# **Chapter 4: Spectroscopy**

# The Inner Workings of Atoms

### **Outline**

- 4.1 Spectral Lines
- 4.2 The Formation of Spectral Lines
- 4.3 Molecules and Molecular Spectra
- 4.4 Spectral Line Analysis

## Summary

This chapter is in many ways a continuation of Chapter 3. The perspective provided to students is inspirational: to understand the largest and most remote objects in the universe we must understand the smallest forms of matter right here on Earth. Atoms, and the particles of which they are made, are the key to unlocking the information stored in the spectra of astronomical bodies.

The one possible difficulty in teaching this material is that so much of it is relevant to the study of the Sun, stars, and objects beyond and not so much to the study of the solar system. In this case you may either choose to cover this chapter in its sequence or delay it until before Chapter 16 (The Sun). Or you may want to do both by covering it now and then reviewing it again later.

This chapter offers the chance to show the optical spectrum and the information it contains in various demonstrations and as the basis for one or more laboratory exercises. Let students experience the spectra of objects directly by issuing them their own gratings. They will see many familiar objects "in a new light."

# **Major Concepts**

- Types of Spectra
  - Emission
  - Absorption
  - Continuous Spectrum
  - Line Spectrum
  - Kirchhoff's Laws
- Atomic structure and the quanta
- Particle nature of light
- The hydrogen atom
- Molecules
- Spectral analysis

# **Teaching Suggestions and Demonstrations**

#### Section 4.1

It is very traditional to allow students to observe the spectra of various gases. Use a gas discharge tube and power supply and give each student a grating to look through. For classroom demonstrations neon, sodium, and mercury usually produce the brightest spectra. For the laboratory environment, hydrogen and helium are very useful. If it is not possible to do this

demonstration in a large lecture environment, allow the students to check out a grating and observe various light sources such as neon lights, street lamps (incandescent, mercury, or sodium), and fluorescent lights. Have them note which colors occur for each of these. There are excellent yet cheap student gratings available from Learning Technologies Inc.

In a laboratory environment, or as a demonstration, measure the wavelengths of the first three Balmer lines (in the red, green, and violet). Use the following wavelengths and colors for approximate measurements.

Violet	Blue	Green	Yellow	Orange	Red
4100	4600	5000	5700	6000	6500 Å

Determine the approximate wavelengths of the first 3 Balmer lines and calculate the energies of the third, fourth, and fifth energy levels (use 10.2 eV for the energy of the second level, the level from which the Balmer lines originate). Use the following formulae provided earlier in the text.

$$\lambda f = v$$
 and  $E = hf$ 

For example, the first line of hydrogen is seen in the red, so  $\lambda$  is estimated to be 6500Å.

$$f = 4.6 \times 10^{14} \text{ s}^{-1}$$
  
 $E = 3.1 \times 10^{-12} \text{ erg}$   
 $E = 1.9 \text{ eV}$   
 $E_3 = 10.2 + 1.9$   
 $E_3 = 12.1 \text{ eV}$ 

The wavelengths for these three lines are 6563, 4861, and 4340 Å.  $E_4 = 12.75$  eV and  $E_5 = 13.06$  eV. By setting the first energy level at zero eV and drawing the energy levels to scale in the usual way, the structure and convergence of the energy levels becomes quite apparent.

### **Section 4.2**

This is a good opportunity to begin a discussion of the basic structure of the atom. The diameter of the ground state electron orbital in a hydrogen atom is about 1Å. The nucleus is about  $10^{-5}$ Å. This makes the atom rather difficult to model in the classroom, and certainly the figures in the text cannot show the nucleus and orbital to scale. **DEMO** For a 1 cm nucleus (you can use a marble), the electron would have to be placed at 100 meters (length of a football field). A 1 mm nucleus is hard to see in most classrooms but does place the electron at 10 m or about 33 ft. Either way, it will be obvious that the atom has mostly space in it; matter occupies little of that space.

