Optical Rectification at Isotropic Chiral Film Composed of Tripod-Like Molecules

Xiao-Ou Wang,* Li-Jing Gong, and Chun-Fei Li

Department of Physics, Harbin Institute of Technology, 92 West Dazhi Street, Harbin 150001, China

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In the paper, the three-coupled-oscillator model presented by us is used to study the optical rectification in isotropic chiral films. The zero frequency hyperpolarizabilities of chiral molecules with a tripod-like structure are calculated. The expressions of the static-electric polarization and the relations between the optical rectification and the microscopic parameters of chiral medium are obtained by theoretical derivation. Furthermore, the relations of the dc electric-dipole polarization with the wavelength of incident light and microscopic parameters of chiral molecules have been simulated numerically.

1. Introduction

It is well-known that second-order nonlinear optical processes are forbidden in the centrosymmetric media,[1] such as crystals with cubic symmetry and most isotropic materials: gases, liquids, amorphous solids, etc. However, the second-order nonlinear optical processes are not forbidden for the isotropic chiral materials consisted of chiral molecules that are naturally noncentrosymmetric. For example, the sum-frequency generation has been recently observed in chiral liquids: limonene[2] and 1,1′-bi-2-naphthol in tetrahydrofuran;[3,4] the difference-frequency and the optical rectification have been predicted to exist in isotropic chiral media.[5,6]

Optical rectification (OR) is the generation of dc electric polarization intensity due to second-order nonlinear optical effect, when a light beam passes through a nonlinear medium. In 1962, Armstrong et al.[7] predicted theoretically this effect. In the same year, Bass et al.[8] observed experimentally OR using a ruby laser and KDP crystals. In 1996, Il'inova et al.[9] investigated OR in chiral liquids. In the same year, Zawdny et al.[5] studied the dc electric-dipole polarization produced by an elliptically polarized light, which was in resonance to the chiral molecules. In 2002, Fischer[10] researched OR in isotropic media consisting of chiral molecules; he found the light-induced dc electric polarization in pinene.

The classical models of chiral molecules are often used for studying the second harmonic generation,[11–15] which has a clear physical picture to explain the optical nonlinearity in different chiral molecular systems. In this paper, we use the new three-coupled-oscillator model[14,15] to study the OR in the isotropic thin films composed of chiral molecules with a tripod-like structure at the direction of reflected light. In section 2, the expression of static electric-dipole polarization and the relationship between molecular zero frequency hyperpolarizabilities and dc electric-dipole polarization of chiral film are presented, and then the dc electric-dipole hyperpolarizabilities of chiral molecules with a tripod-like structure are calculated. In section 3, the relations of the static electric polarizations with the wavelength and the incident angle of the incident light and the microscopic parameters of molecules are simulated numerically.

2. Theory

2.1. dc Electric-Dipole Polarization at the Chiral Films.

As we know the OR phenomenon from the nonlinear optics[1–5] that when a monochromatic optical wave with an electrical field

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}(\omega, \mathbf{r}) \exp(-\mathrm{i}\omega t) + \mathrm{cc} \tag{2.1}$$

passes though an second-order nonlinear medium, a direct current electric-dipole polarization intensity $\mathbf{P}^{(2)}(0)$ can be produced with a nonlinear susceptibility $\chi^{(2)}(0;-\omega,\omega)$.

In a Cartesian coordinate system XYZ, we can write down the following phenomenological expression (the Einstein summation convention is used):

$$P_I^{(2)}(0) = \varepsilon_0 \chi_{IJK}^{(2)}(0;-\omega,\omega)\, E_J^*(\omega,r)\, E_K(\omega,r) + \mathrm{cc} \tag{2.2}$$

where the indices I, J and K refer to the Cartesian laboratory coordinates and may be assigned X, Y and Z.

We discuss here in the case of chiral medium, in which the second-order nonlinear medium is an isotropic thin film consisted of chiral molecules, which are distributed on the surface isotropically. We take the chiral film to be in the $X-Y$ plane and fundamental field at frequency ω to be a monochromatic plane wave that is given by

$$\mathbf{E} = \boldsymbol{e} E_0(\omega) e^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)} \tag{2.3}$$

where $\boldsymbol{e}$ denotes polarization direction, $\mathbf{E}_0(\omega)$ is the amplitude of light field, and $\mathbf{k}$ is the wave vector. We suppose the light beam propagate in the $X-Z$ plane, so that the wave vector is given by

$$\mathbf{k} = -\boldsymbol{e}_Z k \cos\theta_{inc} + \boldsymbol{e}_X k \sin\theta_{inc} \tag{2.4}$$

where $\boldsymbol{e}_X$ and $\boldsymbol{e}_Z$ are the Cartesian unit vectors, θ_{inc} is the angle of incidence (Figure 1), and $k = \omega/c$, where c is the speed of light in vacuum. An arbitrary state of polarization of the incident field is conveniently expanded in the basis of the s- and p-polarized unit vectors, which are

$$\begin{aligned} \boldsymbol{e}_s &= -\boldsymbol{e}_Y \\ \boldsymbol{e}_{Fp} &= \boldsymbol{e}_X \cos\theta_{inc} + \boldsymbol{e}_Z \sin\theta_{inc} \end{aligned} \tag{2.5}$$

where the subscript **F** refers to the fundamental field.

A dc electric-dipole polarization can be generated by interaction between the chiral molecules and the electromagnetic field in the direction of reflected light. Assuming that the nonlinear response is localized within a thin layer, we only consider

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* Corresponding author. Telephone: 86-451-86414132, 13684637917. Fax number: 86-451-86416889. E-mail: wxo@hit.edu.cn.

