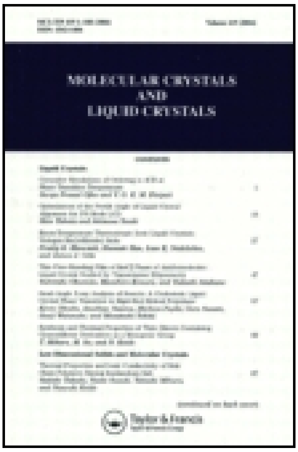

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Electroabsorption Study of Internal Electric Fields in Vacuum-Evaporated Layers of Organic Materials

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ELECTROABSORPTION STUDY OF INTERNAL ELECTRIC FIELDS IN VACUUM-EVAPORATED LAYERS OF ORGANIC MATERIALS

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Abstract The Stark effect in optical absorption of some organic compounds has been analyzed to yield information on the internal electric fields (IEF) occurring in their vacuum-evaporated thin layers. IEF strengths in excess 10^5V/cm have been observed with films of Epindolidione (EPI: $C_{18}H_{12}N_2O_2$) and linear trans - Quinacridone (QAC: $C_{20}H_{12}N_2O_2$) at room temperature. The lower values of IEF have been obtained for QAC, where, in contrast to EPI, the IEF are directed from the non-substrate to substrate side of the samples. No external field dependence of IEF was detected. However, the exact value of IEF depends on the preparation procedure of the layers. The hypothesis has been confirmed that formation of IEF involves a charge generation process on non-identified generation centres associated with defects showing an asymmetry in their characteristics on the substrate and non-substrate side of the samples.

INTRODUCTION

Wherever models of charge transport and charge generation are applied to thin organic layers, which involve potential barriers and structural inhomogeneity, internal electric fields (IEF) should be invoked in addition to external electric fields. The dark current-voltage and photocurrent-voltage behavior of such layers can be greatly affected by IEF, particularly in cases where the quantum efficiency of charge generation and transport is field-dependent. The presence of IEF in thin organic films can be revealed by electromodulation of optical absorption[1-4] and emission[5]. The purpose of this work is to apply the Stark spectroscopy technique to detect IEF in vacuum-evaporated layers of two organic compounds which appeared to be good photoconductors: Epindolidione (EPI)[6,7], $C_{18}H_{12}N_2O_2$, and linear trans-Quinacridone (QAC)[8,9], $C_{20}H_{12}N_2O_2$,

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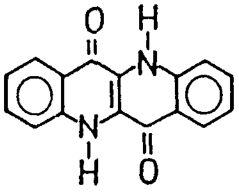
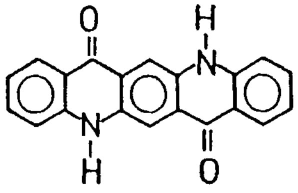


EPI



QAC

DESCRIPTION OF THE METHOD

The absorption spectrum of an aggregate of molecules responds to an electric field (F) via the field-induced change in the transition energy

$$\Delta E(F) = -\Delta\vec{\mu}\cdot\vec{F} - \frac{1}{2}(\Delta p \cdot F^2) \qquad (1)$$

where $\Delta\mu$ and Δp are the changes of the dipole moment and polarizability upon excitation, respectively. The local field that interacts with the aggregate is resultant of the applied, F_e, and an internal field F_i, which may have several origins, the potential barriers and space charge existing in the sample being the most common reasons,

$$\vec{F} = \vec{F}_e \cdot \sin(\omega t) + \vec{F}_i \qquad (2)$$

The change in the light intensity (I) passing through the sample as a function of F can be expressed in terms of a Fourier series

$$\left(\frac{\Delta I}{I}\right) = A + \left(\frac{\Delta I}{I}\right)_{1\omega} \cdot \sin(\omega t) + \left(\frac{\Delta I}{I}\right)_{2\omega} \cdot \cos(2\omega t) + \dots \qquad (3)$$

where, for an isotropic medium[2],

$$\left(\frac{\Delta I}{I}\right)_{1\omega} = -F_i \cdot F_e \cdot B(E) \qquad (4)$$

and

$$\left(\frac{\Delta I}{I}\right)_{2\omega}=\left(\frac{1}{4}\right)\cdot F_e^2\cdot B(E) \tag{5}$$

In (4) and (5) B stands for the function expressing the shape of the electroabsorption spectrum[10]. The first and second harmonics of ΔI/I are thus interrelated by a simple equation

$$\left(\frac{\Delta I}{I}\right)_{1\omega}=-\frac{4F_i}{F_e}\cdot\left(\frac{\Delta I}{I}\right)_{2\omega} \tag{6}$$

The value and direction of F_i can be obtained from this relationship if the first and second harmonic electroabsorption signals are known for a given external field.

RESULTS AND DISCUSSION

The electroabsorption studies were performed on vacuum-evaporated layers of EPI an QAC contained between two semitransparent Al electrodes (see the inset in Fig.1a).

