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Dispersions of Electroabsorption Susceptibilities: Application to a Polymeric Langmuir-Blodgett Film

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Abstract

The relation between the dispersions of nonlinear optical susceptibilities $\chi^{(n)}(\omega;\omega,0\dots 0)$ and $\chi^{(n-1)}(\omega;\omega,0\dots 0)$ (for electro-optic process) of organic polymeric materials is studied based on the premises that the microscopic polarizabilities $\alpha, \beta, \gamma, \delta, \dots$ are derivatives of their next lower order polarizabilities, with respect to the effective internal field F across the polarizable π -conjugated systems[1], and that these derivative relationships are still valid when dynamic (frequency-dependent) processes are considered[2]. Electroabsorption spectroscopy has been used to determine the dispersion of $\chi_{113}^{(2)}$ and $\chi_{1133}^{(3)}$ of a polyamic acid salt Langmuir-Blodgett film containing covalently bonded azobenzene NLO chromophores. The results are consistent with our prediction, and confirm the validity of the derivative relationships proposed by Marder et al.[1,2]. This LB film also gives appreciable values of both $\chi_{113}^{(2)}$ (26pm/v) and $\chi_{1133}^{(3)}$ (2×10^{-11} esu).

Key words: electroabsorption spectroscopy, nonlinear optical susceptibility.

I. Introduction

Organic nonlinear optical materials[3] have received considerable attention for their potential use in optical communication systems such as in transmission, modulation, switching and storage of the optical signals. In particular, organic polymeric materials[4,5] offer certain advantages over conventional inorganic materials including diverse synthetic design (molecular engineering) to enhance optical nonlinearity, high switching speeds, potential low cost, facile thin-film processability, and low dielectric properties. Both 2nd order as well as 3rd order optical nonlinearity of polymeric systems are of interest. Polymeric systems have been designed to possess optimal second and third order nonlinearities. It is of interest to study the relationship among different orders of nonlinearity in such systems. It will help to understand further the laws governing the nonlinear optical properties of polymers and guide in the design of nonlinear optical polymers with desired properties.

Recently, Marder et. al.[1] have proposed that the microscopic polarizabilities α , β , γ , δ ,... are derivatives of their next lower order polarizabilities, with respect to the effective internal field F across the polarizable π -conjugated systems. They have also developed frequency-dependent derivative relationships for dynamic process through simulation calculations of harmonic generations, and the results show that the derivative relationships for static internal field remain valid when dynamic processes are considered[2]. It is further proposed in this paper that in electro-optic process, the internal field is under the influence of probing photon, thus is a function of the probing photon energy $F(\omega)$. Based on this assumption and the previous research results, we infer that the electroabsorption spectrum of $\chi^{(n)}$ is proportional to $\frac{d\chi^{(n-1)}}{d\omega}$ (ω is the optical frequency of the probing photon), and the extrema in the spectra of real and imaginary part of $\chi^{(n-1)}$ will occur at the optical frequencies where the corresponding part of $\chi^{(n)}$ spectrum crosses zero.

Electroabsorption spectroscopy can determine both complex spectra of $\chi_{113}^{(2)}$ and $\chi_{1133}^{(3)}$. By measuring the signal at the modulation frequency, we can determine the dispersion of $\text{Im}\left(\frac{\chi_{113}^{(2)}}{\tilde{n}}\right)$ (\tilde{n} is the complex refractive index). The real part can then be obtained by Kramers-Kronig relation to determine $\chi_{113}^{(2)}$. Similarly, $\chi_{1133}^{(3)}$ can be determined by measuring the signal at twice the modulation frequency.

The Langmuir-Blodgett (LB) technique[6] is one of the established techniques to obtain ordered molecular assemblies. By arranging the chromophores in a noncentrosymmetric ordering, we can obtain a material with appreciable values for $\chi^{(2)}$ and $\chi^{(3)}$.

In part II, the derivative relationships proposed by Marder et al.[1,2] are reviewed, and the dispersion relationship between $\chi^{(n)}(\omega;\omega,0,\dots,0)$ and $\chi^{(n-1)}(\omega;\omega,0,\dots,0)$ for electro-optic process is derived. In part III-V, the spectra of $\chi_{113}^{(2)}$ and $\chi_{1133}^{(3)}$ of a polyamic acid salt Langmuir-Blodgett film containing covalently bonded azobenzene in the polymer(see Figure 1) were determined through electroabsorption spectroscopy. The results are consistent with our prediction, confirm the derivative relationships proposed by Marder et al.[1,2], and show appreciable values of $\chi^{(2)}$ and $\chi^{(3)}$.

