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Primary optical excitations and excited-state interaction energies in sexithiophene

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Based on a unique combination of angle-resolved transmission spectroscopy and transmission data at high pressure, we identify the primary photoexcitations and the relevant excited-state interaction energies in a sexithiophene crystal. Optical excitations include charge-transfer excitons and Davydov polaritons. By extrapolation, we predict that in sexithiophene at hydrostatic pressures above 180 kbar, intermolecular excitations are lower in energy than intramolecular ones. The results are representative for a wide class of π-conjugated molecular semiconductors because (1) the pertinent interaction energies and lengths scales are nearly identical and (2) published data on different molecules are consistent with our interpretation.

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Linear π-conjugated molecules, such as oligothiophenes, oligophenylenes, and oligophenylene-vinylenes, are attracting increasing attention for their use in electronic and optoelectronic devices.[1] Despite the high technological interest, the knowledge of their fundamental electronic and optical properties remains inadequate for various aspects. Our interest is to address to the nature and interacting energies of the primary photoexcitations, for which long-lasting and unresolved controversies exist.[2–6]

In the crystal, the lowest molecular excitation gives rise to as many intramolecular exciton bands as the number of nonequivalent molecules in the unit cell. The energy difference between the lowest and highest exciton transitions, the so-called Davydov splitting (E_{DS}), represents a fundamental energy scale, which provides an estimate of the intermolecular interaction strength in the excited state. Experimental optical spectra feature, however, complex patterns, which have precluded an unequivocal evaluation of E_{DS}.

In crystals, excitons with small wave vector $\mathbf{k}$ couple to photons with the same quasimomentum to yield a new particle called polariton.[7] The latter describes the photon-exciton dynamics when the interaction energy (E_{EPI}) with photons exceeds any line broadening (strong-coupling regime). The polariton concept is the extension of the weak-coupling limit case, in which photons and delocalized excitations of matter are treated as independent particles. In linear π-conjugated molecules, the lowest π-π^* transition exhibits a very large oscillator strength ($\gg 1$). Therefore, we expect that polaritons, rather than bare excitons, are the primary photoexcitations in the crystal. The ensuing optical response can differ substantially from the one predicted in the weak-coupling regime.

Besides intramolecular Frenkel excitons, crystals also support excitations for which the bound electron and hole reside on different molecules [charge-transfer excitons (CTE)]. The energy difference E_B between these two kinds of excitations provides an estimate of the intermolecular interaction energy between electrons and holes. Positive (negative) E_B implies that stable exitations have an intramolecular (intermolecular) character. The identification of CTE's is, however, not simple, as their oscillator strength is very weak. Even though electro-optical modulation techniques have been also used to probe CTE's, a conclusive estimate of E_B has not be given yet.[8,9]

E_{DS}, E_B and E_{EPI} depend on basic quantities such as intermolecular coupling, screening, and oscillator strength. A comparative analysis suggests that these quantities are similar in oligothiophenes, oligophenylenes, and oligophenylene-vinylenes. In this paper, we focus on the optical properties of sexithiophene single crystals. The picture we draw from the present experimental results provides the basis for understanding the photophysics of this new, emerging class of molecular materials.

We report on angle-resolved transmission spectra and transmission data at high hydrostatic pressure. The former experiments allow us to distinguish the mixed exciton-photon nature of the excited states; the latter data permit to discriminate between the intramolecular and the intermolecular excitations. We demonstrate that the combined use of these two techniques represent an all optical approach to determine both E_{DS} and E_B. Finally, experiments indicate that E_B can become negative for pressure above 180 kbar.