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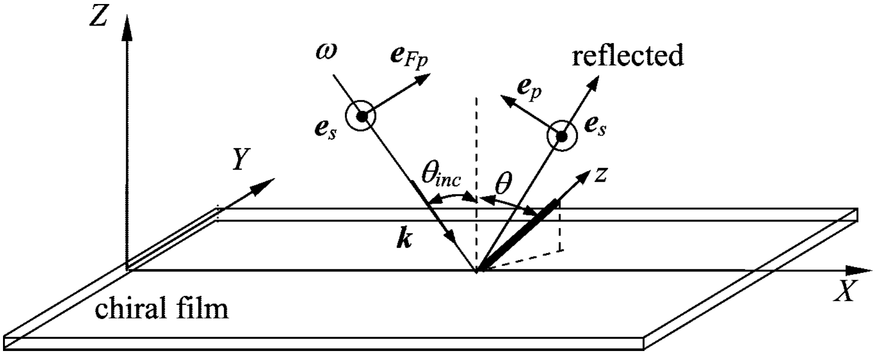

Figure 1. Laser beam at frequency ω incident on the sample at angle $\theta_{\rm inc}$. The surface normal is along the z axis. Also shown are the p and s unit vectors for each field.

electric-dipole approximation. In addition, the nonlinear layer is assumed to be sufficiently thin so that linear effects do not mix the p- and s-polarized components of the fields.

From Figure 1, the s- and p-polarized unit vectors in the reflected direction are

$$\boldsymbol{e}_S = -\boldsymbol{e}_Y \qquad \boldsymbol{e}_P = -\boldsymbol{e}_X \cos\theta_{inc} + \boldsymbol{e}_Z \sin\theta_{inc} \tag{2.6}$$

Thus, we can obtain the expressions of $P_I^{(2)}(0)$ in the all state of polarization based on eqs 2.2, 2.3 and 2.6.

For the isotropic chiral film, the s-polarized components of the static electric-dipole polarization in the reflected directions, we have

$$P_{sX}^{(2)}(0) = 2\varepsilon_0|E_0|^2\chi_{XYY}^{(2)}(0;-\omega,\omega)e_Ye_Y \tag{2.7a}$$

$$P_{sY}^{(2)}(0) = 2\varepsilon_0|E_0|^2\chi_{YYY}^{(2)}(0;-\omega,\omega)e_Ye_Y \tag{2.7b}$$

$$P_{sZ}^{(2)}(0) = 2\varepsilon_0|E_0|^2\chi_{ZYY}^{(2)}(0;-\omega,\omega)e_Ye_Y \tag{2.7c}$$

The p-polarized components also can be written

$$P_{pX}^{(2)}(0) = 2\varepsilon_0|E_0|^2[\chi_{XXX}^{(2)}(0;-\omega,\omega)e_Xe_X + \chi_{XXZ}^{(2)}(0;-\omega,\omega)e_Xe_Z + \chi_{XZX}^{(2)}(0;-\omega,\omega)e_Ze_X + \chi_{XZZ}^{(2)}(0;-\omega,\omega)e_Ze_Z] \tag{2.8a}$$

$$P_{pY}^{(2)}(0) = 2\varepsilon_0|E_0|^2[\chi_{YXX}^{(2)}(0;-\omega,\omega)e_Xe_X + \chi_{YXZ}^{(2)}(0;-\omega,\omega)e_Xe_Z + \chi_{YZX}^{(2)}(0;-\omega,\omega)e_Ze_X + \chi_{YZZ}^{(2)}(0;-\omega,\omega)e_Ze_Z] \tag{2.8b}$$

$$P_{pZ}^{(2)}(0) = 2\varepsilon_0|E_0|^2[\chi_{ZXX}^{(2)}(0;-\omega,\omega)e_Xe_X + \chi_{ZXZ}^{(2)}(0;-\omega,\omega)e_Xe_Z + \chi_{ZZX}^{(2)}(0;-\omega,\omega)e_Ze_X + \chi_{ZZZ}^{(2)}(0;-\omega,\omega)e_Ze_Z] \tag{2.8c}$$

However, in any isotropic chiral film, the macroscopic quadratic nonlinearity, the second-order nonlinear susceptibility $X_{IJK}^{(2)}(0)(0;-\omega,\omega)$ is related to the corresponding orientationally averaged molecular hyperpolarizability $\beta_{ijk}(0;-\omega,\omega)$. It can be written as:

$$\chi_{IJK}^{(2)}(0;-\omega,\omega) = Nf_{\rm L}^3\langle(I\cdot i)(J\cdot j)(K\cdot k)\rangle\beta_{ijk}(0;-\omega,\omega) \tag{2.9}$$

where i, j, k and I, J, K refer to the molecular and the laboratory frames, respectively. $\langle\ \rangle$ represents the averaging operation. N is the molecular surface density; f_L^3 is the local field factor of modifications in three directions. From eq 2.9, we derive the nonvanishing-independent components of $X_{IJK}^{(2)}(0;-\omega,\omega)$ for tripod-like molecules using three-coupled-oscillator.

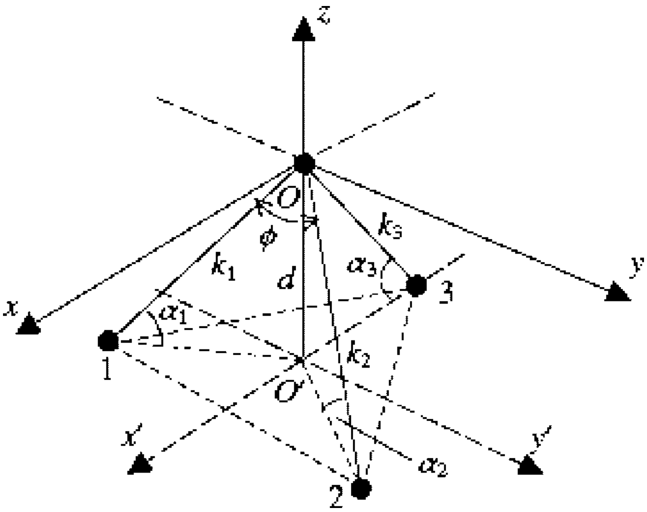

Figure 2. Schematic diagram of the three-coupled-oscillators model.

