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NONLINEAR OPTICAL PROPERTIES OF ORGANIC MATERIALS: A THEORETICAL STUDY

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Replacement of electronic switching circuits in computing and telecommunication systems with purely optical devices offers the potential for extremely high throughput and compact information processing systems. The potential application of organic materials containing molecules with large nonresonant nonlinear effects in this area have triggered intensive research during the last decade. Interest on this area was due to two facts: (a) that many organic materials show nonlinearities that are orders of magnitude larger than those of conventional inorganic materials such as lithium niobate and potassium dihydrogen phosphate, and (b) that organic materials much flexibility in terms of molecular designs.

Some of the desirable characteristics that these materials should have are that they be transparent to the frequency of the incident laser and its second or third harmonic, that they have a high damage threshold and, in the case of second-order effects, that their crystal structure or molecular orientation be acentric. Since polymeric assemblages can enhance the nonlinear response of organic molecules severalfold, efforts have been directed toward the synthesis of thin films with interpenetrating lattices of electroactive molecules. The goal of this theoretical investigation is to predict the magnitude of the molecular polarizabilities of organic molecules that could be incorporated into films. These calculations are intended to become a powerful tool to assist material scientists in screening for the best candidates for optical applications.

There are two possible approaches in the theoretical prediction of the magnitude of molecular susceptibilities of organic molecules: the sum-over-state approach, which is based on a perturbative expansion in terms of molecular eigenstates, and the finite-field-perturbation approach, which diagonalizes a molecular Hamiltonian that includes a static-field dipolar perturbation. In the first approach, a perturbation expansion in terms of excited states of the unperturbed molecule is used. In the second approach, ground state energies are calculated directly by a variational method in the presence of a perturbing field. In either case, any semiempirical or ab-initio method may be utilized. In general, ab-initio theories are used in attempting to reproduce absolute magnitudes but semiempirical models have been useful to detect trends among related molecules. For a summary of theoretical screening methods, please see Penn, Cardelino, Moore, Shields and Frazier, 1991 [5]).

The procedure that was developed for the present calculations is based on the static-field approach, and is a modification to the method developed by Dewar and Stewart, 1984 [2] for calculating molecular linear polarizabilities. When a molecule is placed in an electric field, a given component of its polarization can be expressed by the following summation:

$$p_q = \mu_q + \sum_j \alpha_{qj} F_j + \sum_{jk} \beta_{qjk} F_j F_k + \sum_{jkl} \gamma_{qjkl} F_j F_k F_l + \ldots \qquad [1]$$

where p_q represents the **q** component of the polarization, F_i the **i** component of the applied electric field, μ the permanent dipole moment, α the linear polarizability, β the second-order polarizability, γ the third-order polarizability, etc. The magnitude of the vector part of β, corresponds to the effective measure of hyperpolarizability for second harmonic generation (SHG):

$$\beta_{vec} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad [2]$$

where x, y, and z are the molecular coordinate axes. The symmetry of β with respect to interchange of the last two indices determines that the vector components be:

$$\beta_q = \beta_{qqq} + (\sum_j \beta_{qjj} + 2 \sum_j \beta_{jqj})/3 \qquad [3]$$

Finally, the value of the average (scalar part) third-order polarizability γ, which is related to third-harmonic generation, can be expressed as:

$$\gamma = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{xxzz})/5 \qquad [4]$$

Dewar and Stewart [2] method utilizes four isolated point charges (or sparkles, with no associated electrons or atomic orbitals) in the description of the molecule, allowing for the corresponding changes in polarization and energy to be calculated directly. The polarization and energy are obtained within the MNDO approximation, implemented in the MOPAC [4] quantum mechanical package.

The computer coding required for the calculation of second-order polarizabilities was developed before the summer of 1991 (Cardelino et al., 1991 [1]). The original version of MOPAC used involved the use of fields along the three Cartesian coordinates. In order to obtain the 27 required elements of the β tensor, calculations with fields along the bisector of all quadrants were added to MOPAC. In total, molecules are subjected to electrical fields of 14 different strengths along each of the molecular axes and along the bisector line of each quadrant. Thus, MOPAC is used to obtain polarization data which are subsequently utilized by another program to perform polarization expansions in terms of field strengths.

The procedure to obtain second-order polarizabilities was applied to nitroanilines (Cardelino, Moore and Stickel, 1991 [1]) and benzophenone derivatives (Moore and Cardelino, 1991 [3]). During the summer of 1991, this code was reviewed and substantially simplified. The simplified procedure was applied to mono-, di-, and tri-substituted naphthalene, quinoline and isoquinoline. A manuscript to be submitted for publication is under preparation.

