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Optical Rectification in Isotropic Thin Film Composed of Chiral Molecules with a Tripod-Like Structure *

WANG Xiao-Ou(王晓鸥)**, GONG Li-Jing(宫丽晶), LI Chun-Fei(李淳飞)

Department of Physics, Harbin Institute of Technology, Harbin 150001

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Optical rectification (OR) effect in the isotropic thin film consisting of chiral molecules with a tripod-like structure is investigated. The expressions of static-electric polarization in the isotropic chiral thin films and the relations between the OR and microscopic parameters of chiral medium are obtained by theoretical derivation. Furthermore, the relations of static electric polarization with the wavelength of incident light and parameters of chiral molecules are simulated numerically.

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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 non-ordered materials: gases, liquids, amorphous solids, etc. However, the second-order nonlinear optical processes are not forbidden for the isotropic chiral materials consisting of chiral molecules that are naturally non-centrosymmetric. For example, the sum-frequency generation has recently been 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. It was theoretically predicted by Armstrong *et al.* and firstly observed by Bass *et al.* in a potassium-dihydrogen-phosphate crystal in the same year of 1962.[7] In 1989, Yuh *et al.*[8] and Rosencher *et al.*[9] have found the OR characteristic of materials containing various asymmetric quantum well structures, which is greater than other materials in 10^6 times. In 2004, Kadlec *et al.* provided an important theoretical basis on OR in new THz radiation.[10]

In 1996, Il'inova *et al.*[11] 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 that is in resonance with chiral molecules; and Fischer *et al.*[12] in 2002 investigated OR in isotropic media consisted of chiral molecules, and estimated the light-induced dc electric polarization in pinene.

In this Letter, we investigate the dc electric-dipole polarization in the isotropic thin films of chiral molecular materials with a tripod-like structure using the three-coupled-oscillator model.[13] Firstly, we obtain the expression of static electric polarization in the isotropic surface composed of chiral molecules and the relation between molecular hyperpolarizabilities and second-order susceptibilities of chiral film. That is the basis of OR. Secondly, we compute the dc electric-dipole hyperpolarizabilities of chiral molecules with a tripod-like structure. Finally, we simulate numerically the relations of the static electric polarization with the wavelength of incident light, the incident angle, and microscopic parameters of molecules.

It is very well known from nonlinear optics[1−5] that an intense monochromatic optical wave with the circular frequency ω: $\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}(\omega,\boldsymbol{r})\exp(-i\omega t) +$ c.c. and that in an isotropic medium composed of chiral molecules a static macroscopic dipole polarization at zero frequency $P^{(2)}(0)$ is produced due to quadratic optical nonlinear susceptibility $\chi^{(2)}_{IJK}(0;-\omega,\omega)$.

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

$$P^{(2)}_I(0) = \varepsilon_0\chi^{(2)}_{IJK}(0;-\omega,\omega)E^*_J(\omega,r)E_K(\omega,r) + \text{c.c.} \tag{1}$$

We discuss the case in which the thin film is composed by chiral molecules and distributed on the surface isotropically, the so-called isotropic chiral film. We take the chiral surface to be in the $X-Y$ plane and fundamental field at frequency ω to be a monochromatic plane wave given by

$$\boldsymbol{E} = \boldsymbol{e}E_0(\omega)e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}, \tag{2}$$

where $\boldsymbol{e}$ denotes polarization direction of light, $\boldsymbol{k}$ is the wave vector of the optical waves, and the amplitude $E_0(\omega)$ is assumed to be constant. This field is taken to propagate in the $X-Z$ plane, the wave vector of which given by

$$\boldsymbol{k} = -\boldsymbol{e}_Z k\cos\theta_{\text{inc}} + \boldsymbol{e}_X k\sin\theta_{\text{inc}}, \tag{3}$$

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

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** Email: wxo@hit.edu.cn

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the basis of the s- and p-polarized unit vectors

$$\boldsymbol{e}_s = -\boldsymbol{e}_Y, \quad \boldsymbol{e}_{F_p} = \boldsymbol{e}_X \cos\theta_{\rm inc} + \boldsymbol{e}_Z \sin\theta_{\rm inc}, \tag{4}$$

where the subscript F refers to the fundamental field.

Due to the nonlinear interaction, static electric polarization is generated by the chiral molecules with the electromagnetic field in the reflected directions. We assume that the nonlinear response is localized within a thin layer, and also suppose that the higher multipole contributions are negligible but allow the possibility that the nonlinearity of the active material has contributions beyond the 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 Fig. 1, the p-polarized unit vectors in the reflected directions is

$$\boldsymbol{e}_p = -\boldsymbol{e}_X \cos\theta_{\rm inc} + \boldsymbol{e}_Z \sin\theta_{\rm inc}. \tag{5}$$

Thus, we can obtain the expressions of $P_I^{(2)}(0)$ in the all state of polarization based on Eqs. (1), (2), (4) and (5).

