

# Exciton Band Structure of Pentacene Molecular Solids: Breakdown of the Frenkel Exciton Model

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Employing inelastic electron scattering we demonstrate here the determination of the exciton dispersion in a molecular solid. The failure of the applied tight-binding description provides strong evidence for a necessary reconsideration of the traditional, Frenkel-exciton based, understanding of the lowest-lying electronic transitions in organic semiconductors.

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The band structure of quasiparticles, moving in a periodic, translationally invariant potential, is at the heart of solid state physics. In general, the band structures determine many physical properties and without a detailed knowledge of them, a rationalization of the solid's properties is not conceivable. Consequently, experimental techniques that allow the determination of quasiparticle dispersions are of enormous importance. Within those techniques inelastic scattering methods play a substantial role, and have led to a broad fundamental understanding of, for instance, the phonon degrees of freedom. Inelastic electron scattering to probe charge excitation of solids is applied to a considerably lesser extent despite the basic importance of charge excitations for the optical properties of materials.

Organic molecular solids are the subject of intense research due to their potential applications in novel organic devices. They are comprised of closed-shell molecular units, which only interact weakly in the condensed phase. As a consequence, it is generally assumed that the electronic properties of molecular solids are to a large extent determined by those of the individual molecular building blocks, which are only slightly modified in the solid by the weak intermolecular interactions. This assumption is the basis of the description of many observed physical properties, among them charge excitations in organic molecular solids [1–3]. The energetically lowest-lying charge excitations are consequently associated with excitons that are confined to one molecular building block, often termed as molecular Frenkel excitons [1–4]. These Frenkel excitons can move through the solid as a result of the (weak) intermolecular interactions [1–3]. Despite the tremendous importance of the exciton dispersion for an understanding of the optical properties, an experimental determination of the full exciton band structure in any organic molecular solid has not been reported so far.

Pentacene (C<sub>22</sub>H<sub>14</sub>) can be regarded as a model compound for molecular solids and its single crystals have been used to investigate and to determine fundamental proper-

ties of this material and of the class of organic molecular solids in general [2,5,6]. Furthermore, organic devices based upon pentacene single crystals have also led to significant insight into the device physics [7,8].

We have used inelastic electron scattering, often also called electron energy-loss spectroscopy (EELS) [9], to directly measure the exciton band structure within the reciprocal  $a^*b^*$  plane of pentacene. Large, high-quality single crystals of pentacene were obtained by directional sublimation of two- or three-times purified pentacene. They were grown at temperatures between 280 and 220 °C in closed, evacuated Pyrex ampoules and a horizontal two-zone furnace was used. Typical crystal dimensions were 5–15 mm length, 2–5 mm width, and 0.05–0.25 mm thickness. For our studies using EELS, thin, single-crystalline pentacene films (thickness  $\sim 100$  nm) were cut from the large, flat surface of a single crystal using an ultramicrotome equipped with a diamond knife. Subsequently, the films were mounted onto standard electron-microscopy grids and transferred to the spectrometer. The EELS measurements were carried out using a 170 keV spectrometer described elsewhere [9]. We note that at this high primary beam energy, only singlet excitations are possible [9]. The energy and momentum resolution were set to be 180 meV and 0.03 Å<sup>-1</sup>, respectively. Importantly, in addition to inelastic investigations, the spectrometer also allows electron diffraction measurements, which have been employed for identifying the high-symmetry crystal directions for the exciton band-structure studies. These diffraction measurements prove that our pentacene samples are indeed single crystals.

We have determined the loss function  $\text{Im}[-1/\epsilon(\mathbf{q}, \omega)]$  for various momentum transfers  $\mathbf{q}$ , parallel to the directions of the corresponding reciprocal lattice vectors. Furthermore, as molecular crystals often are damaged by fast electrons, we repeatedly checked our samples for any sign of degradation.

In Fig. 1 we show the evolution of the energetically lowest excitation in the loss function for different momen-

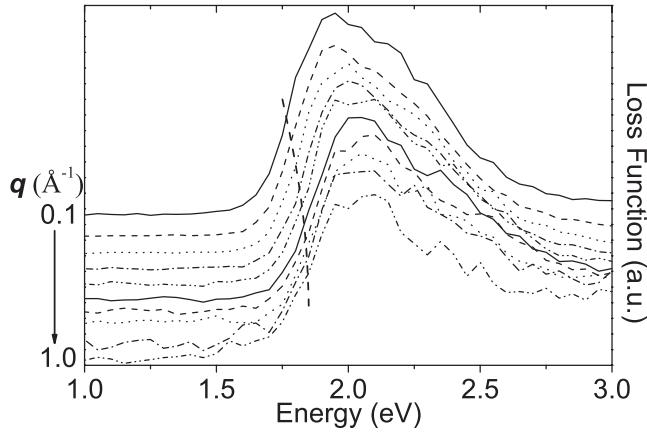


FIG. 1. The loss function of pentacene for momentum transfers parallel to the (110) direction in reciprocal space. The (vertical) dashed line indicates the position of the leading edge (see text for details).

