Model calculation of the optical properties of 3,4,9,10 perylene tetracarboxylic dianhydride (PTCDA) thin films

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Abstract. – The marked difference between the optical absorption of dissolved PTCDA monomers and crystalline films is analysed in terms of the deformation of an effective internal vibrational mode of the molecule and transfer of Frenkel excitons between different molecular sites in the crystal. It is shown in detail that the coupling between equivalent molecules in different crystal unit cells, especially among stack neighbours, dominates over exciton transfer between the two different molecules in the crystal basis. The first type of interaction leads to a pronounced deformation of the expected Poisson progression over subsequent vibrational levels while the latter is responsible for a small Davydov splitting and consequently different absorption lineshapes along different crystal axes.

Organic materials with semiconducting properties have become interesting candidates for various technological applications, ranging from field effect transistors over light emitting diodes to solar cells. For molecular solids, the material properties derive from an interplay between strong covalent bonds within each molecule and much weaker electric multipole and van-der-Waals interactions between different molecular sites.

One of the archetypal materials of this class, 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), crystallizes in the monoclinic centro-symmetric space group $P2_1/c$ (C^5_{2h}) with two nearly coplanar molecules in the unit cell [1], cp. Fig. 1. Molecules of consecutive planes arrange in tilted stacks, with a smaller interplanar distance than in non-polar materials like graphite or perylene due to the electrostatic interactions of the partly charged carboxyle and anhydride groups. While the short distance between consecutive molecules along the stacks leads to a large overlap of their π-orbitals and favours charge transport, the electronic interaction between the two different molecules in the unit cell is expected to be much smaller, resulting in a large anisotropy of the mobility [2,3].

Concerning the optical properties, the presence of neighbouring molecules in the crystal introduces new degrees of freedom with respect to isolated molecules or dissolved monomers: Transfer of Frenkel excitons, and completely different types of optical excitations like charge transfer (CT) excitons. The first model proposed for the optical properties of crystalline PTCDA films applied the concept of three-dimensional Wannier-Mott excitons to optical absorption [4] and electro-absorption [5] in organic quantum-well structures. Subsequent analyses were based on non-interacting monomer transitions (Frenkel excitons) and CT excitons [6],

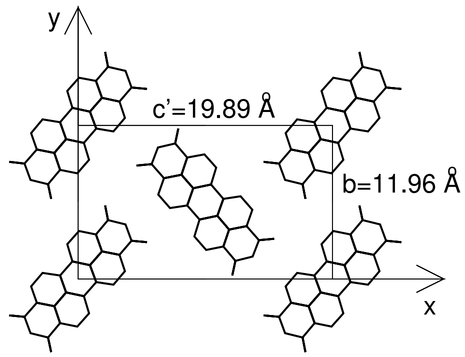

Fig. 1 – Crystal unit cell of α-PTCDA, in the plane most closely coinciding with the molecular planes, where $\mathbf{c}'$ corresponds to the $(\mathbf{c} - 2\ \mathbf{a})$ direction of the published crystal basis vectors [1]. The HOMO-LUMO transition dipoles are oriented along the long axes of the molecules forming an angle of $\varphi = 50.4^0$ with $\mathbf{c}'$.

which lead to the concept of mixed Frenkel-CT states, each with its vibronic replicas, as proposed in a dimer model [7, 8]. Finally, this approach was adjusted to the one-dimensional stack geometry, including Frenkel excitons with several vibronic levels and CT excitons [9].

While all of these investigations accounted for a possible CT exciton, none included the full crystal geometry with two molecules in the unit cell. Here we present such a microscopic model in the framework of Frenkel excitons coupled to intramolecular vibrations, neglecting any CT contribution. This approximation can be motivated by two independent estimates of the ratio between the transition dipoles of CT and Frenkel excitons of 0.14 [9] and 0.15 [10], resulting in a relative oscillator strength of about 2 - 3 %. In recent quantum chemical calculations of dimers, we obtained similar estimates for the relative oscillator strengths [11].