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

$$P_{sZ}^{(2)}(0) = 2\varepsilon_0 |E_0|^2 \chi_{ZYY}^{(2)}(0; -\omega, \omega). \tag{6}$$

The p-polarized components also can be written

$$\begin{aligned} P_{pX}^{(2)}(0) = & -2\varepsilon_0 |E_0|^2 \cos\theta_{\rm inc} \sin\theta_{\rm inc} [\chi_{XXZ}^{(2)}(0; -\omega, \omega) \\ & + \chi_{XZX}^{(2)}(0; -\omega, \omega)], \end{aligned} \tag{7a}$$

$$\begin{aligned} P_{pY}^{(2)}(0) = & -2\varepsilon_0 |E_0|^2 \cos\theta_{\rm inc} \sin\theta_{\rm inc} [\chi_{YXZ}^{(2)}(0; -\omega, \omega) \\ & + \chi_{YZX}^{(2)}(0; -\omega, \omega)], \end{aligned} \tag{7b}$$

$$\begin{aligned} P_{pZ}^{(2)}(0) = & 2\varepsilon_0 |E_0|^2 [\chi_{ZXX}^{(2)}(0; -\omega, \omega) \cos^2\theta_{\rm inc} \\ & + \chi_{ZZZ}^{(2)}(0; -\omega, \omega) \sin^2\theta_{\rm inc}]. \end{aligned} \tag{7c}$$

From the above discussion, we know that the light-induced dc electric polarization have a connection with the macroscopic dielectric susceptibility $\chi_{IJK}^{(2)}(0; -\omega, \omega)$. The $\chi_{IJK}^{(2)}(0; -\omega, \omega)$ have time reversibility conservation for the macroscopic symmetry of the medium. However, the nonvanishing components of the tensor $\chi_{IJK}^{(2)}(0; -\omega, \omega)$ exist for the isotropic medium composed of chiral molecule. The number of nonvanishing components of $\chi_{IJK}^{(2)}(0; -\omega, \omega)$ lies on the molecular configuration of chiral molecules, because $\chi_{IJK}^{(2)}(0; -\omega, \omega)$ is related to the corresponding orientationally averaged molecular hyperpolarizability $\beta_{ijk}(0; -\omega, \omega)$.

For the second-order process in isotropic film, we have

$$\chi_{IJK}^{(2)}(0; -\omega, \omega) = N f_L^3 \langle (I\cdot j)(J\cdot j)(K\cdot k) \rangle \beta_{ijk}(0; -\omega, \omega), \tag{8}$$

where i, j, k and I, J, K refer to the molecular and the laboratory frames, respectively. The brackets represent the averaging operation. N is the molecular surface density; f_L^3 is the local field factor of modifications in three directions. Based on the statistical theory suggested by Nakaon *et al.*,[14] we derive the nonvanishing-independent components of $\chi_{IJK}^{(2)}(0; -\omega, \omega)$ for chiral molecules with a tripod-like structure using three-coupled-oscillator, as follows:

$$\begin{aligned} \chi_{ZZZ}^{(2)}(0;\omega, -\omega) = & \frac{1}{2} N f_L^3 \cos\theta [\sin^2\theta \\ & \cdot (\beta_{xxz}^{eee} + \beta_{xzx}^{eee} + \beta_{yyz}^{eee} + \beta_{yzy}^{eee} \\ & + \beta_{zxx}^{eee} + \beta_{zyy}^{eee}) + \cos^2\theta \beta_{zzz}^{eee}], \end{aligned} \tag{9a}$$

$$\begin{aligned} \chi_{ZXX}^{(2)}(0;\omega, -\omega) = & \frac{1}{4} N f_L^3 \cos\theta [\sin^2\theta (-\beta_{xxz} - \beta_{xzx} \\ & - \beta_{yyz} - \beta_{yzy} + 2\beta_{zzz}) \\ & + (1 + \cos^2\theta)(\beta_{zxx} + \beta_{zyy})], \end{aligned} \tag{9b}$$

$$\begin{aligned} \chi_{XXZ}^{(2)}(0;\omega, -\omega) = & \frac{1}{4} N f_L^3 \cos\theta [\sin^2\theta (-\beta_{xxz} - \beta_{yzy} \\ & - \beta_{zxx} - \beta_{zyy} + 2\beta_{zzz}) \\ & + (1 + \cos^2\theta)(\beta_{xxz} + \beta_{yyz})], \end{aligned} \tag{9c}$$

