Nonlinear Optical Materials

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The current state of materials development in nonlinear optics is summarized, and the promise of these materials is critically evaluated. Properties and important materials constants of current commercial materials and of new, promising, inorganic and organic molecular and polymeric materials with potential in second- and third-order nonlinear optical applications are presented.

THE MORE COMMONLY EXPERIENCED INTERACTIONS OF light with matter, such as refraction, reflection, and diffraction, occur in the linear domain. That is to say, the magnitude of the observed effect changes linearly with light intensity. Light absorption and photochemical events such as plant and bacterial photosynthesis can also be described as one-photon linear events. Most optical nonlinear responses were not demonstrated until the advent of the laser, as a direct consequence of the extremely high photon fluences that can be obtained under laser irradiation. Nonlinear optics (NLO) is the study of the interaction of intense electromagnetic fields with materials to produce modified fields that are different from the input field in phase, frequency, or amplitude.

Some nonlinear optical processes are familiar to physicists, chemists, and other scientists because they are in common use in our laboratories. Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. The process occurs within a nonlinear medium, usually a crystal. Such frequency-doubling processes are commonly used to produce green light (532 nm) from, for example, a Nd-YAG (yttrium-aluminum-garnet) laser operating at 1.06 μm (Fig. 1). However, nonlinear processes will also be useful in optical communications and signal processing, laser medicine, parallel image processing, and the emerging field of integrated optics. The search for new and efficient materials in which to carry out nonlinear optical processes has been an active one since SHG was first observed in single-crystal quartz by Franken and co-workers (*1*) in 1961. These early workers frequency-doubled the output of a ruby laser (694.3 nm) into the ultraviolet (347.15 nm) with a conversion efficiency of only about 10^{-4} percent in their best experiments, but the ground had been broken. Remarkably rapid progress has been made during the past 5 years. This review presents the current state of the art in materials design for NLO.

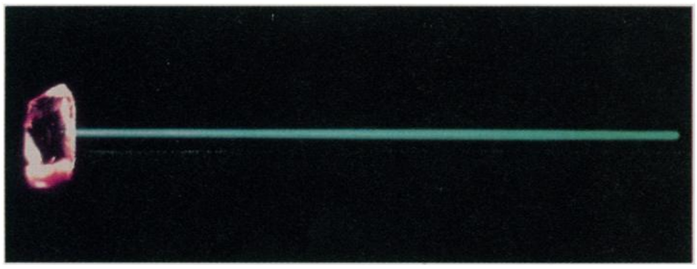

Fig. 1. Second harmonic generation of green light (532 nm) from near-infrared (1.06 μm) light in a potassium titanyl phosphate crystal.

Polarization in intense electric or electromagnetic fields can be described both at the molecular level and in the bulk. Molecular polarization is described by the field-dependent molecular dipole moment expansion,

$$\mu = \mu_0 + \alpha \cdot \mathbf{E} + \beta \cdot \mathbf{E} \cdot \mathbf{E} + \gamma \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \ldots \quad (1)$$

in which μ_0 is the intrinsic dipole moment of the molecule and **E** is the electromagnetic field vector. The coefficients α, β, and γ are, respectively, the polarizability, hyperpolarizability, and the second hyperpolarizability constants of the molecule. They describe the responsivity of the molecule to electromagnetic perturbation. When molecules are condensed into the solid or liquid phase, the polarization of the ensemble must be described. The analogous Eq. 2 describes the bulk polarization of condensed matter, valid in the dipole approximation, where the expansion coefficients (χ) are now known as the first-, second-, and third-order susceptibilities, respectively, of the material:

$$\mathbf{P} = \mathbf{P}_0 + \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{E} \cdot \mathbf{E} + \chi^{(3)} \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \ldots \quad (2)$$

Many organic and inorganic materials are highly polarizable and thus are good candidates for study. However, because **E** is a vector, the net polarization of a material depends on its symmetry properties with respect to the orientation of the impinging fields. It can be shown (*2*) that the odd-order terms in Eqs. 1 and 2 are orientationally independent, but that the even terms vanish in a centrosymmetric environment. Thus, materials for second-order NLO must be orientationally noncentric to be functional. No such restriction applies to third-order materials.

After the discovery of SHG in quartz, other NLO effects were rapidly discovered (*3*). Parametric amplification was observed in lithium niobate ($LiNbO_3$) by two-wave mixing in temperature-tuned single crystals in 1965 (*4*). The first observation of SHG in an organic material (benzpyrene) was made in 1965 by Rentzepis and Pao (*5*).

At the end of the 1960s, the Kurtz and Perry powder SHG method was introduced (*6*). In this method, a powdered sample is irradiated with a laser and scattered light is collected and analyzed for its harmonic content with the use of suitable filters. For the first time, rapid, qualitative screening for second-order NLO effects was possible. The stage was set for a rapid introduction of new materials, both inorganic and organic. Early NLO history is chronicled more extensively by Zyss and Chemla (*7*).

A variety of reviews and monographs have been published during

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the last 5 years. These report on various aspects of NLO theory, practice, and materials properties (*8–14*).

Materials for Linear Optics Applications

In order to apply NLO in practice, light must first interact with the NLO material. In laboratory experiments, free space interconnections are usually used for this purpose. That is, lenses and mirrors are used to direct the beam to the material under study. In any practical use of NLO, such simplistic solutions will not be possible, for reasons both of safety and rugged construction of the device. Light will need to be moved around in space within the device. In many second-order devices, whether they are color-specific lasers such as doubled diode or YAG lasers or electro-optic (EO) modulators such as spatial light modulators (SLMs), waveguide or fiber optic connections will be used. In other integrated optics applications, beam steering can be accomplished with holographic optical elements (HOEs). Holograms of this type are produced by spatially modulating the optical index of refraction of a material. Tomlinson and Chandross have reviewed early efforts in this area (*15*). Some materials systems are now commercial. Du Pont (*16*) and Polaroid (*17*) have developed holographic imaging systems based on photopolymerization, in which the optical index is altered through loss of double bonds during a radical-initiated cross-linking. Because these systems form volume-phase holograms, high diffraction efficiencies are possible, and both transmission and reflection holographic modes can be used. Holograms can also be formed in a variety of inorganic materials, especially silver halide (AgX) photographic films selectively cross-linked with dichromate reagents. These systems generally operate by modulating the absorption of the film rather than the refractive index, so their diffraction efficiency is lower. Similarly, a variety of photochromic materials (both organic and inorganic) can be used to form amplitude-modulated HOEs (*15*).