Excitons and polaritons in uniaxial molecular crystals. In a molecular crystal, the exciton energy can be expressed as a lattice sum over the *instantaneous* Coulomb interactions between the excited and the unexcited molecules located at different crystal sites. This sum can be split into two parts, which describe the short- and the long-range contributions. The latter gives rise to the angular dependence of the exciton energy. In contrast to the short-range forces, the long-range contribution is fairly well approximated by dipole-dipole interaction, and can be evaluated analytically in the framework of the continuum optical model.[10,11] For any angle β between $\mathbf{k}$ and the transition dipole $e\mathbf{d}$, the exciton frequency reads

$$\Omega^2 = \omega_T^2 + \omega_P^2 2 d^2 m_e \omega_T \cos^2(\beta)/(\hbar \varepsilon_\infty), \tag{1}$$

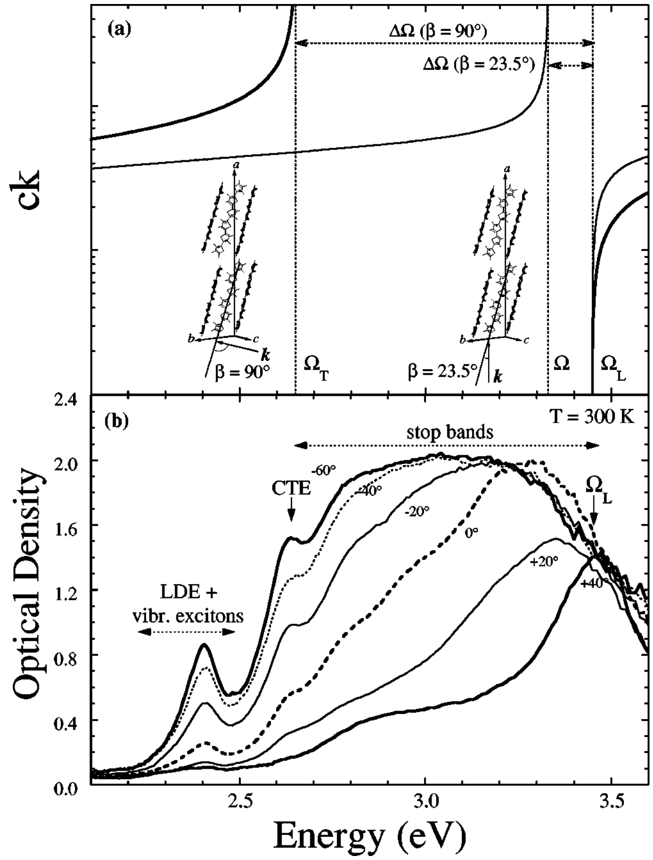

FIG. 1. (a) Polaritons dispersion [from $(ck/\Omega_L)^2=\varepsilon_\infty(\Omega_L^2-\omega^2)/(\Omega_T^2-\Omega^2)$[10]] for different angle β (23.5°, 90°) between the molecular axis and the propagation vector **k**. The crystal system of $T6$ is monoclinic and belongs to the space group $P21/n$ with four nonequivalent molecules arranged in a herringbone fashion in the unit cell (inset 1). Sexithiophene molecules are inclined by 23.5° with respect of the a axis of the unit cell. (b) c polarized absorption spectra of $T6$ single crystal as a function of the incident θ angle between the light beam and the normal to the sample surface (b-c plane). The investigated sample (thickness $\leqslant 1$ μm) was placed between two quartz plates. LDE stands for lower Davydov exciton and CTE for charge-transfer excitons.

where $\omega_p^2=4\pi me^2/m_e\nu_c$ is the plasma frequency, ν_c being the volume of the unit cell, and m the number of nonequivalent molecules; ω_T is the short-range contribution to the exciton frequency, which coincides with the energy of transverse excitons ($\beta=90°$). The second term in Eq. (1) corresponds to the long-range contribution; it vanishes for transverse excitons ($\mathbf{k}\perp\mathbf{d},\Omega=\omega_T$) and is maximum for longitudinal excitations (Ω_L), ($\mathbf{k}\|\mathbf{d},\Omega=\Omega_L$).

