Eur. Phys. J. B **10**, 681–686 (1999)

THE EUROPEAN
PHYSICAL JOURNAL B
EDP Sciences

Electro-optical properties of excitons in polydiacetylene chains

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Received 5 November 1998 and Received in final form 23 February 1999

Abstract. We show how to compute the optical functions (reflectivity, transmission, and absorption) of polydiacetylene chains diluted in their monomer matrix exposed to a uniform electric field in the chain direction, in the excitonic energy region. Adopting a model electron-hole potential, we derived an analytical expression for the effective chain susceptibility, which gives the optical functions. The resulting absorption shows excitonic peaks below the gap and Franz-Keldysh oscillations above the gap. The method has been applied for a 3BCMU polydiacetylene chain, showing a good agreement with experimental spectra.

PACS. 78.66.-w Optical properties of specific thin films, surfaces, and low-dimensional structures – 71.35.-y Excitons and related phenomena – 71.36.+c Polaritons (including photon-phonon and photon-magnon interactions)

1 Introduction

The electronic properties of polymers can be modelled by considering the chain as a strongly correlated one-dimensional system [1,2]. So in consequence their optical spectra can be considered as those of excitons in a cylindrical quantum wire (QWW). By applying a moderate electric field along the chain (QWW) axis one observes the quadratic Stark shift for excitation energies below the gap and Franz-Keldysh oscillations above the gap [3]. From the analysis of the electro-absorption spectra microscopic data as, for example, the positions of excitonic transitions, their oscillator strengths, and the electron effective masses along the chain axis, can be obtained. Therefore there is a need for a simple mathematical procedure which relates the optical spectra with the microscopic properties.

In what follows we present an approach which is based on the dynamical matrix theory. In Section 2 we describe the constitutive equations for an exciton in an homogeneous electric field as appropriate to a PDA chain and the consequent approach to the solution of Maxwell's equations. In Section 3 we give the computing procedure for the calculation of the optical functions. Applications to the case of 3BCMU and 4BCMU PDA chains are given for various choices of the relevant parameters in Section 4. In Section 5 we present conclusions and discuss the experimental consequences.

2 Density matrix formulation for polydiacetylene chains in a homogeneous electric field

Below we concentrate our attention on optical properties of PDA chains in the excitonic energy region, when a homogeneous electric field is applied in the chain direction. As we have recently shown for the case of superlattices [4], optical properties of a low dimensional system can be discussed by adapting the Stahl coherent wave approach when the low dimensional semiconductor is treated as an effective anisotropic medium in which the quasi-free carriers propagate and interact. Below we adopt the Stahl's method for the case of PDA treated as a quantum wire subject to a homogeneous electric field applied in the wire direction, and show how to calculate the optical functions.

We consider a platelet, parallel to the yz-plane, containing polymer chains parallel to the surface and oriented in the z-direction. The chains will be considered as QWWs of radius a with infinite potential barriers. We will discuss the linear response of the platelet to a normally incident electromagnetic wave, linearly polarized in the z-direction,

$$E(\mathbf{R},t) = E_{x0}\exp(\mathrm{i}\mathbf{k}\mathbf{R} - \mathrm{i}\omega t), \quad k_0 = \frac{\omega}{c}, \tag{1}$$

and exposed to the electric field $\mathbf{F} = (0,0,F)$. In the case of 3BCMU and poly-4BCMU we adopt the model proposed in [3], assuming excitonic transitions labelled by the index $\nu = \nu_0, \nu_a, \nu_b, \nu_c, \nu_S, \ldots$, with corresponding transition matrix elements $\mathbf{M}_\nu$. In the density matrix approach the linear response will be described by a set

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[b] This work was performed under the auspices of *C. N. R.* (*Consiglio Nazionale delle Ricerche*). G. Czajkowski acknowledges the *Scuola Normale Superiore* for its invitation and hospitality.

