Chapter 4
Interactions of Light and Matter

Light and Matter

Taking measurements and observing our surroundings requires interactions. In some cases, that is the interaction between objects with mass, such as through the sense of touch. In other cases, the interactions are between light and matter, such as with sight. Let's start by looking at how light and matter interact through two fundamental methods. First, think of a window on a sunny day. If there is nothing blocking that window, light will shine in through the glass. This is because the glass is **transparent** to the visible light from the sun, and therefore this light is **transmitted** through the window. Second, think of the wall around a window. While the light can transmit through the window, it is blocked by the surrounding walls. We say that the walls are **opaque**, and they **absorb** the visible light from the sun, preventing it from reaching you inside.

The interactions described above should seem pretty obvious to you because they are experiences you have on a daily basis. The question is: why do light and matter interact in the first place? We have seen that light and matter are fundamentally different. Light, for example, has no mass, can move through a vacuum, and is created through the osillation of orthogonol electric and magnetic fields. Matter, on the other hand, is defined as having mass, can not move as fast as light (*c*), and is involved in the macroscopic interactions we see everyday. So how can these two fundamentally different entities interact? What makes some objects opaque and others transparent to light? The first answer to these questions is that atoms are made up of individually charged particles which produce electric fields. The fields of these particles can interact with the electric and magnetic fields that create light waves. The second answer lies in a condition known as resonance.

Resonance

Every material has what is called a natural frequency. An example of natural frequency that we have seen in our lives is the plucking of a guitar string. In this example, the natural frequency of the string can be heard in the sound it produces. When you tighten the string, you change the sound. This means that by changing the tension or length of the guitar string, you are changing its natural frequency. While it is helpful to think of examples that we see in our everyday lives, molecules do not contain guitar strings. However, they also have natural frequencies based on how their atoms are bonded together. Waves, such as light, also have frequencies. Because of this, light and matter can interact when the frequency of light matches the natural frequency of a molecule. This interaction is known as **resonance**.

The Absorption of Light

Light interacts with matter in a number of ways, including absorption, reflection, refraction, emission, and scattering. In this course we will focus on two of these: absorption and emission. **Absorption** of light occurs when the matter is in resonance with frequency of the light – i.e., when the frequencies match ($\nu_{\text{light}} = \nu_{\text{matter}}$). As a result, knowing the frequencies of light that are absorbed by a particular atom or molecule can give us information about its structure.

The absorption of light occurs as the oscillating electric field of the light tugs and pulls on the electron cloud of the matter and causes the matter to oscillate at the same frequency. The light must expend energy in order to make the matter start moving at this frequency. The total amount of energy used to excite one atom is equal to:

$$E_{light} = h\nu_{light} \qquad [4.1]$$

$h\nu_{light}$, where h is Planck's constant (6.626×10^{-34} J·s) and ν is the frequency of the light (and the matter). The amount of energy required to excite a single atom can be very small. As a result, scientists often use a different unit for energy other than the joule. This unit is called an electron volt ($1\ eV = 1.6\ \times 10^{-19}\ J$). When the the frequency of light and matter are not equal ($\nu_{light} \neq \nu_{matter}$), they are not in resonance and therefore no absorption takes place. Instead, the matter is transparent to this specific frequecy of light, and the light will pass through.

Worked Example 4.1: What is the energy (in J) of red light with wavelength 656 nm?

Solution: to calculate the energy transferred by light of a given wavelength we use the expression for the energy of light, $E_{light} = h\nu$. The relationship between frequency (ν) and wavelength (λ), ν = c/λ, can be used to transform this expression into one that we can use to solve for the energy:

$$E_{light}\ =\ h\nu\ = \frac{hc}{\lambda} = \frac{(6.626\ \times\ 10^{-34}\ \mathrm{Js})\left(3.00\ \times\ 10^{8}\ \frac{\mathrm{m}}{\mathrm{s}}\right)}{656\ \times 10^{-9}\ m} = 3.03\ \times\ 10^{-19}\ \mathrm{J}$$

This is the total amount of energy transferred when one atom absorbs red light with wavelength 656 nm.

