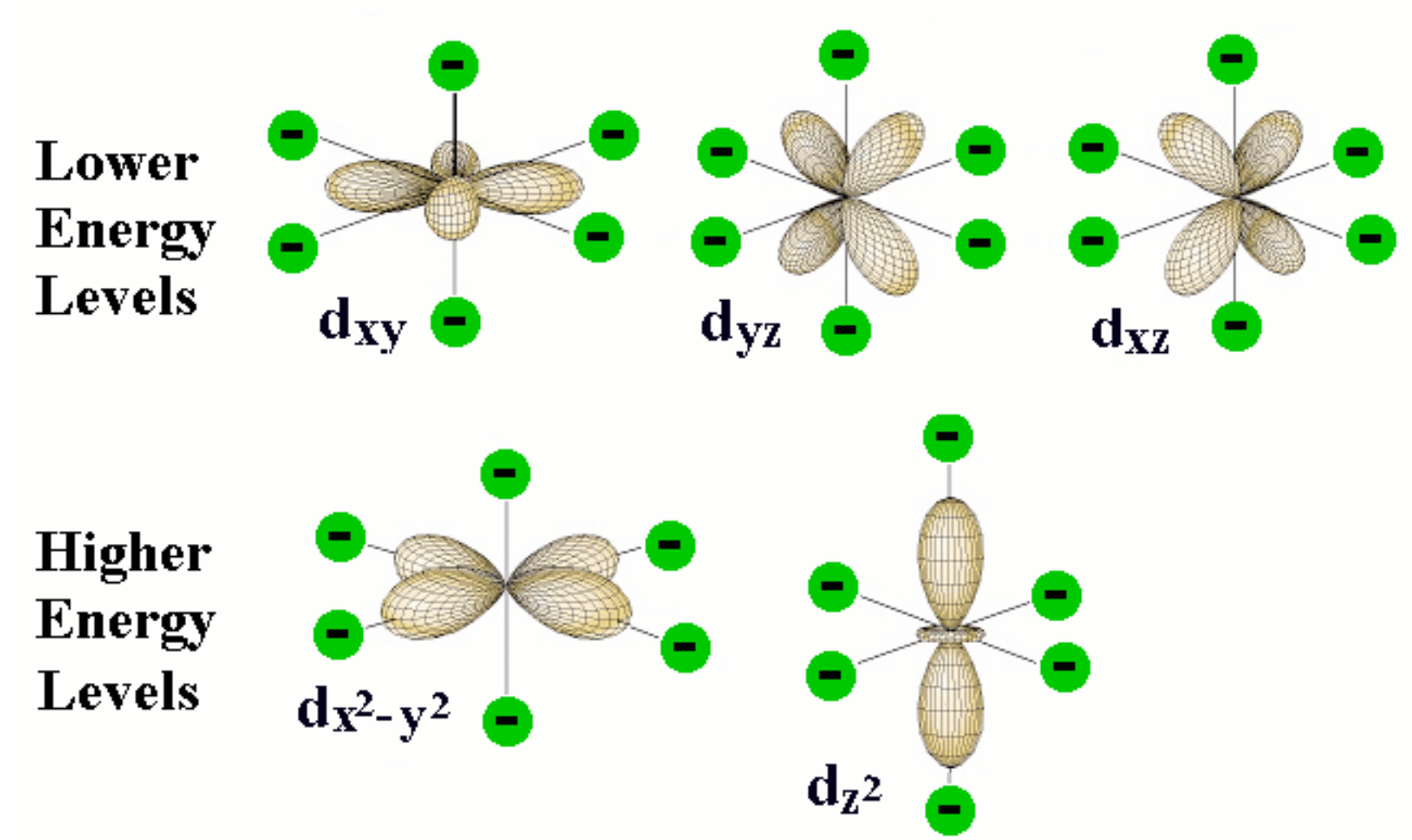
Crystal Field Effects

The electronic energy levels of an isolated ion are usually split and displaced when located in a solid. Unfilled d orbitals are split by interaction with surrounding ions and assume new energy values. These new energy values (transitions between them and consequently their spectra) are primarily determined by the valence state of the ion (Fe^{2+}, Fe^{3+}), coordination number, and site symmetry.

