Absorption of electromagnetic radiation

The process whereby the intensity of a beam of electromagnetic radiation is attenuated in passing through a material medium by conversion of the energy of the radiation to an equivalent amount of energy which appears within the medium; the radiant energy is converted into heat or some other form of molecular energy. A perfectly transparent medium permits the passage of a beam of radiation without any change in intensity other than that caused by the spread or convergence of the beam, and the total radiant energy emergent from such a medium equals that which entered it, whereas the emergent energy from an absorbing medium is less than that which enters, and, in the case of highly opaque media, is reduced practically to zero.

No known medium is opaque to all wavelengths of the electromagnetic spectrum, which extends from radio waves, whose wavelengths are measured in kilometers, through the infrared, visible, and ultraviolet spectral regions, to x-rays and gamma rays, of wavelengths down to 10^{-13} m. Similarly, no material medium is transparent to the whole electromagnetic spectrum. A medium which absorbs a relatively wide range of wavelengths is said to exhibit general absorption, while a medium which absorbs only restricted wavelength regions of no great range exhibits selective absorption for those particular spectral regions. For example, the substance pitch shows general absorption for the visible region of the spectrum, but is relatively transparent to infrared radiation of long wavelength. Ordinary window glass is transparent to visible light, but shows general absorption for ultraviolet radiation of wavelengths below about 310 nanometers, while colored glasses show selective absorption for specific regions of the visible spectrum. The color of objects which are not self-luminous and which are seen by light reflected or transmitted by the object is usually the result of selective absorption of portions of the visible spectrum. Many colorless substances, such as benzene and similar hydrocarbons, selectively absorb within the ultraviolet region of the spectrum, as well as in the infrared. *See also:* COLOR; ELECTROMAGNETIC RADIATION.

Laws of absorption

The capacity of a medium to absorb radiation depends on a number of factors, mainly the electronic and nuclear constitution of the atoms and molecules of the medium, the wavelength of the radiation, the thickness of the absorbing layer, and the variables which determine the state of the medium, of which the most important are the temperature and the concentration of the absorbing agent. In special cases, absorption may be influenced by electric or magnetic fields. The state of polarization of the radiation influences the absorption of media containing certain oriented structures, such as crystals of other than cubic symmetry. *See also:* STARK EFFECT; ZEEMAN EFFECT.

Lambert's law. Lambert's law, also called Bouguer's law or the Lambert-Bouguer law, expresses the effect of the thickness of the absorbing medium on the absorption. If a homogeneous medium is thought of as being constituted of layers of uniform thickness set normally to the beam, each layer absorbs the same fraction of radiation incident on it. If I is the intensity to which a monochromatic parallel beam is attenuated after traversing a thickness d of the medium, and I_0 is the intensity of the beam at the surface of incidence (corrected for loss by reflection from this surface), the variation of intensity throughout the medium is expressed by Eq. (1),

$$I = I_0 e^{-\alpha d} \tag{1}$$

in which α is a constant for the medium called the absorption coefficient. This exponential relation can be expressed in an equivalent logarithmic form as in Eq. (2),

$$\log_{10}(I_0/I) = (\alpha/2.303)d = kd \tag{2}$$

where $k = \alpha/2.303$ is called the extinction coefficient for radiation of the wavelength considered. The quantity $\log_{10}(I_0/I)$ is often called the optical density, or the absorbance of the medium.

Equation (2) shows that as monochromatic radiation penetrates the medium, the logarithm of the intensity decreases in direct proportion to the thickness of the layer traversed. If experimental values for the intensity of the light emerging from layers of the medium of different thicknesses are available (corrected for reflection losses at all reflecting surfaces), the value of the extinction coefficient can be readily computed from the slope of the straight line representing the logarithms of the emergent intensities as functions of the thickness of the layer.

Equations (1) and (2) show that the absorption and extinction coefficients have the dimensions of reciprocal length. The extinction coefficient is equal to the reciprocal of the thickness of the absorbing layer required to reduce the intensity to one-tenth of its incident value. Similarly, the absorption coefficient is the reciprocal of the thickness required to reduce the intensity to $1/e$ of the incident value, where e is the base of the natural logarithms, 2.718.

