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AP Chemistry 1

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2.2 Quantum Theory and the Bohr Model of the Atom

Warm Up

1. (a) List three properties of waves such as water waves or visible light.

   ____

   (b) What would you expect to happen when two water waves moving in opposite directions met each other?

   ____

2. (a) List three properties of solid objects or particles such as the marbles in a bag.

   ____

   (b) What would you expect to happen when two marbles moving in opposite directions met each other?

   ____

3. Are any of your answers to question 1 identical to question 2? (Stay tuned…)

   ____

Waves Behaving like Particles? Well Hit Me with a Planck!

A serious challenge to Rutherford's atomic model arose almost immediately. A very secure prediction of the physics available at the end of the 1800s was that accelerating charges should radiate energy. Because orbiting electrons are accelerating charges, electrons in atoms should lose energy. That prediction was catastrophic for Rutherford's model. It meant that all atoms, and so also all matter, should collapse in a fraction of a second as their electrons lost energy and spiraled into the nucleus! Obviously, a significant piece of the atomic puzzle was missing and even Rutherford himself was ready to abandon his view of the atom. Yet, his conclusions and his nuclear model were correct. The real problem was that the physics of the day needed to be re-written to explain the behavior of electrons in atoms.

To begin to understand how the solution came about, we must consider the work of German physicist Max Planck. In 1900, this conservative professor began nothing short of a revolution in physics. He proposed that energy, long considered to be strictly a wave phenomenon, could be shown to behave like particles in the form of very tiny, discreet energy packets or bundles he called quanta (plural for quantum). Planck called this the quantum theory and arrived at his conclusions (reluctantly) by studying the energy radiated from heated solids. Planck developed the following equation for the energy associated with each packet or quantum:

$$\boldsymbol{E = hv}$$

where $\boldsymbol{E}$ = energy, $\boldsymbol{v}$ = frequency, $\boldsymbol{h}$ = a very tiny proportionality constant ($h = 6.626 \times 10^{-34}$ J·s) called Planck's constant. According to Planck, energy could only be absorbed or emitted in whole numbers of quanta, that is, one quantum of energy ($E = hv$), two quanta ($E = 2hv$), three quanta ($E = 3hv$) and so on, but nowhere in between. Think of each energy quantum as a glass marble in a bag of identical marbles (Figure 2.2.1). In the same way that you could only ever add or remove a specific amount of glass from the bag in the form of a whole number of marbles, so too could amounts of energy only be absorbed or emitted in the form of whole numbers of quanta.

Figure 2.2.1 *Quanta of energy are like marbles in bag. The marbles can only be removed as whole units.*

At the end of the 1800s, the behavior of waves and the behavior of particles were seen as very different and mutually exclusive. Waves were disturbances that moved through space, could pass through and interfere with each other, and could have any value within a range. Particles were objects with definite boundaries that bounced off each other when they collided and could only exist in certain whole-number quantities. A firm experimental and mathematical foundation supported the idea that waves were fundamentally different from particles. To now suggest that waves could behave like particles was almost sacrilegious! Planck himself wrote about his work: "By nature, I am peacefully inclined and reject all doubtful adventures. …However, a theoretical interpretation had to be found at any cost….I was ready to sacrifice every one of my previous convictions about physical laws."

Planck's theory wasn't taken very seriously at first. But in 1905, a 26-year-old clerk in a Swiss patent office named Albert Einstein wrote five papers that changed the scientific world forever. One of those papers used the quantum theory to explain a phenomenon involving light called the "photoelectric effect" that had baffled physicists until then. According to Einstein, the only way to make sense of the photoelectric effect was to consider light as being composed of tiny discreet packets of energy. (These were later called "photons" by American chemist Gilbert Lewis.) Einstein's paper was the first practical application of the quantum theory and as a result, the theory soon began to gain widespread acceptance. In 1921, Einstein was awarded the Nobel Prize in physics for his explanation of the photoelectric effect.