Neutrons can be added to the nucleus to make it heavier; protons can be added to make different elements. Electrons must be added to equal the number of protons, but notice, as in Figure 4.11, many of these electrons will be in orbitals much farther out than in the original model. Using a plastic bag of marbles to represent a heavy element nucleus with lots of protons and neutrons, note that the nucleus does not appear that much larger for heavier elements, compared to the overall size of the atom. No diagram in any text, such as Figure 4.11, can give the scale of this amazing property of atoms. To put the atomic scale into perspective, mention that if the nucleus were modeled by a BB, then the size of the electron orbits would be about the size of a soccer

field. Similarly, if a nucleus of hydrogen, for example, were the mass of a bowling ball, then the mass of each electron would be approximately that of a BB.

Quantization does not occur on the macroscopic scale and is therefore more difficult to understand. The most important concepts to develop are that it requires energy to move up to a higher energy level and the energy levels are quantized. DEMO Attach two rubber balls to each other with a rubber string. Use a larger ball to represent the nucleus and a smaller ball for the electron. The lowest energy state is represented by the balls pulled apart but without the string being stretched. Holding the balls vertically, show that energy (work, actually) must be added to the electron in order for it to be in a higher energy level. When released from that higher energy level, it freely gives up that energy. Continue the demonstration using the concepts of the absorption and emission of light.

**DEMO** A very simple but effective demonstration of quantized emission and absorption is to use a couple of tennis balls and a step ladder. Give the tennis balls to a couple of students in the first row and then stand next to the ladder, which should be situated within an easy toss of the students and visible to all. Explain to the class that the balls represent photons of light. Now, have one student toss a ball (gently) to you and move up one rung on the ladder upon catching it. You have represented an atom engaged in the absorption process. Repeat with the second student and move up another rung. To demonstrate emission, simply toss the balls, one at a time, to other students. Be sure to move down one rung each time you toss a ball away.

#### Section 4.3

Traditionally, the best demonstration of a molecule is to use 3-D, molecular models that could be borrowed from your chemistry instructor colleagues down the hall. **DEMO** If you can find one with some flexibility built in, then use it to show how vibrational and rotational modes are possible. If you can find several models, it is a good idea to let the students pass them around while you discuss the model that you are holding. Of course, if you do not have access to readymade molecular models, then you can easily make a few yourself using anything from straws and marshmallows to Tinkertoys.

#### Section 4.4

By now the students are familiar with the Doppler Effect. Remind the students that the spectral lines consist of very narrow ranges of wavelengths, even consider one wavelength for discussion purposes. DEMO Draw a vertical line on the board or on an overhead transparency. Now, ask the students how the wavelength will change if the emitting atom were moving toward you. Assuming that you were able to elicit the correct response, draw a line just to the left of your original line. This represents the same line only shifted slightly toward shorter wavelengths. "What if the atom is moving away from you?" Accordingly, draw a line just to the right of the original. You should now be looking at a broadened line.

This is yet another example for the scientific process at work. Explain the difference between idealized situations and the "real world." Although the spectrum generated by a given atom might be easily predicted and observed in the laboratory, spectra that arrive from distant stars or nebulae may not be so "perfect." This variation from ideal conditions is not to be considered detrimental, but rather an advantage to the astronomer. Theories of how various phenomena effect spectral content are devised to explain alterations in expected observations of spectra. For example, the presence of a Doppler shift in the light due to motion of the emitting molecule could account for the broadening of the lines.

# **Student Writing Questions**

- 1. Pick an item that is colorful. Describe in detail why it appears colorful; which colors are being reflected and which absorbed? When we say "the shirt is red," is the shirt really red?
- 2. Select various sources of artificial lighting, like a computer screen, calculator display, glow-in-the-dark posters. Describe, in terms of Kirchhoff's laws, how each is able to emit light.
- 3. Go back to Chapter 1 and consider the small scale of matter. Describe how you might zoom in on the tip of your finger and what you would see at each magnification. Keep zooming until you are able to see individual atoms. How much are you having to magnify in order to see at this small scale?
- 4. Look around and find objects whose color is indicative of temperature; think in terms of Wien's law. What are these objects and what would you guess to be their temperatures? How common is color an indicator of temperature?
- 5. In an astronomy laboratory experiment, students are going to observe the spectrum of the Sun. But when they get ready to make their observations they are told to observe the light coming from a bright, white cloud in the sky. Why is this?