Beer's law. This law refers to the effect of the concentration of the absorbing medium, that is, the mass of absorbing material per unit of volume, on the absorption. This relation is of prime importance in describing the absorption of solutions of an absorbing solute, since the solute's concentration may be varied over wide limits, or the absorption of gases, the concentration of which depends on the pressure. According to Beer's law, each individual molecule of the absorbing material absorbs the same fraction of the radiation incident upon it, no matter whether the molecules are closely packed in a concentrated solution or highly dispersed in a dilute solution. The relation between the intensity of a parallel monochromatic beam which emerges from a plane parallel layer of absorbing solution of constant thickness and the concentration of the solution is an exponential

one, of the same form as the relation between intensity and thickness expressed by Lambert's law. The effects of thickness d and concentration c on absorption of monochromatic radiation can therefore be combined in a single mathematical expression, given in Eq. (3),

$$I = I_0 e^{-k'cd} \tag{3}$$

in which k' is a constant for a given absorbing substance (at constant wavelength and temperature), independent of the actual concentration of solute in the solution. In logarithms, the relation becomes Eq. (4).

$$\log_{10}(I_0/I) = (k'/2.303)cd = \epsilon cd \tag{4}$$

The values of the constants k' and ε in Eqs. (3) and (4) depend on the units of concentration. If the concentration of the solute is expressed in moles per liter, the constant ε is called the molar extinction coefficient. Some authors employ the symbol a_M, which is called the molar absorbance index, instead of ε.

If Beer's law is adhered to, the molar extinction coefficient does not depend on the concentration of the absorbing solute, but usually changes with the wavelength of the radiation, with the temperature of the solution, and with the solvent.

The dimensions of the molar extinction coefficient are reciprocal concentration multiplied by reciprocal length, the usual units being liters/(mole)(cm). If Beer's law is true for a particular solution, the plot of log (I_0/I) against the concentrations for solutions of different concentrations, measured in cells of constant thickness, will yield a straight line, the slope of which is equal to the molar extinction coefficient.

While no true exceptions to Lambert's law are known, exceptions to Beer's law are not uncommon. Such exceptions arise whenever the molecular state of the absorbing solute depends on the concentration. For example, in solutions of weak electrolytes, whose ions and undissociated molecules absorb radiation differently, the changing ratio between ions and undissociated molecules brought about by changes in the total concentration prevents solutions of the electrolyte from obeying Beer's law. Aqueous solutions of dyes frequently deviate from the law because of dimerization and more complicated aggregate formation as the concentration of dye is increased.

Absorption measurement

The measurement of the absorption of homogeneous media is usually accomplished by absolute or comparative measurements of the intensities of the incident and transmitted beams, with corrections for any loss of radiant energy caused by processes other than absorption. The most important of these losses is by reflection at the various surfaces of the absorbing layer and of vessels which may contain the medium, if the medium is liquid or

gaseous. Such losses are usually automatically compensated for by the method of measurement employed. Losses by reflection not compensated for in this manner may be computed from Fresnel's laws of reflection. *See also:* REFLECTION OF ELECTROMAGNETIC RADIATION.

Scattering

Absorption of electromagnetic radiation should be distinguished from the phenomenon of scattering, which occurs during the passage of radiation through inhomogeneous media. Radiant energy which traverses media constituted of small regions of refractive index different from that of the rest of the medium is diverted laterally from the direction of the incident beam. The diverted radiation gives rise to the hazy or opalescent appearance characteristic of such media, exemplified by smoke, mist, and opal. If the centers of inhomogeneity are sufficiently dilute, the intensity of a parallel beam is diminished in its passage through the medium because of the sidewise scattering, according to a law of the same form as the Lambert-Bouguer law for absorption, given in Eq. (5),

$$I = I_0 e^{-\tau d} \tag{5}$$

where I is the intensity of the primary beam of initial intensity I_0, after it has traversed a distance d through the scattering medium. The coefficient τ, called the turbidity of the medium, plays the same part in weakening the primary beam by scattering as does the absorption coefficient in true absorption. However, in true scattering, no loss of total radiant energy takes place, energy lost in the direction of the primary beam appearing in the radiation scattered in other directions. In some inhomogeneous media, both absorption and scattering occur together. *See also:* SCATTERING OF ELECTROMAGNETIC RADIATION.

Physical nature

Absorption of radiation by matter always involves the loss of energy by the radiation and a corresponding gain in energy by the atoms or molecules of the medium.

The energy of an assembly of gaseous atoms consists partly of kinetic energy of the translational motion which determines the temperature of the gas (thermal energy), and partly of internal energy, associated with the binding of the extranuclear electrons to the nucleus, and with the binding of the particles within the nucleus itself. Molecules, composed of more than one atom, have, in addition, energy associated with periodic rotations of the molecule as a whole and with oscillations of the atoms within the molecule with respect to one another.

The energy absorbed from radiation appears as increased internal energy, or in increased vibrational and rotational energy of the atoms and molecules of the absorbing medium. As a general rule, translational energy is not directly increased by absorption of radiation, although it may be indirectly increased by degradation of

electronic energy or by conversion of rotational or vibrational energy to that of translation by intermolecular collisions.