of coupled equations: constitutive equations for the coherent amplitudes $Y_\nu(\mathbf{r}_\mathrm{e}, \mathbf{r}_\mathrm{h})$ (nine for the case of 3BCMU, six for 4BCMU) from which the polarization can be obtained and used in Maxwell's equations. The constitutive equations have the form:

$$\partial_t Y_{12\nu} + \frac{\mathrm{i}}{\hbar} H_{\mathrm{eh}\nu} Y_{12\nu} = \frac{1}{\hbar}\left[\mathrm{i}\mathbf{M}_\nu(\mathbf{r})\mathbf{E}(\mathbf{R}) - \Gamma_\nu Y_{12\nu}\right], \quad (2)$$

where Y_{12} contains the dependence on spatial coordinates of the hole and of the electron, $\mathbf{r} = \mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{h}$ is the relative electron-hole coordinate, and $\mathbf{R}$ the center-of-mass coordinate; $\mathbf{M}_\nu(\mathbf{r})$ are the transition dipole densities describing the coherence between the radiation field and the motion of the carriers [4,5]. We have considered relaxation times $\hbar/\Gamma$ as phenomenological quantities. The operator $H_{\mathrm{eh}\nu}$ is the exciton effective mass Hamiltonian:

$$\begin{aligned} H_{\mathrm{eh}\nu} = {} & E_{\mathrm{g}\nu} - \frac{\hbar^2}{2m_{\mathrm{e}z\nu}}\partial^2_{z_e} - \frac{\hbar^2}{2m_{\mathrm{h}z\nu}}\partial^2_{z_\mathrm{h}} \\ & - \frac{\hbar^2}{2m_{\mathrm{e}\perp\nu}}\left(\partial^2_{x_\mathrm{e}} + \partial^2_{y_\mathrm{e}}\right) - \frac{\hbar^2}{2m_{\mathrm{h}\perp\nu}}\left(\partial^2_{x_\mathrm{h}} + \partial^2_{y_\mathrm{h}}\right) \\ & + eF(z_\mathrm{h} - z_\mathrm{e}) + V_{\mathrm{eh}\nu}(\mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{h}) \\ & + V_{\mathrm{e}\nu}(x_\mathrm{e}, y_\mathrm{e}) + V_{\mathrm{h}\nu}(x_\mathrm{h}, y_\mathrm{h}). \end{aligned} \quad (3)$$

The potential term representing the Coulomb interaction in an anisotropic medium is

$$V = -\frac{e^2}{4\pi\epsilon_0\epsilon_\mathrm{b}\left[(x^2+y^2) + z^2\epsilon_\parallel/\epsilon_z\right]^{1/2}}, \quad (4)$$

where we introduce the two effective dielectric constants, $\epsilon_\parallel$, and ϵ_z, respectively, and define $\epsilon_b = \sqrt{\epsilon_\parallel\epsilon_z}$.

The coherent amplitudes Y_ν, with the transition dipoles give the total polarization of our effective anisotropic medium:

$$\mathbf{P}(\mathbf{R}) = 2\int \mathrm{d}^3\mathbf{r}\,\mathrm{Re}\left[\sum_\nu M_\nu(\mathbf{r}) Y_\nu(\mathbf{r}, \mathbf{R})\right]. \quad (5)$$

The above equation (5), with the constitutive equations (2), connects the polarization with the electric field. Both polarization and electric field must obey Maxwell's equations, which must be solved to obtain the propagation modes. One advantage of the procedure here presented with respect to other approaches is that microscopic theory and macroscopic theory are treated on the same footing and the problem of *additional boundary conditions* finds its natural solution in the conditions which the geometry of the problem imposes on $Y_{12\nu}$. The above formulation contains all the ingredients for the calculation of all QWW (PDA) optical functions. Here we will concentrate the attention on calculation of the optical absorption which will be obtained from the susceptibility.

3 Electro-optical functions of polydiacetylene chains

Similarly to the procedure adopted in a previous paper, [4] we separate the Hamiltonians of equations (2, 3) into a "kinetic+electric field" part $H_{\mathrm{kin+F}}$ and a potential term V, and obtain from (2)

$$H_{\mathrm{kin+F}} Y = \mathbf{ME} - VY, \quad (6)$$

which coincides with the Lippmann-Schwinger equation, once the Green function G appropriate to the "kinetic+electric field" part is adopted for the coherent amplitudes

