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Electrooptic Effect in Langmuir–Blodgett Films of 2-(Docosylamino)-5-nitropyridine Probed by Surface Plasmon Waves

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Measurements of electrooptic modulation of surface plasmon resonance have been carried out on horizontally transferred Langmuir–Blodgett films of 2-(docosylamino)-5-nitropyridine. The observed Pockels response is approximately constant for different numbers of layers in multilayered films and is proportional to the strength of the modulating field. The calculated second-order susceptibility values are $\sim 2 \times 10^{-13}$ m V^{-1}, 2 orders of magnitude lower than those derived from second harmonic generation studies. The presence of the Pockels effect is attributed to off-diagonal terms in the second-order susceptibility.

Introduction

There is a continuing interest in the use of organic materials in optical devices utilizing second-order nonlinear effects such as frequency mixing and the electrooptic effect.[1,2] One of the features of organic materials as opposed to commonly used inorganic electrooptic crystals is that the Pockels (linear electrooptic) effect in organics is mostly electronic in origin and, therefore, could provide extremely rapid electrooptic modulation. The advantages of using organic compounds for electrooptic devices are 2-fold. First, the flexible chemistry of organics allows one to easily modify the structure of a molecule, so it can be specifically tuned for the application of interest. Second, relatively easy processability of organics permits fabrication of molecular structures by using a variety of techniques. For example, one may link a long hydrocarbon chain to a nonlinear molecular entity (a chromophore). This provides a way in which to build ultrathin molecular layers of well-ordered structures using the Langmuir–Blodgett (LB) technique.

The molecular assemblies made with the LB method can be conveniently studied in geometries facilitating the propagation of bound electromagnetic modes. The large optical field associated with bound waves can be utilized to obtain spectroscopic and optical parameters of a material even with monolayer thicknesses.[3] The propagation characteristics of bound waves can be modulated with an externally applied field, and by monitoring these changes, the nonlinear optical properties of a material can be evaluated. In this paper we report electrooptic (Pockels effect) measurements of 2-(docosylamino)-5-nitropyridine (DCANP) LB layers using surface plasmon (SP) waves to probe variations in the refractive index.

DCANP
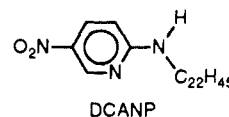
Cross and co-workers[4,5] reported a measurement of the Pockels effect in LB films of hemicyanines where, as is usual for Z-type deposited LB films, the predominant component of the second-order nonlinear susceptibility is found in a direction normal to the film plane.[6] We present a similar study performed on LB films of DCANP. An interesting feature of LB films of DCANP obtained by Y-type deposition is that they exhibit a strong second harmonic generation (SHG), with the intensity of the effect being quadratically dependent on the number of bilayers.[7] It was shown that for Y-type LB films there was a cancellation of the *zzz* components (*z* being the film surface normal) of the third-rank tensor $\chi^{(2)}$ describing the second-order nonolinear optical properties. However, the chromophore of DCANP (in vertically transferred films) lies at an angle of 30 ± 10° with respect to the surface of the substrate in such a way that the in-plane components of

(1) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons: New York, 1991.
(2) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S.; Zyss, J., Eds.; Academic Press, Inc.: Orlando, FL, 1987.
(3) Swalen, J. D. *J. Phys. Chem.* 1979, *83*, 1438.
(4) Cross, G. H.; Girling, I. R.; Peterson, I. R.; Cade, N. A. *Electron. Lett.* 1986, *22*, 1111.
(5) Cross, G. H.; Girling, I. R.; Peterson, I. R.; Cade, N. A.; Carls, J. D. *J. Opt. Soc. Am. B.* 1987, *4*, 962.
(6) Girling, I. R.; Jethwa, S. R.; Stewart, R. T.; Earls, J. D.; Cross, G. H.; Cade, N. A.; Kolinsky, P. V.; Jones, R. J.; Peterson, I. R. *Thin Solid Films* 1988, *160*, 355.
(7) Decher, G.; Tieke, B.; Bosshard, Ch.; Gunter, P. *J. Chem. Soc., Chem. Commun.* 1988, 933.
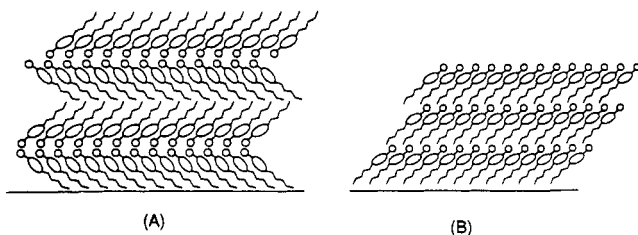
Figure 1. Postulated structures of 2-(decosylamino)-5-nitropyridine LB films obtained (A) by vertical (Y) deposition (see ref 7) and (B) by horizontal (X) lifting.