II. Relation between $\chi^{(n)}(\omega;\omega,0,\dots,0)$ and $\chi^{(n-1)}(\omega;\omega,0,\dots,0)$

Let $\lambda^{(n)}$ be the nth hyperpolarizability of a one dimensional nonlinear chromophore, that is $\alpha = \lambda^{(1)}$, $\beta = \lambda^{(2)}$, $\gamma = \lambda^{(3)}$, $\delta = \lambda^{(4)}$, etc.. The π electrons can only move along the chromophore orientation direction \hat{z} . As described by Marder et al.[1], these polarizabilities are functions of the effective internal field F across the polarizable π -conjugated systems, and are derivatives of their next lower order polarizabilities, with respect to the effective internal field F. That is :

$$\lambda^{(n)}(F) = \frac{d\lambda^{(n-1)}(F)}{dF} \quad (\text{II.1})$$

This relation can be easily proved by expanding the dipole moment μ of the chromophore as a function of external field E acting on it. Let us suppose that μ is in the chromophore orientation direction \hat{z} and it is a function of the local field E_L , which is composed of the external field E_z and the internal field F along z direction, i.e. $E_L = E_z + F$. We only consider the z component because the perpendicular components can not make the π electrons move perpendicular to \hat{z} , and we assume that F is independent of the intensity of the external field E_z . We then have:

$$\mu(E_z + F) = \mu(F) + \sum_{n=1} \frac{1}{n!} \frac{\partial^n \mu(F)}{\partial F^n} E_z^n \quad (\text{II.2})$$

$$\text{By defining } \lambda^{(n)}(F) = \frac{\partial^n \mu(F)}{\partial F^n} \quad (\text{II.3})$$

$$\text{we have: } \mu(E_z + F) = \mu(F) + \sum_{n=1} \frac{1}{n!} \lambda^{(n)}(F) E_z^n \quad (\text{II.4})$$

$$\text{and } \lambda^{(n)}(F) = \frac{d\lambda^{(n-1)}(F)}{dF} \quad \text{which is (II.1)}$$

Marder et al. have further demonstrated that this derivative relationship is still valid when dynamic (frequency-dependent) processes are considered[2]. Thus it should also be valid for electro-optic process.

When we perform an electroabsorption measurement, we use photons to probe the nonlinear optical property. The internal field observed through the photonic detector is under the influence of the probing photon (we can not see the uninfluenced internal field). Photons with different energy interact with the molecular system differently, and cause different internal fields. Therefore, the effective internal field F should be a function of the probing photon energy, i.e. $F = F(\omega)$, where ω is the optical frequency of the probing photon. We assume further that the dependence of μ on ω only comes from the local field $E_L = E_z + F$. Then the dependence of $\lambda^{(n)}$ on ω only comes from the internal field $F(\omega)$.

Therefore, the derivative relation (II.1) could be written as:

$$\frac{d\lambda^{(n-1)}}{d\omega} = \frac{d\lambda^{(n-1)}(F)}{dF} \frac{dF(\omega)}{d\omega} = \lambda^{(n)} \frac{dF(\omega)}{d\omega} \quad (\text{II.5})$$

This relationship indicates that the dispersion of the ω derivative of a polarizability is proportional to its next higher order polarizability.

Let us derive the relation between macroscopic nonlinear optical susceptibilities $\chi^{(n-1)}$ and $\chi^{(n)}$ from the microscopic relationship (II.5). The i th component of polarization per unit volume \vec{P} coming from this kind of nonlinear chromophore is given by:

$$P_i = N \langle \mu(E_z + F) \alpha_{zi} \rangle \quad (\text{II.6})$$

where N is the number of chromophores per unit volume. α_{zi} is the projection factor from z direction of the molecular coordinate to the i th direction of the laboratory coordinate. $\langle \rangle$ means to average over different chromophore orientations. The external field (optical field and applied electric field) along z direction comes from the projection of its components in laboratory frame 1,2,3:

$$E_z = \sum_{j=1}^3 \alpha_{zj} E_j \quad (\text{II.7})$$

Using (II.4) and (II.7), we have:

$$P_i = N\mu(F) \langle \alpha_{zi} \rangle + N \sum_{n=1} \frac{\lambda^{(n)}}{n!} \sum_{j_1 \dots j_n} \langle \alpha_{zi} \alpha_{zj_1} \dots \alpha_{zj_m} \dots \alpha_{zj_n} \rangle E_{j_1} \dots E_{j_m} \dots E_{j_n} \quad (\text{II.8})$$

where E_{j_m} is the j_m th component of the m th electric field. α_{zj_m} is the projection factor from the j_m th direction on the laboratory frame to the z direction on the molecular frame.