Our model parameters are derived from microscopic estimates of the dipole-dipole interaction between the molecular HOMO-LUMO transition dipoles, density functional calculations for an isolated molecule [12], spectra in solution [13], and a comparison with the linear absorption and the refractive index of poly-crystalline PTCDA films grown on quartz glass [14]. Measurements of the absorption of PTCDA dissolved in dimethyl sulfoxide (DMSO) at low concentrations show that the monomer absorption spectrum consists of four clearly resolved peaks with an energy difference of about 0.17 eV [6, 13]. In calculations of the monomer absorption based on the elongation of the A_g breathing modes in the relaxed excited state, it became clear that this apparent vibronic spacing is not due to a single internal mode, but rather an average over the most strongly elongated modes which also dominate the resonant Raman spectra [12, 15].

As in previous exciton models applied to crystalline PTCDA, we assume that the vibronic structure in the monomer absorption can be modelled by a single *effective* internal mode with an energy of $\hbar\omega = 0.17$ eV, and an exciton-vibrational coupling constant g. With these simplifications, the relative intensities of the vibronic subbands of the monomer are simply given by the squared Franck-Condon factors between the lowest vibratonic state in the electronic ground state, $|0_g\rangle$, and the νth vibronic state in the potential energy surface of the optically excited state, $|\nu_e\rangle$:

$$S_\nu^2 = \langle 0_g|\nu_e\rangle^2 = e^{-g^2}\frac{g^{2\nu}}{\nu!}, \tag{1}$$

giving the expected Poisson progression of argument g^2. Previous estimates for g^2 range from 0.67 for PTCDA dissolved in DMSO [8] to a calculated value of 1.18 for the isolated molecule [12,16]. Compared to the polar solvent DMSO, we expect a weaker dielectric influence of the surrounding PTCDA crystal, so that we assume $g^2 = 1.0$ in the following. In the solid, we have to allow for exciton transfer between different molecular sites. With Pauli operators $b^+_{i\alpha\nu}$ and $b_{i\alpha\nu}$ for creation and annihilation of a Frenkel exciton on level ν at molecule α in the unit cell at site $\mathbf{R}_i$, a model Hamiltonian in Heitler-London approximation can be expressed as [17, 18]:

$$H = \sum_{i\alpha\nu} E_{0\nu} b^+_{i\alpha\nu} b_{i\alpha\nu} + \sum_{i\alpha\nu} \sum_{j\beta\mu} t_{i\alpha\nu;j\beta\mu} b^+_{i\alpha\nu} b_{j\beta\mu} \ , \tag{2}$$

where $E_{0\nu} = E_{00} + D + \nu\hbar\omega$ is the exciton on-site energy in the νth vibronic level, composed of the transition energy E_{00} between the lowest vibronic levels, an environment-dependent shift D, and a vibronic part. For an optically excited molecule, this Hamiltonian is based on the eigenstates of the elongated internal mode, just as for an isolated molecule, while all non-excited molecules remain in the lowest vibronic level due to $\hbar\omega \gg k_B T$. The transfer matrix element $t_{i\alpha\nu;j\beta\mu}$ has to return the molecule β in unit cell j into the lowest vibronic level of the electronic ground state, while the molecule α in unit cell i is promoted into an excitonic transition towards the vibronic sublevel ν of the excited state potential. Therefore, this transfer matrix element can be decomposed into an electronic and a vibronic part,

$$t_{i\alpha\nu;j\beta\mu} = T_{i\alpha;j\beta} S_\nu S_\mu . \tag{3}$$

This treatment differs somewhat from the Holstein model, where the transfer is usually not formulated in terms of vibronic eigenstates. However, for a Holstein model including a pointlike coupling to a dispersionless phonon branch as in our approach [19], it is easily shown that such eigenstates for localized modes diagonalize the vibrational part of the Hamiltonian. Therefore, this complete set of basis states appears also as the natural choice for the formulation of the transfer part [9, 17, 18]. More complicated couplings between electronic and vibronic excitations, e.g. nonlocal terms [20], are beyond the scope of the present model.