$\chi^{(2)}$ do not vanish by mutual cancellation.[7-9] In other words, the molecules are ordered in the xy plane and the order is preserved for consecutive layers. Figure 1A shows the postulated structure of the Y-type deposited films.[7] It can be seen that although the films lack a polar character in the direction perpendicular to the surface, there is a possibility of constructive addition of molecular nonlinearities along the surface.

Our results of SHG on Y-type LB films of DCANP are essentially identical to those of Gunter and co-workers.[7,8] We also performed a study of SHG on horizontally transferred LB films of DCANP.[10] Also, in this case, SHG is mostly due to the in-plane components of $\chi^{(2)}$, namely, $\chi_{xxx}^{(2)}$ and $\chi_{yyy}^{(2)}$, as evidenced by the angular dependence of the SHG signal. Figure 1B presents our postulated structure for the horizontally deposited films. By measuring the angular dependence of second harmonic intensity in different polarizations, we find that the maximum signal in p polarization is at the normal incidence, which shows the dominance of the in-plane component $\chi_{xxx}^{(2)}$ over the $\chi_{zzz}^{(2)}$ component. Performing the SHG measurements as described in ref 7, we find that the angle between the chromophore and the substrate plane is almost zero (0 ± 10°). The SHG is stable in time over a period of several months, which indicates that no significant reorganization of molecules on the surface takes place. Although horizontally lifted films are different in structure from those obtained by the vertical Y-type deposition, the preferential arrangement of molecular chromophores being almost flat on the substrate makes the zzz component of $\chi^{(2)}$ much smaller than the xxx and yyy components.[10] We show in this study that the in-plane components of the second-order nonlinear susceptibility also give rise to electrooptic modulation in surface plasmon reflectivity and that this method may be conveniently used to determine the effective Pockels coefficient. In the present case it leads to the determination of the off-diagonal components of $\chi^{(2)}$.

Experimental Section

(a) Preparation of Langmuir–Blodgett Films. LB films of DCANP were transferred at 18 mN m⁻¹ at 288 K by horizontal lifting using a custom-built Teflon trough. A solution of DCANP in chloroform was slowly spread onto a subphase of doubly distilled deionized water. After solvent had evaporated (typically ~15 min), the film was slowly compressed while the surface pressure was continuously monitored until a surface pressure of 18 mN m⁻¹ was reached. This surface pressure was maintained for ~10 min, and the substrate was gradually brought down in contact with the film. The excess film around the substrate was swept out with an aspirator suction pump prior to lifting off the

film-coated substrate. The substrate was tilted at an angle of approximately 5° and then slowly raised vertically. The subphase in contact with the substrate gently "peels" off, thus minimizing any possible disturbances to the transferred layer. The subsequent LB layers were transferred by repeating the same procedure after the former (first) layer had dried for ~5 min.

For the electrooptic studies the LB films were deposited onto silver films (thickness ≃500 Å) which were made by thermal evaporation onto chemically cleaned glass microscope slides at a deposition rate of 6 Å s⁻¹. An uncoated portion of the same substrate was used to obtain the surface plasmon curve for the bare silver for calibration.