Quick Check

1. Briefly state what it means for something to be a "quantized."

   ____

2. Give three common examples of things considered to be "quantized."

   ____

   ____

3. According to Planck, could an amount of energy equal to 2.5*hv* be absorbed or emitted by an object? Explain.

   ____

   ____

The Bohr Model

One of the scientists who paid particular attention to the work of Planck and Einstein was a young Danish physicist named Niels Bohr. As a young grad student, Bohr had met Ernest Rutherford at the Cavendish Laboratory in Cambridge and then worked with Rutherford at the University of Manchester. Bohr believed in the nuclear atomic model and started to see a way to "save" it using the quantum theory. If energy was indeed quantized and so could be seen to have only certain values and not others, perhaps the energies associated with electrons orbiting the nucleus had similar restrictions.

Bohr was working on this idea at Rutherford's laboratory in Manchester in 1912. In the middle of his experiments and calculations, he returned to Copenhagen to get married. He was so excited about his work that he managed to convince his new bride to cancel their honeymoon and return to England with him. Soon thereafter, Niels Bohr completed one of the most brilliant papers on atomic structure ever written. In doing so, he managed to rescue Rutherford's nuclear model of the atom.

Scientific theories are carefully constructed on a firm foundation of data gathered from a multitude of meticulously documented, rigorously controlled, and perpetually repeatable experiments. Bohr's theory was no exception. In the previous section, we discussed the conduction of charges through gases in glass discharge tubes. Those experiments in the later years of the 1800s not only led to Thomson's discovery of the electron, but also provided Bohr with valuable data for his ideas about the nature of those electrons in atoms.

Quantum Theory Rescues the Nuclear Model

Bohr knew that when high voltage was applied across the electrodes of a sealed glass tube containing a gas such as hydrogen, the gas was heated and emitted light. As part of his investigations, Bohr looked at this light through a spectroscope. A spectroscope is a device similar to a prism, which separates the light into its component wavelengths. When Bohr viewed the light from the heated hydrogen through the spectroscope, he saw only a series of colored lines against a black background, rather than a continuous rainbow of color. For hydrogen, the same pattern of four colored lines was always seen: a red, blue-green, blue, and violet line (Figure 2.2.2). For each gaseous element used, a bright-line pattern unique to that element called a **bright-line spectrum** always appeared (much like a bar code on a modern grocery item).

The phenomenon had mystified scientists. None could explain why only certain colors of light, each corresponding to specific wavelength, frequency, and energy, were emitted by the heated gases — until Bohr. Bohr realized that by applying quantum principles to the behavior of hydrogen's lone electron, he could not only account for the existence of the bright-line spectrum, but also save Rutherford's nuclear model of the atom.

Figure 2.2.2 *Hydrogen's bright-line spectrum*

Bohr's Postulates

Bohr's postulates for hydrogen are summarized below:

1. The hydrogen atom had only certain **allowed energy levels** or **stationary states.** Each of these states corresponded to a circular electron orbit of a fixed size. The larger the allowed orbit, the greater the energy associated with it. No other orbits existed in the atom. Each allowed energy state was given an integer number "*n*" that Bohr called a **quantum number** with allowed values that ranged from 1 to ∞ (i.e., *n* could equal 1, 2, 3…etc). The lowest energy (smallest) orbit corresponded to the lowest allowed energy state called the **ground state** and was designated as $n = 1$. The larger orbits of greater energy were designated as $n = 2$, $n = 3$, $n = 4$, etc. and were said to be **excited states**.

2. As long as an electron moved in an allowed orbit or stationary state, the electron (and therefore the atom) did not radiate or absorb energy.

3. The electron could only move from one allowed orbit to another if it absorbed or emitted an amount of energy exactly equal to the energy difference between the two orbits, ΔE. This meant that the hydrogen atom could only change from one stationary energy state to another.

Bohr's Postulates — Another Look

Postulate 1 employed Planck's theory by quantizing the energies allowed for the hydrogen atom (and thus the electron). Because only certain-sized orbits were allowed, the atom was restricted to existing in only certain energy states and not others. Think of the electron as a ball on a staircase. Just as the ball can only rest on any particular stair and so have only certain amounts of potential energy and not others, so too is the electron restricted to only specific energies.

Postulate 2 meant that the nuclear model of the atom proposed by Rutherford would not collapse as predicted. Although the postulate violated the laws of classical physics, Bohr insisted that it must be true, even though he didn't know why.

