Detection of Electronic Excited States in Conjugated Polymers by Picosecond Transient Strain Spectroscopy

G. S. Kanner,[1,2] S. Frolov,[2] and Z. V. Vardeny[2]
[1]*Los Alamos National Laboratory, CST4, MS G755, Los Alamos, New Mexico 87545*
[2]*Physics Department, University of Utah, Salt Lake City, Utah 84112*

(Received 1 June 1994)

We describe a new type of spectroscopy based on picosecond transient strain in absorption photomodulation that can be used to detect and identify both allowed and forbidden optical transitions in solid thin films. We have applied the new spectroscopy to a variety of conducting polymer films such as polythiophene, *trans* and *cis* polyacetylene, and poly(diethynyl-silane), in which we measured energy levels of various excitonic states with odd and even symmetry that are, respectively, allowed and forbidden in the optical absorption.

PACS numbers: 78.47.+p, 42.65.An, 78.66.Qn

The luminescence efficiency and the resonant and subgap third-order nonlinear optical properties of conducting polymers are determined by the energies and symmetries of a subset of the excited states, including a series of singlet excitons with odd (B_u) and even (A_g) parity lying below the continuum band threshold. Among them, the lowest B_u exciton ($1B_u$), a dominant A_g exciton (hereafter, the mA_g), and a B_u exciton near the continuum band (hereafter, the nB_u) are particularly important in determining the spectra of the real ($\chi^{(3)\prime}$) and imaginary ($\chi^{(3)\prime\prime}$) parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ [1]. The relative energies of the $1B_u$ and the lowest A_g ($2A_g$) excitons determine the photoluminescence (PL) quantum efficiency γ [2]: If $E(2A_g) < E(1B_u)$, then γ is small because of the dipole forbidden character of the lowest singlet. Conversely, for $E(2A_g) > E(1B_u)$, γ is large and the polymer might be considered as the active material for display applications such as light emitting diodes [3].

Several cw optical techniques including electroabsorption [4], third harmonic generation [5], two photon absorption [6], and PL [7], as well as various excitation spectroscopies [8], are commonly used for measuring the exciton energy levels in conducting polymers. In this Letter we introduce a *transient* method, based on picosecond transient strain spectroscopy [9], for detecting odd and even parity excitons in these materials.

A feature often observed in picosecond transient absorption photomodulation (PM), in which the dynamics of photoinduced changes $\Delta T(t)$ in transmission T is measured, is an oscillation caused by a propagating strain pulse, superimposed on the electronic portion of the ΔT signal [9–12]. Figure 1(a) depicts the strain generation process [10]. A thin solid film of thickness d, bonded to a transparent substrate, is illuminated through the substrate by a picosecond pump light pulse, which is absorbed within the optical penetration depth ξ. The consequent heating of this layer creates a thermal stress, causing an acoustic wave to be launched into the film. The spatial and temporal dependencies of the strain η can be derived by solving a 1D wave equation, with a thermal generation term, for a semi-infinite film [10]. Assuming zero displacement at the interface between the substrate and the film at $z = 0$,

$$\begin{aligned}\eta(z,t) &= K[e^{-z/\xi}(2 - e^{-vt/\xi}) - e^{-|z-vt|/\xi}] \\ &= \eta_{\mathrm{ss}} + \eta_{\mathrm{ds}}(t), \qquad (1)\end{aligned}$$

where z is the distance into the film from the interface, t is time after photoexcitation, v is the longitudinal sound velocity, and K is a constant proportional to the heat transferred to the film from the pump pulse. The first term, η_{ss}, in Eq. (1) is time independent for $t \gg \xi/v$, whereas the second one, η_{ds}, corresponds to a portion of the strain that propagates back and forth inside the film. Equation (1) describes the stain for times before the propagating strain pulse first reaches the free surface ($z = d$); upon arrival at this surface η_{ds}, the dynamic strain, is reflected with a change in sign, but η_{ss}, the static strain, remains intact near the substrate-film interface. The spatial profile of the strain for $t < d/v$ and for $d/v < t < 2d/v$ is shown in the upper and lower parts of Fig. 1(b), respectively.