(b) Surface Plasmon and Electrooptic Measurements. Surface plasmons are bound surface electromagnetic waves, which originate from the oscillation of free charges along a metal–dielectric boundary.[11] The electric field associated with these waves is evanescent in nature, peaks out at the boundary, and decays exponentially into both media. The penetration depth of the field in the metal is much shorter than in the dielectric layer due to the smaller skin depth metals typically have. The field in the dielectric layer can be utilized to determine the optical parameters of the dielectric.[12]

Surface plasmon waves can be excited with optical fields by employing attenuated total reflection methods. When a beam of p-polarized light is incident on a glass–silver interface at an angle larger than the critical angle, the beam is totally internally reflected. The evanescent field in the metal gives rise to the surface plasmon wave if the wave vector components of the two waves, along the interface, are matched. If the intensity of the reflected beam is monitored as a function of the incident angle, a reflectivity minimum is observed when the optimum coupling takes place. The angular position of this minimum depends on the wavelength, the type of the metal, and its thickness. If the metal thickness is optimized, the intensity of the reflected beam at the minimum can almost be nullified.

The presence of a thin dielectric layer on the metal shifts the angular position of the SP resonance dip to a higher angle, and fitting the reflection curve with the theory, one can obtain the optical parameters of the dielectric. The refractive index of the monolayer can be altered by applying an electric field (Pockels effect) across the film; the changes induced by the applied field can be detected by the variations in the reflectivity (ΔR) which register as the angle of incidence is scanned. Generally, electric field induced change in the refractive index is very small ($\Delta n \simeq 10^{-5}$) and may be buried in the laser noise, so one has to use lock-in detection to monitor it. The change in the reflectivity (ΔR) caused by the modulation of the complex dielectric function $\epsilon = \epsilon_r + i\epsilon_i$ is[13] $\Delta R = (\partial R/\partial \epsilon_r)\Delta\epsilon_r + (\partial R/\partial \epsilon_i)\Delta\epsilon_i$. The changes in the real and the imaginary parts of the complex permittivity can be related to the real and the imaginary parts of the second-order nonlinear susceptibility $\chi^{(2)}$.

Both the surface plasmon and the Pockels effect experiments were carried out with the attenuated total reflection method using the Kretschman[14] configuration as shown in Figure 2. The bare silver film or the DCANP film(s) coated silver film on a glass substrate was kept in optical contact with the base of a BK-7 prism using an index matching fluid. The prism film assembly was mounted on a computer-controlled θ–2θ rotation stage, and a p-polarized He–Ne laser beam (≃0.5 mW at 632.8 nm) was internally incident on the glass silver interface. The reflected signal beam was monitored with a photodiode, passed through an A–D converter, and read by a microcomputer.

The electrooptic measurements were performed by using the LB film covered silver film and an ITO- (indium tin oxide) coated glass slide as the two electrodes, which were separated at a distance of 6 μm by using a thin Mylar spacer. An electric field of the order of 10⁶ V m⁻¹ was created across the LB films by applying a 5-kHz ac voltage of between 25 and 98 V (peak to peak). The

(8) Bosshard, Ch.; Decher, G.; Tieke, B.; Gunter, P. *Proc. SPIE Int. Soc. Opt. Eng.* **1988**, *1017*, 141.

(9) Bosshard, Ch.; Kupfer, M.; Gunter, P.; Pasquier, C.; Zahir, S.; Seifert, M. *Appl. Phys. Lett.* **1990**, *56*, 1204.

(10) Wijekoon, W. M. K. P.; Karna, S. P.; Talaptra, G. B.; Prasad, P. N., manuscript in preparation.

(11) Shen, Y. R. *Principles of Nonlinear Optics*; John Wiley and Sons: New York, 1984.

(12) Pockrand, I.; Swalen, J. D.; Gordon, J. G., II; Philpott, M. R. *Surf. Sci.* **1977**, *74*, 237.

(13) Loulergue, J. C.; Dumont, M.; Levy, Y. *Thin Solid Films* **1988**, *160*, 399.

