

GENERAL CHEMISTRY SECTION I: BONDING

LECTURE 1. WAVE PARTICLE DUALITY OF LIGHT

Time out for a first lesson on active learning. Most people make a cursory glance at an outline or summary and head immediately for the meat of the material. This is a really dumb and lazy idea. Instead, think how much better you would be able to create a context for the material if you would **memorize the summary**. For example, see if you can describe out loud to yourself the material in the outline below. After all, you will see me do it to start the lecture and it is the main reason I don't really need to look at my notes during lecture—I have already proven to myself I know what I will be talking about.

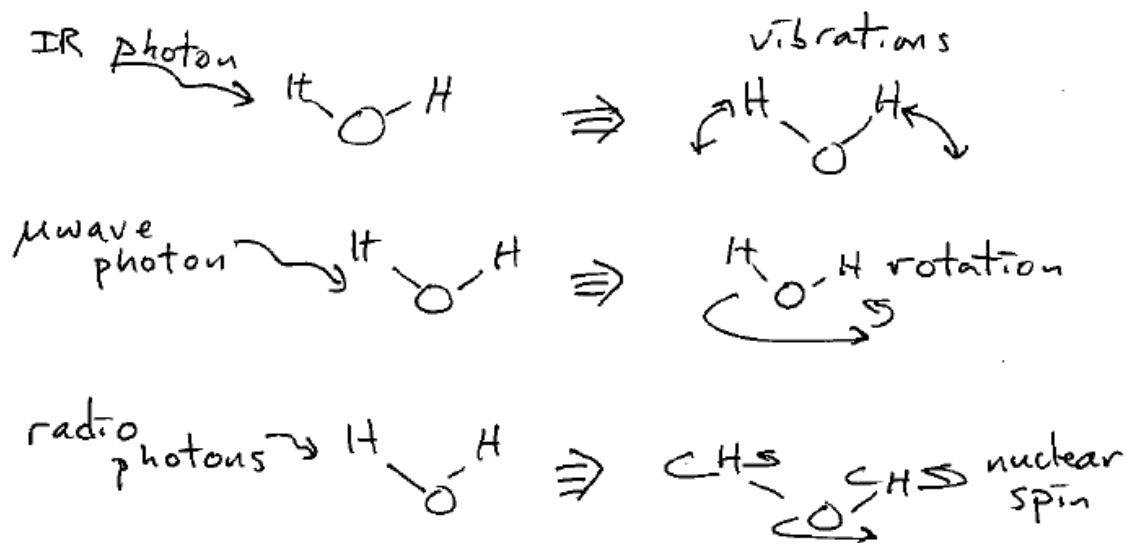
An overview of any first chapter on general chemistry taught from an “atoms up” approach requires an argument for how light interacting with matter paved the way for a quantum mechanical revolution that revealed the electronic configuration of atoms. Here is a summary of the argument.

- The best way to interrogate atomic and subatomic particles is with electromagnetic radiation (light). So it is important to understand the properties like wavelength and frequency.
- The classical interpretation of light as a wave breaks down explaining black bodies and the photoelectric effect. So Planck and Einstein redefined light as a particle with discrete energies.
- deBroglie says that there is a duality (wave and particle) to both light and matter.
- The uncertainty principle provides a lower bound for measurement uncertainty in asking the question, where are electrons located in an atom?
- Schrödinger develops quantum mechanics so he can identify the wave functions that describe physical systems like the particle in a box.

- Balmer and Rydberg see discrete lines in atomic spectra. Schrödinger explains them with quantum mechanics.
- Using an appropriate potential energy function, the quantum number describing size of atoms, n , generates correct energy levels.
- Two more quantum numbers, ℓ and m_ℓ , explain orientation and shape of the orbits formed by electrons.
- A final quantum number, m_s , explains the discrete nature of electron spin.

