Second Harmonic Generation

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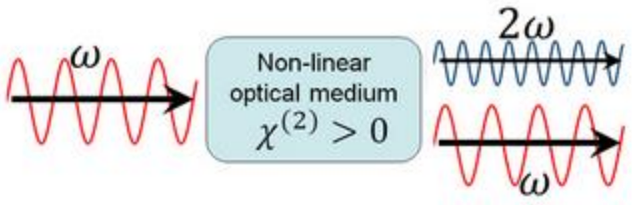
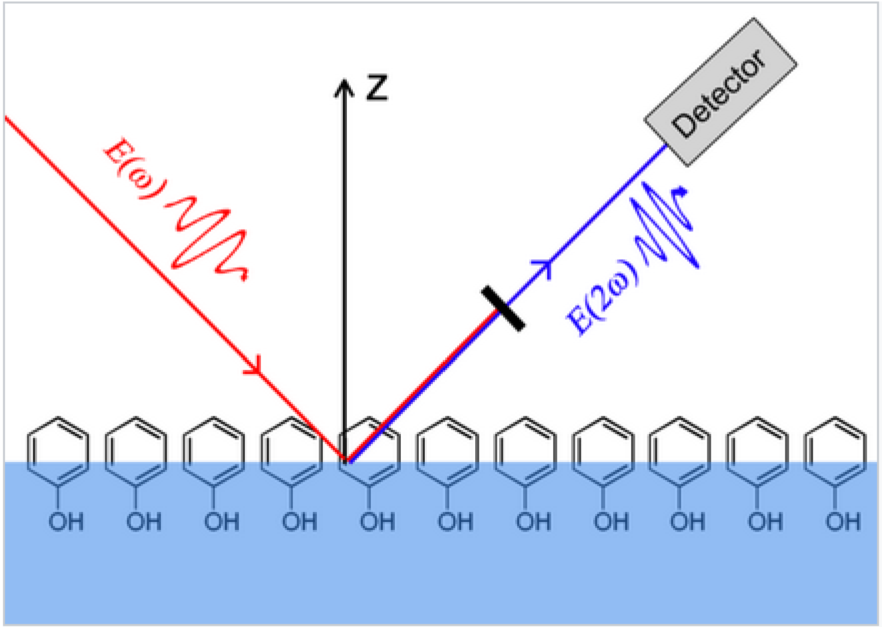
1. Theory

◇ The Nonlinear Optical Susceptibility



$$\tilde{P}(t) = \epsilon_0[\chi^{(1)}\tilde{E}(t) + \chi^{(2)}\tilde{E}^2(t) + \chi^{(3)}\tilde{E}^3(t) + \cdots]$$
$$\equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots . \qquad (1.1.2)$$

The quantities $\chi(2)$ and $\chi(3)$ are known as the second- and third-order nonlinear optical susceptibilities, respectively

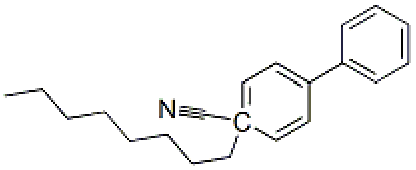


A depiction of the second harmonic generation set up for measuring the orientation of phenol at the air-water interface.

2. Application

Alignment of liquid crystals on a photosensitive substrate studied by surface optical second-harmonic generation (SSHG)

4-N-Octyl-4-CyanoBiphenyl(8CB)

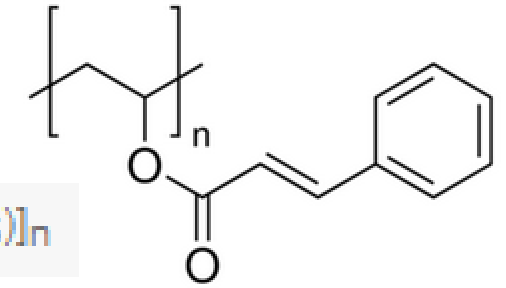


liquid crystal film: 8CB

Substrate: PVCN

Poly(vinyl cinnamate)

$[CH_2CH(O_2CCH{=}CHC_6H_5)]_n$



Olenik, I. Drevenšek, et al. *Physical Review E* 61.4 (2000): R3310.

