# Second-Order Nonlinear Optical Characterization Techniques An Introduction

## Thierry Verbiest Koen Clays Vincent Rodriguez



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### Contents

Pref	face	ix
The	Authors	xiii
<b>C</b> 1		
Cha	pter 1 General aspects of second-order nonlinear optics	1
1.1	Linear optical phenomena	1
	1.1.1 Interaction of light with matter	1
	1.1.2 Wave propagation in optical media	3
	1.1.3 Tensor properties of polarizability and susceptibility	7
1.2	Nonlinear optical phenomena	8
1.3	Examples of nonlinear optical phenomena	9
1.4	Symmetries in second-order nonlinear optics	. 11
1.5	Second-order polarizabilities and susceptibilities	. 21
1.6	Beyond the electric-dipole approximation	. 24
Refe	erences	. 26
Cha	pter 2 Determination of molecular symmetry	
	with hyper-Rayleigh scattering	. 27
2.1	Hyper-Rayleigh scattering: General principles	. 27
2.2	Experimental techniques and equipment	. 34
2.3	Determination of molecular symmetries	. 41
2.4	Switching the first hyperpolarizability at the molecular level	. 48
2.5	Probing aggregation and supramolecular structure in solution	. 53
2.5 Refe	Probing aggregation and supramolecular structure in solution	. 53 . 59
2.5 Refe	Probing aggregation and supramolecular structure in solution	. 53 . 59
2.5 Refe <b>Cha</b>	Probing aggregation and supramolecular structure in solution erences	. 53 . 59
2.5 Refe <b>Cha</b>	Probing aggregation and supramolecular structure in solution erences opter 3 Characterization of interfaces, surfaces, and thin films	. 53 . 59 <b>. 63</b>
2.5 Refe <b>Cha</b> 3.1	Probing aggregation and supramolecular structure in solution erences pter 3 Characterization of interfaces, surfaces, and thin films Second-harmonic generation and sum-frequency generation	. 53 . 59 <b>. 63</b>
<ul><li>2.5</li><li>Refe</li><li>Cha</li><li>3.1</li></ul>	Probing aggregation and supramolecular structure in solution erences pter 3 Characterization of interfaces, surfaces, and thin films Second-harmonic generation and sum-frequency generation from surfaces: General principles	. 53 . 59 . 63
2.5 Refe <b>Cha</b> 3.1	Probing aggregation and supramolecular structure in solution erences pter 3 Characterization of interfaces, surfaces, and thin films Second-harmonic generation and sum-frequency generation from surfaces: General principles	. 53 . 59 . 63 . 63