By comparing with the definition of the macroscopic nonlinear susceptibilities, we have:

$$\chi_{ij_1 \dots j_n}^{(n)}(\omega; \omega, 0, \dots, 0) = N \frac{\lambda^{(n)}}{n!} \langle \alpha_{zi} \alpha_{zj_1} \dots \alpha_{zj_n} \rangle \quad (\text{II.9})$$

For the case of electroabsorption, the optical field is very weak such that it can not significantly change the chromophore orientation. Thus $\alpha_{z_j m}$ and $\langle \alpha_{z_i} \alpha_{z_j} \dots \alpha_{z_n} \rangle$ are not dependent on ω . Then we can derive the derivative relation for the macroscopic nonlinear susceptibilities from the relationship for microscopic nonlinear susceptibilities (II.5):

$$\frac{d\chi_{ij_1 \dots j_{n-1}}^{(n-1)}(\omega; \omega, 0, \dots, 0)}{d\omega} = n \chi_{i' j'_1 \dots j'_n}^{(n)}(\omega; \omega, 0, \dots, 0) \frac{dF(\omega)}{d\omega} \frac{\langle \alpha_{z_i} \alpha_{z_j} \dots \alpha_{z_n} \rangle}{\langle \alpha_{z_{i'}} \alpha_{z_{j'_1}} \dots \alpha_{z_{j'_n}} \rangle} \quad (\text{II.10})$$

From above equation, we can see that

$$\frac{d\chi^{(n-1)}(\omega; \omega, 0 \dots 0)}{d\omega} \propto \chi^{(n)}(\omega; \omega, 0 \dots 0) \frac{dF(\omega)}{d\omega} \quad (\text{II.11})$$

If $\frac{dF(\omega)}{d\omega}$ is a smooth real function, then the extrema in real and imaginary part of $\chi^{(n-1)}$ will occur at the position (in ω) where the corresponding part of $\chi^{(n)}$ is zero, provided that $\chi^{(n-1)}$ and $\chi^{(n)}$ are generated by the same one dimensional chromophore. The following experiment will confirm this prediction.

III Experimental Details

80 bi-layers of a polyamic acid salt Langmuir-Blodgett film containing covalently bonded azobenzene NLO chromophore (fig 1.) was formed on an indium tin oxide (ITO)-glass substrate. The polymer film was asymmetrically transferred with transfer ratio of 1 in the upstroke and a small transfer ratio of 0.3 during the downstroke. The thickness of this 80 bilayer film is 965 \AA . An aluminum electrode (300 \AA) was deposited on top of the LB film. An oscillating electric field ($f = 1 \text{ KHz}$, $V_{p-p} = 25.5 \text{ V}$) was applied to the sample. A beam of polarized light coming from a tungsten lamp through a monochromator was incident normally on the sample. The electroabsorption signal ΔI_f and ΔI_{2f} , which is defined as the change of the output intensity I , was detected by a lock-in amplifier set at the electrical modulation

frequency (f) and twice of the electrical modulation frequency ($2f$) respectively. The sign of ΔI_f and ΔI_{2f} were determined by comparing the amplified signals from the lock-in amplifier and the reference signal from the function generator simultaneously on an oscilloscope. The d.c. output intensity I (without the electric field) was measured at each optical frequency. A computer was used to synchronize the change of wavelength of the monochromator and the data reading of the lock-in amplifier. The experimental setup is shown in Figure 2. The measurements were performed from wavelength of 470nm to 730nm for both f and $2f$ signal. The results of $\frac{\Delta I_f}{I}$ and $\frac{\Delta I_{2f}}{I}$ are shown in Figure 3. The dispersions of the real and imaginary part of the complex refractive index $\tilde{n} = n + iK$ of this LB film were measured by an ellipsometer and a UV-visible spectrometer, and are shown in Figure 4(a) and 4(b).