$$\begin{aligned} \chi_{XZX}^{(2)}(0;\omega, -\omega) = & \frac{1}{4} N f_L^3 \cos\theta [\sin^2\theta (-\beta_{xxz} - \beta_{yyz} \\ & - \beta_{zxx} - \beta_{zyy} + 2\beta_{zzz}) \\ & + (1 + \cos^2\theta)(\beta_{xxz} + \beta_{yzy})], \end{aligned} \tag{9d}$$

$$\begin{aligned} \chi_{XYZ}^{(2)}(0;\omega, -\omega) = & \frac{1}{4} N f_L^3 2\cos^2\theta (\beta_{xyz} - \beta_{yxz}) \\ & - \sin^2\theta (\beta_{xzy} - \beta_{yzx} - \beta_{zxy} + \beta_{zyx})], \end{aligned} \tag{9e}$$

$$\begin{aligned} \chi_{XZY}^{(2)}(0;\omega, -\omega) = & \frac{1}{4} N f_L^3 [2\cos^2\theta (\beta_{xzy} - \beta_{yzx}) \\ & - \sin^2\theta (\beta_{xyz} - \beta_{yxz} + \beta_{zxy} - \beta_{zyx})], \end{aligned} \tag{9f}$$

$$\begin{aligned} \chi_{ZXY}^{(2)}(0;\omega, -\omega) = & \frac{1}{4} N f_L^3 [2\cos\theta (\beta_{zxy} - \beta_{zyx}) \\ & + \sin^2\theta (\beta_{xyz} - \beta_{xzy} - \beta_{yxz} + \beta_{yzx})], \end{aligned} \tag{9g}$$

where θ represents Euler's angles (namely, polar angle with respect to the surface normal, the Z axis in the laboratory frame, see Fig. 1). In the above equations, β_{ijk} namely $\beta_{ijk}(0; -\omega, \omega)$, can be derived using the method in Refs. [13,15]. The expressions of $\beta_{ijk}(0; -\omega, \omega)$ are written as

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

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

with

$$
\begin{aligned}
B_1 &= f_1 D_1(0)^{-1} D_1(\omega)^{-1} D_1(-\omega)^{-1}, \\
C &= f_1 D_1(0)^{-1} D_1(\omega)^{-1} D_2(-\omega)^{-1} D_1(-\omega)^{-1}, \\
E &= f_1 D_1(0)^{-1} D_1(\omega)^{-1} D_3(-\omega)^{-1} D_1(-\omega)^{-1} A_{13}, \\
F &= f_1 D_1(0)^{-1} A_{12} D_2(\omega)^{-1} D_1(\omega)^{-1} D_1(-\omega)^{-1}, \\
G &= f_1 D_1(0)^{-1} A_{13} D_3(\omega)^{-1} D_1(\omega)^{-1} D_1(-\omega)^{-1}, \\
H_1 &= f_2 D_2(0)^{-1} D_1(0)^{-1} A_{12} D_2(\omega)^{-1} D_2(-\omega)^{-1}, \\
N_1 &= f_3 D_3(0)^{-1} D_1(0)^{-1} A_{13} D_3(\omega)^{-1} D_3(-\omega)^{-1}, \\
B_2 &= f_1 D_2(0)^{-1} D_1(0)^{-1} A_{21} D_1(\omega)^{-1} D_1(-\omega)^{-1}, \\
H_2 &= f_2 D_2(0)^{-1} D_2(\omega)^{-1} D_2(-\omega)^{-1}, \\
I &= f_2 D_2(0)^{-1} A_{21} D_2(\omega)^{-1} D_2(-\omega)^{-1} D_1(-\omega)^{-1}, \\
V &= f_2 D_2(0)^{-1} A_{23} D_2(\omega)^{-1} D_3(-\omega)^{-1} D_2(-\omega)^{-1}, \\
K &= f_2 D_2(0)^{-1} A_{21} D_2(\omega)^{-1} D_1(\omega)^{-1} D_2(-\omega)^{-1}, \\
M &= f_2 D_2(0)^{-1} A_{23} D_3(\omega)^{-1} D_2(\omega)^{-1} D_2(-\omega)^{-1},
\end{aligned}
$$

where the meanings of α and A_{ij} $(i, j = 1, 2, 3)$ can be found in Ref. [15].