Equation (1) neglects propagation effects that are accounted for in the polariton picture. When the exciton-photon coupling is switched on, the two branches of the new quasiparticles show an anticrossing behavior with a gap $\Delta\Omega=\Omega_L-\Omega$, called *stop band,* with $\hbar\Delta\Omega$ being a measure of E_{EPI}.[7] Figure 1(a) shows the polariton dispersion for two angles between the molecular axis and the propagation vector of the light. $\Delta\Omega$ decreases for $\beta\rightarrow 0$, since the electric field of the light becomes perpendicular to the transition dipole moment. At sufficiently large **k**, retardation effects are negligible and the instantaneous results, provided by Eq. (1), are recovered [see Fig. 1(a)]. Incoming light with frequency within $\Delta\Omega$ cannot propagate inside the crystal and light is entirely reflected. Reflectivity smaller than unity is indeed observed, as damping processes permit a fraction of light to travel through the sample.[10] In simple transmission experiments, this leads to a weak transmission (high apparent absorbance) for light frequencies within $\Delta\Omega$. Finally, it is worth stressing that the stop band is a specific retardation phenomenon. Conversely, the blueshift of the optical resonance as a function of β is due to the instantaneous long-range dipolar coupling.

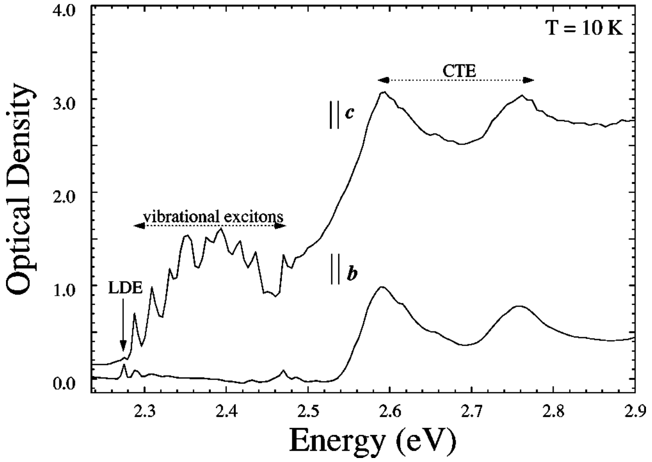

FIG. 2. Absorbance spectra of the sexithiophene single crystal polarized along the c and b axis. LDE stands for lower Davydov exciton and CTE for charge-transfer excitons. The sample thickness is 2.8 μm.

Sexithiophene: Lower Davydov component and vibrational excitons. The lower and upper Davydov components of sexithiophene can be selectively excited by light polarized along the b and c axes of the crystal [see inset, Fig. 1(a)], respectively. According to symmetry properties, the oscillator strength of the lowest molecular transition is mostly transferred to the upper Davydov component.[12] The lower component has a very weak oscillator strength and can be detected only at low temperatures. Figure 2 shows the absorbance spectrum at $T=10$ K; the transition energy to the lower Davydov exciton $\hbar\Omega_{LDE}$ is peaked at 2.276 ± 0.001 eV. Vibronic replica, which are polarized both along c and b, appear as narrow lines at energy lower than 2.6 eV. At room temperature [Fig. 1(b)], spectra notably simplify as all the fine structures broaden; for c polarization, the vibrational excitons collapse into a single peak centered at 2.4 eV.

Sexithiophene: Davydov polaritons and determination of E_{DS}. Figure 1(b) shows the absorbance between 2 and 3.5 eV as a function of the angle θ between the direction of the incoming beam and the normal to the sample surface. The incoming light has wave vector and electric field in the a-c plane in order to excite only the upper Davydov exciton. In these experiments, a very thin sample (thickness $\leqslant 1$ μm) has been used to prevent saturation effects. The main experimental findings are as follows.