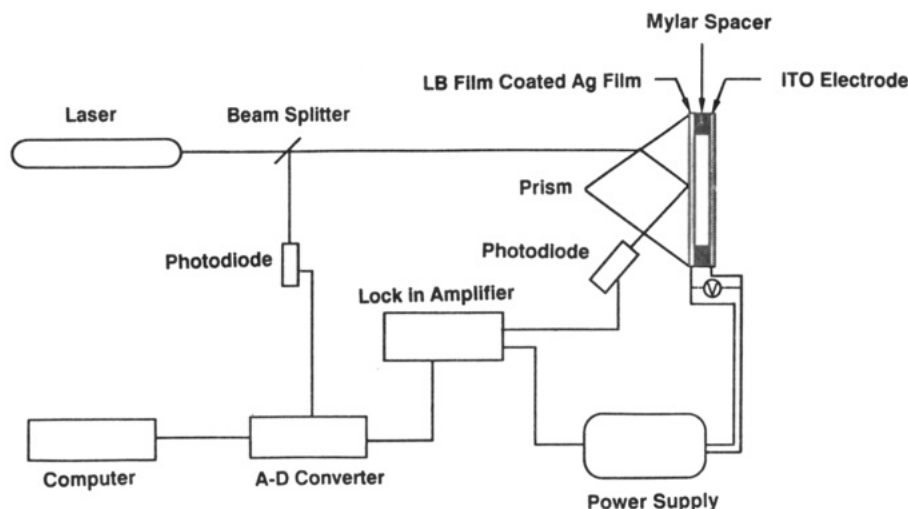(14) Kretschman, E. *Z. Phys.* **1971**, *241*, 313.

Figure 2. ATR experimental geometry employed for surface plasmon and electrooptic investigations.
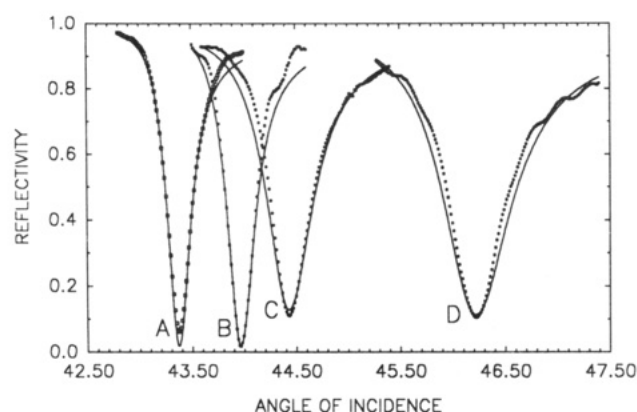

Figure 3. Surface plasmon resonance curves of silver coated with (A) 2, (B) 4, (C) 6, and (D) 10 layers of DCANP. Solid curves are the theoretical fits. All the films were transferred by horizontal lifting.

Figure 4. Differential reflectivity cures of (A) 2, (B) 4, and (C) 10 layers of DCANP-coated silver films. The theoretical curves have been overlaid (solid curves).

Table I

	no. of layers			
	2	4	6	10
layer thickness d, Å	64	130.2	188	312.7
ϵ_r^n	2.218	2.049	1.912	2.091
ϵ_i^n	0	0	0.0816	0.0521
$\Delta\epsilon_r^n$ ($\times 10^{-7}$)	−6.5	−5.7	6.9	−4.0
$\Delta\epsilon_i^n$ ($\times 10^{-7}$)	0	0	7.0	4.8
$\chi^{(2)}(-\omega;\omega,0)$ ($\times 10^{-13}$), mV^{-1}	−1.9	−1.6	−1.8 + 0.7i	−1.0 + 0.7i

signal from the photodiode was fed into a lock-in amplifier synchronized at the frequency of the applied electric field. The output from the lock-in amplifier was passed through the A–D converter and read by the microcomputer. The electrooptic measurements were carried out on mutilayer films of 2-, 4-, 6-, and 10-layer depositions. The voltage dependence of the electrooptic signal was carried out on a 10-layer sample.

