

## Light Absorption in Sea Water

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# Light Absorption in Sea Water

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# Contents

<b>1</b>	<b>Introduction: Absorption of Sunlight in the Ocean</b>	<b>1</b>
1.1	Inflow and Absorption of Sunlight in the Ocean	1
1.2	Case 1 and Case 2 Waters	6
1.3	The Light Absorption Coefficient and its Components in Sea Water	7
<b>2</b>	<b>Light Absorption by Water Molecules and Inorganic Substances Dissolved in Sea Water</b>	<b>11</b>
2.1	Light Absorption Spectra of Small Molecules Such as Water: Physical Principles	11
2.1.1	Vibrational-Rotational Absorption Spectra	13
2.1.2	Electronic Absorption Spectra	28
2.2	The Absorption of Light and Other Electromagnetic Radiation in Pure Liquid Water and Ice	44
2.2.1	Physical Mechanisms of Absorption	45
2.2.2	The Absorption of Electromagnetic Radiation in Pure Liquid Water	52
2.2.3	The Absorption of Electromagnetic Radiation in Ice	64
2.3	Light Absorption by Atoms, Sea-Salt Ions and Other Inorganic Substances Dissolved in Sea Water	73
2.3.1	Dissolved Gases	75
2.3.2	Salts	75
2.3.3	Inorganic Complex Ions	80
<b>3</b>	<b>The Interaction of Light with Organic Molecules Present in Sea Water: Physical Principles</b>	<b>82</b>
3.1	The Characteristic Absorption Properties of Simple Chromophores in Organic Molecules	82
3.2	The Absorption Properties of Complex Organic Molecules with Conjugated $\pi$ -Electrons	93

3.2.1	Linear Polyenes . . . . .	93
3.2.2	Cyclic Polyenes . . . . .	100
3.2.3	Mixed Conjugations ( $\pi$ - and $n$ -Electron) and Photosynthetic Pigments . . . . .	101
3.3	The Influence of Auxochromic Groups and Complexes on the Optical Properties of Organic Compounds in the Sea . . . . .	105
3.3.1	Intramolecular Interactions . . . . .	106
3.3.2	The Solvent Effect . . . . .	108
3.3.3	Organometallic Complexes . . . . .	109
3.3.4	Charge-Transfer Complexes . . . . .	110
<b>4</b>	<b>Light Absorption by Dissolved Organic Matter (DOM) in Sea Water . . . . .</b>	<b>112</b>
4.1	Classification, Origin and General Characteristics of Light Absorption by the Principal Groups of Organic Absorbers in Sea Water . . . . .	115
4.1.1	Occurrence and Origin of Organic Matter in the Ocean . . . . .	115
4.1.2	Principal Organic Absorbers of Light in the Ocean . . . . .	119
4.2	Analysis of the Conditions Governing UV-VIS Absorption by the Principal Organic Absorbers in the Sea . . . . .	121
4.2.1	Amino acids and their Derivatives . . . . .	121
4.2.2	Peptides and Proteins . . . . .	129
4.2.3	Purines, Pyrimidines and Nucleic Acids . . . . .	133
4.2.4	Lignins . . . . .	138
4.2.5	Colored Dissolved Organic Matter (CDOM) . . . . .	139
4.3	The Total Absorption of UV-VIS Radiation by All Organic Substances Dissolved in Sea Water . . . . .	152
4.3.1	Fine Spectral Structure . . . . .	155
4.3.2	Absolute Magnitudes of Absorption Coefficients . . . . .	160
4.3.3	The Slopes of Absorption Spectra . . . . .	163
<b>5</b>	<b>Light Absorption by Suspended Particulate Matter (SPM) in Sea Water . . . . .</b>	<b>167</b>
5.1	The Optical Properties of Dispersing Media: Theoretical Principles . . . . .	169
5.1.1	The Packaging Effect: What is it and How Does it Manifest Itself? . . . . .	170
5.1.2	Light Absorption in Polydispersing Media: A Quantum-Mechanical – Electrodynamical Description . . . . .	172
5.1.3	Elements of Mie Theory . . . . .	175
5.1.4	Some Theoretical Optical Characteristics of Suspended Particles . . . . .	181

5.2	Suspended Particulate Matter in the Sea: Nature, Origins, Chemical, and Physical Properties . . . . .	184
5.2.1	Suspended Particulate Matter in the Sea: Main Types, Origins, and Resources. . . . .	184
5.2.2	The Chemical Composition and Optical Constants of Mineral Particles . . . . .	197
5.2.3	The Chemical Composition and Optical Constants of the Planktonic Components of Organic Particles. . . . .	206
5.2.4	The Chemical Composition and Optical Constants of Organic Detritus . . . . .	228
5.2.5	Sizes and Shapes of Particles . . . . .	252
5.3	Light Absorption Properties of Nonalgal Particles: Results of Empirical Studies . . . . .	271
5.3.1	Light Absorption Spectra of All Suspended Particulate Matter (SPM) and Nonalgal Particles: General Characteristics. . . . .	272
5.3.2	Spectra of the Mass-Specific Light Absorption Coefficients of Nonalgal Particles . . . . .	280
5.3.3	Parameterization of the Particulate Matter Spectra for Oceanic Case 1 Waters. . . . .	291
<b>6</b>	<b>Light Absorption by Phytoplankton in the Sea . . . . .</b>	<b>295</b>
6.1	Abiotic Factors Governing Light Absorption by Phytoplankton in the Sea . . . . .	296
6.1.1	The Trophicity of Marine Basins: A Factor Governing The Resources of Algae and Light Absorption . . . . .	298
6.1.2	The Light Field: A Factor Governing the Composition of Light-Absorbing Pigments in Cells . . . . .	301
6.2	Phytoplankton Pigments and their Electronic Absorption Spectra in the Visible Region . . . . .	311
6.2.1	The Role of Phytoplankton and the Main Types of Phytoplankton Pigments . . . . .	311
6.2.2	The Chemical Structure of Pigments . . . . .	315
6.2.3	The Individual Absorption Properties of Pigment Extracts . . . . .	320
6.2.4	The Individual Absorption Properties of Pigments <i>in Vivo</i> . . . . .	323
6.2.5	The Native Forms of Chlorophyll Pigments . . . . .	328
6.3	Phytoplankton Resources and Chlorophyll <i>a</i> Concentrations in Oceans and Seas . . . . .	331
6.3.1	The Principal Natural Factors Governing Phytoplankton Resources in the World Ocean . . . . .	332
6.3.2	The Distribution of Chlorophyll in the World Ocean . . . . .	334

6.3.3	Vertical Distributions of Chlorophyll <i>a</i> in the Sea . . . . .	337
6.3.4	Statistical Formulas Describing the Vertical Distributions of Chlorophyll Concentration . . . . .	341
6.4	The Composition of Chlorophyll <i>a</i> and Accessory Pigments in Marine Algae . . . . .	343
6.4.1	Pigment Compositions Characteristic of Various Classes of Phytoplankton . . . . .	343
6.4.2	Pigment Compositions in Natural Plant Communities, in Different Types of Sea and at Different Depths . . . . .	346
6.4.3	Photoadaptation and Chromatic Adaptation; Model Descriptions of Pigment Concentrations in Different Seas . . . . .	350
6.5	The Packaging Effect of Pigments in Marine Phytoplankton Cell . . . . .	354
6.5.1	An Approximate Formal Description of the Packaging Effect for Marine Phytoplankton . . . . .	355
6.5.2	The Product $C_{chl}D$ for Phytoplankton in Different Types of Seas: A Preliminary Statistical Description . . . . .	360
6.6	Total Light Absorption by Marine Algae: Results of Empirical Studies . . . . .	362
6.6.1	Methodological Problems. . . . .	362
6.6.2	Light Absorption Spectra of Phytoplankton: A General Outline . . . . .	366
6.6.3	Light Absorption Spectra of Phytoplankton: Fine Structure . . . . .	368
6.6.4	Absolute Values of Total and Specific Absorption Coefficients . . . . .	370
6.7	Model Descriptions of the Absorption Properties of Marine Phytoplankton: A Review . . . . .	376
6.7.1	The Principal Model Descriptions of Light Absorption by Phytoplankton . . . . .	377
6.7.2	Classical Models . . . . .	378
6.7.3	Single-Component, Nonhomogeneous Models . . . . .	379
6.7.4	The Multicomponent, Homogeneous Model . . . . .	382
6.7.5	The Multicomponent, Nonhomogeneous Model . . . . .	383
6.7.6	Complex Utilitarian Models. . . . .	387
6.7.7	Modeled Absorption Properties of Algae in Different Types of Sea . . . . .	389
	<b>References . . . . .</b>	<b>395</b>
	<b>Subject Index . . . . .</b>	<b>429</b>
	<b>List of Symbols and Abbreviations. . . . .</b>	<b>443</b>



# 1 Introduction: Absorption of Sunlight in the Ocean

## 1.1 Inflow and Absorption of Sunlight in the Ocean

The absorption of light by the oceans is a fundamental process in the Earth's harvesting of the vast resources of solar radiation and its conversion into other forms of energy. Of course, light is also absorbed by the atmosphere and the continents, but the scale of the process there is very much smaller than in the oceans, inasmuch as the absorption capability of the atmosphere is lower and the surface area of the land is only about one-third of that of the oceans. At any instant, half the Earth's surface is illuminated by a beam of solar rays (Figure 1.1) which, at this distance from the sun and given the comparative size of the Earth, are practically parallel. Their angle of divergence is that through which we see the Sun from the Earth; that is,  $\Delta\phi \approx 6.8 \times 10^{-5}$  radians, or c. 0.004 of a degree.

