INTRODUCTION TO NONLINEAR OPTICAL EFFECTS IN MOLECULES AND POLYMERS

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PREFACE

Nonlinear optics is a new frontier of science and technology that is to play a major role in the emerging technology of photonics. Photonics, which uses photons for information and image processing, has been labeled the technology of the 21st century, for which nonlinear optical processes provide the key functions of frequency conversion and optical switching. Molecular materials and polymeric systems have emerged in recent years as a new class of promising nonlinear optical materials because they offer the flexibility, both at the molecular and bulk levels, to optimize the nonlinearity and other required properties for device applications. This is a multidisciplinary area, the progress of which depends on active participation from chemists, physicists, material scientists, and engineers. Although several texts on nonlinear optics itself as well as several review books on nonlinear optical effects in organic and polymeric systems exist, there is no monograph or textbook dealing with nonlinear optics of molecules and polymers. Since the interest in this area is growing worldwide, a monograph dealing with this subject and addressing issues specific to molecular and polymeric materials will be of great value to newcomers to the field. It can also be used as a reference book by researchers of varied backgrounds. We hope that this book will be such a monograph for multidisciplinary readership. We have emphasized concepts and avoided mathematical rigor so as to provide useful conceptual information to readers outside the areas of their expertise.

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1

INTRODUCTION

1.1 NONLINEAR OPTICS AND PHOTONICS

Nonlinear optics is expected to play a major role in the technology of photonics. Photonics is emerging as a multidiciplinary new frontier of science and technology that is capturing the imagination of scientists and engineers worldwide because of its potential applications to many areas of present and future information and image processing technologies. Photonics is the analog of electronics in that it describes the technology in which photons instead of electrons are used to acquire, store, transmit, and process information. Examples of nonlinear optical phenomena that are potentially useful in this context are the ability to alter the frequency or color of light and to amplify one source of light with another, switch it, or alter its transmission characteristics through a medium, depending on its intensity. It is the potential for providing these functions in suitable materials and devices that motivates much of the current fundamental and exploratory research in the field of nonlinear optics.

With the advent of lasers, which provide a source of high-intensity coherent light, much progress has been made in the field of nonlinear optics. The strong oscillating electric field of the laser beam creates a polarization response that is nonlinear in character and that can act as a source of new optical fields with altered properties. Among the nonlinear optical processes that have been studied, one of the most visually dramatic is frequency doubling. In the field of optical information storage this process can provide for the conversion of near-infrared laser light from diode lasers into deep blue light. Since the size of a focused spot of light is inversely proportional to its wavelength, second-harmonic generation can increase the capacity of stored information on optical disks immensely. Using related phenomena, one can also build devices, such as frequency mixers, that can act as new light sources or as amplification schemes, light modulators for controlling the phase or amplitude of a light beam, optical switches, optical logic, optical information storage, optical limiters, and numerous ways of processing the information content of data or images.

Optical processing of information and optical computing is one of the most appealing applications of photonics. Major potential advantages are a gain in speed in certain types of switching functions and the reconfigurable connectivity of light sources and detectors with little interference or cross-talk between adjacent channels. Photonic switching can take place with femtosecond speeds, thus providing a gain in speed that is many orders of magnitude over that of electronic processes. Working at optical frequencies provides a tremendous gain in the bandwidth of information processing. Optical processing functions are generally free from interference from electrical or magnetic sources. On the other hand, the weak interactions of optical fields with each other has necessitated the development of materials where in these interactions can be maximized, thus the need for considerable new fundamental understanding of the interaction of light with matter. Based on the prospect of three-dimensional interconnectivity between sources and receptors of light, concepts of optical neural networks that mimic the fuzzy algorithms by which learning takes place in the brain have been proposed and experimentation has begun. Integrated optical circuits, which are counterparts of electric circuits but where optical fibers or channels in waveguides conduct photons, can provide for various logic, memory, and multiplexing operations. Utilizing nonlinear optical effects, analogs of transistors or optical bistable devices with which light controls light have also been demonstrated.

