

Chapter 15

The Interactions of Matter with Light I The Classical Electron Theory of Optics

When a beam of light strikes a piece of matter, many changes can take place, both in the light and in the matter. These changes are of great interest to the chemist because they provide the basis for many of his most important research tools (e.g., the spectroscope, the refractometer, the colorimeter, the polarimeter, light scattering, x-ray diffraction, and the photoactivation of chemical reactions). It is therefore advisable that the chemist understand in some detail what happens when matter and radiation interact. Briefly, some of the more important changes that may occur are these:

The direction of the incident beam can be changed by *reflection* and *refraction*.

The beam can be decomposed into other beams by *diffraction*, *double refraction*, and *scattering*.

If scattering occurs, the scattered light may have the same wave length as the incident beam (*Rayleigh scattering* or *coherent scattering*) or the scattered light may have a different wave length (*Raman scattering* or *incoherent scattering*).

If the incident beam is plane polarized, the plane of polarization may be rotated on passing through the substance (*optical rotation*) and the degree of polarization may be reduced (*depolarization*).

The light beam can disappear, the energy of the light reappearing as heat or sometimes in other forms (*absorption*). The extent of the absorption may depend on the orientation of the plane of polarization in the incident beam (*dichroism*). Absorption may be followed, after a time interval, by re-emission of light that usually has a different color than the incident light (*fluorescence* if the time interval is short and *phosphorescence* if it is long). Light absorption may also produce chemically reactive substances (*photoactivation* and *photochemical reaction*).

Finally, matter can be made to *emit* light if it is properly "excited"—for instance by heat or by bombardment with high velocity electrons, as in a spark gap.

Theories are available that account for these and other interactions in terms of the atomic composition of matter. None of these theories are completely satisfactory, but in this chapter and in the next chapter we shall outline an approach that is adequate for essentially all of the interactions a chemist is likely to encounter.* In this chapter we shall outline the classical approach known as the *electron theory of optics*. This theory was one of the major developments in physics toward the end of the nineteenth century. Much of the theory was worked out by the Dutch physicist, H. A. Lorentz. After 1900 the theory ran into a series of fundamental difficulties, which played a predominant part in the establishment of quantum theory. (Lorentz' book (1) is an interesting and detailed account of the theory that describes the difficulties as they appeared to the pre-quantum theorist.) Although the classical electron theory has proven to be inadequate, it has one very useful attribute: the correct quantum mechanical theory gives many of the same equations for optical properties as did the electron theory. Thus in many instances one has merely to take the old classical equations and reinterpret some of the quantities that appear in them. This will be shown in the next chapter.

The justification for describing the classical electron theory in some detail is clear. The classical theory gives an understandable physical explanation of the optical properties of matter. This explanation is much easier for the average student to grasp in his first encounter with optics than is the much more mathematical quantum theory of radiation. Furthermore, even though the classical theory is wrong, it can be corrected by a mere reinterpretation of some of the basic classical concepts.

A. The Basic Assumptions in the Classical Electron Theory of Optics

Around the year 1900 it seemed that the final concepts were at hand out of which a complete classical theory of the atom could be constructed. J. J. Thomson had discovered that electrons are present in all matter and the

* The interactions for which this approach fails are chiefly those involving radiation of very short wave length, especially where the Compton effect comes into play and where matter is converted into radiation, and *vice versa*.

movements of electrons, controlled by Newton's laws of motion, were expected to account for all phenomena that depend on the internal dynamics of atoms. It was supposed that atoms consist of a massive diffuse cloud of positive charge in which the electrons were embedded in such a way that they could oscillate in simple harmonic motion. Even though this idea had ultimately to be discarded, it is interesting and instructive to look at some of its consequences, particularly as they concern the interactions of radiation with matter.

Our discussion of this theory will be based on a set of simple assumptions, which we shall list together with brief justifications in each instance.

Assumption 1. A charge e in an electric field \mathbf{E} is acted on by a force given by

$$\mathbf{F} = e\mathbf{E} \quad (\text{A-1})$$

in the direction of the field. This can be taken as a definition of an electric field.

Assumption 2. Light consists of oscillating electric and magnetic fields. The directions of both fields are perpendicular to the direction in which the light is propagated. At a time t the electric field associated with a beam of light moving through a vacuum in the positive z -direction is given by

$$\mathbf{E} = \mathbf{E}_0 \cos \omega(t - z/c) \quad (\text{A-2})$$

where \mathbf{E}_0 is a vector whose size and direction are constant in both time and space, c is the velocity of light, $\omega = 2\pi\nu$, and ν is the number of oscillations per second as the light wave passes a fixed point. The constant ω is called the "circular frequency" and ν is called the "ordinary frequency." We shall use the term "frequency" for both of these quantities; the context will always reveal which quantity is referred to.

The magnetic field, \mathbf{H} , at any point in a light wave is equal in magnitude to the electric field, \mathbf{E} , provided that \mathbf{E} is expressed in electrostatic units (e.s.u.) and \mathbf{H} is expressed in electromagnetic units (e.m.u.).* Thus

$$|\mathbf{H}| = |\mathbf{E}| = |\mathbf{E}_0| \cos \omega(t - z/c) \quad (\text{A-3})$$

* Practical electrical and magnetic units are related to electrostatic units (e.s.u.) and electromagnetic units (e.m.u.) in the following way.

Electric field strength	{	1 e.s.u. = 300 volts/cm.
		1 e.m.u. = 10^{-8} volts/cm.
Magnetic field strength	{	1 e.s.u. = 3.34×10^{-11} gauss
		1 e.m.u. = 1 gauss
Quantity of electricity	{	1 e.s.u. = 3.34×10^{-10} coulomb
		1 e.m.u. = 10 coulombs

The two fields, \mathbf{E} and \mathbf{H} , differ, however, in their directions, being perpendicular to each other and to the direction of propagation, such that \mathbf{E} , \mathbf{H} , \mathbf{z} form a right handed system (*cf.* page 26), as shown in Fig. 15-1. That is, light is a transverse wave.

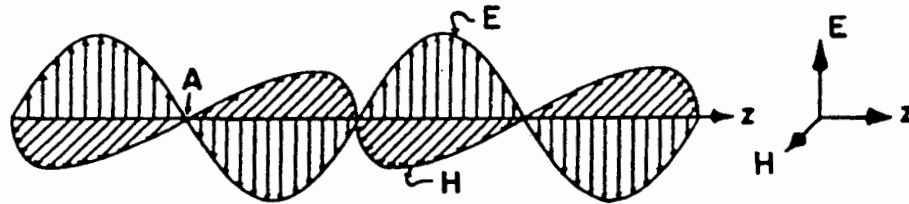


FIG. 15-1. The structure of a light wave moving toward the right. Note that when the electric field, \mathbf{E} , is pointing toward the top of the page, the magnetic field, \mathbf{H} , points out of the plane of the paper toward the reader.

A beam of light having a finite cross section consists of a bundle of parallel rays each having the structure shown in Fig. 15-1. For a given value of the coordinate z , the magnitudes of \mathbf{E} and \mathbf{H} are identical for all rays. That is, \mathbf{E} and \mathbf{H} are constant in each plane normal to the z -direction within the light beam. Such a beam of light is said to have a *plane wave front*.

The justification of Equations (A-2) and (A-3) and of Fig. 15-1 is to be found in Maxwell's equations, which rest in turn essentially on the laws of electromagnetic induction. Although Equations (A-2) and (A-3) and Fig. 15-1 are all that we shall need to know about light for our present purposes, it is of some interest to give a qualitative discussion of the nature of the relationship between the laws of induction and the structure of the light wave. (For a more quantitative discussion, see 2, Chapter 10; 3, Chapters 16 and 17; and 4, pp. 397*ff.*)

Consider the situation at point A in the light wave in Fig. 15-1. An observer located at this point would find that the electric field increases in the vertical direction with time, and he might note that it is similar to the changing field that would be produced if either a flow of positive charges took place in the upward vertical direction or a flow of negative charges took place in the downward vertical direction. Such a flow of charge corresponds in either case to a flow of positive current in the upward direction and, according to the well-known electromagnetic laws, would be encircled by a magnetic field as shown in Fig. 15-2A. Similar vertical current elements would exist in the light rays next to point A in a plane perpendicular to the direction of propagation. As seen in Fig. 15-2B, however, the portions of these circular magnetic fields that are parallel to the direction of propagation will tend to cancel each other, whereas the components normal to the direction of propagation tend to reinforce. The net result is a magnetic field normal to both \mathbf{z} and \mathbf{E} at all points in the wave front passing through A , as shown in Fig. 15-2C.

The currents that we have assumed as generators of the magnetic field are known as *polarization currents*. It is easy to see how they might arise in the presence of matter through the displacements of electrons. In order to account for the propagation of light through a vacuum, Maxwell had to assume that

these currents also exist in free space. This seemed to Maxwell to require the existence of a polarizable medium pervading all of space, which he termed the "ether." The nature of this ether has provided theoretical physics with one of its most fruitful and difficult problems.

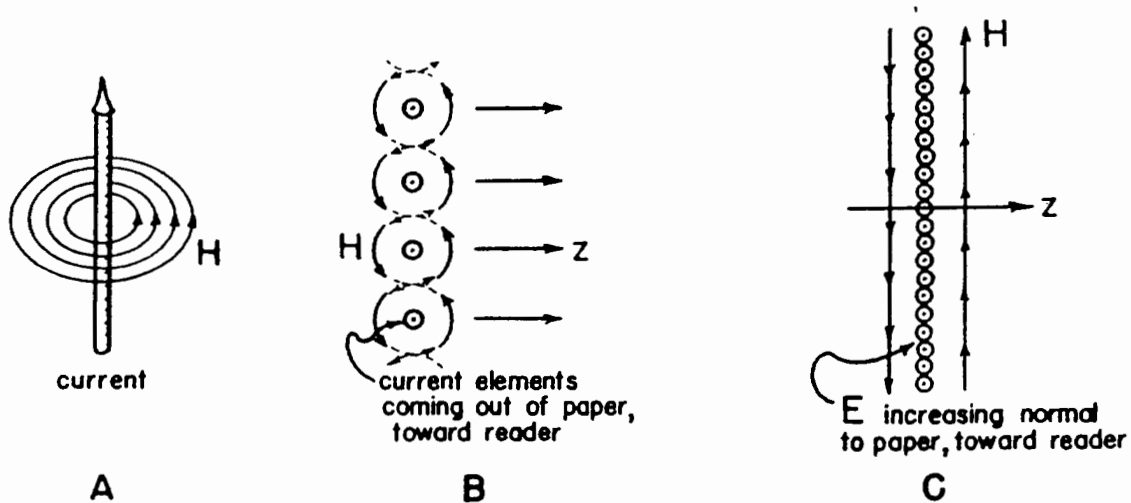


FIG. 15-2. Qualitative explanation of the origin of the fields in a light wave.

A. Magnetic field about a current element.

B. Magnetic field about a row of parallel current elements.

C. Magnetic field on either side of a layer in which the electric field increases in a direction parallel to the layer. This is the situation in the plane normal to z passing through point A in Fig. 15-1.

A stationary observer at point A in Fig. 15-1 would note that the magnetic field also changes with time. According to the laws of magnetic induction, this should result in an electric field that tends to induce an electric current in any conductor encircling the changing magnetic field. By arguments similar to those given above, we see that the changing magnetic field can account for the distribution of the electric fields in the light wave shown in Fig. 15-1. Thus a light wave can be said to arise from the interactions of the changing magnetic and electric fields associated with the flow of the polarization current. The electric field pattern sustains the magnetic field pattern and *vice versa*, in accordance with the laws of electromagnetic induction.