$$Y = G\mathbf{ME} - GVY. \quad (7)$$

The solution of equations (6, 7) and the corresponding Maxwell equations represent a nontrivial computational problem since we deal with a system of integro-differential equations in a 6-dimensional configuration space. As it can be seen from reference [6], even the solution of a Schrödinger equation for the semiconductor QWW geometry constitutes a problem for which analytical solutions are not known and only approximative methods can be used. Since we tend to construct a simple calculational procedure for interpreting optical data, we assume some simplifications similar to that of references [7,8], where a special choice of the electron-hole interaction potential and of the dipole density was adopted. Since the lateral extension of a polymer chain is small compared to an excitonic Bohr radius (being of the order of a few nm), we separate the relative and the center-of-mass motion in the xy-plane, neglecting then the effects coming from the lateral center-of-mass motion. This means that our effective mass Hamiltonian will have the form:

$$\begin{aligned} H_{\mathrm{eh}\nu} = {} & E_{\mathrm{g}\nu} - \frac{\hbar^2}{2m_{\mathrm{e}z\nu}}\partial^2_{z_\mathrm{e}} - \frac{\hbar^2}{2m_{\mathrm{h}z\nu}}\partial^2_{z_\mathrm{h}} \\ & - \frac{\hbar^2}{2\mu_{\perp\nu}}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right) - \frac{\hbar^2}{2M_{\perp\nu}}\nabla^2_{R_\perp} \\ & + eF(z_\mathrm{h} - z_\mathrm{e}) + V_{\mathrm{eh}\nu}(\mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{h}), \end{aligned} \quad (8)$$

where $\rho = \sqrt{(x_\mathrm{e} - x_\mathrm{h})^2 + (y_\mathrm{e} - y_\mathrm{h})^2} = \sqrt{x^2 + y^2}$. Similar as in the case of quantum dots [9,10], we separate the center-of-mass motion, which is relevant for the macroscopic electrodynamical equations, from the relative electron-hole motion. Due to this assumption, the coherent amplitudes take the form

$$Y_\nu(\mathbf{r}_\mathrm{e}, \mathbf{R}) = Y_\nu(\mathbf{r}_\mathrm{e})\exp(\mathrm{i}\mathbf{kR} - \mathrm{i}\omega t). \quad (9)$$

In the geometry considered ($\mathbf{E} \parallel \mathbf{b}$, $\mathbf{F} \parallel \mathbf{b}$, $\mathbf{E}$ being the electric field vector of the incident wave and $\mathbf{b}$ the direction of the chain axis) [11,3], only the k_z component of $\mathbf{k}$ is relevant and we arrive at the following equations for the coherent electron–hole amplitude of the ν-exciton:

$$\begin{aligned} & \left[E_{g\nu} - \hbar\omega - \mathrm{i}\Gamma_\nu + \frac{\hbar^2}{2M_{z\nu}}k_z^2 - \frac{\hbar^2}{2\mu_{\parallel\nu z}}\partial^2_z \right. \\ & \left. - \frac{\hbar^2}{2\mu_{\perp\nu}}(\partial^2_\mathrm{x} + \partial^2_\mathrm{y}) + eFz + V_{\mathrm{eh}\nu}(z, \rho)\right] Y_\nu(\rho, z) \\ & = M_\nu(\rho, z)E_0, \end{aligned} \quad (10)$$

where E_0 is the amplitude of the electromagnetic wave propagating in the medium. Below, for the sake of simplicity, we use the components of the dipole densities with the coherence radii $r_{0\nu}$ along the z-axis and zero along the planes perpendicular to the chain axis, of the form:

$$\mathbf{M}_\nu(\mathbf{r}) = \mathbf{M}_{0\nu}\frac{\delta(\rho - r_{0\nu})}{2\pi\rho}\delta(z). \tag{11}$$