Quantum theory. In order to construct an adequate theoretical description of the energy relations between matter and radiation, it has been necessary to amplify the wave theory of radiation by the quantum theory, according to which the energy in radiation occurs in natural units called quanta. The value of the energy in these units, expressed in ergs or calories, for example, is the same for all radiation of the same wavelength, but differs for radiation of different wavelengths. The energy E in a quantum of radiation of frequency ν (where the frequency is equal to the velocity of the radiation in a given medium divided by its wavelength in the same medium) is directly proportional to the frequency, or inversely proportional to the wavelength, according to the relation given in Eq. (6),

$$ E = h\nu \tag{6} $$

where h is a universal constant known as Planck's constant. The value of h is 6.63×10^{-34} joule-second, and if ν is expressed in s^{-1}, E is given in joules per quantum. *See also:* QUANTUM MECHANICS.

The most energetic type of change that can occur in an atom involves the nucleus, and increase of nuclear energy by absorption therefore requires quanta of very high energy, that is, of high frequency or low wavelength. Such rays are the γ-rays, whose wavelength varies downward from 0.01 nm. Next in energy are the electrons nearest to the nucleus and therefore the most tightly bound. These electrons can be excited to states of higher energy by absorption of x-rays, whose range in wavelength is from about 0.01 to 1 nm. Less energy is required to excite the more loosely bound valence electrons. Such excitation can be accomplished by the absorption of quanta of visible radiation (wavelength 700 nm for red light to 400 nm for blue) or of ultraviolet radiation, of wavelength down to about 100 nm. Absorption of ultraviolet radiation of shorter wavelengths, down to those on the border of the x-ray region, excites electrons bound to the nucleus with intermediate strength.

The absorption of relatively low-energy quanta of wavelength from about 1 to 10 micrometers suffices to excite vibrating atoms in molecules to higher vibrational states, while changes in rotational energy, which are of still smaller magnitude, may be excited by absorption of radiation of still longer wavelength, from the short-wavelength radio region of about 1 cm to long-wavelength infrared radiation, some hundredths of a centimeter in wavelength.

Gases. The absorption of gases composed of atoms is usually very selective. For example, monatomic sodium vapor absorbs very strongly over two narrow wavelength regions in the yellow part of the visible spectrum (the so-called D lines), and no further absorption by monatomic sodium vapor occurs until similar narrow lines appear in the near-ultraviolet. The valence electron of the sodium atom can exist only in one of a series of energy states separated by relatively large energy intervals between the permitted values, and the sharp-line absorption

spectrum results from transitions of the valence electron from the lowest energy which it may possess in the atom to various excited levels. Line absorption spectra are characteristic of monatomic gases in general. *See also:* ATOMIC STRUCTURE AND SPECTRA.

The visible and ultraviolet absorption of vapors composed of diatomic or polyatomic molecules is much more complicated than that of atoms. As for atoms, the absorbed energy is utilized mainly in raising one of the more loosely bound electrons to a state of higher energy, but the electronic excitation of a molecule is almost always accompanied by simultaneous excitation of many modes of vibration of the atoms within the molecule and of rotation of the molecule as a whole. As a result, the absorption, which for an atom is concentrated in a very sharp absorption line, becomes spread over a considerable spectral region, often in the form of bands. Each band corresponds to excitation of a specific mode of vibration accompanying the electronic change, and each band may be composed of a number of very fine lines close together in wavelength, each of which corresponds to a specific rotational change of the molecule accompanying the electronic and vibrational changes. Band spectra are as characteristic of the absorption of molecules in the gaseous state, and frequently in the liquid state, as line spectra are of gaseous atoms. *See also:* BAND SPECTRUM; LINE SPECTRUM; MOLECULAR STRUCTURE AND SPECTRA.

Liquids. Liquids usually absorb radiation in the same general spectral region as the corresponding vapors. For example, liquid water, like water vapor, absorbs infrared radiation strongly (vibrational transitions), is largely transparent to visible and near-ultraviolet radiation, and begins to absorb strongly in the far-ultraviolet. A universal difference between liquids and gases is the disturbance in the energy states of the molecules in a liquid caused by the great number of intermolecular collisions; this has the effect of broadening the very fine lines observed in the absorption spectra of vapors, so that sharp-line structure disappears in the absorption bands of liquids.

Solids. Substances which can exist in solid, liquid, and vapor states without undergoing a temperature rise to very high values usually absorb in the same general spectral regions for all three states of aggregation, with differences in detail because of the intermolecular forces present in the liquid and solid. Crystalline solids, such as rock salt or silver chloride, absorb infrared radiation of long wavelength, which excites vibrations of the electrically charged ions of which these salts are composed; such solids are transparent to infrared radiations of shorter wavelengths. In colorless solids, the valence electrons are too tightly bound to the nuclei to be excited by visible radiation, but all solids absorb in the near- or far-ultraviolet region. *See also:* CRYSTAL OPTICS; INTERMOLECULAR FORCES.