Assumption 3. If the electric field at a point in a vacuum is \mathbf{E} (measured in e.s.u.) and the magnetic field is \mathbf{H} (measured in e.m.u.), then the energy density, in ergs per cubic centimeter, stored in the field at that point is

$$W = \frac{1}{8\pi} (|\mathbf{E}|^2 + |\mathbf{H}|^2) \quad (\text{A-4})$$

This very general result can be proven from Maxwell's equations (see M. Abraham and R. Becker (2, page 145)). In a light wave, since $|\mathbf{E}| = |\mathbf{H}|$, the energy density is

$$W = |\mathbf{E}|^2/4\pi \quad (\text{A-4a})$$

Assumption 4. When a moving electric charge changes its velocity, it emits electromagnetic radiation. Simple arguments (depending ultimately on Maxwell's equations; see Compton and Allison (5, Appendix II)) show that if an observer is located at a distance r from a charge that is accelerated at a rate a , he will notice a pulse of radiation in which the magnitude of the electric field is

$$| \mathbf{E} | = (ea \sin \theta)/rc^2 \quad (\text{A-5})$$

where e is the magnitude of the charge, c is the velocity of light, and θ is the angle between the direction of acceleration and the vector \mathbf{r} drawn from the charge to the observer. The electric field \mathbf{E} is normal to \mathbf{r} and in the same plane as \mathbf{r} and the direction of acceleration. Since it takes time for light to move from one point to another, this expression gives the field at a distance r due to an acceleration that occurred at a time r/c previously.

The physical basis of Equation (A-5) is not difficult to understand. If a charged particle moves with constant velocity, it carries with it its lines of force, which are straight. If the velocity of the particle is increased, the lines of force also tend to move with the new velocity, but because of the finite rate of propagation of electric fields the adjustment of the lines of force to the change in velocity will take place only out to a distance $r = ct$, where t is the time since the acceleration began and c is the velocity of light. Beyond a spherical surface of radius ct the lines of force continue to move with the original velocity of the particle. Now the lines of force which leave the particle after it has been speeded up must be continuous with those that left it before the acceleration. As can be seen from Fig. 15-3, this is possible only if the lines are "kinked," and if the kinks move outward with the speed of light along the lines of force. These kinks therefore constitute a pulse of radiation. We see from Fig. 15-3 that the kinks tend to be small ahead of and behind the charge and are largest in directions lateral to the direction of acceleration. This is the origin of the $\sin \theta$ term in (A-5). The kinks are also sharper (giving a larger pulse, and hence larger values of \mathbf{E}) the greater the acceleration, and the fields will be greater, the larger the charge, whence the terms e and a in the numerator of (A-5). The factor r in the denominator arises because of the spreading of the energy of the pulse over larger and larger areas at greater distances from the charge; the area varies as the square of r , so the energy density varies as the inverse square of r and the field strength (*cf.* Equation (A-4a)) must vary inversely with r . (It is interesting that the electrostatic field from a charge varies inversely with the *square* of the distance; thus the radiation field decreases much less rapidly with distance than does the electrostatic field.)

Assumption 4a. If a charge e moves harmonically along the x -axis so that its displacement is

$$x = x_0 \cos \omega t$$

where ω is the circular frequency, then the acceleration of the charge is

$$a = d^2x/dt^2 = -\omega^2x_0 \cos \omega t$$

It will, according to Equation (A-5), emit light in which the magnitude of the electric field strength at a distance r from the charge is*

$$|E| = -\frac{ex_0\omega^2}{rc^2} \sin \theta \cos \omega(t - r/c) \quad (\text{A-5a})$$

If a stationary charge e of opposite sign is present at $x = 0$, we have a so-called *Hertzian dipole oscillator*, which emits radiation having the same

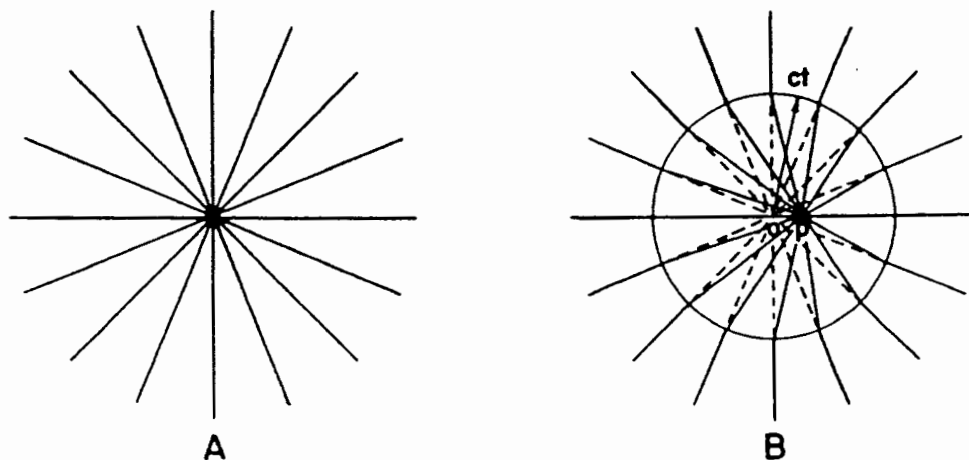


FIG. 15-3. The origin of radiation from accelerated electric charges.

A. Lines of force around a charge moving with constant velocity. The lines are straight and move with the charge.

B. The charge is subjected to a sudden change in velocity at time $t = 0$. If the velocity had not been changed the charge would have been located at point o at time t . Because of the finite velocity of propagation of electrical disturbances, the lines of force beyond a sphere of radius ct will still point toward o , c being the velocity of light. Inside the sphere the lines of force point toward the actual location of the charge, p . Therefore the lines of force are kinked at the surface of the sphere. This kink, moving outward with the velocity of light, is a pulse of electromagnetic radiation.

field strength as (A-5a) at large distances from the dipole. The dipole moment of such an oscillator is

$$m = ex = m_0 \cos \omega t$$

* Strictly speaking, no minus sign should appear in (A-5a) because the magnitude of a vector should be a positive quantity. In this chapter and the next one, however, we shall want to allow for the fact that a vector which is parallel to a given line, may point toward either of the two ends of the line (*i.e.*, the *sense* of the vector must be specified). The sign in equations such as (A-5a) should be taken to specify the sense of the vector, which may change in both space and time. Note that in Equation (A-5) the sense of the vector E is such that when $\theta = 90^\circ$, E points in the same direction as the acceleration if the charge is positive.

where $m_0 = ex_0$, which is the amplitude of the variation of the dipole moment. Thus we can write for the magnitude of the electric field strength in the radiation from a Hertzian dipole

$$|\mathbf{E}| = -(m_0 \omega^2 / rc^2) \sin \theta \cos \omega(t - r/c) \quad (\text{A-5b})$$

This equation is valid only at distances much larger than the wave length of the radiation. Close to the dipole other electromagnetic effects become important, and in particular, at distances small compared with the wave length, the electrostatic field of the dipole becomes predominant and has to be added to (A-5b). This electrostatic field varies inversely with the cube of the distance and therefore dies out much more rapidly than the radiation field. Furthermore, its angular dependence and direction are entirely different from the angular dependence and direction of the radiation field.

The rate at which energy is emitted by a charge undergoing a *constant* acceleration a is the total amount of electromagnetic energy contained in a sphere of radius $r = c$. From Equations (A-4a) and (A-5), this is

$$\begin{aligned} \mathcal{W} &= \int_0^c \int_0^\pi \int_0^{2\pi} (|\mathbf{E}|^2 / 4\pi) r^2 \sin \theta \, d\varphi d\theta dr \\ &= \frac{e^2 a^2}{4\pi c^4} \int_0^c dr \int_0^\pi \sin^3 \theta d\theta \int_0^{2\pi} d\varphi = \frac{e^2 a^2}{4\pi c^4} \cdot c \cdot \frac{4}{3} \cdot 2\pi = \frac{2e^2 a^2}{3c^3} \quad (\text{A-6}) \end{aligned}$$

The mean rate at which a Hertzian dipole emits radiation is therefore

$$\mathcal{W} = \frac{2e^2 \bar{a}^2}{3c^3}$$

where \bar{a}^2 is the mean square acceleration in the dipole. This is

$$\bar{a}^2 = \int a^2 dt / \int dt$$

both integrals being over one cycle. Thus

$$\begin{aligned} \bar{a}^2 &= \omega^4 x_0^2 \int_0^{2\pi/\omega} \cos^2 \omega t \, dt / \int_0^{2\pi/\omega} dt \\ &= \omega^4 x_0^2 / 2 \end{aligned}$$

so that the mean rate of emission is

$$\mathcal{W} = e^2 x_0^2 \omega^4 / 3c^3 \quad (\text{A-7})$$

Introducing the wave length associated with the frequency ω

$$\lambda = 2\pi c/\omega$$

we obtain

$$\mathcal{W} = 16\pi^4 e^2 x_0^2 c / 3\lambda^4 \quad (\text{A-7a})$$

According to this result, we see that if a group of oscillators have the same amplitude, x_0 , but different frequencies, they will emit radiation in inverse proportion to the fourth power of the wave length of the radiation. The reason for this high power is that for harmonic motion the acceleration is proportional to the square of the frequency, and the intensity of the radiation is proportional to the square of the acceleration. We shall see that this simple fact explains the blue color of the sky (page 586).

Assumption 4b. It is possible to show from Maxwell's equations that a magnetic dipole whose moment varies sinusoidally with the time will emit radiation in which the direction of the magnetic field is in the same plane as the direction of the dipole. The field strengths in this radiation have exactly the same magnitudes as those from an oscillating electric dipole of equal amplitude. That is, the amplitude m_0 in (A-5b) can represent either a magnetic or an electric dipole moment, the units of measurement being respectively e.m.u. and e.s.u.

Thus we can have electric dipole radiation and magnetic dipole radiation. Later in this chapter we shall also consider a third type of radiation—that produced by quadrupoles. Of these three types, however, the electric dipole radiation is usually the most important by far. In most of the discussion in this and the next chapter, therefore, the term "dipole" refers to an electric dipole, and the effects of quadrupoles will not be considered.

The four assumptions discussed above are perfectly general and are not restricted to the electron theory of matter. The properties of the electron are introduced in the following assumption.

Assumption 5. The electron is a particle that moves according to the laws of Newtonian mechanics. Its motion is therefore determined by the forces acting upon it. These forces consist of the following:

(i) An inertial force, $\mathbf{f}_1 = -m_e \mathbf{a}$, where m_e is the mass of the electron and \mathbf{a} is its acceleration.

(ii) The restoring force responsible for the harmonic motion the electron is assumed to undergo in the atom, $\mathbf{f}_2 = -k\mathbf{x}$, where \mathbf{x} is the displacement of the electron from its equilibrium position and k is a constant. The origin of this force was never made clear in the classical electron theory.

(iii) The force on the electron due to whatever electric fields are present, $\mathbf{f}_3 = e\mathbf{E}$, where e is the charge on the electron.

(iv) The force on the electron due to any magnetic field that might be present, $\mathbf{f}_4 = e(\mathbf{v} \times \mathbf{H})/c$, where \mathbf{v} and \mathbf{H} are the velocity and magnetic field strength (both vectors) and $(\mathbf{v} \times \mathbf{H})$ represents the vector product (page 26). In a light wave, since $|\mathbf{E}| = |\mathbf{H}|$, this force will be negligible compared with \mathbf{f}_3 as long as the velocity of the electron is small compared with the velocity of light ($|\mathbf{v}| \ll c$). This is always true in chemical systems. We therefore conclude that when light interacts with ordinary matter, it is generally the electric field of the wave that does most of the interacting, rather than the magnetic field. There are, however, some exceptions (e.g., in the phenomenon of optical rotation, where the interactions with both magnetic and electric fields in the light wave are important).

(v) Since a moving electron may dissipate energy in the form of radiation, there must be a force associated with the emission of radiation. This is called the *radiation damping force*. It is convenient for later applications to assume that this force is proportional to the velocity, $\mathbf{f}_5 = -\mu\mathbf{v}$. The constant μ is called the radiation damping coefficient, and its value can readily be calculated for an electron undergoing harmonic motion. The rate of energy dissipation as radiation is $-(\mathbf{f}_5 \cdot \mathbf{v}) = \mu|\mathbf{v}|^2$. The energy radiated per second by the oscillating electron is (taking $\mathbf{x} = \mathbf{x}_0 \cos\omega t$ and $\mathbf{v} = d\mathbf{x}/dt$)

$$\begin{aligned} \mathcal{W} &= (\text{number of cycles per second}) \times (\text{energy radiated per cycle}) \\ &= \nu \int_0^{1/\nu} |\mathbf{f}_5 \cdot \mathbf{v}| dt = \nu\mu x_0^2 \omega^2 \int_0^{1/\nu} \sin^2 \omega t dt \\ &= \nu\mu x_0^2 \omega \int_0^{2\pi} \sin^2 x dx = \mu x_0^2 \omega^2 / 2 \end{aligned}$$

But according to Equation (A-7)

$$\mathcal{W} = e^2 x_0^2 \omega^4 / 3c^3$$

Thus the radiation damping coefficient is

$$\mu = 2e^2 \omega^2 / 3c^3 \quad (\text{A-8})$$

(vi) It is also assumed that the electron can dissipate energy in forms other than light—particularly as heat. The forces responsible for this are called frictional forces, or “damping forces” because they tend to “damp out” the

electronic oscillations. In analogy with ordinary viscous forces, they are assumed to be proportional to the velocity of the electron

$$\mathbf{f}_6 = -\eta\mathbf{v}$$

where η is a constant analogous to a viscosity. The physical origin of these forces was presumed to lie in a sort of “viscous drag” on the electron as it moved through whatever made up the non-electronic portions of the atom. We shall find that collisions between atoms can have the same effects as \mathbf{f}_6 .

