

## Mineral Identification using FTIR Spectroscopy

The unique properties of each mineral are the result of its crystal structure and chemical composition. Although the atoms that comprise a mineral are almost unimaginably small, mineralogists can perform tests on minerals that reveal information about those atoms and the bonds that hold them together. If a mineral is subjected to a stimulus, such as a beam of light, a beam of electrons, or a beam of x-rays, countless numbers of atoms respond in the same way, making the response measurable. You may have seen some of these responses such as the bending of light by a mineral grain in oil to make a Becke line, or the peaks that result from diffraction of x-rays by a mineral powder.

The measurement and study of responses in which a mineral absorbs, reflects, changes, or emits electromagnetic waves is called spectroscopy. Minerals can be investigated by many types of spectroscopy, named according to the wavelengths of the stimuli and/or the method of measurement. By observing the color of minerals, you have already performed a simple spectroscopic experiment. For example, when you shine a white light on a garnet crystal, some wavelengths of the light (the shorter blue ones) are absorbed, whereas other wavelengths of the light (the longer red ones) are reflected. Also, if you have used invisible ultraviolet (UV) light to illuminate certain “fluorescent” minerals, such as calcite from Franklin, NJ, you will have observed the mineral visibly glowing (emitting electromagnetic waves with a longer wavelength than the stimulus). FTIR spectroscopy is similar to these experiments, but uses an infrared source (longer wavelengths than visible light) as a stimulus. You can’t see infrared light with your eyes, but you can “feel” infrared waves as warmth when you are near an electric heater or an active lava flow.

### Some Electromagnetic Wave Fundamentals

Radiant energy, the type of energy that comes from the sun, from a hot woodstove, or from a radioactive mineral is called electromagnetic energy. Electromagnetic energy includes a variety of energy types that act like waves (and also like particles). This type of energy includes such diverse things as x-rays, radio waves, microwaves, heat, and light. Just as a floating object would go up and down as a water wave passes, charged particles like electrons move back and forth as an electromagnetic wave passes. Like waves on water, the distance from one wave crest to the next is called the wavelength ( $\lambda$ ). Wavelengths of a number of electromagnetic wave types are shown in Figure 1 using a logarithmic scale for wavelength, along with the sizes of some familiar materials for comparison.

The energy ( $E$ ) of an electromagnetic wave is related to its wavelength ( $\lambda$ ) by the equation:

$$E = K / \lambda = (h c) / \lambda$$

where  $K$  is a constant. If the wavelength is given in meters (m), the constant  $K$  is  $1.9864 \times 10^{-25}$  J·m (Planck’s constant,  $h$ , times the speed of light,  $c$ ), and the energy is in joules (J). Notice that the energy ( $E$ ) is **inversely** proportional to its wavelength ( $\lambda$ ). This means that long wavelength waves like radio waves have a low energy and are not dangerous to humans (a comfort to mobile phone users!), whereas short wavelength waves like X-rays have a high energy and are