2.2. Three-Coupled-Oscillator Model. There is one kind of chiral molecule; 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 a kind of molecules as shown in Figure 2.

We suppose that the three oscillators move along their bond direction separately. 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 $\gamma_{\rm i}$ ($i = 1, 2, 3$) and they are coupled each other through dipole−dipole interaction with small coupling parameters A_{ij} ($i, j = 1, 2, 3$). Positional vectors $\mathbf{r}_i$ ($i = 1, 2, 3$) of oscillators have an angle α_i with the x'O$'y'$ plane (parallel to xOy plane). ϕ is the angle between two bonds. Assume that $\alpha_1 \approx \alpha_2 \approx \alpha_3 \approx \alpha$ to calculate easy. At the rest position, the oscillators 1, 2, and 3 are located at ($^1/_2d\cot\alpha$, $-(3^{1/2}/2)d\cot\alpha$, $-d$), ($^1/_2d\cot\alpha$, $(3^{1/2}/2)d\cot\alpha$, $-d$), and ($-d\cot\alpha$, 0, $-d$), respectively.[14,15] The relation of bond angle ϕ with α can be expressed as $\cos\alpha = (2\cdot3^{1/2}/3)\sin(\phi/2)$ approximately. We call a, b and c as the elongations of oscillators 1, 2, and 3 from their equilibrium positions, and they can written as $a = a_1{\rm e}^{-{\rm i}\omega t} + a_2{\rm e}^{-{\rm i}2\omega t} + {\rm cc}$, $b = b_1{\rm e}^{-{\rm i}\omega t} + b_2e^{-{\rm i}2\omega t} + {\rm cc}$, and $c = c_1e^{-{\rm i}\omega t} + c_2e^{-{\rm i}2\omega t} + {\rm cc}$ when molecules are excited by the monochromatic wave (eq 2.1).

Considering the linear response of the system, the coupled equations of the oscillators along their respective oscillating direction can be written,

$$D_1(\omega)a^{(1)} + A_{12}b^{(1)} + A_{13}c^{(1)} = \frac{q_1}{m_1}T_1 \qquad (2.10a)$$

$$D_2(\omega)b^{(1)} + A_{21}a^{(1)} + A_{23}c^{(1)} = \frac{q_2}{m_2}T_2 \qquad (2.10b)$$

$$D_3(\omega)c^{(1)} + A_{31}a^{(1)} + A_{32}b^{(1)} = \frac{q_3}{m_3}T_3 \qquad (2.10c)$$

Correspondingly, the zero frequency response of oscillators to the electric field, produced by the second-order nonlinear process, can be given by

$$D_1(0)a_-^{(2)}(0) + \mathrm{A}_{12}b_-^{(2)}(0) + \mathrm{A}_{13}c_-^{(2)}(0) = -f_1a^{(1)}(\omega)a^{(1)}(\omega) \qquad (2.11a)$$

$$D_2(0)b_-^{(2)}(0) + \mathrm{A}_{21}a_-^{(2)}(0) + \mathrm{A}_{23}c_-^{(2)}(0) = -f_2b^{(1)}(\omega)b^{(1)*}(\omega) \qquad (2.11b)$$

$$D_3(0)c_-^{(2)}(0) + \mathrm{A}_{31}a_-^{(2)}(0) + \mathrm{A}_{32}b_-^{(2)}(0) = -f_3c^{(1)}(\omega)c^{(1)*}(\omega) \qquad (2.11c)$$

where A_{ij} (i, j = 1, 2, 3) is the coefficients for weak coupling, $D_i(\omega) = -\omega^2 + \omega_{0i}{}^2 - 2\mathrm{i}\omega\gamma_i$, $D_i(0) = \omega_{0i}{}^2$, (i = 1, 2, 3), f_i are the introduced anharmonic coefficients and can be estimated by $f_il^2 \approx \omega_{0i}{}^2l$, where l is the elongation of oscillator from the equilibrium state,[16] and T_i is the linear combination of the electric field $\mathbf{E}_j$ and its gradient $\partial\mathbf{E}_k/\partial x_j$ and coefficients of which are related to the direction cosines of the field in the direction of oscillation. On the basis of eqs 2.10a–2.10c and 2.11a–2.11c, we can obtain the general expressions of the zero frequency solutions $a_-^{(2)}(0)$, $b_-^{(2)}(0)$ and $c_-^{(2)}(0)$. These solutions are used to derive the electric dipole moments of molecule

$$p_x^{(2)}(0) = \frac{q\cos\alpha}{2}[a_-^{(2)}(0) + b_-^{(2)}(0) - 2c_-^{(2)}(0)] \qquad (2.12a)$$

$$p_y^{(2)}(0) = \frac{\sqrt{3}q\cos\alpha}{2}[-a_-^{(2)}(0) + b_-^{(2)}(0)] \qquad (2.12b)$$

$$p_z^{(2)}(0) = -q\sin\alpha[a_-^{(2)}(0) + b_-^{(2)}(0) + c_-^{(2)}(0)] \qquad (2.12c)$$