3. Results

The first plateau in $P(2\nu,t)$ is generally assumed to coincide with the formation of the first complete monolayer of the LC molecules

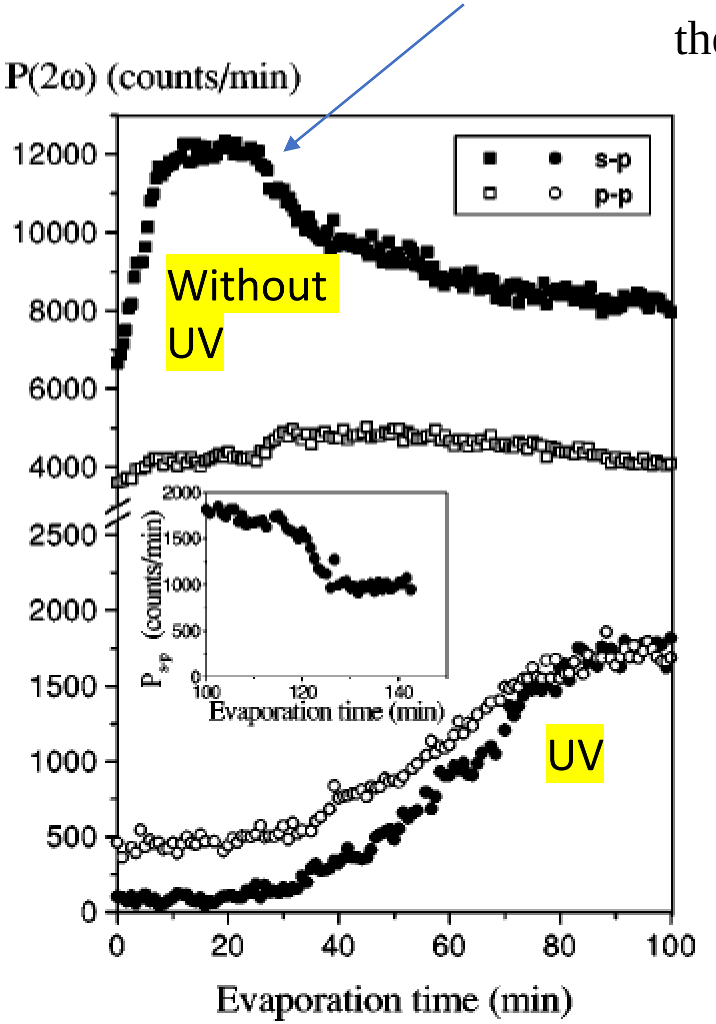
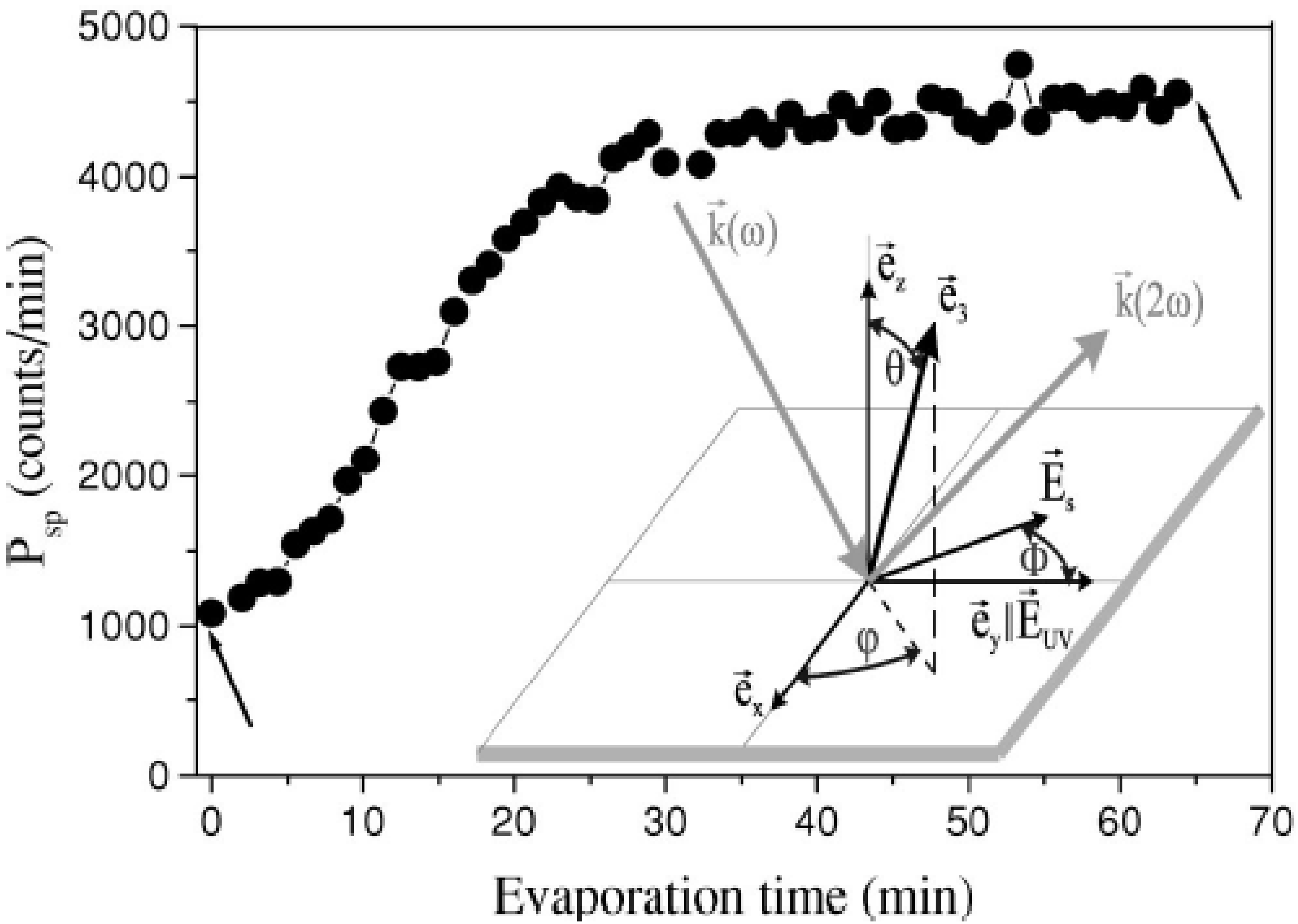