Apart from the field of photonics there are other potentially interesting and important applications of nonlinear optics. Among these are the use of light intensity-dependent transmission properties of materials that might serve useful functions as eye or optoelectronic sensor protection from unwanted or stray sources of laser radiation. Here the medium would become nontransparent at some critical light intensity. Nonlinear optical processes are highly sensitive to many of the microstructural aspects or interfacial characteristics of the medium that exhibits the effect. They may, therefore, be suitable for sensor applications to probe structural relaxations in materials, chemical stimuli of various sorts, pressure, temperature, electric fields, and so on.

1.2 NONLINEAR OPTICAL MATERIALS

Basically, all materials exhibit nonlinear optical phenomena. This includes all forms of matter—gases, liquids, and solids. The power of the optical fields required to observe these effects varies over many orders of magnitude, depending on the detailed nature of the electronic structure of the atomic and molecular constituents of the medium, their dynamical behavior, as well as the symmetry and details of their geometrical arrangement in the medium. The important nonlinear optical materials from the device point of view are generally in solid formats and must meet a wide variety of ancillary material requirements for practical use. In general, they will require extraordinary stability with respect to ambient conditions and high-intensity light sources. They will have to meet many processing requirements for pattern or shape definition, and integration with additional dissimilar materials.

Before the major research issues in the development of new materials for nonlinear optics are discussed, several distinctions and features of materials for application in the field are commented on. The first type, molecular materials, consists of chemically bonded molecular units that interact in the bulk through weak van der Waals interactions. Many organic crystals and polymers typify this class of materials. For these materials the optical nonlinearity is primarily derived from the molecular structure. The expression of the nonlinearity is highly dependent on the geometrical arrangement of the molecules in the condensed medium in the case of second-order nonlinear processes, but much less so for third-order nonlinearities. One can define microscopic nonlinear coefficients (molecular hyperpolarizabilities) that are the molecular equivalents of bulk nonlinear optical susceptibilities. In fact, the bulk susceptibility can be readily related to the susceptibilities of the constituent molecules. The primary step in optimizing optical nonlinearities in this class of materials is at the molecular structural level, which then requires a detailed understanding of the relationship between molecular electronic structure and the nonlinear polarization that can be induced in a molecule. The molecular engineering issues of how to arrange molecules in solids encompass areas of chemistry, polymer science, and materials science.

The second major class of materials is bulk materials. Nonlinearities in these materials are thought of as arising from electrons not associated with individual nucleii, such as those in metals and semiconductors. The optical nonlinearity in this class is determined by the electronic characteristics of the bulk medium and thus requires different theoretical frameworks to account for the origins of nonlinear optical effects. Examples of materials in this category are quantum well structures derived from GaAs and II–VI semiconductors such as CdSe. Inorganic crystals, such as potassium dihydrogen phosphate (KTP) and potassium titanyl phosphate (KTP), are also regarded as bulk materials because no single molecular unit in the ionic lattice can be identified. However, in the systems the nonlinear responses are undoubtedly related to individual bond polarizabilities.

Compared to the more traditional inorganic nonlinear optical materials, the history of organic (or, in general, molecular) nonlinear optical materials is quite new. Although this book refers to one class of molecular materials, namely organic systems, most concepts and discussions are applicable to inorganic and organometallic molecular materials as well. Organic and other molecular materials are increasingly being recognized as the materials of the future because their molecular nature combined with the versatility of synthetic chemistry can be used to alter and optimize molecular structure to maximize nonlinear responses and other properties. Other benefits associated with molecular systems derive from the fabrication methods that are available or under development for building thin-film structures. These and other perceived benefits of organic materials are summarized in the following paragraphs.

Organic structures can be grown into thin crystalline layers, fabricated into structures that can be deposited into thin films layer by layer as in the Langmuir–Blodgett technique, or incorporated into polymers for deposition and processing as highly oriented thin-film structures. The resulting structures can exhibit optimized orientations for many types of nonlinear behavior, especially those of interest for waveguide formats.

Many organic materials, especially high-performance polymers, have high mechanical strength as well as excellent environmental and thermal stability. Recent developments have produced materials with thermal stabilities in excess of 350 °C. In contrast to misconceptions about the fraility of organic materials, the optical damage threshold for polymeric materials can easily be $>10\,GW/cm^2$ with picosecond pulses. In contrast, multiple-quantum well structures derived from GaAs will undergo optical damage at power densities many orders of magnitude lower.