3.2	Exper	imental techniques and equipment	75
	3.2.1	Absolute and relative measurements	75
	3.2.2	Maker fringe technique	76
3.3	Probin	ng the symmetry of interfaces, surfaces, and thin films	80
	3.3.1	Interpreting Maker fringe patterns	80
	3.3.2	Oxide photonic glasses	81
		3.3.2.1 Induction of SONL properties in oxide glasses.	82
		3.3.2.2 Thickness and profile effect of the NLO layer	
		in poled oxide glasses	86
	3.3.3	Organic- and polymer-oriented materials	89
		3.3.3.1 Langmuir–Blodgett (LB) films	91
		3.3.3.2 Poled organic polymer films	93
3.4	Molec	ular orientation at surfaces	96
	3.4.1	Relationship between bulk response and molecular	
		response	96
	3.4.2	Application to an uniaxial polar interface	101
		3.4.2.1 Experimental ODF-based approach	101
		3.4.2.2 Mean-field potential approach: The	
		liquid-oriented model	107
3.5	Surfac	e adsorption and surface reactions	108
Refe	rences.	*	112
Cha	pter 4	Characterization of surface chirality	
Chaj	pter 4	Characterization of surface chirality by second-harmonic generation and	
Cha	pter 4	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115
Cha <sub>j</sub> 4.1	pter 4 Chira	Characterization of surface chirality by second-harmonic generation and sum-frequency generation lity and second-order nonlinear optics:	115
Cha 4.1	pter 4 Chira genera	Characterization of surface chirality by second-harmonic generation and sum-frequency generation lity and second-order nonlinear optics: al principles	<b>115</b> 115
Chay 4.1	pter 4 Chira genera 4.1.1	Characterization of surface chirality by second-harmonic generation and sum-frequency generation lity and second-order nonlinear optics: al principles Chirality and optical activity	<b>115</b> 115 115
<b>Cha</b> 4.1	pter 4 Chira genera 4.1.1 4.1.2	Characterization of surface chirality by second-harmonic generation and sum-frequency generation lity and second-order nonlinear optics: al principles Chirality and optical activity Nonlinear optical activity in second-harmonic	<b>115</b> 115 115
<b>Cha</b> 4.1	pter 4 Chira genera 4.1.1 4.1.2	Characterization of surface chirality by second-harmonic generation and sum-frequency generation lity and second-order nonlinear optics: al principles Chirality and optical activity Nonlinear optical activity in second-harmonic generation	<b>115</b> 115 115 119
Char 4.1	pter 4 Chira genera 4.1.1 4.1.2 4.1.3	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	<b>115</b> 115 115 119
Cha 4.1	pter 4 Chira genera 4.1.1 4.1.2 4.1.3	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	<b>115</b> 115 115 119 126
Chaj	pter 4 Chira genera 4.1.1 4.1.2 4.1.3 4.1.4	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	<b>115</b> 115 115 119 126 128
<b>Cha</b> 4.1	pter 4 Chira genera 4.1.1 4.1.2 4.1.3 4.1.4	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	<b>115</b> 115 115 119 126 128
<b>Cha</b> 4.1	pter 4 Chiral genera 4.1.1 4.1.2 4.1.3 4.1.4	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	<b>115</b> 115 119 126 128 132
Cha <sub>j</sub>	pter 4 Chira genera 4.1.1 4.1.2 4.1.3 4.1.4	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115 115 115 119 126 128 132 133
<b>Cha</b> ;	pter 4 Chira genera 4.1.1 4.1.2 4.1.3 4.1.4 4.1.4	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115 115 115 119 126 128 128 132 133 135
<b>Cha</b> 4.1 4.2	pter 4 Chiral genera 4.1.1 4.1.2 4.1.3 4.1.4 4.1.5 Exper	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115 115 115 119 126 128 132 133 135 136
<b>Cha</b> 4.1 4.2	pter 4 Chira genera 4.1.1 4.1.2 4.1.3 4.1.4 4.1.5 Exper 4.2.1	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115 115 115 119 126 128 132 133 135 136 136
<b>Cha</b> 4.1 4.2	pter 4 Chira genera 4.1.1 4.1.2 4.1.3 4.1.4 4.1.5 Exper 4.2.1 4.2.2	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115 115 115 119 126 128 128 132 133 135 136 136 140
Cha 4.1 4.2	pter 4 Chirai genera 4.1.1 4.1.2 4.1.3 4.1.4 4.1.5 Exper 4.2.1 4.2.2 4.2.3	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115 115 115 119 126 128 132 133 135 136 136 140 140
Cha; 4.1 4.2 4.3	pter 4 Chiral genera 4.1.1 4.1.2 4.1.3 4.1.4 4.1.5 Exper 4.2.1 4.2.2 4.2.3 Secon	Characterization of surface chirality by second-harmonic generation and sum-frequency generation	115 115 115 119 126 128 128 133 135 136 136 140 140 141

4.5	Molec	ular origin	144
4.6	Relati	on with the Faraday effect	
Refe	rences.		147
Chaj	pter 5	Second-order nonlinear optical imaging techniqu	ıes 149
5.1	Gener	al principles	149
	5.1.1	Introduction to nonlinear imaging techniques	149
	5.1.2	Basics of microscopy: Gaussian beam optics	151
	5.1.3	Confocal microscopy	155
5.2	Exper	imental techniques and equipment	158
	5.2.1	Two-photon excited fluorescence imaging	158
	5.2.2	Two-photon excited second-harmonic generation	
		imaging	161
5.3	Appli	cations	
Refe	rences.		166
App	endix.		169

Index 173
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## Preface

This book focuses on characterization techniques that are based on secondorder nonlinear optical processes. Examples of second-order nonlinear optical processes include the linear electro-optic (or Pockels) effect and harmonic generation processes such as second-harmonic generation (SHG) and sum- and difference-frequency generation (SFG and DFG). The first effect has been used mainly in applications such as ultra-fast modulators and switches, whereas harmonic generation processes have been applied in frequency conversion devices. Furthermore, second-harmonic and sum-frequency generation received attention because of their potential as powerful characterization techniques in physical and physico-chemical labs.

