Chapter 1

Linear and Nonlinear Polarizability
A Primer

Galen D. Stucky[1], Seth R. Marder[2], and John E. Sohn[3]

[1]University of California, Santa Barbara, CA 93106
[2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109
[3]AT&T Bell Laboratories, P.O. Box 900, Princeton, NJ 08540

In this introductory chapter the concepts of linear and nonlinear polarization are discussed. Both classical and quantum mechanical descriptions of polarizability based on potential surfaces and the "sum over states" formalism are outlined. In addition, it is shown how nonlinear polarization of electrons gives rise to a variety of useful nonlinear optical effects.

This chapter introduces the reader to linear and nonlinear optical polarization as a background for the tutorial and research articles that follow. We consider first how the passage of light changes the electron density distribution in a material (i.e., polarizes the material) in a linear manner, from both the classical and quantum mechanical perspectives. Next, we examine the consequences of this polarization upon the behavior of the light. Building on this foundation, we then describe, in an analogous manner, the interaction of light with nonlinear materials. Finally, we outline some materials issues relevant to nonlinear optical materials research and development.

Nonlinear optics is often opaque to chemists, in part because it tends to be presented as a series of intimidating equations that provides no intuitive grasp of what is happening. Therefore, we attempt in this primer to use graphical representations of processes, starting with the interaction of light with a molecule or atom. For the sake of clarity, the presentation is intended to be didactic and not mathematically rigorous. The seven tutorial chapters that follow this introduction as well as other works (1–5) provide the reader with detailed treatments of nonlinear optics.

Nonlinear Behavior and Nonlinear Optical Materials

The idea that a phenomenon must be described as nonlinear, at first, has inherent negative implications: we know what the phenomenon is not (linear), but what then is it? As a starting point, Feynman (6) has noted that to understand physical laws, one must begin by realizing they are all approximate. For example, the frictional drag on a ball bearing moving slowly through a jar of honey is linear to the velocity, i.e. $F = -kv$. However, if the ball is shot at high velocity the drag becomes nearly proportional to the square of the velocity, $F = -k'v^2$, a nonlinear phenomenon. Thus, as the speed of the

ball bearing increases, the form of the physical "law" describing the relationship between the drag and the velocity changes. Nonlinear dynamics forms the basis of the new discipline, chaos (7), a nearly universal phenomenon. A process is nonlinear when the response to an input (i.e., the output) changes the process itself. Nonlinear behavior is not unusual, and for most physical processes a linear formulation is generally just the lowest-order approximation to the actual process. This has been emphasized for the behavior of light by Chemla and Zyss (8): "The artificial distinction between linear and nonlinear optics is now obsolete. Optics is in essence nonlinear."

Nonlinear optics is concerned with how the electromagnetic field of a light wave interacts with the electromagnetic fields of matter and of other light waves. The interaction of light with a nonlinear optical material will cause the material's properties to change, and the next photon that arrives will "see" a different material. As light travels through a material, its electric field interacts with other electric fields within the material. These internal fields are a function of the time dependent electron density distribution in the material and the electric fields of the other light waves, if for example, two or more light sources are used. In a **nonlinear optical (NLO)** material, strong interactions can exist among the various fields. These interactions may change the frequency, phase, polarization, or path of incident light. The chemist's goal in the field is to develop materials that control this mediation so that one can modulate or combine photons (wave mixing). In addition, it is necessary to fine tune both the magnitude and response time of the optical processes. To effect this control, we must look more closely at how matter, and specifically the electronic charge density in matter, interacts with light.

Polarizability: A Microscopic View

What causes the electron density of an optical material to couple and polarize with the electromagnetic field of a light wave? To understand this process we need to consider more quantitatively what happens at the molecular level. How does light perturb or couple to the electrons in a molecule?

Light has an electric field, E, that interacts with the charges in a material producing a force (qE, where q is the charge). Figure 1 is a simple schematic that shows the instantaneous displacement (polarization) of the electron density of an atom by the electric field of the light wave. The displacement of the electron density away from the nucleus results in a charge separation, an <u>induced dipole</u> with moment μ (Figure 1b). For small fields the displacement of charge from the equilibrium position is proportional to the strength of the applied field.

$$\text{Polarization} = \mu = \alpha E \tag{1}$$

Thus a plot of polarization as a function of the applied field is a straight line whose slope is the <u>linear polarizability</u>, α, of the optical medium (Figure 1c). If the field oscillates with some frequency, (i.e., electromagnetic radiation, light), then the induced polarization will have the same frequency if the response is instantaneous (Figure 1a). Polarization is a vector quantity with both direction and magnitude.

In this <u>classical</u> model of linear polarizability, the electrons are bound to the atoms by a <u>harmonic potential</u> (Figure 2), i.e., the restoring force for the electron is linearly proportional to its displacement from the nucleus:
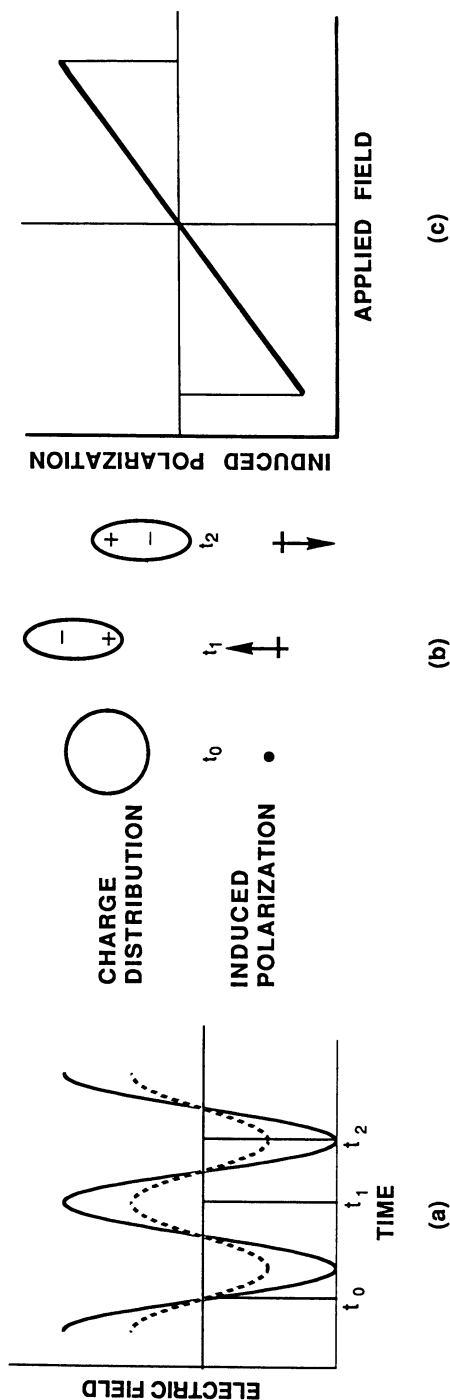
$$F = -\kappa x \tag{2}$$

Figure 1. (a) Plots of the electric field of the applied light wave (solid) and the induced polarization wave (dotted) as a function of time for a linear material; (b) cartoon depicting the polarization of the material as a function of time; (c) plot of *induced* polarization vs. applied field.

The electrons see a potential energy surface:

$$V = 1/2 \, \kappa x^2 \tag{3}$$

Therefore, a symmetrical distribution of electron density exists around the atom with an equal ease of *charge* displacement in both the +x and –x directions.

The oscillating electric field of light affects all charges in the optical medium, not only the electron. For materials that contain electric dipoles, such as water molecules, the dipole themselves stretch or reorient in the applied field. In ionic materials, the ions move relative to one another (Figure 3). Dipolar and ionic motions involve nuclear reorientation.

The magnitude of the polarization depends on whether the charges can move fast enough to keep up with the oscillations of the electric field. Only electrons are efficiently polarized by optical frequency fields since they have small mass. Heavier, and thus more slowly moving, nuclei and molecules are efficiently displaced (polarized) at lower frequencies. If the charges fail to keep up with the field, a phase difference between the polarization and the electric field occurs, i.e., the charge displacement maximizes sometime <u>after</u> the electrons experience the maximum in the electric field of the light wave. The total polarizability, α, consists of an in-phase component, α', and an out-of-phase component, α'', that accounts for absorption ($\alpha = \alpha' + i\alpha''$). Figure 4 shows a plot of α' and α'' as a function of frequency. As a rough generalization, electron polarization, α_e, is the fastest, occurring on the femtosecond time scale (UV/visible); vibrational displacements, α_v, are slower, occurring in the picosecond regime (infrared or lower frequencies); and molecular dipole reorientation, α_d, is generally slower still, occurring on the nanosecond or slower time scale (microwave frequencies or lower). However, most third-order susceptibility measurements on organic based molecules show reorientational effects which are quite fast, sometimes sub nanosecond, which can dominate in this time regime. Heating effects are thus possible on the nanosecond time scale and <u>must</u> be taken into account since they can greatly modify the polarization response. The induced displacement of trapped charges at defect sites (space charges) within solids occurs at audio frequencies at the slowest end of the time scale. It is important, therefore, to write equation 1 as

$$\mu(\omega) = \alpha(\omega) \, E(\omega) \tag{4}$$

indicating that each of the variables is frequency dependent.

