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FOUNDATIONS OF SPECTROSCOPY

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Spectroscopy is the study of the interaction of electromagnetic radiation with matter. When matter is energized (excited) by the application of thermal, electrical, nuclear or radiant energy, electromagnetic radiation is often emitted as the matter relaxes back to its original (ground) state. The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum and the science is appropriately called emission spectroscopy.

Another approach often used to study the interaction of electromagnetic radiation with matter is one whereby a continuous range of radiation (e.g., white light) is allowed to fall on a substance; then the frequencies absorbed by the substance are examined. The resulting spectrum from the substance contains the original range of radiation with dark spaces that correspond to missing, or absorbed, frequencies. This type of spectrum is called an absorption spectrum. In spectroscopy the emitted or absorbed radiation is usually analyzed, i.e., separated into the various frequency components, and the intensity is measured by means of an instrument called a spectrometer.

The resultant spectrum is mainly a graph of intensity of emitted or absorbed radiation versus wavelength or frequency. There are in general three types of spectra: continuous, line, and band. The sun and heated solids produce continuous spectra in which the emitted radiation contains all frequencies within a region of the electromagnetic spectrum. A rainbow and light from a light bulb are examples of continuous spectra. Line spectra are produced by excited atoms in the gas phase and contain only certain frequencies, all other frequencies being absent. Each chemical element of the periodic chart has a unique and, therefore, characteristic line spectrum. Band spectra are produced by excited molecules emitting radiation in groups of closely spaced lines that merge to form bands.

Much of the scientific knowledge of the structure of the universe, from stars to atoms, is derived from interpretations of the interaction of radiation with matter. One example of the power of these techniques is the determination of the composition, the velocities, and the evolutionary dynamics of stars. The source of the incredible amount of energy produced by the sun is nuclear fusion reactions going on within the hot interior (temperature $40 \times 10^6$ K). Two fusion cycles, the carbon cycle and the proton cycle, convert hydrogen nuclei into helium nuclei via heavier nuclei, such as carbon 12 and nitrogen 14. The enormous radiation of energy from the hot core seethes outwards by convection. This radiation consists of the entire electromagnetic spectrum as a continuous spectrum. Towards the surface of the sun (the photosphere), the different elements all absorb at their characteristic frequencies. The radiation that shoots into space toward earth is a continuous emission spectrum with about 22,000 dark absorption lines present in it (Fraunhofer lines), of which about 70% have been identified. These absorption lines - i.e., missing frequencies - prove that more than 60 terrestrial elements are certainly present in the sun.
Plank's constant, $h = 6.63 \times 10^{-34}$ J s.
The speed of light, $c = 3.0 \times 10^8$ m s$^{-1}$. 

RF = Radio frequency radiation 
$\mu$W = Microwave radiation 
IR = Infrared radiation 
VIS = Visible light radiation 
UV = Ultraviolet radiation 
X = X-ray radiation 
$\gamma$ = gamma ray radiation
Radiation may be described in one of two ways: either as a stream of energy pulses (photons) or as energy waves sent out from a source at the speed of light. Scientists use whichever interpretation works best to explain an experiment involving radiation. The photon and wave theories are linked by Plank’s law:

\[ E = h \nu \]

where \( E \) is the photon energy in Joules (J), \( \nu \) is the frequency of the radiation (Hz or s\(^{-1}\)) and \( h \) is Plank’s constant (\( 6.63 \times 10^{-34} \) J s).

Wavelength and frequency are related by

\[ c = \lambda \nu \]

where \( c \) is the speed of light (\( 3 \times 10^8 \) m s\(^{-1}\)), \( \lambda \) is the wavelength of the radiation (often reported in nm), and \( \nu \) is the frequency.

### PREFIXES AND SCIENTIFIC NOTATION

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### Notation

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Some Greek letters which we will use:

- \(\alpha\) = “alpha”; as in \(\alpha\) particle.
- \(\beta\) = “beta”; as in \(\beta\) particle.
- \(\gamma\) = “gamma”; as in \(\gamma\) ray.
- \(\delta\) = “delta”; used with a plus or minus sign to represent partial charges in polarized molecules.
- \(\Delta\) = “della”; a capital delta is used for a change in a quantity.
- \(\lambda\) = “lambda”; used for wavelength.
- \(\nu\) = “nu”; used for frequency.
- \(\mu\) = “mu”; used for the prefix micro.
- \(\pi\) = “pi” is the ratio of the circumference of a circle to its diameter.
- \(\Omega\) = “omega”; a capital omega is used for electrical resistance.
The fisherman rises and falls with the passing waves. The (vertical) distance the fisherman moves through is called the amplitude of the wave. The distance between crests of the wave is called the wavelength. The time it takes for the fisherman to go from one wave top (crest), down to the bottom (trough) and back up to the top is called the period; its inverse is called the frequency. If the sea is choppy we could say that the number of waves going by the fisherman in a second is the frequency.