tum transfers parallel to the (110) direction. Note that the excitation starts around 1.8 eV which is clearly below the band gap  $E_g$  of pentacene ( $E_g > 2.2$  eV [2,10–13]). From Fig. 1 it is evident that there is a clear dependence of the energy of this feature on the momentum transfer. This is

further pointed up in Fig. 2(c) where we show a comparison of the two momentum transfers where the excitation energies are farthest apart. Additionally, Fig. 2 summarizes equivalent results in three other reciprocal-crystal directions: (100), (210), and (120).

To analyze the dispersion of the lowest-lying exciton quantitatively, we have determined the leading edge position of the features as seen in Figs. 1 and 2, which is defined by the energy where the steep increase reaches half its height. This analysis avoids ambiguities that can arise due to a variation of the spectral shape of excitation features in our measurements, which can make the analysis of the peak maxima problematic. We emphasize that in the long-wavelength limit our peak shapes are consistent with the results from optical measurements [14–16], in particular, the leading edge positions analyzed here agree very well.

The results of this analysis are shown in Fig. 3. This figure reveals that excitons in pentacene molecular solids sizably disperse in the  $a^*b^*$  reciprocal-crystal plane, which is in agreement to what can be qualitatively read off Figs. 1 and 2. The maximal exciton band width is about 100 meV and the exciton dispersion is significantly anisotropic. To the best of our knowledge, this represents the first direct determination of the full anisotropic exciton dispersion in a molecular solid.

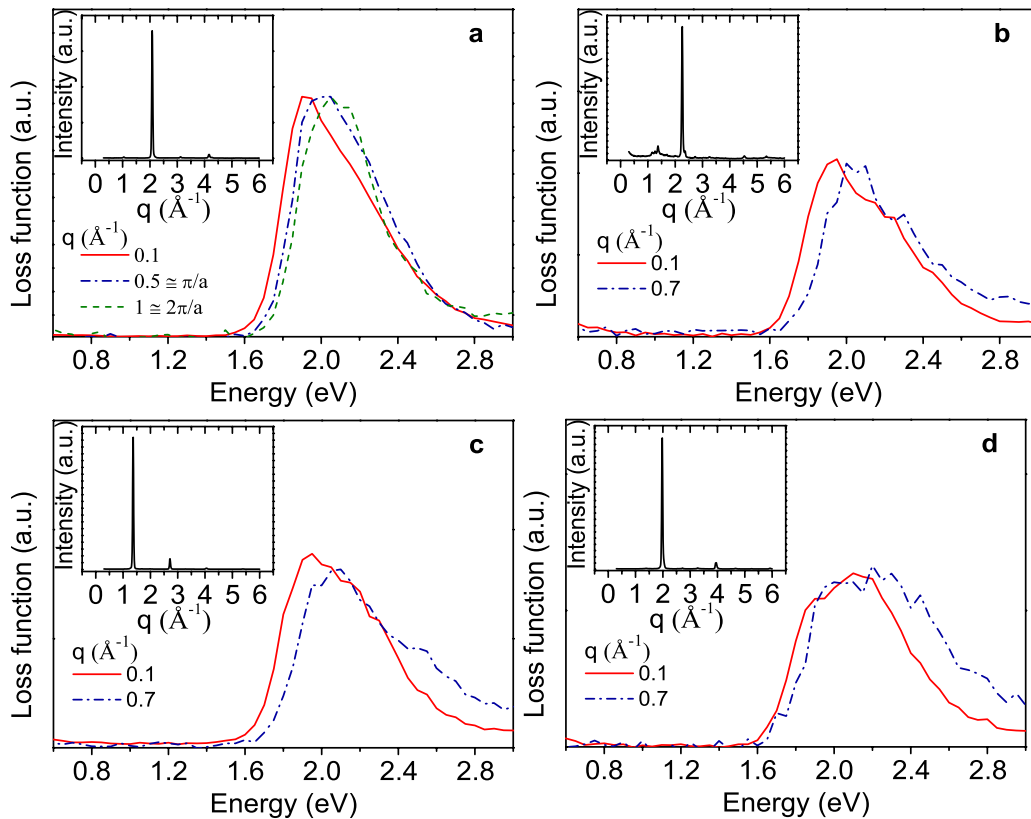


FIG. 2 (color online). The loss function for four different directions in the  $a^*b^*$  plane of pentacene: (a) (100); (b) (210); (c) (110); (d) (120), respectively. The insets show the corresponding Bragg spectra and reveal the high quality of the employed pentacene single crystals.