Blackbody Emission of Earth

All objects, unless they have a temperature of 0 K (absolute zero), radiate electromagnetic energy (i.e., light). It is the temperature of the object that determines the wavelength (and, therefore, energy) of the light that is emitted. The sun, for example, has a surface temperature of around 6000 K and emits visible, infrared, and ultraviolet light. Wein's Law – named after the German physicist Wilhelm Wein – relates the peak wavelength (λ_{max}) and the temperature (T) of the object in K:

$$\lambda = \frac{2.9 \times 10^{6}\ \mathrm{nm{\cdot}K}}{T}$$

Earth is much colder than the sun, with an average temperature around 290 K. This means that the peak wavelength emitted by Earth is:

$$\lambda = \frac{2.9 \times 10^{6}\ \mathrm{nm{\cdot}K}}{290\ \mathrm{K}} = 10{,}000\ \mathrm{nm}$$

Light with wavelength of 10,000 nm is in the infrared region of the EM spectrum (1000 cm^{-1} or 3×10^{-13} Hz).

Practice: what is the wavelength of light (and from what region of the EM spectrum) is emitted by (a) a human with temperature 34 °C (307 K) and (b) a red dwarf star with temperature 3000 K?

A neat applicantion of the concept of resonant frequencies is the absorption of infrared light (IR) emitted from Earth by molecules in the atmosphere, the so-called **greenhouse gases**. Greenhouse gases are molecules that contain IR-active bonds that are resonant with the light being emitted by the planet.

Bond Frequencies

As we said, light only interacts with matter when there is resonance – when the frequency of the light's oscillating electric field matches a natural frequency in the matter. Greenhouse gases are molecules with bonds that vibrate at frequencies that are resonant with the light emitted by Earth – infrared light.

There are two primary factors that affect the frequency at which a chemical bond will vibrate: the strength of the chemical bond (single versus double versus triple bonds) and the masses of the two atoms that are bonded together. We will use a balls-on-spring **model** for our chemical bonds – treating the nuclei like two massive balls connected by a spring. While this model is not an accurate picture of why atoms stay together to make bonds, it is a great model for how bond vibrations occur. The activity on the next page will walk through discovering the factors that affect the frequencies at which bonds oscillate.

Infrared spectra – visualizing and graphing resonance

A spectral graph showing transmittance and wavenumbers can help us determine the resonances between a given type of light and matter. Wavenumbers ($\tilde{\nu}$) are a convenient measure used by spectroscopists and are defined as:

$$\tilde{\nu} = \frac{1}{\lambda} \qquad [4.2]$$

where λ is the wavelength of the light in cm. Infrared light with frequency 3×10^{13} Hz has a wavelength of 10,000 nm (or 10^{-3} cm) and wavenumbers of 1000 cm^{-1}.

Figure 4.1 shows an IR absorption spectrum of ethanol. Each dip in the graph (such as the peak labeled "A" that occurs at 3000 cm^{-1} in Figure 4.1), represents a wavelength that is being absorbed by ethanol. Peak "A" has a transmittance of 0.25, which means that only 25% of IR light hitting the sample goes through, because this light is resonant with bonds in ethanol (the C–H bonds, to be exact).

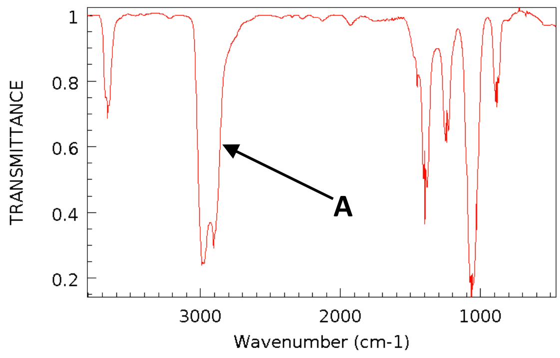


Figure 4.1: IR spectrum of ethanol
Source: http://webbook.nist.gov/chemistry

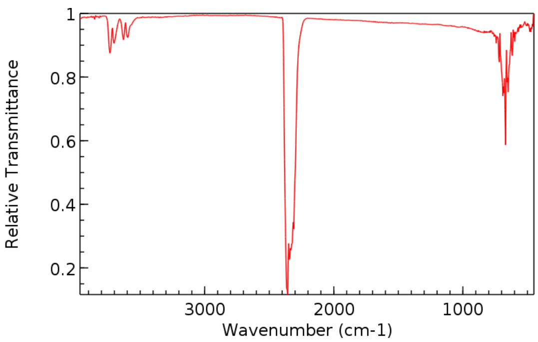


Figure 4.2: IR spectrum of carbon dioxide
Source: http://webbook.nist.gov/chemistry