The amplitudes Y_ν are determined from the Lippmann-Schwinger equation (7). For further considerations we introduce dimensionless quantities,

$$\begin{aligned}
\rho &= \frac{\sqrt{x^2+y^2}}{a_\nu^\star}, \quad \zeta = \frac{z}{a_\nu^\star\sqrt{\alpha_\nu}}, \\
f_\nu &= \frac{F}{F_{\mathrm{I}\nu}}, \\
k_\nu^2 &= \frac{2\mu_{\perp\nu}}{\hbar^2}a_\nu^{\star 2}\left(E_{\mathrm{g}\nu} - \hbar\omega - \mathrm{i}\Gamma_\nu + \frac{\hbar^2 k_z^2}{2M_{z\nu}}\right),
\end{aligned} \tag{12}$$

where $F_{\mathrm{I}\nu}$ is the so-called ionisation field:

$$F_{\mathrm{I}\nu} = \frac{\hbar^2}{2\mu_{\perp\nu} e a_\nu^{\star 3}} = \frac{R_\nu^\star}{a_\nu^\star e}, \tag{13}$$

$R_\nu^\star$ is the excitonic Rydberg for the ν-exciton, $a_\nu^\star$ is the corresponding excitonic Bohr radius, and $\alpha_\nu = \mu_{\perp\nu}/\mu_{z\nu}$ is the anisotropy parameter. With these quantities equations (10) take the form

$$\begin{aligned}
&\left(k_\nu^2 - \partial_\zeta^2 - \partial_\rho^2 - \frac{1}{\rho}\partial_\rho + f_\nu\sqrt{\alpha_\nu}\zeta\right)Y_\nu = \\
&\qquad \frac{2\mu_{\perp\nu}}{\hbar^2}a_\nu^{\star 2}M_\nu(\rho,\zeta)E_0 + \frac{2}{\sqrt{\rho^2+\alpha_\nu\zeta^2}}Y_\nu.
\end{aligned} \tag{14}$$

For the sake of simplicity, we start with the following *ansatz* for the e-h potential [7,8]:

$$\frac{2}{\sqrt{\rho^2+\alpha_\nu\zeta^2}} \quad \to \quad 2\delta(\zeta)\frac{\delta(\rho-\rho_{0\nu})}{\rho}, \tag{15}$$

where the quantities ρ_ν will be fixed by the conditions for resonances. The Green function of equation (14) can be expressed in terms of eigenfunctions of the relative motion [12] and has the form:

$$\begin{aligned}
G_\nu(\rho,\rho';\zeta,\zeta') &= \frac{1}{2(f_\nu\sqrt{\alpha_\nu})^{1/3}} \\
&\times \sum_{n=1}^{\infty}\frac{2}{a_\nu^2[J_1(x_n)]^2}J_0(x_n\frac{\rho}{a_\nu})J_0(x_n\frac{\rho'}{a_\nu})g_{n\nu}(\zeta,\zeta'),
\end{aligned} \tag{16}$$

where J_0, J_1 are Bessel functions of 0th and 1st order, x_n are the roots of $J_0(x)$,

$$J_0(x_n^{(0)}) = J_0(x_n) = 0, \quad n = 1,2,3,..., \tag{17}$$

and

$$\begin{aligned}
a_\nu &= \frac{a}{a_\nu^\star}, \\
g_{n\nu}(\zeta,\zeta') &= g_n^< g_n^>, \\
g_{n\nu}^< &= \mathrm{Bi}\left[(f_\nu\sqrt{\alpha_\nu})^{1/3}\left(\zeta^< + \frac{k_\nu^2 + (x_n^2/a_\nu^2)}{f_\nu\sqrt{\alpha_\nu}}\right)\right] \\
&+ \mathrm{i}\ \mathrm{Ai}\left[(f_\nu\sqrt{\alpha_\nu})^{1/3}\left(\zeta^< + \frac{k_\nu^2 + (x_n^2/a_\nu^2)}{f_\nu\sqrt{\alpha_\nu}}\right)\right], \\
g_{n\nu}^> &= \mathrm{Ai}\left[(f_\nu\sqrt{\alpha_\nu})^{1/3}\left(\zeta^> + \frac{k_\nu^2 + (x_n^2/a_\nu^2)}{f_\nu\sqrt{\alpha_\nu}}\right)\right],
\end{aligned} \tag{18}$$

and Ai(z), Bi(z) are Airy functions (see, for example, [13]). The quantity a describes the limits of extension of the relative lateral motion and is treated at the moment as a free parameter. As we will see below, such a choice guarantees the continuity with normal optical properties by taking the limit $f \to 0$. With the above Green functions and the dipole densities (11), which in our scaled variables take the form

