

Chapter 10

Measured Optical Properties

In the preceding chapter we discussed classical theories of optical constants based on simple hypothetical models. Lest we mislead the reader, we must emphasize that the illustrative materials and frequency ranges in that chapter were carefully selected; everything does not, alas, conform in detail to such simple models. Ultimately, therefore, recourse must be had to measured frequency-dependent optical constants, and to fully understand scattering and absorption by small particles one must be aware of how the optical constants of real materials vary. In this chapter we give synopses of measured optical constants of an insulating solid, a metal, and a liquid: magnesium oxide, aluminum, and water. These materials illustrated simple theoretical dielectric functions in Chapter 9; the emphasis in this chapter is on measurements and their interpretation for a wide range of frequencies, from microwave to far ultraviolet. We also briefly comment on the magnitude of k , the imaginary part of the refractive index, and the validity of using bulk dielectric functions in small-particle calculations.

10.1 OPTICAL PROPERTIES OF AN INSULATING SOLID: MgO

Although not a common solid, magnesium oxide has been available for many years as pure single crystals, which have been studied over a broad wavelength range. Single crystals are cleaved easily for reflection and transmission studies, and small particles are produced by simply burning magnesium ribbon in air. Ultraviolet and infrared optical properties of MgO were used in Sections 9.1 and 9.2 to illustrate the Lorentz model applied to electronic and vibrational absorption. In Fig. 10.1 the real and imaginary parts of the dielectric function are shown for photon energies from far infrared to far ultraviolet. Because investigators of optical properties are usually interested in limited spectral regions, it was necessary to piece together results from several sources which are cited in the figure caption (unfortunately, there is not yet a compendium of optical constants of solids). Note that the imaginary part of the dielectric function is plotted on a logarithmic scale, whereas the real part is shown on a

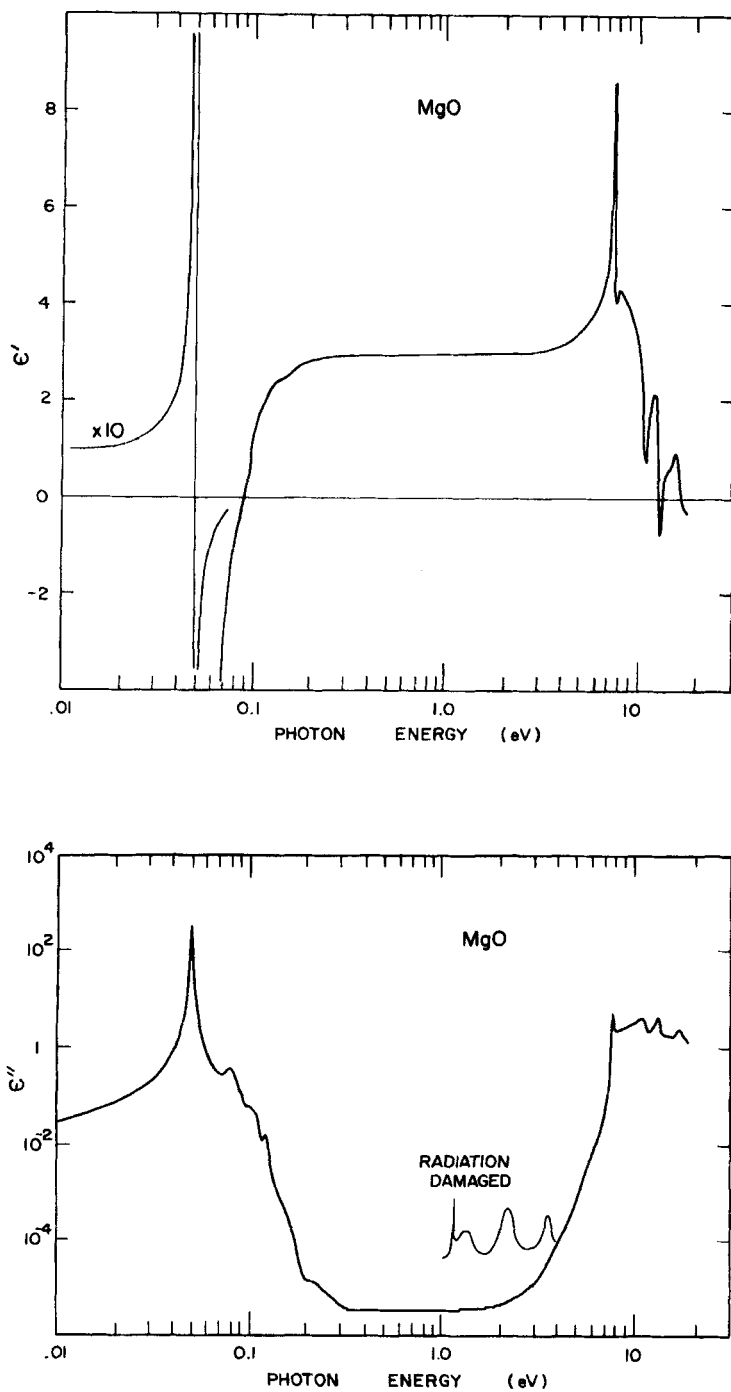


Figure 10.1 Dielectric functions of magnesium oxide. Infrared data are from Jasperse et al. (1966); visible and ultraviolet data are from Roessler and Walker (1967).

linear scale; therefore, structure in the real part appears more prominent than associated structure in the imaginary part.