The Hamiltonian (2) can be block-diagonalized by a Fourier transform to k-space:

$$H(\mathbf{k}) = \begin{pmatrix} H_{AA}(\mathbf{k}) & H_{BA}(\mathbf{k}) \\ H_{AB}(\mathbf{k}) & H_{BB}(\mathbf{k}) \end{pmatrix} \tag{4}$$

where the block $H_{AA}(\mathbf{k})$ stands for the interaction of basis molecule A with all A molecules in the other unit cells, and similarly for the other entries. The different blocks have the following structure concerning the vibronic levels μ, ν:

$$\begin{aligned} H_{AA;\mu\nu}(\mathbf{k}) &= H_{BB;\mu\nu}(\mathbf{k}) = E_{0\nu}\delta_{\mu\nu} + S_\mu S_\nu \sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j} T_{0A;jA} \\ H_{AB;\mu\nu}(\mathbf{k}) &= H_{BA;\mu\nu}(\mathbf{k}) = S_\mu S_\nu \sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j} T_{0A;jB} \end{aligned} \tag{5}$$

For the optical properties discussed below, only the immediate surroundings of the Γ-point of the Brillouin zone, $k = 0$, are required. In the following we assume that the crystallites in an epitaxial film have a *finite* size, and that, on average, the surrounding material contributes only a finite dielectric constant without any well-determined geometric arrangement of the constituent molecules. In this case, the sums in eq. (5) extend only over a finite volume, so that the non-analyticity problems around Γ discussed earlier [17] disappear, and the calculation is reduced to the evaluation of the finite sums $X = \sum_{j\neq 0} T_{0A;jA}$ and $V = \sum_j T_{0A;jB}$. For an estimate of X and V, we have calculated the interaction of the atomic distribution of overlap charges contributing to the HOMO-LUMO transition dipole, accounting for the anisotropic screening of the electrostatic interaction [21] with the bulk dielectric tensor of α-PTCDA [22]. As discussed earlier for cubic systems, the dielectric screening develops on a spatial scale corresponding roughly to the bond length [23], so that for the anisotropic system studied here, we expect that the Coulomb interaction between the transition dipoles of two molecules is always fully screened, except for the stack neighbours. Therefore, we found it convenient to divide the interaction X between the same basis molecules into the parts W arising from the stack neighbours, and the remaining part M of the sum, $X = 2W + M$, where $M = \sum'_{j\neq 0} T_{0A;jA}$ excludes the stack neighbours. The key quantity for the computation of X and V is the size of the transition dipole d. Previous gas phase estimates for the $S_0 - S_1$ transition in PTCDA were in the range $d = 7.4 \pm 0.7$ Debye [9], and from the analysis of the experimental data of Ref. [14], we find a value of $d = 7.3$ Debye, see below. Together with published values for the static dielectric tensor, $\epsilon^0_{||} = \epsilon^0_{xx} = \epsilon^0_{yy} = 4.07$ and $\epsilon^0_{\perp} = \epsilon^0_{zz} = 1.85$ [22], which we assume to be diagonal, this allows an evaluation of the different interactions.

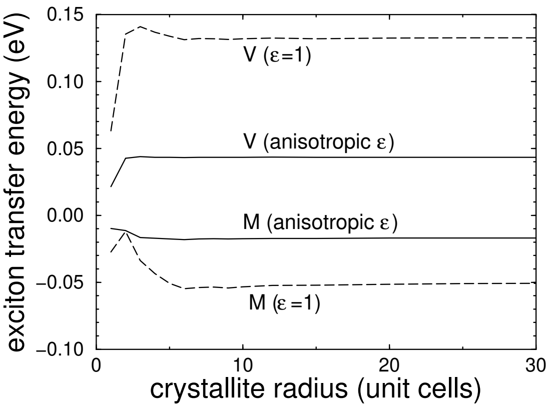

Fig. 2 – Exciton transfer energies M and V, calculated over a sphere in terms of crystal unit cells, for two different model dielectric tensors.

Assuming for simplicity crystallites corresponding to spheres in terms of crystal unit cells, i.e. ellipsoids in real space, we find the size dependence displayed in Fig. 2. As expected, M and V are mainly determined in the immediate surroundings of the reference molecule. At larger distances, the individual contributions scaling with R^{-3} nearly cancel due to the sum over different spatial directions. For the stack neighbours, the assumed screening model is most crucial: Without screening ($\epsilon = 1$), we find $W = 0.121$ eV, while for the bulk value of the anisotropic dielectric tensor, the resulting interaction $W = 0.027$ eV is much lower. A more precise estimate would require a generalization of the Thomas-Fermi screening model [23] to an anisotropic dielectric surrounding, which is beyond the scope of the present work.