(vii) If there are other electrons in the atom, they will exert forces on a given electron according to Coulomb’s law

$$\mathbf{f}_7 = e^2 \sum (\mathbf{r}_i / |\mathbf{r}_i|^3)$$

where \mathbf{r}_i is the distance from the i^{th} electron (considered as a vector) and the sum is a vector sum over all of the other electrons in the atom.

B. The Emission of Light by Excited Atoms and Molecules

a. Emission by a single electron

Suppose that we have an atom containing only one electron, or alternatively, an atom in which the electrons exert no forces on one another. Then $\mathbf{f}_7 = 0$, and in the absence of light the equation of motion of an electron is, according to the classical theory,

$$\mathbf{f}_1 + \mathbf{f}_2 + \mathbf{f}_5 + \mathbf{f}_6 = 0 \quad (\text{B-1})$$

Assuming that the motion takes place only in the x -direction, this gives

$$m_e d^2x/dt^2 + (\eta + \mu) dx/dt + kx = 0 \quad (\text{B-2})$$

The solution of this differential equation is, as can be verified by substitution

$$x = x_0 e^{-\omega' t} \cos \omega_1 t \quad (\text{B-3})$$

where

$$\omega' = (\eta + \mu)/2m_e \quad (\text{B-3a})$$

$$\omega_1^2 = \omega_0^2 - \omega'^2 \quad (\text{B-3b})$$

$$\omega_0^2 = k/m_e \quad (\text{B-3c})$$

Equation (B-3) represents the damped vibrations of an oscillator whose natural frequency in the absence of dissipative forces is $\omega_0/2\pi$ (see Fig. 15-4). Because of the accelerations that it undergoes, the electron must emit radiation in accordance with Equation (A-5). The acceleration can be computed by differentiating (B-3) twice, but the result can be simplified

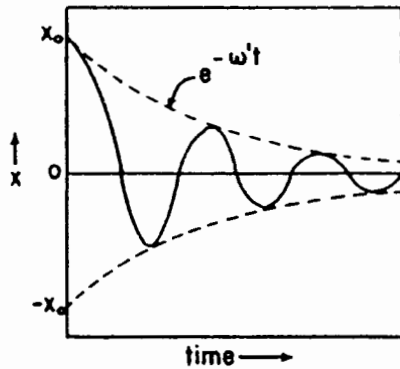


FIG. 15-4. Damped oscillations of an elastically bound electron. In the classical atom the damping would be much less rapid than is shown here.

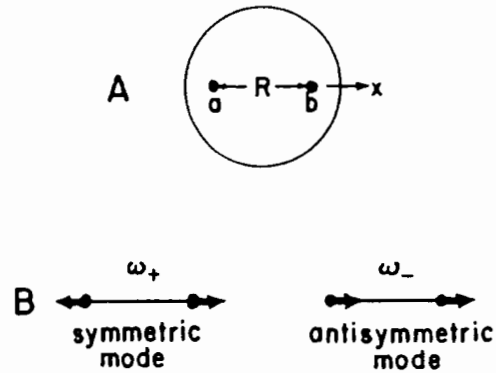


FIG. 15-5. Normal modes of interacting electrons.

because of the fact that ω' is always much smaller than the oscillation frequency ω_1 . Therefore the magnitude of the electric field in the radiation is very nearly

$$|\mathbf{E}| = |\mathbf{E}_0| e^{-\omega't} \cos \omega_1 t \tag{B-4}$$

where $|\mathbf{E}_0| = e^2 \omega_1^2 x_0^2 \sin \theta / rc^2$.

Thus the electron emits a damped train of waves of the same form as the displacement shown in Fig. 15-4. According to the classical electron theory, this is the mechanism of the emission of visible and ultraviolet light by atoms. The electron is set in motion either by heat (through collisions with other molecules) or by bombardment with other electrons (as in a gas discharge or a spark). It then moves according to (B-4), emitting a continuous train of waves whose frequency is close to the natural frequency ω_0 (but always slightly smaller) and whose amplitude decreases exponentially with the time.

b. Emission by coupled electrons

If an atom contains N electrons all moving independently of each other, and if the force constants of the electrons differ from each other and also

differ for displacements in different directions, the atom can emit as many as $3N$ different frequencies.

If the forces between the electrons, represented by \mathbf{f}_7 in Assumption 5, cannot be neglected, the electrons will not move independently, but must be discussed in terms of their $3N$ normal modes of vibration. For instance, consider an atom containing a pair of electrons, a and b , bound with identical force constants, k , to two sites a distance R apart (Fig. 15-5A). Let the x -axis lie along the line joining the two equilibrium positions. Then the forces on electron a will be influenced by the position of electron b and *vice versa* because of the Coulombic repulsion of the electrons. If the displacements of the electrons from their equilibrium positions are x_a, y_a, z_a and x_b, y_b, z_b , the Coulombic repulsion is

$$|\mathbf{f}_7| = e^2 / [(R + x_a - x_b)^2 + (y_a - y_b)^2 + (z_a - z_b)^2]$$

Assuming that the displacements are small, so that their squares can be neglected in comparison with their first powers, this expression can be approximated by

$$|\mathbf{f}_7| \cong (e^2/R^2) \left[1 - 2 \frac{x_a - x_b}{R} \right] \quad (\text{B-5})$$

This force is directed along the x -axis, so that only the vibrations in this direction will be affected; the vibrations in the y and z directions will take place independently as if the two electrons were on separate atoms. Neglecting the contribution of e^2/R^2 to \mathbf{f}_7 since it is independent of the displacement, and neglecting the damping forces, we can write the equations of motion of the two electrons as follows

$$m_e \ddot{x}_a = -k'x_a + (e^2/R^3)x_b \quad (\text{B-6a})$$

$$m_e \ddot{x}_b = (e^2/R^3)x_a - k'x_b \quad (\text{B-6b})$$

where $k' = k + e^2/R^3$. For the normal modes we must look for solutions of the form

$$x_a = x_{a0} \sin \omega t \quad (\text{B-7a})$$

$$x_b = x_{b0} \sin \omega t \quad (\text{B-7b})$$

Substitution into Equations (B-6) results in the relations

$$-\omega^2 m_e x_{a0} = -k'x_{a0} + (e^2/R^3)x_{b0} \quad (\text{B-8a})$$

$$-\omega^2 m_e x_{b0} = (e^2/R^3)x_{a0} - k'x_{b0} \quad (\text{B-8b})$$

which leads in the usual manner to the secular equation

$$\begin{vmatrix} (-k' + \omega^2 m_e) & e^2/R^3 \\ e^2/R^3 & (-k' + \omega^2 m_e) \end{vmatrix} = 0 \quad (\text{B-9})$$

having the roots

$$\omega^2 = (k'/m_e) \pm (e^2/m_e R^3) \quad (\text{B-10})$$

The upper sign leads to the result

$$\omega_+^2 = (k/m_e) + (2e^2/m_e R^3) \quad (\text{B-10a})$$

$$x_{a0} = -x_{b0} \quad (\text{B-11a})$$

In this normal mode the two electrons move with equal amplitudes and opposite phases (see Fig. 15-5B); we shall refer to it as the *symmetric mode*. The other normal mode (lower sign in Equation (B-10)) gives

$$\omega_-^2 = k/m_e \quad (\text{B-10b})$$

$$x_{a0} = x_{b0} \quad (\text{B-11b})$$

In this mode the two electrons have equal amplitudes and the same phase (see Fig. 15-5B); it will be called the *antisymmetric mode*.

It is obvious that the emission from the two electrons in the symmetric mode will tend to cancel, whereas that in the antisymmetric mode will give constructive interference. The frequency ω_- will thus be emitted strongly, whereas ω_+ will be weak. (The intensity of emission of the symmetric mode will be discussed further on page 611; it is an example of so-called quadrupole emission.) The interaction of the electrons has thus removed part of the degeneracy of the normal modes and has altered the intensity of the emission.

In general the coordinate x in Equation (B-3) can be taken as the displacement of a given electron in some normal mode. A similar equation is obtained for each electron in each normal mode. The electric field in the radiation from the entire atom is then simply the resultant of the fields due to all of the electrons in all of the normal modes that happen to be excited. In some normal modes, radiation from different electrons may interfere destructively, so that there will be little or no net emission; in other normal modes, there may be constructive interference with enhanced emission intensity. These normal modes can be called "inactive" and "active," respectively. It is clear that the radiation from active modes should have the form of a damped oscillation, as in Equation (B-4).

The physicists responsible for this theory were greatly puzzled by the fact that the emission spectra of practically all known atoms seem to contain a very large number of frequencies. This is true even of hydrogen, the simplest known atom. It would seem to require that all atoms have an almost unlimited number of normal modes, which is hardly conceivable. We now know that this paradox results from fundamental shortcomings of the theory (*cf.* Chapter 16).

c. Emission by molecules

Similar considerations can be used to explain the emission of light by molecules. If a molecule contains a permanent dipole moment, its over-all rotation will cause the component of the moment in any particular direction to vary sinusoidally with time. The rotating molecule can thus act as a Hertzian oscillator and will emit radiation having the same frequency as the frequency of rotation. For molecules at ordinary temperatures these rotation frequencies correspond to the far infra-red and microwave regions of the spectrum, where we know that there is strong absorption, and hence presumably also emission, by molecules with permanent dipoles. According to the classical theory, however, a molecule can rotate at any frequency, so the emission ought to be continuous over a range of frequencies. This is not observed because, as we now know, rotational motion is quantized. At the time that the classical electron theory was developed, however, these regions of the spectrum had not been investigated with sufficient resolution to show the discontinuous nature of the pure rotational spectra of molecules.

Molecules can not only rotate, but they can also undergo skeletal harmonic vibrations with frequencies equal to the normal mode frequencies of the molecule. If these vibrations result in the movement of the charged ends of the permanent dipoles present in the molecule, they may also cause emission of spectroscopic lines having frequencies equal to the normal mode frequencies. This is the classical explanation of the origin of the infra-red spectra of molecules, lying between approximately 10,000 Å. and 300,000 Å. (1μ to 30μ).

In addition to these over-all molecular motions, we should expect electronic vibrations in molecules, similar to those just postulated in atoms. Molecules should therefore give rise to electronic line spectra in the visible and ultra-violet. This is in fact observed, but there is a complication in that electronic motions are "coupled" to the rotations and vibrations of the molecule. In order to show this, let us for simplicity consider the behavior of a diatomic molecule in which the electrons are undergoing harmonic motion. We should

expect that if the electrons shifted their positions in the bond of diatomic molecule, the strength of the bond would be changed slightly and the atoms at either end of the bond would tend to assume new equilibrium positions. The result is that the motions of the electrons are influenced to some extent by the motions of the atoms. The intensity of the emission by the vibrating electrons will therefore vary as the atoms move; if the two atoms themselves are vibrating, the intensity of the emission by the electrons will fluctuate (or be "modulated") with the much lower frequency of the atomic oscillations. The situation is very similar to that in ordinary "amplitude modulated" radio broadcasting, where a "carrier wave" of high frequency has superimposed on it a message having a much lower frequency (see Fig. 15-6).

