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PREDICTION OF NONLINEAR OPTICAL PROPERTIES OF LARGE ORGANIC MOLECULES

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The preparation of materials with large nonlinear responses usually requires involved synthetic processes. Thus, it is very advantageous for materials scientists to have a means of predicting nonlinear optical properties. For example, correlating the strengths of the nonlinear properties of a family of compounds with different substituents at various bonding sites may be of great utility in selecting good candidates for experimentation.

The prediction of nonlinear optical properties has to be addressed first at the molecular level and then as bulk material. At the molecular level, prediction of these properties must consider both conditions of static and dynamic fields. For relatively large molecules, two types of calculations may be used: the sum-over-states (based on a perturbative expansion in terms of molecular eigenstates in the absence of an external field) and the finite-field approach (which diagonalizes a molecular Hamiltonian with a static-field dipolar perturbation). In the first case, the magnitude of the properties is obtained for a specific dynamic field, and the static field value can be extrapolated to zero frequency. In the second case, the nonlinear terms are obtained for static conditions and a correction for dispersion should be added if they are to be compared with experiments involving electromagnetic radiation.

The finite-field method was selected for this research, because this approach is better suited for larger molecules. A simplified version of the sum-over-states approach is under development to predict dispersion effects. Previously, dispersion corrections were extrapolated from experimental data on molecules similar to the ones investigated. Finally, a molecular mechanics approach is being considered to predict interatomic effects on nonlinear properties. These effects have been estimated previously from empirical data on molecules similar to the ones under study.

a) Progress in static-field calculations

During the summer of 1992, a core correction to the third-order polarizabilities was implemented. The method to calculated static nonlinear polarizabilities is a modification to the method developed by Dewar and Stewart, 1984 for calculating molecular linear polarizabilities. Dewar and Stewart include isolated point charges (or "sparkles") in the description of the molecule, with no associated electrons or atomic orbitals. An appropriate selection of these sparkles simulates the effect of a uniform electric field on a molecule, allowing for the corresponding changes in polarization to be calculated directly. The all valence-electron MNDO Hamiltonian (Dewar and Thiel, 1977) is employed to obtain molecular polarizations in the presence of various static fields. Then, polynomial regressions of polarizations versus fields data are used to calculate all tensor elements of the static second and third-order polarizabilities. Since MNDO is a valence-electron model, a correction for the atomic cores was required for third-order polarizabilities. In second-order polarizabilities, the effect of induced polarization in centrosymmetric structures cancels since they involve squares of the field strengths.

A group of substituted benzene molecules was selected to parameterize atomic core corrections for carbon, hydrogen, oxygen, and nitrogen. Experimental data for these molecules was available from third-harmonic generation (THG) measurements (Cheng et al., 1991). In order to minimize solvent effects, the molecules chosen for comparison were those measured as neat samples. Since the THG measurements were done at 0.649 eV radiation, the experimental values were corrected for dispersion effects. The correction for dispersion of the experimental values was based on the two-state anharmonic model:

$$\gamma_O = \gamma_\omega \ (\ \omega_o{}^2 - \omega^2)^4 \ / \ \omega_o{}^8$$

[1]

where γ_O is the static third-order polarizability, γ_ω is the measured third-order polarizability, ω_o is the resonance frequency (ω_o = 6.9 eV for benzene), and ω is the laser frequency (Zhao et al., 1989). The experimental data were also corrected for bulk effects, as follows: Two EFISH measurements on liquid and vapor benzene were used to obtain a liquid to vapor correction. The liquid-to-vapor correction was assumed to be applicable for all substituted benzene molecules.

A plot of number of atoms in the molecules versus the difference between the predicted third-order polarizabilities and the corrected experimental value showed a correlation of 0.90 (Figure 1, solid line). Using as normalization factors the same non-hydrogen to hydrogen ratios from the core corrections on linear polarizabilities (Dewar and Stewart, 1984), a plot of "H units" versus the difference between predicted and experimental values showed a correlation of 0.91 (Figure 1, dotted line). Thus, the significant correlations indicate that core corrections for third-order polarizabilities were required. By performing multiple regressions with various groups of data, it was found that the core corrections for carbon and hydrogen were highly coupled. In order to overcome this problem, the same carbon to hydrogen ratio from the core correction of linear polarizabilities was used. Thus the following atomic core corrections were obtained: carbon = 0.251 x 10^{-61} SI, hydrogen = 0.217 x 10^{-61} SI, oxygen = 0.386 x 10^{-61} SI, and nitrogen = 0.931 x 10^{-61} SI. Table 1 shows the results.

