12.4 Atomic Absorption and Emission Spectra

Long before Rutherford proposed his planetary model for atomic structure, it was known that matter, when heated intensely, gives off light. Solids, liquids, and very dense gases gave off light with a continuous spectrum of wavelengths. On the other hand, the light emitted when a high voltage was applied to a rarefied gas was quite different. The special behaviour of incandescent rarefied gases, studied for half a century before Rutherford, was now to provide a valuable clue to the structure of the atom.

continuous spectrum a spectrum showing continuous (not discrete) changes in intensity

The **continuous spectrum**, such as that from white light, usually originates from a heated solid and results from the interactions between each atom or molecule and its close-packed neighbours. By contrast, in a hot, rarefied gas, the atoms are far enough apart to ensure that any light emitted comes from individual, isolated atoms. It is for this reason that an analysis of the light emitted by a rarefied gas provides a clue to the structure of the gas atoms themselves.

emission spectrum a spectrum that a substance emits with its own specific set of characteristic frequencies

As early as the beginning of the nineteenth century, it was known that the radiation from electrically "excited" gases was discrete rather than continuous; that is, an excited gas gives off only specific frequencies of light. When this light is passed through a spectroscope, a *bright-line emission spectrum* is observed, containing lines of light of the various frequencies given off by that gas. Each gas emits its own specific set of characteristic frequencies, called its **emission spectrum**, making spectroscopy a particularly accurate method for identifying elements (**Figure 1**).

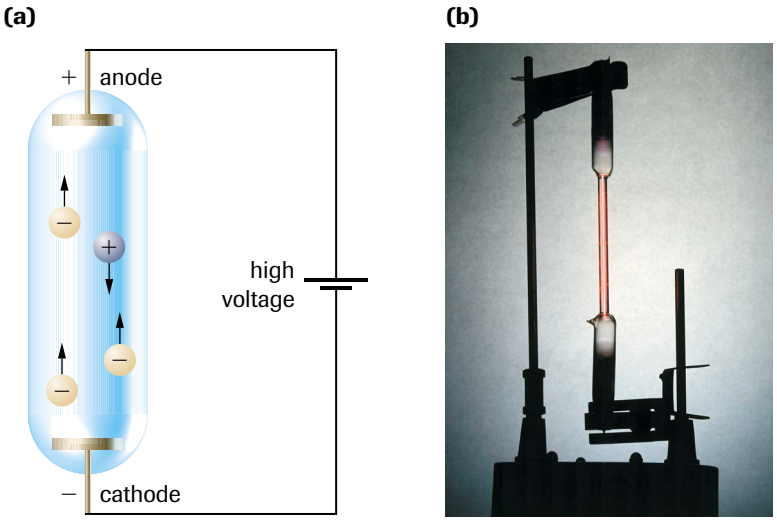


Figure 1
(a) Schematic of a gas discharge tube
(b) Hydrogen is the gas used in this discharge tube.

For example, if a sample of hydrogen gas under low pressure in a vacuum tube is excited by a high electric potential applied between electrodes at the ends of the tube, a pink-purple glow is produced. If this pink-purple light is passed through a spectroscope (Section 10.3), it is found to consist of numerous discrete wavelengths. Four of these are visible in the ordinary school laboratory in the red, blue–green, blue, and violet parts of the spectrum. An additional ten or so lines in the near ultraviolet are discernible by photography with a modest spectrograph. **Figure 2** shows the formation of a typical emission spectrum and the apparatus needed to create it. **Figure 3(a)** shows the visible line spectra of three gases.

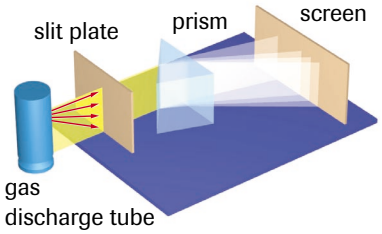


Figure 2
Apparatus used to produce an emission spectrum

A still more extensive examination of the hydrogen emission spectrum, using photographic film sensitive to infrared and far ultraviolet radiation, would reveal that it also contains a number of frequencies in these regions of the electromagnetic spectrum.

It can also be shown that if white light is allowed to pass through a gas, and the transmitted light is analyzed with a spectroscope, dark lines of missing light are observed in the continuous spectrum at exactly the same frequencies as the lines in the corresponding emission spectrum. This so-called **absorption spectrum** is created by light absorbed from the continuous spectrum as it passes through the gas (**Figure 3(b)**).

absorption spectrum the lines of missing colour in a continuous spectrum, at the same frequencies as would be emitted by an incandescent gas of the same element

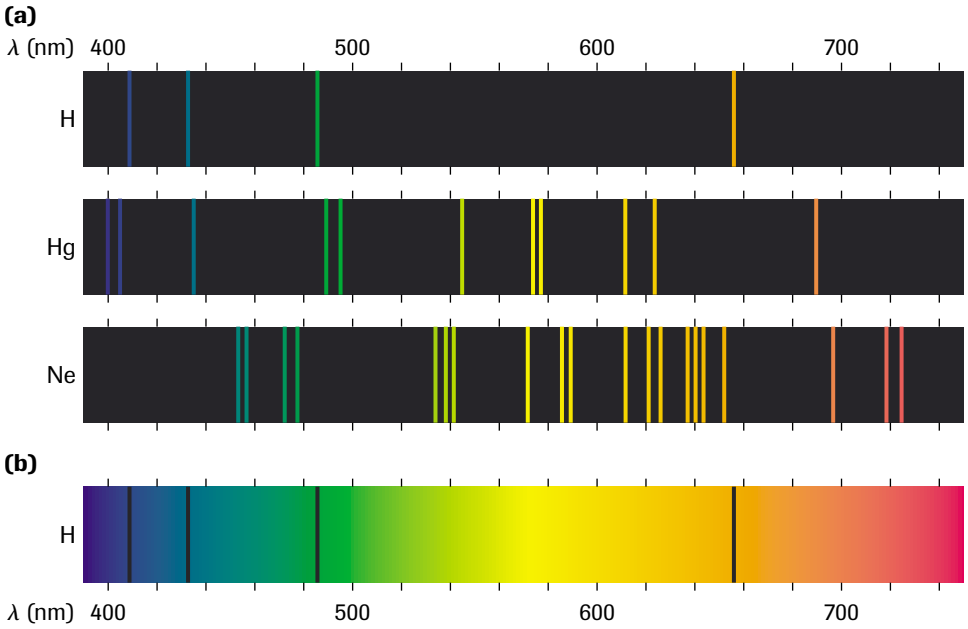


Figure 3
Visible spectra
(a) Line spectra produced by emissions from hydrogen, mercury, and neon
(b) Absorption spectrum for hydrogen. The dark absorption lines occur at the same wavelengths and frequencies as the emission lines for hydrogen in **(a)**.

