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# RELATIONSHIP BETWEEN INTENSITY OF SURFACE SECOND HARMONIC GENERATION AND MOLECULAR STRUCTURE IN HELIX MOLECULAR FILMS

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The relationship between intensity of surface Second Harmonic Generation (SHG) and the pitch, radius and azimuthal angle of molecules on the surface of helix molecular films is analyzed. The values of pitch and radius corresponding to the maximal intensity of SHG have been shown to exist. The theoretical results are compared with the experimental ones reported by Möhlman *et al.*, and the limitation of their conclusion is also pointed out.

**Keywords:** chiral media, helix molecular films, surface SHG
**PACC:** 4265, 7820E

## I. INTRODUCTION

Chiral molecules are well known for possessing nonsymmetrical structure and optical activity. The typical structure of chiral molecule is helical. In the single electron model, the movement of electron is restricted along a helical path, so that the helical motion not only induces the electronic-dipole moment, but also the magnetic-dipole moment, and the magnitude of the latter could be in the same order as that of former[1].

In recent years, much attention has been attracted to the research of nonlinear optical properties of chiral molecules and their media, including the second-order and third-order nonlinearities.[2,3] Especially, helical molecules with conjugated $\pi$ bond exhibit significant nonlinear optical properties.

In this paper we analyze the relationship between intensity of surface SHG and the pitch, radius and azimuthal angle of molecules in helix molecular films. The results of numerical simulation suggest there exists a maximum value of intensity of second harmonic generation (SHG). The theoretical results are compared with the experimental one reported by Möhlman *et al.*[4], and the limitation of their experimental results is also pointed out. Our work provides a theoretical prediction for the experimental research of SHG in chiral molecular films.

## II. THEORY OF SURFACE SHG FOR HELIXMOLECULAR FILMS

Drude presented the helix model to describe the linear optical activity. Inspired by the Drude model, Maki[5,6] *et al.* established the model of one-electron moving along a helical path of which the radius is $\rho$ and the pitch is $\xi$. The equation of electron motion is given by using classical method. With the small-angle approximation and neglecting the higher-order terms of magnetic interaction, the expression of complex amplitudes for the second-order electric and magnetic-dipole moments and the results of macroscopic second-order nonlinear-optical response on the surfaces of helix molecular films are given. The S-polarized component of intensity of surface SHG is

$$I_{2\omega} = -\frac{\pi N_s^2 e^6 \sin^2\theta_{\rm inc}}{4c^3 n^3 m^4 \cos\theta_{\rm inc}} \frac{\gamma\omega^3}{|D(\omega)|^4 |D(2\omega)|^2} \times I_0^2 \frac{b\rho^2\xi^2}{(\rho^2+(\xi/2\pi)^2)^4} \cos\theta(1+3\cos 2\theta) \times \Big[\rho^2(1+3\cos 2\theta)+(\xi/2\pi)^2(1-cos2\theta)\Big], \quad (1)$$

where $n$ is the mean refractive index of the nonlinear surface layer, $\theta_{\rm inc}$ is the angle of incidence of the fundamental light; $f_j$ ,$g_j$ and $h_j$ are the coefficients relevant to the susceptibilities, $\omega$ is the angle frequency of incidence light, $c$ is the velocity of light, $I_0$ is the intensity of the fundamental light. $N_s$ is the surface number density of helical molecules in $cm^{-2}$, $m$ is the mass of electron, $\theta$ is the azimuthal angle of molecules against the direction of the surface normal; $\xi$ and $\rho$ are the pitch and radius of the helical path respectively. $D(\omega)$ is the frequency dispersion of the optical response.