Second-harmonic generation or frequency doubling was first observed in 1961 by Franken and coworkers at the University of Michigan. They focused a ruby laser (wavelength 694 nm) onto a quartz sample and sent the output through a spectrometer. The spectrum was recorded on photographic paper and they were able to show generation of light at the double frequency. An amusing anecdote is that when they published their results in the prestigious journal *Physical Review Letters*, the editor mistook the small dot on the photographic paper at 347 nm for a spot of dirt and removed it from the article. Since then the field has grown continuously and second-harmonic generation has become a very powerful characterization tool with applications in biology, chemistry, and physics.

In the past a lot of interest in second-order nonlinear optical processes was motivated by their potential applications. Meanwhile, harmonic generation was found to be a very powerful characterization tool for the study of surfaces and interfaces. Indeed, due to symmetry reasons, second-harmonic generation is surface specific and has evolved into a mature characterization technique. Recently, sum-frequency generation also has matured into a reliable technique to probe surfaces and interfaces. However, whereas second-harmonic generation usually probes electronic transitions at interfaces, sum-frequency generation is typically used to address vibrational transitions. Both techniques are almost exclusively used by those with a background in nonlinear optics and remain largely unknown techniques for most scientists. With this book we would like to give the nonspecialist reader a taste of these exceptional characterization tools.

Several books on nonlinear optics have been published over the past 40 years. However, these books are often aimed at physicists and require a good understanding of optics, quantum theory, and nonlinear optical processes. Furthermore, several of these books focus on applications or materials design, instead of focusing on the potential of second-order nonlinear optics as a powerful characterization tool. However, many chemists, biochemists, biologists, and materials scientists are interested in using nonlinear optical techniques for characterization of their samples but often do not have the necessary background to become involved in this field. Also, for students at the PhD level who enter the field of nonlinear optics, we believe this book could be very helpful. Hence, there is obviously a need for a multidisciplinary book on this topic, without going too much into mathematical detail. This book is aimed toward a more general readership and provides an elementary description of nonlinear optics and several practical examples of how to use nonlinear optics as a versatile characterization tool. It provides a detailed description on how to implement nonlinear optical techniques for specific purposes, going from determination of molecular symmetries over surface characterization to biological imaging. The aim of the book is not to give a complete overview of all possible nonlinear optical techniques, but instead to focus on those techniques that are relatively easy to describe and implement in the lab.

Although it is usually preferred to use the International System of Units (SI), we have decided to define equations in the Gaussian unit system. The reason is that the majority of literature in the field of nonlinear optics still uses the Gaussian unit system. Furthermore, we believe that equations defined in the Gaussian unit system are physically more meaningful and straightforward. However, the reader probably easily understands SI units and therefore we will occasionally use SI units when discussing the optical parameters. Conversion factors from Gaussian to SI units can be found in any standard textbook on physics and optics, but for completeness we have included an appendix that briefly addresses this topic.

The outline of the book is as follows. Chapter 1 starts with a short introduction of linear optics from a perspective of polarizability and linear susceptibility. Both are fundamental parameters in the description of linear optical processes such as refraction and absorption. At the end of the chapter the linear optical formalism is extended by adding nonlinear terms that describe the second-order nonlinear optical process. Special attention is given to nonlinear susceptibility, a materials parameter that provides a framework for the description of second-order nonlinear optical phenomena.

Chapter 2 deals with incoherent second-harmonic generation, generated during nonlinear light scattering or hyper-Rayleigh scattering. In contrast to its linear analogue, scattered light is doubled in frequency. Since its discovery in the 1960s, little attention was paid to this very weak and "forbidden" process until the early 1990s when it was used as a simple and efficient technique to determine the hyperpolarizability of organic molecules. Since then the number of groups using this technique has grown tremendously. Here we would like to focus on the sensitivity of this technique to molecular symmetry. By analyzing the polarization state of the scattered light, it is possible to determine molecular symmetries and to study supramolecular aggregation.

Chapters 3 and 4 deal with the study of surfaces and interfaces, exploiting the intrinsic surface sensitivity of second-harmonic generation and sum-frequency generation. Chapter 3 starts with a very general introduction and introduces the theoretical framework to analyze secondharmonic generation from surfaces. Applications include the determination of surface symmetry and molecular orientation. Chapter 4 focuses on chiral surfaces and the specific effects—such as second-harmonic generation circular dichroism and second-harmonic generation optical rotatory dispersion—that can be observed in these systems. Using a conceptually simple framework, we gradually introduce the reader to the exceptional optical effects that can be observed in these systems.