It is evident that atoms absorb light of the same frequencies as they emit. Our model of the atom must be capable of explaining why atoms only emit and absorb certain discrete frequencies of light; in fact, it should be able to predict what these frequencies are. Since Rutherford's planetary model made no attempt to account for discrete emission and absorption spectra, modifications were needed.

The Franck–Hertz Experiment

In 1914, a team of two German physicists, James Franck and Gustav Hertz (**Figure 4**), provided another significant contribution to our understanding of atomic structure. They devised an experiment to investigate how atoms absorb energy in collisions with fast-moving electrons.

(a) **(b)**

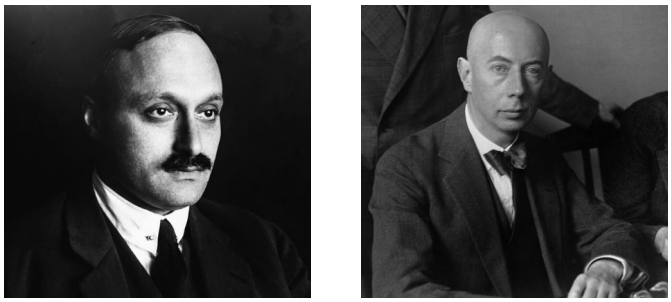


Figure 4
(a) James Franck (1882–1964) and **(b)** Gustav Hertz (1887–1975) received the 1925 Nobel Prize in physics. When the Nazis came to power in Germany, Franck was forced to flee to the United States. In order to carry his gold Nobel Prize medal with him, he dissolved it in a bottle of acid. He later precipitated the metal and recast it.

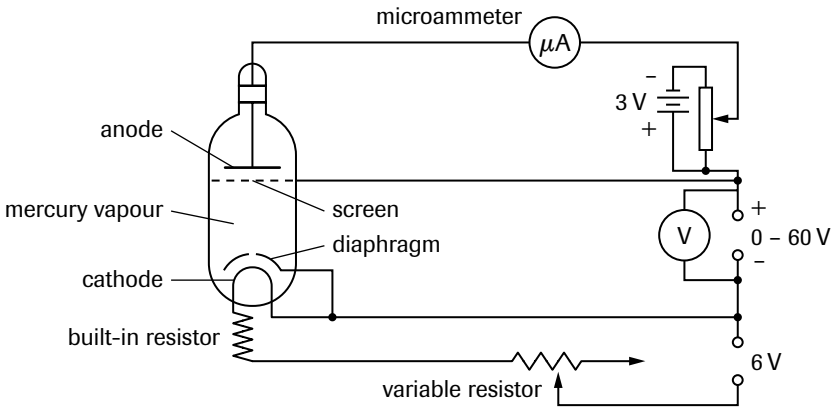


Figure 5
Apparatus used by Franck and Hertz to determine how atoms absorb energy

Franck and Hertz used an apparatus similar to that shown in **Figure 5**. Free electrons emitted from a cathode were accelerated through low-pressure mercury vapour by a positive voltage applied to a wire screen anode, or "grid." Most of the electrons missed this screen and were collected by a plate maintained at a slightly lower voltage. These collected electrons constituted an electric current, measured by a sensitive ammeter.

The experiment consisted of measuring the electric current for various accelerating electrical potential differences. Franck and Hertz found the following:

- As the accelerating potential difference was increased slowly from zero, the current increased gradually as well.
- At a potential of 4.9 V, the current dropped dramatically, almost to zero.
- As the potential was increased further, the current once again began to increase.
- Similar but minor decreases in current occurred at potentials of 6.7 V and 8.8 V.
- Another significant decrease in current occurred at a potential of 9.8 V.

A graph of collected current transmitted through the mercury vapour versus electron accelerating potential difference is shown in **Figure 6**.

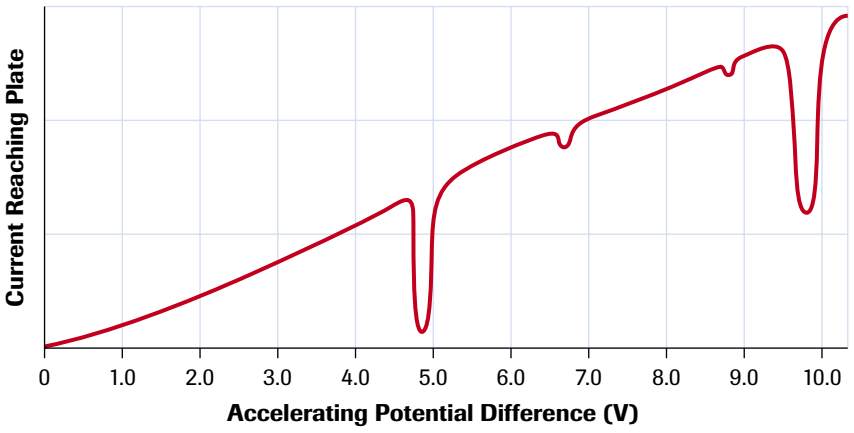


Figure 6
Collected current versus accelerating potential difference

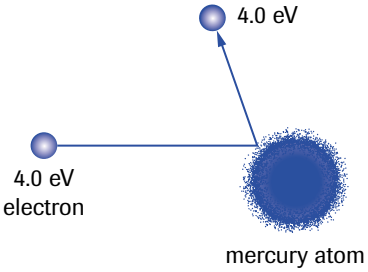


Figure 7
An incident electron with kinetic energy less than 4.9 eV bounces off the mercury atom with no loss of kinetic energy.

An electron accelerated by a potential difference of 4.9 V acquires a kinetic energy of 4.9 eV. Franck and Hertz found that for certain values of bombarding-electron kinetic energy (4.9 eV, 6.7 eV, 8.8 eV, 9.8 eV, ...) the electrons did not pass through the mercury vapour and contribute to the measured plate current. At these specific values, the electrons lost their kinetic energy to collisions with mercury vapour atoms.