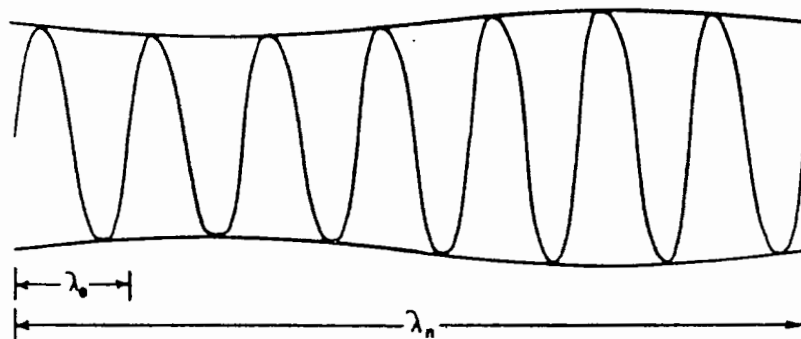


FIG. 15-6. Modulation of light emitted by electrons as a result of nuclear motions in a molecule. The wave length corresponding to the frequency of nuclear motion is λ_n , and that corresponding to electronic motion is λ_e .

Furthermore, the intensity of the electronic radiation from a molecule depends on the orientation of the molecule with respect to the observer, because of the $\sin \theta$ term in Equation (A-5). The orientation changes as the molecule rotates, so the intensity of the observed electronic emission will also be modulated by the frequency of the molecular rotation. As a result of all of these factors, a rotating and vibrating diatomic molecule containing a single electron ought to produce a radiation field that varies with time in the following manner

$$\begin{aligned}
 |E| &= k_1 \sin \omega_1 t + k_2 \sin \omega_2 t + k_3 \sin \omega_3 t + k_{12} \sin \omega_1 t \sin \omega_2 t \\
 &\quad + k_{13} \sin \omega_1 t \sin \omega_3 t + k_{23} \sin \omega_2 t \sin \omega_3 t \\
 &\quad + k_{123} \sin \omega_1 t \sin \omega_2 t \sin \omega_3 t
 \end{aligned}$$

Here the k 's are constants, ω_1 is the frequency of the electron, ω_2 is the frequency of the atomic (infrared) vibration, and ω_3 is the rotational fre-

quency (far infrared). The first three terms represent pure electronic, vibrational, and rotational spectra. The next four terms represent the mutual modulations of these motions.

Now trigonometry shows that, for instance

$$\sin \omega_1 t \sin \omega_2 t = [\cos (\omega_1 - \omega_2)t - \cos (\omega_1 + \omega_2)t]/2$$

and

$$\begin{aligned} \sin \omega_1 t \sin \omega_2 t \sin \omega_3 t = & [\sin (\omega_1 - \omega_2 + \omega_3)t + \sin (\omega_1 - \omega_2 - \omega_3)t \\ & - \sin (\omega_1 + \omega_2 + \omega_3)t - \sin (\omega_1 + \omega_2 - \omega_3)t]/4 \end{aligned}$$

The radiation field \mathbf{E} can therefore be written as the sum of individual sine and cosine terms involving the thirteen frequencies and combinations of frequencies, ω_1 , ω_2 , ω_3 , $|\omega_1 \pm \omega_2|$, $|\omega_1 \pm \omega_3|$, $|\omega_2 \pm \omega_3|$, and $|\omega_1 \pm \omega_2 \pm \omega_3|$. These thirteen frequencies would be observed as thirteen lines if the radiation from such a molecule were passed through a spectroscope; only ω_1 , $|\omega_1 \pm \omega_2|$, $|\omega_1 \pm \omega_3|$, and $|\omega_1 \pm \omega_2 \pm \omega_3|$ involve the electronic motion and will appear in the visible or ultraviolet. We must remember, however, that according to the classical picture the rotational frequency, ω_3 , can assume any value in a molecule. Therefore the visible and ultraviolet emission of a diatomic molecule caused by a single mode of electronic vibration would be expected to cause continuous *regions* of emission, in contrast to the relatively sharp *lines* produced by atoms. This is more or less what is observed; diatomic molecules produce so-called "band spectra" containing very many more lines than the spectra of atoms, and if the resolution of the spectroscope is not high the bands will seem to be continuous regions.

Exercises. (1) Calculate the average rotational frequency of the HCl molecule (interatomic distance 1.27 Å.) and of the ICl molecule (interatomic distance 2.32 Å.) at room temperature. (Assume that the average rotational energy is kT with $k = 1.38 \times 10^{-16}$ erg degree⁻¹molecule⁻¹.) Show that these frequencies lie in the far infrared and microwave regions of the spectrum.

(2) Sketch the emission spectrum that you would expect from a single excited electronic normal mode of a diatomic molecule on the basis of the classical considerations presented above. Assume that the molecule has been heated to some definite temperature, and take account of the fact that, because of the Boltzmann expression, $\exp(-\epsilon/kT)$, only a limited range of rotational frequencies will be found. Assume that the electronic frequency is 30,000 cm.⁻¹, the atomic vibration frequency is 1000 cm.⁻¹, and the rotational frequency covers the approximate range 1 to 10 cm.⁻¹ with a broad maximum around 7 cm.⁻¹.

C. The Widths and Shapes of Spectral Lines

a. Preliminary discussion in terms of line widths

As we have seen on pages 36 and 241, no wave train that lasts for a finite time can be strictly monochromatic. If the train consists of n waves and takes τ seconds to pass by an observer, its frequency will be given by $\nu = n/\tau$, but it is not possible to measure n with much more precision than the nearest whole integer, so the frequency must be indefinite to the extent $\Delta\nu \cong \Delta n/\tau \cong 1/\tau$. Therefore the damped radiation emitted by a vibrating electron does not produce a perfectly sharp line when passed through a spectroscope, but it is spread out over a frequency range of the order of $\Delta\nu$ corresponding to a range of wave lengths of the order of $\Delta\lambda = (c/\nu^2)\Delta\nu$. The quantities $\Delta\nu$ and $\Delta\lambda$ are thus rough measures of the "width" of a spectral line. We shall now show how these quantities may be estimated. In Section *b* we shall give a more precise discussion of the shapes of spectral lines.

A convenient measure of the length of the wave train from an atom or molecule in which electrons oscillate according to Equation (B-3) is the quantity

$$Q = \omega_1/2\pi\omega' \quad (\text{C-1})$$

This quantity is evidently equal to the number of oscillations that occur before the amplitude has dropped to $1/e^{\text{th}}$ of its initial value. We can say that the "duration" of the wave train is therefore of the order of magnitude

$$\tau \cong Q \times (\text{duration of one cycle}) = 2\pi Q/\omega_1 = 1/\omega' \quad (\text{C-2})$$

An upper limit to τ (lower limit to $\Delta\nu$) is set by the radiation damping, which must be present even if no other dissipative forces exist. This limit is given by the expression

$$\tau_{\max} \cong 1/\Delta\nu_{\min} \cong 2 m_e/\mu = 3m_e c^3/e^2\omega_1^2$$

where μ is the radiation damping coefficient defined in Equation (A-8). The corresponding upper limit to Q is

$$Q_{\max} = 2m_e\omega_1/2\pi\mu = 3m_e c^3/2\pi e^2\omega_1$$

For visible light (say wave length = 6000 Å., or $\omega_1 = 3 \times 10^{15}$ sec.⁻¹) we obtain

$$Q_{\max} = 16,000,000$$

$$\tau_{\max} \cong 3 \times 10^{-8} \text{ sec.}$$

$$\Delta\nu_{\min} \cong 3 \times 10^7 \text{ sec.}^{-1}$$

The minimum uncertainty in the wave length of the emitted light is of the order of

$$\Delta\lambda_{\min} = 4\pi^2 e^2 / 3m_e c^2 = 0.00037 \text{ \AA}. \quad (\text{C-3})$$

which is a constant for all regions of the spectrum. Accordingly this should be the lower limit to the sharpness of the spectral line that originates from the vibration of a *single isolated electron*.*

The observed widths of spectral lines from atoms and molecules are usually greater than the value given in (C-3). Three factors contribute to the broadening. In the first place, because of the Doppler effect, thermal motions of the radiating particles along the line of vision change the wave lengths of the emitted light as seen by a stationary observer. Since some of the atoms are moving toward the observer and some are moving away, and since there is a continuous range of velocities, even perfectly monochromatic radiators moving in this way would appear to emit a range of frequencies. This is known as the "Doppler broadening" of a spectral line.

The Doppler shift in frequency due to motion of a radiating body toward or away from the observer is

$$\Delta\nu = \nu_1 v/c \quad \text{or} \quad \Delta\lambda = v/\nu_1$$

where v is the velocity of the emitter, c is the velocity of light, and ν_1 is the frequency that would be observed if the body were not moving. In a gas at a temperature T , the velocity v can be related to the mean thermal energy in a given direction, ($v = \sqrt{2RT/M}$, where M is the molecular weight of the emitter). For a molecular weight of 20 at 300°K. and light of wave length 6000 Å. this gives

$$v = 35,000 \text{ cm./sec.}$$

$$\Delta\lambda = 0.0012 \text{ \AA}.$$

which is several times larger than the limiting width due to radiation damping.

Doppler broadening is most serious in atoms of low atomic weight. It can be reduced by cooling the radiating particles so that they do not move so fast, and also by collimating the particles through a series of slits into a narrow beam in which the velocities normal to the beam are very low.

* If several electrons are coupled together, however, so that there is constructive or destructive interference between the fields produced by different electrons, then the radiation damping can be, respectively, greater or smaller than the values given by these relations.

The second factor affecting the line width is molecular collision ("collision broadening"). If in each collision between atoms or molecules the vibrational state of the electrons is changed, the emitted wave train cannot on the average be any longer than the average time between collisions, Δt . The kinetic theory of gases shows that

$$\Delta t = 1/(\sqrt{2} v n \sigma) \quad (\text{C-4})$$

where v is the mean velocity, n is the number of molecules per cubic centimeter and σ is the effective cross-sectional area for collision. As a result, the frequency and wave length of the emitted line are indefinite by approximately

$$\Delta \nu \cong \sqrt{2} v n \sigma, \quad \text{or} \quad \Delta \lambda \cong \sqrt{2} v n \sigma \lambda^2 / c \quad (\text{C-5})$$

This phenomenon has been used to obtain information about the collision cross sections of radiating atoms (see 6).

The third factor affecting the breadth of spectral lines is the interaction of atoms or molecules when they are brought close together ("interaction broadening"). Under these conditions, the electrons of one particle are influenced by the electrons in neighboring particles, and as a result the vibration frequencies are altered. The magnitude of the frequency shift depends on the distance between the particles, being large when they are close together. These interactions become noticeable in gases at high pressures and in liquids, where the atoms or molecules are not very far apart on the average. Furthermore, the interatomic distances in gases and liquids, and hence the magnitude of the interaction, varies considerably from one pair of particles to another because of the randomness of the structure of gases and liquids. As a result the observed spectrum is a superposition of emission spectra whose natural frequencies cover a range of values and the relatively narrow emission "lines" of an isolated atom or molecule appear to be spread out over continuous bands of frequencies. Broadening from this source can also occur in gases at low pressures when there is a tendency for the atoms to undergo slightly "sticky" collisions because of the formation of weak "quasi-molecules" in which the interatomic distance is not sharply defined.

Interaction broadening and collision broadening in gases can be reduced by lowering the pressure. These types of broadening are particularly important in liquids, and are responsible for the relatively broad absorption regions almost universally observed with colored substances in solution.

b. The shapes of spectral lines

It is not difficult to obtain an expression giving the shape of the spectral line emitted by an oscillator that moves according to Equation (B-3). By the shape of a spectral line is meant the distribution of the intensity in the line with respect to frequency when it is observed through a spectrograph. Spectrographs break down polychromatic radiation into its monochromatic components, and as we have seen in Chapter 2, Section F, these components can be regarded as Fourier components in a Fourier expansion of the electric field, $\mathbf{E}(t)$, emitted by the atom. Since a continuous range of frequencies is involved, a Fourier integral expansion must be utilized (page 33). Thus we may write

$$|\mathbf{E}(t)| = \int_{-\infty}^{\infty} A(k)e^{ikt}dk \quad (\text{C-6})$$

where $\mathbf{E}(t)$ is given by Equation (B-4) when $t > 0$, and $\mathbf{E} = 0$ for $t < 0$. Here $A(k)dk$ is the amplitude of the total electric field strength associated with all components having circular frequencies between k and $k + dk$. Since the intensity of radiation (that is, the energy density of the radiation) is proportional to the square of the field strength, according to Equation (A-4a), the intensity of the radiation in this frequency range must be proportional to $|A(k)|^2$. Thus $|A(k)|^2$ gives the shape of the spectral line directly.