(a) The absorbance spectra do *not* show an excitonlike peak, eventually followed by a vibronic progression, but an intense and very broad band; similar results have been reported for thin polycrystalline films or aggregates in solution of several linear π-conjugated molecules.[5,6]

For decreasing θ:

(b) The lower energy onset of this structure redshifts.

(c) The apparent bandwidth increases considerably. This result compares favorably with the angle-dependent bandwidth observed in parahexaphenyl films.[5]

(d) The broad feature at 2.6 eV and its replica do not shift. The nature of these features, more evident in the 10-K spectra (Fig. 2), is frequently debated, and has been attributed to the transition towards the upper Davydov levels.[4] This explanation is ruled out, as the upper level should be the dominant feature in the a-c polarized spectra.

In order to show that the large width of the band observed in the c-polarized spectra is consistent with the polariton model, we need to evaluate the dipole length d. It can be estimated in two ways: from the absorption spectrum and from the radiative lifetime τ_r of noninteracting sexithiophene molecules in solution. Various groups attempt to measure d following the first approach. Published data shows, however, large discrepancies. Conversely, the measured radiative lifetimes show a negligible scattering. We therefore estimate d from the fundamental law, which relates τ_r and d for an atom or molecule in a medium with refraction index n:[13]

$$d^2=(3/4\hbar c^3)/(ne^2\langle\omega^3\rangle\tau_r), \qquad (2)$$

where $\langle\omega^3\rangle$ is the spectral average of the cubic emission frequency. For sexithiophene in benzene solution $\tau_r=2.2$ ns, $\langle(\hbar\omega)^3\rangle=11.4$ eV,[3] $n=1.51$,[6,14] and thus $d=2.7\pm0.1$ Å. Taking into account the different refraction index, we obtain the same result from the data reported for sexithiophene in dioxane solution.[6,14] This value of d differs by only 8% from the theoretical result obtained through quantum-correlated calculations.[15] The longitudinal exciton frequency can be easily evaluated from the experimental data, $\Omega_L=3.45\pm0.03$ eV [Fig. 1(b)]. From Eqs. (1) and (2), we can now evaluate $\omega_T=2.66\pm0.04$ eV, and thus $\Delta\Omega=0.79\pm0.07$ eV. This value of $\Delta\Omega$ compares favorably with the experimental data. Finally, we note that the pure transverse polariton ($\beta=90°$) can never be excited in our samples due to the crystal refraction index ($n\geqslant1.61$, $\beta\leqslant56°$).

The experimental Davydov splitting between the lower Davydov component at 2.276 eV and the transverse polariton $\hbar\Omega_T=2.65$ eV, reads $E_{DS}=0.38\pm0.04$ eV; E_{DS} depends only on the short-range forces.

Sexithiophene: Charge-transfer excitons and determination of E_B. The transition frequency of the line at 2.6 eV (CTE) does not depend on θ [Fig. 1(b)]; according to Eq. (1), this behavior is consistent with the weak oscillator strength of this resonance. We now address the effect of reducing the intermolecular distance on the energy of Davydov and charge-transfer excitons, respectively.

Shorter distances imply stronger intermolecular interactions. The splitting between lower and upper Davydov exciton should therefore increase.[16] The enhanced repulsion between these states should yield a redshift of the low component of the doublet and a blueshift of the high-energy component. This behavior is quite a general result, which has been also confirmed by quantum-correlated computations.[17]