Here, we only consider the interacting between electric-dipole and electric-dipole, where q is the charge of oscillators supposed as $q_1 = q_2 = q_3 = q$. Comparing with $p_i^{(2)}(0) = \varepsilon_0\beta_{ijk}(0;-\omega,\omega)\,E_j^*(\omega)\,E_k(\omega)$, we can obtain the zero frequency first hyperpolarizabilities $\beta_{ijk}(0;-\omega,\omega)$ of chiral molecules with a tripod-like structure (see Appendix). We derive the nonvanishing-independent components of $\chi_{IJK}^{eee}(0;-\omega,\omega)$ from eq 2.9, as follows:

$$\chi_{ZZZ}^{eee}(0;-\omega,\omega) = \frac{1}{2}\cos\theta[\sin^2\theta(2\beta_{xxz} + 2\beta_{yyz} + \beta_{zxx} + \beta_{zyy}) + 2\cos^2\theta\beta_{zzz}] \qquad (2.13a)$$

$$\chi_{ZXX}^{eee}(0;-\omega,\omega) = \frac{1}{4}\cos\theta[\sin^2\theta(-\beta_{xxz} - \beta_{xzx} - \beta_{yyz} - \beta_{yzy} + 2\beta_{zzz}) + (1 + \cos^2\theta)(\beta_{zxx} + \beta_{zyy})] \qquad (2.13b)$$

$$\chi_{XXZ}^{eee}(0;-\omega,\omega) = \frac{1}{4}\cos\theta[\sin^2\theta(-\beta_{xzx} - \beta_{yzy} - \beta_{zxx} - \beta_{zyy} + 2\beta_{zzz}) + (1 + \cos^2\theta)(\beta_{xxz} + \beta_{yyz})] \qquad (2.13c)$$

$$\chi_{XYZ}^{eee}(0;-\omega,\omega) = \frac{1}{2}\cos^2\theta(\beta_{xyz} - \beta_{yxz}) - \frac{1}{4}\sin^2\theta(\beta_{xzy} - \beta_{yzx} - \beta_{zxy} + \beta_{zyx}) \qquad (2.13d)$$

$$\chi_{XZY}^{eee}(0;-\omega,\omega) = \frac{1}{2}\cos^2\theta(\beta_{xzy} - \beta_{yzx}) - \frac{1}{4}\sin^2\theta(\beta_{xyz} - \beta_{yxz} + \beta_{zxy} - \beta_{zyx}) \qquad (2.13e)$$

$$\chi_{ZXY}^{eee}(0;-\omega,\omega) = \frac{1}{2}\cos^2\theta(\beta_{zxy} - \beta_{zyx}) + \frac{1}{4}\sin^2\theta(\beta_{xyz} - \beta_{xzy} - \beta_{yxz} + \beta_{yzx}) \qquad (2.13f)$$

$$\chi_{XZX}^{eee}(0;-\omega,\omega) = \frac{1}{4}\cos\theta[\sin^2\theta(-\beta_{xxz} - \beta_{yyz} - \beta_{zxx} - \beta_{zyy} + 2\beta_{zzz}) + (1 + \cos^2\theta)(\beta_{xzx} + \beta_{yzy})] \qquad (2.13g)$$

$$\chi_{ZXX}^{eee}(0;-\omega,\omega) = \chi_{ZYY}^{eee}(0;-\omega,\omega) \qquad \chi_{XXZ}^{eee}(0;-\omega,\omega) = \chi_{YYZ}^{eee}(0;-\omega,\omega)$$

$$\chi_{XYZ}^{eee}(0;-\omega,\omega) = -\chi_{YXZ}^{eee}(0;-\omega,\omega) \qquad \chi_{XZX}^{eee}(0;-\omega,\omega) = \chi_{YZY}^{eee}(0;-\omega,\omega)$$

$$\chi_{XZY}^{eee}(0;-\omega,\omega) = -\chi_{YZX}^{eee}(0;-\omega,\omega) \qquad \chi_{ZXY}^{eee}(0;-\omega,\omega) = -\chi_{ZYX}^{eee}(0;-\omega,\omega)$$

where θ is the Euler angle (namely, the polar angle with respect to the surface normal, the Z axis in the laboratory frame, see Figure 1). In the equations above-mentioned, β_{ijk}, is $\beta_{ijk}(0;-\omega,\omega)$.

2.3. Optical Rectification at the Chiral Films Composed of Tripod-Like Molecules. For the isotropic thin film of chiral molecules with a tripod-like structure, eqs 2.7a–2.7c and 2.8a–2.8c can be written

$$P_{\mathrm{s}Z}^{(2)}(0) = 2\varepsilon_0|E_0|^2\chi_{ZYY}^{(2)}(0;-\omega,\omega) \qquad (2.14)$$

$$P_{\mathrm{p}X}^{(2)}(0) = -2\varepsilon_0|E_0|^2\cos\theta_{\mathrm{inc}}\sin\theta_{\mathrm{inc}}[\chi_{XXZ}^{(2)}(0;-\omega,\omega) + \chi_{XZX}^{(2)}(0;-\omega,\omega)] \qquad (2.15a)$$

$$P_{\mathrm{p}Y}^{(2)}(0) = -2\varepsilon_0|E_0|^2\cos\theta_{\mathrm{inc}}\sin\theta_{\mathrm{inc}}[\chi_{YXZ}^{(2)}(0;-\omega,\omega) + \chi_{YZX}^{(2)}(0;-\omega,\omega)] \qquad (2.15b)$$

$$P_{\mathrm{p}Z}^{(2)}(0) = 2\varepsilon_0|E_0|^2[\chi_{ZXX}^{(2)}(0;-\omega,\omega)\cos^2\theta_{\mathrm{inc}} + \chi_{ZZZ}^{(2)}(0;-\omega,\omega)\sin^2\theta_{\mathrm{inc}}] \qquad (2.15c)$$

