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Three-coupled-oscillator model for nonlinear optical response of chiral molecules with tripod-like structure

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Abstract

In this paper, we further study on the relation between the first hyperpolarizability and molecular configuration based on the three-coupled-oscillator model proposed by us. The model is suitable for chiral molecules with the tripod-like structure. We numerically simulate the spectra of first hyperpolarizabilities, and investigate the effects of molecular chiral parameters and coupling coefficients on the hyperpolarizabilities. As an example, we show a calculation of the first-hyperpolarizability spectra for NPAN molecules, which accord well with the experimental result obtained by Barzoukas et al. [M. Barzoukas, D. Josse, P. Fremaux, J. Zyss, J. Opt. Soc. Am. B 4 (1987) 977–986].

Keywords: Molecular chirality; Hyperpolarizabilities; Three-coupled-oscillator model; Tripod-like molecular structure; Second-order optical nonlinearity

1. Introduction

The chiral molecular medium is very attractive to researchers due to its asymmetric structure and unique properties. In recent years, the study for designing and synthesizing molecular materials with larger susceptibilities is one of hot research topics [1–3], which relates to several fields, such as chemistry, biology, medicine and physics.

In order to explain nonlinear optical characteristics, such as the surface second harmonic generation (SHG), in different chiral molecular media, scientists have made great efforts to find the relations between molecular microstructure and nonlinear optical property in chiral molecular systems by using the classical or the quantum mechanics method [4–7]. The one of effective approaches is accomplishing the following three steps: firstly, to establish a chiral molecular model; secondly, to calculate the molecular hyperpolarizability; and finally, to deduce and obtain the susceptibility of the medium.

Recently, some researchers focus on the establishment and correct use of chiral molecular models [8–18]. There are three classical models have been developed: the electron-on-helix (Drude's) model, the coupled oscillator (Kuhn's) model, and the simplified Kirkwood's model. The electron-on-helix model [12–15] is used to describe the chiral molecules with helix structure, in which the conjugated π-electrons are bounded by the molecular backbone and they can move along the helical path, such as helicene, stilbene, bipyridyl, etc. However, this model is too simple to describe the large molecules consisting of several groups separated in space. One must take into account the interaction between groups. Therefore, some coupled-oscillator models have been developed, such as the two-coupled-oscillator model [15,16] and the simplified Kirkwood's model [17]. The former is concerned to the chiral molecules with two weak-coupled electric oscillation centers, which move along the directions orthogonal to each other on two parallel planes having certain

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spacing, such as 1,1′-bi-2-naphthol, tartaric acid, Tröger base, etc. The latter is used to investigate the chiral molecules with two anisotropic groups, which have same structure and different orientation.

However, the different models may give different results in same condition [15]. The above molecular models cannot describe the molecules with some special configurations, for example, the chiral molecules with a tripod-like structure. Therefore, we will develop the three-coupled-oscillator model [18] in this paper. Based on the new model we will deduce the coupled equations and obtain the analytical expressions of the hyperpolarizabilities for describing the optical nonlinearity of such molecules.

The work in this paper is an extension of the original work about three-coupled-oscillator model we proposed [18]. We will further study the relationship between first hyperpolarizabilities and molecular configurations, and will describe the nonlinear optical properties of chiral molecules with a tripod-like structure. In the following sections, we will briefly describe the three-coupled-oscillator model, and then present the dependence of first hyperpolarizabilities on the parameters of molecular configuration (such as bond angles), and show the spectra of first hyperpolarizabilities as a function of second harmonic wavelength. Finally, we will present the spectra of hyperpolarizabilities for NPAN, a typical chiral molecule with tripod-like structure.

2. Result and discussion

2.1. Brief of three-coupled-oscillator model

There is one kind of chiral molecules, their configuration looks like a tripod due to the restriction of spatial structure between multiple groups, such as nitrobenzene derivatives, sulfur compound, and so on. We suggest using the three-coupled-oscillator model to describe such kind of molecules as shown in Fig. 1. Based on this model, we can study on the nonlinear optical properties in this molecular medium.