Results and Discussion

The surface plasmon resonance curves of silver films coated with different number of DCANP LB layers are shown in Figure 3. It can be clearly seen that, as the thickness of the films grows, the depth of the SP resonance curve decreases and the width increases. Since DCANP does not absorb at the probing wavelength, we associate any changes consistent with absorption with the optical losses in the films. For bare silver, the thickness and the dielectric constant were varied until the best fit was found
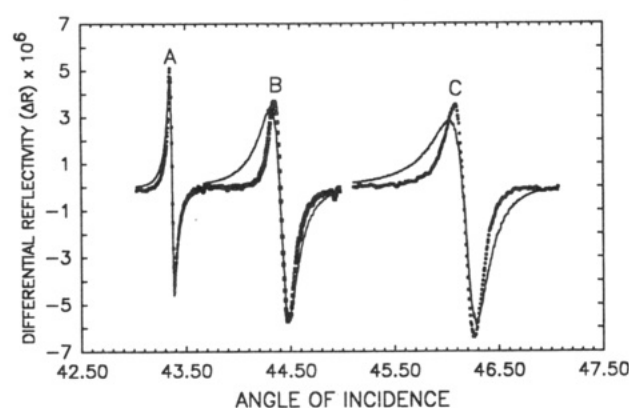
by minimizing the difference between the experimental data and the theory. The parameters thus calculated were used to obtain the best fit for the SP curves of DCANP-coated silver. All calculations have been performed by modifying a program originally written by Swalen.[3] The parameters obtained in the fits are presented in Table I. The appearance of the imaginary part of the dielectric susceptibility for thicker films may be considered an artifact, stemming from the optical losses caused by imperfections in the LB layers. It can be seen that the discrepancies between the experimental data and the theoretical fit intensify as the thickness of the films increases. One obvious inadequacy of the treatment adopted here is that, in fitting the experimental reflectivity curves with the theory, we have treated the LB layers as isotropic even though this assumption is questionable for LB films. Still, the same isotropic model was used to generate the theoretical differential reflectivity curves presented in Figure 4.

The surface plot in Figure 5 gives theoretical electrooptical results for an idealized film ($d = 50$ Å, $n = 1.5$). Curves associated with a refractive index other than 1.5 represent the expected angular dependence of the modulation signal detected by the lock-in amplifier. There has been no attempt to modify the imaginary part of the refractive index, which was given as being negligible.

The experimental curves were fitted by performing the calculation of the change in reflectivity as above with a set of ϵ values changed by a very small quantity. The ratio of the change in the real and the imaginary parts of ϵ was
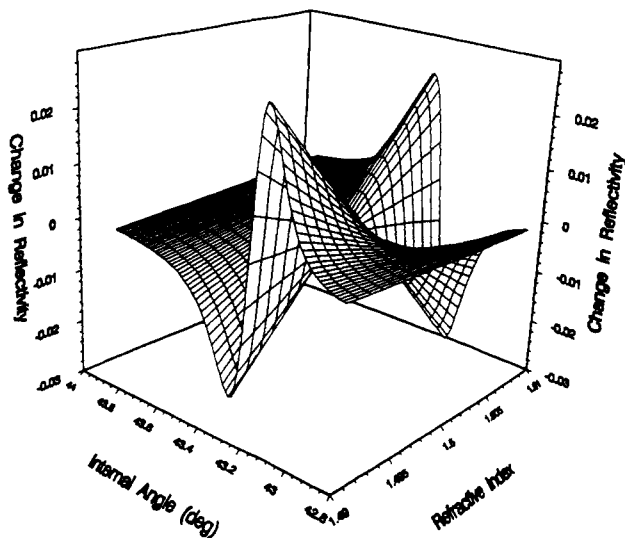
Figure 5. Theoretical electrooptic results for an idealized isotropic film ($d = 50$ Å, $n = 1.5$) with simulated changes in n.