There is a strong correlation between molecular structure and nonlinear properties in the materials composed of chiral molecules. We know from eqs 2.14 and 2.15a–2.15c that the dc electric-dipole polarization depend on the susceptibility tensor $X_{IJK}^{(2)}(0;-\omega,\omega)$ of materials when the incident angle θ_{inc} is chosen for fixed value. Whereas $X_{IJK}^{(2)}(0)(0;-\omega,\omega)$ is related to both the magnitude of the individual molecular nonlinearities [i.e., the hyperpolarizability $\beta_{ijk}(0;-\omega,\omega)$] and the relative distribution of molecules in the medium (see eqs 2.13a–2.13g). And the hyperpolarizabilities $\beta_{ijk}(0;-\omega,\omega)$ are connected with parameters of molecular configuration. Therefore the dc electric-dipole polarization is influenced by the molecular microscopic parameters.

3. Simulation and Discussion

In this section, we simulate numerically the relation between $P_{IJ}^{(2)}(0)$ (I = s, p; J = X, Y, Z) and the microscopic parameters of chiral molecules. We assume that the wavelength of the

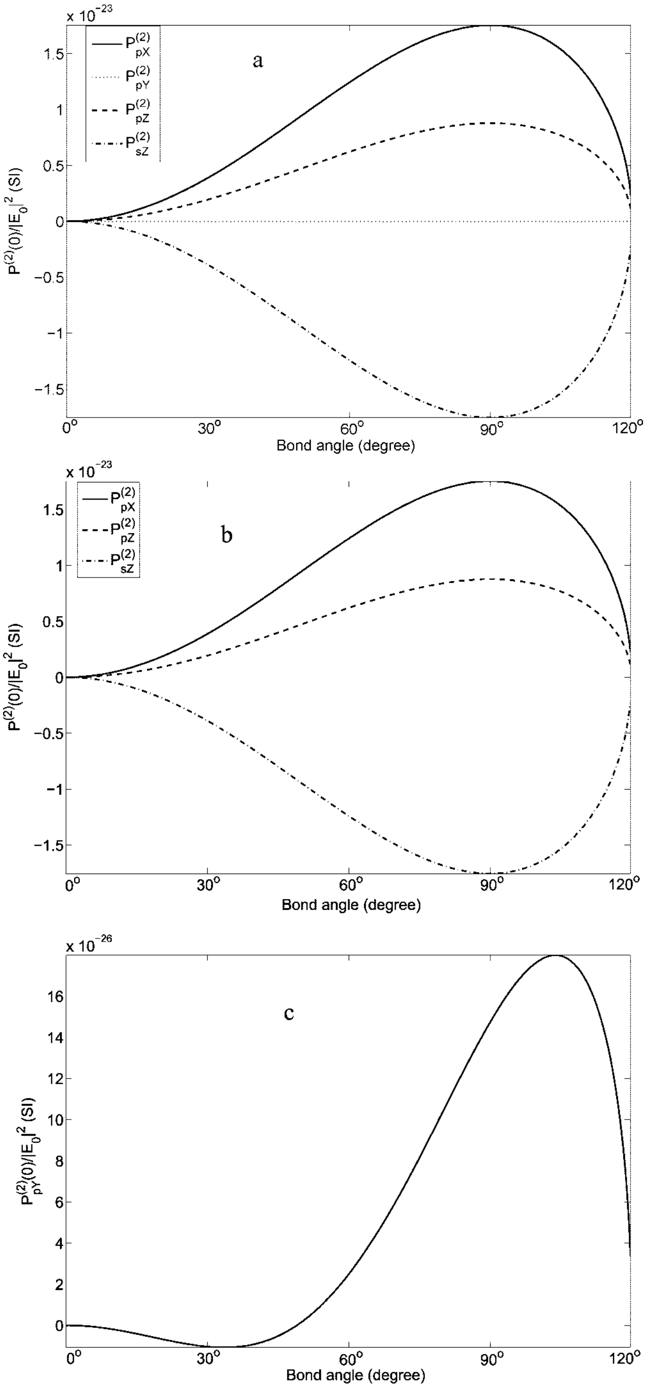

Figure 3. dc electric-dipole polarization $P_{IJ}^{(2)}(0)$ versus bond angle: (a) neglect coupling; (b) (c) consider coupling.

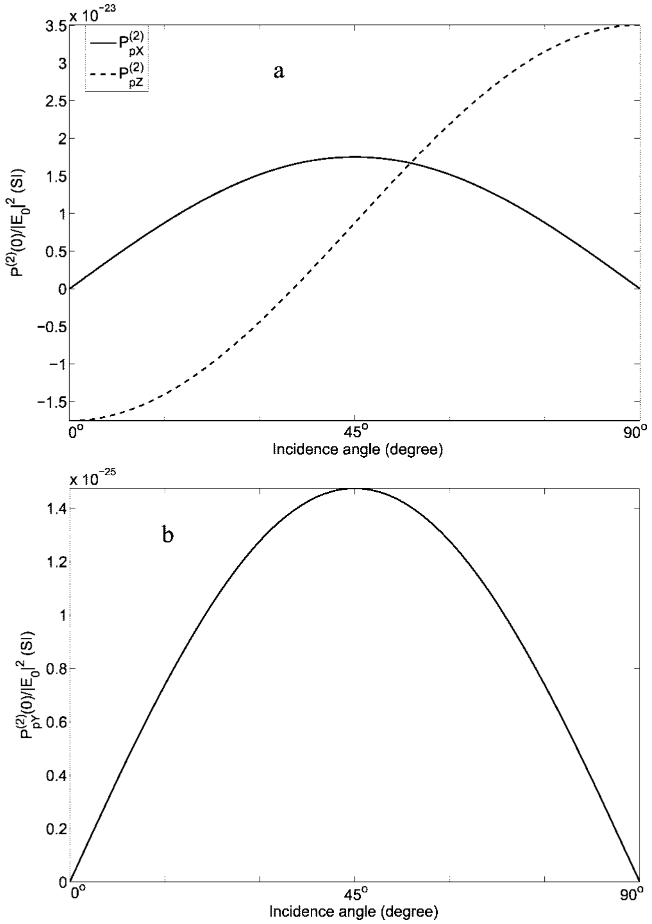

Figure 4. Curves of $P_{IJ}^{(2)}(0)$ versus an incident angle. (a) X and Z directional components and (b) Y directional components of the p-polarized components in the static electric polarization.