Notice, however, that there is no peak at 2000 cm^{-1} in the spectrum of ethanol. Actually, you'll notice that most of the transmittance is near 1 (or 100%) for most wavenumbers/frequencies of IR light. This is because there are are no bonds that are resonant with the IR light of these frequencies, so the light passes through unabsorbed. In other words, ethanol is transparent to most frequencies of IR light. The IR spectrum of carbon dioxide is depicted in Figure 4.2. Notice that the heavier C=O bonds absorb IR light with lower frequency (around 2400 cm^{-1}) than that of the C–H bonds in ethanol. This absorption is in the higher-range of IR light emitted by Earth.

Worked Example 4.2: What is wavelength (in nm) of light with wavenumbers 2400 cm^{-1}?

Solution: wavenumbers are wavelength are inversely related:

$$\lambda = \frac{1}{\tilde{\nu}} = \left(\frac{\text{cm}}{2400}\right)\left(\frac{1\text{ m}}{100\text{ cm}}\right)\left(\frac{1\text{ nm}}{10^{-9}\text{ m}}\right) = 4000\text{ nm}$$

In-class Activity: Oscillations of Springs

In this activity you will use springs with hanging masses to compare the frequency of oscillations (ν) under different scenarios. You will test two setups simultaneously, A and B. In each scenario you will pull the weights down a specific distance, release the weights, and determine the number of oscillations per second (ν).

Predictions (make these before class): Before you begin, make predictions for each of the following scenarios. Circle the correct relation (<, =, or >) for your predictions.

1. If the masses and springs are identical:

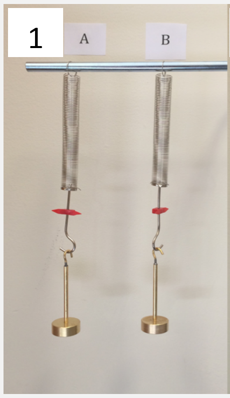
$\nu_A \quad < \quad = \quad > \quad \nu_B$

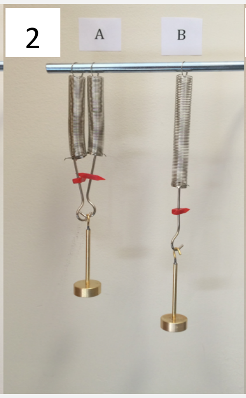
2. If an additional spring is added to setup A (masses are identical):

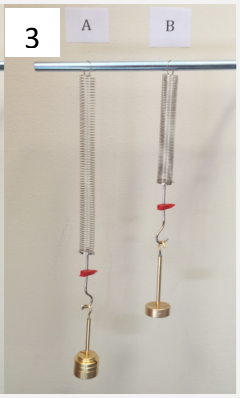
$\nu_A \quad < \quad = \quad > \quad \nu_B$

3. If additional mass is added to spring setup A (springs are identical):

$\nu_A \quad < \quad = \quad > \quad \nu_B$







Testing your predictions (in class): Test the following three scenarios. For each scenario, one person should pull both masses down 2 cm and release them at the same time. As soon as the masses are released, start a timer and count the number of oscillations that occur on each spring over the course of 10 seconds. Coordinate with your partners to determine who is doing each task. Determine the frequency (oscillations/second) by dividing the number of oscillations/10 seconds by 10. Compare the frequencies of A and B by setting up a ratio. *(Continued on following page)*

(See previous page)

Scenarios:
1. Identical: Two identical springs (A and B) with equal masses (70 g each).
2. Two springs on A: Add the extra spring to setup A. Keep the masses the same.
3. Additional mass on A: Remove the extra spring from setup A. Double the mass on spring A to 140 g by adding the extra plates.