Taking into consideration the daily cycles of the Earth's revolutions about its axis and the unevenness of its surface, the mean insolation of the Earth amounts to c.  $342 \text{ W m}^{-2}$ , that is, around one quarter of the solar constant ( $S = 1365 \text{ W m}^{-2}$ ; Wilson (1993)), because the surface area of the Earth is four times as large as its cross-section (Schneider 1992). If we allow for a 26% loss of this radiation due to reflection in the atmosphere and a further 19% due to absorption in the atmosphere (Harrison et al. 1993, Trenberth 1992), the mean insolation of the ocean is 55% of the original value, or c.  $188 \text{ W m}^{-2}$ . In other words, this is the time- and space-averaged downward irradiance of the sea surface. Furthermore, if we bear in mind that c. 6% of the light reaching the sea is reflected from the surface and within the water itself—this is the mean albedo of the sea (Payne 1979)—we have an average flux of radiant energy equal to c.  $177 \text{ W}$  that is constantly being absorbed in the water column beneath every square meter of the sea surface and converted to other forms of energy.

If we take the World Ocean to have a total surface area of 361 million  $\text{km}^2$ , it is unceasingly absorbing a solar radiation flux of c.  $6.4 \times 10^{10} \text{ MW}$ . This energy is consumed in warming and evaporating the waters of the ocean, warming the atmosphere by conduction, the latent heat of evaporation, and

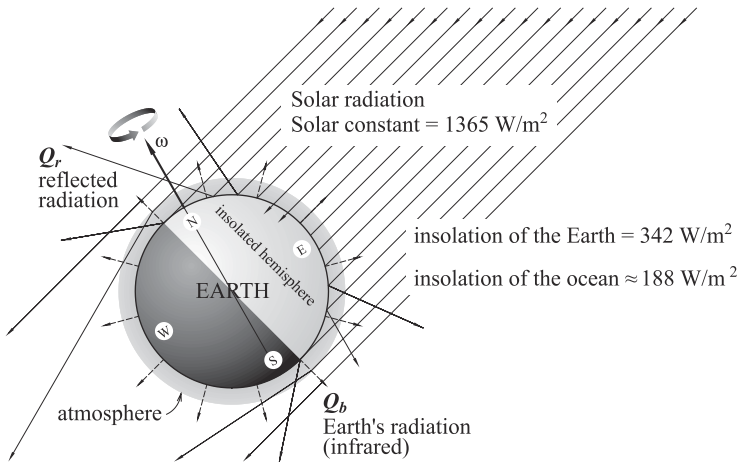


FIGURE 1.1. Solar light fluxes and the Earth. Solar constant: the mean solar radiation flux incident on a plane at right angles to the radiation reaching the top of the atmosphere; insolation of the Earth: the average component at the top of the atmosphere of the above flux (solar constant) perpendicularly incident at every spot on the Earth's surface during the day; insolation of the ocean (and land areas, i.e., the combined surface area of the ocean and land): the insolation of the Earth minus the averaged amount of radiation lost in the atmosphere. (Adapted from Dera (2003).)

the thermal radiation of the sea surface, as well as setting (and maintaining) the masses of water in motion. Finally, less than 1% of this energy drives the photosynthesis of organic matter and photochemical reactions in the sea water (e.g., Dera 2003).

From the point of view of quantum mechanics, this flux of absorbed energy means that an average of  $10^{20}$  collisions between photons and the component molecules of sea water and the absorption of the former by the latter takes place under every single square meter of ocean during every single second. The effect of every elementary collision of a photon with a particle of matter is strictly dependent on the energy of a photon  $E_\nu = h\nu$  (where  $h = 6.62517 \times 10^{-34}$  Js, Planck's constant and  $\nu$  is the frequency of vibrations of a photon, equal to the reciprocal of the period of vibrations  $T = 1/\nu$ , which is linked to the wavelength of the light  $\lambda$  and its velocity  $c$  by the relationship  $c = \nu\lambda$ ). The most likely effects of these collisions, during which photons of the appropriate energy are absorbed, are shown in Table 1.1.

We see in the table how very different the energies of photons are from different frequency bands of the light spectrum and also how large the extent to which the effects of their absorption vary, from the ionization of atoms by the far ultraviolet (UV) to the translation motions induced by the far infrared (IR). It thus becomes essential to know what the spectrum of light incident on the sea is and the changes it is subject to as it penetrates ever deeper into

TABLE 1.1. Relationships between the length of an electromagnetic wave  $\lambda$  (in a vacuum), the frequency of vibrations  $\nu$ , the energy of a photon  $E_\nu$ , the color of the light, and the probable effect of the absorption of a photon.

Wave-length $\lambda$ [nm]	Frequency of vibrations $\nu$ [Hz]	Energy of a photon $E_\nu$ [ $10^{-19}$ J]	Energy of a photon $E_\nu$ [eV]	Number of photons per J of energy [ $10^{18}$ J $^{-1}$ ]	Color of light (type of waves)	Probable effect of the absorption of a photon by a molecule
-1-	-2-	-3-	-4-	-5-	-6-	-7-
100	$3.001 \times 10^{15}$	19.88	12.41	0.503		Ionization,
150	$2.000 \times 10^{15}$	13.25	8.27	0.756	Far	electronic
200	$1.500 \times 10^{15}$	9.93	6.20	1.006	ultraviolet	excitation
250	$1.199 \times 10^{15}$	7.95	4.96	1.258	Ultraviolet	
300	$9.993 \times 10^{14}$	6.62	3.87	1.510		
350	$8.566 \times 10^{14}$	5.68	3.54	1.761	Violet	
400	$7.495 \times 10^{14}$	4.97	3.10	2.012	Blue	
450	$6.662 \times 10^{14}$	4.41	2.76	2.268	Green	
500	$5.996 \times 10^{14}$	3.97	2.48	2.519	Greenish-	Vibrational -
550	$5.451 \times 10^{14}$	3.61	2.25	2.770	Yellow	rotational excitation
600	$4.997 \times 10^{14}$	3.31	2.07	3.021	Orange	
650	$4.612 \times 10^{14}$	3.06	1.91	3.268		
700	$4.283 \times 10^{14}$	2.84	1.77	3.521	Red	
750	$3.997 \times 10^{14}$	2.65	1.65	3.774		
800	$3.748 \times 10^{14}$	2.48	1.55	4.032		
1,000	$2.998 \times 10^{14}$	1.99	1.24	5.025	Infrared	
2,000	$1.499 \times 10^{14}$	0.99	0.62	10.10		
3,000	$9.993 \times 10^{13}$	0.66	0.41	15.15		
5,000	$6.038 \times 10^{13}$	0.40	0.25	25.00	Far infrared	
10,000	$3.019 \times 10^{13}$	0.20	0.13	50.00		Rotational
20,000	$1.509 \times 10^{13}$	0.10	0.06	100.0		excitation,
50,000	$6.032 \times 10^{12}$	0.04	0.03	250.0		translations

Adapted from Dera (2003).

the water. Spectra of the irradiance of the sea surface by sunlight and the changes it undergoes with increasing depth in different seas are illustrated in Figure 1.2. Numerous studies have shown that, under average conditions, c. 50% of the sunlight incident on the sea surface consists of IR bands, some 45% of visible radiation and only around 5% of UV. The figure also shows how quickly the visible light spectrum narrows down with depth in the sea: bluish-green light ( $\lambda \approx 450$  nm) penetrates the farthest in optically clear oceanic waters, whereas greenish-yellow light ( $\lambda \approx 550$  nm) is the most penetrating in sea waters containing large amounts of organic substances. We can also see from Figure 1.2a that light reaching a depth of barely one meter contains practically no more IR, which means that IR radiation is very strongly absorbed by sea water and that all its energy entering the sea is absorbed in the very thin surface layer.