In the model, the three different groups connect to a chiral center (for instance, a nitrogen atom), which can be regarded as three spring oscillators 1, 2 and 3 with weak interaction. We suppose that the three oscillators move along their bond direction separately. A Cartesian coordinates with x-, y-, and z-axes are fixed on the top of the tripod for describing their movement. (x, y, z) is the microscopic frame. The three oscillators have frequencies ω_{0i} and damping coefficients γ_i $(i = 1, 2, 3)$ and they are coupled each other through dipole–dipole interaction with a small coupling parameters A_{ij} $(i, j = 1, 2, 3)$.

The positional vectors $\mathbf{r}_i$ $(i = 1, 2, 3)$ of oscillators has an angle α_i with the $x'O'y'$ plane (parallel to xOy plane). ϕ is the angle between two bonds. Assume that

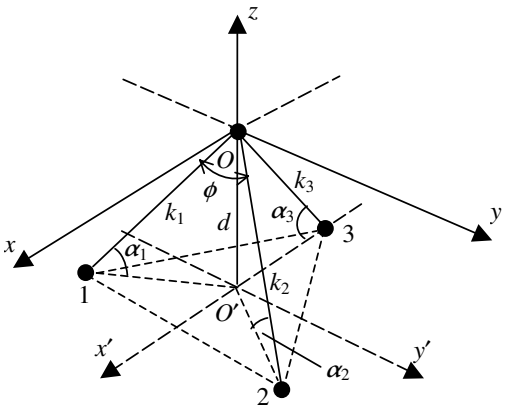

Fig. 1. Schematic diagram of the three-coupled-oscillators model.

$\alpha_1 \approx \alpha_2 \approx \alpha_3 \approx \alpha$ for easy calculate. At the rest position, the oscillators 1, 2, and 3 are located at $(\frac{1}{2}d\cot\alpha, -\frac{\sqrt{3}}{2}d\cot\alpha, -d)$, $(\frac{1}{2}d\cot\alpha, \frac{\sqrt{3}}{2}d\cot\alpha, -d)$, and $(-d\cot\alpha, 0, -d)$, respectively [18]. The relation of bond angle ϕ with α is $\cos\alpha = (2\sqrt{3}/3)\sin(\phi/2)$ approximately. We call a, b and c as the elongation of oscillators 1, 2, and 3 from their equilibrium positions.

If this molecular system is excited by a monochromatic wave, $\mathbf{E}_i(\mathbf{r}, t) = \mathbf{E}_i(\mathbf{r})\exp(-i\omega t) + \text{c.c.}$, the response of oscillators to the electric field has the components at fundamental frequency, second-harmonic frequency and third-harmonic frequency, and so on. We only consider the case up to second-harmonic frequency, thus $a = a_1 e^{-i\omega t} + a_2 e^{-i2\omega t} + \text{c.c.}$, $b = b_1 e^{-i\omega t} + b_2 e^{-i2\omega t} + \text{c.c.}$, and $c = c_1 e^{-i\omega t} + c_2 e^{-i2\omega t} + \text{c.c.}$

Based on the coupled equations of motion for the three oscillators [18], and considering the spatial dispersion (SD) of electric field, $\mathbf{E}_i(\mathbf{r}, t)$ is expanded in the vicinity of the origin point O as

$$E_{ij} = E_j + \frac{\partial E_j}{\partial x}x_i + \frac{\partial E_j}{\partial y}y_i + \frac{\partial E_j}{\partial z}z_i \quad (i = 1, 2, 3;\ \ j = x, y, z). \tag{1}$$

Let us first consider the linear response of the system. The coupled equations of the oscillators along their respective oscillators can be written as:

$$D_1(\omega)a_1 + A_{12}b_1 + A_{13}c_1 = \frac{q_1}{m_1}T_1, \tag{2a}$$

$$D_2(\omega)b_1 + A_{21}a_1 + A_{23}c_1 = \frac{q_2}{m_2}T_2, \tag{2b}$$

$$D_3(\omega)c_1 + A_{31}a_1 + A_{32}b_1 = \frac{q_3}{m_3}T_3, \tag{2c}$$

where we have introduced the following notation: $D_i(\omega) = -\omega^2 + \omega_{0i}^2 - 2i\omega\gamma_i$, and where the subscript 1 means first-order solution. T_i is the linear combination of the electric field E_j and its gradient $\partial E_k/\partial x_j$ $(i = 1, 2, 3,\ j, k = x, y, z)$, coefficients of which are related to the direction cosines of the field in the direction of oscillation.