Electromagnetic radiation: Characteristics

We are interested in electromagnetic radiation because it is used to probe the molecular, atomic, and subatomic nature of matter. Note how different light energies promote different kinds of motion in atoms and molecules.



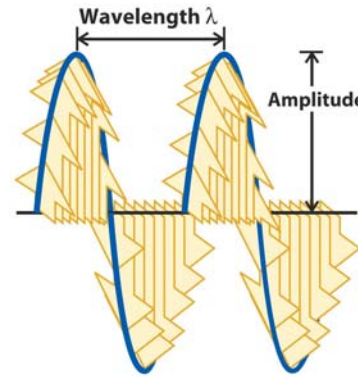
EMR characteristics: EMR radiation is classified by either frequency or wavelength which are inversely related to each other through the constant, c , which is the speed of light.

$$c = \lambda \nu$$

λ = wavelength (length from meters to picometers)

ν = frequency in Hz (sec^{-1})

c = speed of light = 3.0×10^8 m/s



Example: Calculate the wavelength of light from traffic signals (in nm)

Pertinent Data

Green 5.75×10^{14} Hz
 Yellow 5.15×10^{14} Hz
 Red 4.27×10^{14} Hz

Pertinent Equations

$$\nu = c/\lambda$$

$$\hookrightarrow \lambda = c/\nu$$

Pertinent Const & Conversions

$c = 3.0 \times 10^8$ m/s
 $1 \text{ m} = 10^9 \text{ nm}$

Solution

$$\lambda = \frac{3 \times 10^8 \text{ m/s}}{5.75 \times 10^{14} \text{ Hz}} = 5.22 \times 10^{-7} \text{ m} \quad \text{and} \quad 5.22 \times 10^{-7} \text{ m} \left(\frac{1 \times 10^9 \text{ nm}}{1 \text{ m}} \right) = 522 \text{ nm}$$

similarly $5.15 \times 10^{14} \text{ Hz}$ converts to 582nm and $4.27 \times 10^{14} \text{ Hz}$ converts to 702 nm

Is this sensible? Yes, since $\lambda \nu = c$, it makes sense that as $\nu \downarrow$ $\lambda \uparrow$

Note the wide range of wavelengths in the EMR spectrum that are important to chemists because of the interaction with matter. Spectroscopy, which is a measurement of energy changes that result from light interacting with matter, is a very useful investigative tool. State troopers use it to find out your friend's blood alcohol content and the doctor uses it to perform MRI.

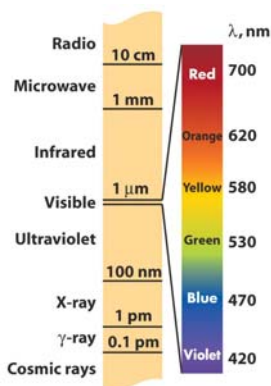


TABLE 1.1 Color, Frequency, and Wavelength of Electromagnetic Radiation

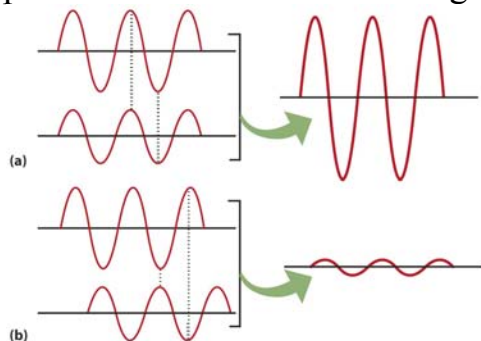
Radiation type	Frequency (10^{14} Hz)	Wavelength (nm, 2 sf)*	Energy per photon (10^{-19} J)
x-rays and γ -rays	$\geq 10^3$	≤ 3	$\geq 10^3$
ultraviolet	8.6	350	5.7
visible light			
violet	7.1	420	4.7
blue	6.4	470	4.2
green	5.7	530	3.8
yellow	5.2	580	3.4
orange	4.8	620	3.2
red	4.3	700	2.8
infrared	3.0	1000	2.0
microwaves and radio waves	$\leq 10^{-3}$	$\geq 3 \times 10^6$	$\leq 10^{-3}$

*The abbreviation sf denotes the number of significant figures in the data. The frequencies, wavelengths, and energies are typical values; they should not be regarded as precise.