# **Answers to End of Chapter Exercises**

#### **Review and Discussion**

- 1. Spectroscopy is the observation and study of spectra. Since light is about the only information received from astronomical objects, this light is the source of all the information about those objects. Spectroscopy is the detailed study of this light and allows many properties of objects to be determined.
- 2. A simple spectroscope is made up of a slit, a prism, and an eyepiece or screen. The slit defines a narrow beam of light. The prism spreads the light out into its various wavelengths or colors. The eyepiece or screen allows the spectrum to be observed.
- 3. The spectrum emitted by a blackbody is known as a continuous spectrum. Light is emitted at all wavelengths but the amount of light emitted at each wavelength varies and depends on the temperature of the blackbody. An absorption spectrum appears like a continuous spectrum but with specific wavelengths missing. Dark vertical lines or bands, which can be quite narrow or very broad, are found throughout the spectrum.
- 4. Gamma rays carry much more energy in every photon than radio waves. They carry enough energy to harm living tissue. In passing through cells, gamma rays can break up important molecules, such as DNA, and also ionize atoms which then cause further cellular damage.
- 5. A photon is a particle of light.
- 6. Color is usually related to wavelength, which in turn is dependent on energy; red is the longest wavelength and violet the shortest wavelength. Since wavelength and frequency are inversely proportional, red has the lowest frequency and energy; violet has the highest frequency and energy.

- 7. Each orbital has a precise energy, like in the Bohr model, but the electron is smeared out in an electron cloud or probability shell. The exact location of the electron cannot be determined.
- 8. The hydrogen atom has one proton in its nucleus and one electron moving around it. The electron is found in one of many possible energy levels or orbitals.
- 9. When a physical quantity is quantized it means that it takes on only specific values rather than a continuous range of values.
- 10. The normal condition for atoms is one in which the number of electrons equals the number of protons in the nucleus. The electrons are in their lowest energy level. When an atom is excited, an electron is found in a higher energy orbital. The precisely-defined energy states or energy levels are referred to as orbitals. They are the regions occupied by electrons that surround the nucleus.
- 11. In order for a photon to be absorbed, it must have an energy that is precisely equal to the energy difference between two energy levels, the lower level which is occupied by an electron. The electron absorbs the photon and moves to the higher energy level. Very quickly thereafter the electron moves back down to the lower energy level by emitting a photon of equal energy to the energy difference between the two levels.
- 12. A star produces a continuous spectrum. However, this light passes through a cooler layer of gas that surrounds the star. Specific wavelengths are absorbed by this gas and the resulting spectrum appears as an absorption spectrum, a continuous spectrum with specific wavelengths missing. Emission lines are not normally found in a stellar spectrum because they are produced in a hot, low density gas. Most stars have a layer of a cool, low density gas forming an absorption spectrum. However, in some cases, a hot, low density layer can form or can be found in clouds of gas between stars and an emission spectrum is seen.
  - Information about the composition and temperature of the cool gas, along with its motions, can be determined from the absorption lines.
- 13. According to Kirchhoff's first law, a luminous solid liquid or dense gas will emit light of all wavelengths and produce a continuous spectrum.
- 14. When the spectrum of the light source is observed, an absorption spectrum is seen because the cloud has absorbed specific wavelengths. But if the cloud is observed, it is seen to emit specific wavelengths, as its atoms that absorbed the light now re-emit the energy.
- 15. The H-alpha absorption line of hydrogen results from electrons jumping from the second to the third atomic orbital. Because the Sun's lower atmosphere is rather cool, relatively few atoms have electrons in the second orbital; most are in the ground state. Hence, in the Sun, the H-alpha line is weak.
- 16. Molecules can rotate and they can vibrate. These two motions have quantized energy levels just like the electrons in an atom. Changes in the rotational or vibrational state of a molecule will produce specific spectral lines unique to each molecule.
- 17. The intensity of a spectral line depends primarily on two factors, the number of atoms of a particular element and the number of those atoms that are able to make the necessary transition between orbitals to produce that spectral line. The first factor gives information on the existence and abundance of an element. The second factor depends on the