Electron Orbits

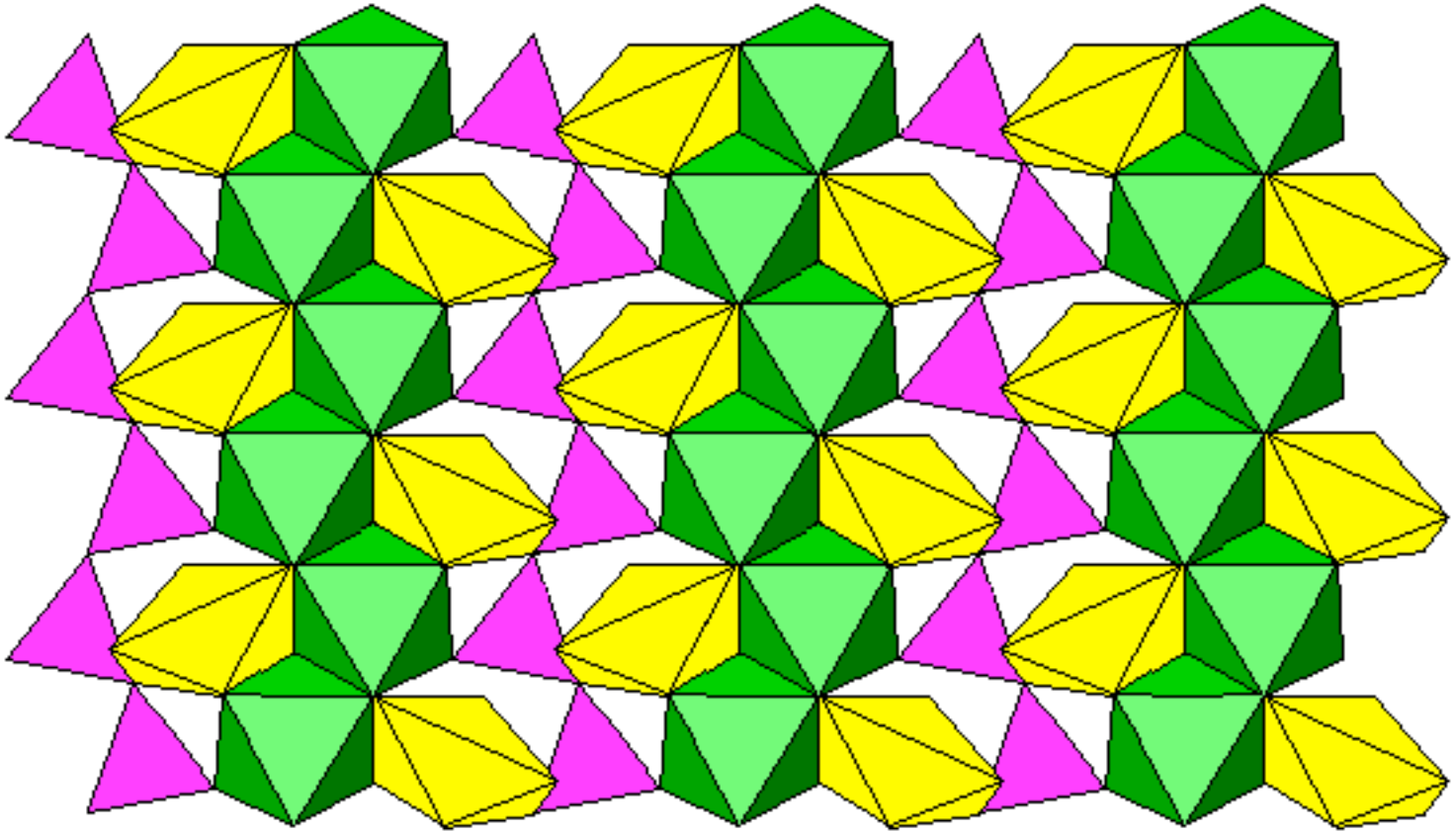


Energy Level Splitting in Solids: Part 1



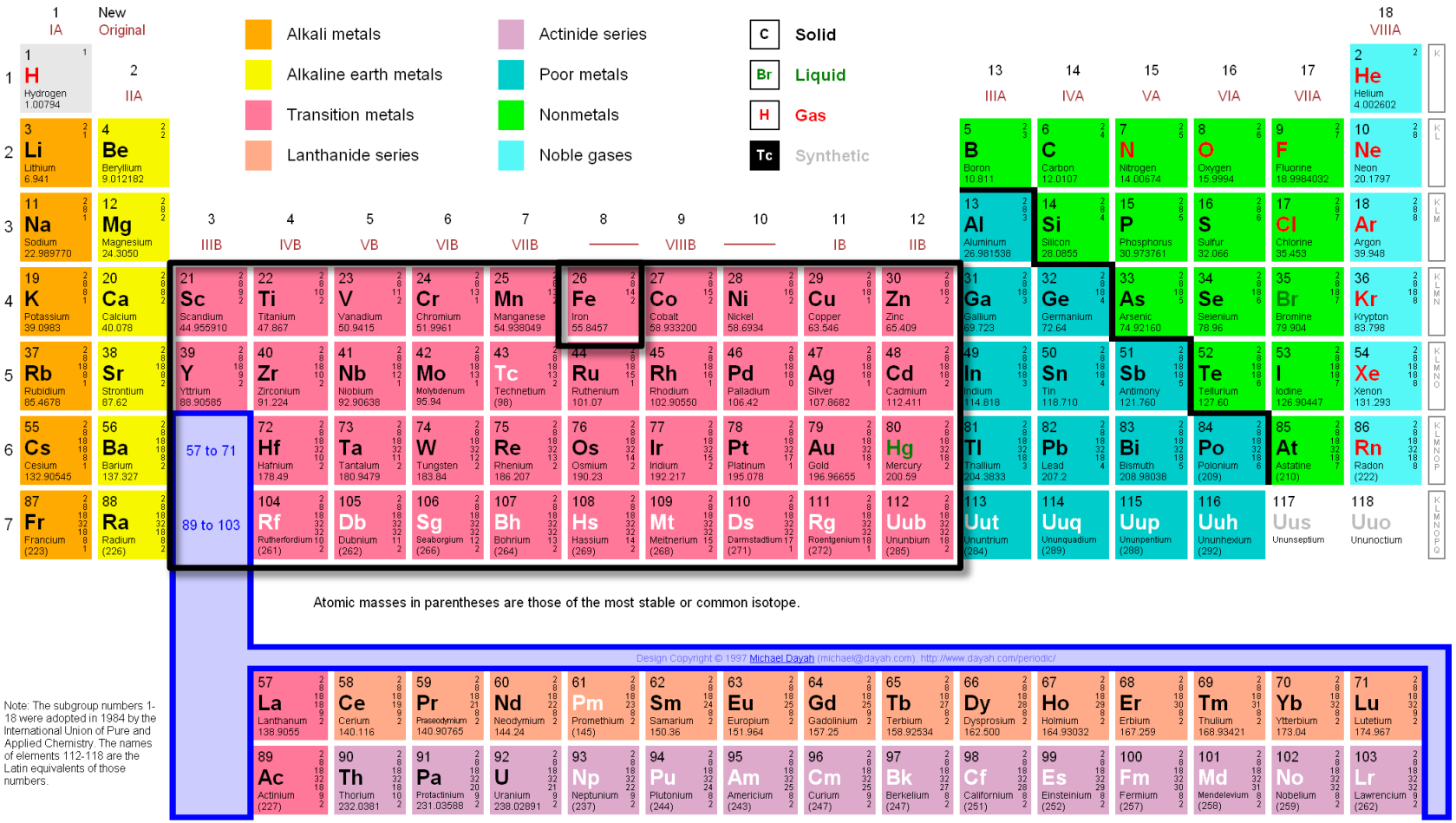
In a free atom these have equal energy, but not in a crystal…

Energy Level Splitting in Solids: Part 2



Distortion of some “sites” in a crystal → further energy splitting
→ *diagnostic of mineralogy*