The imaginary part of the dielectric function of MgO ranges over eight decades, an enormous variation [and recall that ϵ'' enters into the exponent of the transmission equation (2.52)]. There are two distinct absorption regions: absorption by electrons occurs above about 1 eV and that by lattice vibrations below about 0.3 eV. The sharp peak below the minimum band gap energy (~ 7.6 eV), especially prominent in the ϵ' curve (and in Fig. 9.5), is evidently the result of creation of an *exciton*. When a photon with energy slightly below the band gap is absorbed by an electron near the top of a filled band, the electron leaves behind a positively charged hole. Interaction of the hole and the electron can bind the pair together, much like an electron and a proton are bound in a hydrogen atom. The bound electron-hole pair—an excitation which cannot transport charge—is called an exciton. In ionic solids such as the alkali halides and MgO the exciton is tightly bound, and the electron is confined mostly to the vicinity of the negative ion (O^{2-} in MgO). A sequence of progressively closer spaced absorption bands leading up to the continuous transitions is sometimes observed; the electron-hole pair may be thought of as having a sequence of bound-state energy levels like a one-electron atom (e.g., hydrogen). In weakly bound excitons, the electron orbit ranges over many lattice parameters; in this instance the permittivity of free space, which is appropriate for the hydrogen atom, must be replaced by the permittivity of the solid in which the electron moves. The larger permittivity of solids compared with free space has the twofold effect of compressing the hydrogen atom energy levels and increasing the orbital radius of the electron. A notable example of a material showing hydrogen-like energy-level structure near the band gap is CuO_2 , which has a number of exciton bands at low temperatures.

Beyond the exciton peak in the far ultraviolet there is a series of other absorption features in MgO, which are more distinct in Fig. 9.5. These features, a theoretical treatment of which requires electron energy band calculations, are caused by maxima in the combined density of available states for electrons in the ground and excited states.

On the low-energy side of the transparent region there is strong absorption by lattice vibrations. The huge peak near 0.05 eV is the *Reststrahlen* band, which was discussed in Section 9.2. For both energy and momentum to be conserved, only the long-wavelength transverse optical mode phonon can couple strongly to the photon; this interaction produces the dominant infrared peak. A second peak in ϵ'' , some three orders of magnitude less intense, is on the high-energy side of the *Reststrahlen* peak at about 0.08 eV. This is interpreted as the result of excitation of two phonons by a photon, a much less probable event. In the region 0.1–0.2 eV there is weak residual absorption, which is probably related to multiple phonon excitation.

Between the regions of strong absorption by electronic and vibrational transitions there is a region of high transparency where absorption is dominated by impurities and imperfections. Artificial crystals of MgO are thus quite transparent to visible light. This transparent region can be made more interest-

ing by a bit of stimulation. We have inset a separate spectrum of ϵ'' for radiation-damaged MgO in Fig. 10.1 (the variations of ϵ' are too small to be seen in the figure); the dielectric function was obtained by a four-oscillator fit to transmission data of Chen and Sibley (1969). These additional bands in MgO are examples from the rich field of *color centers*, or *F-centers* (from the German *Farbenzentrum*), in transparent crystals. Because the bands absorb differently in different parts of the visible spectrum the originally clear crystals are colored. In the simplest color center, for example, an electron is trapped in the vicinity of a missing negative ion site, which has an effective positive charge. The trapped electron has energy levels to which it can be excited by photons of approximately visible wavelengths. Although the energy levels of the trapped electron can be quite narrowly spaced, absorption of a photon is usually accompanied by production of several phonons along with the electronic excitations; this gives the possibility of photon absorption over a rather broad band of energies, which accounts for the 0.05-eV width of the three MgO absorption bands (Fig. 10.1). The sharp spike on the low-energy side of the first band seems to be a no-phonon band where (as the name implies) the electronic transition is not accompanied by phonon emission and attendant band broadening. Only in rare instances, of which this is one, is the no-phonon band strength comparable with that of broad phonon-assisted bands. There are many other kinds of color centers in crystals. The most extensive work has been done on alkali halide crystals, which can be colored either by irradiation or by heating the solid in its alkali metal vapor. Natural radioactivity is thought to be the agent producing color centers in some crystals highly prized for their color—amethyst, for example. Old bottles left in the sun for many years owe their purple hue to color centers induced by low-level ultraviolet photon bombardment. Impurities must sometimes be present to make radiation-induced energy levels possible. Much work remains to be done before the exact formation mechanisms of all color centers are understood.

Impurity atoms in transparent crystals also frequently have electronic energy levels that contribute to absorption bands in the transparent region. In most instances the electronic transitions are coupled to multiphonon processes, as in F-centers, causing broadening of the absorption bands; sometimes there are no-phonon bands. Not all impurity atoms produce such effects. Particularly important coloring agents are the transition metal atoms, which can yield a variegated collection of absorption bands; the colors of gemstones such as ruby, sapphire, and the garnets are the result of transition metal impurities in otherwise clear crystals, and many colored minerals owe their hues to this same cause. Even the reds and oranges of the Grand Canyon can be traced to iron impurities in crystals of its rocks.