The book concludes with Chapter 5, which discusses second-order imaging techniques. The chapter starts with a short introduction to microscopy in general, followed by an in-depth discussion of two-photon fluorescence (TPF) microscopy and second-harmonic generation microscopy.

#### The Authors

Thierry Verbiest obtained his PhD in physical chemistry in 1993 at the Catholic University of Leuven. After a postdoc at the IBM Almaden Research Center (San José, California), he returned to the University of Leuven and became a professor in the department of chemistry. He has performed research on surfaces, nonlinear optical techniques, and materials. Currently he is involved in magneto-optics and secondharmonic generation from chiral supramolecular materials. He is author or coauthor of more than 100 papers in the field of second-order nonlinear optics.



Koen Clays obtained his PhD in chemistry in 1989 at the Catholic University of Leuven. After a postdoc at Eastman-Kodak (Rochester, New York), he obtained a professor position at the Department of Chemistry, Catholic University of Leuven, Belgium. Recently he also became an adjunct professor at the Department of Physics and Astronomy, Washington State University, Pullman, Washington. His research interests are linear and nonlinear optics of and nanostructured molecular materials. Currently he is involved with research on photonic crystals and complex organic materials for second-order nonlinear optics.



**Vincent Rodriguez** received his PhD in physical chemistry from the University of Bordeaux, France, in 1989. This was followed by postdoctoral studies with Professor H. Schmid at the University of Geneva, Switzerland, before he moved to the Institut Laue-Langevin (European Neutron Research Facilities) in Grenoble, France, as a physicist working on the D16 diffractometer (WANS, SANS). In 1993, he joined the group of Claude Sourisseau at the University of Bordeaux 1 in the Laboratory of Spectroscopies of Molecules and Crystals as an assistant professor in the Department of Chemistry. He is presently a full professor in physical chemistry at the Institute of Molecular Sciences. His primary research was in the field of solid-state materials, and in 1998 he entered the field of nonlinear optics. Over the years, he has contributed in the field of vibrational spectros-



copies as well as nonlinear optics techniques such as second-harmonic generation, hyper-Raleigh scattering, and hyper-Raman scattering. His recent areas of interest concern novel photonic materials for nonlinear optics applications and imaging, molecular switches, and molecular and supramolecular chirality.

#### chapter one

# *General aspects of second-order nonlinear optics*

In this chapter we will give a qualitative overview of the interaction of light with matter, which is necessary to understand the origin of nonlinear optical effects. A rigorous mathematical treatment is beyond the scope of this book and can be found in many standard textbooks on optics (Stratton 1941; Böttcher 1973). Instead we will focus on the basic principles underlying linear and nonlinear optics, bearing in mind the background and interest of the readers for which this book was written.

#### 1.1 Linear optical phenomena

#### 1.1.1 Interaction of light with matter

Light, or electro-magnetic (EM) radiation in general, can be described by a time and space varying electric (E) and magnetic (B) field. For example, the electric field component of a monochromatic wave can be written as

$$E(r,t) = E_0(e^{ik.r-i\omega t} + cc)$$
(1.1)

with a time-dependent phase term,  $\omega t$ , and a space-dependent phase term,  $k.r. \omega$  is the pulsation (equal to  $2\pi v$  with v the frequency) of the EM field,  $k = 2\pi n/\lambda = n\omega/c$  (with  $\lambda$  the wavelength, c the speed of light in vacuum, and n the refractive index) is the wave vector that indicates the direction of light propagation (Figure 1.1), and cc denotes complex conjugate.

Since any material can be thought of as a collection of charged particles—electrons and positively charged cores—the oscillating electric field will interact with these particles. The positive ones will tend to move in the direction of the field, whereas the negative ones move toward the opposite direction of the field. The positively charged cores, however, have much greater mass than the electrons, and for high optical frequencies (in the ultraviolet and visible region of the spectrum), the motions of the electrons are more significant since they are instantaneous (approximately a few femtoseconds). In dielectric media, this charge separation will lead to induced dipole moments ( $\mu$ ) that oscillate with the same frequency as the



Figure 1.1 Schematic representation of an electro-magnetic wave.