The function of the HOE is not simply to move light around in a two-dimensional plane (that is, to function as a waveguide). HOEs can also function as focusing devices (lenses) or frequency splitters (diffraction gratings), which demultiplex frequency-mixed signals, or as other Fourier optical devices. Such functions will be critical to the eventual manufacture of efficient and small optical devices and signal processing elements.

Second-Order Materials

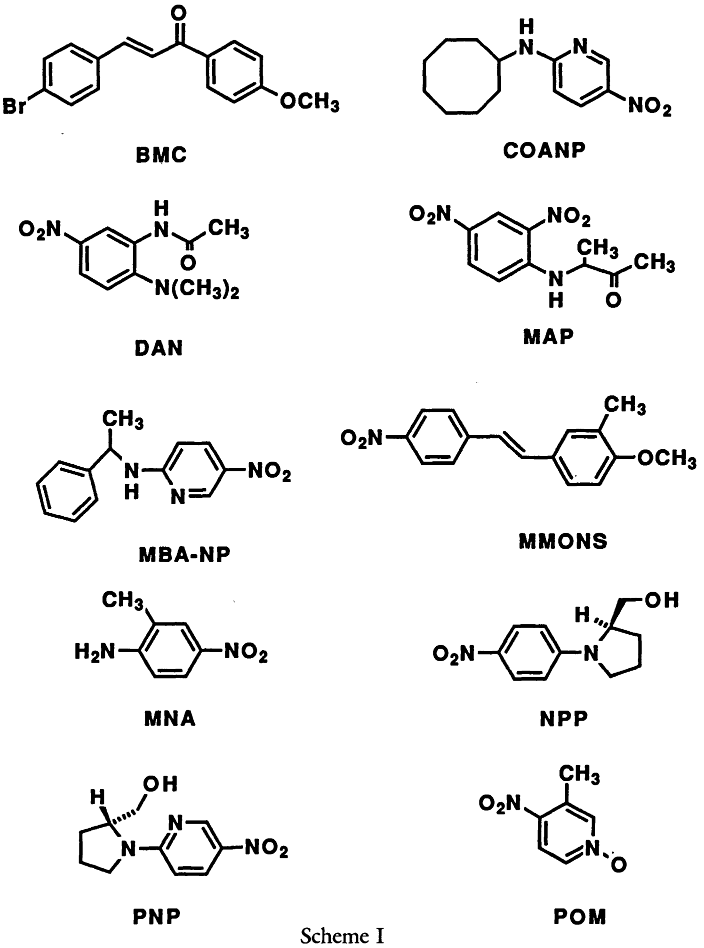
Second-order materials will be used in optical switching (modulation), frequency conversion (SHG, wave mixing), and electro-optic applications, especially in EO modulators (a class of spatial light modulators, SLM). All of these applications rely on the manifestation of the molecular β of the material (the hyperpolarizability) and either the optical coefficients of nonlinearity ($\mathbf{d}_{ijk}$) or the electro-optic coefficient ($\mathbf{r}_{ijk}$). These are the tensor elements that describe the expression of the second-order susceptibility, $\chi^{(2)}$, of the bulk material. Materials will be used as single crystals or as thin polycrystalline films or will be dispersed in polymers and oriented in strong electric fields to provide an acentric environment, in which $\chi^{(2)}$ is nonvanishing by symmetry. Recently, the use of pure, organic glass-forming materials has also been demonstrated (*18*).

Inorganic materials are much more mature in their application to second-order NLO than are organics. Most commercial materials are inorganic, especially for high power use. However, organic materials are perceived as being structurally more diverse and therefore are believed to have more long-term promise than inorganics.

Organic materials. Although most SHG materials are ultimately referenced to quartz (*1*), urea is a common powder standard used in the Kurtz-Perry testing protocol. Urea (*19*) has a molecular β of $\sim 0.5 \times 10^{-30}$ esu, determined at 1.06 μm by EFISH (electric field–induced second harmonic generation). Powder SHG intensities are nearly 400 times the value of quartz. The tetragonal crystal, space group $P\bar{4}2_1m$, is of the point group $\bar{4}2m$, which lacks a center of symmetry. The crystal packing is not especially favorable for SHG (*20*). The nonlinear coefficient of urea is estimated to be 1.4 pm/V (*21*). Urea is a useful NLO material because of its high optical transparency (to 200 nm), its high damage threshold (1 to 5 GW/cm^2) in single-shot applications, and its high birefringence that makes phase matching possible (*21*). It is, however, difficult to grow, and it is mechanically soft and hygroscopic. It was the first organic material in which optical parametric amplification was demonstrated, it can be phase-matched to 238 nm, and it is a superior organic for SHG into the ultraviolet.

A wide variety of organic materials are touted for frequency doubling. Table 1 lists the properties of organic materials that have been studied as single crystals. Scheme I shows structures of the materials listed in Table 1. Each is briefly described below.

4-Bromo-4′-methoxychalcone (BMC) (*22*) is a monoclinic, yellow material, with total transparency from about 420 nm to near 2 μm, although the absorption is anisotropic. Powder SHG values depend on the solvent from which the material is crystallized. 2-*N*-cyclooctylamino-5-nitropyridine (COANP) (*23*) is a yellow, orthorhombic crystal, transparent from about 470 nm to 1.6 μm. Crystals are grown from either ethyl acetate or acetonitrile by gradient mass transport methods to give plates of about 10 by 5 mm^2 and several millimeters thick. 4-(*N*,-*N*-dimethylamino-3-acet-



Scheme I

Table 1. Properties of selected organic NLO crystals. See Scheme I for structures.

Compound	β*	SHG†	Space group	Point group	*d* Coefficients	Cut-off‡	FOM§
BMC		10–70	*Pc*	*m*	$d_{13} \sim 90$	420	
COANP		50	$Pca2_1$	*mm*2	$d_{32} \sim 32$ $d_{31} \sim 15$ $d_{33} \sim 14$	470	100
DAN	36‖	115	$P2_1$	2	$d_{\mathrm{eff}} \sim 27$	~500	420
MAP	22	~5	$P2_1$	2	$d_{21} \sim 17$ $d_{22} \sim 18$ $d_{23} \sim 4$	~500	
MBA-NP		25	$P2_1$	2	$d_{22} \sim 28$	430	
MMONS	18 26¶	750–1250	*Aba*2	*mm*2	$d_{33} \sim 140$ $d_{32} \sim 34$ $d_{24} \sim 82$	510	850
MNA	16 9.5¶	22	I*a*	*m*	$d_{11} \sim 67$	500	
NPP	45‖	50–150	$P2_1$	2	$d_{21} \sim 84$ $d_{22} \sim 29$	500	
PNP		140	$P2_1$	2	$d_{21} \sim 48$ $d_{22} \sim 17$	470	
POM	8.5	13	$P2_12_12_1$	222	$d_{25} \sim 10$	450	

*In esu × 10^{30} at 1.06 μm unless noted. †Powder SHG versus urea. ‡Long wavelength cutoff in nanometers. §Figure of merit, d_{eff}^2/n^3, in $(\mathrm{pm/V})^2$. ‖From (*94*). ¶At 1.9 μm.

amidonitrobenzene (DAN) (*24*) is a monoclinic crystal. Melt growth techniques are used to produce crystals 10 by 5 by 2 mm^3.