- temperature of the gas. Astronomers are thus able to determine the abundance of an element and temperature of the gas from line intensity.
- 18. When an atom produces a spectral line, the wavelength observed depends on the motion of the atom. The Doppler Effect tells us that an atom moving towards us will produce a line that is observed to be shifted to shorter wavelengths; an atom moving away will produce an observed wavelength that is longer. In any hot gas there are atoms moving in all directions; the hotter the gas the faster they move. The net result is a broadening of the spectral line. Mass motions of the gas and stellar rotation will also produce broadening of the line in much the same way.
- 19. If a star is rotating and is oriented so that its equator is approximately in our line of sight, then the light from one side will be approaching us and the other will be receding from us. The light from those two sides will be blue and red shifted, respectively. As the rotation increases, the amount of shifting increases. For a particular spectral line, coming from all parts of the star, a broadening of the line is observed.
- 20. Radial velocity of the star, elemental abundance, temperature, rotation, turbulence, magnetic field, atmospheric pressure.

## **Conceptual Self-Test**

- 1. F
- 2. T
- 3. F
- 4. T
- 5. F
- 6. F
- 7. F
- 8. T
- 9. T
- 10. T
- 11. C
- 12. C 13. D
- 14. C
- 14. C
- 15. B
- 16. B 17. B
- 18. B
- 19. B
- 20. D

#### **Problems**

1. 450 nm blue photon:  $c = f\lambda$ .  $3 \times 10^8$  m/s =  $f \times 450 \times 10^{-9}$  m.  $f = 6.7 \times 10^{14}$  Hz. E = hf, so  $E = 6.63 \times 10^{-34}$  J s  $\times 6.7 \times 10^{14}$  Hz,  $E = 4.42 \times 10^{-19}$  J. In eV this would be  $4.42 \times 10^{-19}$  J /  $1.6 \times 10^{-19}$  J/eV = 2.8 eV. The 200 nm ultraviolet photon will have 2.25 higher energy or  $E = 9.94 \times 10^{-19}$  J and 6.3 eV.

- 2. E = hf, so  $E = 6.63 \times 10^{-34} \text{ J s} \times 10^{11} \text{ Hz}$ ,  $E = 6.63 \times 10^{-23} \text{ J}$ . In eV this would be  $6.63 \times 10^{-23} \text{ J} / 1.6 \times 10^{-19} \text{ J/eV} = 4.1 \times 10^{-4} \text{ eV}$ .
- 3. 2 eV red photon:  $= 3.2 \times 10^{-19}$  J;  $= 4.8 \times 10^{14}$  Hz; = 620 nm. 0.1 eV infrared photon:  $1.6 \times 10^{-20}$  J;  $= 2.4 \times 10^{13}$  Hz; = 12,400 nm or 12.4  $\mu$ m. 5000 eV photon: 1240/5000 = 0.25 nm. See *More Precisely 4-1*.
- 4. E = hf, so energy is proportional to frequency. A 1 nm gamma ray has a frequency of  $3 \times 10^8$  m/s  $= f \times 1 \times 10^{-9}$  m;  $f = 3 \times 10^{17}$  Hz. The 10 MHz radio photon has a frequency of  $10^7$  Hz. The ratio of these two frequencies is  $3 \times 10^{17}$  Hz /  $10^7$  Hz =  $3 \times 10^{10}$ .
- 5.  $c = f\lambda$ .  $3 \times 10^8$  m/s =  $10^8$  Hz ×  $\lambda$ .  $\lambda = 3$  m. 100 eV ×  $1.6 \times 10^{-19}$  J/eV =  $1.6 \times 10^{-17}$  J.  $f = E/h = 1.6 \times 10^{-17}$  J /  $6.63 \times 10^{-34}$  J s =  $2.4 \times 10^{16}$  /s.  $3 \times 10^8$  m/s =  $2.4 \times 10^{16}$  Hz ×  $\lambda$ .  $\lambda = 1.25 \times 10^{-8}$  m. The ratio of these wavelengths is  $3 / 1.25 \times 10^{-8} = 2.4 \times 10^8$  times longer.
- 6.  $\lambda = 589.9 \text{ nm}, f = 3 \times 10^8 \text{ m/s} / 5.899 \times 10^{-7} \text{ m}, f = 5.08 \times 10^{14} \text{ Hz}. E = 3.37 \times 10^{-19} \text{ J} = 2.1 \text{ eV}.$
- 7. Carefully note that the transition is from the third to the second excited state, so the value of n changes from 4 to 3. Using the formula in the *More Precisely 4.2*, the energy in the fourth level is  $E_{10} = 13.6(1-1/10^2)$  eV,  $E_{10} = 13.464$  eV. Likewise,  $E_9 = 13.432$  eV. The difference between these two levels is 0.03190 eV. With  $1.6 \times 10^{-19}$  J in an eV, this energy is  $5.104 \times 10^{-21}$  J. Using E = hf, the frequency of this wave can be calculated.  $5.104 \times 10^{-21}$  J =  $6.63 \times 10^{-34}$  J s  $\times f$ .  $f = 7.70 \times 10^{12}$  Hz. Converting this frequency to wavelength, using  $c = f\lambda$  gives  $3 \times 10^8$  m/s =  $7.70 \times 10^{12}$  Hz  $\times \lambda$ .  $\lambda = 3.90 \times 10^{-5}$  m = 39.0  $\mu$ m, which is in the infrared.