10.2 OPTICAL PROPERTIES OF A METAL: ALUMINUM

In modern times aluminum has become one of the most common metals in the industrialized world; every day we encounter aluminum as cooking ware, foil, and building materials. Aluminum is highly reflecting at all visible wavelengths

and into the far ultraviolet, making it the commonly used coating for high-quality mirrors, including reflecting telescope mirrors. Although aluminum oxidizes readily, the oxide coating inhibits further deterioration by oxidation; this preserves the quality of the surface for most optical applications because the oxide is transparent to visible light.

The dielectric function and reflectance of aluminum, which were displayed in Fig. 9.11, are shown over a broader energy range in Fig. 10.2; note that two

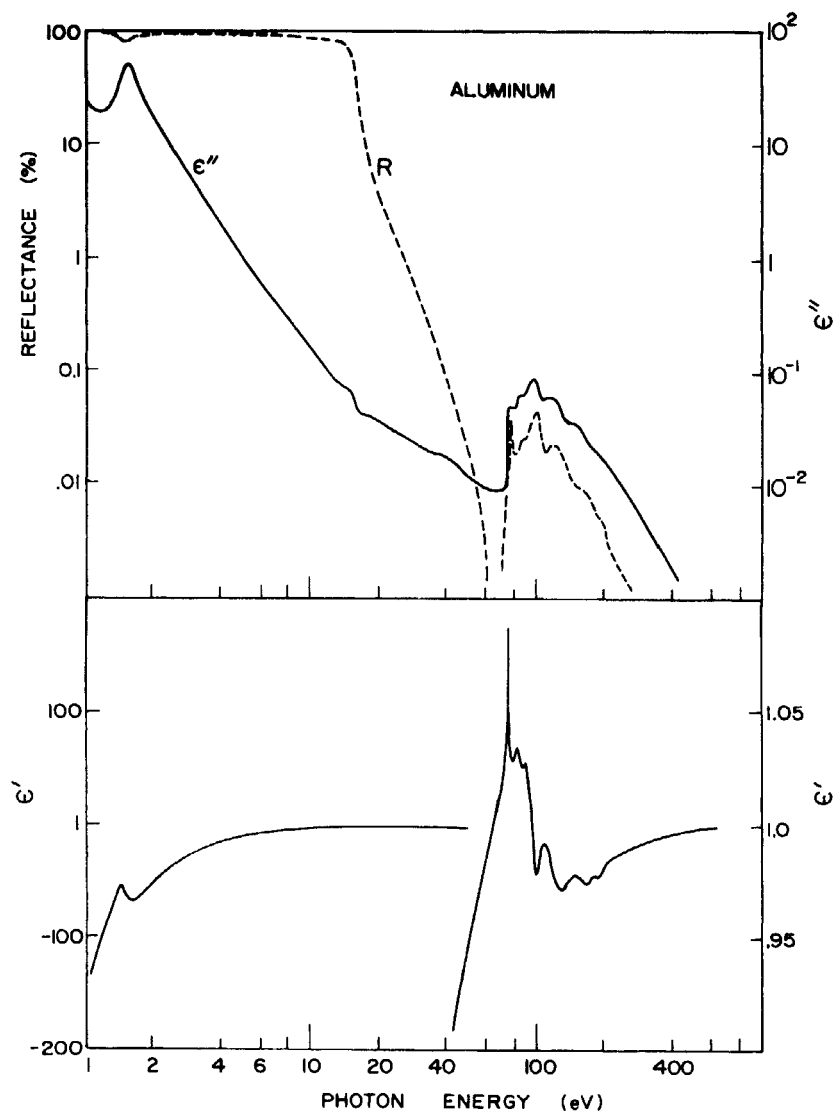


Figure 10.2 Dielectric functions and reflectance of aluminum (Hagemann et al., 1974).

logarithmic scales are needed to properly show structure at both high and low energies. These optical properties were taken from Hagemann et al. (1974), who did experiments in the range 13–150 eV and also surveyed the literature for determinations of optical constants at lower energies; these authors give very useful tables of optical constants for aluminum as well as magnesium, copper, silver, gold, bismuth, carbon, and aluminum oxide.

Below the plasma frequency at about 15 eV the only appreciable deviation from Drude theory occurs near 1.5 eV, where interband electronic transitions produce a peak in ϵ'' and associated structure in ϵ' ; with this exception, ϵ' for aluminum goes monotonically toward negative infinity and ϵ'' toward positive infinity as the energy approaches zero.

Features abruptly appear at about 60 eV, where ϵ' is nearly 1 and ϵ'' has fallen to about 0.01. This signals the onset of absorptive effects associated with deeper lying core electrons in the aluminum atoms; note carefully that the change in scale for ϵ' greatly exaggerates the relative importance of the core transitions. The electron configuration of the aluminum atom is $[\text{Ne}]3s^23p$; that is, two 3s electrons and one 3p electron outside a closed neon-like shell. The three outer electrons only partially fill the electron energy band that is formed when the atoms come together to make up the solid; it is this partially filled band that gives continuous free-electron absorption. Electrons in the neon-like cores are so tightly bound that photons of energy greater than about 60 eV are required to excite them. It is these core electrons that give rise to structure in the dielectric function of aluminum at high energies. Although such core transitions were not mentioned in the chapter on classical theories, they could be modeled reasonably well by a superposition of Lorentzian oscillators.

At energies high compared with the core electron excitation energies, ϵ' again approaches 1 and ϵ'' tends toward zero. In the x-ray region, of course, further excitation of deep-lying electrons will occur, giving absorption structure and attendant variation in ϵ' . These transitions are more properly regarded as atomic transitions: they are little affected by the fact that the atoms are grouped in a solid.