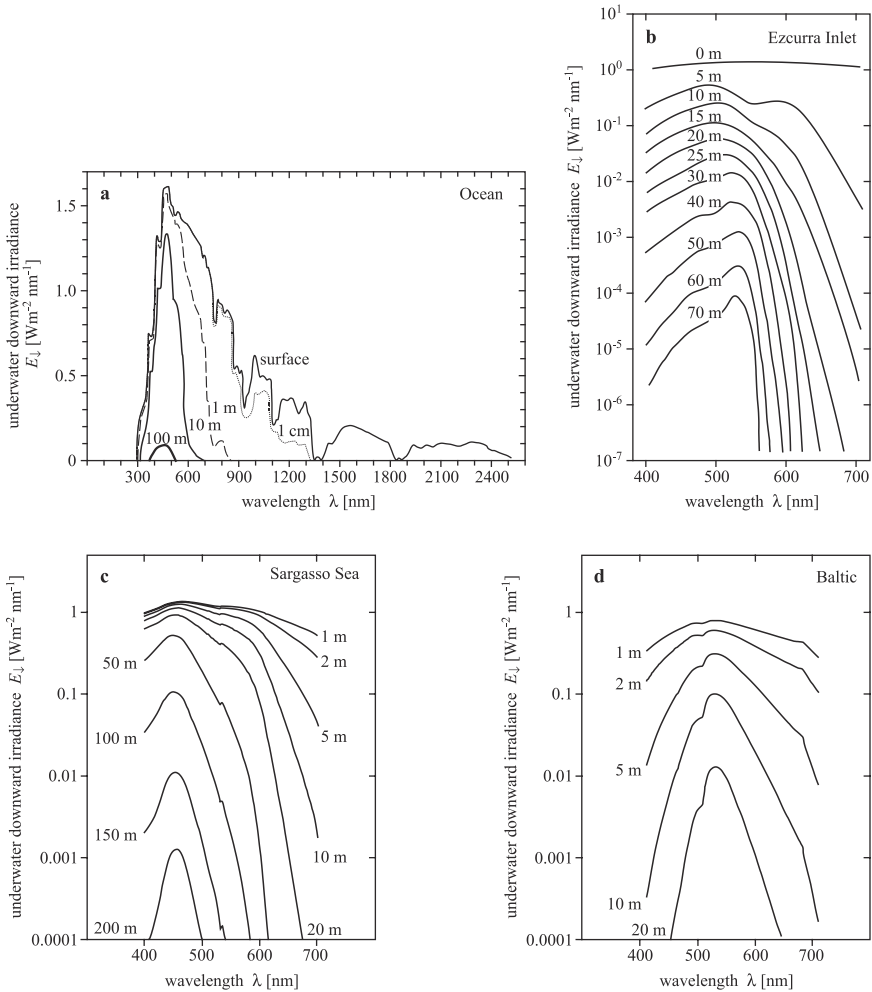


FIGURE 1.2. Spectra of daily downward irradiance in sea waters at various depths: (a) in the ocean over a broad spectral range (Jerlov 1976); (b) in the Ezcurrea Inlet, Antarctica, at around noon in January (from measurements by Woźniak et al. during the second Antarctic Expedition of the Polish Academy of Sciences (Dera 1980); (c) in the clear oligotrophic waters of the Sargasso Sea; (d) in the eutrophic waters of the Baltic Sea (drawn on the basis of data from IO PAN Sopot.) Reproduced from J. Dera, *Marine Physics*, 2nd ed., updated and supplemented, 2003 (in Polish), with the kind permission of PWN, Warszawa.

Water molecules play the most important part in the absorption of solar light energy in the ocean, not only because of their amount (>96% of all the molecules contained in sea water), but also because of their absorption properties: light in the IR band is very strongly absorbed (Chapter 2). Even so,

there is a multitude of other substances in sea water that are also capable of absorbing this energy. The complexity of sea water as a substance means that its optical properties are essentially different from those of pure water. Sea water contains numerous dissolved mineral salts and organic substances, suspensions of solid organic and inorganic particles, including various live microorganisms, and also gas bubbles and oil droplets. Many of these components participate directly in the interactions with solar radiation in that they absorb or scatter photons. Many also participate indirectly by fulfilling diverse geochemical and biological functions, for instance, in photosynthesis, which regulates the circulation of matter in marine ecosystems, and in doing so, affects the concentrations of most of the optically active components of sea water. The resources and the concentrations of the most important sea water components of the World Ocean are listed in Table 2.17, which also gives the principal optical and biological functions of these components.

The occurrence in sea water of suspended particles as well as other inhomogeneities, such as gas bubbles, oil droplets, and turbulence, means that from the optical standpoint it is a turbid medium, a light absorber and scatterer, the optical properties of which vary together with changes in the composition and concentration of the components and depend on the physical conditions prevailing at any given time (Jerlov 1976, Morel and Prieur 1977, Shifrin 1983b,1988, Højerslev 1986, Kirk 1994, Spinard et al. 1994, Mobley 1994, Stramski et al. 2001, Dera 1992, 2003).

Because of this powerful interaction between the molecules and the large number of components in sea water, we observe in the optical spectrum not discrete spectral absorption lines but broad absorption bands. Overlapping to various degrees and in different regions of the spectrum, the absorption bands actually form an absorption continuum with local maxima and minima. The absolute principal minimum of electromagnetic wave absorption in sea water lies in the visible region, as is the case with pure water (Figures 1.3 and 2.11). As we see in Figure 1.3, there is a great variety for different seas (e.g., a large absorption for the Baltic). The huge number of sea water components and the continuous nature of its absorption spectrum preclude any meaningful discussion of the optical properties of each component in turn. Nevertheless, it is possible to distinguish groups of components that are especially actively involved in the absorption of the solar radiation entering the sea water.

Generally speaking, we have to examine the following groups of components, which differ distinctly in their optical properties: water molecules and their associated forms, sea salt ions, dissolved organic matter (DOM), live phytoplankton and suspended phytoplanktonlike particles, and other particulate organic matter (POM; organic detritus, zooplankton, and zooplanktonlike particles), suspended mineral particles, and other components such as oil droplets and gas bubbles. It is thus the aim of the present volume to describe and assess the current state of knowledge of the absorption properties of these optically significant substances and the part they play in the interaction with light in sea water.

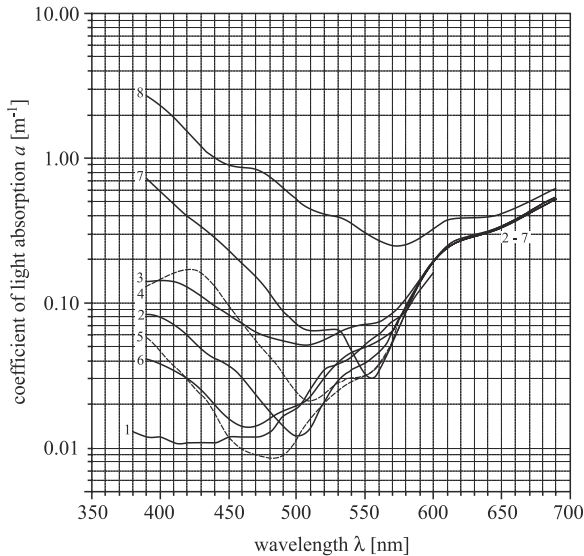


FIGURE 1.3. Spectra of light absorption in the visible range measured in different sea waters, curves: 1. Central Pacific; a very clear, deep-sea water (data from Pelevin and Rostovtseva (2001)); 2. Pacific Ocean, northern zone of subtropical convergence, depth 85 m; 3. Pacific Ocean, North Equatorial Current, depth 200 m; 4. Pacific Ocean, South Equatorial Current, depth 10 m; 5. Pacific Ocean, Tonga Trench, depth 10,000 m; 6. Atlantic Ocean, Sargasso Sea surface water; 7. Baltic Sea, Gotland Deep surface water; 8. Baltic Sea, Gulf of Riga surface water; plots 2 to 8, data selected from Kopelevitch et al. (1974); expedition of the Soviet research vessel “Dmitrii Mendeleev” to the oceans (1971) and other cruises in the Baltic Sea (1970).

## 1.2 Case 1 and Case 2 Waters

In addition to water molecules and salt ions, most of the other substances interacting to a significant extent with light in the open waters of oceans have their origin in the photosynthesis of organic matter in phytoplankton cells. The organic matter produced in this process supplies a whole trophic chain of marine organisms with nutritional energy, and the functioning of the ecosystem in turn gives rise to a range of dissolved and suspended substances: the metabolic and decay products of these organisms. The photosynthetic process is strictly dependent on the concentration of chlorophyll *a* in phytoplankton cells. Hence, the concentration of a mixture of light-absorbing substances in such waters is correlated with the chlorophyll *a* concentration, which can serve both as an index of the trophicity (fertility) of waters and as a parameter of their optical properties. Waters in which the functioning of the local marine ecosystem is practically the only source of substances affecting the optical properties of waters—these substances are thus autogenic—have come to be known as *Case 1 waters* (Morel and Prieur 1977).

