Modelling of dielectric properties of non-linear optic materials based on linear molecules

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Abstract. Dependence of polarizability (LP) and hyperpolarizability (HP) of linear oligomers on the number of monomers in the chain is analyzed. A critical review of previous studies revealed two main issues. Firstly, the specific (per one chain unit) values of both LP and HP monotonously increase along with the chain length, and secondly, both dependencies approach the limit values in sufficiently long chains. A model describing such behavior is proposed. The model parameters are LP and HP of an isolated chain unit and a cross-term, which couples the dipole moments of neighboring units. These parameters have a clear physical meaning. It is shown that the theoretical predictions provided by the model agree well both with the results of accurate quantum-mechanical calculations and with experimental data.

1. Introduction
Nonlinear optics deals with physical phenomena related to the light-matter interaction, in which the dependence of polarization on field strength is nonlinear [1]. The major problem of modern optoelectronics is to find new transparent materials with high optical nonlinearity.

A large body of researches (see [2] and references therein) has discovered anomalously large values of the longitudinal polarizability and second order polarizability in linear molecules with conjugated C-C bonds. Later, a similar enhancement of LP and HP values was found in inorganic chain clusters [3]. Many experimental [4-9] and theoretical [10-21] studies revealed an interesting phenomenon – a marked increase in specific LP and HP with a chain length. For the sufficiently large molecules, the increase slows down and finally approaches a linear growth. Such phenomenon was termed ‘saturation behavior’ [22]. Below we shall refer to it as the Chain Length Effect (CLE).

Most theoretical studies analyzed CLE using quantum-mechanical calculations, whereas some empirical relations were used in the experimental studies. The latter approach has an essential advantage of prognostication power. However, all the empirical formulas for CLE proposed to date had two main shortcomings: (a) none of them was equally well applicable for both short and long chains; (b) empirical parameters for the polarizability and hyperpolarizability expressions were fitted independently. Finally, such approach is purely phenomenological. It does not provide any new insights into the nature of CLE. This study is aimed at searching new expressions that self-consistently describe CLE for the polarizability and second-order hyperpolarizability in chain molecules of arbitrary length.
2. Results and discussion

As a starting point we use the Harmonically Coupled Anharmonic Oscillators Model (HCAOM) proposed in [10]. The model assumes that the \( i \)-th elementary chain unit is an electron in a potential well with a minimum point located at \( X_i \). We also state that the form of each potential well includes harmonic and anharmonic terms, i.e.:

\[
V(x_i) = \frac{1}{2} k (x_i - X_i)^2 + \frac{1}{24} g (x_i - X_i)^4,
\]

where \( k \) and \( g \) are the harmonic and anharmonic coefficients expressed in units of eV/Å\(^2\) and eV/Å\(^4\), respectively. The total Hamiltonian of a chain consisting of \( N \) units is described as a superposition of \( N \) adjoining potential wells with the form given by equation (1). The minima of the wells are assumed to be equidistant and separated by a distance \( d \). The inter-site coupling is assumed to be harmonic with the hardness constant \( t \).

In a homogeneous external field \( F \), the shells are displaced. The displacements \( x_i \) are determined from the equilibrium conditions:

\[
k x_i + \frac{1}{6} g x_i^3 - t(x_{i+1} - 2x_i + x_{i-1}) = YF.
\]

The set of nonlinear equations (2) can be solved numerically by using the power series:

\[
x_i = x_i^{(1)} F + x_i^{(3)} F^3 + \ldots
\]

The dipole moment induced by the field is given by the expression:

\[
\mu = Y \sum_{i=1}^{N} x_i.
\]

Solving equation (2) for different \( F \) values, one can determine the \( \mu(F) \) dependence. The use of the decomposition (3) provides us with the appropriate expression for the specific (per one chain unit) LP:

\[
\alpha_s(N) = \frac{1}{N} \sum_{i=1}^{N} x_i^{(1)}
\]

and the third-order HP:

\[
\gamma_s(N) = \frac{1}{N} \sum_{i=1}^{N} x_i^{(3)}
\]

Equations (1-6) have been successfully used in [10] for modelling dielectric properties of polyene and thiophene molecules. In this paper, the HCAOM is used in order to derive analytic expressions for the \( \alpha_s(N) \) and \( \gamma_s(N) \) dependencies. For this purpose, we turn to the long-chain approximation.

