Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Luminescence 112 (2005) 316–320

JOURNAL OF LUMINESCENCE

www.elsevier.com/locate/jlumin

# Microscopic calculation of axial dispersion for quaterthiophene crystals

M. Laicini[a,*], P. Spearman[b], S. Tavazzi[a], L. Raimondo[a], L. Miozzo[a], M. Moret[a], A. Borghesi[a]

[a]*INFM and Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, Via Cozzi 53, I-20125 Milano, Italy*
[b]*School of Chemical and Pharmaceutical Sciences, Kingston University Kingston upon Thames, KT1 2EE, UK*

---

## Abstract

We present a microscopic calculation of the axial dispersion for the quaterthiophene crystal in a spectral region including the first and higher molecular excited states. After evaluating the complex dielectric tensor near the corresponding Frenkel excitons we observe that two of the principal axes referring to the upper Davydov states rotate with energy within the reflection plane of the monoclinic unit cell. In particular, we show the role of this dispersion in understanding the relationship between the transverse dielectric tensor and the measured optical spectra.

*PACS:* 71.35.Cc; 78.20.Ci; 78.40.Me

*Keywords:* Dielectric tensor; Axial dispersion; Optical spectra

---

## 1. Introduction

Oligothiophenes (nT) are representative of a large class of linear $\pi$-conjugated organic molecules whose solid-state properties have recently received a revival in interest due to their potential in technological applications [1,2]. There are many papers [3–9] devoted to their optical responses both experimentally and theoretically but a deep and complete knowledge of these systems requires further efforts. For example, these materials are very anisotropic, which strongly affects the optical measurements in that the absorbance and reflectance are subjected to the electrodynamic effect of the system that can be understood only by knowledge of the directions of the principal axes of the dielectric tensor.

Here we show a microscopic calculation of the axial dispersion [10], i.e. the rotation with energy of the principal axes of the dielectric tensor built up near Frenkel exciton resonances. We include higher molecular excitations that in the crystal are

---

[*] Corresponding author. Tel.: +39 026 448 5215; fax: +39 026 448 5400.
*E-mail address:* marco.laicini@mater.unimib.it (M. Laicini).

0022-2313/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2004.09.108

described by a complete Hamiltonian accounting for the coupling among them. We report the imaginary part of the dielectric tensor and the axial dispersion by showing the direct correlation with the absorbance spectra.

## 2. Theoretical background

We consider an extension of the Heitler–London Hamiltonian [11] to several molecular excited states:

$$H = \sum_{n\alpha r}(E_r + D_r)B^+_{n\alpha r}B_{n\alpha r} + \frac{1}{2}\sum_{nm}\sum_{\alpha\beta}\sum_{rs} T^{rs}_{n\alpha m\beta}B^+_{n\alpha r}B_{m\beta s}, \tag{1}$$

where $r(s) = 1, \ldots, l$ refers to the $r(s)$th molecular excited state, $\alpha(\beta)$ to the molecule in the unit cell and the index $n(m)$ labels the unit cell of the crystal; $E_r$ is the $r$th electronic excitation energy, $D_r$ is its gas-to-crystal shift energy, $B^+_{n\alpha r}$ is the operator that creates an electronic excitation over molecule $n\alpha$ from the electronic ground state to the $r$th excited electronic state while $B_{n\alpha r}$ is the operator responsible for the de-excitation. Finally, $T^{rs}_{n\alpha m\beta}$ is the resonance-interaction matrix.

In order to diagonalize Hamiltonian (1) we start by defining the following unitary transformations:

$$B^+_{\alpha r}(k) = \frac{1}{\sqrt{N}}\sum_n \mathrm{e}^{-\mathrm{i}kn}B^+_{n\alpha r}, \tag{2}$$

$$a^+_{\mu_r}(k) = \sum_\alpha u^*_{\alpha\mu_r}(k)B^+_{\alpha r}(k). \tag{3}$$

The first one takes into account the delocalization of the exciton while the latter leads to the Davydov states labelled with $\mu_r$. For each wave vector $k$ the Hamiltonian reads:

$$H(k) = \sum_{r\mu_r} E_{\mu_r}(k)a^+_{\mu_r}(k)a_{\mu_r}(k) + \sum_{rs\mu_r\mu_s} G^{rs}_{\mu_r\mu_s}(k)a^+_{\mu_r}(k)a_{\mu_s}(k), \tag{4}$$

where

$$E^{rr}_{\mu_r}(k) = E_r + D_r + \sum_{\alpha\beta} u^+_{\mu_r\alpha}(k)M^{rr}_{\alpha\beta}(k)u_{\beta\mu_r}(k), \tag{5}$$

$$G^{rs}_{\mu_r\mu_s}(k) = \sum_{\alpha\beta} u^+_{\mu_r\alpha}(k)M^{rs}_{\alpha\beta}(k)u_{\beta\mu_r}(k) \tag{6}$$

with

$$M^{rr}_{\alpha\beta}(k) = \sum_n T^{rr}_{n\alpha 0\beta}\mathrm{e}^{\mathrm{i}kn}, \tag{7}$$

$$M^{rs}_{\alpha\beta}(k) = \sum_n T^{rs}_{n\alpha 0\beta}\mathrm{e}^{\mathrm{i}kn}. \tag{8}$$

At $k = 0$ and for a crystal with four inequivalent molecules the unitary matrix $u_{\alpha\mu_r}(k)$ results

$$u_{\alpha\mu} = \frac{1}{2}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}. \tag{9}$$

Thus, Hamiltonian (4) is block diagonalized and each block leads to sub-set of exciton states classified according to symmetry, i.e. the irreducible representations of the factor group ($\mu = \{a_g a_u b_g b_u\}$). The block structure of the matrix in Eq. (4) is due to a zero value of elements $G^{rs}_{\mu_r\mu_s}$ as they refer to a different Davydov state. Finally, each block of $\mu$ symmetry can be diagonalized independently by numerical methods and the resulting eigenfrequencies $\Omega_{\mu t}$ are the new resonances of the Frenkel excitons while their transition dipoles can be computed from the corresponding eigenvectors $w^\mu_{sr}$ by using the following relations:

$$\tilde{a}^+_{\mu t} = \sum_r w^\mu_{tr}a^+_{\mu_r}, \tag{10}$$

$$\boldsymbol{d}_{\mu t} = \langle 0|\mathrm{e}\boldsymbol{x}|\tilde{a}^+_{\mu t}0\rangle, \tag{11}$$

where $|0\rangle$ is the ground state, e the electron charge and $\boldsymbol{x}$ the displacement of the promoted electron.

The transfer exciton matrix in Eqs. (7) and (8) are calculated via Ewald methods[12]. As the first molecular excited state is the most intense, containing the majority of the oscillator strength, we prefer to calculate the matrix $M^{11}_{\alpha\beta}(k)$ by describing the HOMO–LUMO electronic transition as a distribution of discrete charges on the atomic sites accounting for the delocalization of the transition dipole moment [9,13]. The higher less intense molecular transitions are described in point dipole approximation. Moreover, in order to