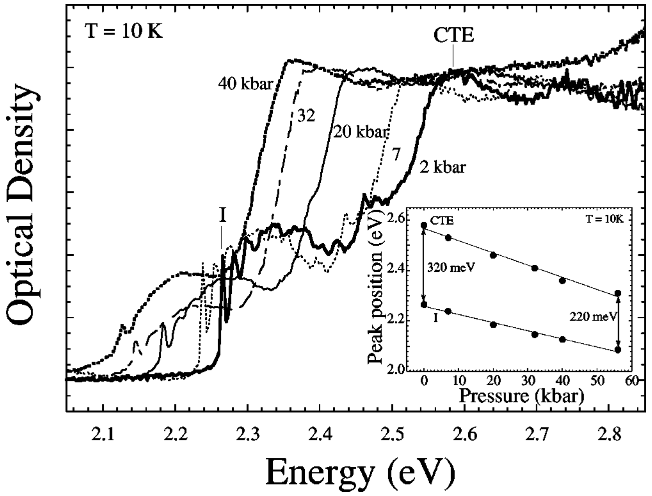

FIG. 3. Transmission spectra of $T6$ single crystal at different pressures. All the spectra are normalized with respect to the maximum. I shows a vibronic replica of the lower Davydov exciton and CTE is the charge-transfer excitons. Inset: Transition energy of I and CTE versus pressure.

The reduced interchain distance, and thus the shorter electron-hole distance, shifts the CTE to lower energies.[18] Moreover, compression of the lattice should improve the stability of charge-transfer excitons with respect to Frenkel excitons. For very short intermolecular distances, we expect that the lowest exciton states should acquire a prominent charge-transfer character.

Figure 3 presents the evolution of the unpolarized absorption spectra as a function of applied pressure at 10 K.[20,12] The vibronic replica I of the lower Davydov excitons and the 2.6-eV peak are very well resolved up to the highest pressure. The pressure dependence of their energies is shown in the inset. The energy difference between the two absorption lines decreases significantly upon decreasing the pressure (320 meV) to 60 kbar (220 meV). This experimental behavior fully confirms the charge-transfer nature of the peak at 2.6 eV at room pressure. We set $E_B=0.314\pm0.005$ eV, by using the low-temperature data. Extrapolating the linear regression of peak I and CTE to even higher pressure, we predict that the splitting between the two peaks closes at ~180 kbar, above which intermolecular excitations should be the lowest stable excitations.

The excitation of CTE's at 2.6 eV is in excellent agreement with the following experimental and theoretical findings:

(1) The features observed experimentally in electroabsorption spectra near 2.7 eV (Ref. 8) and attributed to CTE's in Ref. 9.

(2) Photoexcitation spectroscopy and photoconductivity action spectrum in single crystals.[19] The former shows a sharp decrease of the quantum efficiency for energies above 2.6 eV. Conversely, the latter considerably increases and is

TABLE I. Interaction energies and dipole length in sexithoiphene.

Parameter	Value	Comment
E_B	0.314 ± 0.005 eV	This work, experiment
E_{DS}	0.38 ± 0.04 eV	This work, experiment
E_{EPI}	0.79 ± 0.07 eV	This work, experiment
$\hbar\Omega_L$	3.45 ± 0.03 eV	This work, experiment
$\hbar\Omega_T$	2.66 ± 0.04 eV	This work, experiment
$\hbar\Omega_{LDE}$	2.276 ± 0.001 eV	This work, experiment
d	2.7 ± 0.1 Å	This work, experiment

peaked at Ω_L. These data clearly indicate that exciton ionization takes place for excitations above the charge-transfer states energies.

(3) The sexithiophene photoluminescence is quenched for increasing pressure. The increased charge-transfer nature of the primary excitations in fact facilitates electron-hole separation.[12]

(4) Recent calculations set the position of the CTE in sexithiophene single crystal at 2.66 eV, and provide an estimate of the CTE absorption coefficient $\approx 10^3$ cm^{-1} for light polarized along the b axis,[9] in excellent agreement with experiments.

In conclusion, we have investigated the lowest optical excitations in a sexithiophene single crystal. Transmission spectra feature three distinct kinds of excitations: low-energy intramolecular excitons, intermolecular states, and Davydov polaritons. The signature of the excitation of polaritons is a wide stop band. The signature of charge-transfer excitons is the large stabilization energy these states experience under the application of high pressure.