The strain is detected through its modulation of the optical parameters of the film by measuring $\Delta T(t)/T$ of a time-delayed weak probe pulse [Fig. 1(a)]. The magnitude of the strain-induced change in transmission $(\Delta T/T)_s$ is proportional to the strain $\langle\eta(t)\rangle$, averaged over d [10]. Figure 1(c) shows $\langle\eta(t)\rangle$ for a polythiophene (PT) film calculated by a numerical simulation that includes both the stationary and propagating strain components. The change in sign of $\eta_{\mathrm{ds}}(t)$ in Fig. 1(b) at the free surface is manifested as an oscillation in $\langle\eta(t)\rangle$. The decay of the oscillation in Fig. 1(c) is a result of simulated reflection losses at the interface with the substrate, but, generally, acoustical attenuation must also be taken into account [9,10]. Disregarding heat diffusion out of the absorption region, η_{ss} adds a time-independent component to $[\Delta T(t)/T]_s$; it simply shifts the baseline of the curve in Fig. 1(c) by half the amplitude of the total strain.

0031-9007/95/74(9)/1685(4)$06.00 © 1995 The American Physical Society

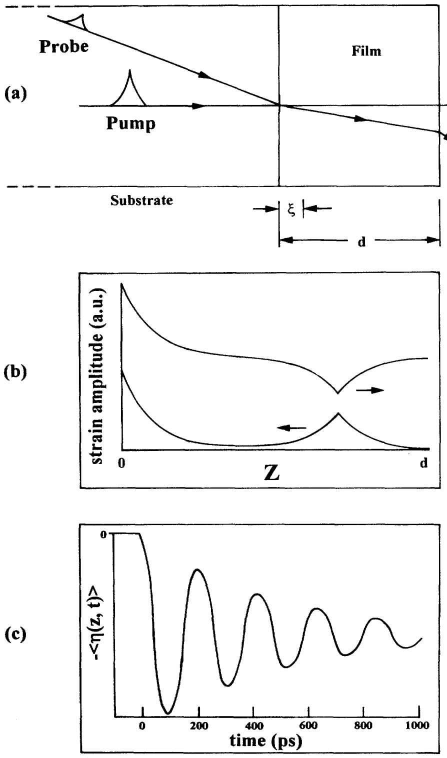

FIG. 1. (a) Experimental geometry for strain generation in a thin film of thickness d by a pump light pulse with absorption depth ξ, and detection via transmission of a time-delayed probe pulse. D symbolizes the detection apparatus. (b) Strain profile [see Eq. (1)] before (upper curve) and after (lower curve) reflection of the propagating strain pulse at the free surface ($z = d$). The arrows denote the direction of propagation. (c) The average transient strain $\langle \eta(t) \rangle$ in a PT film, calculated numerically (see text).

Our detection scheme for measuring the spectrum of the photoinduced strain contribution $(\Delta T/T)_s$ in the picosecond transient PM was described elsewhere [9] for the case in which the pump and probe beams were derived from the same laser. The data reported here were taken with two independent dye lasers for the pump and probe beams, synchronously pumped by a frequency-doubled mode-locked neodymium yttrium aluminum garnet (Nd:YAG) laser at 76 MHz; their cross correlation was 5 ps. The pump wavelength was usually fixed at 580 nm, whereas the probe was varied between 580 and 1020 nm to obtain the transient strain spectrum (TSS). We studied TSS in thin films ($d \simeq 1500$ Å) of electrochemically prepared polythiophene (PT), *cis*-rich $(\mathrm{CH})_x$, and poly(diethynyl-silane) (PDES); all films were deposited on glass or sapphire substrates.

An example of the oscillation in the $\Delta T(t)$ response of PT at a probe photon energy ($\hbar\omega$) of 2 eV is shown in the inset of Fig. 2. The main part of the figure shows the TSS, i.e., the amplitude of $(\Delta T/T)_s$ at the peak of the first oscillation in $\Delta T(t)$ $[(\Delta T/T)_{\mathrm{ds}}$, occurring at 220 ps]

