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## Size of Electron-Hole Pairs in $\pi$ -Conjugated Systems

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We have performed momentum-dependent electron energy-loss studies of the electronic excitations in sexithiophene and compared the results to those from parent oligomers. Our experiment probes the dynamic structure factor  $S(\mathbf{q}, \omega)$  and shows that the momentum-dependent intensity variation of the excitations observed can be used to extract the size of the electron-hole pair created in the excitation process. The extension of the electron-hole pairs along the molecules is comparable to the length of the molecules. Consequently, the primary intramolecular electron-hole pairs are relatively weakly bound. We find no evidence for the formation of excitations localized on single thiophene units.

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There is still growing interest in the physical properties of various  $\pi$ -conjugated systems because many polymers and oligomers have become promising candidates for applications in devices such as organic light emitting diodes [1,2], field effect transistors [2,3], optical converters [4], or molecular switches [5]. In addition,  $\pi$ -conjugated molecules with a finite, well-defined chain length can serve as model systems for the investigation of general and fundamental properties of the whole material class. Moreover,  $\pi$ -conjugated systems bridge molecular and extended electronic states and therefore also allow one to study special cases of Heisenberg, Hubbard, or other models for narrow band solids.

Any potential application in electronic or optical devices and their optimization requires an understanding of the electronic structure of the system in question. Hereby, the excited electronic states are of particular interest in polymers or oligomers as they are directly related to processes such as light absorption and emission, photoconductivity, or exciton formation. One of the remaining questions is the following: To what extent does exciton formation play a role in the excited state and how large is the related exciton binding energy? Exciton binding energies ranging from 0.1 to more than 1 eV have been discussed previously [6–13]. Directly connected with the exciton formation and binding energy is the spatial extension of a possible excitonic state, i.e., the size of the electron-hole pair formed in the excitation process.

In this contribution we present a detailed analysis of optically allowed and forbidden electronic excitations of highly oriented sexithiophene ( $\alpha$ -6T) thin films which have been studied using electron energy-loss spectroscopy (EELS) in transmission. The results are compared to those from parent  $\pi$ -conjugated oligomers. EELS is a measure of the dynamic structure factor  $S(\mathbf{q}, \omega)$  and thus probes the form factor of the electronic excitation in question. We demonstrate that the momentum-dependent in-

tensity variation of different electronic excitations can be used to extract the size (or separation) of the electron-hole pair created in the corresponding excitation process which then additionally gives an estimate for the electron-hole binding energy. To our knowledge, this represents the first determination of the spatial extension of electronic excitations via a momentum-dependent study of  $S(\mathbf{q}, \omega)$ . Previously, those data were only analyzed on the basis of a quasiband structure which completely neglects excitonic effects [14,15]. Our results argue against the intrinsic formation of strongly confined excitons (i.e., excitons that are spatially confined to a single thiophene or even smaller unit) in  $\pi$ -conjugated systems by light absorption or inelastic electron scattering.

Thin, crystalline  $\alpha$ -6T films ( $\sim 1000$  Å) have been grown by evaporation onto a KBr (001) single crystal under UHV conditions. The evaporation rate was  $0.1$  Å/s and the substrate was held at room temperature. Electron diffraction and direction dependent EELS studies showed that the films were highly oriented such that the momentum transfer in our measurements could be aligned predominantly parallel to the long axis of the  $\alpha$ -6T molecules. The EELS measurements were carried out using a 170 keV spectrometer described elsewhere [16]. We note that at this high primary beam energy only singlet excitations are possible. The energy and momentum resolution were chosen to be 120 meV and  $0.05$  Å $^{-1}$ , respectively. The loss function  $\text{Im}[-1/\epsilon(\mathbf{q}, \omega)]$ , which is proportional to the dynamic structure factor  $S(\mathbf{q}, \omega)$ , has been measured for various momentum transfers,  $q$ . Thus, our experiment is equivalent to polarization dependent optical absorption studies with the light polarization vector being parallel to the molecular axis, but it additionally allows one to study the excitation properties of the electronic system as a function of  $q$ . The measured loss functions have been corrected for contributions from the elastic line and multiple scattering [16]. The optical

conductivity,  $\sigma(\mathbf{q}, \omega) = \omega \epsilon_0 \text{Im}[\epsilon(\mathbf{q}, \omega)]$ , which is a measure for the single particle excitations has been derived performing a Kramers-Kronig analysis of the loss function. The absolute value of the loss function at low momentum transfer was determined using the refractive index  $n \sim 2.2$  [17]; at higher momentum transfers the oscillator sum rule was applied [16].