Figure 4 also illustrates that both α' and α'' change dramatically at certain frequencies. These are **resonant** frequencies, natural frequencies for transitions between quantum states. At these frequencies, transitions to higher energy rotational, vibrational, or electronic states lead to large charge displacements. In the search for large optical responses, resonant or near resonant optical frequencies have been used. Unfortunately, at or near-resonant frequencies, photons are no longer weakly perturbed as they travel through the optical medium; non-radiative decay from the high-energy or excited states to the ground state can result in sample heating and loss of photon efficiency.

The polarization for a medium may not be the same in all directions for a molecule or a collection of atoms in a thin film or crystal. For example, a field oriented along the long axis of 2,4-hexadiyne induces a polarization, and a field oriented perpendicular to the long axis induces a smaller polarization (Figure 5). Simply explained (ignoring conjugation effects), application of the electric field along a row of atoms (Figure 5a) induces a series of atomic dipoles in which the positive end of one induced dipole is attracted to the negative end of the neighboring dipole, thus reinforcing the polarization. Reinforcement of the dipoles does not occur with the field perpendicular to the row of atoms (Figure 5b).
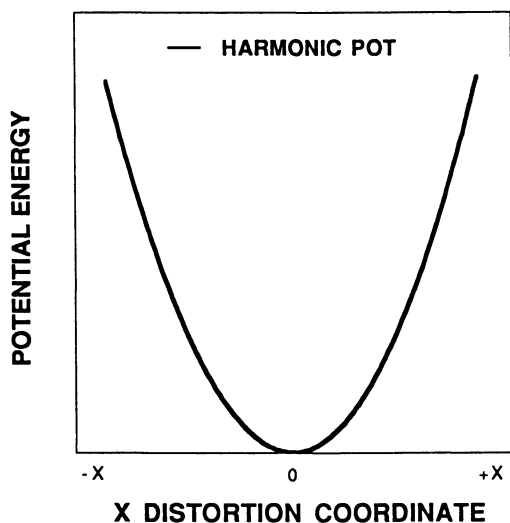
Figure 2. Plot of potential energy vs. distortion coordinate for a material with a harmonic potential.
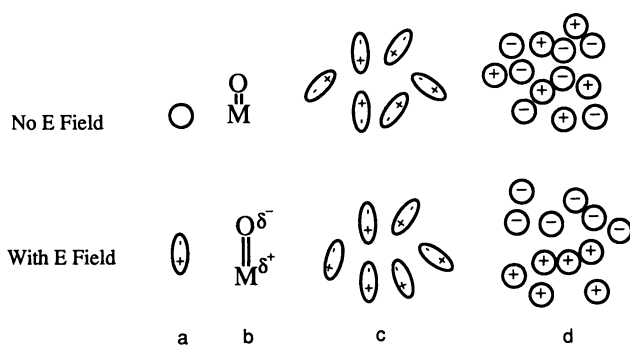

Figure 3. Different mechanisms for inducing polarization through (a) redistribution of electron density, (b) bond stretching, (c) alignment of dipoles, and (d) separation of ions.
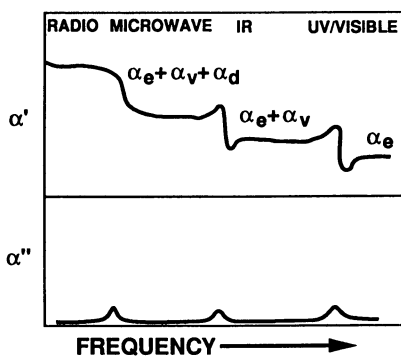
Figure 4. Plot of polarizability of a material as a function of the frequency of the applied field.Top:Real polarizability. Bottom: Imaginary polarizability.
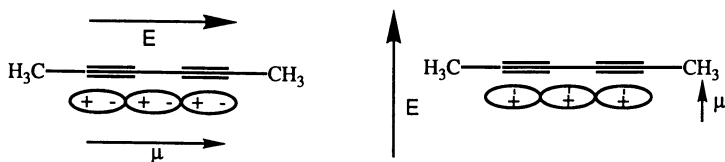

Figure 5. Cartoon illustrating the magnitude of induced polarization with the electric field applied along the long axis of a molecule (left) and induced polarization with the electric field applied perpendicular to the long axis of a molecule (right).

To understand the anisotropic nature of polarizability, consider a molecule as a balloon (Figure 6). Deforming it (applying a field) along the x axis changes the dimension (polarization) of the balloon not only in the x direction but also in the y and z directions. Therefore, three terms, each describing the polarizability along each of the three axes, describe the effect of a field along the x direction. Since the field can be applied in three orthogonal directions, a total of nine terms are required to fully define the polarizability. Taken together, these nine terms are called the polarizability tensor, α_{ij}. Mathematically, α_{ij} is written as a 3 x 3 matrix with elements α_{ij} (i,j = 1, 2, 3). Since both μ and E are vectors and α_{ij} is a tensor, equation 4 is more properly written in terms of the vector components, $\mu_i(\omega)$

$$\mu_i(\omega) = \sum_j \alpha_{ij}(\omega) E_j(\omega) \tag{5}$$

where $\alpha_{ij}(\omega)$ is the <u>linear polarizability</u> of the molecule or atom since it defines the linear variation of polarization (induced dipole moment) with the electric field. However, because of anisotropy in molecular electron density distribution, the direction of the induced dipole moment is not always the same as the electric field that generated the moment.

Polarizability: A Quantum Mechanical Point of View

So far we have described polarization in a classical manner, a useful approach from a phenomenological point of view, but quantitatively inadequate for quantum confined particles like the electrons in molecules (9, 10). We briefly outline the quantum mechanical approach for a small molecule. The polarization of electron density in a molecule by light can be viewed in terms of the electric field of the light wave modifying the ground-electronic state. The original ground-state of the molecule is no longer a quantum-state for the molecule when it is perturbed by the electric field of a light wave. We can write the new quantum-state as a linear combination of the ground- and excited-states of the undisturbed system. Generally, the unperturbed excited-states have different electron distributions than the ground-state, so that mixing the excited-states and the ground-states leads to net charge redistribution (polarization). Since the perturbation of the electron density by the electric field of light is caused by a time dependent field, E(t), we must start with the time-dependent Schrödinger equation to describe the time evolution of the polarization:

$$H\Psi = ih\,(\partial/\partial t)\Psi \tag{6}$$

H is the Hamiltonian operator for the total energy, h = Planck's constant / 2π, t is the time, and Ψ is the wave function describing the electronic state. The electric field of the light adds another contribution to the Hamiltonian. Assuming that all the molecules are isolated polarization units, the perturbation part of the Hamilitonian is the electric dipole operator, $-\mu \cdot E$. Thus,

$$H = H^0 - \mu \cdot E \tag{7}$$

where

$$\mu = \sum er_i \tag{8}$$

with the sum over i, the number of electrons in the molecule; r_i is a vector to the ith electron.

The perturbation, $H'' = -\mu \cdot E$, represents the interaction of the light wave electric field with the molecule.   The solutions to the wave equation 6 are given by

$$\Psi_m(r,t) = \sum C_{mn}(t) \, \Psi(o)_n(r,t) \tag{9}$$

so that the $\Psi_m(r,t)$ eigenfunctions describe the new electronic states in terms of linear combinations of the original unperturbed $\Psi(o)_m(r,t)$ electronic states of the molecule. In this way the electric field serves to "mix" the unperturbed molecular states, $\Psi(o)_n(r,t)$.   For example, the perturbed ground state is a combination of the unperturbed molecule's ground and excited-states and therefore has a different electron density distribution than the unperturbed ground-state. Furthermore, since the electric field is time dependent, the amount of excited-state character will vary with time, as will the electron density distribution. Thus an oscillating electric field induces a time dependent polarization in the molecule.

Suppose that the combination of original states includes the ground-state and an excited-state which has a large charge reorganization with a correspondingly large excited-state dipole. One then expects an increase in dipole moment from a light induced mixing of these states.   Garito and coworkers (*11*) (Figure 7) have demonstrated that a large coupling exists between the ground-state and an excited-state in 2-methyl-4-nitroaniline (MNA).   Application of an electric field to the molecule results in extensive charge displacement through the π orbital system and a change in dipole moment.