Unfilled *d* orbitals: the transition metals



Iron is the most geologically abundant transition metal

Electronic Processes

Crystal Field Effects

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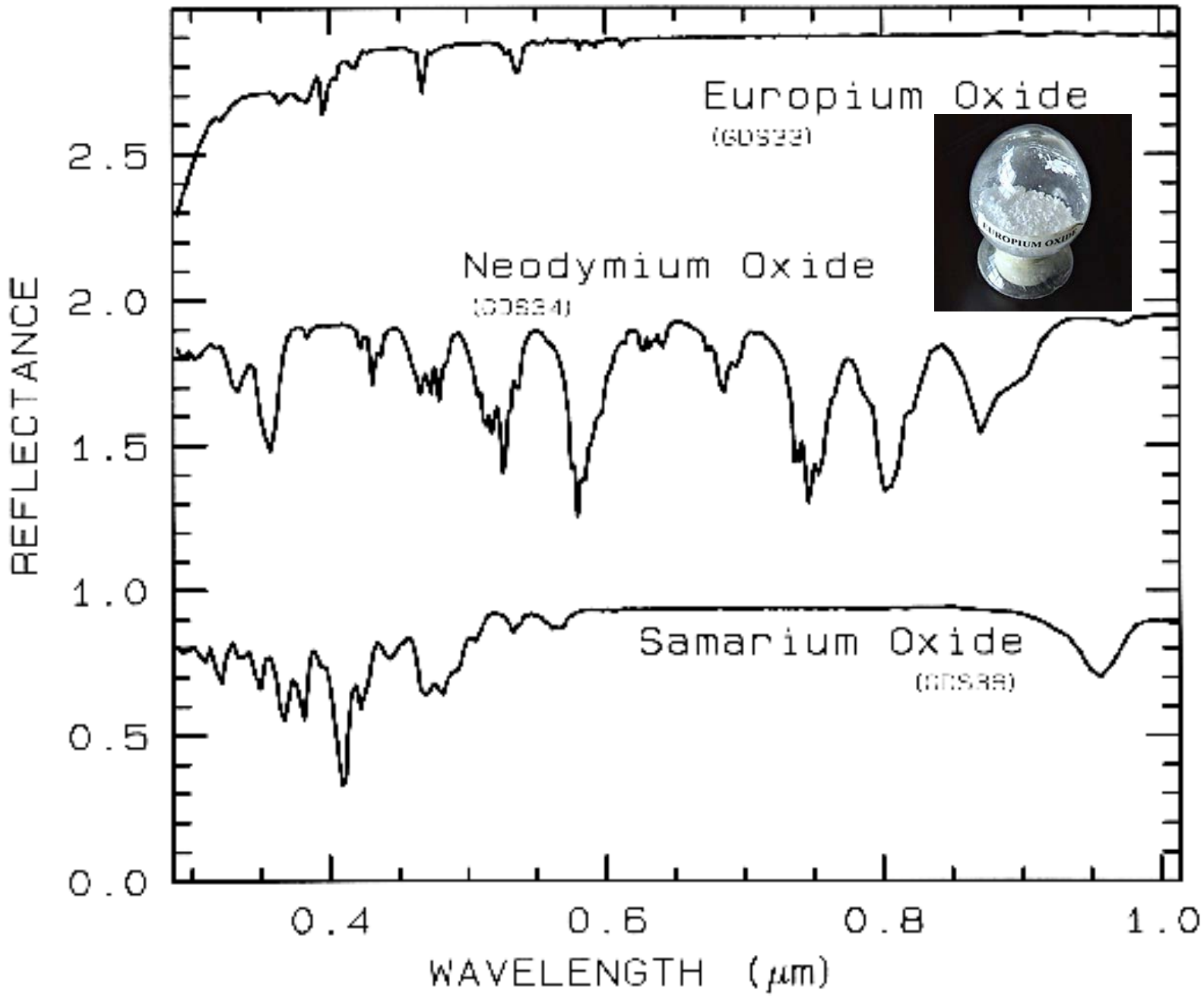
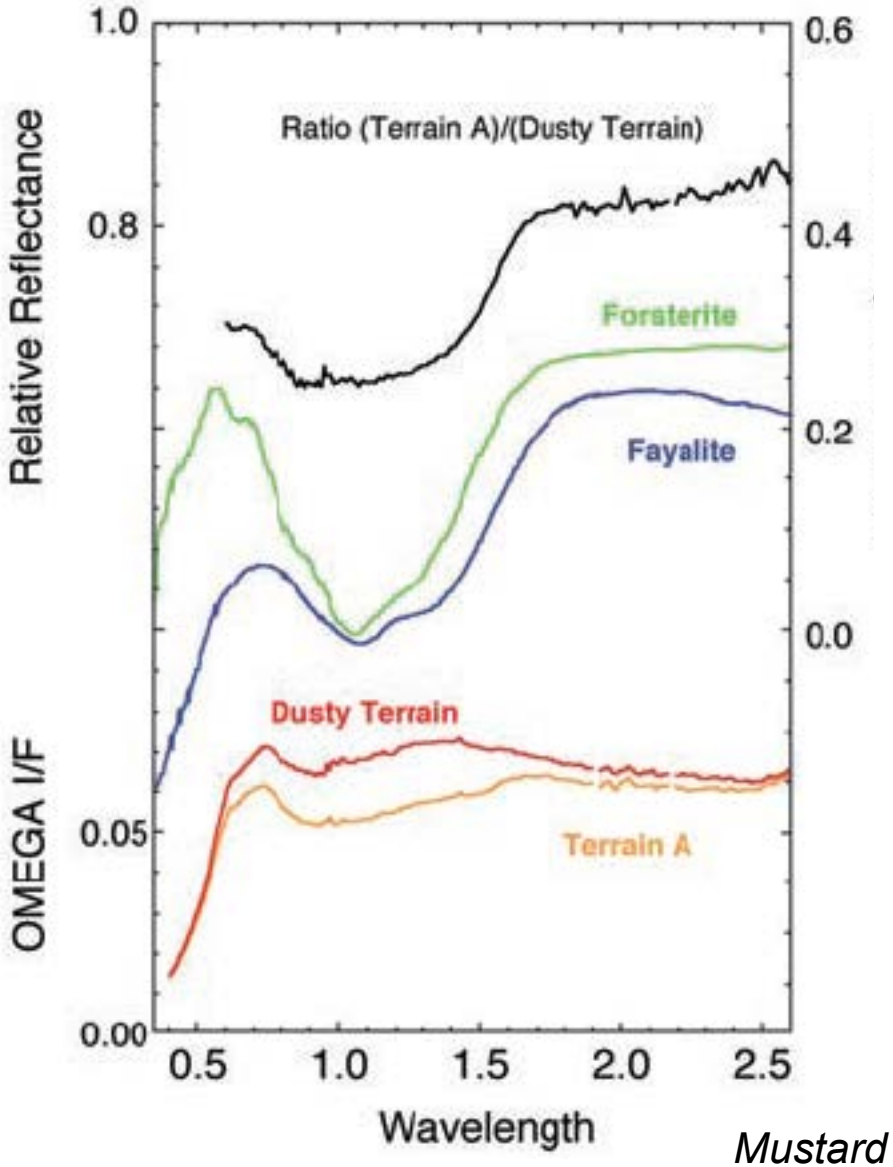
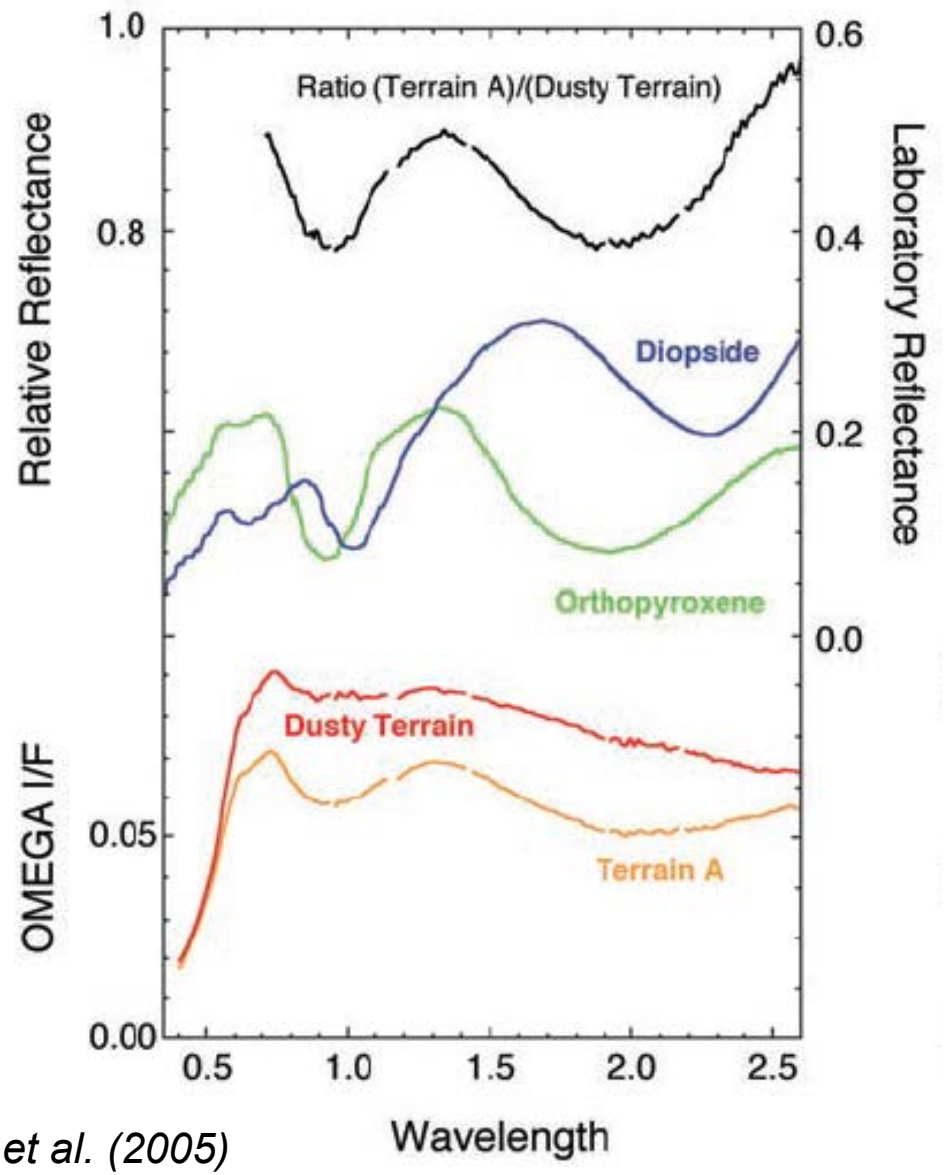
Electronic transitions, crystal field effects