2,4-Dinitrophenyl-(L)-alanine methyl ester (MAP) (*25, 26*) is a comparatively older material that crystallizes on slow cooling from ~34% ethyl acetate–hexane solutions over about 3 weeks as ~0.2-cm^3 monoclinic crystals. The yellow-orange crystals are transparent from about 500 nm to 2.0 μm. At 1.06 μm, laser damage occurred at fluences of ~3 $\mathrm{GW/cm}^2$ for 10-ns pulses. The nitropyridine derivative MBA-NP [(−)-2-(α-methylbenzylamino)-5-nitropyridine) (*26, 27*) is a chiral molecule that crystallizes in the monoclinic form. It is very pale yellow and is transparent from 430 nm into the infrared at 1.8 μm. Damage thresholds near 1 $\mathrm{GW/cm}^2$ are quoted at 1.06 μm. Excellent crystals (up to 7 by 5 by 5 cm^3) of this material are reported to grow from methanol by slow cooling.

3-Methyl-4-methoxy-4′-nitrostilbene (MMONS) (*28*) has the highest reported powder SHG value (1250 times that of urea) among simple stilbene derivatives, but its measured β value is relatively modest, 18 to 26 × 10^{-30} esu (dependent on the wavelength of measurement). The powder SHG value observed depends strongly on the solvent from which it is crystallized. It has been fully characterized for SHG (*29*). Conversion efficiencies (defined as d_{eff}^2/n^3, where d_{eff} is the effective *d* coefficient and *n* is the index of refraction) are 120 times that of KTP (potassium titanyl phosphate, see below); however, its use is limited because of large walkoff, that is, large divergence of the fundamental and second harmonic beams due to dispersion of the index of refraction within the crystal. Crystals larger than 1 cm^3 can be grown from chloroform-ethanol solutions by slow evaporation or by slow cooling. The FOM listed in Table 1 is the highest reported to date for a single-crystal organic material. The electro-optic coefficients have also been determined (for example, $r_{33} = 40$ pm/V, where the subscripts are specific tensor elements for r_{ij}). The extreme ease of crystal growth of MMONS may spur a search for other uses.

2-Methyl-4-nitroaniline (MNA) (*30–32*) is another mature material that has been available since 1975 in Russia and slightly later in the United States. The material played a historical role in helping to establish the connection between molecular charge transfer and enhanced hyperpolarizability. It is monoclinic, with a melting point of 131°C. At 1.06 μm, the yellow crystals have an absorption coefficient of about 1 cm^{-1}. The measured electro-optic coefficient is ~270 pm/V. Unfortunately the material is very difficult to grow in bulk form, although thin films have been grown from the melt. NPP [*N*-(4-nitrophenyl)-(*S*)-prolinol] (*33*) is the levorotatory isomer of this chiral nitroaniline analog. It is monoclinic, and crystals are grown from the melt by Bridgman methods. Femtosecond frequency conversion has been demonstrated in thin plates of NPP.

2-(*N*-(*S*)-prolinol)-5-nitropyridine (PNP) is another prolinol derivative, but in the nitropyridine family (*27*). Crystals 0.5 cm^3 in size result by slow cooling in methanol-water solutions. 3-Methyl-4-nitropyridine-*N*-oxide (POM) (*34*) is the only commercially available organic crystal for SHG, other than urea. POM crystals about 1 cm^3 in size are formed by solution growth from a variety of solvents. It has been very thoroughly characterized. Damage thresholds are reported to be ~1 $\mathrm{GW/cm}^2$ for nanosecond pulses of 1.064-μm light.

Many other organic and some organometallic materials have been examined by the powder SHG method or tested by EFISH techniques, or both. They will not be discussed here, but many of these newer materials could easily supplant those that have been more thoroughly characterized to date. Several compendia of materials responses have been published (*35–37*). The largest single class of second-order organics consists of donor-acceptor substituted aromatics, because these allow highly polarized charge distributions to be established. The class has been extended to stilbenes, diarylacetylenes, diacetylenes, and biaryls. Many acceptor moieties have been described other than the now-classic nitro group. A variety of salts, especially pyridinium ions, can function as acceptors. Fulvenes, dicyano- or tricyanovinyl groups, sulfones, enone, or imine (Schiff base) functionalities can also be used. Donors other than the simple but effective amino or dimethylamino group are suitable. Various heterocyclic groups have been used as donor groups: oxazole, dithiafulvene, and dihydropyrazole.

In addition, various specific classes of molecules have proved to be of special interest. Amino acids are naturally occurring chiral species, some of which show NLO activity (*38*). Intermolecular interactions in halocyano substituted benzenes result in favorable crystal structures and make this class of aromatics attractive (*39*). A growing number of organometallic compounds have been demonstrated to have good SHG powder intensities (*40, 41*). Metal-pyridine and -bipyridine complexes are effective for SHG (*42*). In zero valent Pd and Pt compounds (*43*) it was shown that the group $(R_3P)_3M$–, M = Pt or Pd, is a mimic for methoxy as a donor in donor-acceptor aromatics, just as the ferrocene group can also be used as a donor (*44*). The hyperpolarizability of metalloarene and other metal complexes has been demonstrated by incorporation of the complex as a guest into an inclusion host to provide polar orientation and thus SHG capability (*45, 46*).

Polymeric and thin film organic materials. Second-order NLO applications that require crystalline materials limit the scope of molecular types that can be used to those that crystallize in acentric space groups. Various strategies have been reported to engineer molecules into acentric arrangements so that bulk second-order susceptibility can be usefully expressed. Chiral auxiliaries can be used to break centers of symmetry. Functional groups can be introduced into a basic nonlinear optiphoric structure to encourage formation of acentric crystals through intermolecular forces. Several organic (*45–49*) or inorganic (*50*) guest-host inclusion complexation paradigms can be used to orient a guest in a polar fashion in three-dimensional space, but the most widely practiced method of inducing polar alignment is the poled polymer approach (*51, 52*). In this method, polarizable guests (nonlinear optiphores) are dispersed in a thin polymeric medium, and orientation is effected by poling the film in a strong electric field while at temperatures above the glass transition temperature of the film. One can freeze "permanent" polar order into the structure by cooling the film while the orienting field is still present. Polymeric materials are attractive because they are compatible with manufacturing methods practiced in industry, and they can provide durability, environmental protection, and packaging advantages not provided by crystalline materials.