10.3 OPTICAL PROPERTIES OF A LIQUID: WATER

Optical properties of liquids are similar in many ways to those of solids. Electrically, there are metallic liquids such as mercury and molten iron, but the majority of common liquids are nonmetallic. As an illustration of a liquid we have chosen H_2O , a ubiquitous substance on our planet; water dominates not only atmospheric processes but the chemistry of life.

The optical properties of water have been studied for centuries; the modern results are scattered throughout the literature of many scientific fields. Fortunately, several authors have critically surveyed the literature on H_2O and have assembled collections of optical constants for broad wavelength ranges. These reviews include those by Irvine and Pollack (1968), Hale and Querry

(1973), and Ray (1972); extensive tabulations of n and k , which are very useful for small-particle calculations, are given in the first two papers. Because of more recent data included in the paper by Hale and Querry, and because they ensured that n and k are connected by Kramers–Kronig relations, we have based our figures for liquid H_2O on their paper.

Dielectric functions calculated from refractive indices tabulated by Hale and Querry are plotted in Fig. 10.3; optical constants at wavelengths shorter than $0.2\ \mu\text{m}$ were taken directly from the work of Kerr et al. (1972). In deference to the many workers who do not commonly use electron volts, we include a wavelength scale. As was done for MgO , ϵ' is plotted linearly and ϵ'' is plotted logarithmically. We also include on the ϵ'' plot some results for solid H_2O from Irvine and Pollack; comparison of ice and water gives insight into the similarities and differences between a solid and its liquid. The insulating liquid H_2O is not unlike the insulating solid MgO : the electronic and vibrational excitation regions for both materials are well separated by a highly transparent region. Electronic absorption by H_2O begins to be appreciable at about $0.2\ \mu\text{m}$; strong vibrational absorption bands rise above the continuum between about 1 and $100\ \mu\text{m}$. The major difference between MgO and liquid H_2O occurs longward of the vibrational absorption region: dipole relaxation in H_2O (discussed in Section 9.5) maintains a high level of absorption from the microwave well into the infrared; this also is the cause of the major differences between the optical properties of liquid and solid water.

10.3.1 The Transparent Region

The lowest point in the entire absorption spectrum lies in the visible, where ϵ'' plunges to less than 10^{-8} . A simple calculation shows that water is quite transparent to visible light for path lengths of tens of centimeters. If we ignore reflection, which is only a few percent, then the transmission T by a slab of thickness d is $\exp(-\alpha d)$, where to good approximation α is $2\pi\epsilon''/n\lambda$. In the visible, therefore, α is about $10^{-3}\ \text{cm}^{-1}$. Even in a large glass full of water ($d \approx 10\ \text{cm}$) there is no discernible absorption. However, $T \approx 0.6$ for $d = 500\ \text{cm}$; thus, there is appreciable absorption in a home swimming pool of moderate size. Moreover, there is appreciable differential absorption over the visible spectrum. If we take as blue $\lambda = 4250\ \text{\AA}$, as red $\lambda = 6000\ \text{\AA}$, and use k values from Hale and Querry of 1.3×10^{-9} and 10.9×10^{-9} , respectively, the transmission percentages for a 5-m path length of pure water are the following: blue, 82.5%; red, 32%. Thus, white light transmitted over such a distance should take on a distinctly bluish hue. This apparently can be observed in the clear water of swimming pools, although competing effects such as reflection of the blue sky, color of the pool bottom and sides, impurities and particles in the water, and scattering by the water molecules themselves can render the interpretation complicated. Because absorption in ice and water are similar, light transmitted by pure ice over distances of several meters should also