According to the theory of Fourier transforms, $A(k)$ is given by

$$A(k) = (1/2\pi) \int_{-\infty}^{\infty} |\mathbf{E}(t)| e^{-ikt} dt$$

Using the relation

$$\cos \omega_1 t = (e^{i\omega_1 t} + e^{-i\omega_1 t})/2$$

and remembering that $\mathbf{E}(t) = 0$ for $t < 0$, we find

$$\begin{aligned} A(k) &= (|\mathbf{E}_0|/4\pi) \int_0^{\infty} \left\{ e^{-[i(k - \omega_1) + \omega']t} + e^{-[i(k + \omega_1) + \omega']t} \right\} dt \\ &= (|\mathbf{E}_0|/4\pi) \left[\frac{1}{\omega' + i(k - \omega_1)} + \frac{1}{\omega' + i(k + \omega_1)} \right] \end{aligned} \quad (\text{C-7})$$

If we restrict ourselves to frequencies very close to ω_1 , so that $(k - \omega_1)$ is of the same order as ω' , and recall that $\omega' \ll \omega_1$, the second term in the

brackets in (C-7) can be neglected and we obtain for the shape of the spectral line

$$|A(k)|^2 = (E_0^2/16\pi^2)/[(k - \omega_1)^2 + \omega'^2] \tag{C-8}$$

Replacing the circular frequencies, ω_1 and k , by ordinary frequencies, ν_1 and ν , we find

$$\text{Intensity} = \frac{\gamma/2\pi}{(\nu - \nu_1)^2 + (\gamma/2)^2} \tag{C-9}$$

where

$$\gamma = \omega'/\pi = (\eta + \mu)/2\pi m_e$$

and the numerator is chosen so that the integrated intensity under the curve is unity. This function has the appearance shown in Fig. 15-7. It is

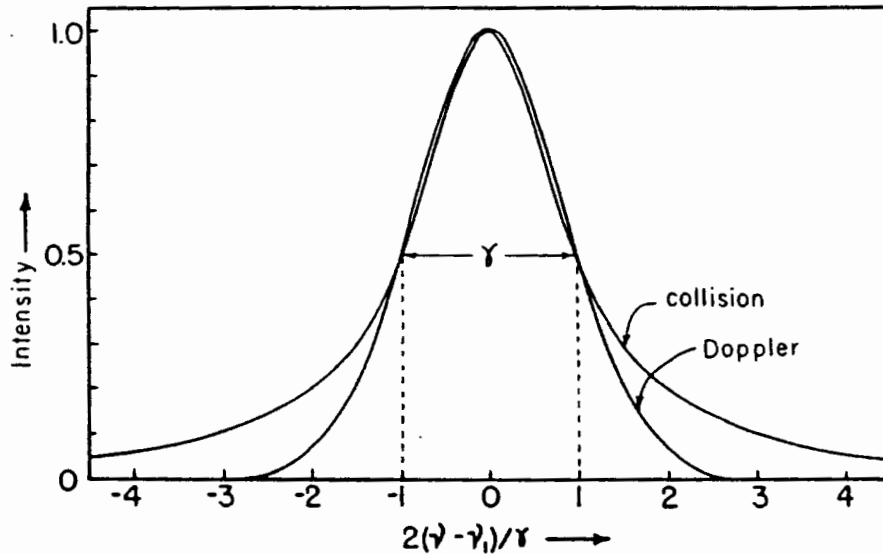


FIG. 15-7. Line shapes due to collision and radiation broadening and to Doppler broadening. Both curves have the same half-width, γ .

sometimes called the *Lorentz formula*. The intensity is a maximum at ν_1 and falls to half of its maximum value when the frequency is larger or smaller than ν_1 by $\gamma/2$. Therefore γ is called the “half width” of the line.*

If dissipation is caused by radiation damping alone, then

$$\gamma = \gamma_0 = \mu/2\pi m_e = 4\pi e^2 \nu_1^2 / 3m_e c^3 \tag{C-10}$$

where γ_0 is called the “natural half width” of a spectral line.

* The term “half width” is sometimes applied to the quantity $\gamma/2$. Strictly speaking, γ is the “width at half maximum intensity” and $\gamma/2$ is “half the width at half maximum intensity.”

Lorentz showed (1, page 37) that when line broadening is caused by collisions as well as by radiation damping, the same line shape as Equation (C-9) is obtained, except that the half width now has the value

$$\gamma = \sqrt{2}\sigma v n / \pi + \gamma_0 \quad (\text{C-11})$$

where σ , v , and n are the same quantities as those appearing in (C-4). Collisions therefore act in the same way on the electron as a viscous drag for which the drag coefficient is $\eta = 2\sqrt{2}\sigma v m_e n$.

The line shape due to Doppler broadening is easily derived in the following way. The frequency observed by a stationary observer when a radiator of frequency ν_1 approaches with velocity v is

$$\nu = \nu_1(1 + (v/c)) \quad (\text{C-12})$$

The Boltzmann principle states that the number of atoms having a velocity component v in a given direction is proportional to $\exp(-Mv^2/2RT)$, where M is the atomic weight. But from Equation (C-12)

$$v^2 = c^2(\nu - \nu_1)^2/\nu_1^2$$

Hence the line shape is given by

$$\text{Intensity} = K \exp \left[- \left(\frac{\nu - \nu_1}{\gamma_D/2} \right)^2 \ln 2 \right] \quad (\text{C-13})$$

where K is a constant and γ_D is the "Doppler half width,"

$$\gamma_D = 2\nu_1 \sqrt{2RT \ln 2 / Mc^2} \quad (\text{C-13a})$$

This shape is that of a Gauss error curve, and as seen from Fig. 15-7 the intensity drops off much more rapidly at large values of $(\nu - \nu_1)$ than it does in the Lorentz formula, Equation (C-9). Therefore, even in the presence of Doppler broadening that has a half width several times that due to radiation damping and collisions, it is possible to observe the effects of the latter in the "wings" of the line.

D. The Response of Bound Electrons to Light

a. The motion of an isotropically bound electron

The equation of motion of an elastically bound electron that is exposed to a beam of monochromatic light is the same as Equation (B-1), except for

the additional force, \mathbf{f}_3 , arising from the interaction of the electron with the incident light

$$\mathbf{f}_1 + \mathbf{f}_2 + \mathbf{f}_3 + \mathbf{f}_5 + \mathbf{f}_6 = 0 \quad (\text{D-1})$$

The magnetic force, \mathbf{f}_4 , is also present, but as has been explained previously, it can be neglected because it is very small compared with \mathbf{f}_3 . If the atom is small compared with the wave length of the light, the spatial variation of the electric field in the light wave (Equation (A-2)) can be disregarded giving

$$m_e d^2x/dt^2 + (\eta + \mu) dx/dt + kx = e|\mathbf{E}_0| \sin \omega t \quad (\text{D-1a})$$

where ω is the circular frequency of the light, x is the displacement of the electron in the direction of \mathbf{E}_0 , the field of the light wave, and k is the force constant in the x -direction.* The electron would be expected to respond to the light by oscillating with it at the same frequency, though perhaps with a different phase. After some time a steady state will have been reached in which the amplitude of the electron's oscillations becomes constant. We can then say that

$$x = x'_0 \sin \omega(t + \delta) = x_0(\sin \omega t + \beta \cos \omega t) \quad (\text{D-2})$$

where x_0 is the amplitude of the component of the oscillation that moves in phase with the light wave, and βx_0 is the amplitude of the component that is 90° out of phase. Substituting (D-2) into (D-1a), we find that

$$\begin{aligned} & \{[-m_e\omega^2 - \beta(\eta + \mu)\omega + k]x_0 - e|\mathbf{E}_0|\} \sin \omega t \\ & + \{[-m_e\omega^2\beta + (\eta + \mu)\omega + \beta k]x_0\} \cos \omega t = 0 \end{aligned} \quad (\text{D-3})$$

This equation must be true for all values of the time t , which can be the case only if the coefficients of $\sin \omega t$ and $\cos \omega t$ vanish. Thus, replacing k/m_e by ω_0^2 , $(\eta + \mu)/2m_e$ by ω' , and $\omega_0/2\pi\omega'$ by Q , we obtain

$$\beta = \frac{(\eta + \mu)\omega/m_e}{\omega^2 - \omega_0^2} = \frac{2\omega\omega'}{\omega^2 - \omega_0^2} = \frac{1}{\pi Q} \frac{\omega\omega_0}{\omega^2 - \omega_0^2} \quad (\text{D-4a})$$

$$x_0 = \frac{e}{m_e} \left[\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + 4\omega'^2\omega^2} \right] |\mathbf{E}_0| = \frac{e}{k} \left[\frac{(\omega_0^2 - \omega^2)\omega_0^2}{(\omega_0^2 - \omega^2)^2 + \omega_0^2\omega^2/\pi^2 Q^2} \right] |\mathbf{E}_0| \quad (\text{D-4b})$$

* For the moment we shall assume that the force constant k is the same for displacements of the electron in any direction (isotropic binding). This means that the solution of (D-1a) will be independent of the orientation of the atom relative to the field in the light. Later, however, we shall consider systems in which k differs in different directions (see pp. 608 ff.).

$$\beta x_0 = -\frac{e}{m_e} \left[\frac{2\omega'\omega}{(\omega_0^2 - \omega^2)^2 + 4\omega'^2\omega^2} \right] |E_0| = -\frac{e}{k} \left[\frac{1}{\pi Q} \frac{\omega\omega_0^3}{(\omega_0^2 - \omega^2)^2 + \omega_0^2\omega^2/\pi^2 Q^2} \right] |E_0| \quad (\text{D-4c})$$

Equations (D-4a, b, and c) describe the steady-state motions of a bound electron in a light wave. Since the positive charge in the environment is assumed to be stationary, the movement of the electron can be said to be responsible for an oscillating induced dipole moment amounting to

$$m = ex \quad (\text{D-5})$$

This induced moment has two components: one component oscillates in phase with the incident light and has the amplitude

$$m_0 = ex_0 \quad (\text{D-5a})$$

and the other component oscillates 90° out of phase with the light wave and has the amplitude

$$m'_0 = -\beta ex_0 \quad (\text{D-5b})$$

The polarizability of an atom or molecule is defined as the induced dipole moment divided by the field strength responsible for the induced moment. We may therefore define an in-phase polarizability of the electron

$$a = m_0/|E_0| = (e^2/k) \left[\frac{(\omega_0^2 - \omega^2)\omega_0^2}{(\omega_0^2 - \omega^2)^2 + 4\omega'^2\omega^2} \right] \quad (\text{D-6a})$$

and an out-of-phase polarizability of the electron

$$\begin{aligned} a' = m'_0/|E_0| &= (e^2/\pi k Q) \left[\frac{\omega\omega_0^3}{(\omega_0^2 - \omega^2)^2 + 4\omega'^2\omega^2} \right] \quad (\text{D-6b}) \\ &= \frac{\omega\omega_0}{\omega_0^2 - \omega^2} \frac{1}{\pi Q} a \end{aligned}$$

We have shown that the quantity ω' determines the contribution of dissipative forces to spectral line widths, and for atoms it is found to be very much smaller than ω_0 . Therefore, except for light waves having frequencies very close to the natural frequency of the electron, ω_0 , we may neglect the term $4\omega'^2\omega^2$ in the denominators of (D-6a) and (D-6b). Using ordinary frequencies, ν and ν_0 , instead of circular frequencies, ω and ω_0 , we then obtain, for the in-phase polarizability of the electron, the expressions

$$a = \frac{e^2}{k} \frac{\nu_0^2}{\nu_0^2 - \nu^2} = \frac{e^2}{k} \frac{\lambda^2}{\lambda^2 - \lambda_0^2} = \frac{e^2}{4\pi^2 m_e} \frac{1}{\nu_0^2 - \nu^2} \quad (\text{D-6c})$$

where $|\nu - \nu_0| \gg \omega'/2\pi$, and λ and λ_0 are the wave lengths corresponding to ν and ν_0 , respectively. Furthermore, Q is generally a very large number (of the order of 10^6), so that when $|\nu - \nu_0| \gg \omega'/2\pi$, we have for the out-of-phase polarizability,

$$\alpha' = 0 \tag{D-6d}$$

Figure 15-8 shows the variation of the in-phase and out-of-phase polarizabilities of the electron with the frequency of the incident light. In order to show more clearly the behavior in the immediate vicinity of ν_0 , Q has been