Postulates 1 and 3 explained the origin and nature of hydrogen's bright-line spectrum. An atomic spectrum could not be continuous (i.e., a complete rainbow of colors) because an atom's energy states could only be certain values and not others. When a sample of hydrogen gas is heated in a discharge tube, the electrons in the hydrogen atoms absorb sufficient amounts of energy to "jump" to larger orbits. (In any one hydrogen atom, only one electron is involved, but in a sample of the gas, the electrons of many hydrogen atoms are undergoing many transitions). Once in a higher energy orbit, any electron could then return to a lower energy orbit by emitting a specific amount of energy corresponding exactly to the difference between the higher and lower energy orbits (Figure 2.2.3). If the frequency of that emitted energy corresponds to any part of the visible spectrum, then a bright line of that specific color would be seen. Four of hydrogen's electron transitions emitted energy in the visible spectrum.

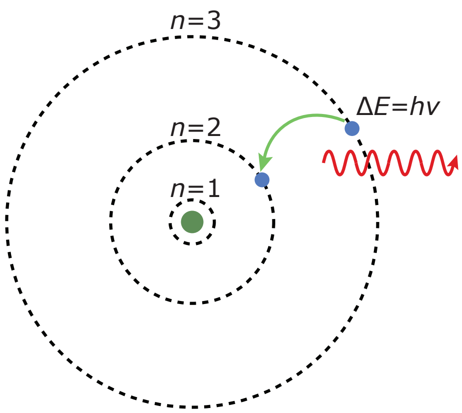


Figure 2.2.3 *When the electron moves to an inner energy level, it emits energy.*

If an excited electron emits energy and drops to $n = 2$ from a higher energy orbit, the wavelength of the emitted energy corresponds to a particular color of visible light. If an electron drops from $n = 3$ to $n = 2$, the energy difference between the two orbits (and therefore the energy emitted) corresponds to that of red light. Hence the red line appears in the emission spectrum. The blue-green line results from an electron transition from $n = 4$ to $n = 2$, the blue line from an electron transition from $n = 5$ to $n = 2$, and the violet line from an electron transition from $n = 6$ to $n = 2$. This series of four bright lines in the visible spectrum is called the Balmer series, named after the Swiss schoolteacher who first derived a mathematical relationship between the lines in hydrogen's visible emission spectrum (Figure 2.2.4).

Bohr's model of the hydrogen atom was successful in explaining the mystery of bright line spectra. His calculations and predictions worked for hydrogen and he even calculated the radius of the orbit for hydrogen's electron in its ground state. In 1922, Niels Bohr was awarded the Nobel Prize in physics.

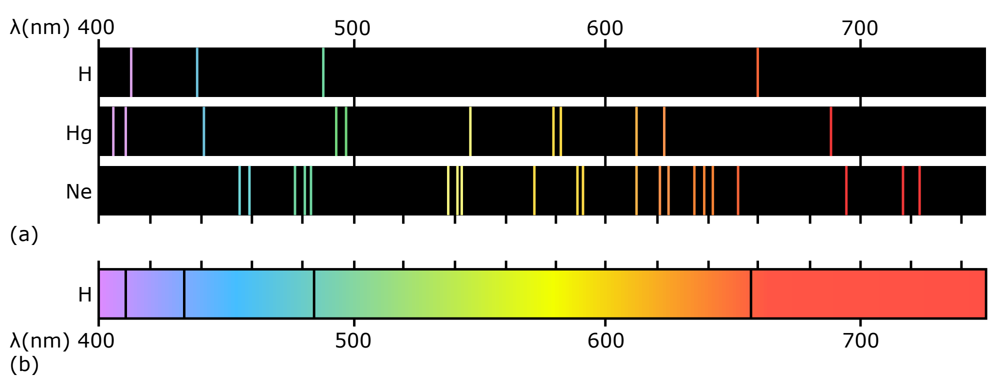


Figure 2.2.4 *(a) The emission spectra of hydrogen, mercury, and neon; (b) The absorption spectrum of hydrogen*

The Emission Spectrum of Hydrogen — Two Views

The diagram on the left in Figure 2.2.5 shows the circular orbits Bohr envisioned for the hydrogen electron and the transitions associated with the Lyman, Balmer, and Paschen emission spectra. The diagram on the right shows that the energy *differences* between various stationary states (n) decrease as the energies of those states increase. The arrows pointing down represent electrons falling to lower energy states and thus emitting energy. Electrons absorbing energy could be indicated by arrows pointing up and would represent absorption spectra.