Several pure polymers have interesting $\chi^{(2)}$ properties, but the more attractive systems for potential application are doped molecular glasses. For example, a poly(ethylene) backbone containing *p*-nitroaniline side groups has been prepared with demonstrated SHG at $d_{\mathrm{eff}} = 31$ pm/V (*53*). The effect of chemically cross-linking a similar, but not chemically identical, system containing *p*-nitroaniline groups as the nonlinear optiphore has also been reported (*54*).

A new potential area for exploitation of SHG is pure organic glass-forming materials. A preliminary report of the first example in this class has recently appeared from IBM laboratories (*18*). Two initial examples were given. (*S*)-2-*N*-α-(methylbenzylamino)-5-nitropyridine (MBA-BP) and COANP both form glasses when cooled rapidly from above the melting temperature. If poling is conducted above the glass transition temperature, orientation is effected. Cooling freezes in polar order. Because no dilution effect occurs in pure glasses as it does in polymer host-guest glasses, this approach seems to offer promise of attaining high SHG levels.

Inorganic materials. Most of the commercial materials available for frequency conversion are inorganic. The merits of several inorganic second-order materials are compared in Table 2. Compared to organics, inorganics are generally more rugged, many allow anisotropic ion exchange which can be used to provide waveguide structures, and they have better purity in crystalline form than organics. For waveguide fabrication, it is easier to prepare thin films of inorganics than films of crystalline organics. Organics, however, have better dielectric constants and generally are easier to synthetically modify when an active class is found. The data in Table 2 are taken from a tabulation by Bierlein (*55*) and from one by Lin and Chen (*56*).

These inorganics represent the current workhorse materials of NLO. Because they are more advanced toward commercialization than organic materials, they will be difficult to displace, technologically, as new devices are developed. For many of the materials listed, commercial samples are available and the materials are used in research or commercial medical or graphic arts laser systems. For some of the materials, waveguide fabrication techniques have been developed and integrated optic devices have been fabricated. Bierlein and co-workers have shown that type I phase-matched SHG in the blue can be generated in KTP waveguide structures from infrared input at high efficiency (*57*). KTP has also been shown to be attractive for other applications such as optical frequency mixing (sum and difference mixing) (*58*) or, in electro-optics, for modulation of Q-switching (*59*).

Table 2. Properties of selected inorganic NLO crystals.

Compound	*d* Coefficients*	Damage (MW/cm^2) threshold†	Cutoff‡	FOM§
β-BaB_2O_4	$d_{11} = 4.1$	10,000	198	26
$Ba_2NaNb_5O_{15}$	$d_{31} = 32$	1	370	
KH_2PO_4	$d_{36} = 1$	500	200	1
LiB_3O_5	$d_{32} = 3.1$	2,000	165	~1
$LiNbO_3$	$d_{31} = 13$	20	400	
$LiIO_3$	$d_{31} = 10$	50	300	50
$KTiOPO_4$	$d_{31} = 15$	20,000	350	215
Urea	$d_{14} = 3$	5,000	210	6

*Relative to KDP as 1. The d_{36} coefficient is quoted as 0.39 pm/V in (*95*). †Damage thresholds are not absolute (experimental conditions can be different). ‡Short wavelength absorption cutoff in nanometers. §The figure of merit, relative to KDP, is a function of the *d* coefficient, the acceptance angle for phase matchability (Δθ), crystal length *L*, wavelength of input λ, field strength **E**, and material index of refraction: FOM ~ $(d^2/n^3)(\mathbf{E}L/\lambda^2)(\Delta\theta)^2$.

Third-Order Materials

Third-order NLO effects include the Kerr effect, optical bistability, optical phase conjugation, photorefractivity, and third harmonic generation (THG). Practical applications of these effects are in optical switching, amplification, beam steering and clean-up, and image processing. The promise of "optical computing" was stated early in the 1980s by several investigators (*60–62*). Digital, serial uses of optics for computation may not provide practical competition for conventional electronic devices for many years, if ever, but optical image processing (*63*) is a vigorous field and it has gained impetus as new materials and processes are discovered and invented. Today, no third-order material applications are practical because the nonlinearities observed to date are two to four orders of magnitude short of what will be required for commercial devices that use lasers of moderate power. New materials breakthroughs will be required before the promise can become reality.

The main components of an "optical computer" are light sources, beam-steering materials, and light modulators. Semiconducting lasers are judged to be the ultimate light source, although most prototype devices are demonstrated with other lasers. Beam-steering materials can be "fixed" (such as holographic optical elements) or "reconfigurable," that is, programmable. Reconfigurable holographic optical elements are known as photorefractives. They can be viewed as a class of phase-conjugate materials, although their actual physical mechanisms of action may not be identical. The time scale for the realization of the photorefractive effect is important: slow materials would be nearly permanent optical memories, whereas fast photorefractives with rapid decay would be transient, the optical equivalent of an electronic DRAM (dynamic random access memory). SLMs spatially modify the phase, amplitude, polarization, or intensity of light that passes through them. They thus have some properties similar to those of photorefractives, which can be used for modulation purposes. However, most SLMs today are electro-optic devices (liquid crystal light valves, optically addressed microchannel plate devices, electro-optic crystals, electrically actuated membranes or mirrors) which are relatively slow in operation (microseconds at the fastest). All-optical SLMs are desired but practically unknown.

No symmetry requirements exist to express third-order susceptibility, so all kinds of materials are potential candidates: liquids, thin films, glasses, and crystals. Eventually, practical considerations such as fabricability may become more important than the magnitude of the nonlinearity. Effects may be grossly classified as those that influence the local index of refraction (so-called n_2 effects) and those that influence the absorption of a material (resonant or photochromic effects). Under the action of either effect the presence of one light beam in a material influences the propagation of a second. For resonant effects optical absorption changes so that the intensity of light is modulated, whereas for resonant or nonresonant n_2 effects the phase of the transmitted signal varies. THG experiments performed far from resonance are a better measure of the inherent ability of a material to respond in a third-order fashion than are resonant experiments.