$$M_\nu(\mathbf{r}) = \frac{M_{0\nu}}{2\pi\rho_{0\nu}a_\nu^{\star 3}}\delta(\rho-\rho_{0\nu})\delta(\zeta), \tag{19}$$

where $\rho_{0\nu} = r_0/a_\nu^\star$, we calculate the coherent amplitudes Y_ν from the Lippmann-Schwinger equations (7) and then the polarization from equation (5). By the assumption (9) we obtain the effective chain dielectric function as

$$\epsilon(\omega) = \frac{c^2k_z^2}{\omega^2} = \epsilon_\infty + \sum_\nu \chi_\nu, \tag{20}$$

where

$$\chi_\nu = 2\frac{M_{0\nu}^2 2\mu_{\perp\nu}}{\epsilon_0\sqrt{\alpha_\nu}a_\nu^\star\hbar^2}\frac{\tilde{g}_\nu}{1-4\pi\tilde{g}_\nu}, \tag{21}$$

and

$$\tilde{g}_\nu = G_\nu(\rho_{0\nu},\rho_{0\nu};0,0). \tag{22}$$

Having the effective chain susceptibility we can compute the electro-optical functions. The results for the absorption coefficient are discussed below.

4 Results for PDA chains

The electroabsorption spectra of isolated 3BCMU and 4BCMU chains diluted in their monomer matrix have been investigated by Horvath *et al.* [3]. The advantage of using isolated chains instead of a fully polymerized sample is that the optical transitions are narrower for isolated chains. Consequently the excitons, the vibronic satellites, and the effect of field broadening can be observed more easily. We have computed the electro-optical functions for polydiacetylene chains named 3BCMU and 4BCMU (formula $\mathrm{R}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\mathrm{R}$, with the side group R

Table 1. Parameter values for 3BCMU and 4BCMU. Energies in eV, $E_{\mathrm{g}\nu}^{(a)}$ for the excitons $\nu = 0, a, b, c, d, S$ (data from Ref. [3]).

quantity	3BCMU	4BCMU
$\mu_\perp$	$0.1m_0$	$0.1m_0$
μ_z	$0.06m_0$	$0.06m_0$
$E_{\mathrm{g}\nu}^{(a)}$	2.482	2.378
$E_{\mathrm{g}D}$	2.646	2.541
$E_{\mathrm{g}T}$	2.743	2.630
$E_{S'}$	1.933	
E_S	1.992	1.909
E_D	2.079	1.989
E_T	2.161	2.075
ν_0	1.896	1.810
ν_a	1.833	1.790
ν_b	1.813	1.747
ν_c	1.775	
ν_d	1.756	
$R_\nu^\star$	0.22	0.22
$a_\nu^\star$	12Å	12Å
ϵ_∞	2.5	2.5
M_0(eÅ)	12.0	11.3

being $(\mathrm{CH}_2)_n - \mathrm{OCO} - \mathrm{NH} - \mathrm{CH}_2 - \mathrm{COO} - \mathrm{C}_4\mathrm{H}_9$ with $n = 3$ and $n = 4$, respectively). The parameters used for calculation are collected in Table 1.

We start with the determination of the potential/and dipole extension radii ρ_ν. To this end we determine the Green function (16) in the limit $f \to 0$. Using the same type of approximation as in [7], we have

$$G_\nu(\rho, \rho'; \zeta, \zeta') \mid_{F=0} \; = \frac{1}{2\pi} \sum_{n=1}^{\infty} \frac{2}{a_\nu^2 [J_1(x_n)]^2} J_0\left(\frac{x_n}{a_\nu}\sqrt{\rho^2 + \rho'^2}\right) g_{n\nu}(\zeta, \zeta'), \tag{23}$$

with

$$g_{n\nu}(\zeta, \zeta') = \frac{\exp(-k_{n\nu} \mid \zeta - \zeta' \mid)}{2k_{n\nu}}, \tag{24}$$

and

$$k_{n\nu}^2 = k_\nu^2 + \frac{x_n^2}{a_\nu^2} \cdot \tag{25}$$

The radii ρ_ν will be determined by positions of the poles in the susceptibility χ_ν, *i.e.* by the equation

$$\tilde{g}_\nu = \frac{1}{4\pi}, \tag{26}$$

where now

$$\tilde{g}_\nu(F = 0) = G_\nu(\rho_{0\nu}, \rho_{0\nu}; 0, 0) \mid_{F=0} \cdot \tag{27}$$