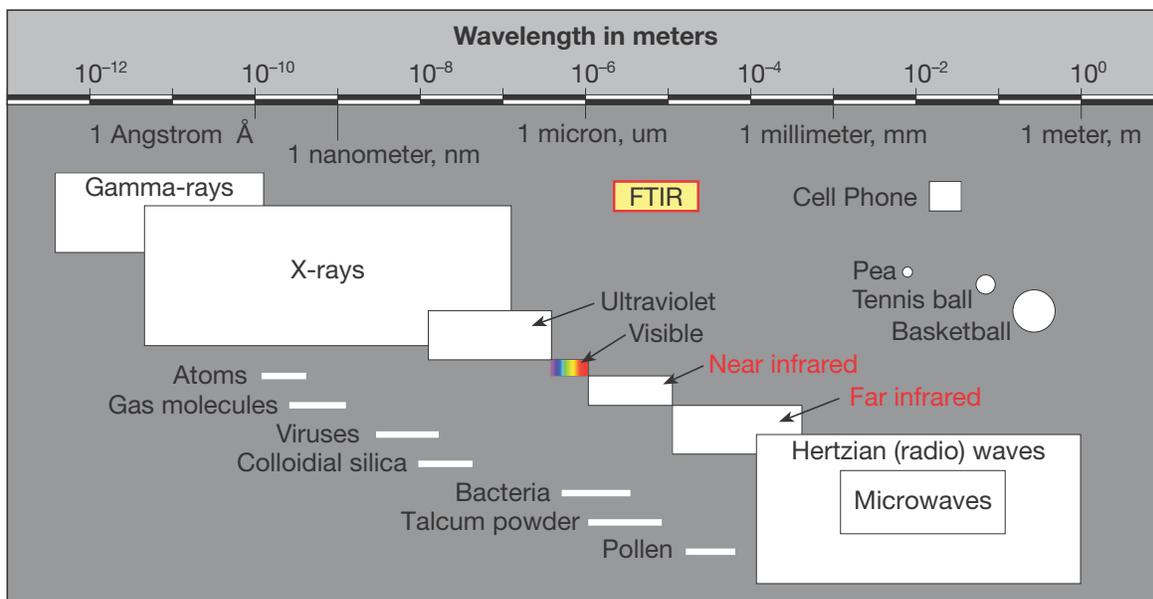


Figure 1. Wavelengths in meters of various types of electromagnetic radiation. The boxes outline the range of wavelengths on the horizontal scale. There is no vertical scale, so the height of the boxes does not matter. Sizes of some familiar objects are also shown for comparison. Notice that the horizontal scale is logarithmic, not linear. This figure is modified from Fig. 9-5 of Dyar and Gunter (2008), created by Dennis Tasa.

Wavelength		Wavenumber	Energy	Frequency	
m	cm	$\text{cm}^{-1}$	J	eV	hertz
1	100	0.01	$1.99\text{E}^{-25}$	$1.24 \times 10^{-6}$	$3.00 \times 10^8$
0.1	10	0.1	$1.99\text{E}^{-24}$	$1.24 \times 10^{-5}$	$3.00 \times 10^9$
0.01	1	1	$1.99\text{E}^{-23}$	$1.24 \times 10^{-4}$	$3.00 \times 10^{10}$
0.001	0.1	10	$1.99\text{E}^{-22}$	$1.24 \times 10^{-3}$	$3.00 \times 10^{11}$
0.0001	0.01	100	$1.99\text{E}^{-21}$	$1.24 \times 10^{-2}$	$3.00 \times 10^{12}$
0.00001	0.001	1000	$1.99\text{E}^{-20}$	$1.24 \times 10^1$	$3.00 \times 10^{13}$
0.000001	0.0001	10000	$1.99\text{E}^{-19}$	$1.24 \times 10^0$	$3.00 \times 10^{14}$
0.0000001	0.00001	100000	$1.99\text{E}^{-18}$	$1.24 \times 10^1$	$3.00 \times 10^{15}$
0.00000001	0.000001	1000000	$1.99\text{E}^{-17}$	$1.24 \times 10^2$	$3.00 \times 10^{16}$

Table 1. Relationships between wavelength, wavenumber, energy, and frequency for electromagnetic radiation

dangerous to humans. Wavelength ( $\lambda$ ) and frequency ( $f$ ) are also inversely related as given by the equation:

$$\lambda = c / f$$

where  $c$  is the speed of light,  $2.9979 \times 10^8$  m/sec,  $f$  is the frequency in hertz ( $s^{-1}$ ) and  $\lambda$  is the wavelength in meters (m). It is customary to report infrared spectra in terms of wavenumbers, which are relatively small, simple numbers equal to  $1/\lambda$  and typically given in units of  $cm^{-1}$ . These relationships are shown in Table 1.

### Infrared Spectroscopy

The wavelengths of infrared energy that will be used in our experiments are 2.5 to 25 microns (wavenumbers of  $4000$  to  $400\text{ cm}^{-1}$ ). You can see these wavelengths marked by the FTIR rectangle in Figure 1. This broadband infrared energy is emitted by a hot bar in the FTIR spectrometer and directed by mirrors to “shine” on a mineral or the powder of a mineral, depending on the sample module. The response of the mineral to the IR stimulus is to absorb selectively some of the IR energies/wavelengths and to reflect back other IR energies/wavelengths. Instead of a single composite infrared “color”, the FTIR spectrometer shows us as a graph of the intensities of infrared energy reflection (the fraction of each wavelength that was not absorbed) as a function of wavenumber. By comparing the infrared spectrum of an unknown mineral to the infrared spectra of known minerals (standards), we will be able to identify many unknown minerals. In other words, we can use the FTIR spectrometer to identify minerals.