applied optical field, and the bulk optical response is the resulting sum of the individual atomic or molecular responses. If the intensity of the incident light is sufficiently low, the relation between the induced dipole moment and the electric field  $E(\omega)$  is given by

$$\mu(\omega) = \alpha(\omega)E(\omega) \tag{1.2}$$

with  $\alpha(\omega)$  the molecular first-order polarizability or linear polarizability. The argument  $\omega$  refers to the frequency of the electro-magnetic radiation. For clarity, this argument is often omitted, but the reader should always realize that the polarizability is a frequency-dependent quantity. Note also that the induced dipole moment will oscillate at the same frequency  $\omega$  as the incident light field and as such acts as a source of radiation. The total dipole moment of the molecule (or molecular polarization) p is then the sum of the permanent dipole moment ( $\mu_0$ ) and the induced dipole moment ( $\mu(\omega)$ ):

$$p = \mu_0 + \mu(\omega) \tag{1.3}$$

The induced polarization of the entire medium, arising from the sum of these induced dipole moments, is given by

$$P(\omega) = \sum_{i} \mu_{i}(\omega) = Nf_{\omega}\alpha(\omega)E(\omega) = \chi^{(1)}(\omega)E(\omega)$$
(1.4)

with  $\chi^{(1)}(\omega)$  the first-order susceptibility (or linear susceptibility). *N* is the number density of molecules and  $f_{\omega}$  a local field factor. The latter accounts for the effects of induced dipoles in the medium through electronic polarization. There are many different forms of local field factors but the most commonly used is the Lorentz–Lorenz correction factor given by

$$f_{\omega} = \frac{n_{\omega}^2 + 2}{3} \tag{1.5}$$

where  $n_{\omega}$  is the refractive index at optical frequency  $\omega$ . Note also that the total polarization of the medium is the sum of the spontaneous (or permanent) polarization  $P^{(0)}$  and the induced polarization  $P(\omega)$ .

The first-order susceptibility contains all information about the optical properties of the macroscopic medium and describes processes such as dispersion, reflection, refraction, absorption, and scattering. As we will see,  $\chi^{(1)}$  is, in general, a complex quantity ( $\chi^{(1)} = \chi' + i\chi''$ ) and related to the refractive index  $n_{\omega}$  and the high frequency dielectric constant,  $\varepsilon_{\omega}$  by

$$n_{\omega}^{2} = \varepsilon_{\omega} = 1 + 4\pi \chi^{(1)}(\omega) \tag{1.6}$$

As a consequence, the refractive index is also a complex quantity, where the real part describes refraction and the imaginary part absorption of radiation.

#### 1.1.2 Wave propagation in optical media

Any interaction of electromagnetic radiation with matter can be understood by using Maxwell's equations. In the Gaussian unit system these are given by

$$\nabla .D = 4\pi\rho$$

$$\nabla .B = 0$$

$$\nabla \times E = -\frac{1}{c}\frac{\partial B}{\partial t}$$

$$\nabla \times B = \frac{1}{c}\frac{\partial D}{\partial t} + \frac{4\pi}{c}J$$
(1.7)

where (*E*, *B*) is the field of the electromagnetic wave (*E*, electric field; *B*, magnetic induction field), *D* is the electric displacement, *c* is the speed of light in vacuum,  $\rho$  is the density of charges, and *J* is the density of current.

If we consider only materials that contain no free charge and no free current (dielectric medium), these equations reduce to

$$\nabla .D = 0$$

$$\nabla .B = 0$$

$$\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t}$$

$$\nabla \times B = \frac{1}{c} \frac{\partial D}{\partial t}$$
(1.8)

The relation between the electric field (*E*) and electric displacement (*D*) is given by the first constitutive relation:

$$D = E + 4\pi P \tag{1.9}$$

Using Equation 1.4 this results in

$$D = E + 4\pi \chi^{(1)}E = (1 + 4\pi\chi^{(1)})E = n^2 E$$
(1.10)

which immediately shows that electric displacement and electric field are simply connected through the refractive index of the medium. Note that we have omitted the frequency argument for clarity. The relation (second constitutive relation) between magnetic induction field and magnetic field intensity is similarly given by

$$B = H + 4\pi M, \tag{1.11}$$

with *M* the magnetization of the medium. In nonmagnetic media this usually reduces to B = H.