Unlike such waters, which are unaffected by the inflow of various substances from rivers, shores, or other external sources, many marine basins, for example, the Baltic Sea, do contain waters that are affected by such inflows. Waters in which allogenic substances (entering from outside the local ecosystem, not produced by it) play a significant part in the interactions with light are referred to as *Case 2 waters* (Morel and Prieur 1977). In these latter waters the dependence of the absorption properties and other optical properties on the chlorophyll *a* concentration is more complex and has to be determined empirically with the aid of statistical methods, separately for particular marine regions and different seasons of the year. The classification of sea waters in accordance with this criterion has become standard in the oceanographic literature. The authors of this concept have stated that more than 98% of oceanic waters are Case 1 waters. This division is, however, merely an approximation of reality, as with many other such approximations necessary for modeling nature and investigating prevailing phenomena. In actual fact, ocean waters always contain certain admixtures not derived from the local ecosystem, for example, windborne sands from the Sahara, volcanic ash and other atmospheric dust, and traces of inflows from the great rivers carried along by the ocean currents. Nonetheless, these admixtures are usually of secondary importance where the optical properties of Case 1 open ocean waters are concerned.

### 1.3 The Light Absorption Coefficient and Its Components in Sea Water

An exact description and the measurement of light absorption in a medium requires the radiant energy transfer equation to be invoked (Preisendorfer 1961). When passing through a medium, light is not only absorbed but also scattered, and, unlike the classical Bouguer–Lambert law of absorption, the radiant energy transfer equation takes both processes into account. In the simplest case, where only one single, thin, parallel, time-invariable beam of light travels a distance  $r$  through a homogeneous medium that itself contains no sources of light, this equation can be written as

$$\frac{dL}{dr} = -cL, \quad (1.1)$$

where  $L \equiv L(r, \lambda)$ , the radiance of this light beam;  $\lambda$  is the wavelength of the light;  $c \equiv c(\lambda)$ , the total volumetric coefficient of light attenuation (for definitions, see Dera (2003, 1992), Højerslev (1986), and Jerlov (1976)).

The dimension of the coefficient of light attenuation is [ $\text{m}^{-1}$ ] and comprises the sum of the coefficients of absorption  $a(\lambda)$  and scattering  $b(\lambda)$ :

$$c(\lambda) = a(\lambda) + b(\lambda). \quad (1.2)$$

In the sea these coefficients are also functions of the coordinates of a given water body and are time-variable. They are the inherent optical properties of the medium (in this case, sea water) and thus characterize only the nature of the medium and are independent of the light's intensity. The correct way of measuring these coefficients, even if different techniques are applied, should lead to identical results. Later on, we cover in detail the light absorption coefficient  $a(\lambda)$  of sea water, which characterizes the absorption properties of this water and its components. A general description of these and other optical properties of sea water can be found in earlier monographs (Jerlov 1976, Mobley 1994, Dera 2003). What the literature lacks, however, is a compact description of the optical absorption properties of sea water in conjunction with a detailed analysis of the properties and the contribution to absorption of the several groups of its components, as well as some individual components that play a particularly important role in certain types of seas. It is the aim of our book to fill this gap and to acquaint the reader with the state of the art in this field.

Determining the optical absorption properties of sea water components has become imperative, particularly in view of the ever-wider applications of remotely sensing, satellite techniques for monitoring the state of the marine environment (Gordon et al. 1988, Karabashev et al. 2002, Arst 2003, Zaneveld et al. 2005a,b). One of the fundamental formulas in the remote sensing of the concentrations of selected sea water components is the one linking the light absorption coefficient  $a(\lambda)$  with the remote reflectance of radiance in the sea  $R_{rs}(\lambda)$  recorded by a satellite (Gordon et al. 1988):

$$R_{rs}(\lambda) = \frac{L_u(\lambda)}{E_d(\lambda)} \approx C \frac{b_b(\lambda)}{a(\lambda) + b_b(\lambda)}, \quad (1.3)$$

where  $L_u$  is the radiance emerging vertically upwards from the sea measured just below the sea surface,  $E_d$  is the downward irradiance just below the sea surface,  $b_b$  is the light backscattering coefficient; that is, in scattering angles from  $90^\circ$  to  $180^\circ$ ,  $C$  is a constant coefficient determined empirically for the given conditions of an investigation. This formula also takes account of the significant part played by the light-scattering coefficient, but the correlations of the absorption coefficients with the reflectance enable one to detect the presence, and even calculate the concentrations, of certain substances in the sea on the basis the remotely measured reflectance  $R_{rs}$  (Sathyendranath et al. 1994, 2001, Platt et al. 1995, Olszewski and Darecki 1999, Lee et al. 1994; Gordon 2002). A well-known application of the reflectance of the sea surface radiance and its correlation with the absorption coefficient of sea water components is the remote sensing of the chlorophyll concentration and hence of primary production in the ocean (Platt and Sathyendranath 1993a,b; Sathyendranath et al. 1989, Morel 1991, Antoine et al. 1996, Woźniak et al. 2004, see also Figure 6.13).



The energy of the light absorbed in unit volume (energy density) of water  $dP/dV$  at depth  $z$  in the sea depends only on the inflow of this light (from all directions) and on the coefficient of light absorption in this volume of water. This is described by the Law of Conservation of Radiant Energy, well known in marine optics, which emerges, for example, from Gershun's equation (1958):

$$\frac{dP}{dV} = -aE_0 \quad [\text{Wm}^{-3}], \quad (1.4)$$

where  $E_0$  is the scalar irradiance at the point of investigation. This equation is exact in the situation where there are no internal light sources in the volume of water under study (for details, see Gordon (2002) or Dera (2003)).

Because the concentrations of the various substances dissolved and suspended in sea water are small, light absorption by the various components or groups of components of sea water is assumed to be additive. This means that the overall absorption coefficient of sea water  $a(\lambda)$  is the sum of the partial coefficients: these express the contribution of various groups of components in the water to the resultant absorption. We can ascribe a separate absorption coefficient to each of these component groups, so that their sum total will express the overall coefficient for sea water:

$$\left. \begin{aligned} a &= a_w(\lambda) + a_s(\lambda) + a_{DOM}(\lambda) + a_p(\lambda) + a_r(\lambda) \\ \text{and } a_p(\lambda) &= a_{POM}(\lambda) + a_{PIM}(\lambda), \quad a_{POM}(\lambda) = a_{pl}(\lambda) + a_{Od}(\lambda) \end{aligned} \right\} \quad (1.5a)$$

or

$$\left. \begin{aligned} a &= a_w(\lambda) + a_s(\lambda) + a_{DOM}(\lambda) + a_{pl}(\lambda) + a_{NAP}(\lambda) + a_r(\lambda) \\ \text{and } a_{NAP}(\lambda) &= a_{Od}(\lambda) + a_{PIM}(\lambda) \end{aligned} \right\}, \quad (1.5b)$$

where the subscripts to the respective partial coefficients denote the following:  $w$  is water;  $s$  is sea salt;  $DOM$  is dissolved organic matter;  $p$  is suspended particulate matter;  $r$  is the remaining substances, including oil droplets, gas bubbles, and others not covered by further subscripts;  $POM$  is particulate organic matter;  $PIM$  is particulate inorganic matter (suspended minerals);  $pl$  is live phytoplankton and bacteria ( $a_{pl}$  is often identified with the total absorption coefficient of all the phytoplankton pigments);  $Od$  is organic detritus (together with nonalgal living organismus as zooplankton);  $NAP$  is nonalgal particles. The dimension of the light absorption coefficients is  $[\text{m}^{-1}]$ .

The partial absorption coefficient related to the mass concentration of a given absorber in sea water is called the *mass-specific light absorption coefficient* of that absorber, and is usually denoted  $a_j^* = a_j/C_j$  (where the subscripts  $j$  denote the absorber in question and  $C_j$  is the mass concentration of the absorber in the water). The dimension of the mass-specific light absorption coefficients of an absorber is  $[\text{m}^{-1}[(\text{mg of the } j\text{th absorber}) \text{m}^{-3}]^{-1}] \equiv [\text{m}^2(\text{mg of the } j\text{th absorber})^{-1}]$ .

In the case of phytoplankton the absorption coefficient is often related to the mass concentration of the principal phytoplankton pigment, that is, to the total chlorophyll *a* concentration in sea water  $C_a$  (the sum of chlorophyll *a* + pheo.). Denoted  $a_{pl}^* = a_{pl}/C_a$ , it is referred to as the *chlorophyll-specific light absorption coefficient* of phytoplankton. Its dimension is  $[m^{-1}[(\text{mg tot. chl } a) \text{ m}^{-3}]^{-1}] \equiv [m^2(\text{mg tot. chl } a)^{-1}]$ .