incident fundamental light is 532 nm, the molecular surface density $N = 4.0 \times 10^{26}$ m^{-2}. The equilibrium elongation l is chosen as 0.116 nm. The plots of the dc electric-dipole polarization $P_{IJ}^{(2)}(0)$ versus bond angle are given in Figure 3, which is under a condition that the resonance center frequency ω_0 is 5.24×10^{15} Hz, the damping coefficients γ_i is $(1/10)\omega_{0i}$ and the chirality relation $\omega_{01}/\omega_{02} = 1.058$, $\omega_{02}/\omega_{03} = 1.056$ and $\omega_{03}/\omega_{01} = 0.895$, separately.

As can be seen from Figure 3, there is a best bond angle to lead $P_{IJ}^{(2)}(0)$ to a maximal value. Therefore, we may properly design the molecular structure to enhance OR effect according to the relation between $P_{IJ}^{(2)}(0)$ and bond angle. The coupling among oscillators is neglected in Figure 3a and considered in Figure 3b,c. From Figure 3, we also see that there is a connection between chiral term $P_{pY}^{(2)}(0)$ and coupling among oscillators, which shows chirality of molecules comes of coupling among oscillators.

When the bond angle is 90°, the curves of $P_{IJ}^{(2)}(0)$ versus the angle of incidence are given in Figure 4. We can see from Figure 4 that there is a best incident angle of light to lead $P_{IJ}^{(2)}(0)$ to a maximal value, which is located at an angle of 45° for $P_{pX}^{(2)}(0)$ and $P_{pY}^{(2)}(0)$, and at an angle of 90° for $P_{pZ}^{(2)}(0)$. Therefore, we may properly choose the incident angle of the light wave to enhance value of $P_{IJ}^{(2)}(0)$, according to the relation of $P_{IJ}^{(2)}(0)$ with incident angle. Equation 2.14 shows that $P_{sZ}^{(2)}(0)$ is not influenced by the angle of incidence.

Usually, we more concern about the some factors (for example, strength of molecular chirality and coupling among molecules) that impact on OR. The study of the spectra of $P_{IJ}^{(2)}(0)$ can give us more information about the relation of OR and the chirality of the molecule, which guide us to design the asymmetric molecule with the better matching relation of chirality. The spectra of $P_{IJ}^{(2)}(0)$ under different chiral components are given in Figure 4. Here, the incident angle of the light wave θ_{inc} is 45° and the bond angle between the molecules is 90°.

We know from Figure 5, when the three oscillators are the same (e.g., no chirality), the $P_{pY}^{(2)}(0)$ is zero (see Figure 5a). Each component of static electric polarization is increased with the chirality of the molecule in the Figure 5b−d, and phenomena of multiple peaks by the coupling among oscillators appear. The emergence of multiple peaks also shows there are different