In summary, the polarization and distortion of electrons can be represented by a field induced mixing of states. This mixing introduces excited-state character but does not result in a long-lifetime population of any excited-states. The instantaneous formation of these polarized states has been referred to in terms of "virtual transitions". The polarization behavior can be written in terms of the ground- and excited-state dipole moments, e.g., <g|μ|g>, <e|μ|e>, and transition moments between the unperturbed molecular states, e.g., <g|μ|e> where g represents the initial ground-state wave function and e an excited state wave function for the unperturbed molecule. The mixing of ground- and excited-states is then described in perturbation theory by summing over the appropriate dipole and transition moments, i.e., a **sum over states.**"

The dipole moments describe the extent of charge separation, and the transition moments measure the mixing of the excited-states into the original ground-state. Extensive mixing of states with concomitant charge reorganization leads to a very soft potential well in the classical picture and, therefore, an increase in polarizability. This "sum over states" approach has been used extensively in the description of organic NLO properties (*12, 13*). Near resonance, the situation changes and real excited-states come into play.

Both the classical and quantum approaches ultimately lead to a model in which the polarizability is related to the ease with which the electrons can be displaced within a potential well. The quantum mechanical picture presents a more quantitative description of the potential well surface, but because of the number of electrons involved in nonlinear optical materials, theoreticians often use semi-empirical calculations with approximations so that quantitative agreement with experiment is not easily achieved.

Polarizability: A Macroscopic View

NLO characterization and device applications are based on bulk materials, not molecules. It is therefore necessary to look at what happens in the laboratory on the
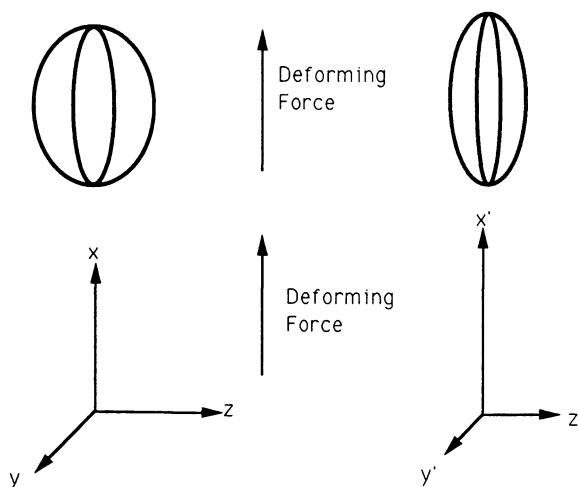
Figure 6. Top: Cartoon illustrating the effect of an arbitrary deforming force applied to a balloon. Bottom: Graphical representation of changes in the x, y and z dimensions when a force is applied along the x direction.
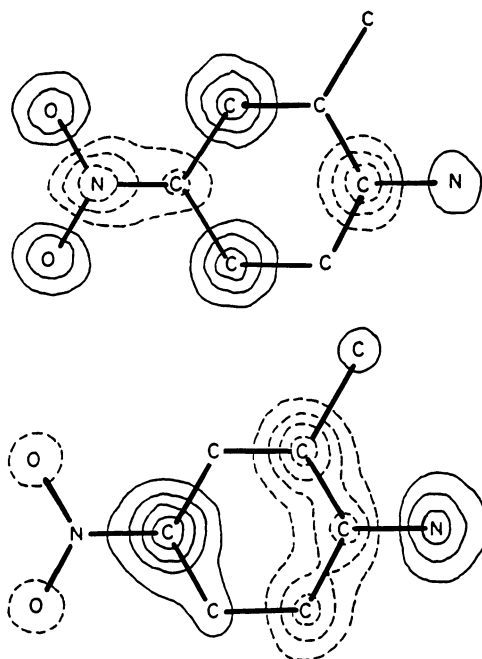

Figure 7. Contour diagram of the wave functions for the MNA ground state (bottom) and a principal excited state (top) showing charge correlations from Garito et. al.
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bulk, macroscopic level. In bulk materials, the linear polarization (cf. equation 5 for atoms or molecules) is given by

$$P_i(\omega) = \sum_j \chi_{ij}(\omega) E_j(\omega) \tag{10}$$

where $\chi_{ij}(\omega)$ is the <u>linear susceptibility</u> of an ensemble of molecules. To relate $\chi_{ij}(\omega)$ to the atomic or molecular polarization described above, it is usually assumed that the atoms or molecules making up the optical material are independently polarized by the light with no interatomic or intermolecular coupling (see below). Within this approximation $\chi_{ij}(\omega)$ is then given by the sum of all the individual polarizabilities, $\alpha_{ij}(\omega)$.

When the electronic charge in the optical material is displaced by the electric field (**E**) of the light and polarization takes place, the <u>total electric field</u> (the "displaced" field, **D**) within the material becomes:

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = (1 + 4\pi\chi)\mathbf{E} \tag{11}$$

Since $\mathbf{P} = \chi\mathbf{E}$ (Equation (10)), $4\pi\chi\mathbf{E}$ is the internal electric field created by the induced displacement (polarization) of charges. Usually, the induced polarization causes the spatial orientation of the internal electric field to differ from the applied electric field and, like $\alpha_{ij}(\omega)$, $\chi_{ij}(\omega)$ is a tensor quantity that reflects the anisotropy of the internal electric field.

The <u>dielectric constant</u> $\varepsilon(\omega)$ and the <u>refractive index</u> $n(\omega)$ are two common bulk parameters that characterize the susceptibility of a material. The dielectric constant in a given direction is defined as the ratio of the displaced internal field to the applied field ($\varepsilon = D/E$) in that direction. Therefore from equation 11,

$$\varepsilon_{ij}(\omega) = 1 + 4\pi\chi_{ij}(\omega) \tag{12}$$

The frequency dependence of the dielectric constant provides insight into the mechanism of charge polarization (see Figure 4). Until now, we were concerned with the effect of light on the medium (ε and χ). Since NLO addresses how the optical material changes the propagation characteristics of light, we must now ask what happens to the light as it passes through the medium.

Linear Polarization of Matter and Linear Optical Effects

As shown in Figure 1, the light wave moves electronic charge back and forth. This motion of charge in turn will re-emit radiation at the frequency of oscillation. For linear polarization, this radiation displays the same frequency as the incident light. However the polarization does change the propagation of the light wave.

We know from everyday experience that when light travels from one medium to another its path can change (Figure 8). For example, a straight stick entering the water at an angle appears to bend as it passes below the surface. This apparent bending is due to the fact that light takes the path of "least time", i.e. the fastest way to get from point A (the part of the stick that is under water) to point B (your eye). Since light travels faster in air than in water, the path of the light in water is shorter than that in air. The direction of the light paths in air and in water is determined by the ratio of the speed of light in air to that in water. The ratio of the speed of light in a vacuum, c, to the speed of light in a material, v, is called the <u>index of refraction</u> (n)

$$n = c/v \tag{13}$$

It is important to note that n is uniquely defined for every material or substance.

At optical frequencies in the absence of dispersion (absorption), the dielectric constant equals the square of the refractive index:

$$\varepsilon(\omega) \quad = n^2(\omega) \qquad\qquad (14)$$

Consequently, we can relate the refractive index to the bulk linear (first-order) susceptibility:

$$n^2(\omega) = 1 + 4\pi\chi(\omega) \qquad\qquad (15)$$

Since $\chi(\omega)$ is related to the individual atomic or molecular polarizabilities, this simple equation relates a property of light (its speed) to a property of the electron density distribution (the polarizability). Now we can see how the optical properties of a material depend on the electron density distribution, which is dictated by chemical structure. Therefore, as the chemist alters the structure, the optical properties change.

Remember that the electric field of light is perpendicular to its direction of propagation. A point source emitting light from the center of an isotropic crystal emanates light outward uniformly in all directions. The position of the wave front defines a sphere (wave surface) whose radius is increasing with time (Figure 9 top). If we chose another material with a larger susceptibility (more polarizable), its wave surface would expand more slowly because the susceptibility relates to the square of the refractive index (Figure 9 middle). At an arbitrary time (t), the wave surface shows a radius inversely proportional to the index of refraction. For non-cubic single crystals, such as a hypothetical crystal of 2,4-hexadiyne (Figure 9 bottom), the index of refraction, and hence, the polarizability varies with the direction that the light travels through the crystal. The hypothetical crystal of 2,4-hexadiyne is uniaxial, where the unique axis is referred to as the optic axis. Other noncubic crystals are characterized by two optical axes and are said to be optically biaxial. A material then, which has an index of refraction that depends on direction, is called birefringent, or doubly refracting. In the following discussion we limit the discussion of anisotropic crystals to those which are uniaxial.