In Fig. 1 we present the optical conductivity,  $\sigma$ , of  $\alpha$ -6T for various momentum transfers parallel to the molecule axis. Strong variations with increasing momentum transfer are visible. At  $q = 0.15 \text{ \AA}^{-1}$   $\sigma$  has a strong maximum at about 2.7 eV (feature I) with weak shoulders at about 3.2 and 3.7 eV (features II and III) followed by a small peak centered at about 4.4 eV (feature IV). The spectrum is fully consistent with those from optical absorption studies [17,18] or EELS measurements in reflection [18] of crystalline  $\alpha$ -6T films. The fine structure of the first absorption feature which has been observed in optical studies and has been associated with phonon satellites [19] or exciton formation [11] is scarcely resolved in our data. Only low energy shoulders at about 2.0 and 2.4 eV can be seen. These have been assigned to aggregates [20] and the lowest Davydov component of the  $1^1B_u$  molecular excitation [21], respectively. An energetically higher lying Davydov component appears at 2.7 eV in optical measurements [21] also consistent with the EELS spectra shown in Fig. 1. In the following, we will not consider those fine structures but we will take the inten-

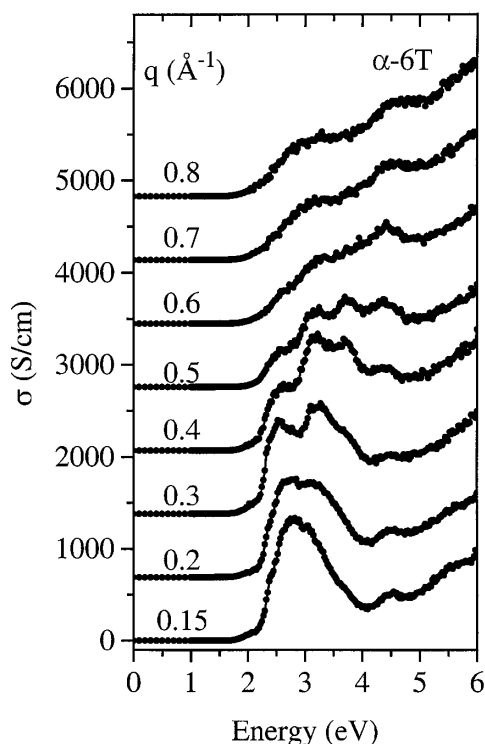


FIG. 1. Optical conductivity,  $\sigma$ , of  $\alpha$ -6T for various momentum transfers  $q$  parallel to the molecules. The curves are offset in the  $y$  direction.

sity of the features I–IV as a measure for the strength of the corresponding electronic excitation as a whole. This is justified by the fact that these features do not change in line shape or energy position as a function of  $q$ ; e.g., the low energy shoulders visible in Fig. 1 do not show an intensity variation different from the main part of feature I (see also discussion below). Following the spectra in Fig. 1 with increasing momentum transfer, feature I decreases in intensity while features II–IV increase successively before they also start to decrease or saturate.

In order to obtain the momentum-dependent intensity variation of the electronic excitations as observed in Fig. 1, we have modeled the optical conductivity with a sum of Lorentz oscillators:

$$\sigma(\omega) = \epsilon_0 \sum_j \frac{\omega^2 f_j \gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 \gamma_j^2}, \quad (1)$$

with  $\omega_j$  being the energy position,  $\gamma_j$  the width, and  $f_j$  the oscillator strength of the corresponding excitation. The result of this fit for the momentum-dependent oscillator strength (or intensity) of the features I–IV is shown in Fig. 2. The momentum position of the intensity maximum clearly shifts to higher momentum transfers on going from excitation I to IV. Such a behavior has also been observed for  $\beta$ -carotene [14] and hexaphenyl [15], which are further representatives of  $\pi$ -conjugated oligomers. The momentum position,  $q_{\text{max}}$ , of the intensity maxima of the first electronic excitations of  $\alpha$ -6T, hexaphenyl, and  $\beta$ -carotene are summarized in Table I.