There is a general relationship for all waves that the velocity of the wave is the product of the wavelength times the frequency.

\[ v = \lambda \nu \]

Measure the wavelength and amplitude, in centimeters, of the fisherman’s wave. If the frequency of the wave is 2.5 Hz, calculate its velocity.
Each of the vertical sequences of pictures above shows a wave moving to the right. Since electromagnetic radiation always travels at the same velocity (in vacuum and nearly so in air) and that velocity is equal to the product of wavelength and frequency, then increasing the frequency must decrease the wavelength.

Does the wave on the left have the same velocity as the wave on the right?
Plank's constant, \( h = 6.63 \times 10^{-34} \) J s.
The speed of light, \( c = 3.0 \times 10^8 \) m s\(^{-1}\). This is the speed of all electromagnetic radiation in a vacuum.

1. A solid state laser has a wavelength (\( \lambda \)) of 650 nm. What color is the laser light? Calculate the frequency (\( \nu \)) and energy (\( E \)) of this light.

2. What is the wavelength range for visible light. Use the ER ruler.

3. Give the approximate wavelength range for yellow light. Use the ER ruler.

4. Give the approximate wavelength range for infrared radiation.

5. Which has the higher energy, red light or blue light?

6. Give the approximate frequency range for visible light.

7. What is the frequency and energy of electromagnetic radiation with a wavelength of \( 1.0 \times 10^4 \) nm? What type of radiation is it?

8. Noting that on the ER ruler the wavelength and energy scales go in opposite directions, if you added a frequency scale, would it go in the direction of the wavelength scale or the energy scale?

9. Atoms have diameters of approximately 0.1 nm. What kind of radiation would have a wavelength of 0.1 nm?

10. What type of radiation has an energy of \( 2.0 \times 10^{-7} \) J?

11. My favorite FM radio station has a frequency of 100 MHz. Calculate the wavelength and energy of the electromagnetic radiation broadcast by my station.

12. X-rays travel at a speed of \( 3.0 \times 10^8 \) m s\(^{-1}\). What speed do radio waves travel at?

13. A microwave oven produces radiation with a frequency of \( 2.5 \times 10^9 \) Hz. This radiation stimulates water molecules to rotate. Calculate the wavelength and use the ER ruler to find the energy of this microwave radiation.

14. A cell phone has an operational frequency of 840 MHz. What type of radiation is this? Calculate the energy of the radiation. Can this radiation go through walls? Why?

15. Would you rather be in a beam of gamma (\( \gamma \)) rays or radio waves? Explain your answer.

16. Suggest the wavelength for the light emitted from the top light in a traffic light.

17. The red Balmer line in the atomic emission spectrum of hydrogen has an energy of \( 3.03 \times 10^{-19} \) J. Calculate the wavelength of the red light in a) m; b) nm; and c) zm. Also calculate the frequency in a) Hz; b) MHz; and c) GHz.
Absorbing a photon increases the energy of a system.

Absorbing a photon increases the size of an electron orbital.

Absorbing an infrared photon can increase the vibrational energy of a molecule.

Absorbing a microwave photon can increase the rotational energy of a molecule.

Absorbing a photon can increase the translational energy of a molecule.

Emitting a photon decreases the energy of a system.

Emitting a photon decreases the size of an electron orbital.

A vibrating molecule can emit an infrared photon and decrease its rate of vibration.

A rotating molecule can emit a microwave photon and decrease its rate of rotation.

A moving molecule can emit a photon and slow up.
The separation of light into its spectral components can be done by refraction or diffraction. The separation of light into its component colors is accomplished by a spectroscope. A spectroscope is simply a box with a slit at one end (to let in light) and a light-separating device at the other end.