When a beam of unpolarized light enters a birefringent crystal at normal incidence (but not along the optic axis), two light beams emerge (Figures 10 and 11). One ray, what we call the <u>ordinary ray</u>, passes straight through the crystal. The other ray, called the <u>extraordinary ray</u>, diverges as it passes through the crystal and becomes displaced. The relative polarization of the two emerging beams is orthogonal.

This interesting result (first observed in calcite by the Vikings) is explained as follows. We can describe a beam of unpolarized light as the superposition of two orthogonally polarized rays (electric fields at 90 degrees to each other) traversing the same path. When both rays encounter the same index of refraction, as in an isotropic medium, or when the direction of propagation occurs along an optic axis (polarized in a direction perpendicular to the optic axis) of an anisotropic crystal, the beams remain collinear and in phase. For light polarized perpendicular to the optic axis, the material appears isotropic and the index of refraction is independent of the direction of propagation. We call this angularly independent index the <u>ordinary index</u> of refraction, n_o. If light is not polarized perpendicular to the optic axis, the index of refraction varies as a function of the direction of propagation. The angularly sensitive index becomes the <u>extraordinary index</u> of refraction, n_e. Generally, for light traveling through a birefringent material in an arbitrary direction, the two orthogonally polarized rays "see" different polarizabilities and thus different refractive indices. One ray
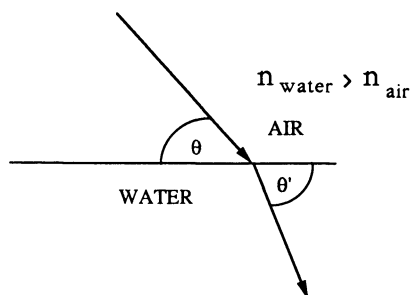
Figure 8. Apparent bending of a stick as it enters water at an arbitrary angle.
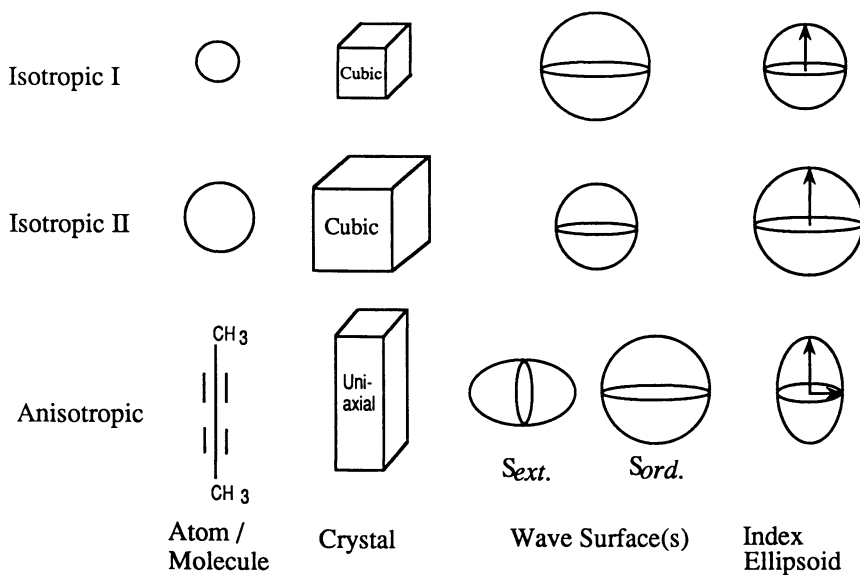

Figure 9. Top: An isotropic atom/molecule and crystal with isotropic polarizabilities will give rise to a spherical wave surface and index ellipsoid. Middle: Another isotropic atom/molecule and crystal with larger isotropic polarizabilities will give rise to a smaller spherical wave surface and a larger spherical index ellipsoid. Bottom: An anisotropic atom/molecule and crystal with anisotropic polarizabilities will give rise to an ordinary spherical wave surface and an ellipsoidal extraordinary wave surface. The index ellipsoid will have major and minor axes.
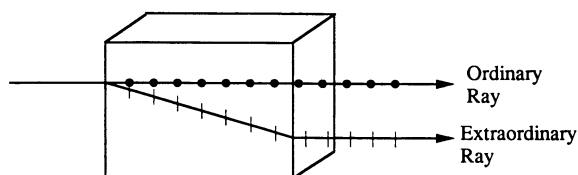
Figure 10. A light beam entering a birefringent crystal at normal incidence (but not along the optic axis) will be divided into an ordinary beam that passes straight through the crystal (line with dots, light polarized perpendicular to the plane of the page). The orthogonally polarized extraordinary beam path (line with dashes, light polarized in the plane of the page) diverges from the ordinary beam as it passes through the crystal.
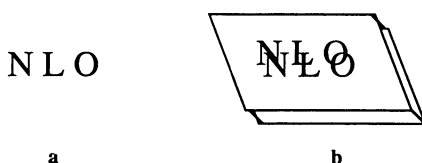

Figure 11. (a) An image (b) appears to be doubled when viewed through a birefringent material.

becomes retarded relative to the other (introducing a phase shift) and may take a different path. A uniaxial material will therefore have two wave surfaces, a spherical ordinary wave surface and an ellipsoidal extraordinary wave surface. Note that the magnitude of the principle axes of the wave surface are inversely proportional to the refractive indices **normal** to the direction of propagation.

In optics, the optical indicatrix (Figures 9 and 12) is a useful construct that characterizes the birefringence of materials. The indicatrix is a surface that specifies the refractive indices of both the O and E rays traveling in any direction through the material. The indicatrix for a uniaxial material is defined by the equation

$$x^2/n_o{}^2 + y^2/n_o{}^2 + z^2/n_e{}^2 = 1 \qquad (16)$$

where n_e is the extraordinary index experienced by waves polarized parallel to the optic axis. The surface described by this equation is an ellipsoid with circular symmetry about the z axis and semiaxes equal to n_o for the circularly symmetric axes and n_e for the unique axis. For a given ray (OP) passing through the material, the intersection of the plane perpendicular to the path of the ray and the indicatrix defines the refractive index ellipse (Figure 12). One axis of the ellipse, which varies with θ (the angle between OP and the optic axis), represents the magnitude and polarization of the index of refraction for the extraordinary ray. The angularly insensitive axis is the index of refraction, n_o, for the ordinary ray. Note that the indicatrix is frequency dependent and that birefringence is critical for exploiting a process called second harmonic generation (see D. Williams's tutorial).

Nonlinear Polarizability: A Microscopic View

Until now we have assumed that the polarization of a molecule or material is a linear function of the applied electric field. In reality, the induced polarization generates an internal electric field that modifies the applied field and the subsequent polarization. This interrelationship is the origin of nonlinear polarization. In this section, we present a physical and chemical model for molecules and materials that describes the source of nonlinear behavior.

Figure 4 clearly illustrates that polarizability is a function of the frequency of the applied field. Changing the restoring force constant, κ (equation (2)) is another way to modify the linear polarizability. Another alternative is to add anharmonic terms to the potential to obtain a surface such as that shown in Figure 13. The restoring force on the electron is no longer linearly proportional to its displacement during the polarization by the light wave, it is now **nonlinear** (Figure 14). As a first approximation (in one dimension) the restoring force could be written as:

$$F = -kx - 1/2k'x^2 \qquad (17)$$

Now the magnitude of the polarization depends on the direction of displacement (Figure 14). For the covalent (e.g. titanyl or vanadyl) M=O bond, in general, one expects that the electron cloud would be more easily polarized towards the oxygen atom. This direction dependency means that the polarization coefficients must be described using tensor quantities.