To derive the optical wave equation, we proceed by taking the curl of  $\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t}$  and use  $\nabla \times B = \frac{1}{c} \frac{\partial D}{\partial t}$  to obtain the general equation of propagation of the electric field E(r,t):

$$\nabla \times (\nabla \times E(r,t)) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} D(r,t) = 0$$
(1.12)

Note that we used the argument (r,t) to indicate the time (t) and spatial variation (r) of E and D. If we use the constitutive relation for D (Equation 1.9), this can be rewritten as

$$\nabla \times (\nabla \times E(r,t)) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} E(r,t) = -4\pi \frac{1}{c^2} \frac{\partial^2}{\partial t^2} P(r,t)$$
(1.13)

Hence, the polarization (*P*) is seen to act as a source term in the wave propagation equation. Substituting *P* with Equation 1.4 yields

$$\nabla \times (\nabla \times E(r,t)) + \frac{(1+4\pi\chi^{(1)})}{c^2} \frac{\partial^2}{\partial t^2} E(r,t) = \nabla \times (\nabla \times E(r,t)) + \frac{n^2}{c^2} \frac{\partial^2}{\partial t^2} E(r,t) = 0$$
(1.14)

Consequently, any propagating wave with velocity c/n and wave vector  $k = n \frac{\omega}{c} = \frac{2\pi nv}{c}$  of the form  $E(r,t) = E_0(e^{ik.r-i\omega t} + cc)$  will satisfy this equation. Hence, it is clear that the polarization of the material is the origin of the refractive index (*n*) of the material.

Let us generalize the meaning of the optical constant of a material by introducing its complex nature (Zernike and Midwinter 1973). In dielectric materials, the charged particles are bound together and the motion of the electrons varies in response to the electric field, E(r,t), in a manner governed by the equation of motion for a classical harmonic oscillator. A simple description of the motion, r(t), for one of the electrons is given in the following equation:

$$\frac{d^2 r(t)}{dt^2} + 2\gamma \frac{dr(t)}{dt} + \omega_0^2 r(t) = -\frac{e}{m} E(r, t)$$
(1.15)

where  $\omega_0$  is the resonance frequency and  $\gamma$  is the damping constant. The term on the right-hand side of Equation 1.15 represents the force exerted on the electron by the applied field that drives the oscillation. If we take the applied optical field of the form

$$E(r,t) = E_0(e^{ik.r - i\omega t} + cc)$$
(1.16)

the solution to Equation 1.15 is of the form

$$r(t) = -\frac{e}{m} E_0 \frac{e^{ik.r - i\omega t}}{\omega_0^2 - 2i\gamma\omega - \omega^2} + cc$$
(1.17)

The motions of the collection of *N* electrons give rise to a macroscopic time-dependent polarization that reads

$$P(t) = -Ner(t) \tag{1.18}$$

and with Equation 1.4 we obtain the following expression for the linear susceptibility at frequency  $\omega$ :

$$\chi^{(1)}(\omega) = \frac{Ne^2}{m} \frac{1}{\left(\omega_0^2 - 2i\gamma\omega - \omega^2\right)}$$
(1.19)

From this equation it is clear that  $\chi^{(1)}$  is frequency dependent and is a complex quantity. The real and imaginary parts of this expression describe refraction and absorption, respectively:

$$\operatorname{Re}[\chi^{(1)}(\omega)] = \chi'(\omega) = \frac{Ne^2}{m} \frac{\left(\omega_0^2 - \omega^2\right)}{\left(\omega^2 - \omega_0^2\right)^2 + (2\gamma\omega)^2}$$
(1.20)

$$\operatorname{Im}[\chi^{(1)}(\omega)] = \chi''(\omega) = \frac{Ne^2}{m} \frac{2\gamma\omega}{\left(\omega^2 - \omega_0^2\right)^2 + (2\gamma\omega)^2}$$
(1.21)

The behavior of these expressions is illustrated in Figure 1.2 where real and imaginary parts of the susceptibility are plotted versus frequency in the region of an optical transition at  $\omega_0$ . At  $\omega_0$ , the absorption of  $\chi''$  is maximal and it has a Lorentzian shape since we consider an assembly of N identical oscillators. In that case, the spectral width of  $\chi''$  is called the homogeneous width. Going from low frequency to  $\omega_0$ , the dispersion of  $\chi'$  is connected to the increase of the backward dephasing of  $P(\omega)$  with  $E(\omega)$ .



*Figure 1.2* Variation of the real and imaginary parts of the linear susceptibility with frequency around a resonant frequency  $\omega_0$ .