## III. RELATIONSHIP BETWEEN INTENSITY OF SHG AND MOLECULAR STRUCTURE

Equation (1) can be simplified as

$$I_{2\omega} = AI_0^2 \frac{\rho^2\xi^2}{(\rho^2 + (\xi/2\pi)^2)^4}(B\rho^2 + C(\xi/2\pi)^2). \quad (2)$$

Then $B = 1 + 3\cos 2\theta$, $C = 1 - \cos 2\theta$ are the coefficients, which are relevant to the azimuthal angle of molecules and

$$A = -\frac{\pi N_s^2 e^6 \sin^2\theta_{\rm inc}}{4c^3 n^3 m^4 \cos\theta_{\rm inc}} \frac{\gamma\omega^3}{|D(\omega)|^4 |D(2\omega)|^2}.$$

$A$ is a constant determined by some constants such as $c$, $n$, $|D(2\omega)|^2$, etc. Select the values of $\rho$, $\xi$ and $\theta$ properly, we can analyze the relationship between the intensity of SHG versus the pitch and the intensity of incidence light by using numerical simulation method.

Assuming $\rho = 3\mu$m and $\theta = 45^0$, Fig.1 shows the surface of $I_{2\omega}$ versus $I_0$ and $\xi$. From the surface one can see the value of $I_{2\omega}$ is not simply inversely proportional to $\xi$. There exists an optimum $\xi$ with which $I_{2\omega}$ can reach the maximum value.

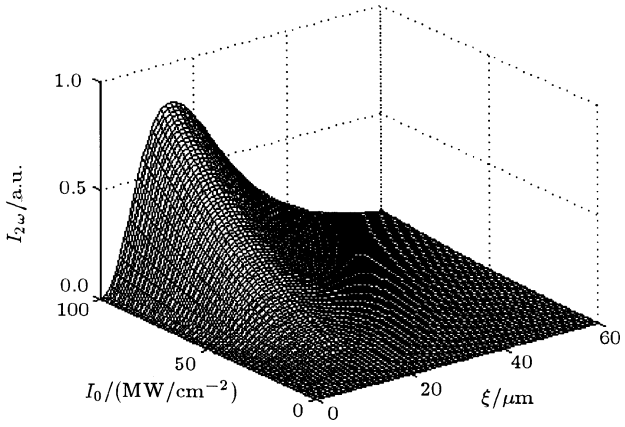



**Fig.1.** Surface of $I_{2\omega}$ versus $I_0$ and $\xi$.

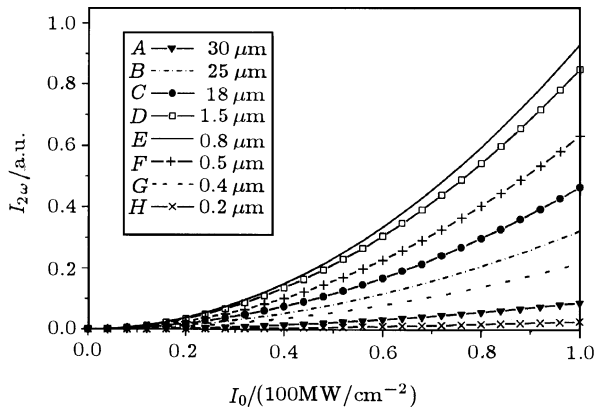



**Fig.2.** Curves of $I_{2\omega}$ versus $I_0$ under different $\xi$.

Figure 2 shows curves of $I_{2\omega}$ versus $I_0$ under different $\xi$. The value of $\xi$ decreases from curve A to H. With long conjugate $\pi$ bond, helical molecules show greater nonlinear optical response to smaller $\xi$. So from curve $A$ to curve $E$, the value of $\xi$ decreases, while the changing ratio of $I_{2\omega}$ to $I_0$ become greater and greater. Because of increasing intensity of the reflected fundamental light and resonant type of SHG, if the pitch approaches integer times of the fundament and/or second-harmonic wavelengths, from curve $E$ to $H$ the value of $\xi$ decreases, and the changing ratio become smaller and smaller. Möhlman and Persons *et al.* realized the SHG in 4-alkoxy-4'nitro-stilbene (ANOS) with incident power density within the range from 0 to 100 MW/cm$^{-2}$ and gave the results as Fig.3 shows. The pitch decreases from $h$ to $a$ and they draw a conclusion as follows: the intensity of SHG tends to be larger for shorter pitch length. That is only fits for curves from $A$ to $E$ of Fig.2, and do not apply to all curves. If the pitch is kept decreasing, the rule applicable to curves $E$ to $H$ would be discovered.