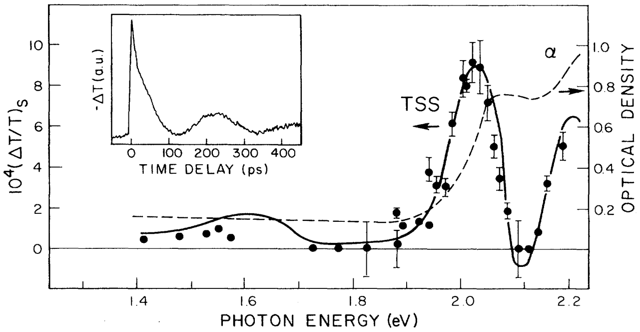

FIG. 2. PT absorption spectrum $\alpha(\omega)$ (dashed line), normalized $\partial\alpha/\partial\omega$ spectrum (solid line), and TSS measured by $(\Delta T/T)_{\mathrm{ds}}$ amplitude at 220 ps (points). The inset shows the oscillation in ΔT at $\hbar\omega(\mathrm{probe}) = 2$ eV.

as a function of $\hbar\omega_{\mathrm{probe}}$. The spectra of the absorption coefficient $\alpha(\omega)$ and its normalized derivative, $\partial\alpha/\partial\omega$, are also shown by dashed and solid lines, respectively, for comparison. The TSS in PT follows closely $\partial\alpha/\partial\omega$, since [9]

$$\left(\frac{\Delta T}{T}\right)_{\mathrm{ds}} = \frac{\partial\alpha}{\partial\omega} \Lambda_i \langle \eta(t) \rangle \frac{d}{\hbar}, \tag{2}$$

where Λ_i is the deformation potential of the ith excited state. We can, consequently, easily identify the energy of the excitonic transition from $1A_g$ to $1B_u$ from the maximum in TSS, corresponding to a shoulder in $\alpha(\omega)$, resulting from the 0-0 transition. In Fig. 2 we find the $1B_u$ exciton in PT to be at 2.03 eV. This is in good agreement with the 0-0 PL band of PT measured in the same film [13].

The analysis of TSS for the *cis*-rich $(\mathrm{CH})_x$ film is more complicated than that for PT. As seen in Fig. 3(a), the resemblance between TSS and $\partial\alpha/\partial\omega$ in *cis*-rich $(\mathrm{CH})_x$ is quite poor [14]; there is only a qualitative correspondence between the positions of the peaks in both spectra. In view of this discrepancy we consider that, in addition to causing a shifting of $\alpha(\omega)$ associated with allowed transitions [Eq. (2)], the photoinduced strain acts as a symmetry-breaking mechanism that permits the detection of optically forbidden states in TSS. Upon uniform heating, hydrostatic pressure, or uniaxial pressure, the inversion symmetry of the film does not change. Hence in conducting polymers with C_{2h} point group symmetry, B_u and A_g excitons do not mix when subject to these perturbations. Therefore, measurements such as thermal or pressure modulation of α and piezoabsorption are expected to yield a first-derivative-type spectrum associated with B_u excitons and their phonon sidebands [15]. However, if the stress is *nonuniform,* the inversion symmetry is broken and new transitions may appear because states of opposite parity are mixed by the perturbation. In the present experimental situation [Fig. 1(a)], the stress is photothermally generated, and, therefore, spatially inhomogeneous with an exponentially decaying spatial profile [$\eta \sim e^{-z/\xi}$, Eq. (1)]. This

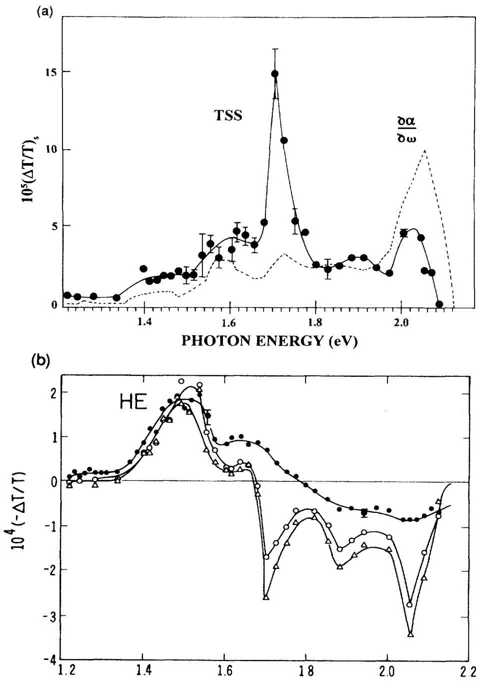

FIG. 3. (a) Normalized $\partial\alpha/\partial\omega$ spectrum (dashed line), and TSS measured by $(\Delta T/T)_{\mathrm{ds}}$ amplitude at 160 ps, (solid circles, full line) in a partially isomerized $(\mathrm{CH})_x$. (b) Normalized transient PM spectra at $t = 0$ (solid circles), $t = 100$ ps magnified by a factor of 4 (empty circles), and $t = 400$ ps magnified by a factor of 6 (triangles), for the same film as in (a). Solid lines are guides to the eye.