http://img.alibaba.com/photo/50502613/Europium_Oxide.jpg

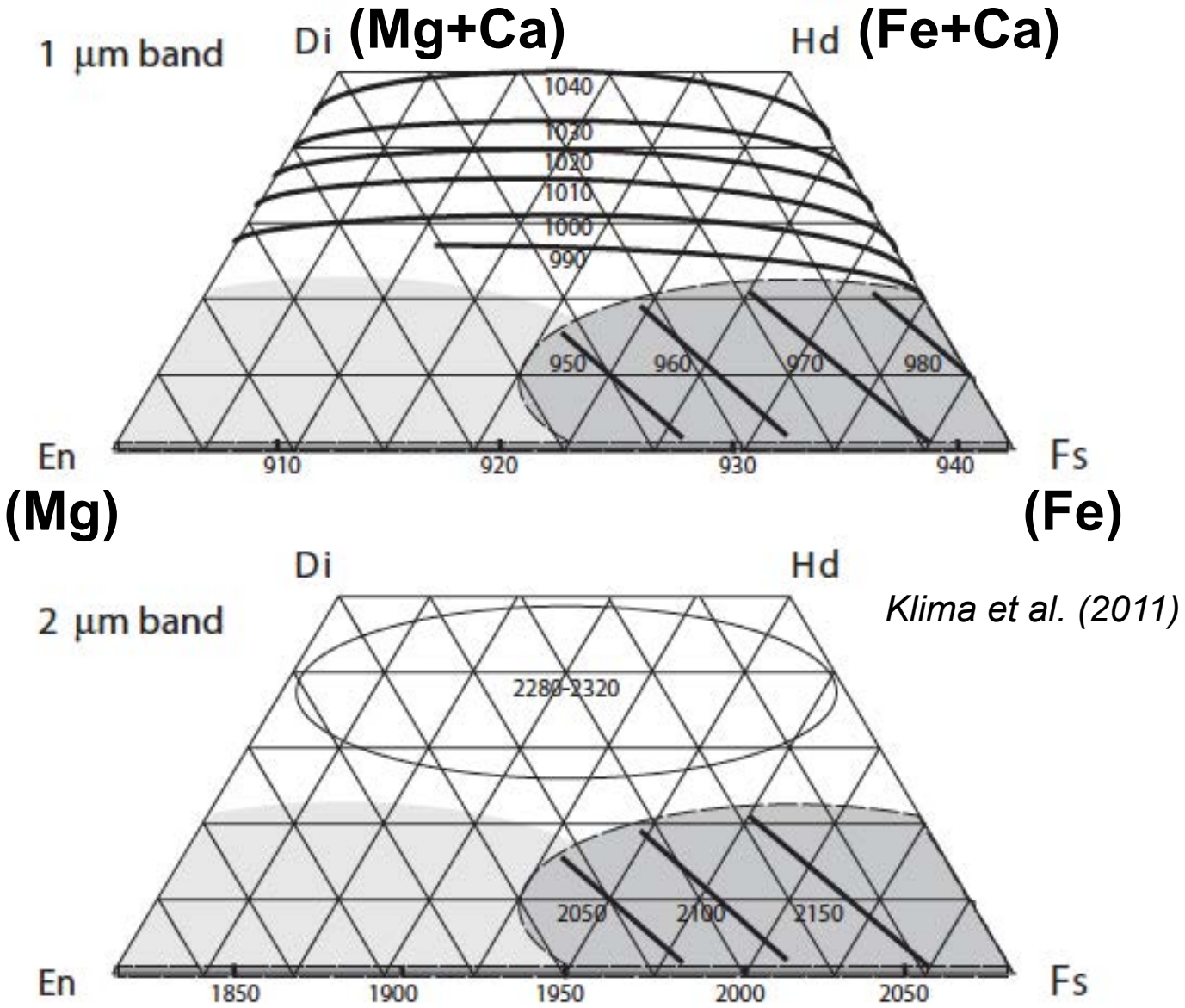
Fe electronic transitions in olivine, pyroxene





