Chemical Reviews®

Volume 94, Number 1 January/February 1994

Optical Nonlinearities in Chemistry: Introduction

Linear optical processes give rise to such familiar phenomena as refraction, light scattering, and absorption. The nonlinear response of a material to the applied optical field is perhaps less familiar but nevertheless widely used by chemists to study a variety of physical and chemical properties. An optical nonlinearity, for example, can result in harmonic light generation, transient grating formation, and excitation of lattice or molecular vibrations.

The field of nonlinear optics had its birth in 1875 with the publication by J. Kerr of his observations of a quadratic electric field induced change in the refractive index of CS_2, now known as the Kerr effect. This discovery was followed shortly in 1883 by the observation of a similar but linear electric field effect in quartz. This latter process is now known as the Pockels effect. These nonlinear effects had limited use until the invention of the laser in 1960, followed the next year by the observation by P. Franken et al. of second-harmonic generation in quartz. Following these events the field of nonlinear optics developed explosively throughout the 1960s, highlighted by the work of N. Bloembergen and co-workers in exploring the full range of nonlinear optical responses of material systems and that of A. D. Buckingham and colleagues in exploring nonlinear processes in atoms and molecules of interest to chemists.

In the decade of the 1970s, the underlying origins of atomic and molecular hyperpolarizabilities were analyzed in more detail. Experimental techniques for the measurement of these molecular nonlinear properties and for the design, synthesis, and growth of crystals that might have practical uses in second-harmonic generation and electrooptic light modulation were developed and refined. In addition, nonlinear effects such as coherent Stokes Raman scattering (CSRS), coherent anti-Stokes Raman scattering (CARS), and four-wave mixing were used to probe vibrational and electronic properties of molecules and crystals.

With the advent of optical fibers in telecommunications in the late 1970s, practical applications for nonlinear optical devices, always recognized as potentially important, became a serious goal. Polymers were developed during this period that showed promise for second-harmonic generation and electrooptic device applications. In addition, nonlinear effects were increasingly used as scientific tools to investigate physical and chemical processes in atoms, molecules, crystals, thin organized films, and polymers. This issue of *Chemical Reviews* provides a detailed look at the current uses of optical nonlinearities in chemistry.

David Shelton and Julia Rice discuss the calculation and gas-phase measurement of second- and third-order hyperpolarizabilities in atoms and small molecules. They show how sophisticated computational techniques along with measurements on isolated atoms and molecules can refine our understanding of the origins of nonlinear processes as well as contribute to the development of tools for predicting these properties. Two issues for future research arise from their discussion. First, they emphasize the need to find a way to relate calculations done on isolated molecules to measurements made in condensed-phase environments. Second, they point out that the most reliable calculations are done using *ab initio* computational techniques. These techniques are much too time consuming for most molecules of practical interest. A need exists for an improved paramaterization of semiempirical calculations to allow these techniques to be used with more quantitative accuracy.

David Kanis, Mark Ratner, and Tobin Marks discuss the use of a variety of electronic structural models and computational techniques to assist in the identification of chromophores with large second-order optical nonlinearities. Knowing in advance that a particular chromophore may reasonably be expected to have a large hyperpolarizability can substantially improve the efficiency of the "highly labor-, expendables-, and facilities-intensive" synthetic organic chemistry. Discussed are origins of the trade-off between large hyperpolarizability and optical transparency that affects the effectiveness of chromophores for second-harmonic generation, the effect of chromophore conjugation length on hyperpolarizability, and the relative effectiveness of double versus triple bonds in nonlinear chromophores. A variety of novel chromophores are described including chromophores containing main group elements such as B, S, and Si, organometallic molecules, and charged chromophores. This paper illustrates very nicely the more generic process by which theoretical models and calculations can guide the synthesis of molecules with desired physical properties.

Third-order nonlinear optical materials have potential use in the "holy grail" of nonlinear optics, all-optical computing. Jean-Luc Brédas, Christine Adant, Peter Tackx, André Persoons, and Brian Pierce review this

0009-2665/94/0794-0001$14.00/0

area from both the molecular and bulk material point of view. A variety of different experimental techniques can be used to measure the third-order hyperpolarizabilities of a chromophore. Each technique may potentially respond to a different combination of physical phenomena, including electrostriction, molecular orientation, and vibrational and electronic processes. Care must thus be used in comparing hyperpolarizabilities measured by different techniques. Here too, the use of computational techniques to identify promising chromophores is described. A variety of third-order systems are discussed, including polyacetylenes, polydiacetylenes, polysilanes, and fullerenes. No material, organic or inorganic, currently possesses the needed combination of high third-order nonlinearity and optical transparency for actual device use. The payoff would be high if a suitable material could be identified.