In line with the partial absorption coefficients we have distinguished here, the several chapters in this book describe and analyze the absorption properties of these various groups of sea water components. We devote the greatest amount of space to the components most strongly differentiating sea and ocean waters from the optical point of view: the water itself, the dissolved organic substances, and the suspended particles of diverse provenance. We place special emphasis on the role of phytoplankton pigments, which are particularly strong and important absorbers of visible light in the sea.

# 2

## Light Absorption by Water Molecules and Inorganic Substances Dissolved in Sea Water

The principal absorber of light and other electromagnetic radiation in seas and oceans is, of course, water as a chemical substance. Above all, this is due to the absolute numerical superiority of  $\text{H}_2\text{O}$  molecules over the molecules of all other substances contained in sea water: for every 100  $\text{H}_2\text{O}$  molecules there are only 3–4 molecules of other substances, chiefly sea salt, but also dissolved organic substances, and the numerous suspended particles of mineral and organic matter, including phytoplankton cells and other live organisms. Although small in quantity, these various substances contained in sea water very significantly differentiate marine areas from the optical point of view. Water itself is a very strong absorber of electromagnetic radiation in the infrared (IR) region; thanks to this property it plays a prominent and indispensable role for life on Earth in that the ocean absorbs solar IR radiation and converts it into heat. This process leads directly to the warming of the ocean's surface waters, causing them to evaporate, and to the heating and circulation of the atmospheric air.

In this chapter we describe the mechanisms and spectra of light absorption by small molecules—principally water molecules—as well as the spectral absorption properties of liquid water, ice, and water vapor, and of the components of sea salt and other mineral substances dissolved in the water. Because of its exceptional significance in Nature, we give the water itself pride of place, describing its absorption spectra with respect not only to visible light but also to a wide spectrum of electromagnetic radiation, from the extremely short  $\gamma$ - and X-rays to long radio waves.

### 2.1 Light Absorption Spectra of Small Molecules such as Water: Physical Principles

As we stated in Chapter 1, the light absorption spectra of matter in its various states are determined by quantum changes in the atomic and molecular energies of that matter as a result of its having absorbed photons. Among these quantum processes we must include the energetic electronic transitions

in atoms, and also the electronic, vibrational, and rotational transitions in molecules, all of which in fact take place simultaneously. We can explain these quantum changes of energy with respect to a molecule most simply if we examine the energy states of a free molecule.

The total energy of a freely moving molecule  $E_M(\Lambda, \nu, J)$  consists of the temperature-dependent energy of its translational motion  $E_{TR}$ , the energy of its rotation about its various axes of symmetry  $E_{ROT}(J)$ , the vibrational energy of its atoms around its equilibrium position  $E_{VIB}(\nu)$ , and the energy of its electrons  $E_E(\Lambda)$ , where  $J$ ,  $\nu$ ,  $\Lambda$ , are respective quantum numbers. We can thus write down this total energy as the sum of these component energies:

$$E_M(\Lambda, \nu, J) = E_E(\Lambda) + E_{VIB}(\nu) + E_{ROT}(J) + E_{TR} \quad (2.1)$$

The first three—quantized—energy constituents on the right-hand side of Equation (2.1) depend on the extent to which the molecule is excited. In other words, they take discrete values, strictly defined by the given quantum (energy) state of the molecule. The energy states of a simple molecule (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ) are defined by the rotational energy (the quantum number or numbers  $J$ ), the vibrational energy (the quantum number or numbers  $\nu$ ), and the electronic energy (given by the quantum number  $\Lambda$ ), defining the absolute value of the projection of the angular momentum on to the molecule's axis.

The absorption or emission by a molecule of a photon of energy  $E_{hv} = h\nu$  invariably involves its transition from one quantum state, described by quantum numbers  $\Lambda$ ,  $\nu$ ,  $J$ , to another quantum state, described by  $\Lambda'$ ,  $\nu'$ ,  $J'$  (in the general case all three quantum numbers change) in accordance with the allowed quantum mechanical selection rules. The energy of this photon is then equal to the difference between the molecule's energies in these two states and can be written as

$$E_{hv} = E_M(\Lambda, \nu, J) - E_M(\Lambda', \nu', J') = \Delta E_E(\Lambda \rightarrow \Lambda') + \Delta E_{VIB}(\nu \rightarrow \nu') + \Delta E_{ROT}(J \rightarrow J') + \Delta E_{TR} \quad (2.2)$$

So it is the sum of the increments (or losses) of energy of the several components in these two states (initial and final), that is, the increments of electronic ( $\Delta E_E$ ), vibrational ( $E_{VIB}$ ), rotational ( $E_{ROT}$ ), and translational ( $E_{TR}$ ) energy. The increments of these first three energy components of the molecule following the absorption of a photon give rise to the three principal types of absorption band, which we discuss presently. The transition of a molecule from one electronic state to another (the selection rule for such transitions is  $\Delta\Lambda = 0, \pm 1$ ) usually brings about changes in the vibrational state (selection rule:  $\Delta\nu = \pm 1, \pm 2, \dots$ ) and the rotational state of the molecule (selection rule:  $\Delta J = 0, \pm 1$ ) as well. A transition during which all three types of molecular energy change as a result of the absorption (or emission) of energy gives rise to an *electronic-vibrational-rotational* spectrum of the absorption of electromagnetic wave energy. This is a band spectrum with a highly complex structure consisting of very many spectral lines forming two or three branches

denoted  $R(\Delta J = 1)$ ,  $P(\Delta J = -1)$ , and  $Q(\Delta J = 0)$ . The lines of these branches lie in the ultraviolet and visible regions of the electromagnetic waves spectrum (in the case of water only in the ultraviolet).

In certain electronic states, a molecule may, as a result of allowed vibrational-rotational energy transitions, change only its vibrational and rotational energy. Transitions of this kind give rise to vibrational-rotational absorption spectra as a result of the absorption (or emission) of relatively low-energy quanta, that is, from the infrared region of electromagnetic waves.

If a molecule is not symmetrical or has a dipole moment other than zero (like the water molecule, for example), then as a result of the absorption (or emission) of energy quanta from the microwave or radiowave ranges, its rotational energy may change without the electronic or vibrational states being affected. What we then have is a rotational absorption band.

This simplified picture of a molecule's internal energy changes reflects the structural complexity of a molecular spectrum of the absorption (or emission) of electromagnetic wave energy. In this chapter we present the theoretical foundations underlying this process, which are essential for understanding the structure of the light absorption spectra of water molecules; it also helps in understanding the absorption band structures of other small molecules. A more detailed treatment of the subject can be found in the numerous monographs on molecular physics, spectroscopy, and quantum mechanics and chemistry, for example, Barrow (1969), Herzberg (1950, 1992), Banwell (1985), Hollas (1992), Haken and Wolf (1995, 1998, 1996, 2002), Kowalczyk (2000), and Linne 2002, to mention but a few. The following works, dealing specifically with the various properties of water, in particular the interaction of water molecules with electromagnetic radiation, are also deserving of attention: Eisenberg and Kauzmann (1969), Lemus (2004), and Chaplin (2006), again, to mention just three. Moreover, Bernath (2002) provides a detailed review of the subject literature, and in the course of this chapter we cite yet other works.

### 2.1.1 *Vibrational-Rotational Absorption Spectra*

Water molecules appear to be the most important ones involved in the process of solar energy absorption because of their untold numbers in the ocean and atmosphere, as well as their crucial optical properties. Of particular significance in Nature is the very strong absorption by water molecules of infrared radiation (IR), as a result of transitions between the vibrational-rotational energy states in these molecules. According to our estimates, this IR absorption by water molecules is equivalent to some 60% of the total solar radiation energy absorbed in the Earth's epigeosphere (i.e., around 70% of the energy absorbed in the atmosphere and some 50% of the energy absorbed in the sea).

How the water molecule interacts with electromagnetic radiation depends closely on its physical properties. Important in this respect are its geometrical

parameters (the positions of the atoms vis-à-vis one another and the configuration of electrons), as well as its dynamic, electrical, and magnetic properties. Table 2.1 lists many of these properties that are directly related to the optical properties of water. We refer frequently to this table in the present (2.1) and the next section (2.2).

As we can see in Table 2.1 (items (1) to (3)), the triatomic molecule of water ( $\text{H}_2\text{O}$ ) has a nonlinear structure: the respective distances between the atoms of oxygen and hydrogen and between the two hydrogen atoms are  $\bar{d}_{\text{OH}} \approx 9.57 \cdot 10^{-11}$  m and  $\bar{d}_{\text{HH}} \approx 1.54 \cdot 10^{-10}$  m (see also Figure 2.4a). These distances are the ones prevailing in the equilibrium state, when the angle HOH  $\bar{\alpha}_{\text{HOH}} \approx 104.5^\circ$ . These parameters define the geometry of the water molecule, in which a rotation through an angle  $\pi$  or  $2\pi$  around the axis of rotation in the planes

TABLE 2.1. Selected physical properties of the water molecule  $^1\text{H}_2\text{}^{16}\text{O}$ , governing its interaction with electromagnetic radiation or associated with its optical properties.