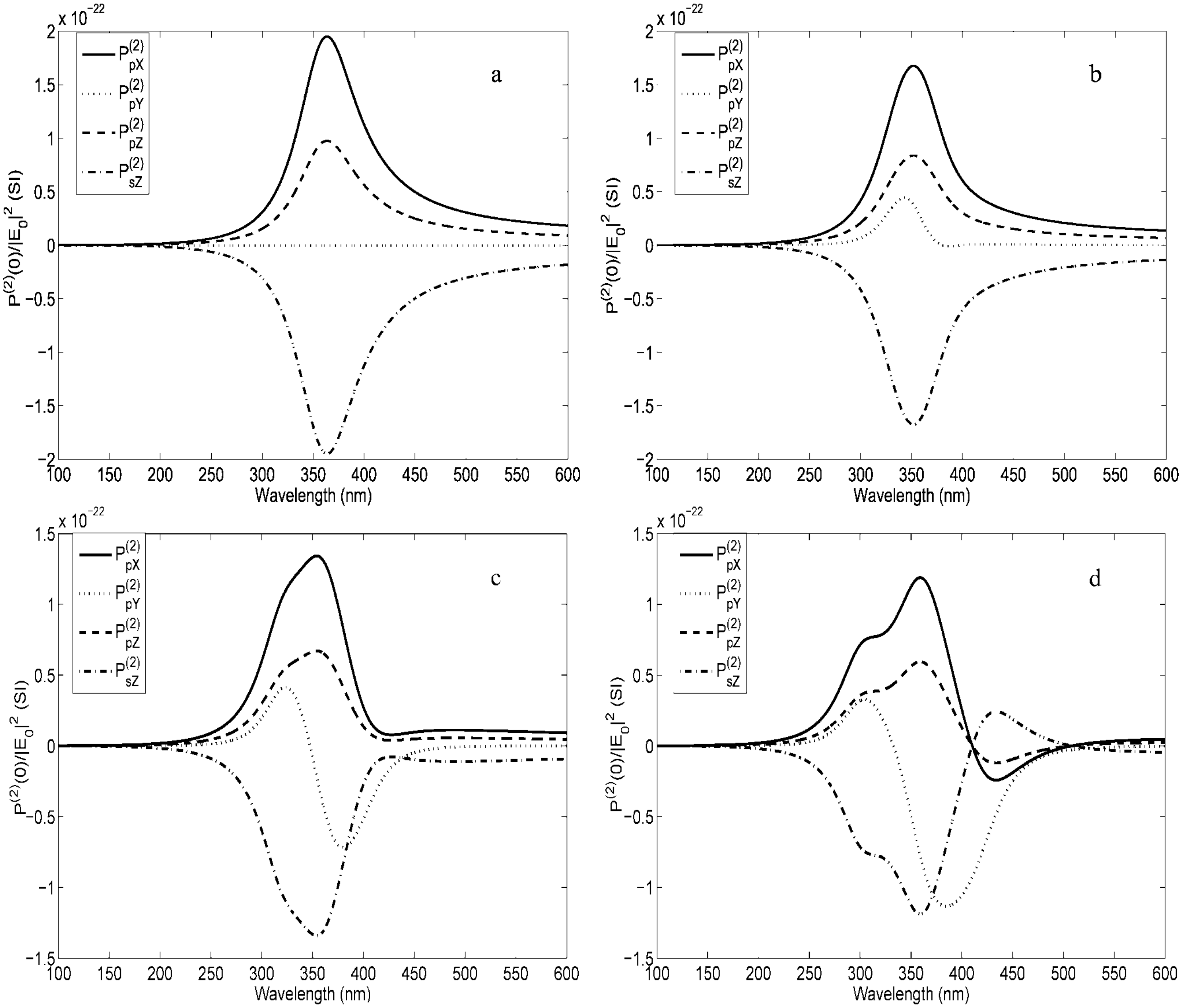

Figure 5. Spectra of $P_{IJ}^{(2)}(0)$ under different chiral components. (a) Three oscillators are the same (e.g., nothing chirality). (b)−(d) Oscillators having the following chiral components: (b) $\omega_{01}/\omega_{02} = 1.056$, $\omega_{02}/\omega_{03} = 1.056$, $\omega_{03}/\omega_{01} = 0.895$; (c) $\omega_{01}/\omega_{02} = 1.125$, $\omega_{02}/\omega_{03} = 1.111$, $\omega_{03}/\omega_{01} = 0.800$; (d) $\omega_{01}/\omega_{02} = 1.200$, $\omega_{02}/\omega_{03} = 1.167$, $\omega_{03}/\omega_{01} = 0.714$.

excitation frequencies among oscillators due to the molecular chirality and coupling action, and interaction among oscillators induces the spatial degeneracy of three oscillators to break up. The position of peaks value can be shifted properly by changing the chirality of molecules in the spectra of optical rectification from the above Figure 5. It is useful for choosing the apt OR wavelength. This indicates the chirality of molecules impacting the optical rectification effect.

4. Conclusion

We studied the optical rectification effect in the isotropic thin film composed of chiral molecules with a tripod-like structure in the direction of reflected light. We see that the dc electric polarization may be induced in the surface made up of randomly oriented chiral molecules, and it achieves the maximal value by changing the microscopic parameters of molecule, such as the bond angle, molecular chirality, and the angle of incidence of light in the isotropic surface. We can conclude that the optical rectification is due to the individual molecular nonlinearities electric dipole polarizability $\beta_{ijk}(0;-\omega, \omega)$, which connects with the molecular configuration, the chirality of molecule and the coupling among molecules. We therefore may properly design the molecular structure to enhance the optical rectification effect to satisfy the needs of the dc signal.

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Appendix

We here only give the expressions of hyperpolarizabilities $\beta_{ijk}(0;-\omega,\omega)$ that contributed to the macroscopic dc electric-dipole polarization in the isotropic thin films:

$$\beta_{xxz} = \frac{1}{8} \cdot \frac{q^3}{\varepsilon_0 m^2} \cos\alpha \sin 2\alpha[(B_1 - B_2 + 2B_3) - C - K - E + 2W - F - I - (H_1 - H_2 - 2H_3) - V + 2R + 2G - 4Q + 2M - 4P + 2(N_1 + N_2 - 2N_3)]$$

$$\begin{aligned}\beta_{xyz}={}&\frac{\sqrt{3}}{8}\cdot\frac{q^3}{\varepsilon_0 m^2}\cos\alpha\sin 2\alpha[-(B_1-B_2+2B_3)+C+K+\\&E-2W-F-I-(H_1-H_2-2H_3)-V+2R]\end{aligned}$$

$$\begin{aligned}\beta_{xzx}={}&\frac{1}{8}\cdot\frac{q^3}{\varepsilon_0 m^2}\cos\alpha\sin 2\alpha[(B_1-B_2+2B_3)-C-K+\\&2E-4W-F-I-(H_1-H_2-2H_3)+2V-4R-G+\\&2Q-M+2P+2(N_1+N_2-2N_3)]\end{aligned}$$

$$\begin{aligned}\beta_{xzy}={}&\frac{\sqrt{3}}{8}\cdot\frac{q^3}{\varepsilon_0 m^2}\cos\alpha\sin 2\alpha[-(B_1-B_2+2B_3)-C-K+\\&F+I-(H_1-H_2-2H_3)+G-2Q-M+2P]\end{aligned}$$

$$\begin{aligned}\beta_{yxz}={}&\frac{\sqrt{3}}{8}\cdot\frac{q^3}{\varepsilon_0 m^2}\cos\alpha\sin 2\alpha[-(B_1+B_2)+C-K+E+\\&F-I+(H_1+H_2)-V-2G+2M+2(-N_1+N_2)]\end{aligned}$$