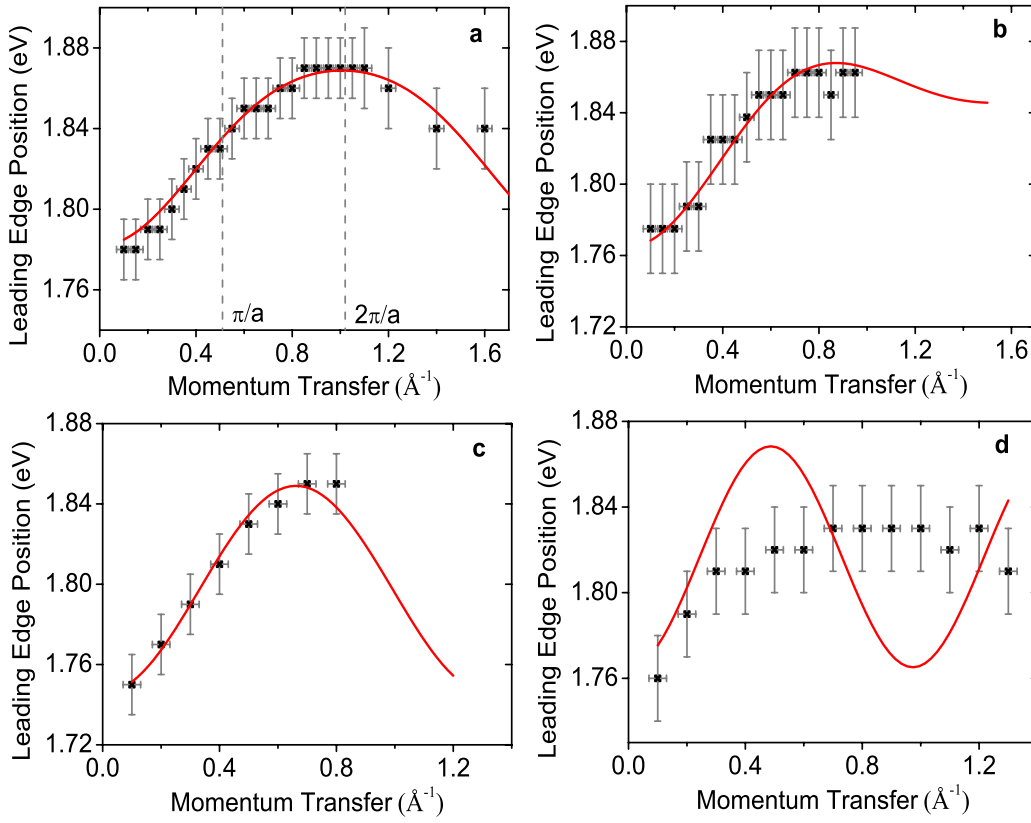


FIG. 3 (color online). The exciton dispersion for different directions: (a) (100); (b) (210); (c) (110); (d) (120), respectively, within the  $\mathbf{a}^*\mathbf{b}^*$  plane of pentacene. The solid curve corresponds to the employed fit according to Eq. (1).

In consideration of the “general belief” that excitons in molecular solids are Frenkel-like and that the intermolecular interactions are very weak, one should be able to model the exciton dispersion in pentacene using a simple tight-binding description that is restricted to next-nearest-neighbor interactions only and has the following functional form [1]:

$$E(\mathbf{q}) = E_0 + t_a \cos(\mathbf{q} \cdot \mathbf{a}) + t_b \cos(\mathbf{q} \cdot \mathbf{b}) + 2t_{ab} \cos\left(\frac{\mathbf{q} \cdot \mathbf{a}}{2}\right) \cos\left(\frac{\mathbf{q} \cdot \mathbf{b}}{2}\right), \quad (1)$$

