Molecular Photonics

Kazuyuki Horie, Hideharu Ushiki, Françoise M. Winnik

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Fundamentals and Practical Aspects

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Horie, Kazuyuki (1.3, 1.4, 2, 5)
Department of Chemistry and Biotechnology, Graduate School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Ushiki, Hideharu (Intro., 1.1, 1.2, 4)
Department of Biomechanics and Intelligent Systems, Graduate School of Bio-applications and Systems Engineering, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183-8509, Japan

Winnik, Françoise M. (3)
Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1

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Preface

The relationship between light and humankind has a long history. Light is always given a positive power, while darkness is associated with illness and depression. According to the Bible God created light on the first day. The Big Bang theory also tells us that a burst of photons occurred together with the explosion of the universe. Every aspect of modern natural science points to the fact that all life on earth needs sunlight for survival.

With the advent of the laser in 1960, humankind entered a new age. The world of advanced technologies gradually moved from the age of electronics to that of optoelectronics and photonics. Everyday we encounter new technologies designated by prefixes, such as "photo" and "opto." *Opt*ical discs, *opt*ical communication, *photo*diodes, and *photo*sensors are ubiquitous. Newspapers are produced electronically by processes based on photosensitive polymers. *Photo*resists form the basis in the manufacture of ICs and LSIs. Over the last ten years, the applications of organic compounds have been reevaluated in various microelectronics fields, not only as necessary support materials, such as dielectrics, but also as materials able to play an active role in devices and systems. Liquid crystal displays, for example, are found everywhere. New organic compounds showing interesting and improved electronic and photonic properties are reported almost every day. New light-triggered materials are designed for molecular or bioelectronic devices.

The academic world however lags behind these changes. If someone wants to study the fundamentals of light science, that individual will have to attend lectures in several university departments. Lectures on optics, laser technology, and optoelectronics will have to be taken in physics and engineering physics departments. Photochemistry in contrast is taught only in chemistry and chemical technology departments, usually as part of a course on spectroscopy, physical chemistry, or organic chemistry. Lectures on organic compounds are very rarely offered in departments of physics and electronic technology.

Well aware of this unfortunate situation, two of the present authors (KH and HU) started to discuss a systematic and unified approach to photochemistry, photophysics, and optics.

Based on their experience teaching the organic chemistry of photomaterials and photophysical chemistry (KH), and the quantum theory of light (HU) in the graduate schools of their respective universities, they wrote "The Science of Hikari-functional Molecules" published in Japanese. The third author (FMW) joined the discussion during her stay in Japan and suggested the publication of an English version of the book. She wrote Chapter 3 of the English version, based on the original Japanese text, and contributed to the editing of the complete volume, text and tables.

The study of the interactions of light and materials constitutes one of the fundamental subjects in natural science and technology. In Japanese, a single word, *hikari*, describes all phenomena related to light. In English, two different prefixes are used: "photo-" from the Greek *photos* (light) and "opto-" from the Greek *optos* (seen). Photochemistry and photophysics deal with light-induced changes in materials and in their electronic states, topics studied mostly by chemists. Optics deals with materials-induced changes in the properties of light, a subject developed primarily by physicists. Both aspects of light/materials interactions have gained equal importance in electronics and photonic materials. Their coalescence has led to the relatively new concept of molecular photonics.