Franck and Hertz proposed an explanation that was simple yet elegant:

- Whenever the kinetic energy of the incident electrons was less than 4.9 eV, they simply bounced off any mercury vapour atoms they encountered, with no loss of kinetic energy, and continued on as part of the current (**Figure 7**). These were elastic collisions with little loss of energy from the electrons, so they still passed between the screen wires, reaching the plate.

- Those electrons with a kinetic energy of 4.9 eV that collided with a mercury atom transferred all their kinetic energy to the mercury atom (**Figure 8**). With no energy remaining, they did not reach the plate, being instead drawn to the positive wire screen.
- At kinetic energies greater than 4.9 eV, electrons colliding with mercury atoms could give up 4.9 eV in the collision, with enough kinetic energy left over to let them reach the plate (**Figure 9**).
- At electron energies of 6.7 eV and 8.8 eV, collisions once again robbed the bombarding electrons of all their kinetic energy. However, these collisions were less likely to occur than those at 4.9 eV, so the effect on the current was less severe.
- At the 9.8 V accelerating potential, the electrons reached the 4.9-eV kinetic energy at the halfway point in their flight. There was a good chance the electrons would lose their kinetic energy in a collision with a mercury atom. The electrons were then reaccelerated. Just before they reached the grid, they lost their energy in a second collision, causing the current to dip at 9.8 V.

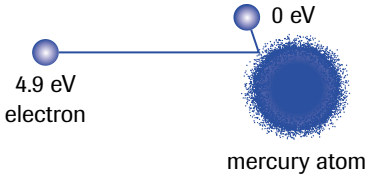


Figure 8
An incident electron with kinetic energy 4.9 eV collides with the mercury atom and loses all its energy.

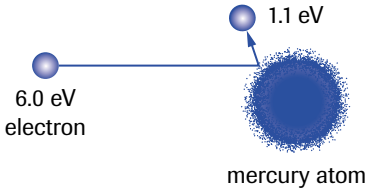


Figure 9
The incident electron with kinetic energy greater than 4.9 eV collides with the mercury atom, losing 4.9 eV of kinetic energy but retaining enough energy to be able to reach the plate.

In a collision between a moving and a stationary puck (Chapter 4), the target puck can absorb any amount of energy from the moving puck in the collision. When the mass of the moving puck is very small in comparison with the stationary puck (as would be the case for a moving electron and a stationary mercury atom), almost no kinetic energy is transferred to the stationary puck, so that the moving puck bounces off with almost all its original kinetic energy. In the electron–mercury atom collision, by contrast, the mercury atom does absorb all of the electron's energy at certain discrete values (4.9 eV, 6.7 eV, 8.8 eV, ...), not what we would expect from classical mechanics. This is the significance of the Franck–Hertz experiment: atoms can change their *internal* energy as a result of collisions with electrons, but only by specific, discrete amounts.

A mercury atom that has not absorbed any extra internal energy as a result of a collision with an electron is normally found in its **ground state**. When it has absorbed 4.9 eV, the smallest amount of energy it is capable of absorbing— its **first excitation energy**—we say the atom is in its *first excited state.* Other greater amounts of internal energy are the second and third excitation energies, respectively. These successive values of internal energy that an atom can possess are called its **energy levels** and can be depicted on an energy-level diagram, such as the one shown in **Figure 10**.

ground state the lowest energy state of an atom

first excitation energy the smallest amount of energy an atom is capable of absorbing

energy levels the various discrete values of internal energy that an atom can possess

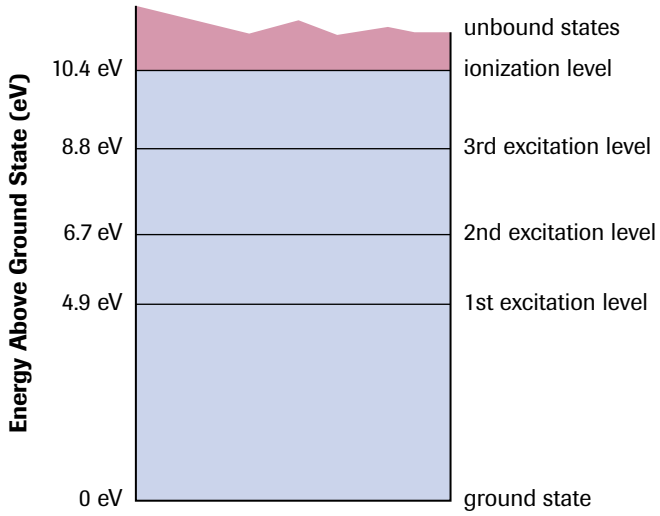


Figure 10
Energy-level diagram for mercury. Although only three excitation levels are shown, there are many more above the third level, spaced progressively closer together up to the ionization level. Beyond the ionization level, electrons are not bound to the nucleus of an atom.

An important difference occurs, though, when the absorbed energy is 10.4 eV or greater. The structure of the mercury atom itself changes. The 10.4 eV of internal energy is too great to be absorbed without the ejection of an electron from the mercury atom, leaving a positive ground-state mercury ion behind. The ejected electron can carry away with it any excess kinetic energy not needed for its release. In this way, the atom can absorb any value of incident energy greater than 10.4 eV. For mercury, 10.4 eV is called its **ionization energy**. The energy-level diagram is a continuum above this energy, rather than a series of discrete levels.

ionization energy the energy required to liberate an electron from an atom

Other elements can be studied with similar electron-collision experiments. Each different electrically neutral element is found to have its own unique ionization energy and set of internal energy levels.

SAMPLE problem 1

Electrons with a kinetic energy of 12.0 eV collide with atoms of metallic element X, in the gaseous state. After the collisions, the electrons are found to emerge with energies of 4.0 eV and 7.0 eV only. What are the first and second excitation levels for atoms of element X?

Solution

Since energy is conserved in the interaction between a free electron and an electron bound to an atom in its ground state,

$$E_n = E_{K,initial} - E_{K,final}$$
$$E_1 = 12.0\text{ eV} - 7.0\text{ eV} = 5.0\text{ eV}$$
$$E_2 = 12.0\text{ eV} - 4.0\text{ eV} = 8.0\text{ eV}$$

The first and second excitation levels are 5.0 eV and 8.0 eV, respectively.