In the remainder of this paper we show that the observed intensity variations can be rationalized considering the

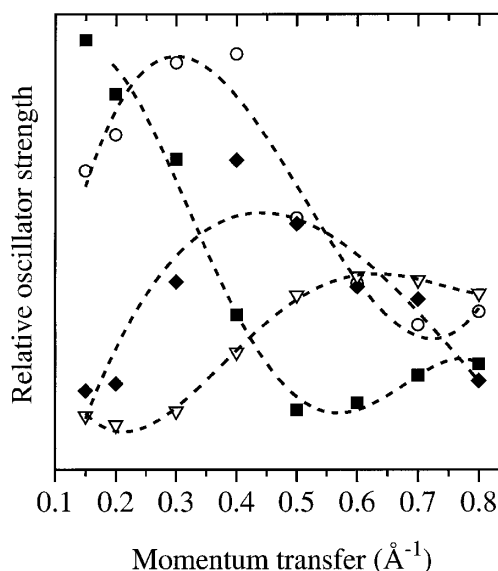


FIG. 2. Intensity variation of the first four excitations observed in Fig. 1 as a function of momentum transfer,  $q$ . Feature I: filled squares; feature II: open circles; feature III: filled diamonds; feature IV: open triangles. The lines are intended as a guide to the eye.

TABLE I. Momentum position  $q_{\max}$  ( $\text{\AA}^{-1}$ ) of the intensity maximum of the first electronic excitations in  $\alpha$ -6T (this study), hexaphenyl [15], and  $\beta$ -carotene (from experiment and theory) [14], and the mean radius  $\langle r \rangle$  ( $\text{\AA}$ ) of the excited state wave function along the long axis of the molecules (see text).

|                           | $q_{\max, \text{II}}$ | $q_{\max, \text{III}}$ | $q_{\max, \text{IV}}$ | $\langle r \rangle_{\text{I}}$ | $\langle r \rangle_{\text{II}}$ | $\langle r \rangle_{\text{III}}$ | $\langle r \rangle_{\text{IV}}$ |
|---------------------------|-----------------------|------------------------|-----------------------|--------------------------------|---------------------------------|----------------------------------|---------------------------------|
| $\alpha$ -6T              | 0.3                   | 0.43                   | 0.64                  | 8                              | 7.3                             | 7.4                              | 6.2                             |
| Hexaphenyl                | $\sim 0.3$            | $\sim 0.4$             | $\sim 0.6$            | $\leq 9$                       | 7.3                             | 8                                | 6.6                             |
| $\beta$ -carotene (expt.) | $\sim 0.2$            | $\sim 0.3$             | $> 0.5$               | 11                             | 10                              | 10                               | $\leq 8$                        |
| $\beta$ -carotene (theo.) | 0.24                  | 0.4                    | 0.54                  | 12                             | 9.1                             | 8                                | 7.4                             |

Taylor expansion of the transition matrix element and that one can directly derive a mean extension of the electron-hole pairs created in the excitations process. The matrix element,  $M$ , for EELS is proportional to  $\langle f | \exp(iqr) | i \rangle$  which can be expanded to

$$M \propto \sum_n \frac{i^n}{n!} (q\langle r \rangle)^n \left\langle f \left| \left( \frac{r}{\langle r \rangle} \right)^n \right| i \right\rangle. \quad (2)$$