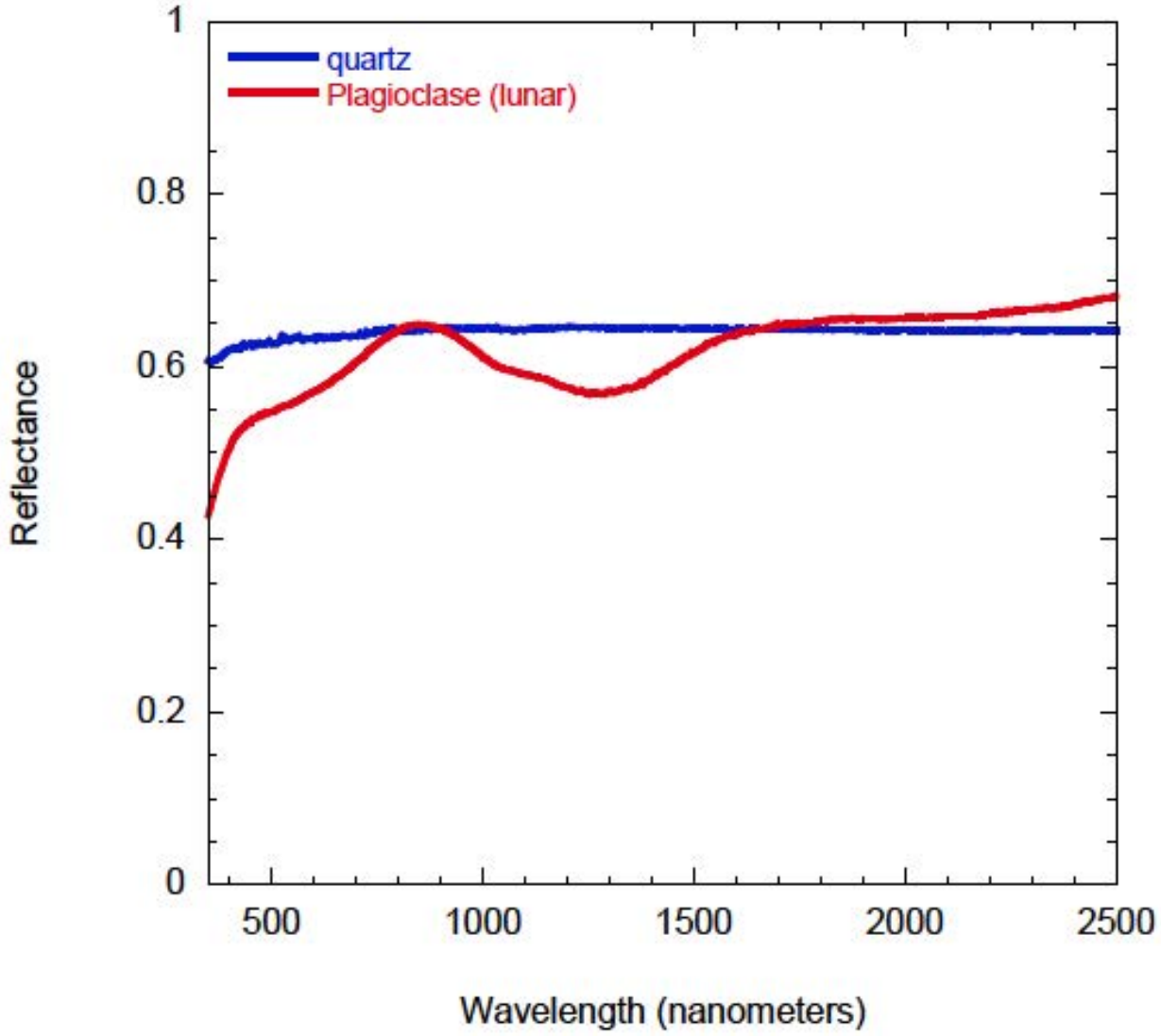
Mustard et al. (2005)

Spectra can indicate pyroxene composition



Klima et al. (2011)

(mostly) Non-Fe-bearing silicate minerals (igneous rock)