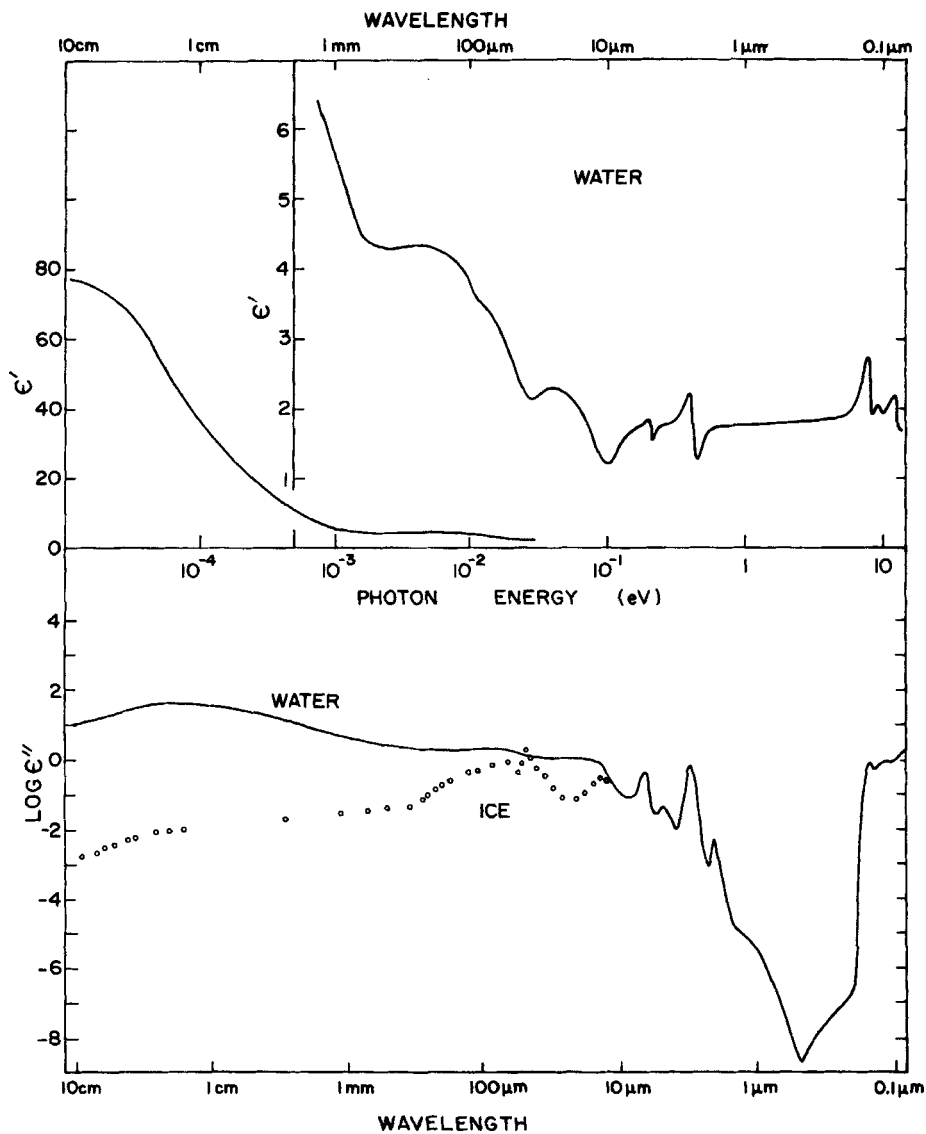


Figure 10.3 Dielectric functions of water (Hale and Querry, 1973). ϵ'' for ice is taken partly from Irvine and Pollack (1968) and partly from an unpublished compilation of the optical constants of ice, from far ultraviolet to radio wavelengths, by Stephen Warren (to be submitted to *Applied Optics*).

appear bluish; this seems to be an important factor in the blue color of glacial crevasses and other large-scale natural ice formations.

10.3.2 The Debye Relaxation Region

At microwave frequencies Debye relaxation is the dominant absorption mechanism in water. The broad maximum in ϵ'' near $\lambda \approx 1$ cm is shown in Fig. 9.15, which also shows how well the simple Debye theory fits experimental data. This suggests that H_2O is not a linear molecule with, say, two hydrogen atoms at equal distances from and on opposite sides of the oxygen atom. Instead, the hydrogen atoms are grouped toward the same side of the oxygen atom; the angle between them is about 105° . The resulting electron distribution favors a higher electron density around a hydrogen atom; this imparts to the molecule a slightly ionic binding character and gives it a permanent dipole moment which can respond to microwave electric fields. Damping of the dipoles, which determines the relaxation time, is highly temperature dependent. Moreover, the molecules abruptly lose their orientational mobility as liquid water freezes to ice, and the Debye relaxation vanishes. The result is a huge change in the dielectric function at microwave frequencies, with effects extending well into the infrared. Because of the frequent coexistence of ice and water and the prevalent use of radar to probe the earth's environment, the difference between the dielectric functions of water and ice can have important consequences. For example, radar reflections from thunderstorms are quite different for rain and hail. Radio waves have been used to map the topography of polar ice sheets by means of reflected signals (Robin et al., 1969); however, it may not be possible to use such techniques for glaciers and other ice masses containing appreciable liquid water.

10.3.3 The Molecular Vibration Region

The infrared absorption bands of water can be grouped into two regions: the molecular bands between 1 and $10\ \mu\text{m}$, and the intermolecular bands between 10 and $100\ \mu\text{m}$. In the first region the absorption bands are similar to those of the free molecule; they occur in the liquid at 1.45, 1.94, 2.95, 4.7, and $6.05\ \mu\text{m}$. The fundamental vibration frequencies of the free (vapor phase) H_2O molecule help elucidate the vibrational modes of the H_2O molecule in the liquid phase. The nonlinear triatomic molecule H_2O has nine degrees of freedom: three describing the translational motion of the center of mass; three rotational degrees of freedom; and three vibrational degrees of freedom. The normal modes of vibration of the free H_2O molecule are illustrated schematically in Fig. 10.4 together with the notation commonly used to denote the three normal frequencies. We may now surmise that the absorption band near $3\ \mu\text{m}$ in liquid and solid H_2O is related to the $\bar{\nu}_1$ and $\bar{\nu}_3$ vibrational modes of the free molecule, which are the O—H stretching modes. The $6.05\text{-}\mu\text{m}$ band in the liquid is the $\bar{\nu}_2$ bending mode of the molecule, which occurs at $6.27\ \mu\text{m}$ in the