Nonresonant third-order materials. The optical Kerr effect is among the most rapid-response NLO effects known, capable of sampling the "instantaneous" intensity of an optical pulse (femtosecond to picosecond response). However, high laser powers (megawatts to gigawatts per square centimeter) are required to induce the effect. The magnitude of the effect depends on the degree of delocalization of electrons in the material and on their orientation with respect to the optical field. Thus, materials with the highest n_2 values are those with the largest number of conjugated, polarizable bond structures, such as poly(diacetylenes) (*64*). Glass discussed a variety of organic and inorganic materials and compared their n_2 coefficients (*13*). A prototype organic n_2 material is CS_2, which has a quoted n_2 coefficient of 8×10^{-14} cm^2/W, which is ~100 times as responsive as silica, but ~1/70 as active as the poly(diacetylene) PTS (1,4-bis-*p*-toluenesulphonyl-1,3-dibutadiyne); the organic MNA (20 times CS_2), and the inorganic $LiNbO_3$ (~0.3 times CS_2) are intermediate in response (*13*). (CS_2 is a well-studied material, but the origin of its response is molecular rotation, so it is used here only as a convenient standard.) Among the best inorganics are semiconductors such as GaAs (12 times CS_2) and InSb (600 times CS_2), a reflection of the polarizability of conduction band electrons. The semiconductor responses, however, are limited to long wavelengths (>10 μm).

A growing number of reports are appearing concerning the $\chi^{(3)}$ of materials as determined by THG experiments. Among organics a variety of poly(diacetylenes) (*13*) and poly(phenylacetylene) have been examined (*65*). Poly(silanes) and germanes exhibit interesting behavior, because they are photochromic and appear to have excitonic, charge-delocalized excited states involving the sigma electrons of the organometallic backbone (*66*).

For inorganic compounds, nonresonant effects reported to date occur among either semiconductors (II-VI or III-V materials) or some of the colorless workhorses of second-order materials, for example, β-BaB_2O_4 (BBO). Bhar *et al.* demonstrated THG in the latter material as well as sum-frequency mixing as methods to produce ultraviolet wavelengths with BBO (*67, 68*). Semiconductors such as GaAs [$\chi^{(3)}$ ~4.8×10^{-11} esu] or Si (2.4×10^{-11} esu) were reported early (*69*). Quantum well (superlattice) structures of GaAs-GaAlAs are anticipated to have enhanced nonresonant $\chi^{(3)}$ values (*70*).

"Quantum dot" materials, or size-quantized semiconductor particles, are related to the quantum well structures, and they have also been recognized to have nonresonant $\chi^{(3)}$ properties that are attractive. A series of small (<30 Å) CdS clusters has recently been shown to exhibit $\chi^{(3)}$ on THG from 1.9 μm with values ranging from 0.05×10^{-10} to 3.3×10^{-10} esu, with larger clusters providing the highest susceptibility (*71*). Particles of CdS with sizes from 30 to 60 Å have been suspended in polymer glasses and examined by THG with exciting light from 1 to 1.5 μm (*72*). Glasses of larger cluster size can be produced by conventional glass technology, and these doped glasses also exhibit THG. With an As_2S_3 glass (*73*) a $\chi^{(3)}$ value of 2.2×10^{-12} esu was found. The earliest work was with CdS_xSe_{1-x} glasses (*74, 75*). Other semiconductors can also be doped into glasses, for example, TiO_2 (*76*). Materials encapsulated in glasses (either polymeric, organic or ceramic, inorganic) would appear to be attractive because of their compatibility with optical fabrication techniques.

Resonant third-order materials. Degenerate four-wave mixing (DFWM), optical limiting, optical bistability, photorefractivity, and optical phase conjugation all operate on the basis of an intensity-dependent change in the refractive index of the absorbing material. Glass (*13*) classified materials according to their nonlinear absorptive n_2 coefficient. GaAs quantum well structures are found to be the best among a variety of absorbing materials ($n_2 \sim 4 \times 10^{-3}$ cm^2/W at 850 nm). Bulk GaAs is substantially less active ($n_2 \sim 2 \times 10^{-5}$ cm^2/W at 870 nm) (*13*) than the quantum well structures. Semiconductors of the II-VI family are also known to be good n_2 materials. The coefficient for CdS excitons (490 nm) is quoted by Glass as 1.6×10^{-6} cm^2/W (*13*). Values for these materials are considerably higher than those for materials in which the excited state involved in the resonance process is not highly delocalized. For example, the n_2 of sodium vapor is only ~5×10^{-11} cm^2/W at 590 nm (*13*). Response times ("turn-on time") can be very rapid (picoseconds) because the origin of the effect is electronic. The absorptive n_2 effect persists for the lifetime of the excited state responsible for the nonlinear response. Thus, the "turn-off time" is related to the lifetime of the material; these values vary from ~20 ns (GaAs) to 2 ns (CdS exciton) for the materials described above.

A number of other NLO materials have been discovered. Among inorganics, the best known are the optical glasses sold commercially by the Schott and Corning glass companies as cutoff filters in the visible region. Originally reported by Jain and Lind, such CdS_xSe_{1-x} doped glasses (*74, 75*) are extremely interesting composite materials. Their optical nonlinearities as determined by phase conjugation or power-dependent optical bleaching are relatively large [$\chi^{(3)} \sim 10^{-8}$ esu], and they have fast response times (picoseconds). An absorption-normalized nonlinearity value, α_2/α_0 (that is, the nonlinear absorption coefficient) is a numerical datum that may have more value than an n_2 value or a $\chi^{(3)}$ value. Peyghambarian and co-workers reported an α_2/α_0 value of -1×10^{-7} cm^2/W for the Corning 3-69 glass filter (*77*). Because these materials are true glasses, they can be fabricated into shapes and polished in the same way that lenses and other optical elements are. However, the materials are susceptible to optical damage and the damage mechanism is intimately connected to the electronic mechanism that governs the optical nonlinearity (*78*).

A new class of optical glasses that may circumvent these difficulties has been described by Wang, Herron, and Mahler (*79*). They have prepared size-quantized semiconductor particles, of sizes ultimately smaller than the commercial glasses, in a variety of polymeric and other porous host structures (*80*). The nonlinearity of a 50 Å CdS cluster composite at 505 nm was reported to be about one-half that of the commercial 3-69 glass at 510 nm. In later experiments it was determined that α_2/α_0 was -6×10^{-7} cm^2/W at 480 nm in the CdS exciton band (*79*), a value six times that for the 3-69 glass. A potential virtue of these composites over the pure glass composites is that there is considerable control over the chemical environment of the semiconductor cluster in the polymer system. Because surface electronic states dominate the linear and nonlinear optical properties of these materials, Wang *et al.* suggested that by manipulation of the surface chemistry it will be possible to modify electronic properties in beneficial ways (*79*).