The use of solids as components of optical instruments is restricted by the spectral regions to which they are transparent. Crown glass, while showing excellent transparency for visible light and for ultraviolet radiation immediately adjoining the visible region, becomes opaque to radiation of wavelength about 300 nm and shorter, and is also opaque to infrared radiation longer than about 2000 nm in wavelength. Quartz is transparent down to wavelengths about 180 nm in the ultraviolet, and to about $4 \ \mu$m in the infrared. The most generally useful material for prisms and windows for the near-infrared region is rock salt, which is highly transparent out to about $15 \ \mu$m. For a detailed discussion of the properties of optical glass *See also:* OPTICAL MATERIALS.

Fluorescence

The energy acquired by matter by absorption of visible or ultraviolet radiation, although primarily used to excite electrons to higher energy states, usually ultimately appears as increased kinetic energy of the molecules, that is, as heat. It may, however, under special circumstances, be reemitted as electromagnetic radiation. Fluorescence is the reemission, as radiant energy, of absorbed radiant energy, normally at wavelengths the same as or longer than those absorbed. The reemission, as ordinarily observed, ceases immediately when the exciting radiation is shut off. Refined measurements show that the fluorescent reemission persists, in different cases, for periods of the order of 10^{-9} to 10^{-5} s. The simplest case of fluorescence is the resonance fluorescence of monatomic gases at low pressure, such as sodium or mercury vapors, in which the reemitted radiation is of the same wavelength as that absorbed. In this case, fluorescence is the converse of absorption: Absorption involves the excitation of an electron from its lowest energy state to a higher energy state by radiation, while fluorescence is produced by the return of the excited electron to the lower state, with the emission of the energy difference between the two states as radiation. The fluorescent radiation of molecular gases and of nearly all liquids, solids, and solutions contains a large component of wavelengths longer than those of the absorbed radiation, a relationship known as Stokes' law of fluorescence. In these cases, not all of the absorbed energy is reradiated, a portion remaining as heat in the absorbing material. The fluorescence of iodine vapor is easily seen on projecting an intense beam of visible light through an evacuated bulb containing a few crystals of iodine, but the most familiar examples are provided by certain organic compounds in solution—for instance, quinine sulfate, which absorbs ultraviolet radiation and reemits blue, or fluorescein, which absorbs blue-green light and fluoresces with an intense, bright-green color. *See also:* FLUORESCENCE.

Phosphorescence

The radiant reemission of absorbed radiant energy at wavelengths longer than those absorbed, for a readily observable interval after withdrawal of the exciting radiation, is called phosphorescence. The interval of persistence, determined by means of a phosphoroscope, usually varies from about 0.001 s to several seconds, but some phosphors may be induced to phosphorescence by heat days or months after the exciting absorption. An important and useful class of phosphors is the impurity phosphors, solids such as the sulfides of zinc or calcium which are activated to the phosphorescent state by incorporating minute amounts of foreign material (called activators), such as salts of manganese or silver. So-called fluorescent lamps contain a coating of impurity phosphor on their inner wall which, after absorbing ultraviolet radiation produced by passage of an electrical discharge through mercury vapor in the lamp, reemits visible light. The receiving screen of a television tube contains a similar coating, excited not by radiant energy but by the impact of a stream of electrons on the surface. *See also:* FLUORESCENT LAMP; PHOSPHORESCENCE.

Luminescence

Phosphorescence and fluorescence are special cases of luminescence, which is defined as light emission that cannot be attributed merely to the temperature of the emitting body. Luminescence may be excited by heat (thermoluminescence), by electricity (electroluminescence), by chemical reaction (chemiluminescence), or by friction (triboluminescence), as well as by radiation. *See also:* LUMINESCENCE.

Absorption and emission coefficients

The absorption and emission processes of atoms were examined from the quantum point of view by Albert Einstein in 1916, with some important results that have been realized practically in the invention of the maser and the laser. Consider an assembly of atoms undergoing absorption transitions of frequency v s^{-1} from the ground state 1 to an excited state 2 and emission transitions in the reverse direction, the atoms and radiation being at equilibrium at temperature T. The equilibrium between the excited and unexcited atoms is determined by the Boltzmann relation $N_2/N_1 = \exp(-hv/kT)$, where N_1 and N_2 are the equilibrium numbers of atoms in states 1 and 2, respectively, and the radiational equilibrium is determined by equality in the rate of absorption and emission of quanta. The number of quanta absorbed per second is $B_{12} N_1 \rho(v)$, where $\rho(v)$ is the density of radiation of frequency v (proportional to the intensity), and B_{12} is a proportionality constant called the Einstein coefficient for absorption. Atoms in state 2 will emit radiation spontaneously (fluorescence), after a certain mean life, at a rate of $A_{21} N_2$ per second, where A_{21} is the Einstein coefficient for spontaneous emission from state 2 to state 1. To achieve consistency between the density of radiation of frequency v at equilibrium calculated from these considerations and the value calculated from Planck's radiation law, which is experimentally true, it is necessary to introduce, in addition to the spontaneous emission, an emission of intensity proportional to the radiation density of frequency v in which the atoms are immersed. The radiational equilibrium is then determined by Eq. (7),