No.	Name or symbol (explanation)	Value	
		In common units	In SI units
-1-	-2-	-3-	-4-
<i>Geometrical Parameters</i>			
1	Mean OH bond length in the ground state $\bar{d}_{\text{OH}}$	0.9572 ( $\pm 0.0003$ ) Å	9.572 ( $\pm 0.003$ ) $\times 10^{-11}$ m
2	Mean HOH bond angle in the ground state $\bar{\alpha}_{\text{HOH}}$	104.52° ( $\pm 0.05^\circ$ )	1.82 rad ( $\pm 8.43 \times 10^{-4}$ rad)
3	Mean distance between H atoms in the ground state $\bar{d}_{\text{HH}}$	c. 1.54 Å	c. $1.54 \times 10^{-10}$ m
<i>Dynamic Parameters</i>			
4	Inert molecular weight $m_{\text{H}_2\text{O}}$	$2.9907243 \times 10^{-23}$ g	$2.9907243 \times 10^{-26}$ kg
5	Moments of inertia in the ground state <sup>(*)</sup> : $I_{\text{H}_2\text{O}}^y$	$2.9376 \times 10^{-40}$ g cm <sup>-2</sup>	$2.9376 \times 10^{-39}$ kg m <sup>-2</sup>
6	$I_{\text{H}_2\text{O}}^z$	$1.959 \times 10^{-40}$ g cm <sup>-2</sup>	$1.959 \times 10^{-39}$ kg m <sup>-2</sup>
7	$I_{\text{H}_2\text{O}}^x$	$1.0220 \times 10^{-40}$ g cm <sup>-2</sup>	$1.0220 \times 10^{-39}$ kg m <sup>-2</sup>
<i>Electric and Magnetic Properties</i>			
8	Relative permittivity (dielectric constants) $\epsilon$	Gas: 1.0059 (100°C, 101.325 kPa) Liquid: 87.9 (0°C), 78.4 (25°C), 55.6 (100°C) Ice Ih: 99 (-20°C), 171 (-120°C)	
9	Relative polarizability $\alpha/\epsilon_0$ (where $\alpha$ = polarizability, $\epsilon_0$ = permittivity of a vacuum)	$1.44 \times 10^{-10}$ m <sup>3</sup>	
10	Dipole moment in the equilibrium state $p_p$	Gas: 1.854 D (debye) Liquid (27°C): 2.95 D Ice Ih: 3.09 D	$6.18 \times 10^{-30}$ A s m $9.84 \times 10^{-30}$ A s m $10.31 \times 10^{-30}$ A s m
11	Volume magnetic susceptibility $\chi = \mu - 1$ (where $\mu$ - relative magnetic permeability) at 20°C	$-7.19 \times 10^{-7}$ [dimensionless] (cgs convention)	$-9.04 \times 10^{-6}$ [dimensionless]

TABLE 2.1. Selected physical properties of the water molecule  $^1\text{H}_2^{16}\text{O}$ , governing its interaction with electromagnetic radiation or associated with its optical properties.—  
Cont'd.

No.	Name or symbol (explanation)	Value	
		In common units	In SI units
-1-	-2-	-3-	-4-
<i>Characteristic Molecular Energies</i>			
12	Bond energy between the constituent atoms in the molecule at temperature 0K	-9.511 eV	$-1.52 \times 10^{-18}$ J
12a	As above, at temperature 25°C	-10.09 eV	$-1.62 \times 10^{-18}$ J
13	Ground state vibrational energy	+0.574 eV	$9.20 \times 10^{-20}$ J
14	Energy of electronic bonds (the difference (12) – (13))	-10.085 eV	$-1.62 \times 10^{-18}$ J
15	The sum of the energies of the discrete constituent atoms in the ground state	-2070.46 eV	$-3.32 \times 10^{-16}$ J
16	The total energy of the molecule at temperature 0 K (sum of (14) + (15))	-2080.55 eV	$-3.33 \times 10^{-16}$ J
16a	The kinetic energy input (equal to-(16))	+2080.55 eV	$3.35 \times 10^{-16}$ J
16b	The potential energy input (equal to 2(16) – (17))	-4411.3 eV	$-7.07 \times 10^{-16}$ J
17	Nuclear repulsion energy	+250.2 eV	$4.01 \times 10^{-17}$ J
18	Electronic excitation energy at light wavelength $\lambda = 124$ nm	c. 10.0 eV	c. $1.60 \times 10^{-18}$ J
19	Ionization potential first (I)	12.62 eV	$2.02 \times 10^{-18}$ J
20	Second (II)	14.73 eV	$2.36 \times 10^{-18}$ J
21	Third (III)	$16.2 \pm 0.3$ eV	$2.60 \times 10^{-18}$ J $\pm 4.81 \times 10^{-20}$ J
22	Fourth (IV)	$18.0 \pm 0.3$ eV	$2.88 \times 10^{-18}$ J $\pm 4.81 \times 10^{-20}$ J
23	Total H–O bond energy at temperature 0K (equal to 1/2 (12))	-4.756 eV	$-7.62 \times 10^{-19}$ J
24	Dissociation energy of H–O bond at temperature 0 K	4.40 eV	$7.05 \times 10^{-19}$ J
25	Dissociation energy of H–OH bond at temperature 0 K (equal to-(12) – (24))	5.11 eV	$8.19 \times 10^{-19}$ J
26	Energy of the lowest vibrational transition	0.198 eV	$3.17 \times 10^{-20}$ J
27	Typical energy of a rotational transition	0.005 eV	$8.01 \times 10^{-22}$ J
28	Change of internal energy per molecule during the formation of water vapor at boiling point	0.39 eV	$6.25 \times 10^{-20}$ J
29	Change of internal energy per molecule during the formation of type Ih ice at temperature 0°C	-0.06 eV	$-9.61 \times 10^{-21}$ J
30	Change of internal energy per molecule during the transition from type Ih ice to type II ice	-0.0007 eV	$-1.12 \times 10^{-22}$ J

(Continued)

TABLE 2.1. Selected physical properties of the water molecule  $^1\text{H}_2^{16}\text{O}$ , governing its interaction with electromagnetic radiation or associated with its optical properties.—Cont'd.

No.	Name or symbol (explanation)	Value	
		In common units	In SI units
-1-	-2-	-3-	-4-
<i><math>^1\text{H}_2^{16}\text{O}</math> Occurrence on the Background of Molar Isotopic Composition of Natural Waters (according to VSMOW<sup>a</sup>)</i>			
Percent of total mass			
31	$\text{H}_2^{16}\text{O}$	99.7317	
32	$\text{H}_2^{17}\text{O}$	0.0372	
33	$\text{H}_2^{18}\text{O}$	0.199983	
34	$\text{HD}^{16}\text{O}$	0.031069	
35	$\text{HD}^{17}\text{O}$	0.0000116	
36	$\text{HD}^{18}\text{O}$	0.0000623	
37	$\text{D}_2^{16}\text{O}$	0.0000026	
38	$\text{HT}^{16}\text{O}$	variable trace	
39	$\text{T}_2^{16}\text{O}$	~ 0	

After various authors, cited in Eisenberg and Kauzman (1969), Haken and Wolf (1995,1998), Dera (2003), and Chaplin (2006); among others.

\* Moment of inertia: (y) = relative to the y-axis passing through the center of mass of the molecule and perpendicular to the HOH plane; (z) = relative to the axis bisecting the angle  $\alpha_{\text{HOH}}$ ; (x) = relative to the axis perpendicular to the (y,z) plane and passing through the center of mass.

<sup>a</sup> The Vienna Standard Mean Ocean Water (VSMOW) for a general number of hydrogen atoms contains 99.984426% atoms of  $^1\text{H}$ , 0.015574% atoms of  $^2\text{H}$  (D), and  $18.5 \times 10^{-16}\%$  atoms of  $^3\text{H}$  (T), and for a general number of oxygen atoms contains 99.76206% atoms of  $^{16}\text{O}$ , 0.03790% atoms of  $^{17}\text{O}$  and 0.20004% atoms of  $^{18}\text{O}$  (see, e.g., Chaplin (2006)).

of symmetry (the plane of the molecule, and the plane perpendicular to it, passing through the oxygen atom) do not affect its configuration. Determined with respect to these axes of rotation, the three moments of inertia of the water molecule are different (see items (5)–(7) in Table 2.1). It is for these reasons that we replace the description of the rotational motion of the water molecule by a quantum description of the motion of an asymmetrical top. This approach makes it very much easier to describe the purely rotational spectrum of the vibrations of the water molecule.