Hereby, the introduction of a mean radius  $\langle r \rangle$  allows one to separate the characteristic dimensionless ( $q\langle r \rangle$ ) dependence of the matrix element from the (now also dimensionless)  $q$ -independent excitation probability  $\langle f | (r/\langle r \rangle)^n | i \rangle$ . In the case of excitations with a *specific* multipole character (e.g., dipole excitations), the latter has a finite value only for the corresponding  $n$  (e.g.,  $n = 1$ ). Thus, the momentum dependence of the excitation intensity  $I_n$  ( $\propto |M|^2$ ) of an excitation with a *specific* multipole character can be written as

$$I_n \propto \frac{n!^{-2} (q\langle r \rangle)^{2n}}{N}, \quad N = \sum_n \frac{(q\langle r \rangle)^{2n}}{n!^2}. \quad (3)$$

$N$  is a sum over the intensities of all excited (final) multipole contributions and represents a normalization factor which guarantees the oscillator strength sum rule. In Fig. 3 we show the intensities  $I_n$  as a function of  $q\langle r \rangle$  for  $n = 1$  to 4. Maxima are found at  $q\langle r \rangle = 0, 2.2, 3.2,$  and 4 for  $n = 1, 2, 3,$  and 4, respectively.

The mean radius  $\langle r \rangle$  as introduced in Eq. (2) gives a measure for the extension of the electron-hole wave function  $\Psi_{eh}(\mathbf{r})$  in the excited state which represents the probability amplitude to find the electron at a certain distance  $\langle r \rangle$  assuming that the hole is fixed ( $\mathbf{r}$  denotes the relative coordinate  $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$ ). This can be seen from the dynamic structure factor  $S(\mathbf{q}, \omega)$  which, in analogy to the static atomic structure factor  $S(\mathbf{q})$ , is the Fourier transform of the electron distribution around the hole in the excited state,  $|\Psi_{eh}(\mathbf{r})|^2$ . Assuming an electron-hole pair with a hydrogenlike  $1s$  wave function having a (Bohr) radius of  $1 \text{ \AA}$ ,  $S(\mathbf{q}, \omega)$  adopts a  $q$  dependence which is also shown in Fig. 3 (open circles) and which is in reasonable agreement with the  $q$ -dependent intensity variation of a dipole excitation with the same mean radius as expected from Eq. (3). From Fig. 3 the error of our approximation regarding the mean radius of the excited state wave function can be estimated to be of the order

of 20%–25%. We emphasize that this uncertainty does not affect the conclusions discussed below. Additionally, Fig. 3 shows that higher order excitations occur at higher momentum transfers. The similarity between the intensity variations observed for  $\alpha$ -6T (Fig. 2), hexaphenyl [15], or  $\beta$ -carotene [14] and those calculated according to Eq. (3) (Fig. 3) is striking. It strongly indicates that the spatial charge distributions of the excited states, which in  $\alpha$ -6T correspond to the excitation energies of 3.2, 3.7, and 4.4 eV, are predominantly of higher order multipole character. Taking this into account, a comparison of the intensity maxima predicted by Eq. (3) (see Fig. 3) and those found in the momentum dependence of the optical conductivity can be used to derive an estimate of the mean radius  $\langle r \rangle$  of the excited state wave functions  $\Psi_{eh}(\mathbf{r})$ . Furthermore, the observed intensity of feature I, which is of particular interest as it represents the lowest lying, optically allowed singlet excitation, reaches its minimum

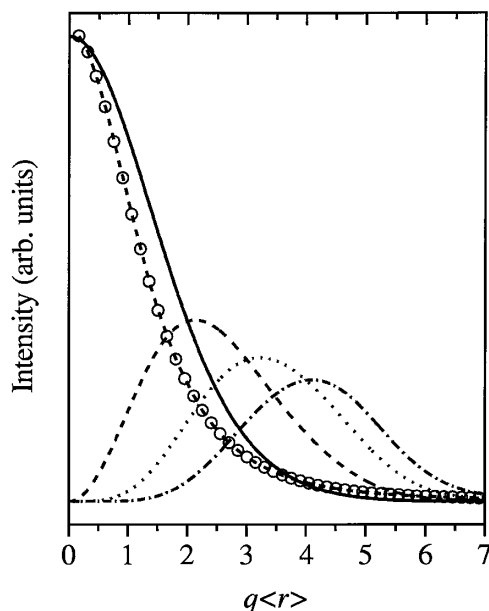


FIG. 3. Intensity of the  $n$ th multipole excitation according to Eq. (3) ( $n = 1$ : solid line;  $n = 2$ : dashed line;  $n = 3$ : dotted line;  $n = 4$ : dash-dotted line). Additionally shown is the  $q$  dependence of the dynamic structure factor for a hydrogenlike electron-hole excitation with a Bohr radius of  $1 \text{ \AA}$  (dashed line with open circles, see also text).