$$\begin{aligned}\beta_{yyz}={}&\frac{3}{8}\cdot\frac{q^3}{\varepsilon_0 m^2}\cos\alpha\sin 2\alpha[(B_1+B_2)-C+K-E+F-\\&I+(H_1+H_2)-V]\end{aligned}$$

$$\begin{aligned}\beta_{yzx}={}&\frac{\sqrt{3}}{8}\cdot\frac{q^3}{\varepsilon_0 m^2}\cos\alpha\sin 2\alpha[-(B_1+B_2)+C-K-2E+\\&F-I+(H_1+H_2)+2V+G-M+2(-N_1+N_2)]\end{aligned}$$

$$\begin{aligned}\beta_{yzy}={}&\frac{3}{8}\cdot\frac{q^3}{\varepsilon_0 m^2}\cos\alpha\sin 2\alpha[(B_1+B_2)+C-K-F+I+\\&(H_1+H_2)-G-M]\end{aligned}$$

$$\begin{aligned}\beta_{zxy}={}&-\frac{\sqrt{3}}{4}\cdot\frac{q^3}{\varepsilon_0 m^2}\sin\alpha\cos^2\alpha[(B_1-B_2+2B_3)+C+K-\\&F-I-(-H_1+H_2-H_3)+2G+2Q-2M-2P]\end{aligned}$$

$$\begin{aligned}\beta_{zyx}={}&-\frac{\sqrt{3}}{4}\cdot\frac{q^3}{\varepsilon_0 m^2}\sin\alpha\cos^2\alpha[(B_1-B_2+2B_3)-C-K+\\&2E+2W+F+I-(-H_1+H_2-H_3)-2V-2R]\end{aligned}$$

$$\begin{aligned}\beta_{zyy}={}&-\frac{3}{4}\cdot\frac{q^3}{\varepsilon_0 m^2}\sin\alpha\cos^2\alpha[-(B_1-B_2+2B_3)-C-\\&K-F-I-(-H_1+H_2-H_3)]\end{aligned}$$

$$\begin{aligned}\beta_{zxx}={}&-\frac{1}{4}\cdot\frac{q^3}{\varepsilon_0 m^2}\sin\alpha\cos^2\alpha[-(B_1-B_2+2B_3)+C+\\&K-2E-2W+F+I-(-H_1+H_2-H_3)-2V-2R-\\&2G-2Q-2M-2P-4(-N_1-N_2+N_3)]\end{aligned}$$

$$\begin{aligned}\beta_{zzz}={}&-\frac{q^3}{\varepsilon_0 m^2}\sin^3\alpha[-(B_1-B_2+2B_3)+C+K+E+W+\\&F+I-(-H_1+H_2-H_3)+V+R+G+Q+M+P-\\&(-N_1-N_2+N_3)]\end{aligned}$$

Here

$$B_1=f_1D_1(0)^{-1}\,D_1(\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$C=f_1D_1(0)^{-1}\,D_1(\omega)^{-1}\,D_2(-\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$E=f_1D_1(0)^{-1}A_{13}D_1(\omega)^{-1}\,D_3(-\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$F=f_1D_1(0)^{-1}A_{12}D_2(\omega)^{-1}\,D_1(\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$G=f_1D_1(0)^{-1}A_{13}D_3(\omega)^{-1}\,D_1(\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$H_1=f_2D_2(0)^{-1}\,D_1(0)^{-1}A_{12}D_2(\omega)^{-1}\,D_2(-\omega)^{-1}$$

$$N_1=f_3D_3(0)^{-1}\,D_1(0)^{-1}A_{13}D_3(\omega)^{-1}\,D_3(-\omega)^{-1}$$

$$B_2=f_1D_2(0)^{-1}\,D_1(0)^{-1}A_{21}D_1(\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$H_2=f_2D_2(0)^{-1}\,D_2(\omega)^{-1}\,D_2(-\omega)^{-1}$$

$$I=f_2D_2(0)^{-1}A_{21}D_2(\omega)^{-1}\,D_2(-\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$V=f_2D_2(0)^{-1}A_{23}D_2(\omega)^{-1}\,D_3(-\omega)^{-1}\,D_2(-\omega)^{-1}$$

$$K=f_2D_2(0)^{-1}A_{21}D_2(\omega)^{-1}\,D_1(\omega)^{-1}\,D_2(-\omega)^{-1}$$

$$M=f_2D_2(0)^{-1}A_{23}D_3(\omega)^{-1}\,D_2(\omega)^{-1}\,D_2(-\omega)^{-1}$$

$$N_2=f_3D_3(0)^{-1}\,D_2(0)^{-1}A_{23}D_3(\omega)^{-1}\,D_3(-\omega)^{-1}$$

$$B_3=f_1D_3(0)^{-1}\,D_1(0)^{-1}A_{31}D_1(\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$H_3=f_2D_3(0)^{-1}\,D_2(0)^{-1}A_{32}D_2(\omega)^{-1}\,D_2(-\omega)^{-1}$$

$$N_3=f_3D_3(0)^{-1}\,D_3(\omega)^{-1}\,D_3(-\omega)^{-1}$$

$$P=f_3D_3(0)^{-1}A_{32}D_3(\omega)^{-1}\,D_2(-\omega)^{-1}\,D_3(-\omega)^{-1}$$

$$Q=f_3D_3(0)^{-1}A_{31}D_3(\omega)^{-1}\,D_3(-\omega)^{-1}\,D_1(-\omega)^{-1}$$

$$R=f_3D_3(0)^{-1}A_{32}D_3(\omega)^{-1}\,D_2(\omega)^{-1}\,D_3(-\omega)^{-1}$$

$$W=f_3D_3(0)^{-1}A_{31}D_3(\omega)^{-1}\,D_1(\omega)^{-1}\,D_3(-\omega)^{-1}$$

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