The situation for second-order polymers is quite different and is discussed by Donald Burland, Robert Miller, and Cecilia Walsh. Second-order polymers can be used in frequency doubling and, via the Pockels effect, in electrooptic modulators and switches. Polymers with sufficiently high nonlinearity have been developed, at least for electrooptic applications, and the focus of much of the research in this area has shifted to optimization of a variety of secondary properties such as thermal stability, adhesion, thermal expansion, etc., while simultaneously maintaining high nonlinearity. Because the chromophores in second-order nonlinear polymers are typically oriented by an electric field, the loss of nonlinearity can be used as a means of following very slow relaxation processes in polymers. In fact it is one of the few experimental techniques for investigating these processes that can extend over days or weeks. In this regard, an interesting and as yet unexplained "universal" behavior of the relaxation time as a function of temperature has been observed.

One normally thinks of a second-order nonlinear chromophore as being dipolar. This need not be the case, and Joseph Zyss and Isabelle Ledoux describe a class of octopolar chromophores that possess a nonzero quadratic hyperpolarizability. They use a tensor formulation to identify the symmetry classes of octopolar molecules. The hyperpolarizability of these octopolar molecules cannot be measured using conventional techniques such as electric field induced second-harmonic generation since they do not possess a dipole moment. The technique of harmonic light scattering (also known as hyper-Rayleigh scattering) is described for making these measurements. Once one has identified an octopolar chromophore, one must incorporate the molecule in a matrix in such a way that the bulk system also possesses the correct symmetry. It has not yet been demonstrated that this can be done in such a way that the resulting system possesses the requisite large second-order nonlinearity. Several promising experimental techniques are discussed by which this orientation might be accomplished.

Second-harmonic generation (SHG) can only be observed in systems that are noncentrosymmetric. The interface between two different media is noncentrosymmetric and SHG can be observed from molecules in this region. Robert Corn and Daniel Higgins discuss the use of SHG to probe surface chemistry. The technique has been used to investigate metal, semiconductor, oxide, polymer, and liquid surfaces. Very recently the technique has been used to probe the membrane potential in biological systems. Information about adsorption strength and surface coverage, molecular orientation, interfacial electric fields, reaction kinetics and surface diffusion can be obtained.

A photorefractive system is one which is simultaneously photoconductive and electrooptic. Diffraction gratings or holograms can be produced in a photorefractive material by the photogeneration of mobile charges. The grating is produced by the internal space-charge field that is set up by these charges. The electrooptic effect due to this field produces an index of refraction grating. Such gratings possess novel properties when compared with the more conventional photochemical gratings. Photorefractive polymers are discussed by W. E. Moerner and Scott Silence. Up to 1990 all photorefractive systems were inorganic crystals. In that year both organic crystalline and polymeric photorefractive systems were reported. The early systems were inefficient and slow when compared to the inorganic crystals. In the short intervening period, efficiency and speed have been improved to the point where the polymeric systems have a photorefractive sensitivity matching that of the inorganic crystals.

Most of the papers in this volume concentrate on the real part of the nonlinear susceptibilities, excluding energy absorption via optically nonlinear processes. Lisa Dhar, John Rogers, and Keith Nelson review the important use of optical nonlinear processes to excite elementary collective and molecular motions in systems. This area has recently received a tremendous boost with the development of pulsed lasers with pulse widths shorter than the oscillation period of such an elementary excitation. In this impulsive limit, the nonlinear mixing of wavelengths that we usually associate with multiple sources comes from the spectral bandwidth of a single short pulse. The use of multiple pulses permits a continuous excitation of a particular transition, tremendously amplifying the motion associated with it. Applied to lattice motions in solids, the technique can be used to investigate large amplitude motions, inaccessible by other experimental techniques. When applied to molecules, this type of excitation holds out the possibility of producing bond-specific chemistry by dumping energy into particular molecular vibrations.

Progress in the study and use of nonlinearities has and will continue to be controlled by developments in three other areas. The development of tunable pulsed lasers with precisely controllable pulse shapes will permit the extension of the use of impulsive light scattering. Developments in high-speed optical communications and increases in computational speed of computers will continue to drive the search for fast and efficient second and third order nonlinear materials. And finally, the development of faster computers, parallel processing, and more efficient computer codes will permit accurate calculations of the nonlinear properties of increasingly larger molecules.

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