at  $q \sim 0.55 \text{ \AA}^{-1}$ . Comparing this to the value for  $q\langle r \rangle$  in Fig. 3 where the intensity of the dipole allowed transition becomes essentially zero ( $q\langle r \rangle \sim 4.5$ ), one obtains an estimate for  $\langle r \rangle$  of the dipole allowed excitation I of about 8 Å. An equivalent comparison can also be performed for  $\beta$ -carotene [14] and hexaphenyl [15]. The results for  $\langle r \rangle$  of the first four electronic excitations are presented in Table I. We note that in the measurements the momentum vector,  $\mathbf{q}$ , is oriented predominantly parallel to the long axis of the molecules and that we therefore probe the mean radius  $\langle r \rangle$  of the excited state wave functions along the molecules.

Interestingly, the mean radius  $\langle r \rangle$  of the excited state wave functions of the oligomers compared in Table I indicates a total extension of the electron-hole wave function ( $2\langle r \rangle$ ) of about 15–20 Å; i.e., the electron-hole pairs are spread over the entire molecules independent of the details of the molecular structures. Moreover, from our results there is no evidence for the formation of a split-off, strongly localized excitonic state whose extension would be significantly smaller than the values discussed above as there is no low energy feature visible whose intensity variation with  $q$  is different from the main features. This means that electron-hole pairs in the  $\pi$ -conjugated oligomers discussed here are limited only by the finite length of the corresponding oligomer. The extension of the electron-hole pairs additionally gives an estimate of the electron-hole pair binding energy,  $E_B$ :

$$E_B \sim \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{\langle r \rangle}, \quad (4)$$

which is screened by the static dielectric constant  $\epsilon_r$  ( $\sim 4.8$  for  $\alpha$ -6T [17]). Taking into consideration the size of an electron-hole pair as discussed above, this simple consideration leads to a binding energy  $E_B$  of about 0.3 eV. This also indicates that electron-hole pairs in  $\pi$ -conjugated systems do not form strongly bound excitons with binding energies of 1 eV or larger but they rather are in a weakly bound state.

Recent studies of the intrinsic photoconductivity of PPV-type conjugated polymers [22] arrived at similar conclusions. The thermalization distance which is equivalent to  $\langle r \rangle$  was reported to be 10–20 Å with an electron-hole binding energy of less than 0.4 eV. Theoretical studies [23,24] on the basis of an intermediate neglect of differential overlap (INDO) approach of the excited state wave function  $\Psi_{eh}(\mathbf{r})$  in PPV-type oligomers also found an extension of the first singlet excited state over the entire molecule, in good agreement to our experimental results. Additionally, our results agree well with recent calculations of excitons in conjugated polymers within the density matrix renormalization group approach based upon an extended Hubbard model [25]. These calculations, which take nearest neighbor Coulomb interaction into account, predict the electron-hole separation in the dipole-allowed

$B_u$  channel to scale with the system size; i.e., they also do not find strongly confined and tightly bound excitons.

Consequently, we conclude that in  $\pi$ -conjugated systems strongly confined excitations ( $\langle r \rangle$  of the order of 2 Å) are not intrinsically formed in electronic excitation processes but that the related electron-hole pairs are spread over many monomer units with their size probably limited only by the molecule length or by structural imperfections. A possible appearance of strongly confined excitons must therefore be due to relaxation processes after the primary excitation. For instance, structural relaxation could lead to “polaron excitons” or impurities could trap electron-hole pairs and thus result in further localization and a higher binding energy. This emphasizes the importance of structural properties of polymer or oligomer films and impurities therein for the performance of devices such as organic light emitting diodes.

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