The electroabsorption (EA) spectra are plotted in Fig.1. Their shapes are similar to a first (EPI) and second (QAC) derivative of the absorption spectrum with main bands near 486 nm, 452 nm and 420 nm for EPI[4], and near 558 nm, 523 nm and 490 nm for QAC[4].

Almost perfect identity of 1ω and 2ω harmonic spectra for EPI and their remarkable similarity for QAC allow relationship (6) to be employed for determination F_i. The values obtained in this way are $F_i=2.5\times10^5$V/cm and $F_i\leq1.0\times10^5$V/cm, for EPI and QAC, respectively.

A remarkable possible deflection of such determined F_i for QAC from its real value can result from a finite contribution of the first derivative terms to $(\Delta I/I)_{1\omega,2\omega}$. The effect is seen in Fig. 2b, where, in contrast to eqn.(4), $(\Delta I/I)_{2\omega}\neq0$ for $U_{rms}=0$. $(\Delta I/I)_{1\omega}=0$ at a finite U_{rms} implies operation of the IEF opposite to the applied field. This is not the case with EPI, where the plotted lines pass the origin of the coordinate system (Fig.2a). The action of a steady-state field (F_{DC}) can be predicted from a modified relationship (6):

$$\left(\frac{\Delta I}{I}\right)_{1\omega}=-\frac{4(F_i+F_{DC})}{F_e}\cdot\left(\frac{\Delta I}{I}\right)_{2\omega} \tag{7}$$

The negative slope of $(\Delta I/I)_{1\omega}$ versus F_{DC} plot for EPI proves F_i and F_{DC} to be antiparallel (Fig. 3).

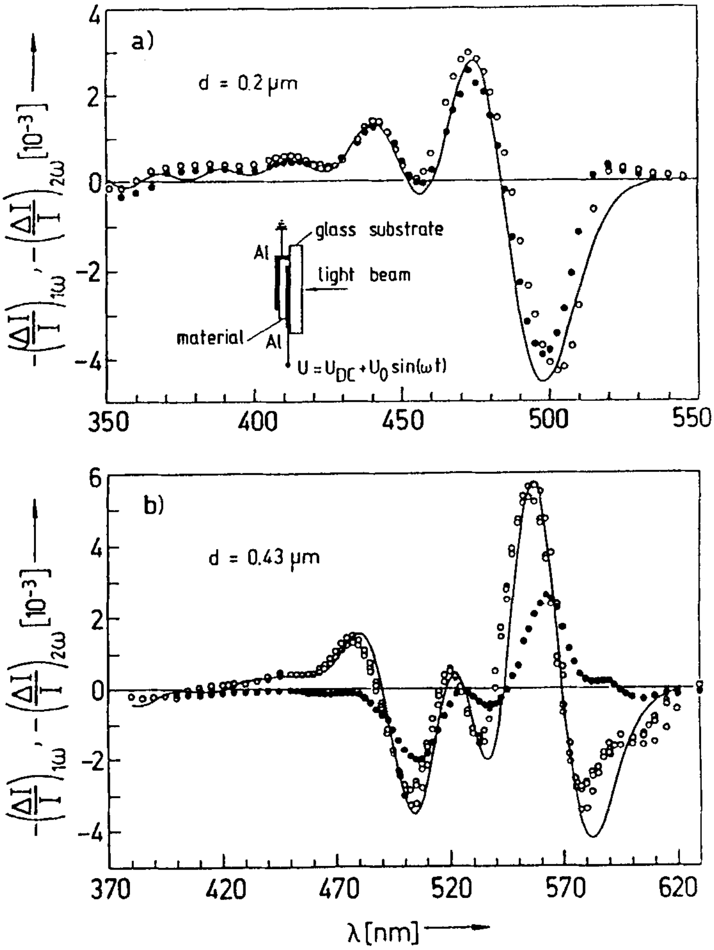


FIGURE 1 Electroabsorption spectra of EPI(a) and QAC(b) films detected at the first (full circles) and second (open circles) harmonic of the applied sinusoidal electric field frequency 1kHz. The field amplitude $F_0=7.0\times10^5$V/cm (a) and $F_0=8.2\times10^5$V/cm (b). The solid lines represent the fitting curves according to eqn.(5) with B(E) following the first derivative of the absorption band for EPI and the second derivative for QAC. Sample thicknesses, d, are given in the figure.

Such features of F_i can be explained by asymmetrical trapping of electrons which originate from electron-hole pairs produced by light in the near electrode layers of the samples (holes are mobile charge carriers in both EPI[6] and QAC[9]) as shown in Fig.4.