Second and third-order polarizabilities have been predicted for diacetylene compounds containing pyrryl or substituted amines and a variety of functional groups. This work has been recently submitted for publication (Cardelino et al., 1992).

Second-order polarizabilities have been calculated for nitro- and amino-substituted quinolines and isoquinolines. The work was initiated from discussions with Dr. Wayne Hyde, a JOVE participant. Organic synthesis of these materials is in progress at the Northwestern State University of Louisiana. A paper on this work will shortly be submitted for publication (Moore et al., 1992).

Second-order polarizabilities have been calculated for substituted nitrobenzenes. The work was initiated from discussions with another JOVE participant, Dr. Ronald Clark. Synthesis of these materials is under way at the New Mexico Highland University.

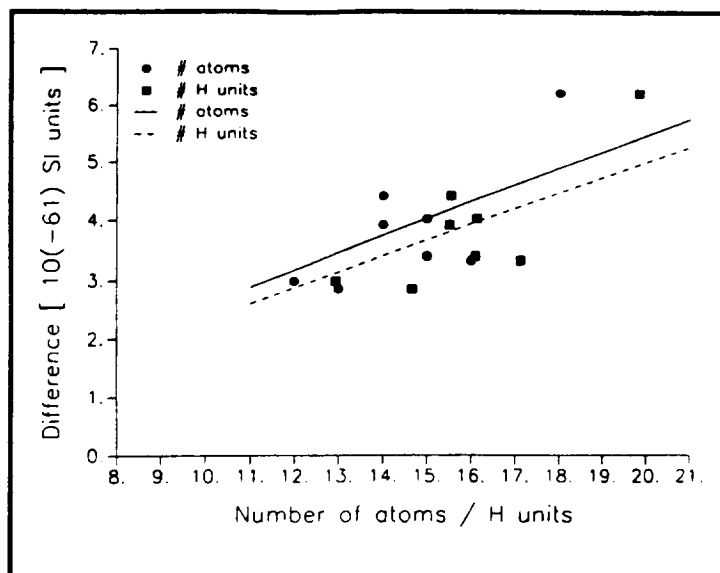| Table 2- Third-Order Polarizabilities of Monosubstituted Benzenes		
	Predicted value 10-61 C m4	**THG** V-3
H	3.3	3.5
CH3	4.2	4.1
OCH3	4.8	4.3
NH2	4.9	4.8
N(CH3)2	6.3	7.2
CN	4.7	3.8
C(O)H	4.6	4.8

Figure 1 - Number of atoms (or number of "hydrogen units") versus the difference between predicted and experimental values of substituted benzenes.

b) Progress in dispersion effects

The basis for predicting the dispersion effects of nonlinear polarizabilities is time-dependent perturbation theory. At low intensities the β and γ terms are constant. In order to detect second and third harmonics, the molecules must be exposed to the intense radiation of lasers. Under these circumstances, the nonlinear polarizabilities become dependent on the frequency of the incident light.

During the summer of 1992, a method to estimate transition dipole moments was developed. To approximate the required transition dipole moments, the zero-differential-overlap method was applied to ground and excited states. Unoccupied molecular orbital wavefunctions from ground state calculations in the absence of external fields were used to construct various excited states. The dipole moments were separated into atomic point charge and hybridization contributions.

Since the goal is to design a method suitable for predicting dispersion effects on large molecules, the relative importance of the perturbative terms will be considered. Inclusion of indirect or direct summations, the number of terms in each summation, corrected expressions for the excited states and molecular orbital energies will be studied.

c) Progress on bulk effects

In our previous work, the effect of intermolecular interactions on the second and third-order polarizabilities have been estimated from experimental data fit to solvent molecular refraction or solvent dielectric

constant. In the case of neat samples, the effect on a parent compound was assumed valid for the substituted molecules.

Calculations performed on dimethylamino nitrobenzene have proven to be very sensitive to conformational isomerization. It is of great importance to know what the structure of the molecule is in the crystalline state. This problem will be examined using a molecular mechanics approach. Estimations of heats of sublimation and fusion, as well as hardness of crystals will also be done. Knowing these properties will help determine the feasibility of growing crystals of a given substance and its utility in various applications.

During the summer of 1992, the molecular mechanics program MM3 was modified to be run in a 486 personal computer.

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