Just as linear polarization leads to linear optical effects, such as refractive index and birefringence, nonlinear polarization leads to other and usually more subtle (nonlinear) effects. It is precisely these effects we hope to understand and exploit. In Figure 14, application of a symmetric field (i.e., the electric field associated with the light wave) to the anharmonic potential leads to an asymmetric polarization response. This polarization wave shows diminished maxima in one direction and accentuated
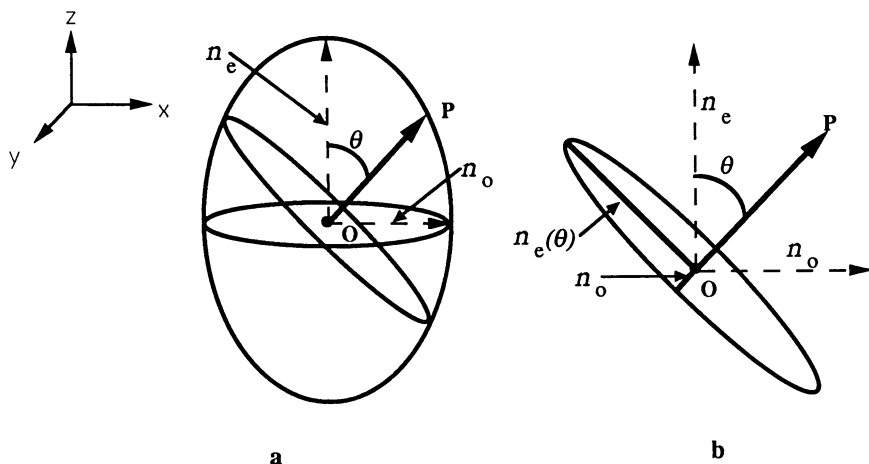
Figure 12. (a) Index ellipsoid defined by n_e and n_0 with a ray of light propagating in an arbitrary direction OP; (b) an ellipse that is formed by the intersection of the plane normal to OP and the index ellipsoid. The principal axes of this ellipse are the angularly dependent index n_e (θ) and the angularly independent index n_0.
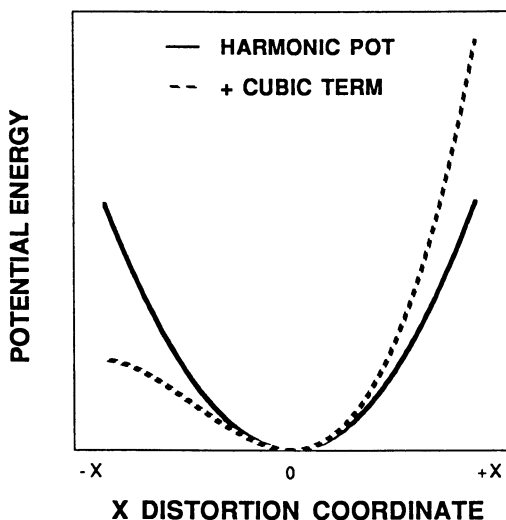

Figure 13. Plot of potential energy vs. distortion coordinate for a material with a harmonic potential and a material with an additional cubic anharmonic term.
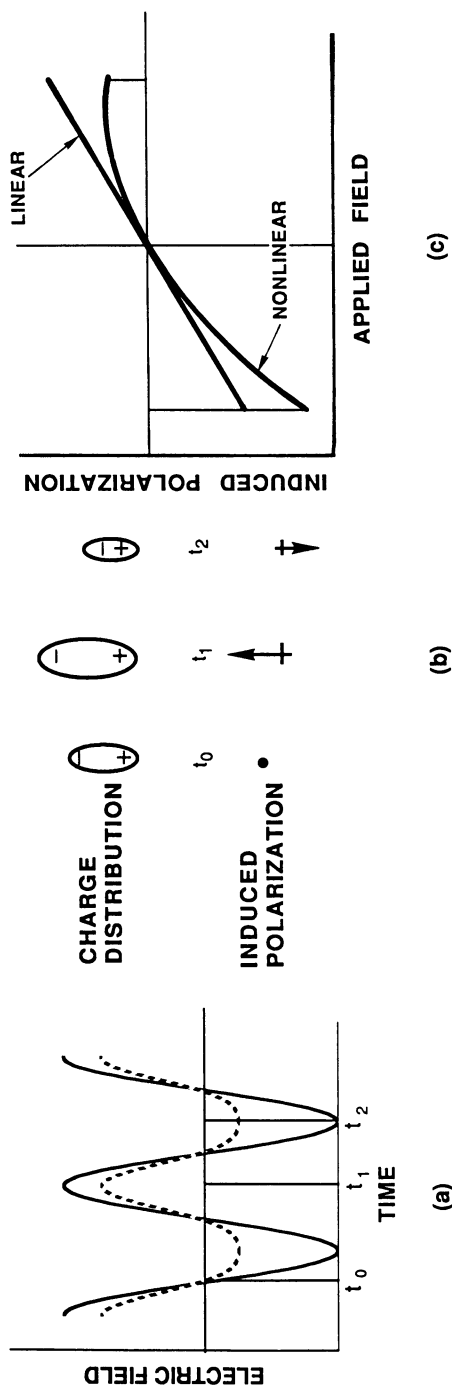
Figure 14. (a) Plots of the electric field of the applied light wave (solid) and the induced polarization wave (dotted), as a function of time, for a second-order nonlinear material; (b) cartoon depicting the polarization of the material as a function of time; (c) plots of induced polarization vs. applied field for both linear and second-order nonlinear materials.

maxima in the opposite direction. This asymmetric polarization can be decomposed into a DC polarization component and polarization components at the fundamental and second harmonic frequencies. This Fourier analysis of the resultant second-order NLO polarization is shown in Figure 15. Since only asymmetric polarization leads to second-order NLO effects, these effects can only be induced by molecules and materials lacking a center of symmetry.

The mathematical formulation of the nonlinear polarization is unknown but a common approximation is to expand the polarizability as a Taylor series:

$$\mu_i = \mu^0_i + (\partial\mu_i/\partial E_j)_{E_0} E_j + 1/2(\partial^2\mu_i/\partial E_j\partial E_k)_{E_0} E_jE_k + $$
$$1/6(\partial^3\mu_i/\partial E_j\partial E_k\partial E_l)_{E_0} E_jE_kE_l + ...(18)$$

or

$$\mu_i = \mu^0_i + \alpha_{ij}E_j + \beta_{ijk}/2\ E_jE_k + \gamma_{ijkl}/6\ E_jE_kE_l + ... \qquad (19)$$

where as indicated, μ^0_i is the static dipole in the absence of an electric field.

The series expansion breaks down as an approximation with increasing field strength, i.e. it is most accurate for relatively small fields and polarizations. Obviously, this description is not valid when the electric field strength (e.g. from a laser light beam) approaches the strength of the atomic fields that bind electric charges (10^8–10^9 V/cm). Fortunately, most nonlinear effects are observed at electric fields of 10^3–10^4 V/cm (laser intensities in the kilowatt to megawatt per cm^2 range) and the above expressions are generally applicable (1). The above expansion is not appropriate at or near a resonance frequency. The reader is therefore advised to use care in the application and interpretation of equation 18.

Physically, the higher-order (i.e., nonlinear) terms such as ß relate to the potential well anharmonicity. Miller has suggested that to a first approximation the second-order polarizability is directly proportional to the linear polarizability (first-order) times a parameter defining the anharmonic potential (14, 15). This relationship works best for inorganic materials. In organic molecules the relationship becomes complex because the linear polarizability and the anharmonicity are not necessarily independent variables (see tutorial by D. N. Beratan).

The terms beyond αE are not linear in E; they are referred to as the nonlinear polarization and give rise to nonlinear optical effects. Also note that at small fields the polarization will more nearly approximate a linear response; however, with increasing field strength, nonlinear effects become more important. Since $\alpha \gg \beta, \gamma$, there were few observations of NLO effects before the invention of the laser with its associated large electric fields.

Just as α is the linear polarizability, the higher order terms β and γ (equation 19) are the first and second hyperpolarizabilities, respectively. If the valence electrons are localized and can be assigned to specific bonds, the second-order coefficient, ß, is referred to as the bond (hyper) polarizability. If the valence electron distribution is delocalized, as in organic aromatic or acetylenic molecules, ß can be described in terms of molecular (hyper)polarizability. Equation 19 describes polarization at the atomic or molecular level where first-order (α), second-order (ß), etc., coefficients are defined in terms of atom, bond, or molecular polarizabilities. μ is then the net bond or molecular polarization.
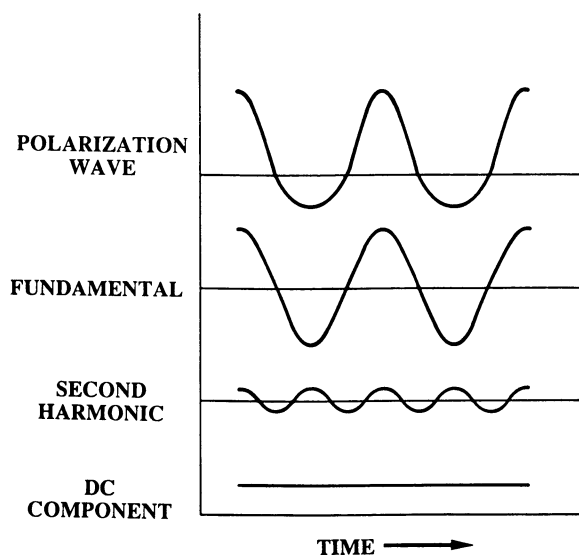
Figure 15. Fourier analysis of an asymmetric polarization wave showing that it is comprised of components at the fundamental frequency, second harmonic frequency, and zero frequency (DC).