Because the energy of the two levels are so similar, the calculation needs to be carried out to more decimal places.  $E_{100} = 13.59864$  eV,  $E_{99} = 13.598612$  eV. The difference is  $2.76 \times 10^{-5}$  eV or  $4.416 \times 10^{-24}$  J.  $4.416 \times 10^{-24}$  J =  $6.63 \times 10^{-34}$  J s × f.  $f = 6.66 \times 10^{9}$  Hz. This is 6660 MHz which is in the radio range. Its wavelength is  $3 \times 10^{8}$  m/s =  $6.66 \times 10^{9}$  Hz ×  $\lambda$ .  $\lambda = 0.045$  m or 4.5 cm.

 $E_{1000} = 13.5999864 \text{ eV}$ ,  $E_{999} = 13.59998637 \text{ eV}$ . The difference is  $2.7 \times 10^{-8} \text{ eV}$  or  $4.32 \times 10^{-27} \text{ J}$ .  $4.32 \times 10^{-27} \text{ J} = 6.63 \times 10^{-34} \text{ J} \text{ s} \times f$ .  $f = 6.52 \times 10^{6} \text{ Hz}$ . This is 6.52 MHz, which is in the short wave radio range. Its wavelength is  $3 \times 10^{8} \text{ m/s} = 6.52 \times 10^{6} \text{ Hz} \times \lambda$ .  $\lambda = 46.0 \text{ m}$ .

- 8. From the fourth level (third excited state) there are  $4\rightarrow 3$ ,  $3\rightarrow 2$ ,  $2\rightarrow 1$ , or  $3\rightarrow 1$ ,  $4\rightarrow 2$ ,  $2\rightarrow 1$ ,  $4\rightarrow 1$  for a total of 7. The wavelengths are all given in *More Precisely 4-1*.
- 9. This calculation is exactly the same as for Problem 7. Here, the transitions are between levels 2 and 3, 4, 5, 6, 7, and 8. The wavelengths are 656.3, 486.1, 434.1, 410.3.
- 10. Ly $\alpha$  = 121.6 nm.  $\lambda$  = 121.6(1 + 3,000/300,000) = 122.8 nm
- 11. The H- $\alpha$  line has a wavelength of 656.3 nm. Using the Doppler formula from Chapter 3 gives  $656/656.3 = 1 + v / (3 \times 10^8 \text{ m/s})$ .  $v = -5.94 \times 10^5 \text{ m/s}$  or -137 km/s.
- 12.  $5 \times 10^{-19} \text{ J} = 6.63 \times 10^{-34} \text{ J s} \times f, f = 7.54 \times 10^{14} \text{ Hz}.$
- 13. The Doppler equation given in Chapter 3 can also be expressed as