Scenario	**Oscillations/10 s**		**Frequency (Hz)**		ν_A/ν_B
	A	**B**	**A**	**B**	
1					
2					
3					

Chlorofluorocarbons (CFCs)

Chlorofluorocarbons (CFCs) are organic molecules – originally trademarked by DuPont under the name "Freon" – that contain carbon, fluorine, and chlorine atoms (Figure 4.3). In their original role, CFCs were widely used as refrigerants and in aerosols (like spray deodorant). Unfortunately, the chemical structure and properties of CFCs tend to make them some of the most environmentally-dangerous substances.

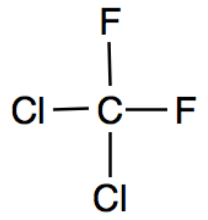


Figure 4.3: Diagram of a CFC molecule

CFCs are problematic for two different, but equally scary, reasons: (1) they are anthropogenic compounds (i.e., we made them and put them in the atmosphere) that persist in the atmosphere and absorb IR radiation (are resonant with IR light); and (2) they are easily broken apart by radiation to produce chlorine radicals that react with ozone.

Since discovering the deleterious effect of CFCs on ozone (O_3) in the atmosphere, the world has united to all but ban the production and use of CFCs (they are still used in submarines). However, it wasn't just CFC's role as a greenhouse gas that led to CFC regulation; rather, it was the reactivity of CFCs that leads to destruction of ozone that was the primary factor.

UV light causes the CFC molecule to break, releasing a Cl atom. That chlorine atom will then react with ozone in the atmosphere to produce oxygen gas (O_2) and the molecule ClO (chlorine + oxygen). The ClO will then react with more ozone, continuing the cycle. The process continues until two Cl ions interact and form chlorine gas (Cl_2).

In fact, had the world not agreed to the Montreal Protocol, NASA scientists estimated that complete worldwide ozone depletion would have been achieved by the year 2060.

To investigate the affect that CFCs have on the ozone layer, select CFC-12 from the choices in the Atmosphere simulation applet (https://kcvs.ca/details.html?key=cfc). Is CFC-12 transparent to UV light? Explain using the results of your exploration with the applet.

Activity: Chlorofluorocarbons and the reason we no longer use them. Ever.

Dichlorodifluoromethane (also known as CFC-12 or Freon-12) was one of the original propellants in Silly String. In the structure of CFC-12 (Figure 4.3), we see two IR-active bonds: C–F and C–Cl.

1. Based on your intuition, will these bonds absorb IR radiation in the higher or lower region of the spectrum? Explain your choice. Use the Infrared Spectra and Molecular Vibration applet (https://kcvs.ca/details.html?key=irSuite) to check your answer (hint: look at the spectrum of dichloromethane, CH_2Cl_2).

   High frequency (~3000 cm^{-1}) mid-range (~2000 cm^{-1}) low frequency (~1000 cm^{-1})

2. Is CFC-12 "transparent" to (a) visible light? (b) IR radiation? (c) microwave radiation? Justify your answers based on your experiences and intuition.

3. Use the CFCs in the Atmosphere applet (https://kcvs.ca/details.html?key=cfc) to simulate the absorption of electromagnetic radiation by CFC-12. Were your answers to question 2 correct? What happens when IR and microwave radiation are absorbed by CFC-12?

4. CFCs represent the tiniest fraction of the atmosphere (1.2 ppb = parts per billion; for reference there is 400,000 ppb CO_2 in the atmosphere). Explain how the absorption of IR radiation by CFCs can lead to atmospheric heating. You may find it useful to work through the Collisional Heating by CO_2 in the Atmosphere simulation applet (https://kcvs.ca/details.html?key=collisionalHeating). Move the line on the graph to a resonant frequency/wavenumber. Then select "atmosphere" at the bottom left of your screen. Observe what happens when light is absorbed by the CFC.

Practice: Use the Infrared Spectral Windows applet to investigate the Global Warming Potential for some prevalent greenhouse gases ((https://kcvs.ca/details.html?key=irWindows).