adjusted for a minimum of the deviations of the calculated curve from an experimental profile. After the minimum was attained, the factor used to normalize the theoretical curve with respect to the experimental one (both of them presented as $\Delta R/R$) was used to calculate the absolute values of changes of ϵ_r and ϵ_i induced by the electric field. It has been verified that, for small changes of ϵ_r and ϵ_i, the resulting theoretical modulation curves preserve their shapes, and therefore, the normalization procedure can be used (see Figure 5). The results of the fitting are presented in Table I. As before, the presence of the change in the imaginary part of ϵ due to the electric field (electroabsorption contribution) should be taken in the context of the previous discussion on the imaginary contribution to the experimental results.

The change of the dielectric function with the applied electric field can be expressed either in the form of the Pockels coefficient r_{ijk}, defined by $\Delta(1/n_{ij}) = r_{ijk}E_k$ or in terms of the second-order nonlinear susceptibility $\chi_{ijk}^{(2)}$, defined by power expansion of the polarization. The latter expansion leads to $\chi^{(2)}(-\omega;\omega,0) = (\Delta\epsilon)/2E$, where E is the effective electric field in the LB film(s). This equation was used to calculate the $\chi^{(2)}$ values given in Table 1. The results indicate that the magnitude of the electrooptic response in DCANP films does not change significantly with the variation in the film thickness. Apparently, a conclusion can be reached that the molecular contributions from consecutive layers are summed up with little cancellation due to randomization of orientations. Therefore, the macroscopic susceptibility $\chi^{(2)}$ remains approximately constant for different numbers of layers.

SHG measurements on films of DCANP show that the zzz component of the second-order susceptibility is very small both for vertically transferred and for horizontally transferred films.[10] This is what should be expected for Y-type films, since the presence of a plane of symmetry (see Figure 1A) causes cancellation of the zzz component of any third-rank tensor. As mentioned before, when the horizontally transferred LB layers were tested for second harmonic generation, we found that the SHG pattern is not very different from that of the Y-type films and the maximum signal is obtained for normal incidence of the fundamental beam both in s and p polarizations. This means that the main effect is generated by the in-plane components $\chi_{xxx}^{(2)}$ and $\chi_{yyy}^{(2)}$. The conclusion which can be derived from this result is that, although the presence of

$\chi_{zzz}^{(2)}$ is not forbidden by symmetry (see Figure 1B), this component is very small.

It follows that, in our experimental geometry for surface plasmon measurements, we can expect contributions to the dielectric function variation to be brought about mainly by the off-diagonal $\chi^{(2)}$ terms. Specifically, if we assume that the multilayer films possess the average planar symmetry of m (C_s) (as could be the case for Y-type films), then all components of $\chi^{(2)}$ having odd numbers of z indices disappear and the change of ϵ can be expressed as $\Delta\epsilon_{xz} = 2\chi_{xxx}^{(2)}E_z$, $\Delta\epsilon_{yz} = 2\chi_{yzz}^{(2)}E_z$, other components of the ϵ tensor being unchanged. When no symmetry exists at all, which may be the case for our horizontally transferred films, there will be additional contributions from $\chi_{zzz}^{(2)}$ as well as from the off-diagonal components $\chi_{xyz}^{(2)}$, $\chi_{xxz}^{(2)}$, and $\chi_{yyz}^{(2)}$. Assuming that the chromophores make a small angle with the surface, one predicts that the zzz component should be smaller than the off-diagonal components. It should be noted that, because of the experimental geometry (the dc field in the z direction), the biggest components of the second-order susceptibility, i.e., $\chi_{xxx}^{(2)}$ and $_{yyy}^{(2)}$, cannot contribute to the Pockels effect. Therefore, when comparing the present results to those of SHG, one should expect the nonlinearity measured by the surface plasmon electrooptic modulation method to be smaller. Indeed, the $\chi^{(2)}(-\omega;\omega,0)$ value of DCANP obtained with electrooptic measurement is 2 orders of magnitude smaller than $\chi^{(2)}(-2\omega;\omega,\omega)$ obtained with SHG measurement (1.4×10^{-11} m V^{-1}). This is not surprising since, in these two particular cases, different Cartesian components of $\chi^{(2)}$ are probed.