Any electron transitions from an excited state down to $n = 1$ result in the emission of energy in the ultraviolet region of the electromagnetic spectrum (the Lyman series). Any transitions from excited states down to the third and fourth orbits result in energies in the infrared region being emitted (the Paschen and Brackett series respectively).

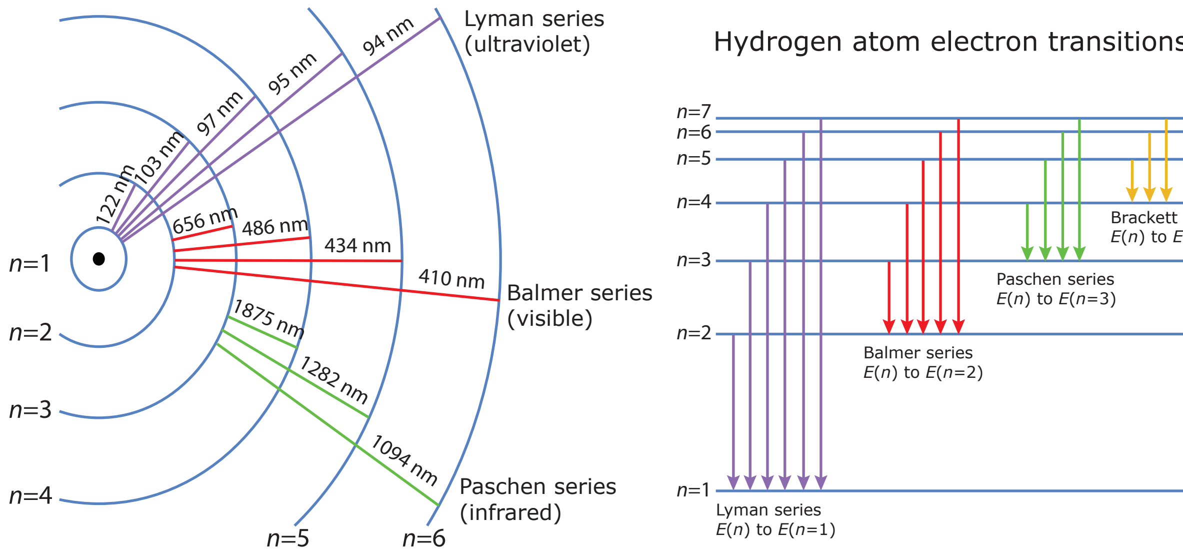


Figure 2.2.5 *The Lyman, Balmer, and Paschen emission series for hydrogen*

Quick Check

1. Describe the appearance of hydrogen's "bright-line" spectrum.

 ____

2. Briefly indicate how electrons generate each visible line in hydrogen's emission spectrum.

 ____

 ____

3. Which electron transitions in the emission spectrum generate lines in the UV region of the electromagnetic spectrum?

 ____

Using Some Simple Equations

In 1885, a Swiss schoolteacher named Johann Balmer found an equation that was able to determine the wavelengths of the lines in the visible portion of hydrogen's emission spectrum. Three years later, the Swedish physicist Johannes Rydberg derived an equation that could be used to calculate the wavelengths of all of hydrogen's spectral lines. This is worth mentioning because if a mathematical relationship exists for a natural phenomenon, it usually means there's a theoretical foundation waiting to be discovered. Both Balmer's and Rydberg's equations were based on data, rather than theory. Neither equation had any physical meaning in terms of atomic structure, but both worked.

The physical meaning was supplied by Niels Bohr. Bohr derived an equation for the energy associated with the electron in each allowed orbit. He correctly predicted the visible, ultraviolet, and infrared spectral lines in hydrogen's emission spectrum by calculating the energy differences between those stationary states.

Although a rigorous mathematical treatment of this material is not intended here, we will present two equations that are quite straightforward. The first equation gives the change in energy ΔE

(energy of photon released) when an electron initially in a higher energy orbit (with a higher quantum number n_h) drops to a lower energy orbit (and so with a lower quantum number n_l).

$\Delta E = b\left(1/n_l^2 - 1/n_h^2\right)$

where b is a constant with value of 2.18×10^{-18} J.