$$B_{12} N_1 \rho(v) = A_{21} N_2 + B_{21} N_2 \rho(v) \tag{7}$$

where B_{21} is the Einstein coefficient of stimulated emission. The Einstein radiation coefficients are found to be related by Eqs. (8*a*) and (8*b*).

$$B_{12} = B_{21} \tag{8a}$$

$$A_{21} = (8\pi h v^3/c^3) \cdot B_{21} \tag{8b}$$

In the past when one considered radiation intensities available from terrestrial sources, stimulated emission was very feeble compared with the spontaneous process. Stimulated emission is, however, the fundamental emission process in the laser, a device in which a high concentration of excited molecules is produced by intense illumination from a "pumping" source, in an optical system in which excitation and emission are augmented by back-and-forth reflection until stimulated emission swamps the spontaneous process. *See also:* LASER; OPTICAL PUMPING.

There are also important relations between the absorption characteristics of atoms and their mean lifetime τ in the excited state. Since A_{21} is the number of times per second that a given atom will emit a quantum spontaneously, the mean lifetime before emission in the excited state is $\tau = 1/A_{21}$. It can also be shown that A_{21} and τ are related, as shown in Eq. (9),

$$= 7.42 \times 10^{-22} f v^2 \qquad (v \text{ in s}^{-1}) \qquad (9)$$

to the f number or oscillator strength for the transition that occurs in the dispersion equations shown as Eqs. (13) to (17). The value of f can be calculated from the absorption integrated over the band according to Eq. (18).

Dispersion

A transparent material does not abstract energy from radiation which it transmits, but it always decreases the velocity of propagation of such radiation. In a vacuum, the velocity of radiation is the same for all wavelengths, but in a material medium, the velocity of propagation varies considerably with wavelength. The refractive index n of a medium is the ratio of the velocity of light in vacuum to that in the medium, and the effect of the medium on the velocity of radiation which it transmits is expressed by the variation of refractive index with the wavelength λ of the radiation, $dn/d\lambda$. This variation is called the dispersion of the medium. For radiation of wavelengths far removed from those of absorption bands of the medium, the refractive index increases regularly with decreasing wavelength or increasing frequency; the dispersion is then said to be normal.

In regions of normal dispersion, the variation of refractive index with wavelength can be expressed with considerable accuracy by Eq. (10),

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad (10)$$

known as Cauchy's equation, in which A, B, and C are constants with positive values. As an approximation, C may be neglected in comparison with A and B, and the dispersion, $dn/d\lambda$, is then given by Eq. (11).

$$\frac{dn}{d\lambda} = \frac{-2B}{\lambda^3} \tag{11}$$

by Thus, in regions of normal dispersion, the dispersion is approximately inversely proportional to the cube of the wavelength.

Dispersion by a prism. The refraction, or bending, of a ray of light which enters a material medium obliquely from vacuum or air (the refractive index of which for visible light is nearly unity) is the result of the diminished rate of advance of the wavefronts in the medium. Since, if the dispersion is normal, the refractive index of the medium is greater for violet than for red light, the wavefront of the violet light is retarded more than that of the red light. Hence, white light entering obliquely into the medium is converted within the medium to a continuously colored band, of which the red is least deviated from the direction of the incident beam, the violet most, with orange, yellow, green, and blue occupying intermediate positions. On emergence of the beam into air again, the colors remain separated. The action of the prism in resolving white light into its constituent colors is called color dispersion. *See also:* OPTICAL PRISM; REFRACTION OF WAVES.

The angular dispersion of a prism is the ratio, $d\theta/d\lambda$, of the difference in angular deviation $d\theta$ of two rays of slightly different wavelength which pass through the prism to the difference in wavelength $d\lambda$ when the prism is set for minimum deviation.