### What is happening?

When a wavelength of infrared light is absorbed, energy is added to the mineral. The absorbed energy will create some type of change in the mineral. If you add heat energy to air (as with a hot air balloon), it will rise because the energized air particles start moving around faster, bumping into each other and moving farther apart so the air becomes less dense and will rise. Minerals will not rise in our experiments, but the absorbed energy affects the atoms that make up the mineral and the bonds that hold them together. The atoms in a mineral are in constant motion relative to one another, constrained by the bonds that connect them. Similar to gas molecules, the higher the temperature of a mineral, the faster the atoms move. A simple way to envision this is to imagine that the atoms in a mineral are spheres connected by springs (see Figure 2) and that they move back and forth (they vibrate) relative to one another.

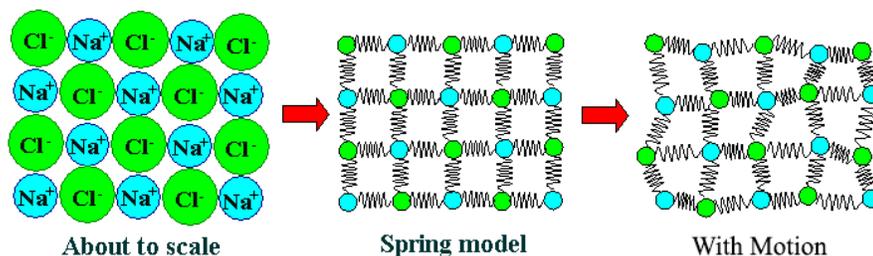


Figure 2. Representation of the halite structure as atoms connected by springs. Atoms are constantly in motion, so the model on the right is in some ways more accurate than the one in the middle. Modified from [http://www.tf.uni-kiel.de/matwis/amat/iss/kap\\_4/illustr/i4\\_1\\_1.html](http://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/i4_1_1.html)

Two spheres connected by a spring will move back and forth with a specific frequency, like a playground swing. For a playground swing (a simple pendulum) the period **T** in seconds (s) is given by:

$$T (s) = 2\pi \sqrt{L/g}$$

where L is the length of the pendulum in meters and g is the acceleration of gravity (9.8 ms<sup>-2</sup>). If you push the swing at the right time, you can add energy to the swing and it will go higher, but the period and frequency (**f** = 1/**T**) will remain the same. For two atoms connected by a bond (= spring), the period of vibration T in seconds is given by

$$T (s) = 2\pi \sqrt{M/k}$$

where **M** is an average of the masses of the two atoms [**M** = (**m**<sub>1</sub>**m**<sub>2</sub>)/(**m**<sub>1</sub>+**m**<sub>2</sub>)] and **k** is a restoring force constant (in units of N/m). For the two-atom, spring-like oscillator, the frequency of vibration (**f** = 1/**T**) is given by