Electronic Processes

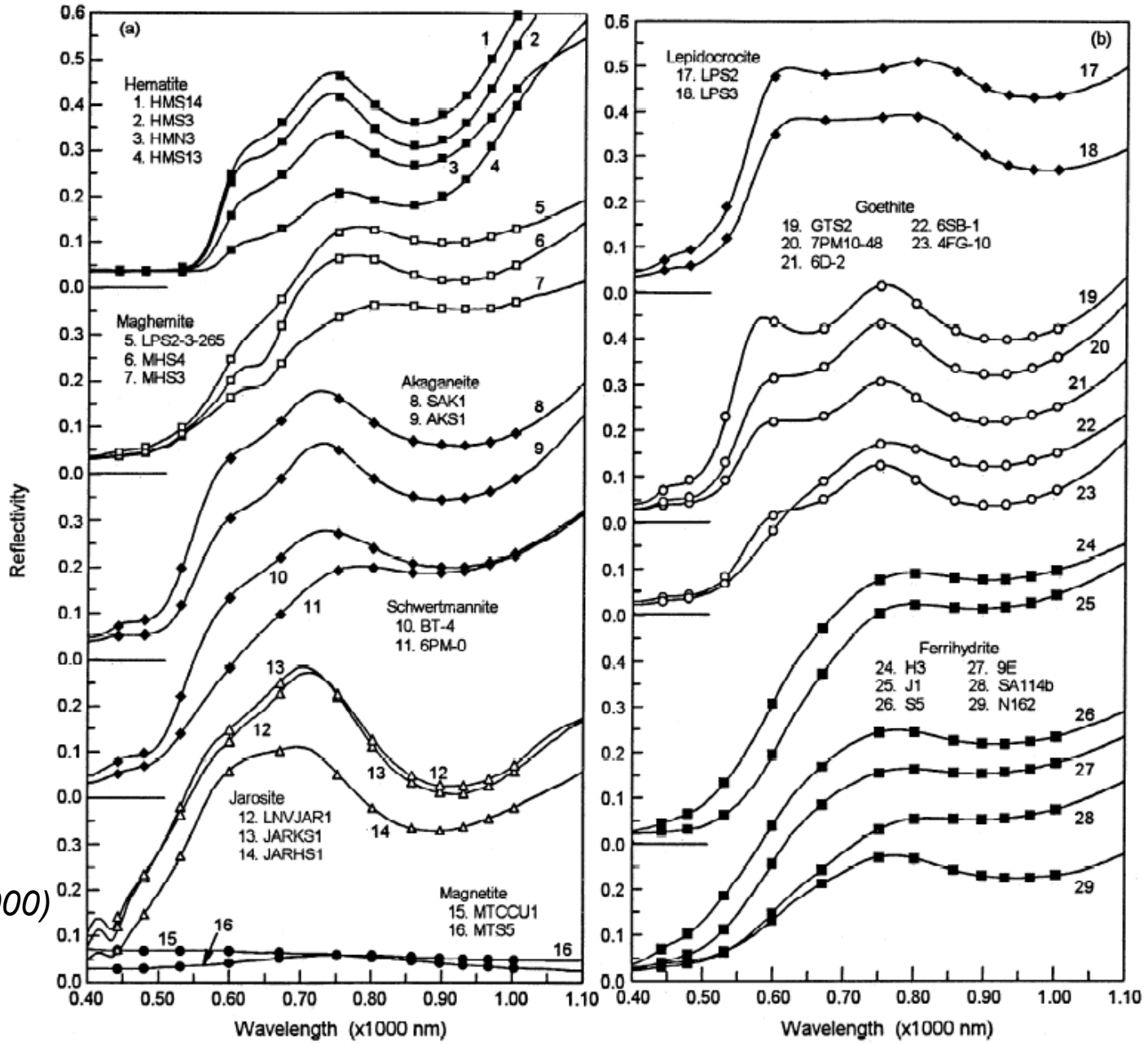
Charge-Transfer Absorptions

Absorption bands can also be caused by charge transfers, or inter-element transitions where the absorption of a photon causes an electron to move between ions. The transition can also occur between the same metal in different valence states, such as between Fe2+ and Fe3+. Absorptions are typically strong. A common example is Fe-O band in the uv, causing iron oxides to be red.

http://en.wikipedia.org/wiki/Image:Hematite.jpg

http://www.galleries.com/minerals/silicate/olivine/olivine.jpg

Electron charge transfer: why Mars is red!



Morris et al. (2000)

Electronic Processes

Conduction Bands

In metals and some minerals, there are two energy levels in which electrons may reside: a higher level called the "conduction band," where electrons move freely throughout the lattice, and a lower energy region called the "valence band," where electrons are attached to individual atoms. The yellow color of gold and sulfur is caused by conduction-band absorption.