The second equation arises from the fact that, according to Planck's equation, the energy of this photon, $\Delta E = h\nu$. Because $\nu = c/\lambda$, we can replace ΔE with hc/λ. Now dividing both sides of the equation by hc yields:

$1/\lambda = b/hc\left(1/n_l^2 - 1/n_h^2\right)$

This equation allows us to solve for the wavelength λ of the spectral line we would observe when the electron lost energy as it made the above transition.

The combination of the constants, b/hc, is itself a constant. Remembering that Planck's constant, $h = 6.626 \times 10^{-34}$ J·s and that the speed of light, $c = 3.00 \times 10^8$ m/s, we can combine these three constants to give $b/hc = 1.097\,30 \times 10^7\ \text{m}^{-1}$. Let's use this to calculate the wavelength of the spectral line we would see when hydrogen's electron made the transition from $n = 4$ down to $n = 2$.

Sample Problem — Calculating the Wavelength of Emission Spectral Lines

Calculate the wavelength λ (in nm) of the spectral line seen in hydrogen's emission spectrum when hydrogen's electron falls from the fourth allowed orbit ($n = 4$) to the second allowed orbit ($n = 2$).

What to Think about

1. Consider the equation:
   $1/\lambda = (1.097\,30 \times 10^7\ \text{m}^{-1})\left(1/n_l^2 - 1/n_h^2\right)$
   The values of n_l and n_h are given in the question: $n = 4$ and $n = 2$.

2. Convert this to nanometers.
   This value corresponds exactly to the green line seen in hydrogen's emission spectrum.

How to Do It

$$1/\lambda = (1.097\,30 \times 10^7\ \text{m}^{-1})\left(1/n_l^2 - 1/n_h^2\right)$$
$$= (1.097\,30 \times 10^7\ \text{m}^{-1})\left(1/2^2 - 1/4^2\right)$$
$$= (1.097\,30 \times 10^7\ \text{m}^{-1})(0.1875)$$
$$= 2.0574 \times 10^6\ \text{m}^{-1}$$

$$\lambda = \frac{1}{2.0574 \times 10^6\ \text{m}^{-1}} = 4.8604 \times 10^{-7}\ \text{m}$$

$$4.860 \times 10^{-7}\ \cancel{\text{m}} \times \frac{1.0 \times 10^9\ \text{nm}}{\cancel{\text{m}}} = 486.04\ \text{nm}$$

Practice Problem

1. Use equation $\Delta E = b\left(1/n_l^2 - 1/n_h^2\right)$ and the value for b given above to calculate the energy released when an excited hydrogen electron drops from the fourth allowed orbit ($n = 4$) to the second allowed orbit ($n = 2$).

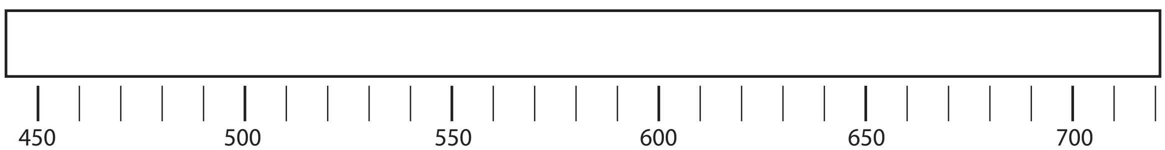
2.2 Activity: The Art of Emission Spectra

When the light emitted by vaporized and then thermally or electrically excited elements is viewed through a spectroscope, a unique line spectrum is observed for each element. In this activity, you will reproduce the emission spectra for lithium, cadmium, sodium, and strontium by coloring in the most visible spectral lines on diagrams representing those spectra.

Materials
- centimeter ruler
- various colors of felt pens or colored pencils, including: blue, red, yellow and black

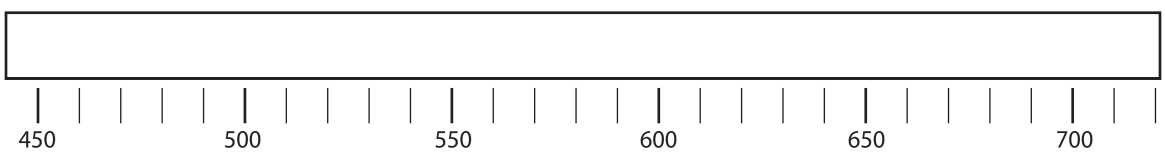
Procedure
1. Using felt pens or colored pencils, draw vertical lines of the appropriate color at each of the indicated wavelengths on the spectral diagrams for the elements listed below.
2. Once all the colors are drawn, use a black felt pen or colored pencil to shade in all of the remaining space on each diagram. Be careful not to blacken out any of the colored vertical lines.
3. After completing the diagrams, look up the emission spectrum of any other element of your choosing and draw that spectrum on the blank diagram below. You will discover that some atomic spectra include many lines while others contain only a few. Some suggestions are helium, mercury, potassium, or calcium.