Practice

Understanding Concepts

1. An electron with a kinetic energy of 3.9 eV collides with a free mercury atom. What is the kinetic energy of the electron after the collision?
2. **Figure 10** is the energy-level diagram for mercury. An electron with a kinetic energy of 9.00 eV collides with a mercury atom in the ground state. With what energies can it scatter?
3. The following data were collected when a gaseous sample of a metallic element was bombarded with electrons of increasing kinetic energy:
   (i) Electrons with $E_K < 1.4$ eV collided elastically with the gas atoms.
   (ii) Electrons with $E_K = 1.8$ eV scattered with $E_K = 0.3$ eV.
   (iii) Electrons with $E_K = 5.2$ eV scattered with $E_K = 3.7$ eV or $E_K = 1.9$ eV.
   What are the most likely values for the first two energy levels of this element?

Answers

1. 3.9 eV
2. 4.14 eV; 2.33 eV; 0.16 eV
3. 1.5 eV; 3.3 eV

Analyzing Atomic Spectra

Another Franck–Hertz observation provides more information about the internal energy levels in atoms. When bombarded with electrons whose energy is less than 4.9 eV, the mercury vapour gave off no light. But for electron energies just greater than 4.9 eV, light was emitted. When this light was examined with a spectroscope, it was found to consist of a single frequency of ultraviolet light, of wavelength 254 nm.

It seems that when atoms absorb energy in collisions with electrons, they quickly emit this excess energy in the form of light. Recall from Section 12.1 that Planck's hypothesis stated that light consists of photons whose energy and wavelength are related by the equation

$$E_p = \frac{hc}{\lambda}$$

Thus, ultraviolet light from mercury vapour consists of photons of energy

$$E_p = \frac{(6.63 \times 10^{-34}\ \text{J·s})(3.00 \times 10^{8}\ \text{m/s})}{2.54 \times 10^{-7}\ \text{m}}$$

$$E_p = 7.83 \times 10^{-19}\ \text{J} = 4.89\ \text{eV}$$

This was a significant discovery. Atoms that will only absorb energy in 4.89-eV packages re-emit the energy in the form of photons of exactly the same energy. In other words, mercury atoms raised to their first excitation level by collisions with electrons de-excite, returning to their ground state by emitting a photon whose energy is equal to the difference between the energy of the first excited state and the ground state.

What would we expect to find upon analyzing light from the same mercury atoms when the energy of the bombarding electrons is increased above the second excitation level, say to 7.00 eV? There should be a line in the spectrum composed of photons emitted when the atom de-excites from its second excitation level, of 6.67 eV, to the ground state. The expected wavelength is

$$\lambda = \frac{hc}{E_p}$$

$$= \frac{(6.63 \times 10^{-34}\ \text{J·s})(3.00 \times 10^{8}\ \text{m/s})}{(6.67\ \text{eV})(1.60 \times 10^{-19}\ \text{J/eV})}$$

$$\lambda = 1.86 \times 10^{-7}\ \text{m, or } 186\ \text{nm}$$

Although this line is more difficult to observe in the spectrum of mercury, since its wavelength is too short to be detected on normal photographic film (let alone with the naked eye), special film, sensitive to ultraviolet radiation, does confirm its presence.

There are, however, additional lines in the spectrum of mercury that do not correspond to de-excitations from the various excited states to the ground state. Apparently there are other photons emitted as the atom gives off its excess energy in returning from the second excited level to the ground state. A line observed at a wavelength of 697 nm provides a clue. The energy of these photons is

$$E_p = \frac{hc}{\lambda}$$

$$= \frac{(6.63 \times 10^{-34}\ \text{J·s})(3.00 \times 10^{8}\ \text{m/s})}{6.97 \times 10^{-7}\ \text{m}}$$

$$E_p = 2.85 \times 10^{-19}\ \text{J, or } 1.78\ \text{eV}$$

Since the first excitation level (and hence the lowest) in mercury is 4.89 eV, this photon cannot correspond to a transition from any excited state to the ground state. A careful examination of the energy levels of mercury shows the difference between the first and second excitation levels to be

$$E_2 - E_1 = 6.67\ \text{eV} - 4.89\ \text{eV}$$
$$E_p = 1.78\ \text{eV}$$

DID YOU KNOW ?

Cecilia Payne-Gaposchkin

Based on absorption spectra from sunlight, it was assumed that all of the elements found on Earth were present in the Sun and other stars. In 1925, the British-born astronomer Cecilia Payne-Gaposchkin, while working at Harvard, found that stellar atmospheres are composed primarily of helium and hydrogen. Her discovery formed the basis of the now-accepted theory that the heavier elements are synthesized from hydrogen and helium.

It thus appears that a mercury atom can de-excite from the second excitation level to the ground level in two stages, first emitting a 1.78-eV photon to decrease its energy to the first excitation level, then emitting a 4.89-eV photon to reach the ground state. Further examination of the complete spectrum of mercury reveals other lines corresponding to downward transitions between higher excitation levels.

In general, for the emission spectrum of any element, we can write

$$E_p = E_i - E_f$$

where E_p is the energy of the emitted photon, E_i is the energy of the higher energy level, and E_f is the energy of the lower energy level.

In terms of the wavelength of the spectral line,

$$\lambda = \frac{hc}{E_h - E_l}$$

SAMPLE problem 2

An unknown substance has first and second excitation levels of 3.65 eV and 5.12 eV, respectively. Determine the energy and wavelength of each photon found in its emission spectrum when the atoms are bombarded with electrons of kinetic energy (a) 3.00 eV, (b) 4.50 eV, and (c) 6.00 eV.

Solution

(a) Since the first excitation energy is 3.65 eV, no energy is absorbed, and there is no emission spectrum.

(b) With incident electrons of energy 4.50 eV, only upward transitions to the first excitation level are possible.

$E_p = ?$

$\lambda = ?$

$$\begin{aligned} E_p &= E_i - E_f \\ &= 3.65 \text{ eV} - 0 \text{ eV} \\ E_p &= 3.65 \text{ eV} \end{aligned}$$

$$\begin{aligned} \lambda &= \frac{hc}{E_p} \\ &= \frac{(6.63 \times 10^{-34} \text{ J·s})(3.00 \times 10^8 \text{ m/s})}{(3.65 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} \\ \lambda &= 3.41 \times 10^{-7} \text{ m or } 341 \text{ nm} \end{aligned}$$

The energy and wavelength of each photon are 3.65 eV and 341 nm, respectively.