$$\frac{\text{change in wavelength}}{\text{true wavelength}} = \frac{\text{velocity}}{\text{speed of light}}$$

$$\frac{\text{change in wavelength}}{656.3 \text{ nm}} = \frac{12 \text{ km/s}}{300,000 \text{ km/s}}$$

change in wavelength = 0.026 nm

total width = 
$$0.052 \text{ nm}$$

or 0.00008 of the original wavelength

14. Using the Doppler equation from Problem 8 and half the width gives

$$\frac{0.25 \text{ MHz}}{1200 \text{ MHz}} = \frac{v}{300,000 \text{ km/s}}$$

$$v = 63 \text{ km/s}$$

15. From Problem 8, the thermal broadening is 12 km/s. Using this as the Sun's equatorial velocity, and a distance of one circumference traveled in one rotation period gives:

$$12 \text{ km/s} = \frac{2 \times \pi \times 700,000 \text{ km}}{P}$$

$$P = 370,000 \text{ s} = 4.2 \text{ days}$$

Rotation = 0.24 revolutions per day

## **Resource Information**

#### Student CD Media

#### **Movies/Animations**

Classical Hydrogen Atom I Classical Hydrogen Atom II

### **Interactive Student Tutorials**

Emission Spectra Absorption Spectra

### **Physlet Illustrations**

Bohr Atom and Spectra

### **Transparencies**

T-29	Figure 4.2	Continuous and Emission Spectra	p. 85
T-30	Figure 4.3	Elemental Emission	p. 86
T-31	Figure 4.4	Solar Spectrum	p. 86
T-32	Figure 4.5/6	Absorption Spectrum (of Sodium)	p. 87
T-33	Figure 4.7	Kirchhoff's Laws	p. 88
T-34	Figure 4.8/9	Bohr Atom and Modern Atom	p. 89

T-35	Figure 4.10	Atomic Excitation	p. 94
T-36	Figure 4.11	Helium and Carbon Atoms	p. 95
T-37	Figure 4.13	Molecular Emission	p. 97
T-38	Figure 4.17	Thermal Broadening	p. 100
T-39	Figure 4.18	Rotational Broadening	p. 100

# **Suggested Readings**

Collins, D. "Video Spectroscopy — Emission, Absorption, and Flash." *The Physics Teacher* (December 2000). p. 561. Uses a diffraction grating attached to a color video camera to display spectra.

Cornell, E. "Stopping Light in its Tracks." *Nature* (25 January 2001). p. 461. Takes the concept of interaction between light and matter into the lab and modern technology.

Englert, Berhold Georg; Scully, Marlan O; Walther, Herbert. "The duality in matter and light." *Scientific American* (Dec 1994). p. 86. Describe experimental work which supports the idea of wave-particle duality.

Gibbs, W. Wayt. "The infinitesimal gets smaller: the single electron transistor." *Scientific American* (July 1997). p. 34. Describes results from a new method to image the motion of individual electrons in atoms.

Goldberg, Leo. "Atomic spectroscopy and astrophysics." *Physics Today* (Aug 1988). p. 38. A review of atomic spectroscopy and its role in the development of modern astrophysics.

Kaler, James B. "Stars in the cellar: classes lost and found." *Sky & Telescope* (Sept 2000). p. 38. A discussion of spectral classification of stars. See the suggested readings for Chapter 17 for additional articles on stellar spectra.

Newton, J. "Imaging the Sun in H $\alpha$ ." *Astronomy* (June 2003). p. 78. Discussion of why H $\alpha$  lines are important, includes several nice images of the Sun through an H $\alpha$  filter.

Palmquist, B. "Interactive Spectra Demonstration." *The Physics Teacher* (March 2002). p. 140. A creative method for modeling emission, absorption, and continuous spectra that involves throwing balls and jumping on chairs!

Pasachoff, J. "The Bohr Staircase." *The Physics Teacher* (January 2004). p. 38. Takes the "stepladder" idea discussed above, but uses a ladder with the step spacing matching the energy levels of the hydrogen atom.

# **Notes and Ideas**

Class time spent on material: Estimated:	Actual:	
Demonstration and activity materials:		
Notes for next time:		