The angular dispersion of the prism given in Eq. (12)

$$\frac{d\theta}{d\lambda} = \frac{d\theta}{dn} \cdot \frac{dn}{d\lambda} \tag{12}$$

is the product of two factors, the variation, $d\theta/dn$, the deviation θ with refractive index n, and the variation of refractive index with wavelength, the dispersion of the material of which the prism is made. The latter depends solely on this material, while $d\theta/dn$ depends on the angle of incidence and the refracting angle of the prism. The greater the dispersion of the material of the prism, the greater is the angular separation between rays of two given wavelengths as they leave the prism. For example, the dispersion of quartz for visible light is lower than that of glass; hence the length of the spectrum from red to violet formed by a quartz prism is less than that formed by a glass prism of equal size and shape. Also, since the dispersion of colorless materials such as glass or quartz is greater for blue and violet light than for red, the red end of the spectrum formed by prisms is much more contracted than the blue.
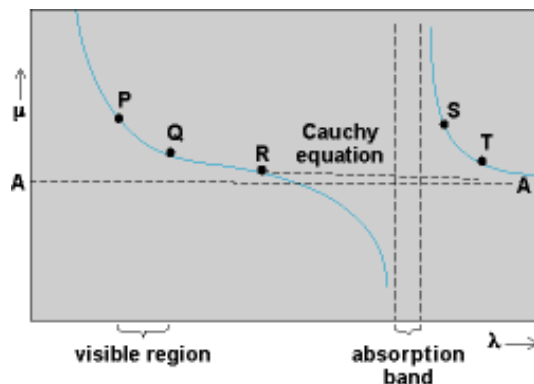
Fig. 1 Curve showing anomalous dispersion of quartz. A is limiting value of *n* as λ approaches infinity. (*After F. A. Jenkins and H. E. White, Fundamentals of Optics, 4th ed., McGraw-Hill, 1976*)

The colors of the rainbow result from dispersion of sunlight which enters raindrops and is refracted and dispersed in passing through them to the rear surface, at which the dispersed rays are reflected and reenter the air on the side of the drop on which the light was incident. *See also:* METEOROLOGICAL OPTICS; RAINBOW.

Anomalous dispersion. The regular increase of refractive index with decreasing wavelength expressed by Cauchy's equation breaks down as the wavelengths approach those of strong absorption bands. As the absorption band is approached from the long-wavelength side, the refractive index becomes very large, then decreases within the band to assume abnormally small values on the short-wavelength side, values below those for radiation on the long-wavelength side. A hollow prism containing an alcoholic solution of the dye fuchsin, which absorbs green light strongly, forms a spectrum in which the violet rays are less deviated than the red, on account of the abnormally low refractive index of the medium for violet light. The dispersion of media for radiation of wavelengths near those of strong absorption bands is said to be anomalous, in the sense that the refractive index decreases with decreasing wavelength instead of showing the normal increase. The theory of dispersion shows, however, that both the normal and anomalous variation of refractive index with wavelength can be satisfactorily described as aspects of a unified phenomenon, so that there is nothing fundamentally anomalous about dispersion in the vicinity of an absorption band. *See also:* DISPERSION (RADIATION).

Normal and anomalous dispersion of quartz are illustrated in **Fig. 1**. Throughout the near-infrared, visible, and near-ultraviolet spectral regions (between P and R on the curve), the dispersion is normal and adheres closely to Cauchy's equation, but it becomes anomalous to the right of R. From S to T, Cauchy's equation is again valid.

Relation to absorption. Figure 1 shows there is an intimate connection between dispersion and absorption; the refractive index rises to high values as the absorption band is approached from the long-wavelength side and falls to low values on the short-wavelength side of the band. In fact, the theory of dispersion shows that the complete dispersion curve as a function of wavelength is governed by the absorption bands of the medium. In classical electromagnetic theory, electric charges are regarded as oscillating, each with its appropriate natural frequency

ν_0, about positions of equilibrium within atoms or molecules. Placed in a radiation field of frequency ν per second, the oscillator in the atom is set into forced vibration, with the same frequency as that of the radiation. When ν is much lower or higher than ν_0, the amplitude of the forced vibration is small, but the amplitude becomes large when the frequency of the radiation equals the natural frequency of the oscillator. In much the same way, a tuning fork is set into vibration by sound waves corresponding to the same note emitted by another fork vibrating at the same frequency. To account for the absorption of energy by the medium from the radiation, it is necessary to postulate that in the motion of the atomic oscillator some frictional force, proportional to the velocity of the oscillator, must be overcome. For small amplitudes of forced oscillation, when the frequency of the radiation is very different from the natural period of the oscillator, the frictional force and the absorption of energy are negligible. Near resonance between the radiation and the oscillator, the amplitude becomes large, with a correspondingly large absorption of energy to overcome the frictional resistance. Radiation of frequencies near the natural frequency therefore corresponds to an absorption band. *See also:* SYMPATHETIC VIBRATION.