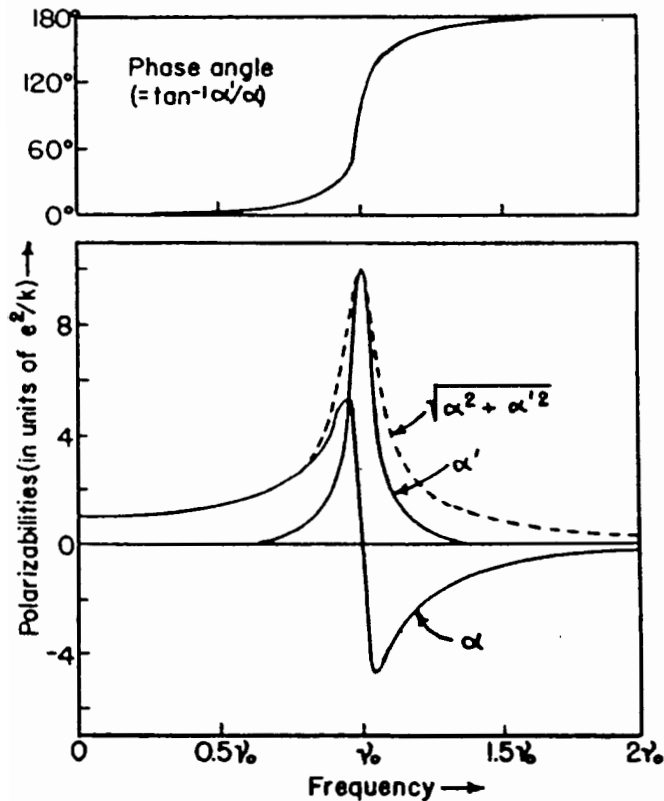


FIG. 15-8. Frequency variation of the polarizability and phase for a system in which $\pi Q = 10$.

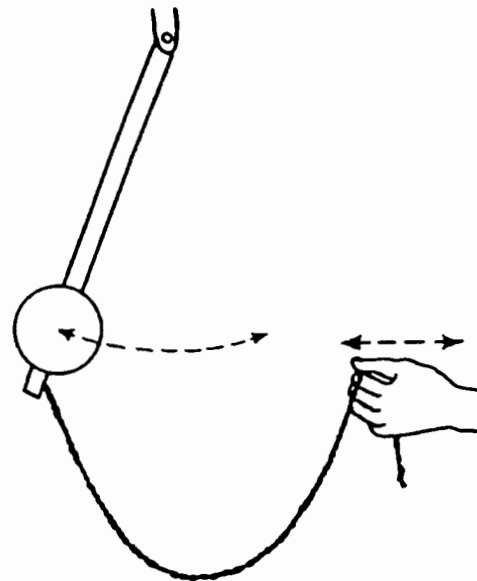


FIG. 15-9. Model illustrating the behavior of an oscillating system when subjected to a periodically applied force.

given the unusually low value of $10/\pi$. Except in the immediate vicinity of ν_0 , Equations (D-6c) and (D-6d) dominate the behavior. At very low frequencies, $\alpha \cong e^2/k$, which is the static polarizability as measured in a constant field. As the frequency is raised, α increases, going through a maximum at $\nu = \nu_0(1 - (1/\pi Q))^{1/2}$. At still higher frequencies α decreases, going through zero at $\nu = \nu_0$ and attaining negative values. It reaches a minimum at $\nu = \nu_0(1 + (1/\pi Q))^{1/2}$ and then approaches zero asymptotically from below. The out-of-phase polarizability merely goes through a sharp and

very large maximum at $\nu = \nu_0$. Thus if the frequency of the radiation is much less than the natural frequency of the electron, the electron oscillates in phase with the light. If the radiation has a much higher frequency than the electron's natural frequency, the electron moves 180° out of phase with the light. Only when the frequency of the light is close to the natural frequency of the electron does the phase differ from 0° or 180° .

It should be emphasized that the value of Q assumed in Fig. 15-8 is very much smaller than values typically found for electronic oscillations in atoms and molecules. Therefore the curve for α' should be much more sharply peaked and the maximum and minimum in α should occur in a much narrower frequency range than is shown in this figure.

This type of response is always found when oscillating systems are subjected to periodic forces. The student can easily verify the general form of the relationships mentioned above in the following way: Set up a pendulum and attach a string to its lower end (Fig. 15-9). Take hold of the other end of the string, allowing it to hang loosely between your hand and the pendulum. Now move your hand back and forth at a definite frequency, ν . The pendulum will begin to swing back and forth with the same frequency as your hand, soon attaining a definite steady-state amplitude and phase. This steady-state amplitude will be larger, the closer the applied frequency is to the natural frequency of the pendulum, ν_0 . The pendulum will move nearly in phase with your hand if ν is less than ν_0 , and it will move with nearly the opposite phase if ν is larger than ν_0 . If ν and ν_0 are nearly equal, the phase difference will be intermediate and if the frictional losses in the pendulum suspension are small the amplitude of oscillation will become very large.

If an atom or molecule contains a number of elastically and isotropically bound electrons that exert no forces on each other, we should expect that as long as the frequency of the incident light is not close to any of the natural frequencies, ν_i , of any of the electrons, the total polarizability of the system will be given by the sum of the polarizabilities of all of the electrons; that is

$$\alpha = (e^2/4\pi^2m_e) \sum_{\substack{\text{all} \\ \text{electrons, } i}} 1/(\nu_i^2 - \nu^2) \quad (\text{D-7})$$

where each electron contributes one term to the sum. Figure 15-10 shows a plot of polarizability *vs.* frequency of the radiation for a hypothetical atom containing three independent electrons whose natural frequencies are in the ratio $\nu_1 : \nu_2 : \nu_3 = 1 : \sqrt{2} : \sqrt{3}$.

According to (D-7), it should be possible to predict the frequency dependence of the polarizability of an atom or molecule from a knowledge of the

natural frequencies ν_i of the electrons in the atom or molecule, since each electron makes a contribution $(e^2/4\pi^2m_e) [1/(\nu_i^2 - \nu^2)]$ to the polarizability, and e and m_e are fundamental constants which are the same for all electrons. Experimental measurements of the frequency dependence of the polarizability show, however, that although (D-7) gives the correct functional form for the frequency dependence outside of the absorption bands of substances, the contributions of most natural frequencies are numerically smaller than predicted. Agreement with the experimental observations is obtained if factors f_i are introduced such that instead of (D-7) we have

$$\alpha = (e^2/4\pi^2m_e) \sum f_i/(\nu_i^2 - \nu^2) \quad (\text{D-8})$$

The constants f_i are called *oscillator strengths* (also sometimes the *effective number of electrons*). In the next section we shall show how oscillator strengths different from unity may arise in the classical theory, and in Chapter 16 we shall give a quantum mechanical interpretation that usually leads to oscillator strengths less than unity.

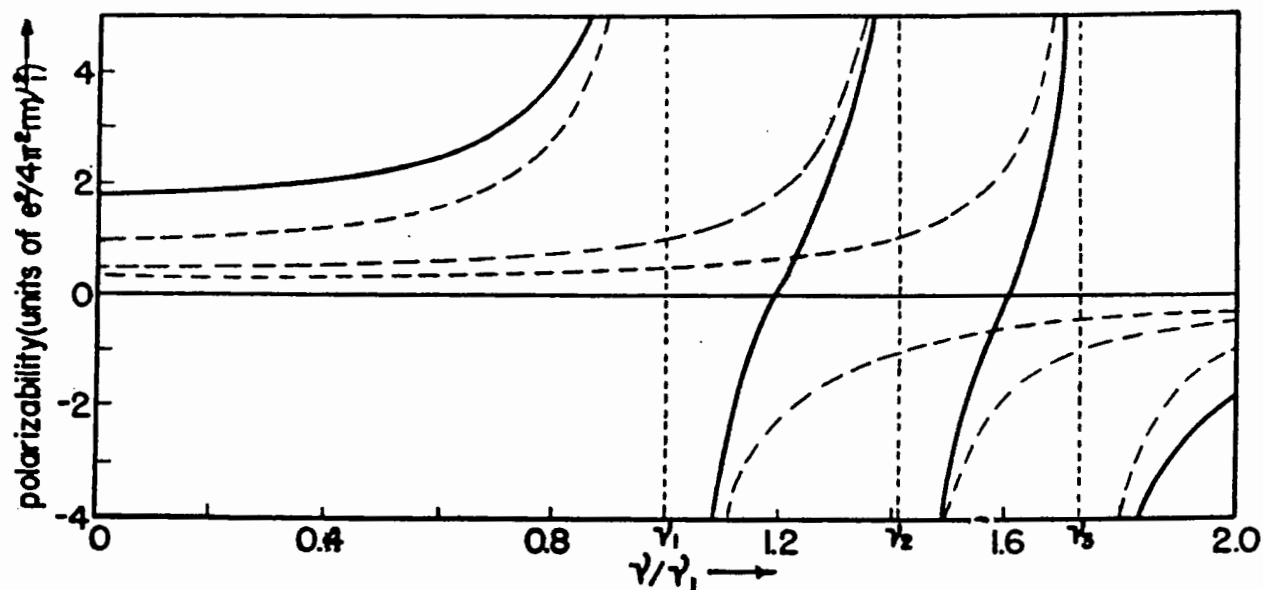


FIG. 15-10. Dependence of the polarizability on the frequency for a hypothetical atom containing three electrons whose natural frequencies are in the ratio $\nu_1:\nu_2:\nu_3 = 1:\sqrt{2}:\sqrt{3}$. The dashed curves give the contributions of the individual electrons. The solid curve is the sum of these dashed curves. The effect of damping is neglected.

b. Response of systems containing interacting electrons

The motions of interacting electrons are best discussed in terms of their normal modes of vibration. Consider, for instance, the system already described on page 558, consisting of an atom containing two electrons.

Assume that the line joining these two electrons is parallel to the electric field in the incident light. Then the equations of motion are (*cf.* Equations (B-6))

$$m_e \ddot{x}_a + (\eta + \mu) \dot{x}_a + k' x_a - (e^2/R^3)x_b = e |E_0| \sin \omega t \quad (\text{D-9a})$$

$$m_e \ddot{x}_b + (\eta + \mu) \dot{x}_b + k' x_b - (e^2/R^3)x_a = e |E_0| \sin \omega t \quad (\text{D-9b})$$

Taking the sum and difference of these two equations and setting

$$\begin{aligned} q_1 = x_a - x_b & \quad \omega_1^2 = \frac{k}{m_e} + \frac{2e^2}{R^3 m_e} \\ q_2 = x_a + x_b & \quad \omega_2^2 = \frac{k}{m_e} \end{aligned} \quad (\text{D-10})$$

we find

$$\ddot{q}_1 + [(\eta + \mu)/m_e] \dot{q}_1 + \omega_1^2 q_1 = 0 \quad (\text{D-11a})$$

$$\ddot{q}_2 + [(\eta + \mu)/m_e] \dot{q}_2 + \omega_2^2 q_2 = 2e |E_0| \sin \omega t \quad (\text{D-11b})$$

Equation (D-11b) has the same form as Equation (D-1a), so its solutions must have the same form as Equations (D-2), (D-3), and (D-4). Equation (D-11a), on the other hand, does not contain any term depending on the field of the light wave, so q_1 must be independent of E_0 ; this normal mode is not excited by a light wave. Thus we may write for the motions induced by the light,

$$q_1 = 0 \quad (\text{D-12a})$$

$$q_2 = q_{20} (\sin \omega t + \beta \cos \omega t) \quad (\text{D-12b})$$

or

$$x_a = x_b = q_2/2 = x_0 (\sin \omega t + \beta \cos \omega t) \quad (\text{D-12c})$$

where x_0 and β are given by Equations (D-4a) and (D-4b), with $\omega_0^2 = k/m_e = \omega_2^2$. The induced dipole moment is

$$m = e(x_a + x_b) = 2ex_0 (\sin \omega t + \beta \cos \omega t) \quad (\text{D-13})$$

If the frequency of the incident light differs appreciably from ω_2 we thus find for the in-phase polarizability

$$\alpha = \frac{e^2}{m_e} \left[\frac{2}{\omega_2^2 - \omega^2} + \frac{0}{\omega_1^2 - \omega^2} \right] \quad (\text{D-14})$$

Therefore we may say that each normal mode of the system makes a contribution to the in-phase polarizability; the contribution of the anti-

symmetric mode is double that of a single isolated electron (first term in Equation (D-14)), and the symmetric mode makes the contribution zero (second term in Equation (D-14)). The same factors appear in the expressions for the out-of-phase polarizability, the antisymmetric mode giving twice as large a value of α' as would be obtained for a single electron, whereas the symmetric mode gives $\alpha' = 0$.