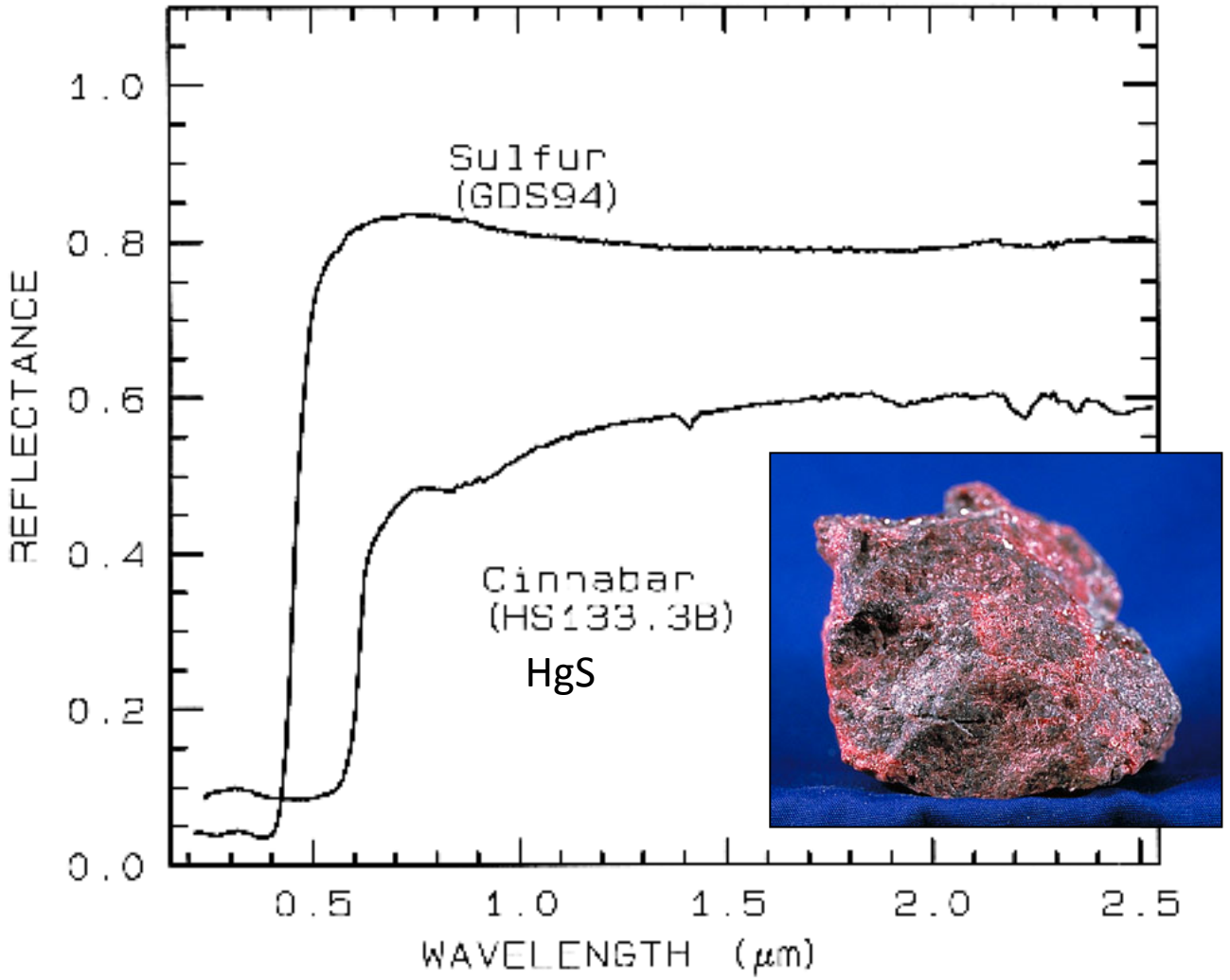
Gold

www.egyptcollections.com

Sulfur

web.syr.edu/~iotz/Gallery.htm

Conduction band processes



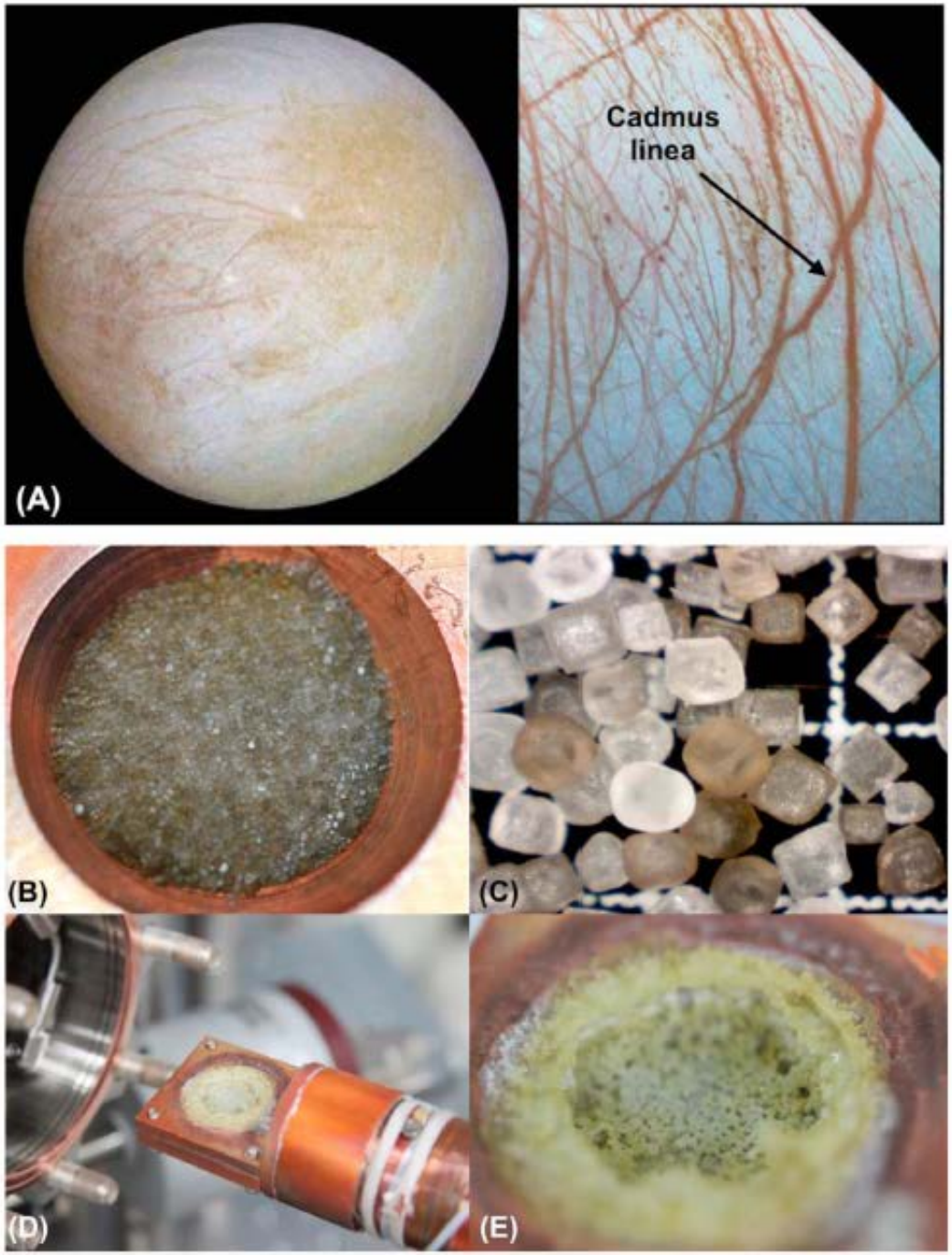
http://www.mii.org/Minerals/Minpics1/Cinnabar.jpg

Electronic Processes

Color Centers

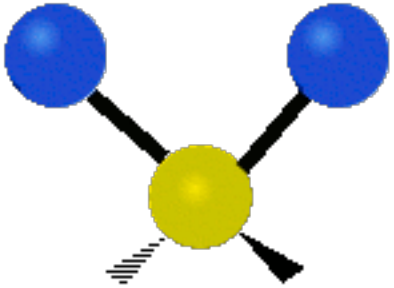
Crystal defects (e.g., induced by radiation) can lead to absorption by materials whose chemical formula otherwise would not suggest any visible/near-infrared features.