Once the applet has loaded, switched to scaled spectra mode: under *Display Options* select "*Scaled Spectra*" and "*Black Body Curve.*" You should see the blackbody IR emission curve for Earth. Now, select a greenhouse gas by clicking on the molecule structure. The selected molecule's scaled spectrum (scaled by global warming potential) will be displayed on top of the blackbody curve. To remove a molecule's spectrum, click on the structure a second time.

a. Investigate the regions of the spectra where the molecules absorb. What do you notice?
b. Why does carbon dioxide have such a large GWP?

Practice Examples

4.1 – What will happen when light of a resonant frequency interacts with a molecule?

4.2 – Which of the following types of bonds would you expect to be held together the strongest and have the highest oscillating frequency? Why? (circle one and explain)

Single bonds (C–C) Double bonds (C=C) Triple bonds (C≡C)

4.3 – Mass also has an effect on the frequency of oscillations. Using mass of the atoms as a predictor, which of the two bonds would have the highest frequency? Why? (circle one and explain)

C – H Bonds C – Cl Bonds

4.4 – Acetyl chloride, has three IR-active bonds: C–H, C–Cl, and C=O. In this representation gray atoms are carbon (C), red = oxygen, white = hydrogen, and green = chlorine. Use the interactive IR spectrum (https://kcvs.ca/details.html?key=irSuite) to determine the stretching frequencies (in wavenumbers, cm^{-1}) of the three bonds. Remember: larger wavenumbers corresponds to larger frequencies.

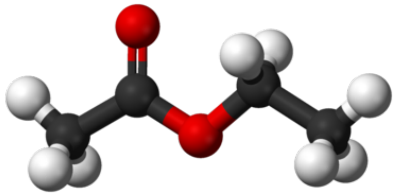
$\tilde{\nu}$(C=O) = __________ cm^{-1} $\tilde{\nu}$(C–Cl) = __________ cm^{-1} $\tilde{\nu}$(C–H) = __________ cm^{-1}

a. Compare the frequencies of C=O and C–Cl bonds. What does this indicate about the relationship between number of bonds and the frequency of the oscillation? Does this agree with your prediction in question 4.2?

b. Compare the frequencies of C–H and C–Cl bonds. What does this indicate about the relationship between mass of the atoms and the frequency of the oscillation? Does this agree with your prediction in question 4.3?

c. Notice that there are single bonds with high frequencies (above 3000 cm^{-1}, such as C–H) and single bonds with very low frequencies (below 1000 cm^{-1}, such as C–Cl). Suggest a reason why the C–H bond stretches at such a high frequency (faster than double and triple bonds).

4.5 – Ethyl ethanoate (structure to the right) is a major component of nail polish remover. It has three IR active bonds: C–O, C=O, and C–H. Use your intuition, and the answers to the above questions to predict the relative order of these bonds' stretching frequencies (in order of decreasing frequency).



4.6 – Use the Infrared Spectra and Molecular Vibration applet to check your answer in #4.5. Remember, in IR spectra high-frequencies are on the left (large wavenumbers, cm^{-1}).

4.7 – Calculate the wavelength (in nm) and frequency (in Hz) of IR light with wavenumbers 1500 cm^{-1}.

4.8 – Infrared light has a range of wavelengths from 10^{-6} m to 10^{-3} m. Calculate the range of frequencies (in Hz) a molecule's natural frequency must be in order to be in resonance with infrared light.

4.9 – Like all objects above absolute zero, both the Earth and the Sun emit radiation. The high temperature of the Sun (6000 K) means that the majority of light emitted from the sun is in the visible region of the spectrum (350 – 800 nm, or 12,500 – 28,600 cm^{-1}), in addition to some UV and infrared light. Earth, on the other hand, is much colder and emits light in the infrared ($\tilde{\nu}$ = 200 – 1400 cm^{-1}).

a. Water can absorb three wavenumbers of infrared light: 600 cm^{-1}, 1500 cm^{-1}, and 3600 cm^{-1}, each corresponding to a different vibrational mode of the water molecule. Indicate whether the following statements are true or false:

T / F Water vapor in the atmosphere absorbs visible light arriving at Earth from the sun

T / F Water in the atmosphere absorbs radiation with ν = 3600 cm^{-1} emitted by Earth.