So why does EMR interact with matter? Think of it as two oscillators interacting constructively or destructively, much like the way you push a child on a swing constructively to go higher or destructively to stop. In spectroscopy:

- Oscillator 1 is the particle motion like the spin of a water molecule
- Oscillator 2 is the electromagnetic radiation like frequency of microwaves

When the microwave is tuned to the frequency at which water spins, an increase in amplitude occurs. Spectroscopists typically monitor this change in amplitude to know that something is going on.



The Dual Nature of EMR of Discovered

Everyone knows that we can think of EMR as a wave. Among the many wave-like properties of light that demonstrate this are phenomena from diffraction to dispersion to the polarization of light. Just pick up a CD or DVD and watch the rainbow of colors flashing off the gratings (grooves), and think: waves.

Sadly, at the turn of the 19th century, several observations of light's behavior that failed to be treated by classical physics suggested that EMR suggested that other explanations were needed. Consider the follow:

- Blackbody radiation—wave theory suggests blackbodies (heat sources) transmit radiation at all ν . They don't.
- Photoelectric effect—wave theory says no energy minima for ejecting electrons from metal surfaces. There is.

And from these conflicts, new theories, developed by Planck and Einstein, were to suggest that light could be described as having a particle nature with discrete energy levels.

Blackbody radiators

Blackbody radiators by definition do not favor one wavelength of EMR over another. What is observed experimentally?

- In 1879 Stefan showed that the intensity is related to the fourth power of temperature.

$$I = (\text{Power} / \text{Area}) = (\text{W} / \text{m}^2) = cT^4 \quad \text{where } c = 5.7 \times 10^{-8} \text{ W} / (\text{m}^2\text{K}^4)$$

- In 1893 Wien demonstrated the inverse relationship of T and the λ_{max} (as T increases, the black body shifts to higher ν). This is why you see the color change on a heating element as the temperature increases.

$$\text{Wien's Law:} \quad T\lambda_{\text{max}} = c_2 / 5 \quad \text{where } c_2 = 1.44 \times 10^{-2}\text{Km}$$

Calculate the temperature in deep space if the maximum λ for EMR is 1.05 mm?

Pertinent Data

$\lambda_{\max} = 1.05 \text{ mm}$

Pertinent Equations

Wien $\Rightarrow \lambda_{\max} T = \frac{c_2}{5}$

Pertinent Const & Conversions

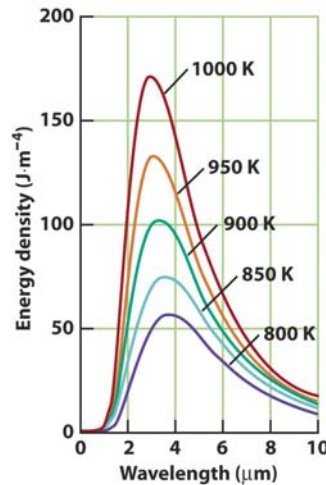
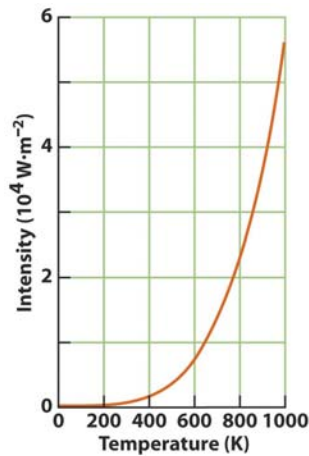
$c_2 = 1.44 \times 10^{-2} \text{ km}$ and $1 \text{ m} = 1000 \text{ mm}$

Solution

$$T = \frac{c_2}{5\lambda_{\max}} = \frac{1.44 \times 10^{-2} \text{ km}}{(5)(1.05 \text{ mm}) \left(\frac{1 \text{ m}}{1000 \text{ mm}} \right)} = 2.7 \text{ K}$$

Is this sensible? Yes, deep space is cold, there are few particles to collide and transfer energy

The experimental data for these observations in support of a classical model for blackbody radiators is shown in the figures below.