At right, NaCl irradiated under Europa-like conditions (Hand & Carlson, 2015)

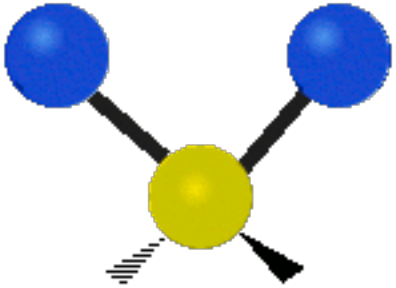


Molecular vibrations

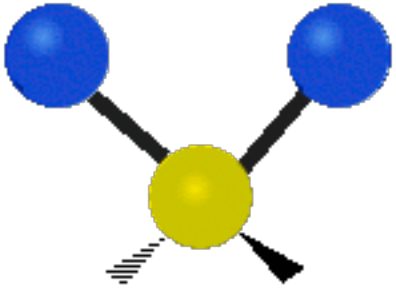
Symmetric stretch



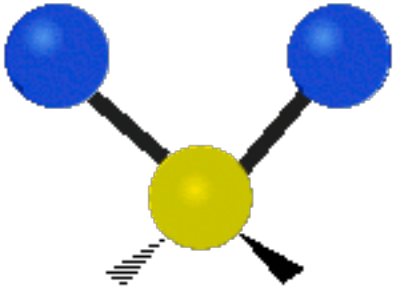
Asymmetric stretch



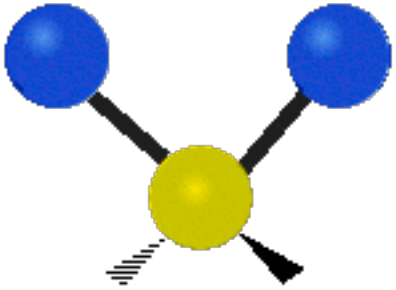
Scissor/bend



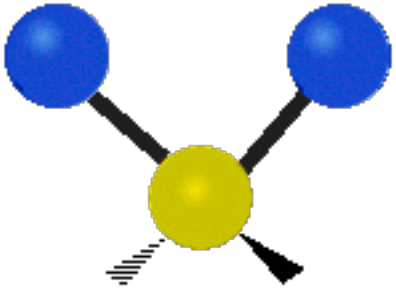
Rocking



Wagging



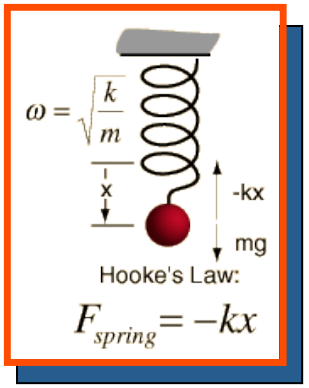
Twist

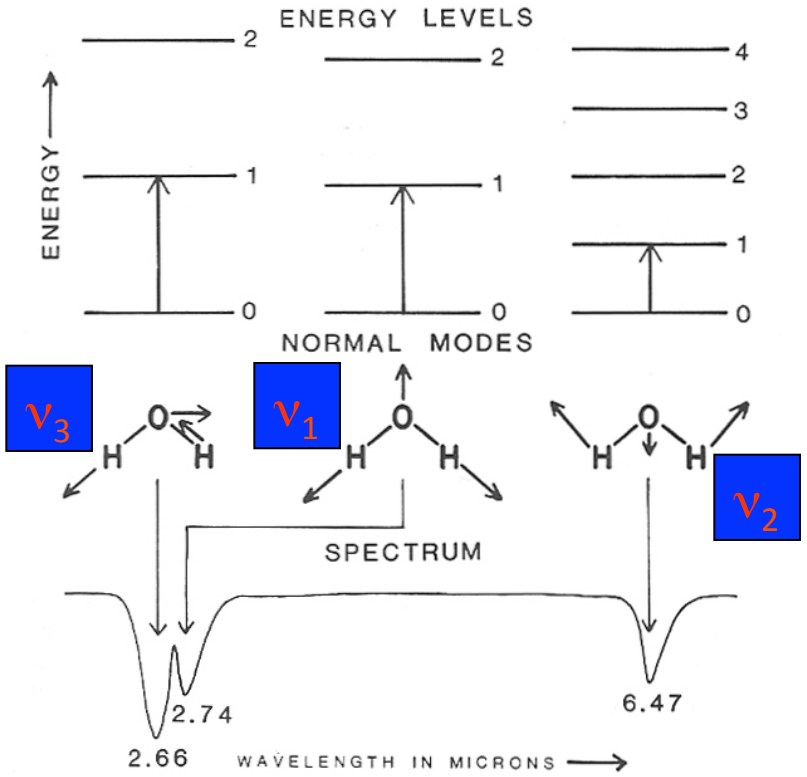


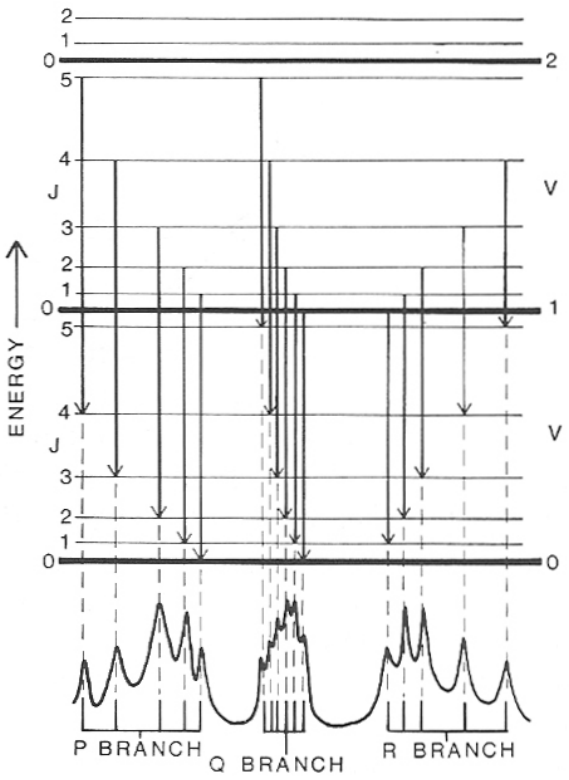
Vibrational Processes

The bonds in a molecule or crystal lattice are like springs with attached weights: the whole system can vibrate. The frequency of vibration depends on the strength of each spring (the bond in a molecule) and their masses (the mass of each element in a molecule). For a molecule with N atoms, there are 3N-6 normal modes of vibrations called fundamentals.* Each vibration can also occur at multiples of the original fundamental frequency (overtones) or involve different modes of vibrations (combinations).

*** In general, a molecule with N atoms has 3N-6 normal modes of vibration but *linear* molecules have only 3N-5 normal modes of vibration as rotation about its molecular axis cannot be observed.**







Vibrational modes

produce simple spectra

Vibrational - rotational modes combine to produce complex spectra with sharp bands

Vibration in water molecules

Water vibrations: ice vs. hydrated minerals

A – D are Europa,

E is Ganymede,

F is model ice spectrum