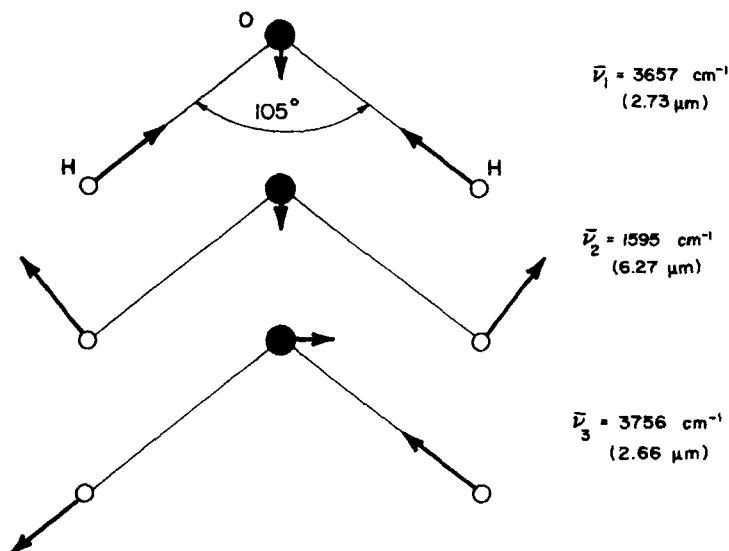


Figure 10.4 Normal modes of vibration of the free water molecule.

free molecule. The other absorption bands in water are more difficult to interpret precisely, but they are evidently overtones and combination bands of the three fundamental vibrations.

There are two broad absorption bands in water at 17 and 62 μm superimposed on the tail of the Debye absorption. Since there are no broad absorption bands in H_2O vapor in this region these bands must be the result of interaction between molecules—intermolecular vibrations. The fact that these bands show larger differences between the liquid and solid phases than the shorter-wavelength molecular vibrations is consistent with this interpretation. There are two kinds of intermolecular vibrations: rotational and translational. The shorter wavelength band, at 17 μm in water and 12 μm in ice, is the rotational band. Note the appreciable shift of this band toward higher frequencies in passing from water to ice, a consequence of the expected “tightening” of the rotational restoring forces as the liquid freezes. The 62- μm band in water is the intermolecular translational band. In ice it is made up of two bands, at 44.8 μm and 62 μm . Largely as a result of much less Debye absorption at these wavelengths, the intermolecular bands in ice are much more dominant than in water. In Table 10.1 we summarize the absorption bands in H_2O that are the result of molecular motions.

There is an important difference between an ionic crystal like MgO and a molecular substance such as liquid or solid H_2O . In the molecular substance there is a clear distinction between molecular and intermolecular modes because the atoms are bound into molecules much more tightly than the molecules are bound to one another. In the ionic crystal there is no such

Table 10.1 Molecular Absorption Bands in Liquid and Solid H₂O

Band Positions (μm)		Type of Molecular Motion
Water	Ice	
1.45	1.52	O—H molecular stretching mode ($\bar{\nu}_1$ and $\bar{\nu}_3$)
1.94	2.0	
2.95	3.08	
4.7	4.5	
6.05	6.05	H—O—H molecular bending mode ($\bar{\nu}_2$)
17	12	Intermolecular rotational
62	45	Intermolecular translational
	62	
1 cm	—	Debye relaxation

distinction; only one dominant absorption mode exists associated with lattice waves in which positive and negative ions move in opposition (the optic mode). One cannot even distinguish a unique cluster of atoms or ions to call a molecule; in a sense, the entire crystal is a molecule. An important consequence of this distinction between ionic and molecular substances is that vibrational absorption in the former is packed into one small frequency range, whereas in the latter there are a number of isolated absorption bands. It follows from the Kramers–Kronig relations, therefore, that ionic crystals usually have much stronger vibrational absorption bands than do molecular substances.

10.3.4 The Electronic Absorption Region

Features in the far-ultraviolet absorption spectrum of H₂O are the result of electronic excitations. The most prominent features in ϵ'' for water occur at 8.2 eV (8.5 eV for ice), 9.8 eV, and 13.5 eV. It is clear from inspection of the dielectric function that the electronic excitations are not exhausted beyond 14.6 eV, the region for which there is no published data; for if this were so, then ϵ'' would be approaching zero and ϵ' would be approaching one from lower values (see Section 9.2 and the high-energy data in Figs. 9.5 and 10.2). Interpretation of the high-energy peaks for H₂O relies heavily on intercomparisons among the liquid, vapor, and solid phases (Kerr et al., 1972). For example, the water band at 8.2 eV is associated with an electronic excitation in the free molecule at 7.5 eV; the energy is shifted in going from the vapor to the liquid or solid because of bonding between molecules. The other two bands are similarly related to corresponding structure in the electronic absorption spectrum of H₂O vapor. This close correspondence between electronic absorption spectra of free molecules and condensed phases is similar to that in the vibrational region. Interpretation of electronic absorption in the ionic crystal MgO, however,

requires a complete energy band calculation for guidance, and molecular spectroscopy is of little help.

10.4 A COMMENT ON THE MAGNITUDE OF k

There are two fields in which great effort has been expended to infer the imaginary part of the complex refractive index of remote particles: the study of interstellar dust and the study of atmospheric aerosols. Determination of k for atmospheric and interstellar particles is a stringent test of methods for inverting data obtained by remote sensing. In both fields values of k in the range 10^{-3} – 10^{-2} at visible wavelengths have frequently been inferred. However, it is rare to find a solid or liquid with these values of k in the visible, and for good physical reasons. Most solids and liquids either have very low values of k (e.g., 10^{-6}) or k of order 1. Intermediate values, such as 10^{-3} , are usually found only at wavelengths where k is rapidly changing from low to high values. For example, k in the visible for MgO is less than 10^{-5} and for water is less than 10^{-8} (see Figs. 10.1 and 10.3); for both materials k is 10^{-3} at about 2000 Å near a rapidly rising absorption edge. The reason for the propensity for either high or low values of k in solids at visible wavelengths lies in the electron energy band structure (see Fig. 9.10). In nonmetallic solids there is very little absorption for photon energies less than the band gap and, consequently, k is small; for photon energies greater than the band gap, however, k is large. Absorption usually rises rapidly as the photon energy increases through the band gap region. Metals, on the other hand, have large values of k at all frequencies below the plasma frequency, which is characteristically in the ultraviolet.