The expression (23) contains an unknown parameter a which can be seen as the maximum relative lateral distance between the electron and the hole. In the case of a semiconductor QWW a can be interpreted as the QWW radius, which is strongly related to the excitonic binding energy. As follows from reference [6], the excitonic binding energy of $2R^\star$ corresponds to a QWW radius of $1.5a^\star$. This value was used in the calculations. By this dimension of the QWW the term with $n = 1$ prevails in the sum (23). Therefore we calculate the radii ρ_ν from the equation

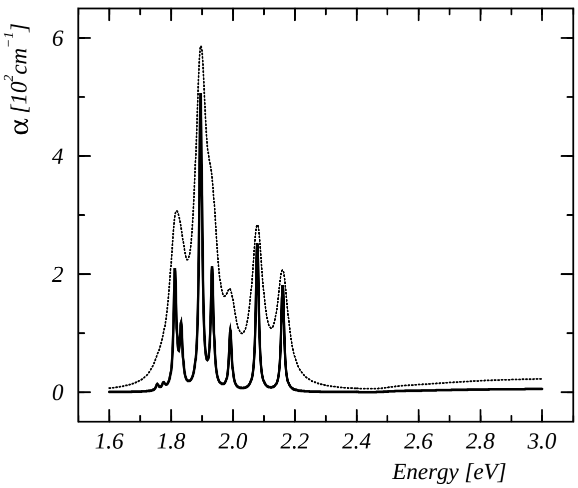


Fig. 1. The absorption coefficient for a 3BCMU PDA chain, calculated for two values of Γ_ν, $0.025R_\nu^\star$ (continuous line), and $0.1R_\nu^\star$ (dotted line). The peaks correspond to excitonic transitions.

$$\frac{1}{a_\nu^2 [J_1(x_1)]^2} J_0\left(\sqrt{2}\frac{x_1 \rho_{0\nu}}{a_\nu}\right) - \frac{1}{4} = 0. \tag{28}$$

In the above equation we took

$$E_{\mathrm{gb}\nu} + \frac{x_1^2}{a_\nu^2} = E_{\mathrm{g}\nu}, \tag{29}$$

where the $E_{\mathrm{gb}\nu}$ correspond to a non-confined situation, and the $E_{\mathrm{g}\nu}$ were treated as known numbers. Having the radii $\rho_{0\nu}$ we insert them into the formula (20) and calculated its real and imaginary part. In particular, the absorption coefficient will be given by

$$\alpha(\omega) = 2\frac{\omega}{c}\mathrm{Im}\,\sqrt{\epsilon}. \tag{30}$$

We have calculated the effective dielectric function for a 3BCMU PDA chain, using the above described method and taking the dipole moments $M_{0\nu}$ from a fit of the experimental absorption given in reference [3]. The results for the absorption, in the case $F = 0$ and for two values of the damping parameter, are shown in Figure 1. The absorption spectrum is dominated by a strong exciton ν_0, at 1.896 eV. (Such a strong excitonic resonance is common to all PDA's.) Below the gap two excitons of notable strength, ν_a (1.833 eV) and ν_b (1.813 eV), are observed. Furthermore, the low energy excitons ν_c (1.775 eV) and ν_d (1.756 eV) can be recognized. Above the excitonic transitions the vibronic fine structure with dominant peaks D