The underlying unity which connects all light-induced phenomena is best appreciated if the book is studied entirely and in the order presented. The introductory chapter reviews the historical background and gives a survey of current light-related research fields. In Chapter 1, the fundamentals of molecular photonics are introduced in terms of the principles of optics, the molecular field theory, the radiation field theory, and the interaction between molecular and radiation fields. The importance of a conceptual understanding of the essence of the interaction between light and materials is emphasized throughout this chapter. Chapters 2 and 3 deal with the light-induced changes in materials. The characteristics of photochemical reactions are summarized in Chapter 2, and typical processes of photophysical chemistry such as excitation energy transfer and photoinduced electron transfer are discussed in Chapter 3. Various examples of photofunctional molecules developed by chemists are given in these chapters. Chapters 4 and 5 are dedicated to the study of the materials-induced changes in light, thus far exploited mostly by physicists. Scattering phenomena and the materials-induced changes in light under the application of an electric, magnetic or acoustic field are presented in Chapter 4. The changes in light by light irradiation, namely multiphoton absorption processes, are introduced in Chapter 5, where nonlinear optical phenomena and coherent spectroscopy are discussed. Throughout the book, key concepts are presented in tabular form consisting of drawings, graphs, tables, or formulae describing a given concept. In each section the most important concepts are summarized in an overview table with specific explanation in the text. We believe that such visual summaries of key concepts of an entire section result in a more active understanding of new topics as they appear in the book. These one-page-size tables might be used for transparencies.

The quantum theory of light developed by Einstein in the beginning of the 20th century gave a unified concept to the particle theory and the wave theory of light. However, the successive developments of the science dealing with light-induced changes in materials and the science dealing with materials-induced changes in light evolved to different streams of science. We feel that the advent of the laser has brought us to a new age, where these two separate streams begin to interact with one another and develop nonlinearly. Molecular photonics has become a truly interdisciplinary field, where both streams are intimately interwoven. This volume attempts, as much as possible, to bring a unified approach to the study of light. Because of the breadth of these fields, a detailed description of each subject could not be provided in the space allocated.

The book is written for scientists, engineers, senior students and graduate students interested in light-related sciences, not only in chemistry, but also in physics, electronic technology, and biology. Any comments on the book from the readers are welcome.

The authors wish to express their special thanks to Mr. Ippei Ohta of Kodansha Scientific Inc. for his encouragement and patience, without which this book would never have been published.

Kazuyuki Horie, Hideharu Ushiki, and Françoise M. Winnik

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Tokyo, Japan

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Introduction

The Concept of Molecular Photonics

At the point of nihility without time nor space, an explosion of dense matter marked the origin of the universe. Immediately after this accident, a fireball of radiation at unbelievably high temperature formed in a tiny volume. Many photons were produced by collisions between quarks and anti-quarks. This is the Big Bang theory of the genesis of the universe. It is not unusual for books on the concept of light to begin with a quotation taken from the Bible on the creation of the world. Indeed, the relationship between mankind and light has a long history and it has been strongly connected to all aspects of life, from antiquity to the modern ages. Man has always been careful to distinguish light from heat. Light is always given a much greater importance throughout the ages. Light is a crucial tool in many religions. Men do not speak badly of light. Note for instance that light is used in the Japanese word Goraiko describing the admiration of the sun, while heat is included in an expression describing hell, Shakunetsu-Jigoku, the scorching heat in hell. Hence it comes as no surprise that man has always been fascinated by the multiple properties of light.

This book is dedicated to the study of light, its interactions with matter, and the transformations of matter triggered by light. We have chosen an integrated approach, inspired by a recent trend trying to merge the physical aspects of light, such as wave optics and field theory, and the more chemical concepts, such as photonics and quantum theory. We have not separated from each other the descriptions of the "photo" and "opto" related areas, but rather we have merged them under the single concept of "Molecular Photonics." Rather than trying to answer the question, "What is light?" we will strive here to illustrate how we, as human beings, understand the concept of light. We will often stress that in order to understand a difficult phenomenon or theory, it is not enough to apply one's mind, but that one's entire being should become involved. In other words, one cannot attain an understanding of the essence of certain phenomena by a unique way or a single concept. We urge the reader to receive all the information with an open mind and to view the various topics described as a gathering of many ideas, observations, and conclusions. In natural sciences, research proceeds when scientists become part of the developments as complex unique human beings.