If the HCAOM is applied to a chain whose length is much larger than the distance between adjoining units \( d \), such chain can be considered as a continuous media. Then, one can replace the discrete variable \( i \) by a continuous variable \( s = id \), and the algebraic equation (4) can be transformed into a differential equation:

\[
k x(s) + \frac{1}{6} g x^3(s) - td^2 \frac{d^2 x(s)}{ds^2} = YF.
\]

The boundary conditions for a chain of length \( L \) can be written as follows:

\[
x(L/2) = 0 \quad \text{and} \quad x(-L/2) = 0.
\]

Solving equation (7) by using the decomposition (3) and the definitions (5-6), one obtains the expressions:

\[
\alpha_s(L) = \alpha_{\text{lim}} \left[ 1 - \frac{1}{s} \tanh(s) \right]
\]

and
\[ \gamma_s(L) = \gamma_{\text{lim}} \frac{3}{32 \cosh^4 s} \left[ 18 + \cosh 4s + 16 \cosh 2s - \frac{1}{s} \left( \frac{40}{3} \sinh 2s + \frac{25}{12} \sinh 4s \right) \right]. \]  \tag{10}

where

\[ \lambda = 2d \sqrt{\frac{t}{k}}, \quad s = \frac{L}{\lambda}, \quad \alpha_{\text{lim}} = \frac{Y^2}{k} \quad \text{and} \quad \gamma_{\text{lim}} = g \left( \frac{Y}{k} \right)^4. \]

To verify these expressions, we compare them with the \( \alpha_s(N) \) and \( \gamma_s(N) \) dependencies obtained by accurate quantum-mechanical calculations. The \( \alpha_s \) and \( \gamma_s \) values for a series of polyene oligomers \( \text{C}_x\text{H}_{N+2} \ (N = 4 + 22) \) have been calculated in \cite{10}. These \( \alpha_s(N) \) and \( \gamma_s(N) \) dependencies are shown in figure 1 by symbols. The data were fitted by the \( \alpha_s(N) \) and \( \gamma_s(N) \) dependencies defined by equations (9-10). They are shown by solid lines.

![Figure 1](image)

Figure 1. LP (a) and HP (b) of polyene oligomers \( \text{C}_x\text{H}_{N+2} \) in dependence on the chain length \( N \). The results of \textit{ab initio} calculations of \cite{10} are shown by symbols; the dependencies corresponding to the analytical formulae (9-10) are shown by solid lines.

Equations (9-10) can be used equally well for fitting the data of real experiments. The \( \alpha_s(N) \) and \( \gamma_s(N) \) dependencies determined in \cite{5} by the degenerate four-wave mixing technique are shown in figure 2 by symbols. Results of the fitting procedure by using equations (9-10) are shown by solid lines.

It should be noted that the analytical dependences in figures 1(a) and 1(b) were obtained for the same value \( \lambda = 7 \). This value characterizes an important physical quantity - the length of delocalization of the dielectric response function. Similarly, the dependences in figures 2(a) and 2(b) were obtained for the value \( \lambda = 9 \).
3. Concluding remarks
In this paper, new analytic expressions describing the chain-length effect for LP and second-order HP are proposed. The expressions are derived from the model of coupled anharmonic oscillators. The parameters of the model, which are the polarizability and hyperpolarizability of an individual unit and the coupling coefficient for the neighboring units, have a clear physical meaning and can be determined either experimentally or from quantum-mechanical calculations. It is shown that the proposed analytical expressions make it possible to describe sufficiently well both the results of accurate quantum-mechanical calculations and the experimental data for various chain oligomers. The main advantage of this approach in comparison with previous analogues is the possibility of a consistent description of both linear and nonlinear optical properties. The proposed formulae allow us, by studying the chain length effect for LP, to predict the chain length dependence for HP.

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