The asymmetrical structure of the water molecule, which can be likened to a three-dimensional anharmonic vibrator, also affects its vibrational states. It is responsible for the fact that water molecules have a high, permanent dipole moment:  $p_p = 1.854$  debye in the equilibrium state (see item (10) in Table 2.1). The value of this dipole moment changes due to the interaction of interatomic forces, which alter the individual interatomic distances in the molecule and also the angle  $\alpha_{\text{HOH}}$  between the OH bonds. The effect of these interactions manifests itself as vibrations of the atoms around their equilibrium positions in the molecule's electric field; generally characteristic of a particular molecule, this effect depends on its structure. The number  $f$  of normal vibrations of a molecule depends on the number of its internal degrees of freedom  $N$ :



$$f = 3N - 5 \text{ for linear molecules.}$$

$$f = 3N - 6 \text{ for nonlinear molecules.}$$

In the water molecule ( $N = 3$ ) there are thus three “modes” of normal vibrations, described by three vibrational quantum numbers:  $\nu_1$  (mode I),  $\nu_2$  (mode II), and  $\nu_3$  (mode III); see Figure 2.1. As this figure shows, the vibrational modes characteristic of the water molecule differ. The excited vibrations of mode I are symmetric stretch vibrations, whereas those of mode II are deformation vibrations, causing the molecule to bend. Mode III vibrations are asymmetric stretch vibrations.

We describe the vibrational energy states of the water molecule by stating the values of all three of its vibrational quantum numbers:  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ . In the ground (not excited) vibrational state the values of all three quantum numbers are zero, so that we can write this state as  $(0,0,0)$ . The vibrational

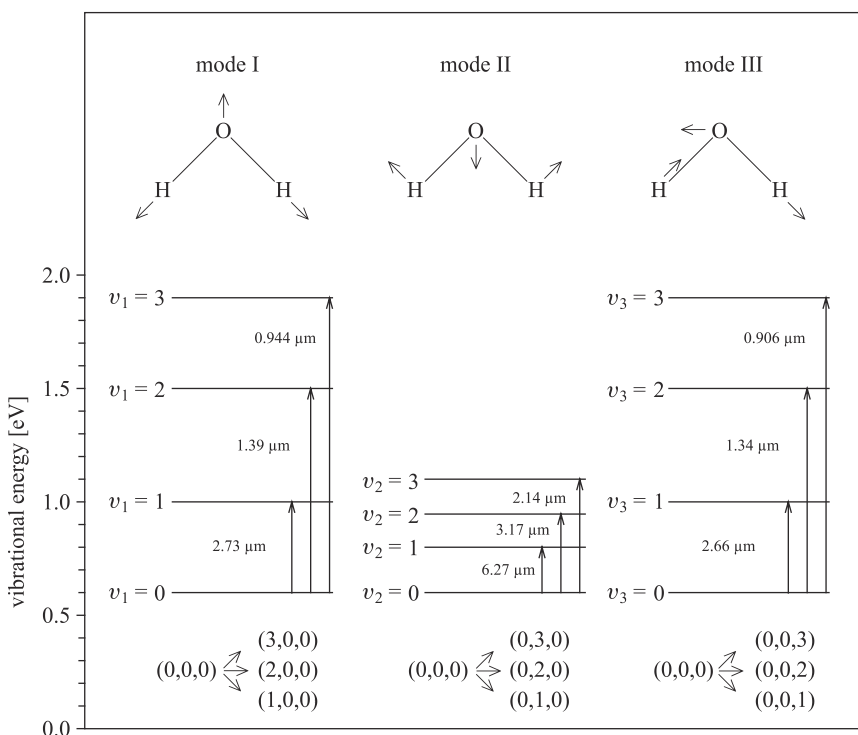


FIGURE 2.1. Normal vibration modes of a water molecule and its characteristic vibrational energy levels in the ground state, and in selected vibrational excited states described by quantum numbers  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ . The figure also gives the approximate wavelengths of light [ $\mu\text{m}$ ] absorbed by such a molecule during its transition from the ground state to these excited states. The exact values of the vibrational energies shown in the figure are given in Table 2.2.

TABLE 2.2. Vibrational energies of the water molecule  $E_{VIB}$  in the ground state and selected simple excited states.<sup>a</sup>

Quantum number $v_1$ or $v_2$ or $v_3$	Mode I ( $v_1$ ) $E_{VIB}$ [eV]	Mode II ( $v_2$ ) $E_{VIB}$ [eV]	Mode III ( $v_3$ ) $E_{VIB}$ [eV]
-1-	-2-	-3-	-4-
0	0.574	0.574	0.574
1	1.03	0.772	1.04
2	1.47	0.965	1.5
3	1.89	1.15	1.94
4	2.34	1.33	2.38
5	2.74	1.51	2.80
6	3.12	1.67	3.21
7	3.55	1.83	3.61

Calculated from data in Eisenberg and Kauzmann (1969) and Lemus (2004).

<sup>a</sup> That is, for the vibrations of one mode.

energy of the water molecule in this state is  $E_{VIB} = 0.574$  eV (i.e.,  $9.20 \times 10^{-20}$  J). In the excited states of the molecule, its vibrational energy is greater, every higher level of excitation being described by the corresponding higher value of the vibrational quantum number. This is exemplified in Table 2.2, which gives the vibrational energies of the water molecule in various “simple” excited states, that is, when it is vibrating in only one of its modes. The data in Table 2.2 show that these energies vary for different modes. The most highly energetic ones are the asymmetric stretch vibrations, that is, mode III. Only slightly less energetic are the symmetric stretch vibrations (mode I). Finally, the vibrations with the lowest energy (less than the previous two types by c. 30–60%, depending on the level of excitation) are the mode II deformation vibrations. These differences exert a fundamental influence on the position of the light absorption spectral bands associated with the molecule’s different vibrational modes (see below), these bands arising as a result of transitions between lower and higher vibrational-rotational energy levels. These transitions can be divided into a number of groups, which we now briefly discuss.

### Fundamental Transitions

Transitions from the ground state to the first excited state in a given mode are recorded in the light absorption spectrum as fundamental absorption bands, which can be written as follows:

$$(0,0,0) \rightarrow (1,0,0) \text{ mode I}$$

$$(0,0,0) \rightarrow (0,1,0) \text{ mode II}$$

$$(0,0,0) \rightarrow (0,0,1) \text{ mode III}$$

If we know the vibrational energy of the ground state  $E_{VIB1}$  and the energies of the first excited state  $E_{VIB2}$  for each of the three vibrational modes (see Table 2.2), we can easily work out the positions in the spectrum of these three

fundamental absorption bands for the water molecule from the differences between these energies.<sup>1</sup> In the spectrum, the fundamental light absorption bands for the vibrational modes I, II, and III of the water molecule lie in the vicinity of the wavelengths  $\lambda = 2.73 \mu\text{m}$ ,  $6.27 \mu\text{m}$ , and  $2.66 \mu\text{m}$ , respectively. As we can see, all three bands lie in the IR region, whereby the longest-wave band (i.e., with the lowest energy of absorbed photons) is due to mode II vibrations. In contrast, the changes in the energy states of the water molecule performing mode I or mode III vibrations cause radiation of a much shorter wavelength, that is, much higher-energy photons to be absorbed (or emitted).

In addition to these three fundamental bands of light absorption or emission, corresponding to molecular transitions from the ground state to the first excited state, or back from the latter state to the former (i.e., transitions for which the condition  $\Delta v_1 = \pm 1$ ,  $\Delta v_2 = \pm 1$ , or  $\Delta v_3 = \pm 1$  is satisfied), the absorption spectrum of the water molecule reveals a whole series of further bands due to energy transitions between various vibrational levels. For analyzing their origin and characteristic features, it is convenient to distinguish four categories of such transitions, namely:

- Harmonic transitions (also known as overtones) from the ground state
- Combination transitions from the ground state
- Harmonic transitions between excited states only
- Combination transitions between excited states only

We now proceed to discuss the meanings of these concepts and the positions of the absorption bands to which they give rise.