stress leads, therefore, to an inhomogeneous perturbation Hamiltonian $H_s(z)$, given by [16]

$$H_s(z) = \Lambda_i \eta(z) = \Lambda_i \eta(z_0) + \Lambda_i \left.\frac{\partial \eta}{\partial z}\right|_{z_0} (z - z_0), \quad (3)$$

where z_0 is the z coordinate of the exciton center and Λ_i is its deformation potential. Using this $H_s(z)$ in second-order time-independent perturbation theory causes B_u and A_g states to mix since $H_s(z)$ destroys the inversion symmetry. Consequently, this mixing causes the forbidden transition to be partially allowed with a probability proportional to $\langle(\partial\eta/\partial z)^2\rangle$, the average square of the strain gradient in the film [16]. This situation is analogous to the application of an external electric field F with a symmetry-breaking Hamiltonian $H_F = eFz$, which leads to an electroabsorption (EA) spectrum with contributions from both B_u and A_g excitons [4]. A_g excitons appear in EA in the form of induced absorption bands centered at $E(A_g)$, which results from the transfer of oscillator strength from adjacent B_u states [4,8]. Although the perturbation Hamiltonians in TSS and EA are not exactly the same, we still expect similar bands for the forbidden A_g states in both spectra since they result from symmetry breaking in both cases. Nevertheless, the spectra obtained with these techniques are strikingly different from each other; for example, the A_g states in EA of $(\mathrm{CH})_x$ [17] are obscured by features associated with the excitonic phonon sidebands, whereas they clearly appear in TSS here.

Based on the above analysis we can now assign the prominent peaks in the TSS of the partially isomerized $(\mathrm{CH})_x$ film in Fig. 3(a) and confirm them by comparing the TSS with results of other optical measurements. First, we attribute the TSS band at 2.05 eV to the $1B_u$ exciton of the *cis* isomer chains in the sample. This is based on a similar feature in the $\partial\alpha/\partial\omega$ spectrum showing that the TSS band is due to an allowed optical transition, and is in agreement with the 0-0 transition of the PL spectrum in *cis*-$(\mathrm{CH})_x$ [18]. Additionally, from the similarity between the spectral features of TSS and $\partial\alpha/\partial\omega$ in the range of 1.5 to 1.65 eV, we assign the prominent shoulder in TSS at 1.58 eV to the $1B_u$ exciton of the *trans* isomer chains in the sample. This band is broader and weaker compared to that of the *cis* isomer chains because of the strong exciton dispersion associated with the inhomogeneity known to exist in the *trans* isomer chains [19]. Our assignment of $1B_u$ (*trans*) at 1.58 eV is in agreement with the energy threshold of the weak infrared PL band previously observed in partially isomerized $(\mathrm{CH})_x$, caused by the *trans* isomer chains [20]. It is also in agreement with 3 times the energy of the "three-photon resonance" in the $\chi^{(3)\prime}$ spectrum of *trans*-$(\mathrm{CH})_x$ observed at ~0.55 eV [5,21]. Finally, since the TSS symmetric band at 1.7 eV does not have an analogous companion in the $\partial\alpha/\partial\omega$ spectrum, we assign it to an A_g exciton. Its higher energy compared to that of the $1B_u$ exciton suggests that it be associated with the mA_g exciton in *trans*-$(\mathrm{CH})_x$. This assignment is in excellent agreement with twice the energy of the "two-photon resonance" observed at 0.85 eV in both $\chi^{(3)\prime}$ [21] and $\chi^{(3)\prime\prime}$ [6] spectra in partially isomerized $(\mathrm{CH})_x$.