The problem with black bodies is that classically there was no reason for a cutoff in frequency at which radiation is absorbed and emitted. But there is – in the ultraviolet region. How do we explain? The answer would await Planck’s development of a particle model for EMR, a decidedly non-classical model for radiation. The idea of a packet of energy allowed Planck to argue that there was insufficient energy in black body radiators at low temperature to emit light at ultraviolet and higher frequency.

Planck described the concept of a photon as a discrete packet of energy that is frequency dependent.

$$E = h\nu$$

$$\nu = \text{EMR frequency, } h = \text{Planck's constant } (6.6 \times 10^{-34} \text{ J s})$$

What is E for a yellow photon with $\nu = 5.2 \times 10^{14} \text{ Hz}$

Pertinent Data

$$5.2 \times 10^{14} \text{ Hz}$$

Equation

$$E = h\nu$$

Const & Conversions

$$h = 6.626 \times 10^{-34} \text{ Js}$$

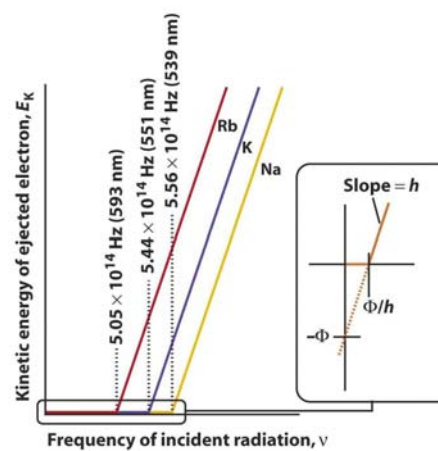
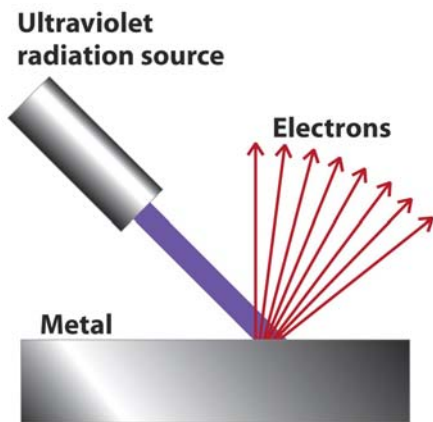
Solution $E = h\nu = (6.626 \times 10^{-34} \text{ Js}) (5.2 \times 10^{14} \text{ sec}^{-1}) = 3.4 \times 10^{-19} \text{ J}$

Is this sensible? Yes, one photon should not produce much energy so answer should be a very small number.

The Photoelectric Effect

The Photoelectric Effect states that if you shine light on a metal, at a certain ν , electrons are emitted. A classical model for the photoelectric effect is not verified experimentally because there is no relationship between the intensity of the incident light and the energy of the expelled electrons. In his Nobel Prize winning work, Einstein explain the inconsistencies of classical theory using the particle model for EMR. He stated that a minimum ejection energy, Φ , was necessary for quantized photons, $h\nu$, to be ejected with a kinetic energy proportional to ν .

$$E_{\text{kin}} = \frac{1}{2} m\nu^2 = h\nu - \Phi,$$



Note the experimental evidence in the figure to the right—a minimum frequency threshold frequency (or energy) is needed before an electron is ejected. Once again a particle model would have to be used to explain an experimental observation.

It was clear that a new theory for EMR needed to be developed that could account for both wave and particle behavior. This became known as the **wave/particle duality of light**.