Because of their unique chemical structures (π bonding), organic molecular materials exhibit the largest nonresonant (nonabsorptive) optical nonlinearities. For inorganic systems, important higher-order nonlinear optical effects (for example, third-order) are resonant (absorptive). Thus, heat dissipation tends to limit the cycle time of devices derived from these materials. For many device applications, such as in all-optical signal processing, the nonlinear optical response time is an important consideration. A nonresonant electronic optical nonlinearity, by its nature, would have the fastest response time, limited only by the width of the driving laser pulse. With current laser technology, femtosecond responses can be achieved and have, in fact, been demonstrated in organic polymers. In contrast, resonant optical nonlinearities have response times limited by the lifetime of the excitation. Other disadvantages associated with resonant optical nonlinearities are beam depletion due to absorption and thermal damage. Further complications arise from thermally induced nonlinearities associated with refractive index changes, which often can dominate the intrinsic electronic optical nonlinearity.

The dielectric constants of organic materials are considerably lower than those of inorganic crystals. This feature has important implications for electrooptic devices in which a low-frequency ac field is used to modulate the refractive index. The low dielectric constant yields a low RC time constant, thus permitting a large operating bandwidth ($>10\,GHz$) modulation. Furthermore, for organic materials the dielectric constants at low frequency are comparable to those at optical frequencies, which leads to minimization of phase mismatch between electrical and optical pulses in high-speed traveling wave devices.

From the above discussion of relative merits, it is clear that organic nonlinear optical materials are promising group of materials. This has provided the rationale for the present monograph which focuses on nonlinear optical effects in organic molecules and polymers.

1.3 BASIC RESEARCH OPPORTUNITIES

Although potential technological opportunities have provided the main impetus for the development of this field, the interest is not solely technological. This field offers challenging opportunities for fundamental research. The challenges are multidisciplinary, ranging from a basic understanding of physics of nonlinear optical interactions to molecular engineering and chemical synthesis of novel organic structures with enhanced optical nonlinearities. As we discuss in this monograph, a basic understanding of the relationship between molecular structure and microscopic optical nonlinearity is still very limited and must be sufficiently developed before we can take full advantage of the tailorability of molecular structures to enhance optical nonlinearity. Once the optical nonlinearity is maximized at the molecular structure level, the question that follows is how it transforms into bulk optical nonlinearity. Therefore, the relation between microscopic and bulk optical nonlinearities is also of fundamental importance. The relevant issues are the roles of (1) the intermolecular interaction and its importance in determining the local fields, (2) bulk excitations, (3) intermolecular charge transfer, and (4) molecular orientation effects. Although certain approximations (such as Lorentz approximation for the local electric field derived from an optical pulse) are widely used, their validity is far from conclusively established.

The effects of the dynamics of excitations and various excited-state resonances on optical nonlinearities of organic systems are not well explored. For inorganic semiconductors, it is well established that in many cases photogenerated or dopant-induced charge carriers have profound effects on nonlinear optical behavior. The role of excitation and the effect of various quantum confinements have been widely studied in inorganic semiconductors. In comparison, these types of studies are highly limited for organic systems. Organic polymers have shown that with appropriate structural features they generate novel types of excitations, such as solitons, polarons, and bipolarons. The role of these new excitations in influencing optical nonlinearities is another area of basic research opportunities.

1.4 MULTIDISCIPLINARY RESEARCH

The field of nonlinear optical effects in organic and polymer systems is truly a multidisciplinary one in which scientists and engineers of varied backgrounds from university and industrial environments can interface their expertise for its expeditious development.