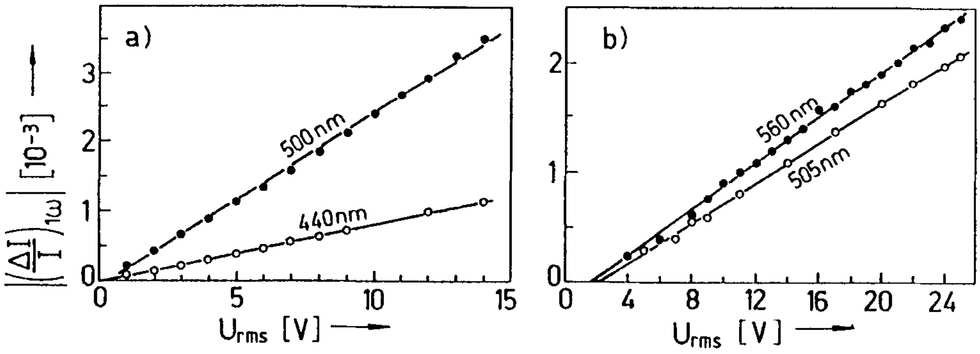


FIGURE 2 The EA signal detected at the first harmonic (1ω) as a function of the rms voltage applied to the EPI (a) and QAC (b) samples from Fig.1 at selected wavelengths.

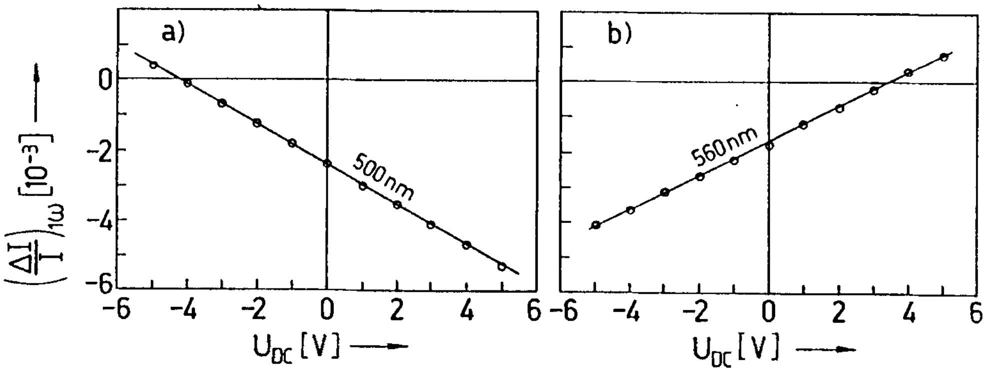


FIGURE 3 The EA signal detected at the first harmonic (1ω) as a function of positive DC voltage applied to the samples of EPI (a) and of QAC (b) from Fig.1. Circles: experimental data for λ=500 nm and U_0=14V for EPI and λ=560 nm and U_0=28 V for QAC. Solid lines: calculated from (7).

The IEF have been found to be sensitive to preparation procedure of the films. For instance, the QAC films obtained by triple subsequent evaporation steps, exposed to the ambient air after each step, showed F_i to be several times greater than that in a one-step-evaporated layer of the same thickness.

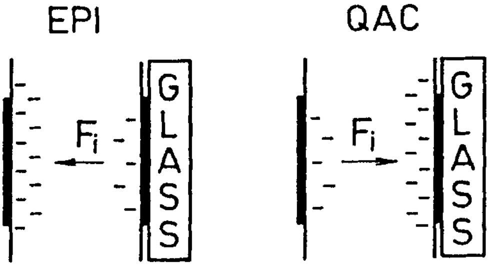


FIGURE 4 IEF in polycrystalline layers of EPI and QAC. Note a difference in the asymmetry of trapping electrons in the near-electrode regions of the samples.

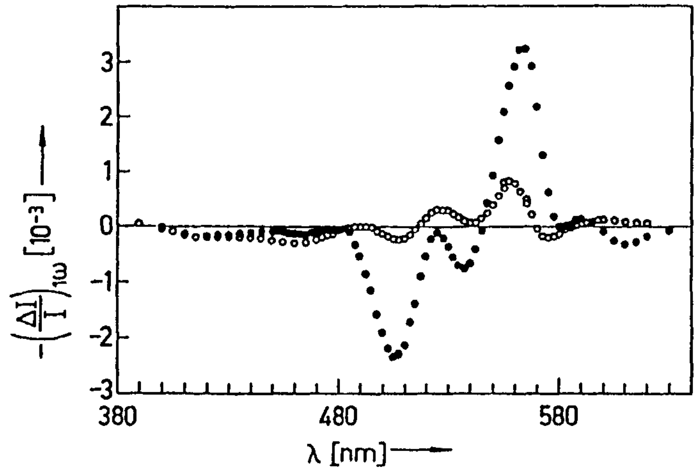


FIGURE 5 Effect of preparation procedure on the first harmonic EA spectrum of a 0.43μm-thick QAC layer. Open circles: one-step-evaporated layer; full circles: triple-step-evaporated layer. F_o=8.2x10^5V/cm.

A slight change in their EA spectra could also be detected (see Fig.5).

In conclusion, an analysis of different harmonic components of electroabsorption signals supplies information on internal electric fields and their origin in thin organic films.

The method is sensitive enough to follow differences in internal field characteristics, due to the preparation procedure of the films.

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