(c) With incident electrons of energy 6.00 eV, excitation to both the first and second levels is possible. Thus, in addition to the photon emitted in (b), we can have

$$\begin{aligned} E_p &= E_h - E_l \\ &= 5.12 \text{ eV} - 0 \text{ eV} \\ E_p &= 5.12 \text{ eV} \end{aligned}$$

and

$$\begin{aligned} E_p &= E_h - E_l \\ &= 5.12 \text{ eV} - 3.65 \text{ eV} \\ E_p &= 1.47 \text{ eV} \end{aligned}$$

The energies of the photons are 1.47 eV and 5.12 eV. The wavelengths, calculated with the same equation as in (b), are 243 nm and 846 nm, respectively. (None of these photons would be visible to the naked eye because one is infrared and the other two are ultraviolet.)

Practice

Understanding Concepts

4. Calculate the energy difference between the two energy levels in a sodium atom that gives rise to the emission of a 589-nm photon.
5. An atom emits a photon of wavelength 684 nm, how much energy does it lose?
6. A substance has its second energy level at 8.25 eV. If an atom completely absorbs a photon ($\lambda = 343$ nm), putting the electron into the third energy level, what is the energy for this level?
7. Electrons are accelerated in a Franck–Hertz experiment through mercury vapour, over a potential difference of 7.0 V. Calculate the energies of all the photons that may be emitted by the mercury vapour.
8. A spectroscope is used to examine white light that has been passed through a sample of mercury vapour. Dark lines, characteristic of the absorption spectrum of mercury, are observed.
   (a) Explain what eventually happens to the energy the mercury vapour absorbs from the white light.
   (b) Explain why the absorption lines are dark.

Answers

4. 2.11 eV
5. 1.82 eV
6. 11.9 eV
7. 4.9 eV; 6.7 eV; 1.8 eV

DID YOU KNOW ?

Energy-Level Problems

The energy levels used in some of the problems are illustrative only and do not necessarily correspond to actual elements or the laws that govern them.

Analysis of Absorption Spectra

As you learned earlier, examination of emission spectra is not the only way in which the internal energy levels of an atom can be probed. Similar information is learned if a beam of white light passes through a sample of the substance. Photons absorbed by the atoms are missing from the transmitted light, causing dark lines (gaps) to appear in the continuous spectrum.

The absorption of the photons by the atoms causes transitions from a lower internal energy level (normally the ground state) to some higher level (an excited state), but only if the energy of the photon is *exactly* equal to the difference between the two energy levels. The relationship between the energy of the photons absorbed and the internal energy levels of the atom is the same as for an emission spectrum, except that the order of the process is reversed, the initial energy level being lower and the final level higher:

$$E_p = E_f - E_i$$

For example, in the absorption spectrum of sodium, dark gaps appear at (ultraviolet) wavelengths of 259 nm, 254 nm, and 251 nm. What energy difference between internal energy levels corresponds to each of these absorption bands?

For the 259-nm line, the energy of the absorbed photon is given by

$$E_p = \frac{hc}{\lambda}$$

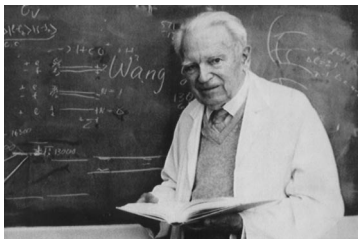
$$= \frac{(6.63 \times 10^{-34}\ \text{J·s})(3.00 \times 10^{8}\ \text{m/s})}{2.59 \times 10^{-7}\ \text{m}}$$

$$E_p = 7.68 \times 10^{-19}\ \text{J, or } 4.80\ \text{eV}$$

Thus, the energy levels in sodium are 4.80 eV apart. Photons of that energy are absorbed from the incoming light, causing electrons in the sodium atoms to jump from the lower to the higher level. Similarly, for the other two lines, the energy differences are 4.89 eV and 4.95 eV, respectively.

DID YOU KNOW ?

Gerhard Herzberg



Dr. Gerhard Herzberg (1904–1999) was born and educated in Germany, where he studied molecular spectroscopy. There he discovered the so-called "Herzberg bands" of oxygen in the upper atmosphere, explaining such phenomena as the light in the night sky and the production of ozone. He left Germany before World War II, settling at the University of Saskatchewan. Although Herzberg considered himself a physicist, his ideas and discoveries did much to stimulate the growth of modern chemical development. He was awarded the 1971 Nobel Prize in chemistry. The Herzberg Institute of Astrophysics in Ottawa is named after him.

This analysis of absorption spectra explains why most gases, including mercury vapour, are invisible to the eye at room temperature. Even the most energetic photons in visible light (deep violet ~3 eV) do not have sufficient energy to excite a mercury atom from the ground state to its first excitation level (4.87 eV) and be absorbed from the white light. Thus, all the photons in the visible light pass through the mercury vapour without being absorbed, rendering the vapour invisible.

You may wonder why the re-emission of photons does not act to fill in the missing spaces in the absorption spectrum. To a limited extent it does. However, the re-emitted photons are radiated in all directions at random, with only a few travelling in the direction of the original beam. Also, for absorption to other than the first excitation level, the de-excitation mode may result in a series of photons, different from the ones absorbed, being emitted.

The emission spectrum of any element contains more lines than its absorption spectrum does. As we saw, lines in an emission spectrum can correspond to downward transitions between two excited states as well as to transitions from any excited state to the ground state. On the other hand, since most atoms are normally in their ground state, only absorptions from the ground state to an excited state are likely. Atoms do not remain in an excited state for a sufficiently long time to make a further absorption to an even higher excited state probable. For example, the emission and absorption spectra of sodium vapour are shown in **Figure 11**.