IV. Theoretical background of Electroabsorption

This film shows $c_{\infty m}$ symmetry: $\chi_{113}^{(2)} = \chi_{223}^{(2)}$, $\chi_{1133}^{(3)} = \chi_{2233}^{(3)}$, $\chi_{123}^{(2)} = \chi_{213}^{(2)} = 0$, and $\chi_{1233}^{(3)} = \chi_{2133}^{(3)} = 0$. The polarization for normal incidence is given by:

$$\dot{P} = \left[1 + 4\pi(\chi_{11}^{(1)} + 2\chi_{113}^{(2)}(\omega; \omega, 0)E_{ac} + 3\chi_{1133}^{(3)}(\omega; \omega, 0, 0)E_{ac}^2) \right] \dot{E}_{opt} \quad (IV.1)$$

where 2 and 3 denote the permutation of the fields[7,8]. $E_{ac} = E_{ac0} \cos(2\pi ft)$ is the applied electric field, \dot{E}_{opt} is the optical field.

The optical field \dot{E}_{opt} sees the effective complex refractive index \tilde{n}_{eff} , which is given by:

$$\tilde{n}_{eff}^2 = 1 + 4\pi(\chi_{11}^{(1)} + 2\chi_{113}^{(2)}(\omega; \omega, 0)E_{ac} + 3\chi_{1133}^{(3)}(\omega; \omega, 0, 0)E_{ac}^2) \quad (IV.2)$$

We have:

$$2\tilde{n}\delta\tilde{n} = 4\pi 2\chi_{113}^{(2)}(\omega; \omega, 0)E_{ac0} \cos(2\pi ft) + 2\pi 3\chi_{1133}^{(3)}(\omega; \omega, 0, 0)E_{ac0}^2 [\cos(2\pi 2ft) + 1] \quad (IV.3)$$

where $\delta\tilde{n} = \tilde{n}_{\text{eff}} - \tilde{n}$ is the change of the complex refractive index due to the applied electric field. The amplitudes of its f and 2f component are then given by:

$$\delta\tilde{n}_f = 2\pi \frac{2\chi_{113}^{(2)}(\omega; \omega, 0)}{\tilde{n}} E_{\text{ac}0} \quad (\text{IV.4})$$

$$\delta\tilde{n}_{2f} = \pi \frac{3\chi_{1133}^{(3)}(\omega; \omega, 0, 0)}{\tilde{n}} E_{\text{ac}0}^2 \quad (\text{IV.5})$$

The relative change of the transmitted light intensity is given by:

$$\frac{\Delta I}{I} = -2 \frac{\omega}{c} \text{Im}(\delta\tilde{n}) t_k \quad (\text{IV.6})$$

where t_k is the thickness of the film.

Then we have the amplitude of the relative change of the transmitted light intensity detected at frequency f and 2f:

$$\frac{\Delta I_f}{I} = -2 \frac{\omega}{c} \text{Im}(\delta\tilde{n}_f) t_k = -4\pi \frac{\omega}{c} t_k E_{\text{ac}0} 2 \text{Im}[\chi_{\text{eff}}^{(2)'}] \quad (\text{IV.7})$$

$$\left(\frac{\Delta I_f}{I} = -\frac{\omega}{c} t_k E_{\text{ac}0} 2 \text{Im}[\chi_{\text{eff}}^{(2)'}] \text{ for SI Units} \right)$$

$$\text{and } \frac{\Delta I_{2f}}{I} = -2 \frac{\omega}{c} \text{Im}(\delta\tilde{n}_{2f}) t_k = -2\pi \frac{\omega}{c} t_k E_{\text{ac}0}^2 3 \text{Im}[\chi_{\text{eff}}^{(3)'}] \quad (\text{IV.8})$$

where $\chi_{\text{eff}}^{(2)'}$ and $\chi_{\text{eff}}^{(3)'}$ are given by:

$$\chi_{\text{eff}}^{(2)'} = \frac{\chi_{113}^{(2)}}{\tilde{n}} \text{ and } \chi_{\text{eff}}^{(3)'} = \frac{\chi_{1133}^{(3)}}{\tilde{n}} \quad (\text{IV.9})$$

(IV.7) is consistent with the result of reference [9], and (IV.8) is consistent with the result of reference [10].