Generalizing this result, we may expect that the contributions of the electronic motions to the in-phase polarizability of an atom or molecule will result in an expression of the form

$$\alpha = \frac{e^2}{4\pi^2 m_e} \sum_{\substack{\text{all normal} \\ \text{modes}}} \frac{f_i}{\nu_i^2 - \nu^2} \quad (\text{D-15})$$

where the dimensionless constants f_i are the *oscillator strengths* mentioned in the previous section, and ν_i is the frequency of the i^{th} normal mode. The oscillator strengths are characteristics of the normal modes and, according to the classical point of view, they can be regarded as an effective number of electrons active in the respective normal modes. In the simple example described above, the oscillator strength of the antisymmetric mode is two, and that of the symmetric mode is zero. If the electrons in a normal mode tend to move in phase, the oscillator strength of that mode will be large. If they tend to move out of phase, it will be small or even zero.

Just as we must introduce the oscillator strength, f_i , into the expression for the contribution of a normal mode to the in-phase polarizability, so we must introduce the same factor into the expression for the out-of-phase polarizability associated with each normal frequency. Thus, when the light frequency is close to one of the normal mode frequencies, ω_i , we shall write Equation (D-6b) in the form

$$\alpha'_i = \frac{f_i e^2}{\pi m_e Q} \frac{\omega \omega_i}{(\omega_i^2 - \omega^2)^2 + (\omega_i \omega / \pi Q)^2} \quad (\text{D-16})$$

where k has been replaced by $m_e \omega_i^2$, and Q has the value corresponding to a single isolated electron.

An oscillator strength different from unity also occurs if electrons are bound anisotropically. For example, consider an atom in which a single electron is constrained to move along a straight line with a characteristic frequency ν_0 . If this line makes an angle θ with the direction of the electric field of the incident light, the component of force, \mathbf{f}_3 , along the path must be written

$$e |E_0| \cos \theta \sin 2\pi \nu t$$

and Equations (D-4b) and (D-4c) will contain an additional factor, $\cos \theta$, on the right. The component of the induced dipole moment in the direction of the applied field also contains a factor of $\cos \theta$, so that the amplitude of the oscillating dipole moment component is

$$\begin{aligned} m_0 &= ex_0 \cos \theta \\ &= \alpha_0 \cos^2 \theta |\mathbf{E}_0| \end{aligned}$$

where α_0 is the polarizability when $\theta = 0$. Suppose that the atom is free to orient at random in all directions relative to the direction of \mathbf{E}_0 . The components of the induced moment perpendicular to \mathbf{E}_0 will cancel, so that the average induced moment lies in the direction of \mathbf{E}_0 . Since the average value of $\cos^2 \theta$ is one-third, the mean in-phase polarizability will have the value

$$\alpha = \frac{e^2}{4\pi^2 m_e} \frac{1/3}{\nu_0^2 - \nu^2}$$

The same factor of one-third also appears in the expression for α' . Thus the oscillator strength is one-third for a randomly oriented linear oscillator.

If we assign oscillator strengths to normal modes in the manner suggested above, it is necessary to reinterpret the oscillator strength of an isolated, isotropically bound electron. Such an electron will have, of course, three independent normal modes, which consist of vibrations in three mutually perpendicular directions. These three normal modes have the same frequency. They therefore contribute three identical terms to Equation (D-15). In order that (D-15) give the same result as (D-6c), which was obtained for the identical system, it is necessary to assign values $f_i = 1/3$ to each of these normal modes.

It is evident that if an atom contains N uncoupled electrons, each capable of three modes of oscillation, then it must be true that

$$\sum_{\substack{\text{all} \\ \text{modes}}} f_i = N \quad (\text{D-17})$$

This is known as the *Kuhn-Thomas sum rule*. We shall see that it is true also in the quantum mechanical modification of the electron theory of optics, in spite of the fact that the oscillator strengths are given an entirely different interpretation from the one just described.

At very high frequencies, when ν is much greater than all of the normal mode frequencies ν_i , Equation (D-15) takes the form

$$\alpha \cong (e^2/4\pi^2 m_e) \sum (-f_i/\nu^2) = -Ne^2/4\pi^2 m_e \nu^2 \quad (\text{D-18})$$

This expression is, in fact, valid for x-rays passing through matter, and was used by J. J. Thomson to calculate the number of electrons in atoms. It is interesting to note that matter has a negative polarizability for x-radiation.

If an oscillation involving several coupled electrons has an oscillator strength f , the damping constant, ω' , appearing in Equation (B-3) will be given by

$$\omega' = 3f \times (\text{damping factor due to each normal mode of a single electron})$$

If radiation damping is the only source of dissipation, this means that

$$\omega' = fe^2\omega_0^2/m_e c^3 \quad (\text{D-19})$$

Exercises. (1) Show that the maximum out-of-phase polarizability of an electron is larger than the static polarizability by a factor πQ .

(2) Show that for large values of Q the maximum and minimum in-phase polarizabilities are $\pm \pi Q/2$ times the static polarizability.

(3) Show that the curve of the half width of the out-of-phase polarizability *vs.* ordinary frequency satisfies $\nu_0/\pi Q = 4\pi\omega'$. Compare this with the half width of the emission line of the same electron.

(4) Show that $x_0^2(1 + \beta^2) = [a'/\omega(\eta + \mu)] |E_0|^2$ (D-20)

(5) Discuss the oscillator strengths of the normal modes of an atom containing three electrons that lie long a straight line, the equilibrium positions of the two end electrons being equidistant from the equilibrium position of the central electron.

c. The absorption of light by bound electrons

The term $(\eta + \mu)dx/dt$ in Equation (D-1a) represents a force that dissipates energy in the form of scattered radiation and heat. It must therefore be responsible for the phenomenon of *light absorption*.

The rate of energy dissipation is the scalar product of the dissipative force multiplied by the velocity of the electron

$$\text{Rate of dissipation} = (\mathbf{f}_5 + \mathbf{f}_6) \cdot d\mathbf{x}/dt = (\eta + \mu) (dx/dt)^2 \quad (\text{D-21})$$

The mean rate of dissipation per second is the dissipation per cycle multiplied by the number of cycles per second

$$\mathcal{W} = \nu \int_0^{1/\nu} (\eta + \mu) (dx/dt)^2 dt \quad (\text{D-22})$$

Using Equations (D-2) and (D-20) to evaluate dx/dt and writing $z = \omega t$, we obtain

$$\begin{aligned} \mathcal{W} &= 2\pi(\eta + \mu)v^2x_0^2 \int_0^{2\pi} (\cos z - \beta \sin z)^2 dz & (D-23) \\ &= 2\pi^2(\eta + \mu)v^2x_0^2 (1 + \beta^2) \\ &= \frac{1}{2}\omega\alpha' |E_0|^2 \end{aligned}$$

If there are n atoms in each cubic centimeter, the rate of energy dissipation per cubic centimeter is

$$n\mathcal{W} = \frac{1}{2}n\omega\alpha' |E_0|^2 \quad (D-24)$$

Exercise. The oscillating electrons are equivalent to a current with a current density of

$$i = ne \, dx/dt$$

The electrons move in the direction of the electric field \mathbf{E} of the light wave, and they therefore consume power at the rate $|\mathbf{E}|i$. The net power consumed per second per cubic centimeter is

$$v \int_0^{1/v} |\mathbf{E}|i \, dt$$

Show that this gives the same result as Equation (D-23).

The tendency of a substance to absorb light is measured experimentally in terms of the *molar extinction coefficient*, ε (also sometimes called the *molar absorptivity* and the *molar absorbancy index*) which is defined by the equation

$$\varepsilon = -(1/M) d(\log_{10}I)/dx = -1/(2.303MI) dI/dx \quad (D-25)$$

where M is the number of moles of the substance per liter, $I(x)$ is the intensity of the light at point x , and dI is the decrease in the intensity that results when the light passes through a layer of substance of thickness dx . When Equation (D-24) is integrated, one obtains the familiar expression

$$I = I_0 10^{-\varepsilon Mx} \quad (D-25a)$$

where I_0 is the intensity of the light falling on the surface of the absorbing medium, and I is the intensity remaining after the light has travelled a distance x through the medium. Equations (D-25) and (D-25a) are, of

course, merely the mathematical expressions of Beer's law and Lambert's law of light absorption.

The molar extinction coefficient defined in this way must be directly related to the energy dissipation, \mathcal{W} , given in Equation (D-24). When a beam of light whose cross-section is one square centimeter passes through a thickness dx of a medium containing n absorbing atoms per cubic centimeter, the energy dissipated in unit time is

$$dI = -n\mathcal{W}dx \quad (\text{D-26})$$

On comparing this result with (D-24) we see that

$$\varepsilon = n\mathcal{W}/2.303MI \quad (\text{D-27})$$

Now the intensity, I , of the incident light is defined as the radiant energy passing through an area of one square centimeter in one second. It is given by the velocity of light multiplied by the radiant energy contained in one cubic centimeter. From Equations (A-4a) and (A-2), the radiation energy in one cubic centimeter is

$$\begin{aligned} (1/4\pi) \int_0^{1 \text{ cm}} |\mathbf{E}|^2 dx &= (|\mathbf{E}_0|^2/4\pi) \int_0^{1 \text{ cm}} \sin^2 \omega(t - x/c) dx \\ &= |\mathbf{E}_0|^2/8\pi \end{aligned} \quad (\text{D-28})$$

Thus we find that

$$I = c|\mathbf{E}_0|^2/8\pi \quad (\text{D-29})$$

Furthermore the number of molecules per cubic centimeter is

$$n = MN/1000 \quad (\text{D-30})$$

where N is Avogadro's number. Combining Equations (D-24), (D-27), (D-29), and (D-30) we find

$$\varepsilon = (4\pi N/2303c)\omega\alpha' \quad (\text{D-31})$$

Thus the out-of-phase polarizability, α' , is directly related to the molar extinction coefficient, which is commonly used to express the ability of matter to absorb light.

According to Equation (D-31), the shape of an absorption band (that is, the dependence of the extinction coefficient on the frequency) should be essentially the same as the curve shown in Fig. 15-8 relating α' and the frequency, the width of the band being determined by the magnitude of the

dissipation factors η and μ . This, however, is almost never the case. In any sample of matter electrons in different atoms never have exactly the same natural vibration frequencies, ν_i . One reason for this is the Doppler effect, which causes a difference in the relative values of the light frequency, ν , and the natural frequencies, ν_i , depending on the direction of motion of the atom relative to the light wave. A much more important cause of variation, however, is the fact that because of thermal fluctuations the environments of all atoms are not the same. This is especially true of atoms in the liquid and solid states. Since the environment affects the values of the normal mode frequencies, the values of ν_i will be different in different atoms. The observed absorption band in a liquid or solid is therefore a superposition of many narrow bands, each having a shape determined by α' in Equation (D-16), but centered on different values of ν_i . Consequently, the over-all shape of the band depends on the interactions between the environment and the electrons.