Among organic materials, the most studied material is undoubtedly poly(acetylene), PA, but films are not stable in air (*81*). The nonlinearity of stress-oriented PA has been documented to be as high as $\chi^{(3)} \sim 10^{-8}$ esu polarized along the polymer axis, arguably the highest nonresonant value reported to date, and its resonant nonlinearities rival those of inorganic semiconductors. Response times are in the femtosecond range (*82*).

Another class of conducting polymer that has been examined for resonant nonlinear response is the poly(thiophene) polymers. DFWM has been reported for poly(alkylthiophene) and for several model oligomers (*83, 84*); $\chi^{(3)}$ values from DFWM are in the range 10^{-11} to 10^{-10} esu at 1.06 μm. The values of $\chi^{(3)}$ increase quite rapidly with increasing degree of polymerization, but high molecular weight species, not yet obtained experimentally, would be required to produce useful nonlinearities. Jenekhe and co-workers have prepared a series of soluble precursor block copolymers consisting of separate segments of poly(thiophene) and its quinoid isomer poly(2,5-bismethylenethiophene) (*85*). The $\chi^{(3)}$ values, measured by picosecond DFWM at 532 nm, are in the range 10^{-8} to 10^{-7} esu, the largest values reported to date for any material.

Photorefractive materials. Among the NLO effects, the photorefractive effect represents the area of greatest current opportunity for chemists because there are few materials know to be photorefractive, and only one organic material among them. Understanding and improvement of photorefractive behavior are prerequisites for the successful implementation of many optical computing concepts, especially for all-optical systems.

Photorefractivity was first discovered (*86*) as an optical damage effect in $LiNbO_3$. The effect is similar to optical phase conjugation (in fact, it is sometimes called self-pumped phase conjugation). During the process, which occurs in crystalline materials, index of refraction patterns are developed in the internal structure of the subject material, so that input light is diffracted as it passes through the material. The index variations are developed by interference of the light as it is reflected internally throughout the crystal. Feinberg has reviewed the phenomenology of the photorefractive effect (*87*).

The most useful of the known photorefractives are $LiNbO_3$ and $BaTiO_3$. Both are ferroelectric materials. Light absorption, presumably by impurities, creates electron-hole pairs within the material that migrate anisotropically in the internal field of the polar crystal, to be trapped eventually with the creation of new, internal space charge fields, which alter the local index of refraction of the material via the Pockels effect. If this mechanism is correct (and it appears established for the materials known to date), then only polar, photoconductive materials will be effective photorefractives. However, if more effective materials are to be discovered, a new mechanism will probably have to be discovered in order to increase the speed and sensitivity of the process, now limited by the mobility of carriers in the materials.

Potential applications of photorefractive materials are manifold. To date, demonstrated effects include real-time holography, correlation filtering, and various "novelty" filter applications, one of which is the development of a microscope that distinguishes moving objects (such as living cells) from a stationary background (*88*). In the latter application $BaTiO_3$ was used as the active material.

A general review of photorefractive materials was presented in 1988 (*12*). Also, two monographs detail theory, physical characterization, and practice of the use of known photorefractives (*89*), and the December 1990 issue of the *Journal of the Optical Society of America B* is devoted to photorefractive materials (*90*). Three classes of inorganic materials dominate: ferroelectric oxides, such as $LiNbO_3$ and $BaTiO_3$; compound semiconductors, such as GaAs and InP; and the sillenite family of oxides, exemplified by $Bi_{12}SiO_{20}$ and $Bi_{12}TiO_{20}$. The semiconductors are sensitive only in the infrared; the other materials operate in the visible. Many of the oxide materials are commercially available, although the available crystals have not been optimized for photorefractivity.

Examples of organic photorefractive crystals, in the sense of the functional inorganic crystals cited above, are rare. However, Gailis, Durandin, and Skudra (*91*) reported that a pyridinium ylide experiences reversible photorefraction, which is attributed to local polarization caused by trapping of photoinduced charges at structural defects in the crystal. A recent report provides the first example of an organic crystal in which true photorefraction has been demonstrated optically (*92*). Sutter and Günter doped the organic second-order material COANP with the electron acceptor 7,7,8,8-tetracyanoquinodimethane to produce a true photorefractive organic single crystal (*92*).

Conclusions

A variety of efficacious NLO materials now exist, and some are generally available. However, improvements are required in several classes of materials before applications will be feasible, and new materials opportunities still exist.

For harmonic conversion and optical parametric conversion of high-power lasers that use single crystals, inorganics appear to be the best choice today. Organic thin films appear to have promise for integrated optic and EO applications, although much work needs to be done to improve thin film technology as it relates to orientational phenomena, film optical uniformity and quality, and, most importantly, stability over time. For third-order applications, organic materials may have advantages over inorganics, both in magnitude of the nonlinearity and fabricability. It is too soon to judge unequivocally. A great deal of fundamental materials research is needed here. New concepts are required to develop new, more efficient examples of photorefractive materials.

An important need is to understand the technology of thin-film formation. New methods of film fabrication and characterization are required. This need, coupled with the continuing needs for understanding the fundamental structure-property relations among NLO materials, demands that chemists continue to seek new solutions if materials for NLO applications are to be successfully developed.

Note added in proof: IBM workers recently reported observation of the photorefractive effect in a doped, photoconductive, polymeric thin film (*93*).