Confirmation of our interpretation of the features in TSS comes from related features in the transient PM spectrum not associated with the ΔT oscillation [Fig. 3(b)], for times 0, 100, and 400 ps. At $t = 0$, most of the pump photon energy is used to form solitonic excitons [22] [HE band in Fig. 3(b)], with only a small amount of excess energy available for thermal strain production. After most of the photoexcitations have recombined, primarily nonradiatively [18], more energy is used to generate strain. Therefore the strain contribution to ΔT increases shortly after exciton recombination, whereas the electronic portion of ΔT is reduced. This is demonstrated in Fig. 3(b), which shows the presence of photobleaching (PB) bands at $t = 100$ ps that are not immediately apparent at $t = 0$. The PB peak energies at 1.58, 1.7 and 2.05 eV are exactly the same as those of the most prominent bands in TSS of Fig. 3(a). We also speculate that the prominent PB band at 1.9 eV in Fig. 3(b), with only a weak analogous band in Fig. 3(a), is due to the elusive nB_u exciton in *trans*-$(\mathrm{CH})_x$; it is in agreement with 3 times the energy of a prominent shoulder in the three-photon resonance band in the $\chi^{(3)\prime}$ spectrum of *trans*-$(\mathrm{CH})_x$, observed at ~0.65 eV [21]. The lack of photoinduced dichroism exhibited in the oscillation amplitude (ΔT_{ds}) and in the long-lived PB (ΔT_{ss}) shows that these two responses are not of electronic origin [23]. Also, the agreement between ΔT_{ds} and ΔT_{ss} spectra [Fig. 3(a) and Fig. 3(b), respectively] shows that ΔT_{ss} does not originate from a simple thermal effect. We attribute, therefore, ΔT_{ss} to the stationary component η_{ss} of the photothermally generated strain [Eq. (1)], which can also mix states of opposite parity because of its spatial nonuniformity.

In some of the conjugated polymers, no strain-induced oscillation ΔT_{ds} has been observed so the only way to detect excitonic states through TSS is that measuring the ΔT_{ss} spectrum caused by the static strain. For example, in Fig. 4 we show transient PM spectra in PDES at $t = 0$ and $t = 100$ ps, and compare them to the $\partial\alpha/\partial\omega$ spectrum. The PM spectrum at $t = 0$ contains a polarized electronic excitation band at 1.5 eV, associated with photoexcited excitons that decay within 2 ps [24], and a band at 1.9 eV followed by a dip at 2 eV, both of which persist beyond 400 ps and are not polarized; the latter two features therefore arise from photoinduced static strain (η_{ss}) in the film. ΔT_{ss} at 100 ps seems to follow $\partial\alpha/\partial\omega$ up to 1.6 eV, but deviates from it around the peak in ΔT_{ss} at 1.9 eV and the dip at 2 eV. As in $(\mathrm{CH})_x$ [Fig. 3(b)] we assign the 1.9 eV band to an A_g exciton that becomes partially allowed in TSS because of the inhomogeneity of the photogenerated strain. Since this A_g exciton is below the dip in TSS (and the analogous peak in $\partial\alpha/\partial\omega$) at 2.02 eV, attributed to the $1B_u$ exciton [24], we assign it to $2A_g$, and thus $E(2A_g) < E(1B_u)$ in PDES. The reason why the $1B_u$ exciton in PDES appears as a dip in TSS rather than a peak [as in PT (Fig. 2) and $(\mathrm{CH})_x$ (Fig. 3)] is the large oscillator strength transferred to the neighboring $2A_g$ state. This is in agreement with the EA spectrum of PDES, which, when corrected by subtracting out the Stark shift of $1B_u$, reveals the transfer of oscillator strength from $1B_u$ to $2A_g$ [25].

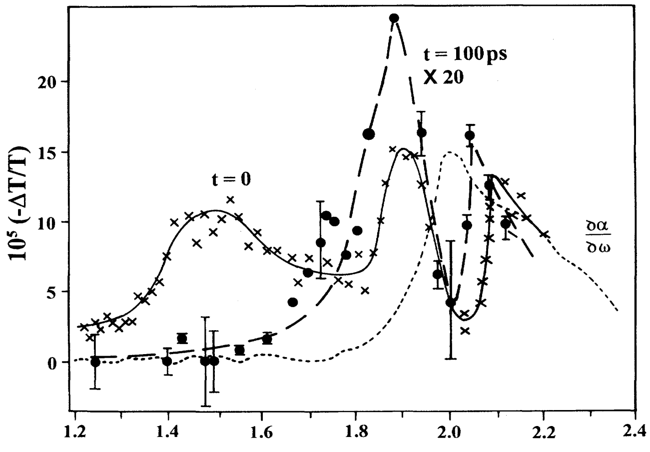

FIG. 4. PDES normalized $\partial\alpha/\partial\omega$ spectrum (short dashed line), PM at $t = 0$ (crosses and full line), and PM at $t = 100$ ps multiplied by a factor of 20 (solid circles and long dashed line).