These environmental effects are most conveniently taken into account in the following way. Suppose that in an isolated atom the electrons have a normal mode whose frequency is ν_{i0} . When the atoms are placed in a solution or in a solid, this normal mode frequency will take on other values because of the interactions with neighboring molecules. Let us define a function $\phi(\nu_i)$ such that $\phi(\nu_i)d\nu_i$ is the fraction of the atoms present in the solution in which the frequency of this i^{th} normal mode lies between ν_i and $\nu_i + d\nu_i$. Then, using Equation (D-16) for the out-of-phase polarizability and replacing the circular frequencies by ordinary frequencies, we find from (D-31) that the molecular extinction coefficient at a particular frequency ν in the absorption band arising from the i^{th} normal mode is

$$\begin{aligned} \epsilon_i &= \frac{2N}{2303} \frac{e^2}{c m_e} \int_0^\infty \frac{f_i \nu^2 \nu_i \phi(\nu_i) d\nu_i}{\pi Q [(\nu_i^2 - \nu^2)^2 + (\nu \nu_i / \pi Q)^2]} \\ &= \frac{N e^2}{2303 c m_e} \int_0^\infty \frac{f_i \nu^2 \phi(\nu_i) d\nu_i^2}{\pi Q [(\nu_i^2 - \nu^2)^2 + (\nu \nu_i / \pi Q)^2]} \end{aligned} \quad (\text{D-32})$$

Since Q is generally much larger than unity, the denominator in the integrand is very large except when ν_i is very close to ν . The entire contribution to the integral therefore comes from the immediate vicinity of $\nu_i = \nu$, so the numerator, which varies relatively slowly with ν_i , can be treated as a constant and can be taken out of the integral, and the quantity $\nu \nu_i$ in the denominator can be replaced by ν^2 . Furthermore,

$$\int (x^2 + b^2)^{-1} dx = (1/b) \tan^{-1}(x/b)$$

Therefore, setting $x = \nu_i^2 - \nu^2$ inside the integral, we obtain

$$\begin{aligned}\epsilon_i &= \frac{Ne^2}{2303 \text{ cm}_e} \frac{\nu^2 f_i \phi(\nu)}{\pi Q} \int_{-\infty}^{\infty} \frac{dx}{x^2 + (\nu^2/\pi Q)^2} \\ &= \frac{\pi Ne^2}{2303 \text{ cm}_e} f_i \phi(\nu)\end{aligned}\tag{D-33}$$

Under these circumstances, the shape of the absorption band is evidently determined by ϕ rather than by Equation (D-16).

Equation (D-33) provides us with an experimental method of finding the oscillator strength of the electronic vibrations responsible for a given absorption band. Suppose that the molar extinction coefficient of an absorption band is plotted against the frequency, and the area under the curve is measured. According to (D-33) this area is

$$\int \epsilon_i d\nu = \frac{\pi Ne^2}{2303 \text{ cm}_e} f_i \int \phi(\nu) d\nu\tag{D-34}$$

But from the definition of ϕ , we have

$$\int \phi(\nu) d\nu = 1\tag{D-35}$$

Therefore

$$f_i = \frac{2303 \text{ m}_e c}{\pi Ne^2} \int \epsilon_i d\nu\tag{D-36}$$

Thus the oscillator strength of a normal mode is directly proportional to the area under its absorption curve. If the frequency is expressed in cm.^{-1} (indicated by the symbol $\tilde{\nu}$), Equation (D-36) gives*

$$f_i = 4.319 \times 10^{-9} \int \epsilon_i d\tilde{\nu}\tag{D-36a}$$

* In this derivation, a small internal field correction has been omitted. If it is included, (D-36) becomes

$$f_i = \frac{2303 \text{ m}_e c}{\pi Ne^2} \frac{9n_0}{(n_0^2 + 2)^2} \int \epsilon_i d\nu\tag{D-36b}$$

where n_0 is the refractive index of the medium in which the absorbing molecule is dissolved [see page 603 and (7)]. Since the index of refraction of most solvents is between 1.3 and 1.6, the correction factor usually lies between 0.69 and 0.86.

The numerical values of the oscillator strengths of absorption bands found in this way will be discussed in detail in the next chapter, but it is interesting to give a few typical values at this point. The absorption bands of the rare earth ions in the visible part of the spectrum give oscillator strengths between 10^{-6} and 10^{-8} . The bands responsible for the colors of the transition metal cations (Cu^{++} , Cr^{+++} , Fe^{+++} , etc.) have oscillator strengths of the order of 10^{-4} . The intense purple of permanganate ion is caused by a band with an oscillator strength of only 0.03. Among the familiar colored substances of everyday life, only the organic dyestuffs give oscillator strengths approaching unity. Values greater than unity are exceptional, and values much greater than unity are never found. This fact is not easy to explain in terms of the classical electron theory, but is readily dealt with by the quantum mechanical theory. Further discussion will therefore be deferred to the next chapter.

The absorption bands of most organic and inorganic molecules in solutions have half-widths of the order of 5000 cm.^{-1} . If we use the approximation

$$\int \epsilon d\tilde{\nu} \cong 5000 \epsilon_{\max}$$

where ϵ_{\max} is the maximum value of the extinction coefficient of the band, then we may estimate an upper limit to the molar extinction coefficient of typical colored substances. Since oscillator strengths greater than unity are unusual, we see from (D-36a) that values of ϵ_{\max} much greater than about 5×10^4 are not to be expected for substances in condensed phases.

In Section Db of this chapter we have seen that the contribution of each normal mode to the in-phase polarizability is proportional to the oscillator strength of the mode. We now see that the oscillator strength also determines the intensity of the absorption of light. *Thus there is a close relationship between the contribution of a band to the polarizability and the intensity of the absorption in the band; weak bands lead to small contributions to the polarizability and strong bands give large contributions.* Evidently the absorption bands responsible for the colors of most substances other than organic dyes give very small contributions to the polarizability.

In the next chapter, we shall need to know the total rate of energy dissipation by a normal mode when an absorbing atom is exposed to "white" light—that is, light that contains all of the frequencies belonging to a given absorption band of the atom. Light of this kind may be described by means of a density function, $\rho(\nu)$, where $\rho(\nu)d\nu$ is the energy per unit volume belonging to frequencies lying

in the range between ν and $\nu + d\nu$. We shall be particularly interested in what happens when $\rho(\nu)$ is constant for the frequencies in some absorption band of a substance. From Equation (D-28), the mean energy density in a light wave is $|\mathbf{E}_0|^2/8\pi$, where $|\mathbf{E}_0|$ is the amplitude of the electric field in the light wave. Thus the total amplitude of the electric field, $|\mathbf{E}_0|$, that arises from the frequencies lying between ν and $\nu + d\nu$ can be found from the relation

$$|\mathbf{E}_0|^2/8\pi = \rho(\nu)d\nu \quad (\text{D-37})$$

The energy absorbed per cubic centimeter by the i^{th} normal mode under these conditions is, from (D-24) and (D-16)

$$\begin{aligned} n\mathcal{W} &= \frac{1}{2}n \int_0^\infty 8\pi\omega a' \rho(\nu) d\nu \\ &= 2n\rho(\nu) \frac{fe^2}{m_e} \int_0^\infty \frac{\omega^2 \omega_i d\omega}{\pi Q [(\omega_i^2 - \omega^2)^2 + (\omega_i\omega/\pi Q)^2]} \end{aligned} \quad (\text{D-38})$$

The integral is evaluated by noting that the integrand is significantly different from zero only when ν is very close to ν_i because of the large value of Q . Using the same procedure as that employed in obtaining (D-33) from (D-32), we find for the energy absorbed in unit time per cubic centimeter

$$n\mathcal{W} = n \frac{fe^2}{m_e} \rho(\nu) \frac{\nu_i^2}{\pi Q} \int_0^\infty \frac{d\nu^2}{(\nu_i^2 - \nu^2)^2 + (\nu_i^2/\pi Q)^2} = \pi n \frac{fe^2}{m_e} \rho(\nu) \quad (\text{D-39})$$

It is important to note that this result is independent of the nature of the dissipative forces. The integrated absorption evidently depends only on the magnitude of the oscillator strength. The dissipative forces (that is, the forces giving rise to the coefficients η and μ and to the Q -factor of a vibration) can at most affect the shape of a band, and not the total amount of the absorption.

Exercises. (1) Show that Equation (D-36) is true even if there is no broadening of the absorption line by interactions with neighboring molecules. [Hint: Substitute (D-16) into (D-31), and integrate over the light frequencies, ν .]

(2) What is the amplitude of the electric field at a point one meter from a 100-watt light bulb, if 10% of the power supplied is converted into light? [Answer: 0.052 millivolts per centimeter.]

(3) The cross-section of a molecule for an absorption process may be defined as the equivalent opaque area that the molecule seems to present to an incident beam of radiation. Thus if there are N molecules per cubic centimeter and if each has a cross-section σ , then a layer of thickness dx would "black out" a fraction $N\sigma dx$ of the area of the layer. As a result of passing through the layer, an incident beam of intensity I would be decreased in intensity by the fractional amount $dI/I = -N\sigma dx$. Comparing this with Equation (D-25), calculate the effective cross-section of a molecule whose molar extinction coefficient is 5×10^4 (corresponding approximately to an oscillator strength of unity). [Answer: $\sigma = 2 \times 10^{-16}$ cm.²]

E. The Scattering of Light and Some of Its Consequences

In Section D of this chapter we have found that when an atom is exposed to light, its electrons undergo oscillations that have the same frequency as the incident light. According to Equation (A-5a), however, any oscillating charge must emit light whose frequency is the same as the frequency of the oscillation. Therefore, when light shines on an atom, the atom must itself emit light of the same frequency as the incident light. The atom is said to *scatter* the incident light. The light that is scattered in this way is responsible for many important optical phenomena, such as refraction, x-ray diffraction, and optical rotatory power.

a. Scattering by an isolated particle

The field strength in the light radiated from an oscillating dipole is given by Equation (A-5b)

$$|\mathbf{E}_s| = - (m_0 \omega^2 / rc^2) \sin \theta \cos \omega(t - r/c) \quad (\text{A-5b})$$

where m_0 is the amplitude of the oscillation of the dipole moment. If an atom is placed in a beam of polarized light whose frequency does not coincide with any of the absorption frequencies of the atom, we may replace m_0 in (A-5b) by $\alpha |\mathbf{E}_0|$, where α is the in-phase polarizability of the atom and $|\mathbf{E}_0|$ is the amplitude of the electric field in the incident light. We shall assume that m_0 lies in the same direction as \mathbf{E}_0 (this means that the polarizability of the atom is the same in all directions, an assumption which will be modified in Section h, below). Then the amplitude of the electric field in the scattered light is

$$|\mathbf{E}_s| = \alpha |\mathbf{E}_0| (\omega^2 / rc^2) \sin \theta \cos \omega(t - r/c) \quad (\text{E-1})$$

where θ is the angle between the direction of polarization in the incident light (that is, the direction of \mathbf{E}_0) and a line drawn from the atom to the observer.

The energy in the light scattered in one second within a solid angle $d\Omega$ in a given direction is

$$\begin{aligned} I_s &= \int_{r=0}^c (|\mathbf{E}_s|^2 / 4\pi) r^2 dr d\Omega \\ &= (\alpha^2 \omega^4 / c^4) I_0 \sin^2 \theta d\Omega \end{aligned} \quad (\text{E-2})$$

where $I_0 = c|\mathbf{E}_0|^2/8\pi$ is the intensity of the incident light (see Equation (D-29)). The total energy scattered in all directions is

$$\begin{aligned} I_{st} &= \int I_s d\Omega = \int_0^{2\pi} \int_0^\pi I_s \sin\theta d\theta d\varphi \\ &= 2\pi(\alpha^2\omega^4/c^4)I_0 \int_0^\pi \sin^3\theta d\theta \\ &= \frac{8\pi\alpha^2\omega^4}{3c^4} I_0 \end{aligned} \quad (\text{E-3})$$

Exercise. Show that if the incident light is not polarized, the energy of the light scattered into the solid angle $d\Omega$ in a direction making an angle χ with the direction of the incident beam is

$$I_s = (\alpha^2\omega^4/2c^4) (1 + \cos^2\chi)I_0 d\Omega \quad (\text{E-4})$$

Also show that the total energy scattered in all directions in this case is the same as Equation (E-3).

b. Scattering by more than one particle

If more than one atom is present in the light beam, the scattered fields from all of the atoms must first be added and the resultant must then be squared in order to find the intensity of the scattered light. Suppose, for instance, that two atoms are separated by a distance small compared with the wave length of the incident light. Then the electric fields in the scattered light will have the same phase and will add, giving a resultant field strength double that obtained from a single atom, while the scattered intensity will be four times that obtained from a single atom. If, on the other hand, the two atoms are farther apart, and are so located that the scattered beams arrive at the observer exactly out of phase (see Fig. 15-11), then the observer will see no scattered light at all. Thus the intensity of scattering from a group of atoms may depend very strongly on the geometrical arrangement of the atoms with respect to one another, as well as on the position of the observer. We can see that the calculation of the intensity of the scattered light in different directions from an array of atoms may be a rather complicated problem. A few general remarks can, however, be made about the properties of the scattered light in certain situations.

(i) The light scattered in the forward direction by any number and ar-