Most of the effort during the summer of 1991 was directed toward extending the procedure for second-order polarizabilities to obtain third-order polarizabilities. Based on equation [1], a polarization expansion for fields along one Cartesian coordinate are as follows:

$$p_q = \mu_q + \alpha_{qi} F + \beta_{qii} F^2 + \gamma_{qiii} F^3 + \ldots \qquad [5]$$

where $F = F_i$. When the fields are along the bisector of a quadrant, the polarization expansion can be expressed with two different equations, depending if the two components have the same or opposite signs:

$$p_q = \mu_q + (\alpha_{qi} + \alpha_{qj}) F + (\beta_{qii} + \beta_{qjj} + 2 \beta_{qij}) F2 + (\gamma_{qiii} + \gamma_{qjjj} + 3 \gamma_{qiij} + 3 \gamma_{qijj}) F^3 \ldots \qquad [6]$$

where $F = F_i = F_j$; and,

$$p_q = \mu_q + (\alpha_{qi} - \alpha_{qj}) F + (\beta_{qii} + \beta_{qjj} - 2 \beta_{qij}) F^2 + (\gamma_{qiii} - \gamma_{qjjj} - 3 \gamma_{qiij} + 3 \gamma_{qijj}) F^3 \ldots \qquad [7]$$

where $F = F_i = -F_j$. Sumation and subtraction of the third-order coefficients of equations [6] and [7] result in:

$$2 \gamma_{qiii} + 6 \gamma_{qijj} \qquad [8]$$

$$2 \gamma_{qjjj} + 6 \gamma_{qiij} \qquad [9]$$

To calculate γ from equation [4], the only terms that are needed are those in which q=i or q=j. If Kleinman symmetry is assumed and if q=i then qij=iij=jii and qiij=iiij=jiii; similarly, if q=j then qij=jij=ijj and qijj=jijj=ijjj. Then, equations [6] and [7] may be written as:

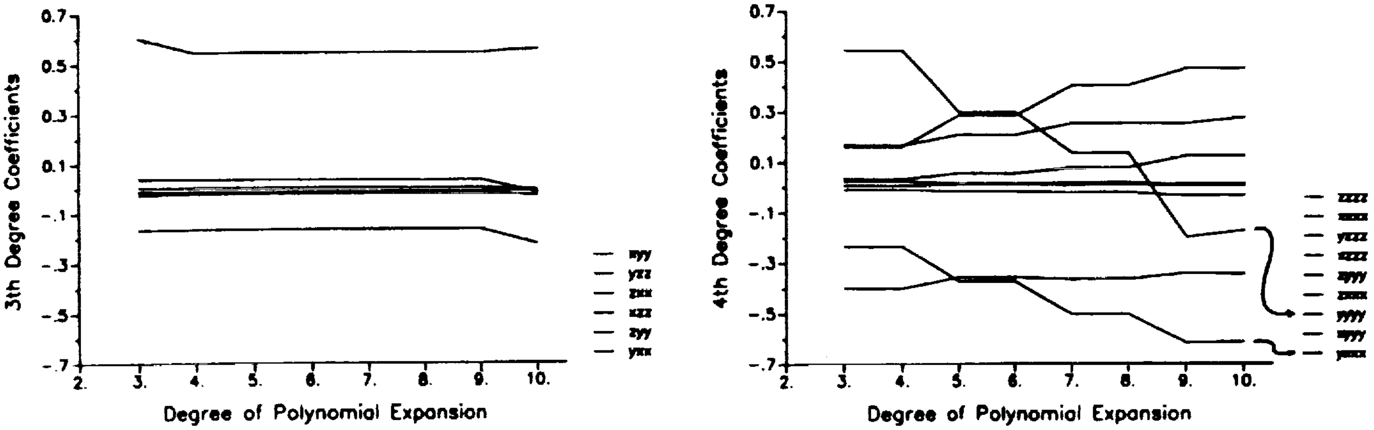
$$p_i - \mu_i - (\alpha_{ii} \pm \alpha_{ij}) F - (\beta_{iii} + \beta_{ijj} \pm 2 \beta_{jii}) F^2 - (\gamma_{iiii} \pm \gamma_{ijjj} \pm 3 \gamma_{jiii}) F^3 = + 3\gamma_{iijj} F^3 \qquad [10]$$

and

$$p_j - \mu_j - (\alpha_{ji} \pm \alpha_{jj}) F - (\beta_{jii} + \beta_{jjj} \pm 2 \beta_{ijj}) F^2 - (\gamma_{jiii} \pm \gamma_{jjjj} + 3 \gamma_{ijjj}) F^3 = \pm 3\gamma_{iijj} F^3 \qquad [11]$$

in which case, all terms in the left side of the equations can be obtained from calculations over fields along only one Cartesian coordinate at a time. In summary, the nonlinear terms needed to obtain the iijj terms are: ijj, jii, ijjj, and jiii. Figures 1 and 2 show the dependence of the coefficients required for the calculation of γ with the degree of the polynomial expansions for one particular molecule. All terms are very stable except for two 4th degree terms: yyyy and yxxx. These instabilities deserve further study. The section of the computer program that performs calculation of γ is under way.

Third-order polarizability calculations will be performed on 1-pyrryl-5-x-(1,3)-dipentyne and 1-pyrryl-6-x-(1,3)-dihexyne, where x will be hydroxyl, nitro, or amino groups. In particular, there has been a patent disclosure by Samuel P. McManus, Donald O. Frazier, and Mark S. Paley on the hydroxyl molecule. During this summer, energy calculations on these molecules were also performed.



Figures 1 and 2. Values of the third and fourth degree coefficients of the expansions of polarization as a function of field strength.

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