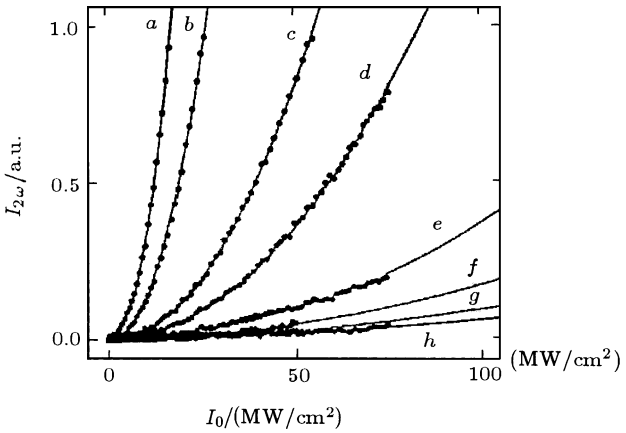



**Fig.3.** Experiment results of Möhlman *et al.*[4]: Curves of $I_{2\omega}$ versus $I_0$ under different $\xi$.

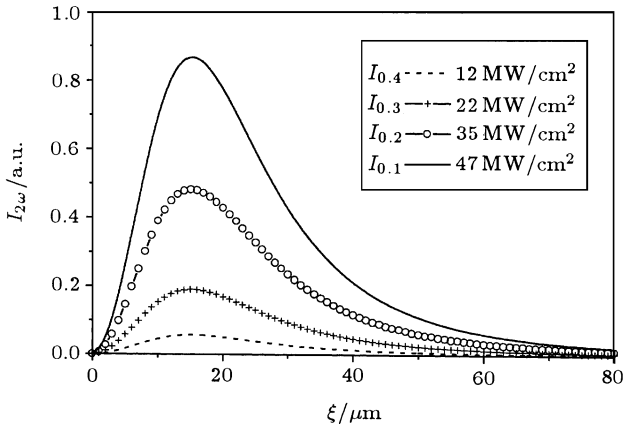



**Fig.4.** Curves of $I_{2\omega}$ versus $\xi$ under different $I_0$.

Figure 4 shows the curves of $I_{2\omega}$ versus $\xi$ under different $I_0$. The intensities satisfy the relation

$I_{01} > I_{02} > I_{03} > I_{04}$. The maximum value of $I_{2\omega}$ under different $I_0$ corresponds to the same $\xi$.

In Eq.(1), $\rho$ and $\xi/2\pi$ are in the same scale, so one can draw the similar conclusion as follows: if $\xi$ is kept constant, there exists only one value of $\rho$ with which the maximum value of $I_{2\omega}$ can be obtained under different $I_0$.

If $\theta = 45^0$ then $B = 1$ and $C = 1$, and $I_0$ is a constant, $C' = AI_0^2(2\omega)$, Eq.(2) can be simplified to

$$I_{2\omega} = C' \rho^2 \xi^2 \left[\rho^2 + (\xi/2\pi)^2\right]^{-3}. \quad (3)$$

Assume $\xi$ is a constant and the value of the derivative of Eq.(3) with respect to $\rho$ is zero, then we can get

$$\rho = \sqrt{2}\xi/(4\pi). \quad (4)$$

It shows that when $\theta = 45^0$ and $\rho = 0.113\xi$ , the maximum value of $I_{(2\omega)}$ can be obtained. When $\theta = 0^0$, the equation is $\rho = \xi/(2\pi) \approx 0.16\xi$. When the intensity of SHG reaches the maximum value, the equation that the pitch and radius satisfy is different to be varying azimuthal angle.

## IV.CONCLUSION

There exists an optimum value for pitch and radius with which the intensity of surface SHG in helical molecular films can gain the maximum value. The equation that the pitch and radius satisfy depends on the azimuthal angle of molecules on the surface of helix films. Our results provide some insight for synthesizing new chiral compounds.

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