Our calculation of the frequency-dependent elements of the dielectric tensor is based on a diagonalization of the Hamiltonian (4) with a consistent parameter set. Due to the symmetry of the Hamiltonian (4) with respect to an exchange of the two basis molecules, all the transition dipoles of the resulting eigenstates $E^{\gamma}_{0\nu}$ have orientations corresponding to $\mathbf{d}^{\gamma}_{0\nu} \propto (\mathbf{d}_A \pm \mathbf{d}_B)$, i.e. they coincide with the cartesian directions $\gamma = x$ and $\gamma = y$ defined by the rectangular unit cell in Fig. 1. The corresponding oscillator strengths can be calculated in the usual way:

$$F_{0\nu}^{\gamma} = \frac{2mE_{0\nu}^{\gamma}}{e^2\hbar^2} \, |\mathbf{d}_{0\nu}^{\gamma}|^2 \tag{6}$$

The imaginary part of the dielectric tensor elements is then obtained from a broadening of the resulting vibronic levels $E_{0\nu}^{\gamma}$ with normalized Gaussians, and the real part by a Kramers-Kronig transform of the imaginary part as given in explicit form in [24]. In order to obtain a smooth interpolation between the static dielectric tensor elements and the high-energy part of the experimental data, we have to include the dispersive tail of higher-lying transitions [15]. For simplicity, we model them as a single transition carrying the whole background coupling strength q_b:

$$\epsilon_b(\omega) = 1 + q_b \frac{\Omega_b^2}{\Omega_b^2 - \omega^2}. \tag{7}$$

The experimental results have been obtained on poly-crystalline films with random azimuthal orientation of the unit cells displayed in Fig. 1 [14]. Therefore, we have calculated the complex square root $n_{||}(\omega) = [\epsilon_{||}(\omega)]^{1/2}$ of the average of the dielectric tensor elements, $\epsilon_{||}(\omega) = \frac{1}{2}[\epsilon_{xx}(\omega)+\epsilon_{yy}(\omega)]$. As the measured data are not fully Kramers-Kronig consistent [14], we have adjusted all of our parameters to the extinction coefficient $\Im[n]$. Keeping the argument of the Poisson distribution fixed at $g^2 = 1.0$, we have optimized the exciton transfer parameters and line broadenings by a mean least squares fit, excluding the tail beyond 3.2 eV and the observed transition pair at about 3.3 eV and 3.5 eV, cp. Table I and Fig. 3.

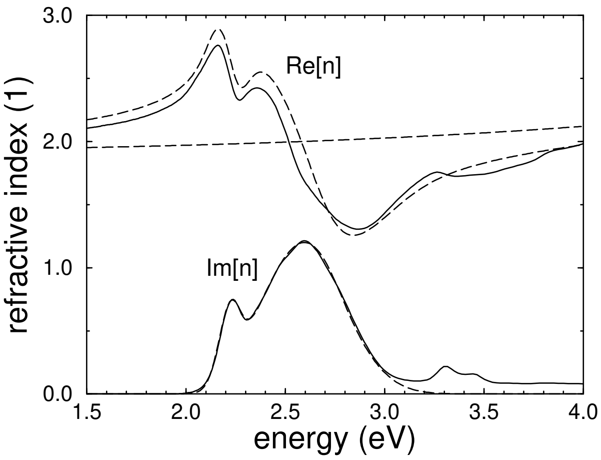

Fig. 3 – Real and imaginary part of the refractive index of PTCDA films. Solid: experimental data [14], dashed: present model calculation for $n_{||}(\omega) = [\epsilon_{||}(\omega)]^{1/2}$ and background for the real part of the refractive index, cp. eq. (7). The model parameters are given in the caption of Table I.

Comparing our best fit parameter $V = 0.056$ eV with Fig. 2, we find that the calculated asymptotic value of $V = 0.043$ eV is lower. However, using this somewhat smaller Davydov splitting parameter for the computation of the dielectric properties, the resulting curves are similar to Fig. 3, except for a slightly smaller value of the extinction coefficient above 2.7 eV. From a comparison of the fitted value $X = 2W + M = 0.137$ eV and the asymptotic value $M = -0.017$ eV for large crystallites, we deduce a transfer to the stack neighbours of about $W = 0.077$ eV, between the calculated values with and without dielectric screening. The sharp