To show that the velocity of the radiation within the medium is changed, it is necessary to consider the phase of the forced vibration, which the theory shows to depend on the frequency of the radiation. The oscillator itself becomes a source of secondary radiation waves within the medium which combine to form sets of waves moving parallel to the original waves. Interference between the secondary and primary waves takes place, and because the phase of the secondary waves, which is the same as that of the atomic oscillators, is not the same as that of the primary waves, the wave motion resulting from the interference between the two sets of waves is different in phase from that of the primary waves incident on the medium. But the velocity of propagation of the waves is the rate of advance of equal phase; hence the phase change effected by the medium, which is different for each frequency of radiation, is equivalent to a change in the velocity of the radiation within the medium. When the frequency of the radiation slightly exceeds the natural frequency of the oscillator, the radiation and the oscillator becomes 180° out of the phase, which corresponds to an increase in the velocity of the radiation and accounts for the fall in refractive index on the short-wavelength side of the absorption band.

The theory leads to Eqs. (13) through (17) for the refractive index of a material medium as a function of the frequency of the radiation. In the equations the frequency is expressed as angular frequency, $\omega = 2\pi\nu$ s^{-1} = $2\pi c/\lambda$ where c is the velocity of light. When the angular frequency ω of the radiation is not very near the characteristic frequency of the electronic oscillator, the refractive index of the homogeneous medium containing N molecules per cubic centimeter is given by Eq. (13a),

$$n^2 = 1 + \frac{4\pi Ne^2}{m} \cdot \frac{f}{\omega_0{}^2 - \omega^2} \tag{13a}$$

$$n^2 = 1 + 4\pi Ne^2 \sum_i \frac{f_i/m_i}{\omega_i{}^2 - \omega^2} \tag{13b}$$

where e and m are the charge and mass of the electron, and f is the number of the oscillators per molecule of characteristics frequency ω_0. The f value is sometimes called the oscillator strength. If the molecule contains oscillators of different frequencies and mass (for example, electronic oscillators of frequency corresponding to ultraviolet radiation and ionic oscillators corresponding to infrared radiation), the frequency term becomes a summation, as in Eq. (13b), where ω_i is the characteristic frequency of the ith type of oscillator, and f_i and m_i are the corresponding f value and mass. In terms of wavelengths, this relation can be written as Eq. (14),

$$n^2 = 1 + \sum_i \frac{A_i \lambda^2}{\lambda^2 - \lambda_i^2} \qquad (14)$$

where A_i is a constant for the medium, λ is the wavelength of the radiation, and $\lambda_i = c/v_i$ is the wavelength corresponding to the characteristic frequency v_i per second (Sellmeier's equation).

If the medium is a gas, for which the refractive index is only slightly greater than unity, the dispersion formula can be written as Eq. (15).

$$n = 1 + 2\pi N e^2 \sum_i \frac{f_i / m_i}{\omega_i^2 - \omega^2} \qquad (15)$$

So long as the absorption remains negligible, these equations correctly describe the increase in refractive index as the frequency of the radiation begins to approach the absorption band determined by ω_i or λ_i. They fail when absorption becomes appreciable, since they predict infinitely large values of the refractive index when ω equals ω_i, whereas the refractive index remains finite throughout an absorption band.

The absorption of radiant energy of frequency very close to the characteristic frequency of the medium is formally regarded as the overcoming of a frictional force when the molecular oscillators are set into vibration, related by a proportionality constant g to the velocity of the oscillating particle; g is a damping coefficient for the oscillation. If the refractive index is determined by a single electronic oscillator, the dispersion equation for a gas at radiational frequencies within the absorption band becomes Eq. (16).

$$n = 1 + \frac{2\pi N e^2}{m} \frac{f(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2 g^2} \qquad (16)$$
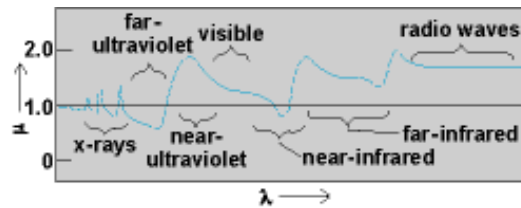
Fig. 2 Complete dispersion curve through the electromagnetic spectrum for a substance. (*After F. A. Jenkins and H. E. White, Fundamentals of Optics, 4th ed., McGraw-Hill, 1976*)