In the materials composed of chiral molecules, there is a strong correlation between molecular structure and nonlinear properties. We know from Eqs. (6) and (7), that the dc electric-dipole polarization depend on the susceptibility tensor $\chi^{(2)}_{IJK}(0; -\omega, \omega)$ of materials when the incident angle $\theta_{\rm inc}$ is chosen for fixed values; whereas $\chi^{(2)}_{IJK}(0; -\omega, \omega)$ 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. (9a)–(9g)]; and $\beta_{ijk}(0; -\omega, \omega)$ are connected with the parameters of molecular configuration. Therefore the dc electric-dipole polarization is influenced by the molecular microscopic parameters.

We numerically simulate the relation between $P^{(2)}_I(0)$ and the microscopic parameters of chiral molecules. We assume the wavelength of the incident fundamental light is 532 nm, the molecular surface density $N = 4.0 \times 10^{26}\,\mathrm{m}^{-2}$. The plots of the dc electric-dipole polarization $P^{(2)}_I(0)$ versus bond angle are given in Fig. 2. We set the molecular parameters as follows: the resonance centre frequency ω_0 is 5.24×10^{15} Hz, the damping coefficients γ_i is $(1/10)\omega_{0i}$, and the chiral relation $\omega_{01}/\omega_{02} = 1.058$, $\omega_{02}/\omega_{03} = 1.056$ and $\omega_{03}/\omega_{01} = 0.895$, respectively.

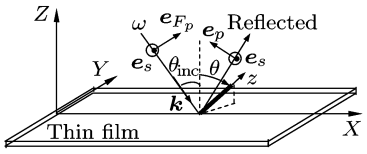


Fig. 1. A laser beam at frequency ω is incident on the sample at angle $\theta_{\rm inc}$. The surface normal is along the z axis, with the p and s unit vectors for each field.

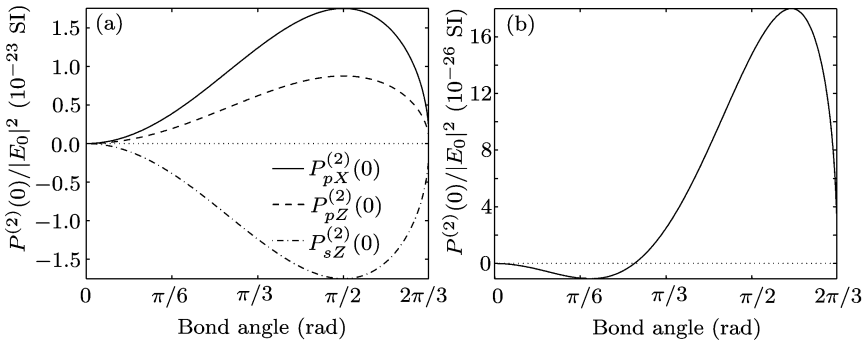


Fig. 2. Plots of the dc electric-dipole polarization $P^{(2)}_I(0)$ versus bond angle. (a) The X and Z directional component of the p-polarized and Z directional component of the s-polarized in the static electric polarization, and (b) the Y directional component of the p-polarized in the static electric polarization, namely $P^{(2)}_{pY}(0)$.

From Fig. 2, we can see that there is a best bond angle to lead $P^{(2)}_I(0)$ to reach maximal value. Therefore, we may properly design the molecular structure to enhance value of OR, according to the relation of $P^{(2)}_I(0)$ with bond angle. We also see that the coupling among oscillators only has an impact on chiral component $P^{(2)}_{pY}(0)$ by studying for the relation between $P^{(2)}_I(0)$ and bond angle. This shows the chirality of molecule root in the coupling among oscillators.

Usually, we concern about the some factors (for ex-

ample, strength of molecular chirality, coupling among molecules) that impact on OR. The study on the spectra of $P_I^{(2)}(0)$ can give us more information about the relation of OR and the chirality of molecule, which guide us to design the asymmetric molecule with the better matching relation of chirality. The spectra of $P_I^{(2)}(0)$ under different chiral components are given in Fig. 3.