It should be noted that two different types of substrates and two film-transferring techniques were used in the SHG and electrooptic measurements. The LB layers were vertically transferred onto octadecyltrichlorosilane- (OTS-) coated glass slides for the SHG measurements while the LB films were horizontally transferred onto fresh silver films for the electrooptic measurements. We recognize that the electronic properties, and hence the linear and nonlinear optical properties, of DCANP layers may be significantly modified due to their interaction with silver.[15] The pyridine moiety has been shown to exhibit enhanced surface phenomena on silver surfaces.[16,17] In order to gain some insight into the substrate–film interaction, Raman spectroscopic studies are planned to be carried out on the horizontally transferred LB layers on silver films using the SP geometry.

We have investigated the dependence of differential reflectivity on the strength of the modulating field with a silver film coated with 10 LB layers of DCANP. The results are presented in the Figure 6. When peak-to-peak differential reflectivity is plotted against the peak-to-peak applied voltage, the data fit into a straight line, confirming that we are probing the linear electrooptic effect (Pockels effect).

Conclusions

To our knowledge, this is the first observation of electrooptic modulation of surface plasmon reflectivity on LB films where nonlinear chromophores lie in a direction almost perpendicular to the modulating field. The technique seems to be useful especially for probing the off-diagonal tensor components of $\chi^{(2)}$. It should be mentioned

(15) Hurst, M.; Munn, R. W. *J. Mol. Electron.* **1986**, *2*, 35.

(16) Jeanmarie, D.; Van Duyne, R. P. *J. Electroanal. Chem.* **1977**, *84*, 1.

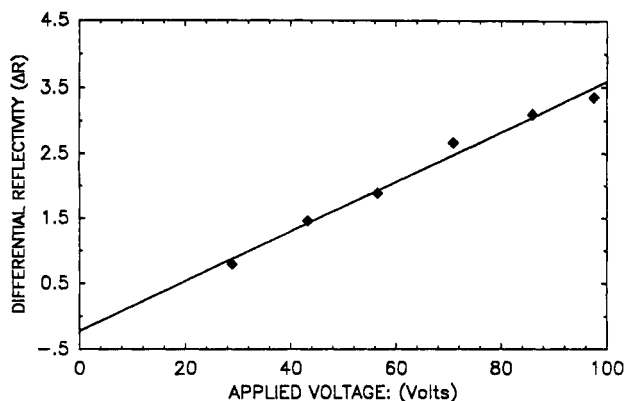(17) Busby, C. C.; Creighton, J. A. *J. Electroanal. Chem.* **1982**, *133*, 183.

Figure 6. Dependence of differential reflectivity (peak to peak) upon the applied voltage (peak to peak) carried out on a 10 LB layer sample of DCANP.

that even in the case of molecules lying almost flat on the substrate plane the order in the layer may be sufficient to give rise to strong second-order effects such as SHG and electrooptic effects. However, several issues must be resolved before a more sophisticated comparison of these results with those of SHG is attempted. First, the theory employed in this paper to fit the experimental data assumes that the dielectric function of the films is isotropic, which is not expected to be rigorously true. Therefore, the nu-

merical values of the susceptibilities derived from the present analysis can only be considered approximate. Second, due to the low frequency of the modulating field in the Pockels effect, there is a possibility that contributions from acoustic material modes (through inverse piezoelectric and elastooptic effect) and optical modes may be present. The former contribution can be avoided by using a higher frequency modulating field; however, the contributions from optical modes (both lattice and internal vibrations) are unavoidable. The consensus among researchers investigating the Pockels effect in organics is that these contributions are much smaller than those derived from the electronic second-order hyperpolarizabilities, β, of organic molecules. However, this problem has not yet been adequately addressed in the literature.