REFERENCES AND NOTES

1. P. A. Franken, A. E. Hill, C. W. Peters, G. Weinrich, *Phys. Rev. Lett.* **7**, 118 (1961).
2. J. L. Oudar and J. Zyss, *Phys. Rev. A* **26**, 2016 (1982).
3. N. Bloembergen, *Nonlinear Optics* (Benjamin, Reading, MA, 1965).
4. J. A. Giordmaine and R. C. Miller, *Phys. Rev. Lett.* **14**, 973 (1965).
5. P. M. Rentzepis and Y. H. Pao, *Appl. Phys. Lett.* **5**, 156 (1964).
6. S. K. Kurtz and T. T. Perry, *J. Appl. Phys.* **39**, 3798 (1968).
7. J. Zyss and D. S. Chemla, Eds., *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic Press, New York, 1987), vol. 1, chap 2.
8. D. J. Williams, *Angew. Chem. Int. Ed. Engl.* **23**, 690 (1984).
9. D. J. Williams, Ed., *Nonlinear Optical Properties of Organic and Polymeric Materials* (ACS Symposium Series 233, American Chemical Society, Washington, DC, 1983).
10. A. Gedanken, M. B. Robin, N. A. Kuebler, *J. Phys. Chem.* **86**, 4096 (1982).
11. S. Basu, *Ind. Eng. Chem. Prod. Res.* **23**, 183 (1984).
12. G. C. Valley, M. B. Klein, A. B. Mullen, D. Rytz, B. Wechsler, *Annu. Rev. Mater. Sci.* **18**, 165 (1988).
13. A. M. Glass, *Science* **226**, 657 (1984).
14. G. D. Stucky, S. R. Marder, S. R. Sohn, Eds., *Materials for Nonlinear Optics: Chemical Perspectives* (ACS Symposium Series 455, American Chemical Society, Washington, DC, 1991).
15. W. J. Tomlinson and E. A. Chandross, *Adv. Photochem.* **12**, 201 (1980).
16. B. M. Monroe, W. K. Smothers, R. R. Krebs, D. J. Mickish, paper presented at the Society of Photographic Scientists and Engineers Annual Conference and Symposium on Hybrid Imaging Systems, Rochester, NY, 1987.
17. R. T. Ingall and H. L. Fielding, *Opt. Eng.* **24**, 808 (1985).
18. M. Eich *et al.*, *J. Opt. Soc. Am. B* **6**, 1590 (1989).
19. C. Cassidy, J. M. Halbout, W. Donaldson, C. L. Tang, *Opt. Commun.* **29**, 243 (1977).
20. J. Zyss and J. L. Oudar, *Phys. Rev. A* **26**, 2028 (1982).
21. J.-M. Halbout and C. L. Tang, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, J. Zyss and D. S. Chemla, Eds. (Academic Press, New York, 1987), vol. 1, chap. II-6.
22. G. J. Zhang, T. Kinoshita, K. Sasaki, Y. Goto, A. Nakayama, paper presented at the Conference on Lasers and Electrooptics, Baltimore, MD, 1989.
23. J. F. Nicoud and R. J. Tweig, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, J. Zyss and D. S. Chemla, Eds. (Academic Press, New York, 1987), vol. 2, appendix 1.
24. R. J. Tweig and K. Jain, in *Nonlinear Optical Properties of Organic and Polymeric Materials*, D. J. Williams, Ed. (ACS Symposium Series 233, American Chemical Society, Washington, DC, 1983), chap. 3.
25. J. L. Oudar and R. Hierle, *J. Appl. Phys.* **48**, 2699 (1977).
26. R. J. Tweig, A. Azema, K. Jain, Y. Y. Cheng, *Chem. Phys. Lett.* **92**, 208 (1982).
27. R. J. Tweig, K. Jain, Y. Y. Cheng, J. I. Crowley, A. Azema, *Polym. Preprints* **23**, 147 (1982).
28. W. Tam, B. Guerin, J. C. Calabrese, S. H. Stevenson, *Chem. Phys. Lett.* **154**, 93 (1989).
29. J. D. Bierlein, L.-K. Cheng, Y. Wang, W. Tam, *Appl. Phys. Lett.* **56**, 423 (1990).
30. L. G. Koreneva, V. F. Zolin, B. L. Davydov, *Molecular Crystals in NLO* (Nauka, Moscow, 1975).
31. B. F. Levine, C. G. Bethea, C. D. Thurmond, R. T. Lynch, J. L. Bernstein, *J. Appl. Phys* **50**, 2523 (1979).