Nonlinear Polarizability: a Macroscopic View

The observed bulk polarization is given by an expression analogous to equation 19:

$$\mathbf{P} = \mathbf{P_o} + \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{E} \cdot \mathbf{E} + \chi^{(3)} \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \ldots \qquad (20)$$

where the $\chi^{(i)}$ susceptibility coefficients are tensors of order $i + 1$ (e.g., $\chi^{(2)}$ has tensor elements $\chi^{(2)}_{ijk}$). $\mathbf{P_o}$ is the built-in static dipole of the sample.

It is of particular interest from both NLO and chemical perspectives to understand how the polarizability changes in the evolution from an isolated atom to a molecule, a cluster of atoms or molecules, an extended array, and ultimately the bulk. Intuitively, one would expect that if the effective potential for the electron extends over several atomic sites, the polarizability and nonlinear optical coefficients might be larger. Indeed, the largest NLO coefficients have been found for semiconductors and unsaturated extended organic molecules both of which have highly delocalized electrons (2).

If the electronic coupling between local clusters of atoms is relatively weak, the bulk polarizabilities can be treated as a simple sum of the localized oscillators in each cluster. If the coupling is strong, a band structure approach should be used. A non-local polarization response must be considered in long conjugated chain compounds, semiconductors, or groups of small clusters that are spatially separated but electronically coupled via resonance tunnelling or similar phenomena. The intermediate situation, the interface between extended and molecular materials, is studied intensely since semiconductor clusters in this regime show unusual NLO behavior. At some point, as polarization dimensions increase, there is a transition from atomic or molecular linear and nonlinear polarizabilities to bulk susceptibilities.

Second-Order Nonlinear Polarization of Matter and Second-Order NLO Effects

Frequency Doubling and Sum-Frequency Generation. A static or oscillating electric field can induce polarization of the electronic distribution, but what has this to do with observable nonlinear optical properties? Earlier, we showed that the induced electronic charge displacement (polarization) by an oscillating electric field (e.g. light) can be viewed as a classical oscillating dipole that itself emits radiation at the frequency of oscillation. For linear first-order polarization, the radiation has the same frequency as the incident light. What is the frequency of this reemitted light for a nonlinear optical material? Recalling that the electric field of a plane light wave can be expressed as

$$\mathbf{E} = \mathbf{E_0} \cos(\omega t) \qquad (21)$$

so that for an arbitrary point in space the polarization (equation 20) can be rewritten as:

$$P = P_0 + \chi^{(1)} E_0 \cos(\omega t) + \chi^{(2)} E_0^2 \cos^2(\omega t) + \chi^{(3)} E_0^3 \cos^3(\omega t) + \ldots \quad (22)$$

Since $\cos^2(\omega t)$ equals $1/2 + 1/2 \cos(2\omega t)$, the first three terms of equation 22 could be written:

$$P = (P_0 + 1/2 \chi^{(2)} E_0^2) + \chi^{(1)} E_0 \cos(\omega t) + 1/2 \chi^{(2)} E_0^2 \cos(2\omega t) + \ldots (23)$$

Physically, equation 23 tells us the polarization consists of a second-order DC field contribution to the static polarization (first term), a frequency component w corresponding to the incident light frequency (second term) and a new frequency doubling component, 2ω (third term) (see Figure 15).

Thus, if an intense light beam passes through a second-order nonlinear optical molecule, light at twice the input frequency will be produced as well as a static electric field. The first process is called second harmonic generation (SHG) and the second is called optical rectification. Frequency mixing of this type is referred to as a three wave mixing process, since two photons with frequency ω have combined to generate a single photon with frequency 2ω. Since the nonlinear oscillating dipole re-emits at all its polarization frequencies, we will observe light at both ω and 2ω. We can extend this analysis could be extended to third- and higher-order terms. By analogy, third-order processes will involve four wave mixing.

As written, equation 22 depicts a simplified picture in which a single field, $E(\omega,t)$ acts on the material. The general picture of second-order NLO involves the interaction of two distinct waves with electric fields E_1 and E_2 with the electrons of the NLO material. Suppose for example that we use two laser beams with different frequencies. The second-order term of equation 23 with two interacting waves of amplitudes E_1 and E_2 at an arbitrary point in space becomes:

$$\chi^{(2)} \cdot E_1 \cos(\omega_1 t) E_2 \cos(\omega_2 t) \tag{24}$$

Trigonometry tells us that:

$$\chi^{(2)} E_1 \cos(\omega_1 t) E_2 \cos(\omega_2 t) =$$
$$1/2 \chi^{(2)} E_1 E_2 \cos[(\omega_1 + \omega_2)t] + 1/2 \chi^{(2)} E_1 E_2 \cos[(\omega_1 - \omega_2)t] \tag{25}$$

This equation shows that when two light beams of frequencies ω_1 and ω_2 interact with the atom(s) in the NLO material, polarization occurs at sum $(\omega_1 + \omega_2)$ and difference $(\omega_1 - \omega_2)$ frequencies. This electronic polarization will therefore, re-emit radiation at these frequencies, with contributions that depend on the relative magnitudes of the NLO coefficient, $\chi^{(2)}$. This combination of frequencies leads to sum frequency generation (SFG).

Phase-matching. To combine polarization waves efficiently, conditions must be met so that the fundamental and the second harmonic light waves reenforce each other. If this requirement is met, then the second harmonic intensity will build as the light propagates throughout the crystal. If this condition is not met, a periodic oscillation of second harmonic intensity occurs as the light travels through the crystal. Therefore, the refractive indices experienced by the interacting waves as they propagate through the medium must match, that is $\eta(\omega) = \eta(2\omega)$, to achieve efficient SHG.

As noted before, the polarizability of a material is frequency dependent so that the wave surfaces are frequency dependent. If one of the wave surfaces at the second harmonic frequency intersects one of the wave surfaces at the fundamental frequency, phase-matched SHG can occur. The ray passing through the origin of the ellipsoids and their point of intersection defines the direction of propagation for phased-matched SHG.

Two types of phase-matching exist for SHG: Type I, where the two fundamental photons are of the same polarization, and Type II, where they are orthogonally polarized. The phase- matching direction and one of the principal vibration directions of the crystal may be coincident in biaxial and uniaxial (birefringent) crystals. This situation, called noncritical phase-matching, is quite

tolerant of the divergence of the incident beam from the most efficient phase-matching direction and hence is highly desirable. Alternatively, a propagation direction might be found in which the ordinary index at the fundamental frequency n_o (ω) is equal to the extraordinary index at the second harmonic frequency $n_E(2\omega)$.

Efficient SHG also requires a large projection of the β tensor along the phase-matching direction. Therefore molecules or atoms within the NLO material must be properly oriented to give the most efficient SHG response. It is generally believed that single crystals, or polymeric thin films doped with NLO chromophores which have been aligned by poling, are the most promising materials for phase-matched SHG. The phase-matching ability is a particularly critical property for the figure of merit for an NLO material (refer to D. J. Williams's tutorial and S. P. Velsko's article for further discussions of phase-matching). Fabrication of high optical quality single crystals or composites with proper phase-matching properties is often the bottleneck in the search for new second-order NLO materials.

In addition to sum-frequency generation (SFG), another important NLO property is optical parametric oscillation (OPO), the inverse of the SFG process. Pump photons decay into signal and idler photons such that $\omega_p = \omega_s + \omega_i$. The frequencies ω_s and ω_i are determined by the phase-matching condition, and output tuning is accomplished by altering the refractive indices experienced by ω_p, ω_s and ω_i. For oscillation to occur, ω_s and ω_i must change so that the pump and output beams phase-match. The phase-matching condition may be altered by changing the incident angle, temperature, or by applying an external potential (electrooptic tuning) as in the Pockels Effect.

Changing the Propagation Characteristics of Light: The Pockels Effect.
As noted above, refractive indices for different frequencies are usually not the same. Furthermore it is possible to change the amplitude, phase, or path of light at a given frequency by using a static DC electric field to polarize the material and modify the refractive indices.