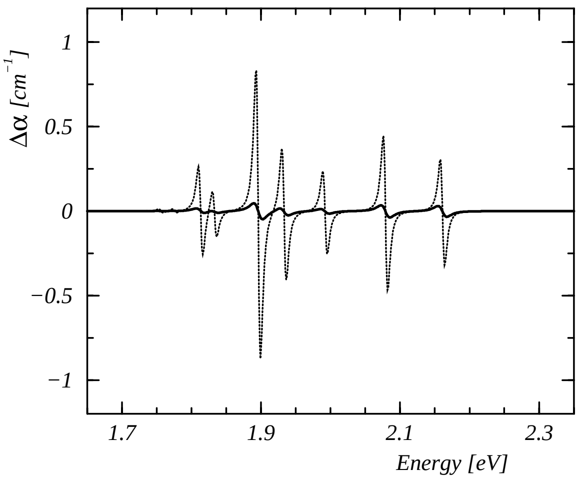


Fig. 2. Variation with field of the excitonic electro-absorption spectrum for a 3BCMU PDA chain, for two values of the relative field strength: $f = 0.01$ (continuous line) and $f = 0.03$ (dotted line). The damping parameter is $\Gamma_\nu = 0.025 R^\star_\nu$.

(2.079 eV) and T (2.161 eV) can be observed. We see that the damping parameter, Γ_ν, can be used to mimic temperature effects since for higher values of this quantity the weaker excitons are no longer resolved and disappear. This effect has also been observed by Horvath *et al.* [3] who measured the absorption spectrum of 4BCMU at several temperatures.

In Figure 2 we display the difference

$$\Delta\alpha = \alpha(F) - \alpha(F = 0), \tag{31}$$

for two values of the applied electric field. Since the field strength is small compared to the excitonic ionisation field, we obtain the red Stark shift for the positions of excitonic transitions and an enhancement of the absorption. All transitions show the same behaviour and the signal of each transition increases with the field.

The effects of excitons and of increasing field strength on the Franz-Keldysh oscillations are shown in Figure 3. We observe an increase of amplitudes and shift of zeros positions with the field. The arrows in the figure indicate the positions of the gaps of the dominant ν_0 exciton, $E_{\mathrm{g}\nu}$, and of the D and the T states, $E_{\mathrm{g}D}$ and $E_{\mathrm{g}T}$. For energies between $E_{\mathrm{g}\nu}$ and $E_{\mathrm{g}D}$ we have continuum states for the ν_0 exciton and discrete states for the D and the T exciton. For energies between $E_{\mathrm{g}D}$ and $E_{\mathrm{g}T}$ we are in the continuum of the ν_0 exciton and the D transition but we have still continuum states for the T transition. In this range we observe interfering Franz-Keldysh oscillations from the continuum of the ν_0 and the D exciton. A similar discussion holds also for energies above $E_{\mathrm{g}T}$.

For a greater field strength, but below the ionisation field, the red shift remains, but the real and the imaginary part of the dielectric function (*i.e.* the excitonic effects) are decreasing. This effect is displayed in Figure 4 near the fundamental excitonic peak (ν_0), and in Figure 5 for both real and imaginary part of the dielectric function.

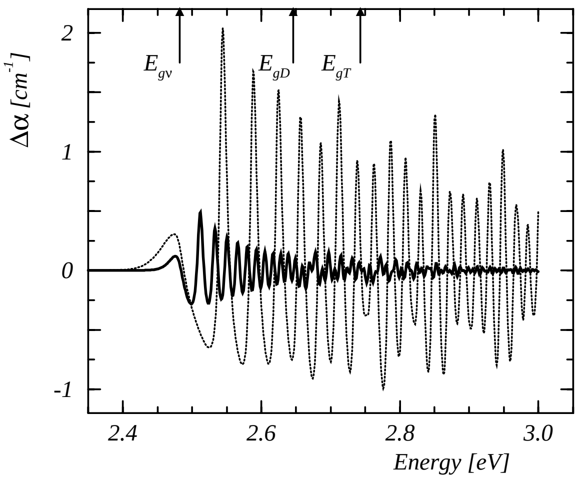


Fig. 3. The same as Figure 2, in the energetic region of Franz-Keldysh oscillations. The arrows indicate the positions of the gaps for the ν_0-exciton and the D, T states.