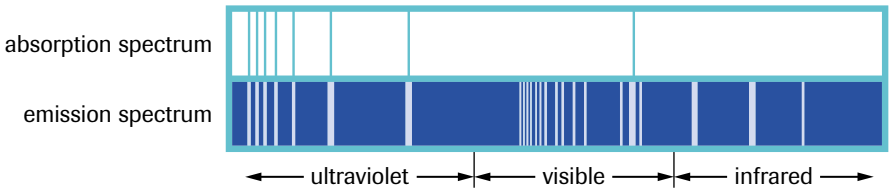


Figure 11
The absorption and emission spectra of sodium vapour

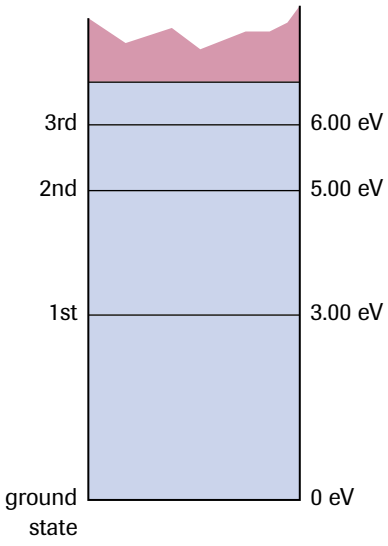


Figure 12
Energy-level diagram for hypothetical element X in question 11

Practice

Understanding Concepts

9. Atoms can receive energy in two different ways. Describe each way, and provide an example.

10. The emission spectrum of an unknown substance contains lines with the wavelengths 172 nm, 194 nm, and 258 nm, all resulting from transitions to the ground state.
(a) Calculate the energies of the first three excited states.
(b) Calculate the wavelengths of three other lines in the substance's emission spectrum.

11. **Figure 12** is the energy-level diagram for hypothetical element X. Calculate all of the wavelengths in both the emission and the absorption spectra.

Answers

10. (a) 4.82 eV; 6.41 eV; 7.22 eV
    (b) 518 nm; 782 nm; 152 nm
11. 1240 nm; 414 nm; 207 nm; 622 nm; 249 nm; 249 nm; 414 nm; 207 nm

Fluorescence and Phosphorescence

When an atom absorbs a photon and attains an excited state, it can return to the ground state through a series of intermediate states. The emitted photons will have lower energy, and therefore lower frequency, than the absorbed photon. The process of converting high-frequency radiation to lower-frequency radiation by this means is called **fluorescence**.

The common fluorescent light applies this principle. Electrons are liberated in the tube as a filament at the end is heated. An applied anode-cathode potential difference accelerates the electrons, which then strike atoms of gas in the tube, exciting them. When the excited atoms return to their normal levels, they emit ultraviolet (UV) photons that

fluorescence the process of converting high-frequency radiation to lower-frequency radiation through absorption of photons by an atom; when the light source is removed, the fluorescence stops

DID YOU KNOW?

Energy-Efficient Lighting
Fluorescent lights are four to six times more energy-efficient than incandescent lights of the same radiated light intensity.

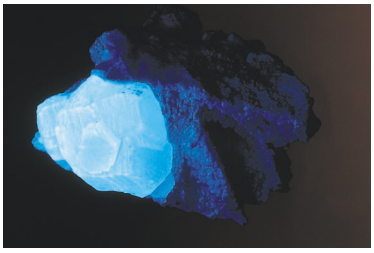
strike a phosphor coating on the inside of the tube. The light we see is a result of this material fluorescing in response to the bombardment of UV photons. Different phosphors emit light of different colours. "Cool white" fluorescent lights emit nearly all the visible colours, while "warm white" fluorescent lights have a phosphor that emits more red light, thereby producing a "warmer" light.

The wavelength for which fluorescence occurs depends on the energy levels of the bombarded atoms or molecules. Because the de-excitation frequencies are different for different substances, and because many substances fluoresce readily (**Figure 13**), fluorescence is a powerful tool for identification of compounds. Sometimes the simple observation of fluorescence is sufficient for the identification of a compound. In other cases spectrometers must be used.

Lasers and fluorescence are often used in crime detection. The radiation from an argon laser causes the perspiration and body oils in fingerprints to fluoresce. In this technique a laser beam illuminates a darkened region where fingerprints are suspected. The forensic technician wears glasses that filter the laser light but allow the fluorescence of the fingerprints to pass through.

Another class of materials continues to glow long after light is removed. This property is called **phosphorescence**. An excited atom in a fluorescent material drops to its normal level in about 10^{-8} s. By contrast, an excited atom of a phosphorescent material may remain in an excited state for an interval ranging from a few seconds to as long as several hours, in a so-called **metastable** state. Eventually, the atom does drop to its normal state, emitting a visible photon. Paints and dyes made from such substances are used on the luminescent dials and hands of watches and clocks and in the luminescent paints applied as a safety measure to doors and stairways.

(a)



(b)

Figure 13
(a) When ultraviolet light is directed at certain rocks—in this case, witherite attached to a piece of barite—they fluoresce.
(b) When the light source is removed, the fluorescence stops.

Lasers

The principle of the **laser** was first developed for microwave frequencies in the *maser* (the "m" stands for microwaves), developed by the American physicist Charles H. Townes in the 1950s. (Townes shared the 1964 Nobel Prize in physics with Basov and Prochorov for this work.) The first maser used ammonia gas. Subsequently, other substances, including ruby, carbon dioxide, argon, and a mixture of helium and neon, were found to have "masing" or "lasing" action. Although there are several different types of lasers, the general principles involved can be illustrated in the action of the helium–neon laser, the type most commonly used in classroom and laboratory demonstrations.

An excited atom can emit photons either through **spontaneous emission** or through **stimulated emission**. The absorption of a quantum of energy by a helium atom raises an electron to a higher energy level. The electron usually moves spontaneously to a lower energy level in a relatively short time ($\sim 10^{-8}$ s), emitting a photon. There is no amplification in spontaneous emission, since the energy absorbed by the atoms is nearly equal to what is radiated.

First predicted by Einstein, stimulated emission can produce amplification, but only under certain conditions. If a photon passes an excited neon atom, it may stimulate the atom to emit a photon additional to the incident photon and identical to it. Consequently, although one photon approaches the atom, two identical photons leave. For stimulated emission to take place, the incident photon must have exactly the same frequency as the photon emitted by the atom. The two photons leaving the atom then not only have the same frequency and wavelength but also travel in the same direction, exactly in phase, and with the same polarization properties. In other words, the emitted light exhibits **coherence**.