In order to understand the concept of "Molecular Photonics," it is crucial for the reader to undertake a study of fundamental principles. Chapter 1 "Fundamentals of Molecular Photonics" includes four sections dedicated to optics, the molecular field theory, the radiation field theory, and the interactions between the molecular field and the radiation field. Fundamental principles are often treated in an introductory chapter, leading the reader to think that they are of little importance and that they can be understood with ease. This trend of relegating the fundamentals to a brief introduction is getting increasingly common in natural sciences. We do not follow it in this book, since we strongly believe that in order to grasp the fundamental aspects of molecular photonics, many complex abstract concepts need to be understood. Natural sciences have grown over the years by innumerable twists and turns, reflecting the commitments and personality of researchers over many centuries. Some of the difficulties in understanding the fundamental aspects of any science can be alleviated if one uses intuition together with solid reasoning. Intuition is needed to see the relationship between a virtual image, an equation, and a plot of experimental data. We are well aware of the importance of this relationship based on intuition. We explain each fundamental concept of "Molecular Photonics" through tables and figures produced by an original computer system. Unlike many natural sciences books which tend to avoid equations at all cost, we take time here to derive equations. Mathematical equations can be of tremendous help to understand abstract concepts. An equation clarifies the predictions of an entire discussion without any ambiguity. The use of equations is very important to balance the intuitive aspects of the natural sciences. Taking note of the physical meaning of equations, without worrying too much about the mathematical derivations, is a useful first step for the readers not accustomed to use them.

0.1 Light as an Electromagnetic Wave

Modern research on light is based on two apparently irreconcilable observations, on the one hand light behaves as an electromagnetic wave, as demonstrated by Hertz in 1888, and, on the other hand, light has a particulate nature as described by the quantum hypothesis put forward by Einstein in 1905. In this book the study of molecular photonics starts from these two inconsistent concepts. We think that by keeping this contradiction constantly in mind, it will become possible at last to answer the question, "How do we, as human beings, understand the concept of light?" This opinion is not like that of a manager, who will try to solve the inconsistency of two thoughts by adopting forcibly an agreement suggested by an outsider. We believe that final understanding will be achieved when both opinions will be accepted intuitively.

First, following Hertz's view, we will describe light as an electromagnetic wave. Table 0.1 lists typical wavelength and energy values of the electromagnetic waves covering the entire spectral range, from radio waves to γ-Rays. Also given in Table 0.1 are the inventors' names, the physical phenomena, practical emission sources, detectors and research fields associated with each type of electromagnetic wave. The electromagnetic spectrum encompasses the range of typical light, from the near-infra red to the near ultraviolet. Therefore in order to understand the fundamental properties of light, it is mandatory to study electromagnetic waves in general. While the wave-particle dual nature of light is often discussed, hardly anyone ever mentions the wave-particle dual nature of the electromagnetic wave. Light indeed occupies a very special place in our lives. We experience it every day, such that, intuitively, we already understand many of its properties.

The dual nature of light has several unexpected consequences and it has important implications in the study of the interactions of matter with light. We can discuss at length the behavior of light as an electromagnetic wave, what really matters, however, is how light interacts with molecules and atoms, the basic building blocks of matter. The light-induced electronic transitions in a molecule must be viewed in this context. In contemporary science,

Table 0.1 Spectral Map of Electromagnetic Wave

Electromagnetic Wave

Fr	300kHz	3MHz	30MHz	300MHz	3GHz	30GHz	300GHz	3THz	30THz	300THz	3PHz	30PHz	300PHz	3EHz	30EHz
W.L.	1km	100m	10m	1m	10cm	1cm	1mm	100 μm	10 μm	1 μm	100nm	10nm	1nm	1 Å	0.1 Å
cm^{-1}					0.1	1	10	100	1000	10000					
Energy	1.24neV	12.4neV	124neV	1.24 μ eV	124 μ eV	124 μ eV	1.24meV	12.4meV	124meV	1.24eV	12.4eV	124eV	1.24keV	12.4keV	124keV
	120 μ J	1.2mJ	12mJ	120mJ	1.2J	12J	120J	1.2kJ	12kJ	120kJ	1.2MJ	12MJ	120MJ	1.2GJ	12GJ
	28.8 μ cal	286 μ cal	2.86mcal	28.6mcal	286mcal	2.86cal	28.6cal	286cal	2.86kcal	28.6kcal	286kcal	2.86Mcal	28.6Mcal	286Mcal	2.86Gcal
Temperature	14.4 μ K	144 μ K	1.44mK	14.4mK	144mK	1.44K	14.4K	144K	1.44kK	14.4kK	144kK	1.44MK	14.4MK	144MK	1.44GK