with the lattice vectors  $\mathbf{a}$  and  $\mathbf{b}$ . The transfer integrals  $t_a$ ,  $t_b$ , and  $t_{ab}$  comprise interactions with the next-nearest-neighbors in all possible multipole orders (dipole-dipole and higher terms) in  $\mathbf{a}$ - and  $\mathbf{b}$ -direction, and the unit-cell diagonal. Note that the parameter  $t_{ab}$ , describing the interaction between the two inequivalent molecules, contains the phenomenon of Davydov splitting [1]. Consequently, we have tried to model the data as shown in Fig. 3 using this approach. The surprising and unexpected result is that such a description of the exciton dispersion in pentacene is not possible. The measured dispersion curves set strong restrictions for the relative values of the hopping parameters  $t$ . First, Fig. 3(a) reveals the intriguing fact that the dispersion for a momentum parallel to  $\mathbf{a}^*$  has twice the

periodicity as expected from the pentacene Brillouin zone. This can only be modeled using Eq. (1) when  $|t_a| \ll |t_{ab}|$ . The fit shown in Fig. 3(a) reflects  $t_a = -2.3$  meV and  $t_{ab} = -10.9$  meV. In general, the transfer integrals can result from the interaction of the excitation multipoles of two adjacent molecules or from the overlap of the exciton wave function of the two corresponding molecules. Assuming a pointlike dipole-dipole exciton transfer [1] leads to the prediction that the transfer integrals  $t_a$  and  $t_{ab}$  should be of the same size and of opposite sign, in clear contradiction to our results. Thus, at this point we can already rule out that the exciton transfer in pentacene single crystals is governed by this mechanism.

Second, after having determined  $t_a$  and  $t_{ab}$ , only one free parameter ( $t_b$ ) is left to model the other three data sets shown in Fig. 3 which is motivated by the almost perfect orthogonality between  $\mathbf{a}^*$  and  $\mathbf{b}^*$  [6]. Therefore the contribution parallel to  $\mathbf{b}^*$  is negligible for fitting the data in the (100) direction. However, it is not possible to describe these data with any satisfactory agreement, but we arrive at the situation as shown in Fig. 3, in which the data and the model based on the Frenkel-exciton picture substantially disagree. Consequently, we are left with the unexpected and surprising conclusion that the exciton dispersion in pentacene cannot be described within this Frenkel-like framework, which is only of nearest-neighbor type. Even

more, the inclusion of further parameters (extended tight-binding model) will not improve the situation since these parameters represent only small corrections within a Frenkel-exciton description due to the exponential decay of a molecular wave function or the  $1/r^3$  decay of the dipole-dipole interaction.

Our results thus provide strong evidence that a microscopic description of the energetically lowest-lying excitons in pentacene as Frenkel excitons must be wrong and larger excitons should be considered, for instance so-called charge-transfer (CT) excitons, for which electrons and holes are separated by at least one intermolecular distance. The binding energy of CT excitons with respect to the band gap  $E_g$  can be estimated within a point-charge approach [3] using

$$E_g - E_{CT} = \frac{e^2}{4\pi\epsilon\epsilon_0 r_{CT}}, \quad (2)$$

whereas  $r_{CT}$  denotes the distance of the molecules which participate in the charge-transfer excitation and  $\epsilon \sim 2.5$  [14] is the dielectric constant. Such an analysis gives for pentacene a CT exciton energy of roughly 1 eV below the band gap. However, this point-charge based calculation only represents a crude estimate and optical data suggest much smaller values [15]. Nevertheless, more advanced calculations arrive at a very similar value [17]. The band gap  $E_g$  of pentacene is surprisingly not well known, the values reported range from 2.2 to 2.8 eV [2,10–13,15]. This uncertainty notwithstanding, the CT excitons are expected at the lowest energies, i.e., at those energies where the excitons are measured as shown and discussed above. This is fully consistent with our conclusion above that a Frenkel-type model cannot rationalize the dispersion of these excitons.

This is further illustrated by elaborate *ab initio* calculations [18] based on the Bethe-Salpeter equation which have already suggested that the lowest (singlet) excited state is expected to be predominantly of CT character and that even unbound electron-hole pairs are supposed to be observable for representatives of the oligoacenes larger than pentacene [19]. In this regard our data may serve as the first strong experimental support for these theoretical predictions.

In conclusion, we have shown that the excitonic dispersion behavior in pentacene obtained from EELS measurements does not fit into the nowadays commonly accepted framework of Frenkel-like electron-hole pairs and it re-

mains to be seen whether a more general CT or mixed CT-Frenkel picture will make a successful description of the observed dispersion feasible, still an open question and a task for thorough calculations.

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