Suppose there is a large group of atoms with more atoms in the excited state than in the ground state, and suppose that the energy-level difference for the atoms is exactly the same as the energy of the photons in the incident light beam. A first photon interacting

phosphorescence the property of some materials that allows them to emit light after excitation has been removed

metastable state of sustained excitation by electrons in which they can remain excited for comparatively long times

laser acronym for Light Amplification by Stimulated Emission of Radiation; source of monochromatic, coherent light

spontaneous emission emission of a photon by an electron as a result of the absorption of a quantum of energy by an atom; the electron moves spontaneously to a lower energy level in a relatively short time ($\sim 10^{-8}$ s)

stimulated emission process in which an excited atom is stimulated to emit a photon identical to a closely approaching photon

coherence property of light in which photons have the same frequency and polarization, travel in the same direction, and are in phase

population inversion the condition in which more atoms are in a metastable state than in the ground state

with an excited atom could produce a second photon; these two photons could stimulate the emission of two more; and those four, four more. A chain reaction would quickly occur, amplifying the light. Unfortunately, however, the number of atoms in the ground state is, under normal conditions, greater than in the excited state.

When more atoms are in a metastable condition than are in the ground state, we say there is a **population inversion**. For laser action to take place, both population inversion and the conditions for stimulated emission must exist in the lasing medium.

The red light of the helium–neon laser is produced in a narrow glass tube (capillary tube) containing a mixture of 85% helium and 15% neon, at low pressure. A metal cathode is outside the tube and an anode inside one end of the tube. A potential difference of approximately 8 kV creates a strong electric field that provides a continuous source of energy for the laser, much like a gas discharge tube. Fused to the capillary tube at one end is a 99.9% reflective flat mirror. At the other end, another mirror reflects 99% of the light, transmitting 1%. It is this transmitted light that is the output of the laser (**Figure 14**).

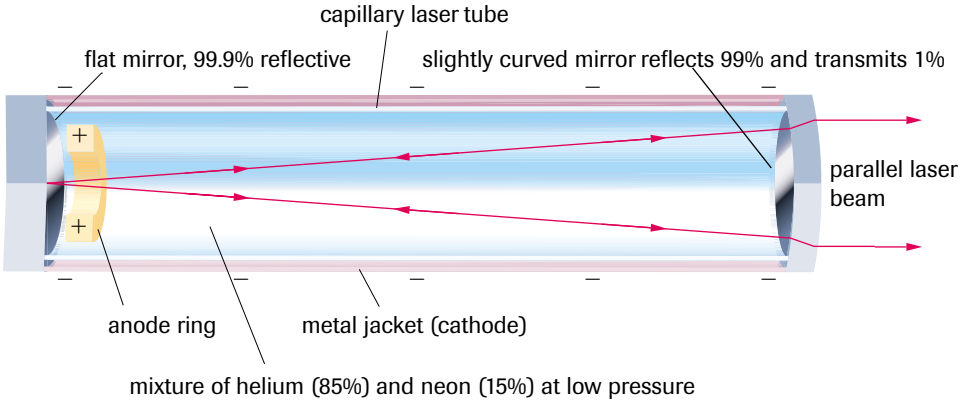


Figure 14
Structure of a helium–neon laser

The strong electric field along the length of the laser tube causes free electrons to gain kinetic energy as they are accelerated toward the positive anode. There is a high probability that an energetic electron will collide with a helium atom before reaching the anode, putting the atom into its excited state as one of its electrons jumps to a higher energy level. The thermal motions of the excited helium atoms result in collisions with neon atoms in the laser tube. During such collisions, a helium atom may revert to its ground state, passing energy to the neon atom. Conveniently, helium has exactly the same energy in its excited state as the neon atom requires to raise it to its metastable state. When an excited neon electron makes a downward transition (**Figure 15**),

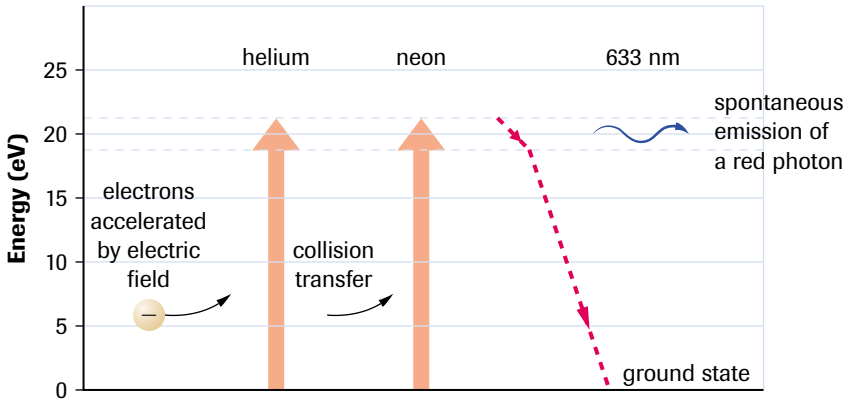


Figure 15
Energy absorption, collision transfer, and spontaneous emission of neon light

DID YOU KNOW ?

John Polanyi

John Polanyi (1929–) worked initially at the National Research Council in Ottawa and then at the University of Toronto in the early 1950s. Using an infrared spectrometer, he measured the light energy emitted by the newly formed products of a chemical reaction. The product molecules emitted a very faint light (invisible to the human eye) called *infrared chemiluminescence*. Polanyi's ability to measure the vibrational and rotational motions in the product molecule earned him the 1986 Nobel Prize in chemistry. Because he understood the source of this faint light, he was able to propose vibrational and chemical lasers, the most powerful sources of infrared radiation ever developed.

1.96 eV of energy is released, and a photon with a wavelength of 633 nm is created. Since there is a population inversion in the tube, this photon stimulates the emission of an identical photon from an adjacent neon atom that, in turn, produces more stimulations along the tube. To strengthen the output of coherent light, the mirrors at each end of the tube reflect the light along the axis of the tube, back and forth through the laser medium. Further reinforcement is achieved with each passage of photons along the tube as a multitude of neon atoms are stimulated to produce 633-nm photons. The mirrors reflect most, but not all, of the light. They transmit a small percentage of the light with each reflection, sufficient to produce the bright laser beam emerging from the laser aperture (**Figure 16**).

The type of laser described above is a *continuous* laser. In such a laser, when the atoms are stimulated and fall down to a lower energy level, they are soon excited back up, making the energy output continuous. In a *pulsed* laser, on the other hand, the atoms are excited by periodic inputs of energy, after which they are stimulated to fall to a lower state. The process then recycles, with another input of excitation energy.