The dispersions of $\text{Im}[\chi_{\text{eff}}^{(2)'}]$ and $\text{Im}[\chi_{\text{eff}}^{(3)'}]$ are obtained through the measurement of the dispersions of $\frac{\Delta I_f}{I}$ and $\frac{\Delta I_{2f}}{I}$, and the real parts of $\chi_{\text{eff}}^{(2)'}$ and $\chi_{\text{eff}}^{(3)'}$ are determined by Kramers-Kronig relation[8,11]:

$$\text{Re}[\chi_{\text{eff}}^{(2),\prime}(\omega)] = \frac{2}{\pi} \int_{\omega_i}^{\omega_f} \frac{\omega' d\omega'}{\omega'^2 - \omega^2} \text{Im}[\chi_{\text{eff}}^{(2),\prime}(\omega')] \quad (\text{IV.10})$$

$$\text{Re}[\chi_{\text{eff}}^{(3),\prime}(\omega)] = \frac{2}{\pi} \int_{\omega_i}^{\omega_f} \frac{\omega' d\omega'}{\omega'^2 - \omega^2} \text{Im}[\chi_{\text{eff}}^{(3),\prime}(\omega')] \quad (\text{IV.11})$$

where ω_i and ω_f are initial and final optical frequencies respectively.

Thus the complex spectra of $\chi_{\text{eff}}^{(2),\prime}$ and $\chi_{\text{eff}}^{(3),\prime}$ are determined. The dispersions of $\chi_{113}^{(2)}$ and $\chi_{1133}^{(3)}$ are subsequently determined from (IV.9).

V. Results and Discussion

The results are shown in Figure 5 and 6. We can see that this LB film gives appreciable near resonance values for both 2nd and 3rd order nonlinear optical susceptibilities ($\chi_{113}^{(2)} \sim 26 \text{pm/v}$, $\chi_{1133}^{(3)} \sim 2 \times 10^{-11} \text{esu}$).

From the dispersions of $\text{Im}[\chi_{113}^{(2)}]$ and $\text{Im}[\chi_{1133}^{(3)}]$, we can see that the maximum of $\text{Im}[\chi_{113}^{(2)}]$ is close to the position where $\text{Im}[\chi_{1133}^{(3)}]$ crosses zero. The two extrema of $\text{Re}[\chi_{113}^{(2)}]$ are also close to the two zero points in $\text{Re}[\chi_{1133}^{(3)}]$. These behavior are consistent with the prediction that $\frac{d\chi^{(2)}(\omega)}{d\omega} \propto \chi^{(3)}(\omega) \frac{dF(\omega)}{d\omega}$.

We can also see from these spectra that $\text{Im}[\chi_{1133}^{(3)}] > 0$ in the region where $\frac{d\text{Im}[\chi_{113}^{(2)}]}{d\lambda} < 0$ ($\frac{d\text{Im}[\chi_{113}^{(2)}]}{d\omega} > 0$), and that $\text{Im}[\chi_{1133}^{(3)}] < 0$ in the region where $\frac{d\text{Im}[\chi_{113}^{(2)}]}{d\lambda} > 0$ ($\frac{d\text{Im}[\chi_{113}^{(2)}]}{d\omega} < 0$). The real parts of these spectra have the same behavior. Thus we can infer that $\frac{dF(\omega)}{d\omega} > 0$ throughout the range of the measurement.

The relation between $\chi^{(1)}$ and $\chi^{(2)}$ is not relevant here, because contribution to $\chi^{(1)}$ is from all segments of the polymeric material, while $\chi^{(2)}$ and $\chi^{(3)}$ are dominated by the nonlinear azo chromophore.

VI. Conclusion

The dispersion relationship (II.11) between the nonlinear optical susceptibilities $\chi^{(n)}(\omega; \omega, 0, \dots, 0)$ and $\chi^{(n-1)}(\omega; \omega, 0, \dots, 0)$ (for electro-optic process) generated by the same one dimensional chromophore for organic polymeric materials is derived. The dispersions of $\chi_{113}^{(2)}$ and $\chi_{1133}^{(3)}$ of a polyamic acid salt Langmuir-Blodgett film containing covalently bonded azobenzene NLO chromophore were determined by electroabsorption spectroscopy. The experimental results are consistent with our prediction (II.11), and confirm the validity of the derivative relationships proposed by Marder et al.[1,2]. This LB film also gives appreciable near resonance values of both $\chi_{113}^{(2)}$ and $\chi_{1133}^{(3)}$.

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Figure Captions

Figure 1. The molecular structure of the polyamic acid salt deposited as a LB monolayer.

Figure 2. The experimental setup for electroabsorption studies.

Figure 3. Relative change of the detected intensity $\Delta I_f/I$ and $\Delta I_{2f}/I$.

Figure 4. (a) The dispersion of the real part of refractive index; (b) The dispersion of the imaginary part of refractive index.

Figure 5. The dispersion of $\chi_{113}^{(2)}(\omega;\omega,0)$. Uncertainty: ± 0.8 pm/v for the real part, ± 0.26 pm/v for the imaginary part.