TABLE I – *Transition energies of the Davydov doublets $E^x_{0\nu}$ and $E^y_{0\nu}$, their respective oscillator strengths $F^x_{0\nu}$ and $F^y_{0\nu}$ per molecule, the polarization ratio $F^y_{0\nu}/F^x_{0\nu}$, and the full width at half maximum (FWHM). Model parameters: $d = 7.3$ Debye, $g^2 = 1.0$, $\nu_{max} = 4$, $X = 0.137$ eV, $V = 0.056$ eV, $E_{00} + D = 2.180$ eV, $q_b = 2.72$, $\hbar\Omega_b = 8.5$ eV, and $\epsilon^0_{||} = \frac{1}{2}[\epsilon^0_{xx} + \epsilon^0_{yy}] = 4.07$. For simplicity, the static limits ϵ^0_{xx} and ϵ^0_{yy} are modelled with the same strength q_b of the higher-lying transition.*

ν		0	1	2	3	4
$E^x_{0\nu}$	[eV]	2.204	2.381	2.539	2.696	2.862
$F^x_{0\nu}$		0.122	0.216	0.177	0.067	0.016
$E^y_{0\nu}$	[eV]	2.222	2.415	2.577	2.713	2.865
$F^y_{0\nu}$		0.091	0.211	0.350	0.214	0.045
$F^y_{0\nu}/F^x_{0\nu}$		0.74	0.98	1.98	3.20	2.85
$FWHM_\nu$	[eV]	0.120	0.283	0.293	0.40	0.40

increase of the broadening σ_ν between $\nu = 0$ and $\nu = 1$ is included phenomenologically in the present model calculation based on a single *effective* internal mode. However, in a vibronic model including several internal modes, such an increased broadening arises naturally from the interaction between different nearly degenerate basis states.

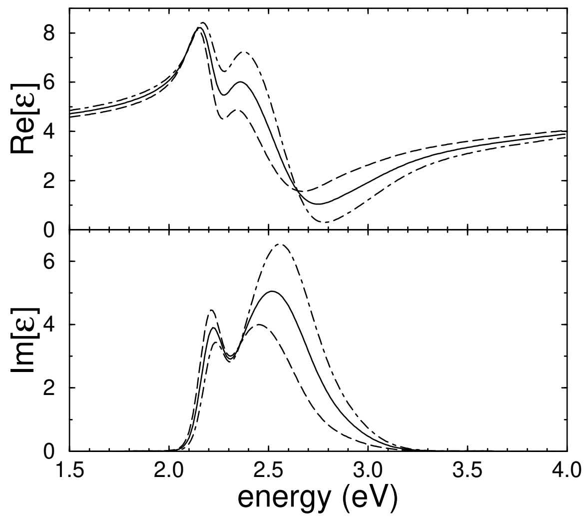

Fig. 4 – Diagonal components of the frequency-dependent dielectric tensor, assuming the same background for both directions. Dashed: $\epsilon_{xx}(\omega)$, dash-dotted: $\epsilon_{yy}(\omega)$, solid: average, cp. Fig. 3.

While the above comparison with the experimental data was based on the average over the two different diagonal elements of the frequency-dependent dielectric tensor, these elements themselves involve oscillator strengths depending in a non-trivial way on the vibronic level, cp. Table I. In Fig. 4, we show explicitly the two components ϵ_{xx} and ϵ_{yy}, resulting in qualitative agreement with recent ellipsometry data [25].

The present model based on the deformation of an effective internal vibration and the transfer of Frenkel excitons is easily generalized to wavevectors throughout the first Brillouin zone. The resulting dispersion relations of the excitonic transitions $E^\gamma_{0\nu}$ produce minima at the surface of the Brillouin zone which can be related to the red-shifted photoluminescence [11]. Concerning electro-absorption spectra, the present approach would require extensions towards the inclusion of CT states and a field-dependence of the molecular polarizabilities.

In conclusion, we have interpreted the refractive index and extinction coefficient of polycrystalline epitaxial films of PTCDA with a model calculation based on the transfer of Frenkel excitons. The good agreement with the experimental data suggests that no strong CT contribution is involved in the region of the lowest optical transitions. The predicted anisotropy for the frequency-dependent dielectric tensor may serve as a guideline for the future interpretation of the anisotropic optical properties of larger PTCDA crystals [25].

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