FIG. 1. Second-harmonic signal during the evaporation of 8CB on the unexposed PVCN substrate (squares) and on the PVCN substrate exposed to unpolarized uv light for 20 min (circles).



3. Results

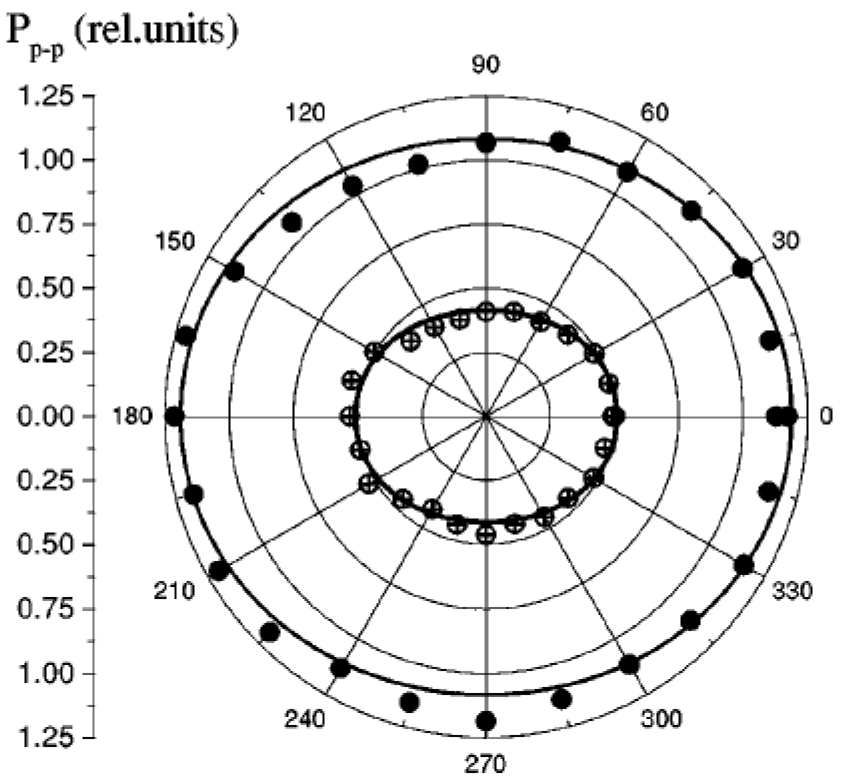


FIG. 3. Dependencies of $P_{s\text{-}p}$ and (top) $P_{p\text{-}p}$ (bottom) on the sample rotation angle Φ: μ bare PVCN substrate after 60 min of LP uv irradiation (crossed circles), and μ the same substrate with the deposited 8CB monolayer (closed circles). $\Phi=0$ corresponds to the s polarization parallel to the uv polarization (see the inset of Fig. 2). The magnitudes are given relative to the corresponding signal for the unexposed substrate. Solid lines are fits to Eq. (5).