Figure 6. The dispersion of $\chi_{1133}^{(3)}(\omega;\omega,0,0)$. Uncertainty: $\pm 1.0 \times 10^{-12}$ esu for the real part, $\pm 2.0 \times 10^{-13}$ esu for the imaginary part.

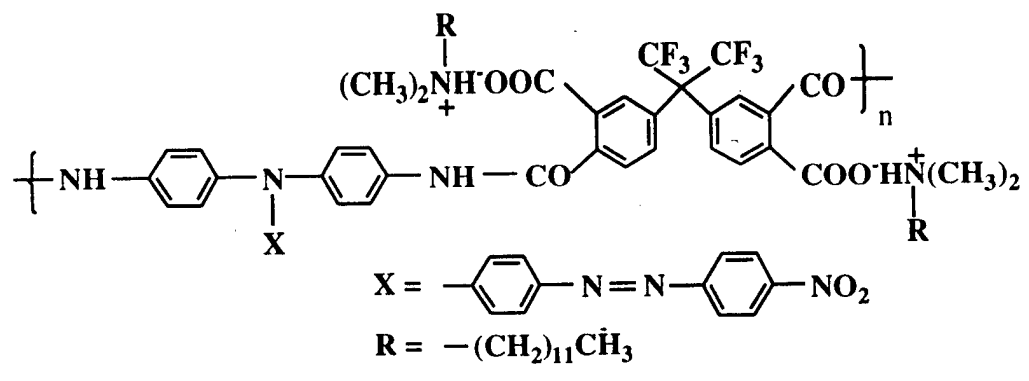


Figure 1

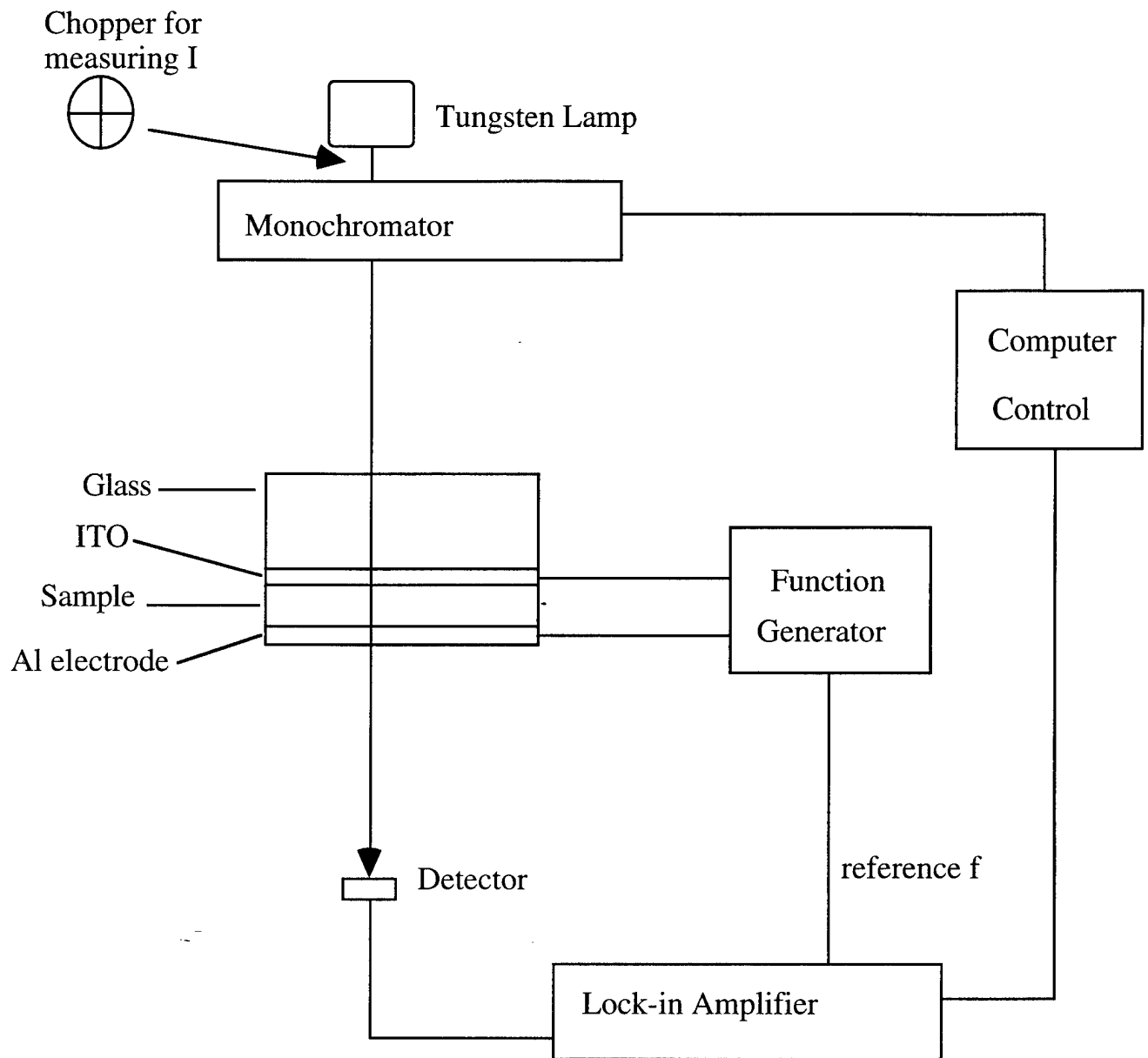
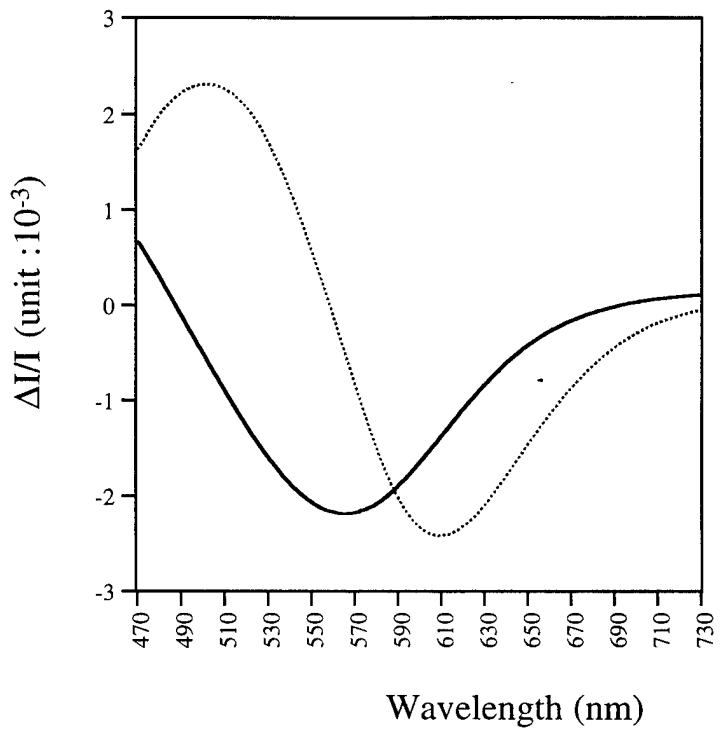