In conclusion, we have shown that TSS is a potentially useful technique for detecting both allowed and forbidden optical transitions, and is particularly suitable for conjugated polymers, for which the lowest singlet exciton is often at energies accessible to mode-locked dye and Ti:sapphire lasers. We have demonstrated the TSS capability in measuring singlet excitons with B_u and A_g symmetries in a group of π-conjugated polymers such as those with $E(1B_u) > E(2A_g)$ [PT and *cis*-$(\mathrm{CH})_x$], as well as polymers with $E(2A_g) < E(1B_u)$ [*trans*-$(\mathrm{CH})_x$ and PDES].

The work at the University of Utah was supported in part by the NSF (DMR 92-22947), by ONR Grant No. N00014-94-1-0853, and by the DOE FG-03-93ER45490.

[1] S.N. Dixit, D. Guo, and S. Mazumdar, Phys. Rev. B **43**, 6781 (1991); S. Mazumdar and F. Guo, J. Chem. Phys. **100**, 1665 (1994).
[2] Z.G. Soos, S. Etemad, D.S. Galvo, and S. Ramasesha, Chem. Phys. Lett. **194**, 341 (1992).
[3] J.H. Burroughes *et al.*, Nature (London) **347**, 539 (1990).
[4] D. Guo *et al.*, Phys. Rev. B **48**, 1433 (1993).
[5] W.S. Fann *et al.*, Phys. Rev. Lett. **62**, 1492 (1989).
[6] C. Halvorson and A.J. Heeger, Chem. Phys. Lett. **216**, 488 (1993).
[7] C.J. Baker, O.M. Gelsen, and D.D.C. Bradley, Chem. Phys. Lett. **201**, 127 (1993).
[8] J.M. Leng *et al.*, Phys. Rev. Lett. **72**, 156 (1994).
[9] G.S. Kanner, Z.V. Vardeny, and B.C. Hess, Phys. Rev. B **42**, 5403 (1990).
[10] C. Thomsen, H.T. Grahn, H.J. Maris, and J. Tauc, Phys. Rev. B **34**, 4129 (1986).
[11] J. Wiesenfeld, Appl. Phys. Lett. **47**, 143 (1985).
[12] G.L. Eesley, B.M. Clemens, and C.A. Paddock, Appl. Phys. Lett. **50**, 717 (1987).
[13] Z. Vardeny, E. Ehrenfreund, J. Shinar, and F. Wudl, Phys. Rev. B **35**, 2498 (1987).
[14] G.S. Kanner, G. Lanzani, and Z.V. Vardeny, Mol. Cryst. Liq. Cryst. **256**, 135 (1994).
[15] R.L. Tober, J.P. Ferraris, and R. Glosser, Phys. Rev. B **33**, 8768 (1986).
[16] M. Raikh (private communication).
[17] S.D. Phillips *et al.*, Phys. Rev. B **40**, 9751 (1989).
[18] L. Lauchlan, S. Etemad, T.C. Chung, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. B **24**, 3701 (1981).
[19] E. Ehrenfreund, Z. Vardeny, O. Brafman, and B. Horovitz, Phys. Rev. B **36**, 1535 (1987), and references therein.
[20] E.A. Imhodff, D.B. Fitchen, and R.E. Stahlbush, Solid State Commun. **44**, 329 (1982).
[21] C. Halvorson, T.W. Hagler, D. Moses, Y. Cao, and A.H. Heeger, Chem. Phys. Lett. **200**, 364 (1992).
[22] J. Orenstein and G.L. Baker, Phys. Rev. Lett. **49**, 1043 (1982).
[23] Z.V. Vardeny, Synth. Metals **28**, D203 (1989).
[24] K.S. Wong *et al.*, Appl. Phys. Lett. **58**, 1695 (1991); G.S. Kanner, Ph.D. thesis, University of Utah, 1991.
[25] S. Jeglinski, Z.V. Vardeny, Y. Ding, and T.J. Barton, Mol. Cryst. Liq. Cryst. **256**, 87 (1994).