The LP uv irradiation induces an apparent anisotropy of $P_{s\text{-}p}(\Phi)$ and $P_{p\text{-}p}(\Phi)$.

4. Analysis

$$P(2\omega) = A|[L\hat{e}(2\omega)]\chi_s^{(2)} : [L\hat{e}(\omega)][L\hat{e}(\omega)]|^2 P^2(\omega)$$

$$= A|\chi_{eff}|^2 P^2(\omega), \quad (2)$$

where $P(\omega)$ is the power of incident fundamental beam, $\hat{e}(\omega)$ and $\hat{e}(2\omega)$ are polarization vectors of the incident and the second harmonic beam respectively, L is the Fresnel transformation matrix [21], and $A = \omega^2 \sec^2\Omega / 2\varepsilon_0 c^3 S$ with $\Omega = 45°$ the angle of incidence and S the spot size of the beam.

8CB on the unexposed substrate:

$$(\chi^m_{eff,s\text{-}p} / \chi^m_{eff,p\text{-}p}) = 5.5 \pm 2.4$$

8CB on the exposed substrate:

$$(\chi^m_{eff,s\text{-}p} / \chi^m_{eff,p\text{-}p}) = 1.6 \pm 0.3$$

$$\chi^m_{eff,s\text{-}p} = (\chi^m_{zxx} \sin^2\Phi + \chi^m_{zyy} \cos^2\Phi) L_{zz}(2\omega) L^2_{yy}(\omega) \sin\Omega, \quad (5)$$

$$\chi^m_{eff,p\text{-}p} = \chi^m_{zzz} L_{zz}(2\omega) L^2_{zz}(\omega) \sin^3\Omega + (\chi^m_{zxx} \cos^2\Phi + \chi^m_{zyy} \sin^2\Phi) \cos^2\Omega \sin\Omega \times [L_{zz}(2\omega) L^2_{xx}(\omega) - 2L_{xx}(2\omega) L_{zz}(\omega) L_{xx}(\omega)].$$

4. Analysis

Assuming a δ function distribution of the molecular tilt angles:

$$f_s(\theta) = \delta(\theta - \theta_0)$$

The nonlinear optical susceptibility χ^m can be described by three independent nonzero components

$$\chi^m_{zzz} = N_s \langle \cos^3 \theta \rangle \beta_{333},$$

$$\chi^m_{zxx} = \chi^m_{xzx} = N_s \langle \sin^2 \theta \cos \theta \cos^2 \varphi \rangle \beta_{333}, \qquad (4)$$

$$\chi^m_{zyy} = \chi^m_{yzy} = N_s \langle \sin^2 \theta \cos \theta \sin^2 \varphi \rangle \beta_{333},$$

8CB on the unexposed substrate:

$$\theta_0 = 65^\circ \pm 2^\circ$$

8CB on the exposed substrate:

$$\theta_0 = 76^\circ \pm 5^\circ$$

Conclusion: The photomodification thus increases the surface tilt angle of the molecules in the adjacent 8CB monolayer.

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Assuming a δ function distribution of the molecular tilt angles:

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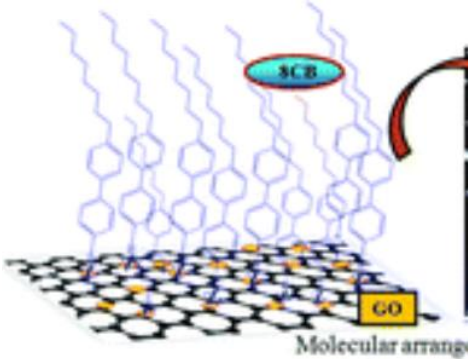
$$\chi^m_{zxx} = \chi^m_{xzx} = N_s \langle \sin^2 \theta \cos \theta \cos^2 \varphi \rangle \beta_{333}, \qquad (4)$$

$$\chi^m_{zyy} = \chi^m_{yzy} = N_s \langle \sin^2 \theta \cos \theta \sin^2 \varphi \rangle \beta_{333},$$

Ns actually only gives the density of the polar oriented 8CB molecules, while the molecules attached to the surface in head to tail “pairs” do not contribute to the SSHG signal



$Ns(without\ UV) : Ns(with\ UV)$
= 1:4

Conclusion: This suggests that the photochemical reactions increase the surface polarity of the PVCN.

Thanks!