Our discussion so far has been confined to pure materials. It might be supposed that any value of k could be achieved by introducing controlled amounts of impurities or defects; however, this is generally not so. A solid cannot be doped to arbitrary levels; in addition, the impurity must produce absorption in the band gap region. Although some atoms, most notably transition metal atoms, do give absorption bands when incorporated into some solids, it is usually difficult to have enough impurities to give $k = 0.01$; we illustrate this with a story.

A Dirty Silicate Story A friend of one of the authors is an astronomer—as well as a professional mineral dealer—who became interested in “dirty silicates” as candidates for interstellar dust. He therefore selected for determination of k the blackest natural silicate mineral in his possession, the coal-black mineral hornblende, which contains a high concentration of impurities such as iron. A slice about 100 μm thick was polished, and transmission was measured in a recording spectrophotometer. The fact that appreciable light was transmitted for all near-infrared and visible wavelengths indicated that k was rather small. Calculations indeed confirmed that k was less than 10^{-4} between about 6 and 0.3 μm. And yet this was the blackest silicate in the possession of a professional collector. It is not easy to find $k = 0.01$ in the band gap region of

a solid; on the other hand, where interband or intraband transitions occur, it is not easy to find such a low value.

The example in the preceding paragraph also illustrates that a macroscopic sample that looks black does not have a k of order 1; if it did have such a high k value, it would probably look shiny. Let us emphasize this with a quantitative example. Suppose that a 1-mm-thick wafer of a black solid transmits 1% of the light incident on it. If we neglect reflection losses (typically small for nonconductors), then k is approximately (see Section 2.8) $(\lambda/4\pi h)\ln(I_i/I_t)$. For $\lambda = 0.5 \mu\text{m}$, $h = 0.1 \text{ cm}$, and $I_i/I_t = 100$, k is about 2×10^{-4} . *Thus, black materials need not have k values in the visible much greater than 10^{-4} . A k of 10^{-4} , which might seem small at first glance, is in fact huge: it gives rise to appreciable absorption of visible light in all but very thin samples.*

10.5 VALIDITY OF BULK OPTICAL CONSTANTS IN SMALL-PARTICLE CALCULATIONS

Before continuing into Chapters 11–13, where we use bulk optical constants in small-particle calculations, it is well to pause and remind ourselves that bulk optical constants, without modification, may not always apply to small particles. Up to this point we have tacitly assumed that the interaction of electromagnetic waves with particles can be treated in the continuum approximation—the electromagnetic theory of Part 1—with constitutive relations independent of size; dielectric functions, such as those presented in this chapter and the preceding one, are for bulk matter. It requires no great insight, however, to realize that matter cannot be subdivided indefinitely without change in optical properties. For example, optical absorption by atomic aluminum is clearly not the same as that by bulk metallic aluminum, and the absorption spectrum of molecular MgO bears little resemblance to that of crystalline MgO. The question to ask, therefore, is not if, but at what size, optical constants appropriate to small particles deviate appreciably from those of bulk matter. This question cannot be answered simply and precisely because there may be several reasons for the breakdown of bulk optical constants, the relative importance of each of which depends on the type of material, particle size, and frequency. For example, in sufficiently small metallic particles the electron mean free path is limited by the particle boundary, with consequences for their optical properties; this is discussed in Section 12.1. Other effects are increased spacing between electronic and vibrational energy levels and the increased importance of surface states in particles with large surface-to-volume ratios; these have been surveyed by Huffman (1977).

Although we admit that these effects must surely appear in small particles, we cannot countenance the uncritical invocation of vague and esoteric “quantum size effects,” as is sometimes done, to dispose of optical phenomena in small particles that are not understood. Often the correct interpretation may be much simpler: particle shape, for example, which we shall discuss in Sections 12.3 and 12.4. Our best advice, based on calculations (Martin, 1973; Chen et

al., 1978, for example) and those experiments which have been done with sufficient care to allow unambiguous interpretation, is that quantum size effects are unimportant except for particle sizes well below 1000 Å, in most instances below 100 Å. We shall bring evidence to bear in support of this assertion in Chapter 12.

10.6 SUMMARY OF ABSORPTION MECHANISMS AND TEMPERATURE EFFECTS

There are many ways in which electromagnetic waves can interact with matter in its condensed phases, liquid and solid. Some of these have been treated with simple models in Chapter 9, and examples are given in this chapter. Lest we leave the reader with an oversimplified view of optical constants we list in Table 10.2 several absorption mechanisms in solids together with the spectral regions in which they are important. References, primarily review articles and monographs, are also included to guide the reader in further study.

Most optical studies of condensed matter have been made near room temperature, but there are applications in which optical properties are required at high temperatures (e.g., particles as solar radiation absorbers) or at low temperatures (e.g., interstellar dust grains). Although we cannot discuss all possibilities, the following brief comments may be helpful.