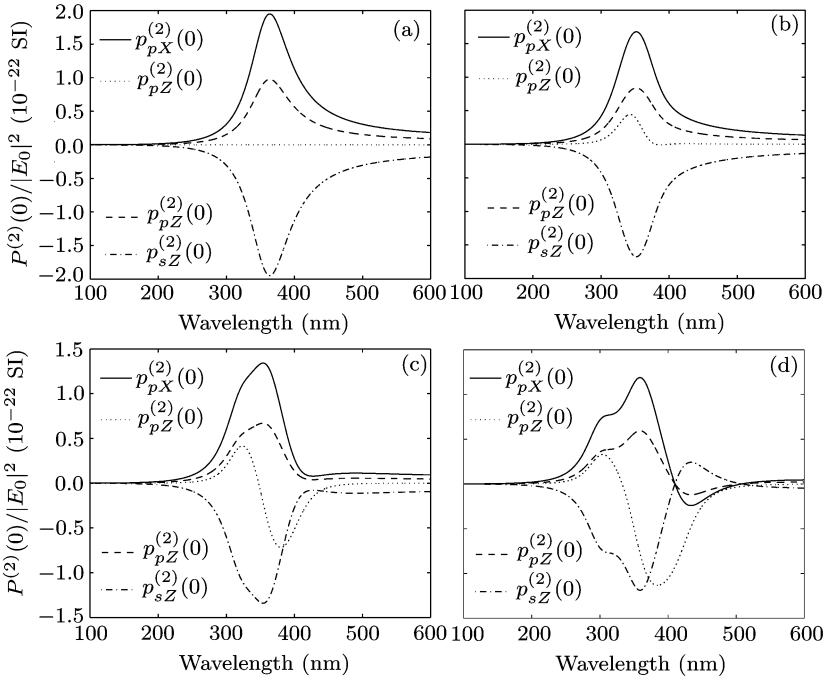


Fig. 3. Spectra of $P_I^{(2)}(0)$ under different chiral components. (a) Three oscillators are the same (e.g. nothing chirality); (b)–(d) having following chiral components: (b) $\omega_{01}/\omega_{02} = 1.056$, $\omega_{02}/\omega_{03} = 1.056$, $\omega_{03}/\omega_{01} = 0.895$; (c) $\omega_{01}/_{02} = 1.125$, $\omega_{02}/\omega_{03} = 1.111$, $\omega_{03}/\omega_{01} = 0.800$, (d) $\omega_{01}/\omega_{02} = 1.200$, $\omega_{02}/\omega_{03} = 1.167$, $\omega_{03}/\omega_{01} = 0.714$.

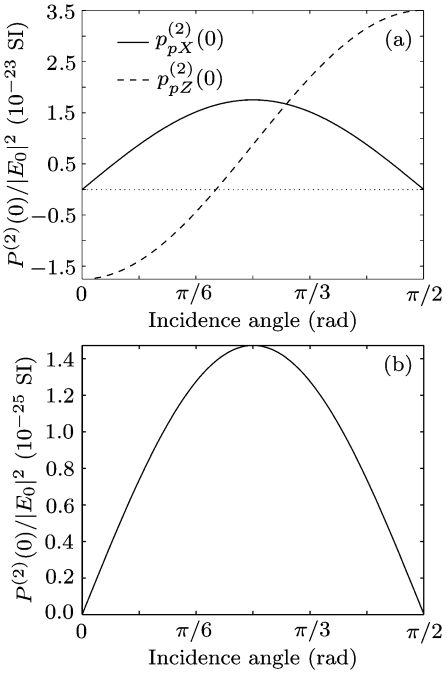


Fig. 4. Curves of $P_I^{(2)}(0)$ versus an incident angle. (a) X and Z directional components and (b) Y directional components of the p-polarized in the static electric polarization.

We known from Fig. 3 that properly changing the chirality of molecules may shift the position of peaks value in the spectra of OR, and the phenomena of multiple peaks appear due to the coupling among oscillators, it is useful for choosing proper OR wavelength.

The curves of $P_I^{(2)}(0)$ versus an angle of incidence are given in Fig. 4, which is under a condition that the resonance centre wavelength λ_0 is 360 nm, the damping coefficients γ_i is $(1/10)\omega_{0i}$, bond angle is $\pi/2$, and chirality relation $\omega_{01}/\omega_{02} = 1.058$, $\omega_{02}/\omega_{03} = 1.056$, $\omega_{03}/\omega_{01} = 0.895$. The system is excited by a monochromatic wave (wavelength is 532 nm). The equilibrium elongation l is chosen to be 0.116 nm. From Fig. 4, we can see that there is a best incident angle of light to lead $P_I^{(2)}(0)$ to reach the maximal value. Therefore, we may properly choose the incident angle of light wave to enhance value of $P_I^{(2)}(0)$, according to the relation of $P_I^{(2)}(0)$ with the incident angle.

We have studied the relation between the OR in the isotropic surface of chiral molecular with a tripod-like structure and microscopic parameters (molecular configuration, molecular chirality) and the angle of light incidence. We can conclude that by properly changing the chirality of molecules, it may shift the position of peaks value in the spectra of OR and the phenomena of multiple peaks appear due to the coupling among oscillators, it is useful for choosing proper OR wavelength. There is a best incident angle of light wave for OR (see Fig. 4). We also find from us investigation that the chirality of molecule comes of the coupling between three oscillators.

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