Consider the special case $\omega_2 = 0$ (equation 24) in which a DC electric field is applied to the crystal. The optical frequency polarization (P_{opt}) arising from the second-order susceptibility is

$$\chi^{(2)}E_1E_2(\cos \omega_1 t) \tag{26}$$

where E_2 is the magnitude of the voltage applied to the nonlinear material. Remember that the refractive index is related to the linear susceptibility (equation 15), that is, given by the second term of equation 23

$$\chi^{(1)}E_1(\cos \omega_1 t) \tag{27}$$

so that the total optical frequency polarization becomes

$$P_{opt} = \chi^{(1)}E_1(\cos \omega_1 t) + \chi^{(2)}E_1E_2(\cos \omega_1 t) \tag{28}$$

$$P_{opt} = [\chi^{(1)} + \chi^{(2)}E_2] \; E_1(\cos \omega_1 t) \tag{29}$$

The applied voltage in effect changes the linear susceptibility and thus the refractive index of the material. This effect, known as the linear electrooptic (LEO) or Pockels effect, modulates light as a function of applied voltage. At the atomic level, the applied voltage is anisotropically distorting the electron density within the material. Thus, application of a voltage to the material causes the optical beam to "see" a different

material with a different polarizability and a different anisotropy of the polarizability than in the absence of the voltage. Since the anisotropy changes upon application of an electric field, a beam of plane polarized light will (1) have its plane of polarization rotated by an amount related to the strength and orientation of the applied voltage and (2) travel at a different velocity and possibly in a different direction.

Quantitatively, the change in the refractive index as a function of the applied electric field is given by the general expression:

$$1/\underline{n}_{ij}^2 = 1/n_{ij}^2 + r_{ijk}E_k + s_{ijkl}E_kE_l + ... \qquad (30)$$

where $\underline{n}_{ij}$ = the induced refractive indices, n_{ij} = the refractive index in the absence of the electric field, r_{ijk} = the linear or Pockels coefficients, and s_{ijkl} = the quadratic or Kerr coefficients. The optical indicatrix, therefore, changes as the electric field within the sample changes (Figure 16). Electrooptic coefficients are frequently defined in terms of r_{ijk} (5). The "r" coefficient is a tensor (just as is α). The first subscript refers to the resultant polarization of the material along a defined axis and following subscripts refer to the orientations of the applied electric fields. Since the Pockels effect involves two fields mixing to give rise to a third, r_{ijk} is a third rank tensor.

The LEO effect has many important technological applications. Light travelling through an electrooptic material can be modulated by refractive index changes induced by an applied electric field (Pockels effect). Devices exploiting this effect include optical switches, modulators, and wavelength filters. Modulators include the phase modulator that shifts the optical phase by altering an applied voltage, and the Mach-Zehnder intensity modulator. In the latter, the incoming field component is split between two waveguide "arms," where an applied voltage induces a relative phase shift between the optical paths, which results in either constructive or destructive interference upon recombination of the two beams (Figure 17).

Comments on NLO and Electrooptic Coefficients. Typically, the Pockels effect is observed at relatively low frequencies (up to gigahertz) so that slower nonlinear polarization mechanisms, such as vibrational polarizations, can effectively contribute to the "r" coefficients. The tensor used traditionally by theorists to characterize the second-order nonlinear optical response is χ_{ijk}. Experimentalists use the coefficient d_{ijk} to describe second-order NLO effects. Usually the two are simply related by equation 31 (*16*):

$$d_{ijk} = 1/2\chi_{ijk} \qquad (31)$$

The "r" coefficient characterizes the low frequency electrooptic nonlinearity and the "d" coefficient the optical frequency nonlinearity. The conversion from "r" coefficients to "d" or "χ" coefficients must take into account the frequency dependence of the dielectric properties.

Thus, just as linear polarizabilities are frequency dependent, so are the nonlinear polarizabilities. Perhaps it is not surprising that most organic materials, with almost exclusively electronic nonlinear optical polarization, have similar efficiencies for SHG and the LEO effect. In contrast, inorganic materials, such as lithium niobate, in which there is a substantial vibrational component to the nonlinear polarization, are substantially more efficient for the LEO effect than for SHG.

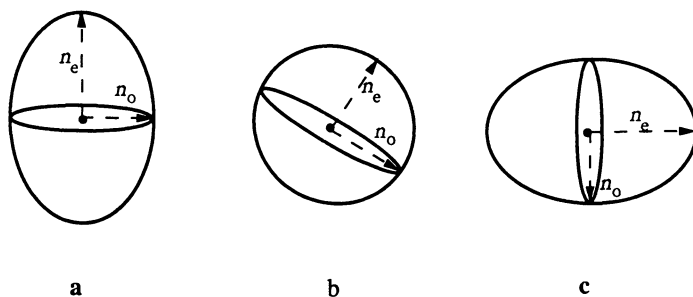a   b   c

Figure 16. Index ellipsoid of an anisotropic material (a) in the absence of an applied field, (b) in a medium field, and (c) in a strong field.
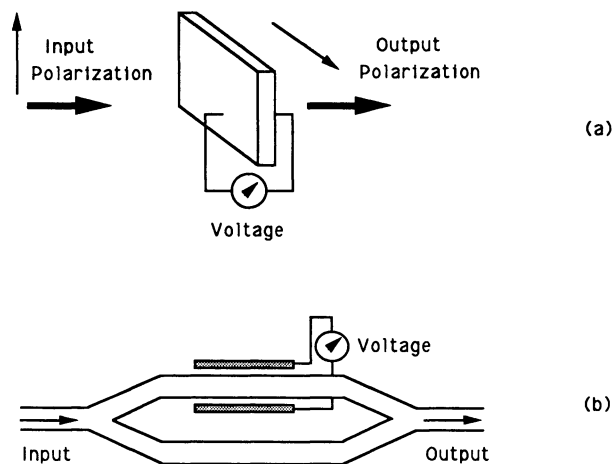

Figure 17. (a) Transverse electrooptic modulator that rotates polarization of an incoming light beam as a function of applied electric field and (b) a travelling Mach-Zehnder interferometer that introduces a phase shift to the light beam in one arm as a function of applied field.

Third-Order Nonlinear Polarization of Matter and Third-Order NLO Effects

Second-order optical nonlinearities result from introduction of a cubic term in the potential function for the electron, and third-order optical nonlinearities result from introduction of a quartic term (Figure 18). Two important points relate to the symmetry of this perturbation. First, while negative and positive β both give rise to the same potential and therefore the same physical effects (the only difference being the orientation of the coordinate system), a negative γ will lead to a different electron potential than will a positive γ. Second, the quartic perturbation has mirror symmetry with respect to a distortion coordinate; as a result, both centrosymmetric and noncentrosymmetric materials will exhibit third-order optical nonlinearities. If we reconsider equation 23 for the expansion of polarization of a molecule as a function of electric field and assume that the even-order terms are zero (i.e., that the molecule is centrosymmetric), we see that polarization at a given point in space is:

$$\mu = \mu_0 + \alpha E_0 \cos(\omega t) + \gamma/6 \, E_0^3 \cos^3(\omega t) + \ldots \tag{32}$$

If a single field, $E(\omega)$, is acting on the material, trigonometry reveals:

$$\gamma/6 \, E_0^3 \cos^3(\omega t) = \gamma/6 \, E_0^3 [3/4 \cos(\omega t) + 1/4 \cos(3\omega t)] \tag{33}$$

thus,

$$\mu = \mu_0 + \alpha E_0 \cos(\omega t) + (\gamma/8) \, E_0^3 \cos(\omega t) + (\gamma/24) \, E_0^3 \cos(3\omega t) \tag{34}$$

or:

$$\mu = \mu_0 + [\alpha + (\gamma/8) \, E_0^2] E_0 \cos(\omega t) + (\gamma/24) \, E_0^3 \cos(3\omega t) \tag{35}$$

The above equation states that the interaction of an intense beam with a third-order NLO material will create an electric field component at the third harmonic. In addition, there is an electric field component at the fundamental frequency, and we note that the $[\alpha + (\gamma/8) \, E_0^2]$ term of equation 35 is similar to the term leading to the linear electrooptic effect. Likewise, the application of an intense voltage will also induce a refractive index change in a third-order NLO material. These two effects are known as the optical and DC Kerr effects, respectively. The sign of gamma will determine if the third-order contribution to the refractive index is positive or negative in sign. Materials with positive gamma are called self focusing; those with negative gamma are known as self defocusing.