Lasers are used in a wide variety of medical applications: in eye surgery (**Figure 17**), for the destruction of tissue, for the breaking up of gallstones and kidney stones, for optical-fibre surgery, for the removal of plaque from clogged arteries, for cancer treatment, and for cauterization during conventional surgery. In addition, lasers are useful in research into the functions of the cell. In industry, lasers are used for the welding and machining of metals, for the drilling of tiny holes, for the cutting of garment cloth, for surveying and distance measurements, for fibre-optics communication, and for holography.

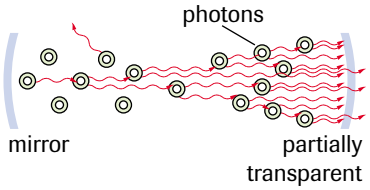


Figure 16
The chain-reaction effect of stimulated emissions in the laser tube

SUMMARY Atomic Absorption and Emission Spectra

- A continuous spectrum given off by a heated solid is caused by the interactions between neighbouring atoms or molecules. An emission spectrum or line spectrum is emitted from electrically "excited" gases.
- An absorption spectrum occurs when some of the light from a continuous spectrum is absorbed upon passing through a gas. Atoms absorb light of the same frequencies that they emit.
- The Franck–Hertz experiment showed that the kinetic energy of incident electrons is absorbed by mercury atoms but only at discrete energy levels.
- An atom is normally in its ground state. The excited states or energy levels are given by the discrete amounts of energy the atom can internally absorb.
- Ionization energy is the maximum energy that can be absorbed internally by an atom, without triggering the loss of an electron.
- In the emission spectrum, the energy of the emitted photon equals the change in the internal energy level: $E_p = E_h - E_l$.
- When a photon is absorbed, its energy is equal to the difference between the internal energy levels: $E_p = E_h - E_l$.
- Atoms can receive energy in two ways: by collisions with high-speed particles, such as electrons, and by absorbing a photon.
- Once raised to an excited state, an atom can emit photons either through spontaneous emission or through stimulated emission. Light amplification requires stimulated emission.

DID YOU KNOW ?

Geraldine Kenney-Wallace

Geraldine Kenney-Wallace, born and initially educated in England, took her Ph.D. in chemical physics at the University of British Columbia. In 1974, Kenney-Wallace organized Canada's first ultra-fast laser laboratory at the University of Toronto where she was professor of physics and chemistry. In 1987, she achieved time scales of 8×10^{-14} s for research into molecular motion and optoelectronics. After serving as President of McMaster University in Hamilton, she returned to research in the U.K. She has received 13 honorary degrees.

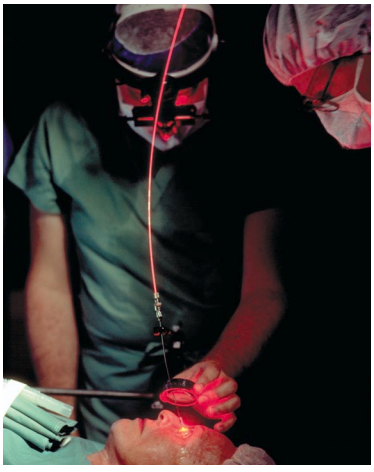


Figure 17
Laser being used in eye surgery

- Some substances or combinations of substances have metastable excited states. A population inversion occurs when more atoms are in a metastable condition than in the ground state.
- For laser action to take place, both population inversion and the conditions for stimulated emission must exist in the lasing medium.
- Lasers are of two types: continuous and pulsed.

Section 12.4 Questions

Understanding Concepts

1. Compare and contrast continuous, line, and absorption spectra.
2. Explain why the Franck–Hertz experiment was so important in the development of the quantum model of the atom.
3. Compare spontaneous emission with stimulated emission.
4. In what ways does laser light differ from, and in what ways does it resemble, light from an ordinary lamp?
5. Explain how a 0.0005-W laser beam, photographed at a distance, can seem much stronger than a 1000-W street lamp.
6. A certain variation of a helium—neon laser produces radiation involving a transition between energy levels 3.66×10^{-19} J apart. Calculate the wavelength emitted by the laser.
7. A laser suitable for holography has an average output power of 5.0 mW. The laser beam is actually a series of pulses of electromagnetic radiation at a wavelength of 632.8 nm, lasting 2.50×10^{-2} s. Calculate
   (a) the energy (in joules) radiated with each pulse
   (b) the number of photons per pulse

Applying Inquiry Skills

8. The energy-level diagram of atom X is shown **Figure 18**. Assuming that atom X is in its ground state, what is likely to occur when
   (a) a 9.0-eV electron collides with the atom
   (b) a 9.0-eV photon collides with the atom
   (c) an 11.0-eV photon collides with the atom
   (d) a 22.0-eV electron collides with the atom

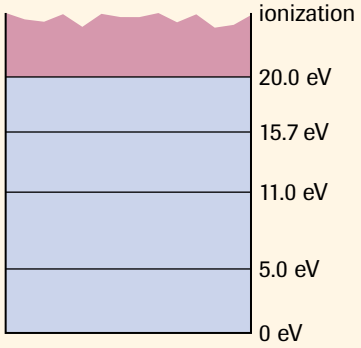


Figure 18
Energy levels for atom X

9. Outline a method in which an astronomer can determine the approximate average temperature of the surface of a star by analyzing its spectrum.

Making Connections

10. What can the absorption spectrum of sunlight tell you about the composition of the gases at the Sun's surface?
11. The emission line spectrum for hydrogen from a distant star is shifted toward the red end of the visible spectrum. What conclusion can be drawn about the star?

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12. In addition to the gas lasers, there are many other types: solid-state, excimer, dye, and semiconductor. One of the most powerful lasers used to cut metal and other dense surfaces is the carbon dioxide (CO_2) gas laser. Research the Internet and other sources, and find out how the CO_2 gas laser works and how it has been applied. Present your findings in a creative way.

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13. A missile shield for North America that uses lasers to knock out incoming missiles has been researched and tested since the 1980s. Research this technology and answer the following questions:
   (a) How would the shield work? In particular, what types of lasers have been proposed?
   (b) What are some of the major technical challenges?
   (c) Why do some consider that the production of these devices could provoke the proliferation of missiles?

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