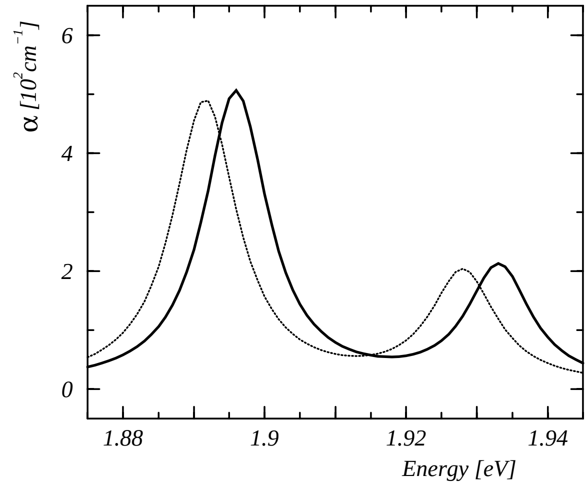
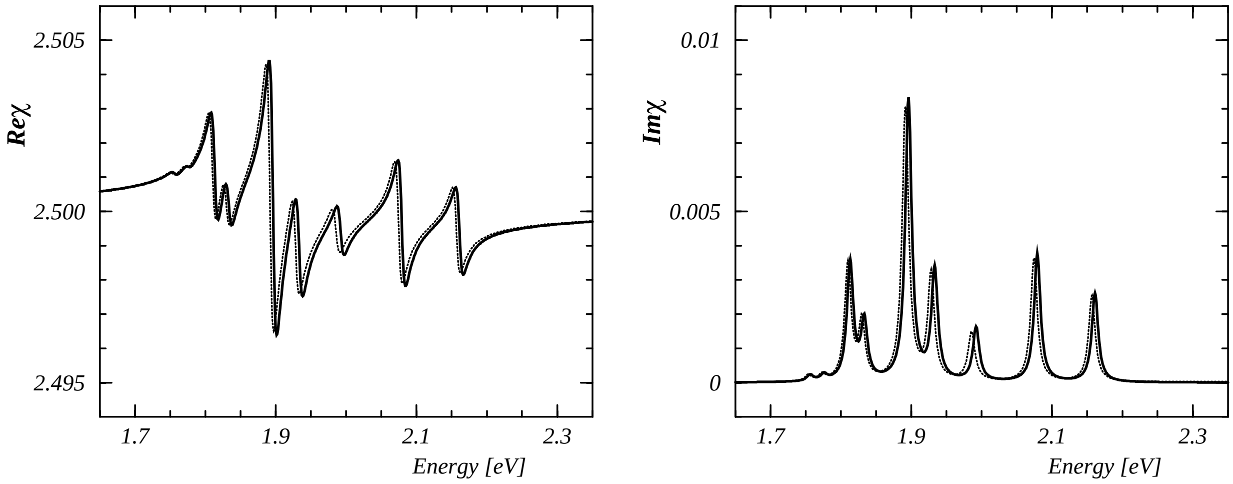


Fig. 4. The Stark red shift in the absorption for the 3BCMU ν_0 excitonic transition for $\Gamma_\nu = 0.025 R^\star_\nu$: $f = 0$ (continuous line) and $f = 0.5$ (dotted line).

Such an effect has been observed recently in semiconductor quantum dots [14]. The real part of the complex susceptibility (Fig. 5a) is related to the reflectivity of the material, whereas its imaginary part (Fig. 5b) is essentially the absorption spectrum. Due to the different gap energies of the excitons, $E_{\mathrm{g}\nu}$, $E_{\mathrm{g}D}$, $E_{\mathrm{g}T}$, the red shift of the resonances differs for a given field strength (see *e.g.* Fig. 5b)

5 Conclusions

We have developed a simple mathematical procedure for calculating the electro-optical functions for a matrix containing polymer chains, treated as quantum wires, when the electric field is applied along the chain axis. We derived an analytical expression for the effective



(a) (b)

Fig. 5. (a) Real and (b) imaginary part of the effective dielectric function of a 3BCMU PDA chain for two values of the applied field and $\Gamma_\nu = 0.025R^\star_\nu$: $f = 0$ (continuous line) and $f = 0.5$ (dotted line).

dielectric function from which the optical functions can be obtained. The method was applied for polydiacetylene 3BCMU chains and the results agree well with experimental data. This agreement obtained despite the crude approximations made confirms the existence of Wannier excitons in PDA chains and their influence on the optical functions. In the paper we used the intrinsic band parameters determined by Horvath *et al.* [3], but, for cases when their values (effective masses, oscillator strengths, intrinsic damping) are not known the method described can be used for determining the parameters from optical absorption data.

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