Figure 2. Experimental setup of electroabsorption.

Figure 3. Relative change of detected intensity $\Delta I/I$.



- 1f signal, detected at the modulation frequency.
- 2f signal, detected at twice of the modulation frequency.

Figure 4(a). The real part of refractive index.

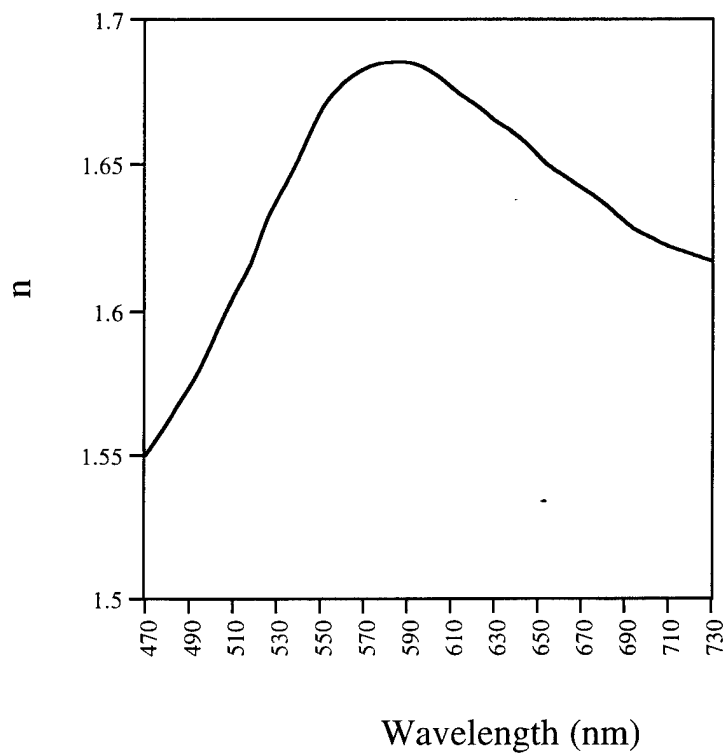


Figure 4(b). The imaginary part of refractive index

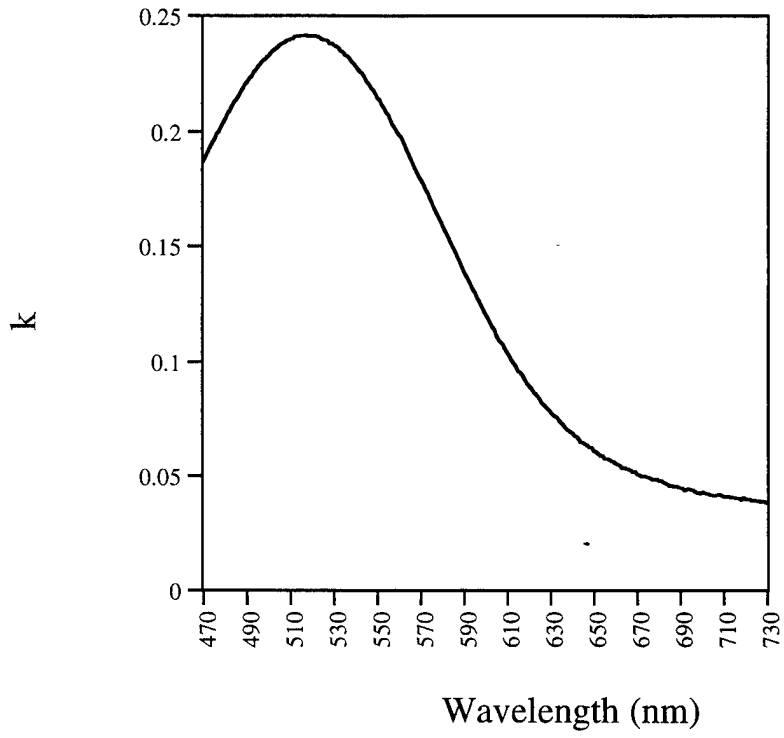


Figure 5. Dispersion of $\chi^{(2)}_{113}$

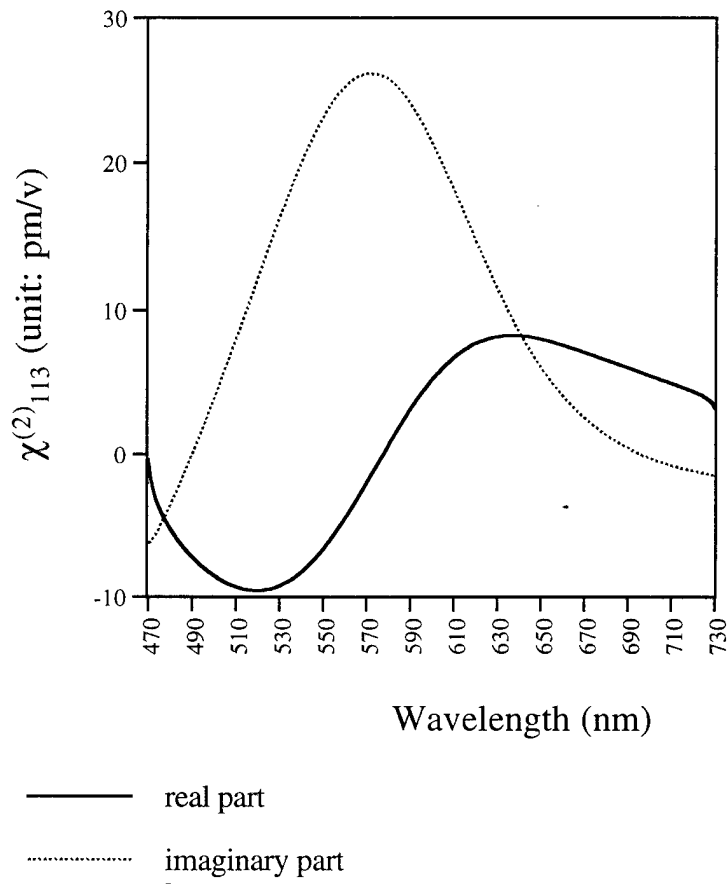


Figure 6. Dispersion of $\chi^{(3)}_{1133}$