In general, temperature tends to affect more greatly low-frequency (infrared and far infrared) than high-frequency (visible and ultraviolet) absorption mechanisms. At room temperature ($\sim 300^\circ\text{K}$) $k_B T$ corresponds to about 0.025 eV ($\lambda \approx 10 \mu\text{m}$); thermal energies are therefore quite small compared with ultraviolet photon energies, so temperature changes only slightly perturb ultraviolet absorption mechanisms. Of the two major types of absorption mechanisms, vibrational and electronic, the former are far more temperature dependent. Infrared absorption bands of ionic solids, associated with collective lattice oscillations, commonly increase in width and decrease in height with increasing temperature; the frequency of peak absorption tends to shift to lower values, although the shift is small except for large temperature changes ($100\text{--}1000^\circ\text{K}$). Excellent examples are given by Jasperse et al. (1966), who studied the *Reststrahlen* band in LiF from 7.5 to 1060°K and that in MgO from 8 to 1950°K . Far-infrared ($> 100 \mu\text{m}$) absorption in crystalline solids may change by several orders of magnitude as temperature increases, although absorption in amorphous solids tends to be independent of temperature (Mitra and Nudelman, 1970).

Temperature changes do not appreciably affect ultraviolet optical properties of both metals and insulators, although at low temperatures absorption bands associated with excitons and electron band transitions are usually sharper, and frequencies of peak absorption may shift slightly. In the soft x-ray region, transitions of core electrons buried in the interior of atoms hardly notice temperature changes.

Table 10.2 Summary of Absorption Mechanisms

Spectral Region	Type of Absorption	References
Microwave > 1 mm	Debye relaxation in polar matter	Debye (1929)
	Electron energy splitting in rare earth ions	Hadni (1970a)
Far infrared ~ 1 mm (1000 μm) to ~ 100 μm	Phonon-difference processes	Hadni (1970b)
	Superconducting band gap	Tinkham (1970b)
	Defect-induced vibrations	Genzel (1969)
	Impurity-induced vibrations	McCombie (1970)
Infrared ~ 100 to ~ 2 μm	Intramolecular vibrations	Sherwood (1972)
	Intermolecular vibrations	Sherwood (1972)
	<i>Reststrahlen</i> absorption in ionic crystals	Mitra (1969); Plendl (1970)
	Two-phonon and multiphonon processes	Bendow (1978)
	Magnetic excitation in magnetic insulators	Tinkham (1970a)
	Intraband electron transitions in metals	Nilsson (1974); Glicksman (1971)
	Free carriers in semiconductors	Dixon (1969); Moss (1959)
	Electron states of impurities	McClure (1959b); Burns (1970)
	No-phonon lines and phonon sidebands	Silsbee (1969); Rebane (1974)
	No-magnon lines and magnon sidebands	McClure (1974)
Near visible ~ 2 μm to ~ 3000 Å	Electron defect states (color centers)	Markham (1966)
	Transition-metal-ion energy levels	DiBartolo (1974); Crosswhite and Moos (1967)
	Electron band gaps in semiconductors	Harbeke (1972)
	Electron band tailing in amorphous semiconductors	Tauc (1972)
	Exciton bands (single and series)	Nikitine (1969); Reynolds (1969)
	Band-to-band transitions of electrons	Phillips (1966)
Far ultraviolet ~ 3000 to ~ 500 Å	Molecular electron transitions	McClure (1959a)
	Electron plasma oscillations in metals	Steinmann (1968); Glicksman (1971)
Extreme ultraviolet, soft x-ray ~ 500 to ~ 20 Å	Core electron transitions	Brown (1974)

Recall, however, that temperature changes often give rise to phase changes such as solid-to-liquid, magnetic, and superconducting phase transitions, with associated appreciable changes in optical properties at all wavelengths. We mentioned in Section 9.5 that the Debye relaxation mechanism, which dominates the radio-frequency behavior of liquid water, practically vanishes in the transition to ice. Similarly, superconducting band gap absorption disappears above the transition temperature.

NOTES AND COMMENTS

Optical properties of solids encompasses a field of study too extensive to be covered adequately in a single volume. Monographs that emphasize different aspects of the subject, together with the topics they treat especially well, are listed below.

Wooten (1972): Metals.

Greenaway and Harbeke (1968): Semiconductors.

Sherwood (1972): Infrared lattice vibrations.

Burns (1970): Ions in crystals.

Some of the most comprehensive coverages of optical properties are found in the following proceedings of summer schools and conferences: Tauc (1966), Nudelman and Mitra (1969), Mitra and Nudelman (1970), Abelès (1972), Mitra and Bendow (1975); the first two are especially recommended.

The following articles in the series *Solid State Physics* offer comprehensive reviews of various topics.

McClure (1959ab): Molecules and ions in crystals.

Stern (1963): Optical properties in general.

Markham (1966): Color centers.

Phillips (1966): Fundamental electronic spectra.

Glicksman (1971): Metals.

Brown (1974): Extreme ultraviolet spectra of solids.

Nilsson (1974): Metals and alloys.

Bendow (1978): Transparent insulators.

The first two volumes in a compilation of optical data on all the metallic elements, in the photon energy range 0.1–500 eV, have been recently published by Weaver et al. (1981ab).

Two highly recommended papers on the color of water are those by Bancroft (1919) and by Raman (1922). The first of these contains lengthy quotes from earlier work.

Molecular vibrations are treated in great detail in the books by Herzberg (1945) and by Wilson et al. (1955).