Wave Name	Radio Wave (LF) (MF) (HF) (VHF) (UHF) (SHF) / Microwave (EHF) / Infrared Radiation: Far IR, Near IR / V.L. / Ultraviolet Radiation: Near UV, Vacuum UV / X-Rays: Soft X-ray, Hard X-ray / γ-Rays
Discoverer	H.R.Hertz (1888) / F.W.Herschel (1800) / Newton / J.W.Ritter (1801) / W.C.Röntgen (1895) / A.H.Becquerel (1896)
Phenomena	motion of electron or atomic nucleus in electromagnetic field / molecular rotation vibration / electronic transition / electronic transition of inner orbital / nuclear reaction
Emission Source	LC circuit / magnetron / klystron / maser / heat-source / mercury lamp / laser / discharge tube / synchrotron orbital radiation / nuclear decay
Detector	antenna and detector / radio telescope / thermocouple / photocell / photomultiplier tube / fluorometer / photograph / Geiger-Müller tube / scintillator
Use	communication / radio / television / radar / microwave communication / aeroradar / HF-heating / IR-photography / heat-source / photoreation / lighting / material analysis / material structure analysis
Field	electrical and electronic engineering / astrophysics / molecular structure / molecular chemistry and physics / photo-reaction / structure analysis / high-energy physics

this idea resulted in the birth of a new discipline dedicated to the study of "the interaction of the radiation field with the molecular field." Central to this study is Equation (0.1) based on perturbation theory:

$$\boldsymbol{H} = \boldsymbol{H}_{\mathrm{R}} + \boldsymbol{H}_{\mathrm{M}} + \boldsymbol{H}_{\mathrm{I}} \tag{0.1}$$

where $\boldsymbol{H}$, $\boldsymbol{H}_{\mathrm{R}}$, $\boldsymbol{H}_{\mathrm{M}}$, and $\boldsymbol{H}_{\mathrm{I}}$ are the Hamiltonian operators for the total radiation, the radiation field, the molecular field, and the interaction of the radiation field with the molecular field, respectively. The $\boldsymbol{H}_{\mathrm{I}}$ term is central to the study of the interaction of the radiation field with the molecular field, but one needs to understand also the $\boldsymbol{H}_{\mathrm{M}}$ and $\boldsymbol{H}_{\mathrm{R}}$ terms, in order to extract the $\boldsymbol{H}_{\mathrm{I}}$ term. Chapter 1 deals with the fundamentals of optics and photonics in terms of the three operators, $\boldsymbol{H}_{\mathrm{R}}$, $\boldsymbol{H}_{\mathrm{M}}$, and $\boldsymbol{H}_{\mathrm{I}}$.

0.2 The Study of Optics and Photochemical Effects: a Historical Perspective

Historical perspectives are very important in a course of natural science. One becomes aware of facts rarely presented in a general history course. How was a discovery made? What was the purpose of a specific experiment? What was the researcher trying to achieve in the general scientific context of his time? Trends can be uncovered, which lead from one discovery to the next. We will see then that science is not a gathering of two-dimensional information but, rather, a dynamic human drama in a four-dimensional space.