Measure the angle at which the blue end of the spectrum is diffracted (1). Use the equation for diffraction to calculate the spacing of the diffraction grating. Repeat for the red end of the spectrum (2).

For a diffraction grating with the width of the lines given as $d$, for light of wavelength $\lambda$, the angle of diffraction is given by the equation

$$n\lambda = d \sin \theta$$

Here $n$ is called the order of diffraction (usually 1) and $\theta$ is the angle of diffraction.

If you put a camera at the position of the virtual spectrum and pointed it at the diffraction grating, would you be able to photograph the spectrum? If you put the camera in place of the eye, would you be able to photograph the spectrum?

Measure the angle at which the blue end of the spectrum is diffracted (1). Use the equation for diffraction to calculate the spacing of the diffraction grating. Repeat for the red end of the spectrum (2).
Unlike solid objects waves can occupy the same space at the same time. When they do their amplitudes add. This is strictly true for both electromagnetic waves and the waves of quantum mechanics. But the amplitudes of both kinds of waves are signed, that is, they are both positive and negative. When amplitudes of the same sign are superimposed upon each other then the combined amplitude is greater. This is called constructive interference. When amplitudes of opposite signs are superimposed upon each other then the net amplitude is decreased and sometimes cancelled. This is called destructive interference.

\[ n\lambda = d \sin \theta \]

The picture on the right illustrates the geometry of a diffraction grating. Two (of the thousands) of slits in the grating allow light to pass through. The separation between the slits is \( d \). The angle at which we observe the waves is \( \theta \). The wavelength of the light is \( \lambda \).

You can see that the waves are in the same relative position (the same phase) along their direction of travel, because one wave has exactly one wavelength farther to travel than the other one, which gives rise to constructive interference and which produces light which can be seen on a screen or in the eye.

By trigonometry you can see (Picture number 12 on the NEXT page may help) that \( \lambda = d \sin \theta \).

You would also have constructive interference if one wave traveled exactly two wavelengths, or any integral number \( n \), further than the other one, which is how we obtain the general equation \( n\lambda = d \sin \theta \).
Far from a source, light travels as a parallel wavefront.

But the barrier has an opening through which light can pass.

Suppose we insert a screen in the way of the light.

Now if we look at the screen...

Use this diagram to explain why $x = ds\sin(\theta)$.

$x$ is the extra distance light path 1 must travel to meet light path 2 at a spot on a distant screen.
A high voltage supply produces a 2000 V difference across the tube.

The cathode is heated to drive electrons off into the tube.

Electrons gain kinetic energy as they are pulled toward the anode.

The electron hits a hydrogen (H) atom.

The electron will use its kinetic energy to excite the H atom.

A line spectrum is emitted.

The H atom will emit visible light at different wavelengths. The visible light escapes.

If the atoms had collided before emission of radiation, then the energy would have been dissipated into motion.

Line emission and absorption spectra come from low pressure gases containing atoms.

Why does collision with an electron excite an atom but collision with another atom does not?

In a gas, what factors control the time interval between atomic collisions?
The cathode is heated to drive electrons off into the tube.

Electrons gain kinetic energy as they are pulled toward the anode.

The electron hits a mercury (Hg) atom.

The electron will use its kinetic energy to excite the Hg atom.

The Hg atom will emit visible or ultraviolet light or both. The visible light escapes.

The UV photon will excite the phosphors on the inside of the tube.

The phosphors will fall back to their original state and emit visible light.

Spectrum of ‘Warm’ Fluorescent Light Bulb
In the part of the sun where the continuous spectrum is produced, called the photosphere, atoms are entirely ionized, giving rise to a gas of free protons and electrons called a plasma. Because they are not bound to an atom, these particles can have any energy state.

The sun is powered by nuclear reactions in the core. Eventually the energy works its way upward through the radiative zone until it reaches the photosphere, from where it escapes into space (and to earth). What frequency range of radiation would you expect to occur in the radiative zone and what sort of effects would that radiation have if it could reach the earth directly?
Atoms are spherically symmetric but molecules have shapes which permit them to vibrate and rotate. These vibrations and rotations provide new energy levels which are also quantized.

Explain why the spherical symmetry of atoms prevents them from having vibrational and rotational energy levels.

MOLECULAR ENERGY LEVELS
As we know, electrons can occupy different electronic energy states.

In molecules the electronic states are subdivided into vibrational states.