At the same time an absorption constant κ enters the equations, related to the absorption coefficient α of Eq. (1) by the expression $\kappa = \alpha c/2\omega\mu$. Equation (17)

$$\kappa = \frac{2\pi Ne^2}{m} \frac{f\omega g}{(\omega_0{}^2 - \omega^2)^2 + \omega^2 g^2} \tag{17}$$

shows the relationship. For a monatomic vapor at low pressure, Nf is about 10^{17} per cubic centimeter, ω_0 is about 3×10^{15} per second, and g is about 10^{11} per second. These data show that, when the frequency of the radiation is not very near ω_0, ωg is very small in comparison with the denominator and the absorption is practically zero. As ω approaches ω_0, κ increases rapidly to a maximum at a radiational frequency very near ω_0 and then falls at frequencies greater than ω_0. When the absorption is relatively weak, the absorption maximum is directly proportional to the oscillator strength f. In terms of the molar extinction coefficient ε of Eq. (4), it can be shown that this direct relation holds, as seen in Eq. (18). The integration in Eq. (18)

$$f = 4.319 \times 10^{-9} \int \epsilon\, d\overline{v} \tag{18}$$

is carried out over the whole absorption spectrum. The integral can be evaluated from the area under the curve of ε plotted as a function of wave number $\overline{v}$ v cm^{-1} = v (s^{-1})$/c = 1/\lambda$.

The width of the absorption band for an atom is determined by the value of the damping coefficient g; the greater the damping, the greater is the spectral region over which absorption extends.

The general behavior of the refractive index through the absorption band is illustrated by the dotted portions of **Fig. 2**. The presence of the damping term $\omega^2 g^2$ in the denominator of Eq. (17) prevents the refractive index from becoming infinite when $\omega = \omega_0$. Its value increases to a maximum for a radiation frequency less than ω_0, then falls with increasing frequency in the center of the band (anomalous dispersion) and increases from a relatively low value on the high-frequency side of the band.

Figure 2 shows schematically how the dispersion curve is determined by the absorption bands throughout the whole electromagnetic spectrum. The dotted portions of the curve correspond to absorption bands, each associated with a distinct type of electrical oscillator. The oscillators excited by x-rays are tightly bound inner elections; those excited by ultraviolet radiation are more loosely bound outer electrons which control the dispersion in the near-ultraviolet and visible regions, whereas those excited by the longer wavelengths are atoms or groups of atoms.

It will be observed in Fig. 2 that in regions of anomalous dispersion the refractive index of a substance may assume a value less than unity; the velocity of light in the medium is then greater than in vacuum. The velocity involved here is that with which the phase of the electromagnetic wave of a single frequency ω advances, for example, the velocity with which the crest of the wave advances through the medium. The theory of wave motion, however, shows that a signal propagated by electromagnetic radiation is carried by a group of waves of slightly different frequency, moving with a group velocity which, in a material medium, is always less than the velocity of light in vacuum. The existence of a refractive index less than unity in a material medium is therefore not in contradiction with the theory of relativity.

In quantum theory, absorption is associated not with the steady oscillation of a charge in an orbit but with transitions from one quantized state to another. The treatment of dispersion according to quantum theory is essentially similar to that outlined, with the difference that the natural frequencies ν_0 are now identified with the frequencies of radiation which the atom can absorb in undergoing quantum transitions. These transition frequencies are regarded as virtual classical oscillators, which react to radiation precisely as do the oscillators of classical electromagnetic theory.

Selective reflection

Nonmetallic substances which show very strong selective absorption also strongly reflect radiation of wavelengths near the absorption bands, although the maximum of reflection is not, in general, at the same wavelength as the maximum absorption. The infrared rays selectively reflected by ionic crystals are frequently referred to as reststrahlen, or residual rays. For additional information on selective reflection. *See also:* REFLECTION OF ELECTROMAGNETIC RADIATION.

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Bibliography

M. Born and E. Wolf, *Principles of Optics*, 7th ed., Cambridge University Press, Cambridge, U.K., 1999

R. W. Ditchburn, *Light*, 3d ed., Academic Press, London, 1976, Dover, New York, reprint 1991

I. S. Grant and W. R. Phillips, *Electromagnetism*, 2d ed., Wiley, Chichester, U.K., 1990

B. D. Guenther, *Modern Optics*, Wiley, New York, 1990

E. Hecht, *Optics*, 4th ed., Addison-Wesley, Reading, MA, 2002

F. A. Jenkins and H. E. White, *Fundamentals of Optics*, 4th ed., McGraw-Hill, New York, 1976

E. E. Kriezis, D. P. Chrissoulidis, and A. C. Papagiannakis (eds.), *Electromagnetics and Optics*, World Scientific, Singapore, 1992

Optical Society of America, *Handbook of Optics*, 3d ed., 5 vols., 2010

A. Sommerfeld, *Lectures on Theoretical Physics*, vol. 4, Academic Press, New York, 1954

Additional Readings

P. W. Milonni and J. H. Eberly, *Laser Physics*, 2d ed., John Wiley & Sons, Hoboken, NJ, 2010

F. Träger, *Springer Handbook of Lasers and Optics*, 2d ed., Springer, Dordrecht, Netherlands, 2012