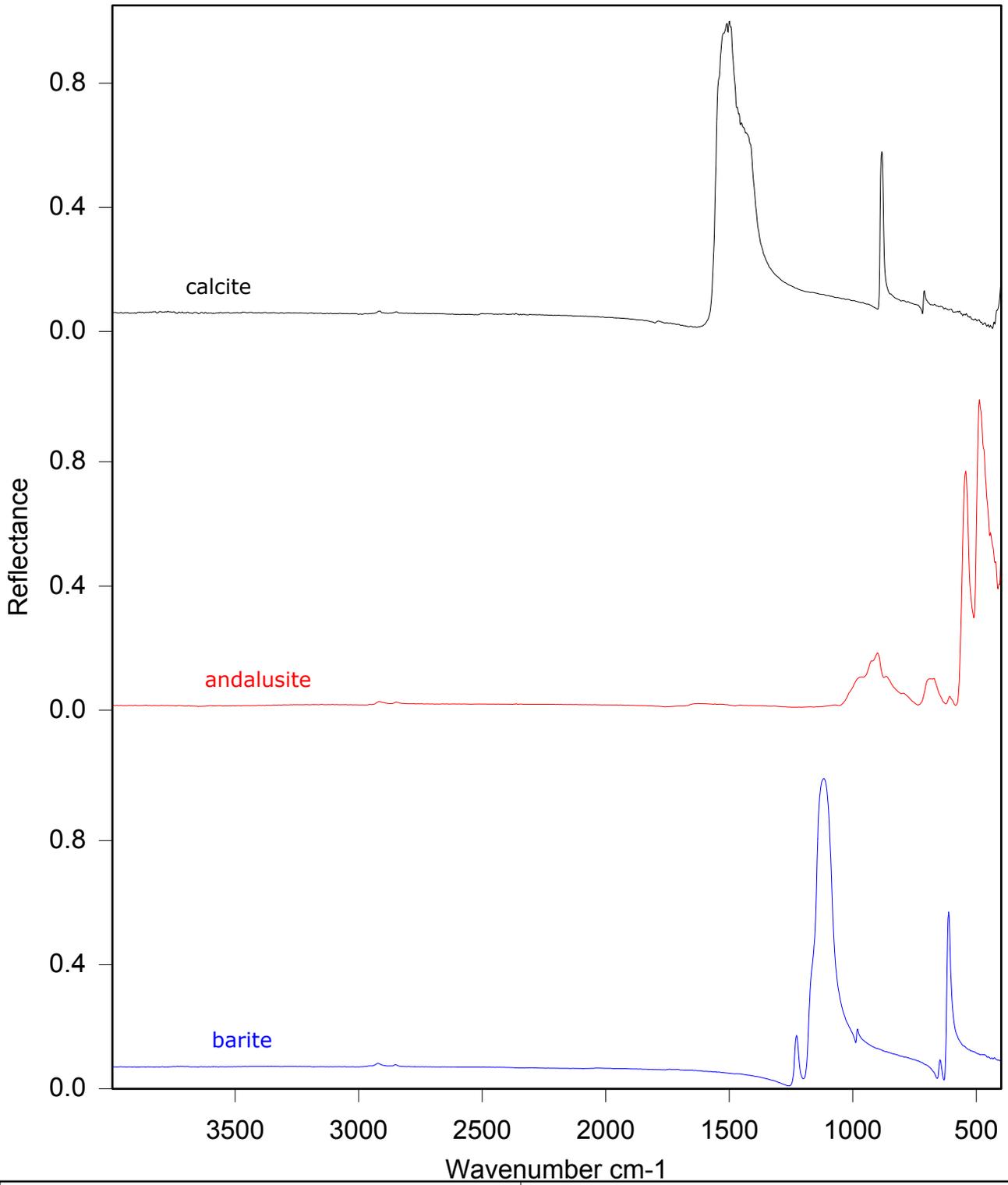
$$f (s^{-1}) = (1/2\pi)\sqrt{k/M}$$

Just as it is possible to add energy to a moving swing or pendulum, it is possible to add energy to a vibrating bond, although the processes is complicated by multiple bonds to each atom and quantum effects (only certain energy levels are possible). Infrared energy is the right order of magnitude to affect the vibrations of bonds. Depending on the types of bonds in a particular mineral, different IR wavelengths will be absorbed. Each mineral has a unique chemical composition and structure and therefore a unique grouping of chemical bonds. The energy vs. wavelength graph of infrared absorption produced by the FTIR spectrometer is due to the absorption properties of all the bonds of the mineral sample you are investigating, and is therefore unique to that mineral.

### *Bruker Alpha FTIR Spectrometer*

In lab we will use a Bruker Alpha ® FTIR spectrometer to identify minerals. Alpha ® FTIR spectrometer comes with two data collection modules: a front reflection module for large mineral samples, and and ATR module for mineral powders. For the front reflection module, we will hold our samples against a window (hole) on the front of the spectrometer. For the ATR module, we will place a small amount of powder on a diamond window and press the powder against the diamond with a clamp.

Figure 3 shows FTIR reflection spectra for the minerals calcite, andalusite, and barite. You can see from the spectra that the graphs of reflection intensity vs. wavenumber are fairly different for these minerals. For many hand samples it will be possible to confirm a mineral identification with an IR spectrum. However, the quality of the spectrum and its match with known mineral spectra will depend on the character of the sample. Large samples with good cleavages or flat crystal surfaces work best for the front reflection method. We will use the MHC FTIR reflection database to identify reflection spectra.



Calcite_chip	Instrument type and / or accessory
Andalusite_Chiastolite	Front-Reflection
Barite_Clear_Crystal	Front-Reflection

Figure 4 shows FTIR-ATR spectra for dolomite and barite powders. Again the spectra are quite different, and can be used for mineral identification. We will use the RRUFF FTIR ATR database to identify ATR spectra. Figure 5 shows a comparison of a front reflection spectrum and an ATR spectrum for the mineral dolomite. The spectra are similar and are responding to the same structure and bonds. The difference is due to the nature of the data collection method, which means that the spectra should be compared with the appropriate database.