The input from quantum theorists and physicists can significantly contribute to the understanding of nonlinear optical processes. Synthetic chemists can contribute significantly to the understanding of structure–property relationships by providing sequentially built and systematically derivatized structures. Measurements of optical nonlinearities on these varied structures provide a testing ground for theoretical models. The efforts of synthetic chemistry can lead to new molecular and polymeric structures to enrich the knowledge base, which currently is rather limited. The participation of polymer and material scientists and engineers is just as important. They can contribute by developing new molecular composite materials, designing processing schemes to improve optical quality, properly characterizing the bulk structures of the materials, and fabricating various device structures. Fabrication of optical quality films and fibers is an area of great need because organic systems tend to exhibit significant light scattering. Input from experimentalists and laser spectroscopists in measurement of nonlinear optical effects and study of excited-state dynamics is also needed. Important input for device processes involves the study of nonlinear optical processes in optical waveguides. Therefore, active participation of optical physicists and electrical engineers is essential. A strong input from device engineers is necessary to implement the device concepts in systems. Finally, it is clear that the most effective approach to help bring this field to maturity relatively quickly will require cross-talk and interactive feedback between participants of various backgrounds. This mode of interaction requires each group to be aware of the relevant issues outside its own area of expertise.

1.5 SCOPE OF THIS BOOK

This book is written with the objective of multidisciplinary appeal. Consequently, mathematical rigors are avoided and the focus is more on conceptual details. There are many excellent books that focus on the theory of nonlinear optical effects and we have left the detailed theoretical formulations to these works. Although several books containing expert reviews in the area of nonlinear optical effects in organic molecules and polymers exist by now, there is still a void as far as a monograph on this topic is concerned. The need for such a book became more apparent when one of the authors (PNP) was invited to offer a tutorial course on this topic at a meeting of the SPIE (the international society for optical engineers). The idea of writing a book in this field was conceived while teaching this course for several years at various SPIE meetings. The composition of the registrants for this tutorial course has been multidisciplinary and over the years participants have constantly emphasized the need for a comprehensive and multidisciplinary monograph in this field. We have written this book with the objective that it would serve as a valuable guide to researchers working in this area in two ways: (1) by providing them with useful information in the areas outside their expertise and (2) by serving as a useful reference book. Since this area is experiencing a continuous rapid expansion, the book will be useful to newcomers who would like to build a working knowledge of this field in a relatively short time. It is our hope that the book can also be used for advanced level courses at universities and tutorial courses at various professional society meetings.

We begin by providing a brief background in the theory of nonlinear optical phenomena (Chapter 2), keeping in mind that the subject should also be readable to synthetic chemists, materials scientists, and engineers who may not be well versed in electromagnetic theory. Consequently, the concepts are developed using minimal mathematical detail. In Chapter 3 the theory of nonlinear optical effects in organic structures is developed, where the uniqueness of bonding in these structures and its manifestations in microscopic optical nonlinearities are discussed. The concepts of σ and π bonding in organic systems are briefly discussed to provide background for those who may not be familiar with them.

In Chapters 4 and 5 the various second-order nonlinear optical processes and the chemical and bulk structures required for observing these processes are discussed. These chapters should provide some synthetic guidance to chemists and suggest material issues to material scientists and engineers. Descriptions of various measurement techniques follow in Chapter 6. Experimental details are provided, as well as a discussion of the relative merits of each method and care needed in interpretation of the measurements. These discussions should be helpful to those interested in setting up a laboratory for experimental measurements of optical nonlinearities in organic structures. Chapter 7 provides a survey of data on second-order optical nonlinearities of various organic molecules and polymers. We list for various organic structures studied, the measurement technique, the nonlinear optical coefficients, and the nature of the bulk phase in which the measurement is made. In addition to providing the data in tabular forms, we discuss some specific molecules and polymers that have received increased attention. The same sequence of topics is followed in the subsequent chapters (Chapters 8–10) dealing with third-order nonlinearities. These surveys and discussions, we hope, will serve as a useful reference for researchers in this field.

The final topics discussed are related to device structures. A review of nonlinear optical processes in optical waveguides is provided in Chapter 11, as well as a discussion of relevant materials issues. Chapter 12 deals with some specific device structures to give a flavor of various applications of nonlinear optical phenomena in organic systems. Again, in addition to a discussion of device structure and device process, the material requirements are addressed. The objective is a multidisciplinary appeal so that these device-related chapters are useful not only for device scientists and engineers, but also for chemists and material scientists by giving them a qualitative feel for this topic and an awareness of materials requirement. We conclude with a discussion of the current status of this field and future directions of research (Chapter 13). This discussion is somewhat subjective and reflects our opinions based on participation in many international conferences, symposia, and workshops in this area.