32. G. F. Lipscomb, A. F. Garito, R. S. Narang, *Appl. Phys. Lett.* **75**, 1509 (1981).
33. J. Zyss, J. F. Nicoud, M. Coquillay, *J. Chem. Phys.* **81**, 4160 (1984).
34. J. Zyss, D. S. Chemla, J. F. Nicoud, *ibid.* **74**, 4800 (1981).
35. S. Okada and H. Nakanishi, *Kagaku Kogyo* **37**, 364 (1986).
36. R. J. Twieg, "Organic materials for SHG" (Final Report, LLNL-2689405, Lawrence Livermore National Laboratory, Livermore, CA, March 1985).
37. D. F. Eaton, in *Materials for Nonlinear Optics: Chemical Perspectives*, G. D. Stucky, S. R. Marder, J. E. Sohn, Eds. (ACS Symposium Series 455, American Chemical Society, Washington, DC, 1991), p. 128.
38. B. A. Fuchs, C. K. Syn, S. P. Velsko, *Appl. Opt.* **28**, 4465 (1989).
39. D. S. Donald, L.-T. Cheng, G. Desiraju, G. R. Meredith, F. R. Zumsteg, Abstract Q9.2, Fall meeting of the Materials Research Society, Boston, 27 November to 2 December 1989.
40. C. C. Frazier, M. A. Harvey, M. P. Cockerham, E. A. Chauchard, C. H. Lee, *J. Phys. Chem.* **90**, 5703 (1986).
41. D. F. Eaton, A. G. Anderson, W. Tam, Y. Wang, *J. Am. Chem. Soc.* **109**, 1886 (1987).
42. W. Tam and J. C. Calabrese, *Chem. Phys. Lett.* **133**, 244 (1987).
43. ———, *ibid.* **144**, 79 (1988).
44. M. L. H. Green *et al.*, *Nature* **330**, 360 (1987).
45. A. G. Anderson, J. C. Calabrese, W. Tam, I. D. Williams, *Chem. Phys. Lett.* **134**, 392 (1987).
46. W. Tam, D. F. Eaton, J. C. Calabrese, I. D. Williams, Y. Wang, A. G. Anderson, *Chem. Mater.* **1**, 128 (1989).
47. S. Tomaru, S. Zembutsu, M. Kawachi, Y. Kobayashi, *J. Chem. Soc. Chem. Commun.* **1984**, 1207 (1984).
48. Y. Wang and D. F. Eaton, *Chem. Phys. Lett.* **120**, 441 (1985).
49. I. Weisbuch, M. Lahav, L. Leiserowitz, G. R. Meredith, H. Vanherzeele, *Chem. Mater.* **1**, 114 (1989).
50. S. D. Cox, T. E. Gier, J. D. Bierlein, G. D. Stucky, *J. Am. Chem. Soc.* **110**, 2986 (1989).
51. G. R. Meredith, J. G. Van Dusen, D. J. Williams in (*9*), p. 109; *Macromolecules* **15**, 1385 (1982); K. D. Singer, S. E. Sohn, S. J. Lalama, *Appl. Phys. Lett.* **49**, 248 (1986).
52. J. D. Le Grange, M. G. Kuzyck, K. D. Singer, *Mol. Cryst. Liq. Cryst.* **150b**, 567 (1987).
53. M. Eich *et al.*, *J. Appl. Phys.* **66**, 2559 (1989).
54. M. Eich, B. Reck, D. Y. Yoon, C. G. Wilson, G. C. Bjorklund, *ibid.*, p. 3241.
55. J. D. Bierlein, personal communication.
56. J. T. Lin and C. Chen, *Lasers Optronics* (November 1987), p. 59.
57. C. J. van der Poel, J. D. Bierlein, J. B. Brown, S. Colak, *Appl. Phys. Lett.* **57**, 2074 (1990).
58. H. Vanherzeele, *Opt. Lett.* **14**, 728 (1989).
59. J. D. Bierlein and C. B. Arweiler, *Appl. Phys. Lett.* **49**, 917 (1986).
60. E. Abraham, C. T. Seaton, S. D. Smith, *Sci. Am.* **248**, 85 (February 1983).
61. J. Hecht, *High Technol.* (*Boston*) **3**, 55 (October 1983).
62. Y. S. Abu-Mostafa, D. Psaltis, *Sci. Am.* **258**, 88 (March 1987).
63. J. L. Horner, *Optical Signal Processing* (Academic Press, New York, 1987).
64. D. S. Chemla, *Rep. Prog. Phys.* **43**, 1191 (1980).
65. D. Neher, A. Wolf, C. Bubeck, G. Wegner, *Chem. Phys. Lett.* **163**, 116 (1989).
66. R. D. Miller and J. Michl, *Chem. Rev.* **89**, 1359 (1989).
67. G. C. Bhar, U. Chaterjee, S. Das, *J. Appl. Phys.* **66**, 5111 (1989).
68. A. Penzkofer, P. Qiu, P. Ossig, in *Nonlinear Optics of Organics and Semiconductors: Proceedings of the International Symposium in Tokyo, July 25–26, 1988*, T. Kobayashi, Ed. (Springer Proceedings in Physics, vol. 36, Springer-Verlag, Berlin, 1989), p. 312.
69. J. Wynne, *Phys. Rev.* **178**, 1295 (1969).
70. Y.-C. Chang, *J. Appl. Phys.* **58**, 499 (1985).
71. L.-T. Cheng, N. Herron, Y. Wang, *ibid.*, **66**, 3417 (1989).
72. Y. Ohashi *et al.*, in *Nonlinear Optics of Organics and Semiconductors: Proceedings of the International Symposium in Tokyo, July 25–26, 1988*, T. Kobayashi, Ed. (Springer Proceedings in Physics, vol 36, Springer-Verlag, Berlin, 1989), p. 81.
73. H. Nasu, Y. Ibara, K. Kubodera, *J. Non-Cryst. Solids* **110**, 229 (1989).
74. R. K. Jain and R. C. Lind, *J. Opt. Soc. Am.* **73**, 647 (1983).
75. N. F. Borrelli, D. W. Hall, H. J. Holland, D. W. Smith, *J. Appl. Phys.* **61**, 5399 (1987).
76. S. Friberg and P. W. Smith, *IEEE J. Quantum Electron.* **QE-23**, 2089 (1987).
77. O. R. Olbright, N. Peyghambarian, S. W. Koch, L. Banyai, *Opt. Lett.* **12**, 413 (1987).
78. B. Van Wonterghem, S. M. Saltiel, T. E. Dutton, P. M. Rentzepis, *J. Appl. Phys.* **66**, 4935 (1989).
79. Y. Wang, N. Herron, W. Mahler, *J. Opt. Soc. Am. B* **6**, 809 (1989).
80. Y. Wang and W. Mahler, *Opt. Commun.* **61**, 233 (1987).
81. S. Gray, *Photonics*, 125 (September 1989).
82. A. J. Heeger, D. Moses, M. Sinclair, *Synth. Metals* **15** (1986).
83. M.-T. Zhao, B. P. Singh, P. N. Prasad, *J. Chem. Phys.* **89**, 5535 (1988).
84. N. Fukaya, A. Heinamaki, H. Stubb, *J. Mol. Electron.* **5**, 187 (1989).
85. S. A. Jenekhe, W.-C. Chen, S. Lo, S. R. Flom, *Appl. Phys. Lett.* **57**, 126 (1990).
86. A. Ashkin *et al.*, *ibid.* **9**, 72 (1966).
87. J. Feinberg, *Phys. Today* **39**, 46 (October 1986).
88. R. S. Cudney, R. M. Pierce, J. Feinberg, *Nature* **332**, 424 (1988).
89. P. Günter and H.-J. Huignard, *Photorefractive Materials and Their Application*, vols. I and II (Topics in Applied Physics 61 and 62, Springer-Verlag, Berlin, 1988).
90. G. Roosen, J.-P. Huignard, M. Cronin-Golomb, Eds., *J. Opt. Soc. Am. B* **7** (December 1990).
91. A. Gailis, A. D. Durandin, V. Skudra, *Latv. PSR Zinat. Akad. Vestis. Fiz. Teh. Zinat. Ser.* **119**, 122 (1983); *Chem. Abstr.* **100**, 14630a (1984).
92. K. Sutter and P. Günter, *J. Opt. Soc. Am. B* **7**, 2274 (1990).
93. S. Ducharme *et al.*, *Phys. Rev. Lett.* **66**, 1846 (1991).
94. M. S. Paley *et al.*, *J. Org. Chem.* **54**, 3374 (1989).
95. D. Eimerl, *Ferroelectrics* **72**, 95 (1987).

Computations Underlying the Execution of Movement: A Biological Perspective

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To execute voluntary movements, the central nervous system must transform the neural representation of the direction, amplitude, and velocity of the limb, represented by the activity of cortical and subcortical neurons, into signals that activate the muscles that move the limb. This task is equivalent to solving an "ill-posed" computational problem because the number of degrees of freedom of the musculoskeletal apparatus is much larger than that specified in the plan of action. Some of the mechanisms and circuitry underlying the transformation of motor plans into motor commands are described. A central feature of this transformation is a coarse map of limb postures in the premotor areas of the spinal cord. Vectorial combination of motor outputs among different areas of the spinal map may produce a large repertoire of motor behaviors.

THE CENTRAL NERVOUS SYSTEM (CNS) CONTROLS THE events from the planning to the execution of movements. To specify a plan of action, the CNS must first transform sensory information into motor goals such as the direction, amplitude, and velocity of the intended movement. In higher vertebrates, these motor goals are represented by the activity of populations of neurons in different cortical and subcortical areas (*1*). Recordings of the electrical activity of single neurons from the parietal and frontal cortices of monkeys show a correlation between neural activity and the direction of the movement of the arm (*1*). Furthermore, on the basis of these recordings, a number of investigators have argued that the activity of cortical cells is represented in spatial coordinates without any specification about how muscles are to be engaged to

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