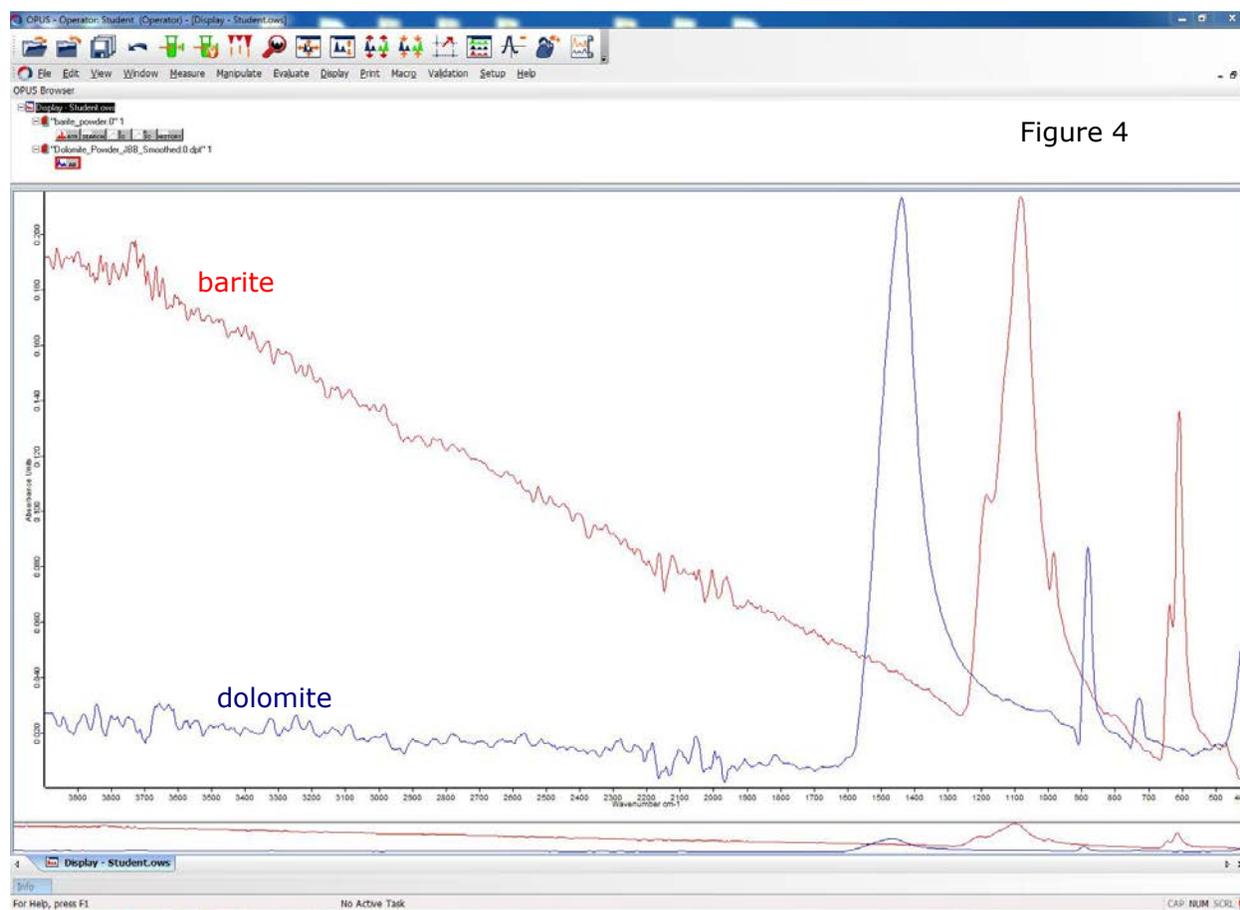


Figure 4

### Bruker Alpha FTIR Spectrometer

In lab we will use a Bruker Alpha ® FTIR spectrometer. We will hold our samples against a window (hole) on the front of the Alpha spectrometer. Using OPUS ® software, the spectrometer will compare the infrared energy reflected from our sample to the original infrared source using an “interferometer”. FTIR stands for Fourier Transform InfraRed spectroscopy. The Fourier Transform part is a mathematical step that converts the interference effects from the interferometer to a graph of reflection intensity vs. wavenumber. As with many modern instruments, you will need to interact with a software interface (OPUS) to make FTIR measurements. Software instructions will be given to you in lab.

*Additional reading about pendulums and oscillators*

<http://hyperphysics.phy-astr.gsu.edu/hbase/pend.html>

<http://hyperphysics.phy-astr.gsu.edu/hbase/shm.html>

<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/hosc.html>