The electronic-vibrational states are also subdivided into rotational states.

Transitions between electronic levels give line spectra.

Transitions between vibrational-electronic states give more complex spectra.

Transitions between electronic-vibrational-rotational states give rise to spectra that appear to have bands.

and many more
It can be established from the Uncertainty Principle of quantum mechanics that high energy transitions in atoms or molecules tend to be very fast. Also, as atomic nuclei are very heavy compared to electrons, the nuclei move much slower than the electrons. Therefore the FRANK-CONDON PRINCIPLE states that during electronic transitions in a molecule, the nuclei can be assumed to be in the same place before and after the transition. This has significant effects upon the appearance of band spectra.

Pictures 1 and 2 show molecular electronic transitions. In picture 1 we see a transition between two states with the same nuclear separation. In picture 2 we see two transitions between states with different nuclear separations. Transition B, however, still involves no nuclear movement and is allowed by the Frank-Condon Principle. Transition C would require nuclear motion and is thus disfavored by the Frank-Condon Principle.

Picture 3 is similar to picture 2 with some changes. The vibrational states of the upper electronic state have been added and dashed lines show the region in which appreciable transitions can actually occur. We have also added the arrows for the transitions which would occur.

Explain how the transitions shown in picture 3 can be correlated to the spectral lines in picture 4. Explain why the line appearing in picture 4 cluster to the left of the spectral band.
Molecules produce band spectra.

Suppose you see bands in the spectrum of an interstellar cloud. What can you deduce about the nature and condition of the cloud?
LASERS

Light Amplification by Stimulated Emission of Radiation.

What does that mean?

We begin with a system of molecules.

Energy is pumped into the system, exciting the molecules.

One of the molecules de-excites by emitting a photon.

That photon stimulates another molecule to emit.

...and so on...

The photons are reflected by the mirrored surface on the left of the system. They continue to stimulate further emission.

Resulting in an intense beam of photons of the same wavelength and phase.

Compare and Contrast pictures 8, 9 and 10. Describe the relationship between the different waves. What are possible sources for each of the wave patterns pictured?

Using an internet search engine, such as www.google.com, perform an advanced search for 'chemical lasers'. Describe the chemistry of at least two kinds of chemical laser. What is the most powerful laser owned by the United States and what is its power range?

Describe a half dozen different uses of lasers in everyday life. What kind of lasers are used?

The original development work which led to the laser was carried out in the interest of microwave spectroscopy.
FOUNDATIONS OF SPECTROSCOPY
SIMPLE SPECTRA

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In the examples at right, the continuous spectrum a is reduced by the absorption pattern b to give the resulting spectrum c.
The following questions refer to the sixteen spectra on the last two pages.

1. In spectrum number 1, measure the wavelength of the four visible lines.
2. In spectrum number 2, what is the frequency of the green line?
3. Referring to spectrum number 3, what is the wavelength of the light emitted by the laser?
4. Describe the origin of the light which produces spectrum number 4.
5. Describe the origin of the light which produces spectrum number 5.
6. What is the energy of the photons which produce the sodium yellow line?
7. List the four visible lines of lithium gas in decreasing order of frequency.
8. Using a chart of known spectra, determine the nature of the unknown gas in spectrum number 8.
9. Describe the source of the black lines which appear in spectrum number 9.
10. Referring to the fluorescent light description page which appears later in this module, explain why spectrum number 10 has both a continuum and discrete lines.
11. Why doesn’t the red line appear in spectrum number 11?
12. Referring to spectrum number 12, what colors of light are absorbed by the green leaf?
13. What happens to the light which is absorbed by the blue solution?
14. How would spectrum number 14 change if fluorescent light replaced the incandescent bulb as the light source?
15. What would spectrum number 15 look like if blue dye were added to the yellow dye?
16. Find a good question to ask about spectrum number 16.
17. The yellow flame in the Bunsen burner is given by the sodium from sodium chloride. How do sodium ions get to be sodium atoms? See the Bonding Module.
18. Why is the yellow part of the continuous spectrum narrower than the green or red parts?
19. What might be responsible for the variations in thickness of the atomic emission lines?
20. Draw the combined spectrum of H, Li, Hg and Na.
21. Using the solution absorption spectra, explain how you could make black ink?
22. What do you find unusual about the spectrum of a leaf?
23. What do you think the spectrum of an autumn leaf would look like?