Table 0.2 presents a summary of the history of modern research in light. In this table we present modern developments in light research from the fundamentals of optics (17th century), to the electromagnetic field, the molecular field, the radiation field, the interaction of the radiation field and the molecular field, leading finally to "Molecular Photonics," as we know it today. The understanding of light-induced phenomena grew through the controversy between the wave and particle theories, the formulation of Maxwell's electromagnetic theory, the measurement of the speed of light, the development of the spectral measurement method, the formulation of the quantum theory, the discovery of the laser, *etc.*

The dawn of modern research in light can be traced to the early 17th century, with the discovery of the telescope. Thereafter optics developed rapidly. Merging of research in optics and electrostatics resulted in the classical electromagnetic theory, culminating in the formulation of Maxwell's electromagnetic theory. In 1888 Hertz discovered the electromagnetic wave and declared victory for the wave theory of light. These major events define the first period in modern light research. At the same time, however, a new technique, the spectral measurement method based on the flame reaction, was gathering momentum in research, leading to the establishment of the periodic table. The new method gave a fatal blow to the wave theory of light. It coincided with the birth of the quantum theory which took over in the 20th century. Therefore, during this first period the historical flow took many twists and turns, torn in two different directions, by the quantum theory and the wave theory. The wave theory became quantum electrodynamics, *via* the discoveries of the microwaves, VHF, and UHF, leading to the creation of the laser from the maser. This line of progress yielded the concept of field based on wave optics. A second line, closely linked to the quantum theory, resulted in molecular spectroscopy and excited-state chemistry, and the creation of various

Table 0.2 Historical Chart of Modern Light Research

	Classification of Age	Optics	Radiation Field	Molecular Field
		Invention of the telescope		
		The law of refraction		
17th	Age of Optics	The law of diffraction		
Century		Discovery of the spectral principle and birefringence	Research in static electricity	
		Controversy between wave and particle theories for light		
18th	Age of Static Electricity		Research of conductor	
			Discovery of the electric charge	
		Achromatic condition		
Century				Law of light absorption
			Coulomb's law	
	Age of Electromagnetics			
		Interference of light	Discovery of IR and UV	
		Discovery of polarization		
		Measurement of light wavelength	Ampere's law	Measurement of spectra
19th			Biot-Savart law	
	Age of Spectroscopic Methods		Faraday's law of induction	Stokes' law
Century				Spectroscopic method
		Measurement of light velocity	Derivation of Maxwell's equations	Equation of spectral lines
		Discovery of optical rotatory dispersion	Discovery of electromagnetic wave	Zeeman effect
				Photoelectric effect
	Age of the Old Quantum Theory	Discovery of magnetic birefringence	Invention of the wireless	Quantum and light quantum theory
			X-ray diffraction	Bohr's theory of atom
	Age of Electromagnetic Wave Spectra		Discovery of the ultrashort wave	
20th	Age of Molecular Spectroscopy		Discovery of meter wave	Establishment of wave mechanics
			Radiotelescope	
Century			Invention of the maser	Discovery of Raman effect
			Invention of the laser	Energy transfer
	Age of the Laser		Development of nonlinear optics by laser	Excimer Emission
			Discovery of the quantum Hole effect	Establishment of organic photochemistry

instrumental analytical techniques, *via* the explanation of the atomic and molecular structures. This historical flow from the appearance of the quantum theory to that of the laser can be classified as the second age in modern light research. Recently, the merging of these two separate lines which led to the discovery of the laser has opened the third period in modern research, considered by many as "light's golden age."

0.3 Recognition of Photo- and Opto-Related Areas

In this chapter we will attempt to uncover the events, in recent history, that led to the formulation of the concept of "Molecular Photonics." What are the research areas supported by the concept of "Molecular Photonics?" What are the relationships between the fundamental fields described previously and "Molecular Photonics?" These questions need to be answered. We will draw a picture of "Molecular Photonics" starting form several related fields (see Table 0.3).

The interaction of the radiation field with the molecular field has two aspects: "the change of the medium by light" and "the change of light by the medium." Traditionally, the former is included in the chemistry curriculum while the latter is part of the physics curriculum. The rationale behind this separation remains unclear. The light-induced transformations of a medium are of two types, photochemical reactions following the rules of organic chemistry, and photophysical processes based on quantum chemistry, chemical kinetics, and molecular spectroscopy. The interactions describing the change of light by the medium are divided further into effects related to electrodynamics, quantum mechanics, and statistical mechanics. We propose then that "Molecular Photonics" is the main concept which includes all light-related research and, consequently, we have adopted in this book the following approach. First we describe fundamental concepts of optics (Section 1.1), the molecular field theory (Section 1.2), and the radiation field theory (Section 1.3). The concept of "Molecular Photonics" emerges naturally, as the meeting point of these fundamental concepts in modern research of light.