The transition frequencies of transverse polaritons and charge-transfer states allow us to determine the short-range intermolecular energy $E_{DS}=0.38\pm0.04$ eV, and the electron-hole interaction energy $E_B=0.314\pm0.005$ eV (see Table I).

The conclusions drawn from the present experiments should be of quite general validity, as similar interaction strengths are expected for a wide class of linear-conjugated molecular semiconductors with high applicative interest.

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[1] See, e.g., F. Garnier, R. Hajlaoui, A. Yassar, and P. Srivastava, Science **265**, 1684 (1994); J.H. Schön, Ch. Kloc, A. Dodabalapur, and B. Batlogg, *ibid.* **290**, 963 (2000); C. Zenz, G. Cerullo, and G. Lanzani, Phys. Rev. B **59**, 14 336 (1999).

[2] *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Band Model*, edited by N. S. Sariciftci (World Scientific, Singapore, 1997).

[3] P. Petelenz and M. Andrzejak, Chem. Phys. Lett. **343**, 139 (2001).

[4] M. Muccini, M. Schneider, C. Taliani, M. Sokolowski, E. Umbach, D. Beljonne, J. Cornil, and J.L. Brédas, Phys. Rev. B **62**, 6296 (2000).

[5] E. Zojer, N. Koch, P. Puschnig, F. Meghdadi, A. Niko, R. Resel, C. Ambrosch-Draxl, M. Knupfer, J. Fink, J.L. Brédas, and G. Leising, Phys. Rev. B **61**, 16 538 (2000).

[6] D. Oelkrug, H.J. Egelhaaf, J. Gierschner, and A. Tompert, Synth. Met. **76**, 249 (1996).

[7] P. Y. Yu and M. Cardona, *Fundamental of Semiconductors* (Springer, Berlin, 1999).

[8] S. Möller, G. Weiser, and F. Garnier, Phys. Rev. B **61**, 15 749 (2000).

[9] M. Andrzejak, P. Petelenz, M. Slawik, and R. W. Munn, J. Chem. Phys. (to be published).

[10] M.R. Philpott, Annu. Rev. Phys. Chem. **31**, 97 (1980), and reference therein.

[11] E.E. Koch *et al.*, Chem. Phys. **3**, 362 (1974).

[12] M.A. Loi, A. Mura, G. Bongiovanni, Q. Cai, C. Martin, H.R. Chandrasekhar, M. Chandrasekhar, W. Graupner, and F. Garnier, Phys. Rev. Lett. **86**, 732 (2001).

[13] D. L. Dexter, *Solid State Physics*, edited by F. Seitz and D. Turbull (Academic, New York, 1958), Vol. 6.

[14] R.S. Becker, J.S. de Melo, A.L. Maganita, and F. Elisei, J. Phys. Chem. **100**, 18 683 (1996).

[15] F. Kouki, P. Spearman, P. Valat, G. Horowitz, and F. Garnier, J. Chem. Phys. **113**, 385 (2000).

[16] A. Otto, R. Keller, and A. Rahman, Chem. Phys. Lett. **49**, 145 (1977); R. Sonnenschein, K. Syassen, and A. Otto, J. Chem. Phys. **74**, 4315 (1981).

[17] J. Cornil, D.A. dos Santos, X. Crispin, R. Silbey, and J.L. Brédas, J. Am. Chem. Soc. **120**, 1289 (1998).

[18] J.A. Gisby and S.H. Walmsley, Chem. Phys. Lett. **135**, 275 (1987); J.A. Gisby and S.H. Walmsley, Chem. Phys. **122**, 271 (1988).

[19] Raman, absorption, and luminescence data show a smooth reversible behavior versus applied pressure, indicating that no phase transition occurs (up to 80 kbar).

[20] G. Horowitz, S. Romdhane, H. Bouchriha, P. Delannoy, J.-L. Monge, F. Kouki, and P. Valat, Synth. Met. **90**, 187 (1997).