T / F Water in the atmosphere absorbs infrared radiation emitted by Earth

b. The O–H bond stretches with a wavenumber of 3600 cm^{-1}. What do you predict about the stretching frequency of C–O single bonds? Explain your reasoning.

ν(O–H) < ν(C–O) ν(O–H) = ν(C–O) ν(O–H) > ν(C–O) Need more info

c. Are C–O bonds transparent to infrared light with a wavenumber of 3600 cm^{-1}? Explain.

d. Carbon dioxide gas is clear and colorless, but does absorb infrared radiation from the atmosphere. In carbon dioxide, the carbon atom is double-bonded to each oxygen atom (C=O). What do you predict about the stretching frequency of the C=O double bonds compared to the C–O single bonds? Explain your reasoning.

ν(C=O) < ν(C–O) ν(C=O) = ν(C–O) ν(C=O) > ν(C–O) Need more info

e. Is carbon dioxide transparent? Explain.

4.10 – Based on Figure 4.1 and the absorption of light by ethanol, sketch a graph representing the emission of light by ethanol. (*Hint: Make sure to indicate the resonant wavenumbers for ethanol.*)

4.11 – What is the range of wavelengths (in nm) of infrared radiation emitted by Earth? Is this lower or higher energy than the visible light reaching Earth?

4.12 – In addition to being good at absorbing infrared radiation, water also has a strong absorption in the microwave region of the spectrum. Absorbing microwaves causes water molecules to rotate quickly leading to increased temperatures. This is the principle behind using microwave ovens to heat food – really you are just heating up the water in the food, which is why microwaved chicken tastes like boiled chicken (it is). It's always why you need to add water to rice or pasta before microwaving (so you don't dehydrate them).

a. Standard microwave ovens have an operating frequency of 2500 MHz (1 MHz = 10^6 Hz). What is the wavelength of the microwaves in a standard oven? Can you "see" these microwaves?

b. Are microwaves transparent? Explain.

4.13 – Spectroscopists often use isotopes to help identify molecules. Frequently, hydrogen atoms (^1H) are replaced by deuterium atoms (^2H). The ^1H–O stretch absorbs infrared light of 3600 cm^{-1}. Assuming that the strength of the bond remains the same, circle the appropriate relationship for the statements below.

a. The frequency of the light absorbed by the ^1H-O stretch is (*greater than / less than / equal to*) the frequency of the light absorbed by the ^2H-O stretch.

b. The wavelength of the light absorbed by the ^1H-O stretch is (*greater than / less than / equal to*) the wavelength of light absorbed by the ^2H-O stretch.

4.14 – Indicate whether the following statements about atmospheric warming are true or false.

T / F A major source of warming is the absorption of sunlight by greenhouse gases.

T / F A major source of warming is IR light in the 3500 cm^{-1} region.

T / F The primary source of warming is absorption of IR light by the atmospheric O_2 and N_2.

T / F The primary source of warming is absorption of IR light given off by Earth.

T / F Water vapor is a major contributor to atmospheric warming.

4.15– How many times more energetic is light corresponding with wavelength 5.0 nm than light with wavelength 100 nm?

4.16 – Consider light that is in resonance with matter. Circle all that must be true.

a. $|\Delta E_{light}| < |\Delta E_{cloud}|$ $|\Delta E_{light}| = |\Delta E_{cloud}|$ $|\Delta E_{light}| > |\Delta E_{cloud}|$

b. $|\Delta E_{cloud}| < h\nu_{light}$ $|\Delta E_{cloud}| = h\nu_{light}$ $|\Delta E_{cloud}| > h\nu_{light}$

4.17– A molecule of substance A is resonant with the red light with wavelength of 700 nm and a molecule of substance B is resonant with the blue light (400 nm). Which statement is the most accurate?

a. When substance A absorbs light it absorbs more energy than substance B.
b. When substance B absorbs light it absorbs more energy than substance A.
c. Because each molecule absorbs one quantum of light, the amount of energy absorbed by each substance is the same.
d. There is no energy absorbed because temperature of the surrounding does not change.