The interactions of the radiation field with the molecular field are often compared with heat-induced phenomena. Thermal energy is supplied gradually to a system, in contrast, light as an energy pack gives a large amount of energy (a photon) to a molecular system in a short time. According to Table 0.1, a molecule can gain large energy, about 100,000 K in temperature scale in a flash lasting no more than 10^{-15} s. Heat- and light-induced phenomena are as different from each other as the live of a middle class worker and that of a gambler who has won the jackpot! We all appreciate how human behavior of the rich differs from that of the middle class. One molecule gradually wastes the energy obtained by heat. The molecule struck by light immediately changes its personality. Moreover the behavior of these molecules depends on these environments. The light-induced phenomena reproduce daily events in human society on the microscopic scale.

Science philosophers often argue about the relative merits of the analytical and synthetic approaches to scientific research. A synthetic viewpoint cannot be created without analysis, and conversely, the systemization and development of a theory necessitates analysis. Analysis is a scientific tool or method which becomes meaningful only if it derives from a synthetic view of phenomena probed by experiments. The proposed new concept of "Molecular Photonics" cannot escape this methodology. It may be seen as a dogma at first. But through

Table 0.3 Classification of Modern Light Research and Interaction between the Radiation Field and the Molecular Field

	Fundamentals and Background of Molecular Photonics
Change of the Medium by Light	Molecular Field Theory: Old Quantum Theory, Atom and Molecule, Hybridized Orbital, Molecule with π-electron, Molecular Orbital Method
	Organic Chemistry
	Chemical Kinetics
	Molecular Spectroscopy
Change of Light by the Medium	Radiation Field Theory: Maxwell's Equation, Canonical Equation of Radiation Field, Quantization of Harmonic Oscillator, Quantization of Radiation Field
	Fundamentals of Optics: Refraction, Reflection, Interference, Diffraction, Polarization
	Quantum Mechanics
	Quantum Statistical Mechanics

First Classification	Second Classification	Various Phenomena	
Photochemical Reactions (Chapter 2)	(n, π^*) Transition; (π, π^*) Transition	Photocycloaddition Reactions, Photoisomerization, Electrocyclic and Photofragmentation Reactions, etc.	Chemistry Curriculum
Photophysical Processes (Chapter 3)	Intramolecular Processes	Absorption, Emission, Internal Coversion, Intersystem Crossing, Deactivation, etc.	Chemistry Curriculum
	Intermolecular Processes	Excimer, Exciplex, Energy Transfer, Electron Transfer,etc.	Chemistry Curriculum
Optical Effects by Outer Perturbation (Chapter 4)	Light Scattering	Rayleigh Scattering, Raman Scattering, Brillouin Scattering, etc.	
	Electrooptical Effects	Pockels Effect, Kerr Effect, Electrooptical Effect in Liquid Crystals,	Curriculum
	Magnetooptical Effects	Zeeman Effect, Faraday Effect, Voigt Effect, etc.	Curriculum
	Sonooptical Effects	Bragg Reflection, Raman-Nath Diffraction, etc.	
Optical Effects by Inner Perturbation (Light) (Chapter 5)	Saturated Absorption and Multi-photon Absorption	Optical Bistability, Lamb Dips, Hole Burning, Frequency Transformation, etc.	Physics
	Coherent Spectroscopy	CARS, RIKES, FWN, etc.	Physics
	Time-resolved Coherent Spectroscopy	Photon Echoes, Stimulated Photon Echo, etc.	

its many twists and turns between analysis and synthesis, the search for understanding becomes pleasurable and full of unsuspected discoveries. It is not a monotonous journey. It changes course abruptly as soon as a conclusion has been reached, implying, maybe, that real human beings are the driving force behind the progresses of the natural sciences.