Li



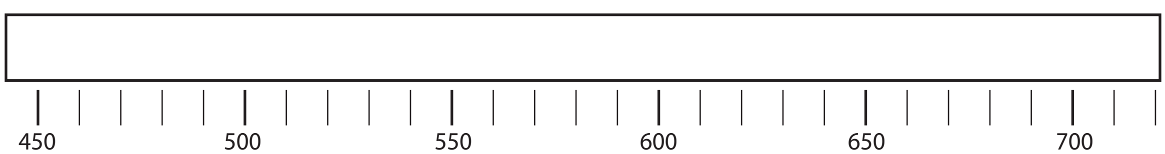
Lithium: 4 colored lines — one blue at ~460 nm, one blue at ~496 nm, one yellow at ~610 nm, and one red at ~670 nm

Cd



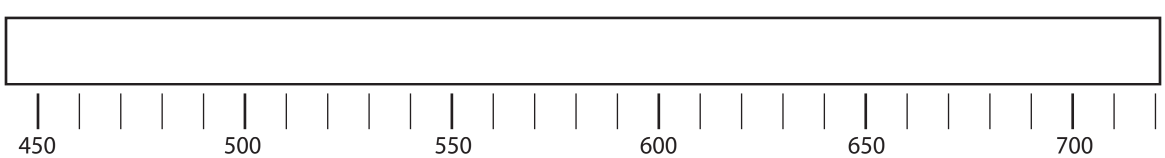
Cadmium: 5 colored lines — three blue at ~467 nm, ~470 nm, and ~508 nm, one yellow at ~609 nm, and one red at ~642 nm

Na



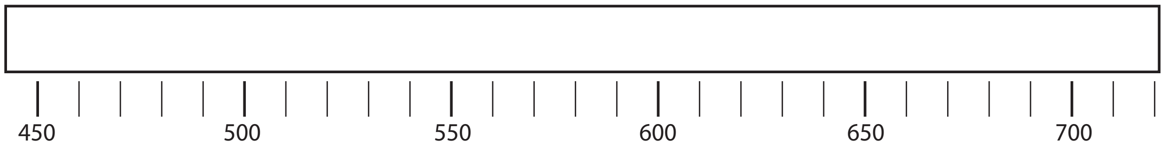
Sodium: 2 bright yellow lines close together at ~590 nm

Sr



Strontium: 7 colored lines — 4 blue at ~460 nm, ~482 nm, ~488 nm, and ~495 nm, and three red at ~670 nm, ~686 nm, and ~715 nm.

Emission Spectrum of Your Choice



Results and Discussion

1. When we view the light emitted by heated or electrically excited vapor with the naked eye, we don't see the separate bright lines you've drawn above. Rather we see a single color resulting from the combination all of those individual bright lines. Many cities use sodium vapor lamps for street lighting. Can you predict what color of light those lamps emit?

2. The principle involving the emission of light resulting from excited electrons is the foundation of many modern conveniences and tools in our society from fluorescent lighting to lasers. Find out what the letters in the word "laser" stand for and find out at least 10 applications of lasers in our society.

2.2 Review Questions

1. Explain the serious problem initially associated with Rutherford's atomic model.

2. State Planck's quantum theory in your own words.

3. Why was this theory not accepted by most physicists at first?

4. What finally convinced the scientific community that Planck's theory was credible?

5. Explain how the work of Planck and Einstein contributed to Bohr's theory about electron behavior.

6. State how Bohr's theory "saved" Rutherford's nuclear atomic model.

7. Briefly explain why hydrogen's visible emission spectrum does not resemble a continuous spectrum or rainbow

8. Describe what you would expect to see if hydrogen's visible emission and absorption spectra were superimposed upon each other.

9. Explain why, when hydrogen's electron transitions occur from excited states down to $n = 1$ or to $n = 3$, no visible spectral lines are observed.