Degenerate four wave mixing is another interesting manifestation of third-order NLO materials. Two beams of light interacting within a material will create an interference pattern (Figure 19) that will lead to a spatially periodic variation in light intensity across the material. As previously noted, the induced change in refractive index of a third-order nonlinear optical material is proportional to the magnitude of the applied field. Thus if the beams are interacting with a third-order NLO material, the result will be an index of refraction grating. When a third beam is incident on this grating a new beam of light, called the phase conjugate beam, is diffracted from the grating. In short, three beams (two writing beams and one probe beam) create a fourth beam, i.e. four-wave mixing. A potential use of this phenomena is in phase conjugate optics, which takes advantage of a special feature of the diffracted beam: its path
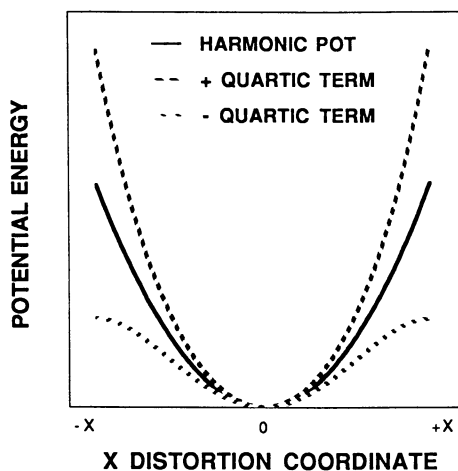
Figure 18. Plot of potential energy vs. distortion coordinate for a material with a harmonic potential and a material with positive and negative quartic anharmonic terms.
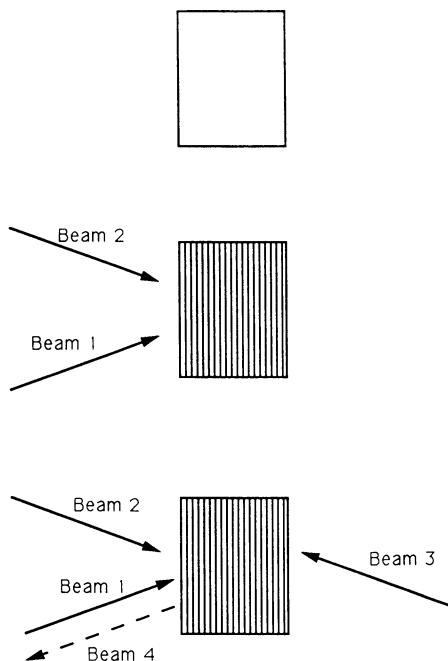

Figure 19. Top: A phase conjugate material in the absence of an applied field. Middle: Beams 1 and 2 create a refractive index grating. Bottom: Beam 3 interacts with the grating creating beam 4 that is the *phase conjugate* of beam 1.

exactly retraces the path of one of the writing beams. As a result, a pair of diverging beams "reflected" from a phase conjugate mirror will converge rather than diverge as from an ordinary mirror (Figure 20). This remarkable property means that distorted optical images can be reconstructed using phase conjugate optical systems (Figure 21).

Issues Relating to Nonlinear Optical Materials

A chemist attempting to design NLO materials is confronted with a variety of questions. Is the goal to map out structure/property relationships that will improve fundamental understanding of NLO phenomena or is it to fulfil requirements for a particular device application? These important goals have different challenges associated with them. We shall provide a brief introduction relating chemical structure to linear and nonlinear polarizability, then end with some comments relating to device issues.

Systematic studies of well-defined materials in which specific structural variations have been made, provide the basis for structure/property relationships. These variations may include the effect of charge, hybridization, delocalization length, defect sites, quantum confinement and anharmonicity (symmetric and asymmetric). However, since NLO effects have their origins in small perturbations of ground-state electron density distributions, correlations of NLO properties with only the ground state properties leads to an incomplete understanding of the phenomena. One must also consider the various *excited-state* electron density distributions and transitions.

It is necessary to understand how a structural change affects the variable to be studied. If possible the structural variation should have only a small effect on other variables. In addition, remember that results are not only sensitive to the material used in the study, but also to the method of measurement. It is often meaningless to compare measurements by different techniques or at different frequencies. The tutorials that follow, in particular the tutorial by J. Perry on characterization techniques, will provide the reader with some insight into these issues.

How does one engineer linear and nonlinear polarizability? If this were fully understood, this book would not exist. As chemists we bring some intuitive understanding of what factors affect polarizability. For example, the organic chemist knows that the electrons in polyacetylene are more polarizable than those in butane. Likewise, the inorganic chemist knows that semiconductors are more polarizable than insulators. These simple observations suggest that the extent of electron delocalization is related to the linear polarizability. In organic molecules the extent of delocalization is affected by the hybridization, degree of coupling, and number of orbitals (and electrons) in the electronic system of interest. We also see that molecules/materials with strong, low-energy, absorption bands tend to be highly polarizable. The linear polarizability derived from perturbation theory

$$\alpha \quad \sim \quad \sum_{\substack{\text{excited} \\ \text{states}}} \langle g|\mu|e\rangle^2/E_{ge} \tag{36}$$

is in accord with these observations. Therefore, it is not surprising that cyanine dyes and semiconductors with their large oscillator strengths and small HOMO–LUMO gaps are highly polarizable.

For second-order nonlinear polarization, the problem becomes more complex. As can be seen in Figure 13 the anharmonic polarization shows the largest deviation from the linear polarization with large distortion values. Therefore, if the material is not polarizable (i.e., if the electrons can only be perturbed a small distance from their equilibrium positions), then the anharmonicity will not be manifested. For large second-order nonlinearities we need a material that offers both a large linear
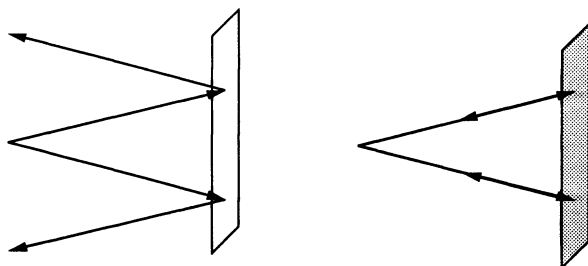
Figure 20. Left: A diverging set of beams reflected off of a normal mirror continue to diverge. Right: A diverging set of beams reflected off of a phase conjugate mirror exactly retrace their original path and are therefore recombined at their point of origin.
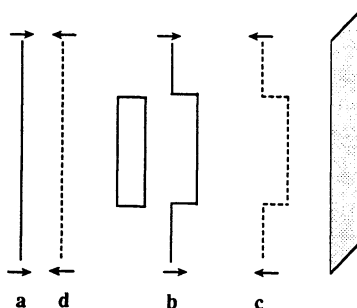

a   d   b   c

Figure 21. (a) A planar wave (b) passes through a distorting material that introduces an aberration and (c) the material interacts with a phase conjugate mirror creating the phase conjugate image. (d) When the phase conjugate wave passes through the distorting material on the reverse path the original aberration is cancelled producing an undistorted image.

polarizability and a large anharmonicity. In organic donor-acceptor molecules, it is easier to polarize the electrons toward the acceptor than towards the donor. Thus these systems have an asymmetric anharmonic term and not surprisingly organic donor acceptor molecules have some of the largest known values of β. It is not sufficient for a molecule to have a large β. In order to observe second-order NLO effects the bulk material must also be non- centrosymmetric. As noted before, the molecules must be oriented in a manner that optimizes the phase-matching of the fundamental and sum frequencies. Since ~75% of all non-chiral molecules crystallize in centrosymmetric space groups and thus have vanishing $\chi^{(2)}$, proper alignment of the chromophore in the bulk material is a major impediment to achieving the goal of engineering a material with a large $\chi^{(2)}$. The electronic driving force for crystallization in a centrosymmetric space group is the cancellation of destabilizing dipole-dipole interactions between adjacent molecules in the crystal lattice. Several approaches have been tried with varying degrees of success to overcome this obstacle (see tutorials by D. Williams and D. Eaton).

The structure/property relationships that govern third-order NLO polarization are not well understood. Like second-order effects, third-order effects seem to scale with the linear polarizability. As a result, most research to date has been on highly polarizable molecules and materials such as polyacetylene, polythiophene and various semiconductors. To optimize third- order NLO response, a quartic, anharmonic term must be introduced into the electronic potential of the material. However, an understanding of the relationship between chemical structure and quartic anharmonicity must also be developed. Tutorials by P. Prasad and D. Eaton discuss some of the issues relating to third-order NLO materials.

The synthesis of materials for device applications has very different requirements. Here, the most important questions are: What does the device do and what factors will affect its performance? The magnitude of the desired optical nonlinearity will always be one of many criteria that will ultimately dictate the material of choice. In many instances the magnitude of the nonlinearity will not be the most important parameter. Depending on the device applications, other considerations such as optical transparency, processability, one- and two-photon optical stability, thermal stability, orientational stability, and speed of nonlinear response will all be important. Our current understanding of NLO materials suggests that these variables are frequently interrelated and that there is often no ideal NLO material. The material of preference for a given application will typically be one that is the best compromise for a variety of variables. Tutorials by G. Stegeman and R. Zanoni, and by R. Lytel outline some of the NLO device applications and the related materials issues.

Many challenging materials issues addressable by chemists currently exist. Chemists bring to the field a chemical understanding of materials that physicists and engineers do not have. Chemists form the bridge between theoretical models for nonlinear polarizability and real NLO materials. As a result, they have an excellent opportunity to make a large, positive, impact on the field of nonlinear optics.

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