### Harmonic and Combination Transitions from the Ground State

In the water molecule, inasmuch as it is anharmonic, further transitions are allowed from the ground state to higher excited states in a given mode (i.e., as a result of which one of the three vibrational quantum numbers changes:  $\Delta v_1$  or  $\Delta v_2$  or  $\Delta v_3 > 1$ ). As a consequence of these transitions, harmonic absorption bands are formed, also known as overtones. We can write these transitions as above, but with higher values of the quantum numbers  $v'_1, v'_2, v'_3 = 2, 3, \dots$ ; for example,  $(0,0,0) \rightarrow (0,2,0)$  denotes a mode II transition from the ground state to the first state of harmonic vibrations. The quantum mechanical selection rules also allow transitions in the water molecule from the ground state to narrower vibrational energy states with a simultaneous change of more than one vibrational quantum number. An example of such a change is  $(0,0,0) \rightarrow (3,1,1)$ , which means that on absorbing a photon, the molecule passes from the ground state to an excited state that is a mixture of

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<sup>1</sup> The wavelength of a photon absorbed (or emitted) by a molecule is given by the obvious relationship  $\lambda = hc/(E_{VIB2} - E_{VIB1})$ , derived from Equation (2.2), where  $E_{VIB1}$  is the ground state energy (i.e.,  $(0,0,0)$ ;  $E_{VIB2}$  is the excited state energy (i.e., in this particular case  $(1,0,0)$ ,  $(0,1,0)$ , or  $(0,0,1)$ ).

all three vibrational modes, because all three quantum numbers have changed by  $\Delta v_1 = 3$ ,  $\Delta v_2 = 1$ ,  $\Delta v_3 = 1$ . Transitions of this type give rise to so-called combination absorption bands.

There may be a large number of such harmonic and combination absorption bands. In practice we find several tens of them in any spectrum (Eisenberg and Kauzmann 1969, Lemus 2004). The more important of these bands, recorded experimentally, are listed in Table 2.3 together with the definition of

TABLE 2.3. Vibrational bands of light absorption by  $\text{H}_2\text{O}$  molecules excited from the ground state.

Quantum numbers of excited states		Quantum numbers of excited states	
$v_1, v_2, v_3$	Wavelength [ $\mu\text{m}$ ]	$v_1, v_2, v_3$	Wavelength [ $\mu\text{m}$ ]
-1-	-2-	-1-	-2-
0,1,0	6.27	1,2,2	0.733
0,2,0	3.17	2,2,1	0.732
1,0,0	2.73	1,7,0	0.732
0,0,1	2.66	2,0,2	0.723
0,3,0	2.14	3,0,1	0.723
1,1,0	1.91	0,7,1	0.723
0,1,1	1.88	1,2,2	0.719
0,4,0	1.63	0,2,3	0.711
1,2,0	1.48	4,0,0	0.703
0,2,1	1.46	1,0,3	0.698
2,0,0	1.39	0,0,4	0.688
1,0,1	1.38	1,5,1	0.683
0,0,2	1.34	1,3,2	0.662
0,5,0	1.33	2,3,1	0.661
1,3,0	1.21	2,1,2	0.652
0,3,1	1.19	3,1,1	0.652
2,1,0	1.14	0,3,3	0.644
1,1,1	1.14	4,1,0	0.635
0,6,0	1.13	1,1,3	0.632
0,1,2	1.11	3,2,1	0.594
0,4,1	1.02	2,2,2	0.594
2,2,0	0.972	3,0,2	0.592
1,2,1	0.968	2,0,3	0.592
0,2,2	0.950	4,2,0	0.580
3,0,0	0.944	1,2,3	0.578
2,0,1	0.942	5,0,0	0.573
1,0,2	0.920	4,0,1	0.572
0,0,3	0.906	1,0,4	0.563
1,3,1	0.847	3,3,1	0.547
1,1,2	0.824	3,1,2	0.544
2,1,1	0.823	2,1,3	0.544
1,1,2	0.806	4,1,1	0.527
0,1,3	0.796	3,0,3	0.506
2,4,0	0.757	5,0,1	0.487
1,4,1	0.754	3,1,3	0.471
0,4,2	0.744	4,0,3	0.444

Based on data gleaned from Lemus (2004).

the type of transition. We should bear in mind, however, that the intensities of the spectral lines in bands corresponding to harmonic vibrations and also in combination bands, are several orders of magnitude less than the intensities of the fundamental lines.

As we can see from Table 2.3, these harmonic and combination absorption bands of the water molecule lie in the near-infrared region of the spectrum, and some of them encroach into the visible region. This means that such photons are absorbed in the transitions, whose energies exceed those of the photons absorbed during fundamental transitions. Absorption of these photons is reflected in the spectrum by the fundamental absorption bands in the vicinity of wavelengths 2.73  $\mu\text{m}$  (mode I), 6.27  $\mu\text{m}$  (mode II), and 2.66  $\mu\text{m}$  (mode III). These last wavelengths, characteristic of the fundamental bands of light absorption by the water molecule, constitute the longwave boundaries (at the longwave end of the spectrum) of the sets of wavelengths corresponding to all the possible absorption bands due to molecular transitions from the ground state to diverse excited states.

On the other hand, at the shortwave end, there is no such boundary due to vibrational transitions. Theoretically, however, we could expect there to be, in this region of the spectrum, shortwave boundaries connected with molecular dissociation, separating the several vibrational-rotational absorption spectra from the continuum absorption spectrum. These boundaries are delineated by the wavelengths of photons, whose absorption (associated with the transition from the ground vibrational state to an excited state with quantum numbers taking infinitely large values) causes the water molecule to dissociate, or more precisely, causes first the H–OH bond, then the H–O bond, to break down (see Table 2.1, items 24 and 25). These are waves of length c. 0.28  $\mu\text{m}$  breaking the H–O bond (dissociation energy c. 4.4 eV) and c. 0.24  $\mu\text{m}$  for the H–OH bond (dissociation energy c. 5.11 eV). On the longwave side of these boundaries the absorption spectrum should consist of separate bands, corresponding to the excitation of successively higher vibrational states. On the shortwave side, however, it should be a continuum, inasmuch as there can be no question of any quantized, discrete energy levels being present in such a configuration. Quite simply, the excess energy of the absorbed photon, beyond that required to dissociate a molecule, may be converted into the kinetic energy (of any value) of these dissociated fragments of the molecule.

Theoretically, therefore, we can also expect there to be vibrational-rotational absorption bands due to transitions of the water molecule to very high vibrational energy states, lying not only in the visible region of electromagnetic waves, but also in the ultraviolet. Empirically, however, such absorption bands are not recorded for water. This is very likely because they are of very low intensity, because the probability of energy transitions of the molecule decreases sharply as the energy of the photons increases. Direct photodissociation of the water molecule only by vibrational-rotational excitation, in the absence of electronic excitation, is so very unlikely as to be practically impossible. Being a single-photon process, it is forbidden by the

selection rules for vibrational transitions, which only allow transitions involving a small change in the vibrational quantum numbers. It is also forbidden by the Franck–Condon principle (see, e.g., Barrow (1969) and Haken and Wolf (1995)). Photodissociation is, however, possible as a result of the absorption of high-energy photons, which give rise to transitions between the electronic energy states of the molecule. We return to the problem of photodissociation in Section 2.1.2.

### Harmonic and Combination Transitions Between Excited States

Apart from the aforementioned fundamental vibrational transitions and their overtones and combination transitions from the ground state, whose absorption bands lie in the near-IR and visible regions of the spectrum— $\lambda \leq 6.27 \mu\text{m}$  (i.e., the fundamental band of mode II)—the water molecule can, as a result of vibrational transitions, also absorb radiation of a longer wavelength, in the region of  $\lambda > 6.27 \mu\text{m}$ . The differences in vibrational energy between successive, ever higher vibrational states diminish with the increasing quantum numbers characterizing these states (see, for instance, the successive vibrational energies given in Table 2.2). Therefore, if vibrational transitions, both harmonic and combination, are going to take place solely between excited states, they can be induced not only by photons with energies higher (shorter wavelengths) than those required for transitions from the ground state (because the quantum numbers of ground states are sufficiently low and those of the final states sufficiently high), but also by lower-energy photons (i.e., longer wavelengths;<sup>2</sup> because the quantum numbers of the initial and final states are sufficiently high and the differences  $\Delta v$  sufficiently low).

In practice, however, transitions between excited states are far less probable than fundamental transitions or overtones and combination transitions from the ground state. Hence, the absorption bands due to transitions between excited states are far less intense. This is because under normal illumination conditions (e.g., when the sea is illuminated by daylight) the number of molecules not excited (or in very low states of excitation) far exceeds the number of highly excited molecules. So the probability of “coming across” (and absorbing a photon from) a highly excited molecule is many orders of magnitude lower than that of coming across (and absorbing a photon from) a molecule in the ground or a low excited state.

### Transitions Between the Vibrational States of Different Isotopes of Water

We should also mention that in natural aquatic environments, or other environments containing water in different states of aggregation, in addition to the

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<sup>2</sup> For example, the following simple transitions for the case of mode II:  $(0,1,0) \rightarrow (0,2,0)$ , and  $(0,2,0) \rightarrow (0,3,0)$ , and so on, are due to the absorption of photons of  $6.42 \mu\text{m}$ ,  $6.57 \mu\text{m}$ , and so on, that is, of a longer wavelength than the fundamental band at  $6.27 \mu\text{m}$ .