Eur. Phys. J. B **59**, 25–28 (2007)
DOI: 10.1140/epjb/e2007-00256-6

THE EUROPEAN
PHYSICAL JOURNAL B

Anisotropic dynamic response of pentacene single crystals

R. Schuster[1], M. Knupfer[1,a], D.R.T. Zahn[2], and H. Berger[3]

[1] IFW Dresden, Postfach 270116, 01171 Dresden, Germany
[2] Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz, Germany
[3] Institute of Physics of Complex Matter, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Received 14 June 2007

Abstract. We have investigated the polarization and momentum dependence of singlet excitons in pentacene molecular crystals using inelastic electron scattering. Our results demonstrate that both the direction as well as the absolute value of the momentum are decisive for the spectral intensity of these excitons. Possible implications of this observation for a microscopic understanding of excitons in organic molecular crystals are discussed.

PACS. 78.20.-e Optical properties of bulk materials and thin films – 71.35.-y Excitons and related phenomena – 78.30.Jw Organic compounds, polymers

1 Introduction

Pentacene is one of the most promising materials for potential applications in organic (opto-)electronic devices, motivated by, for instance, remarkably high charge carrier mobilities of about 1 cm^2/Vs in well ordered films [1–4]. Moreover, pentacene single crystals can be grown with very high quality [1], which renders this material also an excellent model compound for the investigation of fundamental physical properties of organic molecular solids in general. In view of both, applications and fundamental research, the electronic excitations in pentacene play an important role. For instance, studies of these excitations using optical techniques are often applied in order to characterize thin films in organic devices [5–8].

The optical properties of pentacene and related oligoacenes have been studied previously with the aim to microscopically understand their behavior. Despite the huge number of studies in the past fundamental issues in regard of the electronic excitations still remain puzzling. One of the unsolved issues is the nature and the dynamics of excitons in organic molecular solids, among them pentacene. 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 in the solid are only slightly modified by the weak intermolecular interactions [9,10]. This assumption is the basis of the description of many observed physical properties, among them electronic excitations in molecular crystals [9–12]. The energetically lowest lying electronic excitations are consequently associated with excitons that are confined to one molecular building block — often termed as molecular Frenkel excitons [9–13]. On the basis of the Frenkel exciton approach the strong anisotropy of the optical response of pentacene has been rationalized by the so-called Davydov components [12], which are essentially polarized along the **a** and **b** crystal axes, respectively [14]. These Davydov components arise from the interaction of the excitation dipoles of the two symmetrically inequivalent molecules in one pentacene unit cell [12]. In addition, due to the usually weak inter-molecular interaction, the dispersion of the Frenkel excitons is expected to follow that of a simple tight-binding model, which takes solely next nearest neighbor interactions into account [11,12], and these interactions, additionally, are believed to be of predominant dipolar character.

More recently, ab-initio approaches containing density functional theory calculations for the ground state, the G-W approximation for the electronic self energy and the Bethe-Salpeter equation taking into account excitonic effects (see e.g. Refs. [15–17]) predicted the energetically lowest lying singlet excitons in pentacene to be of predominant charge transfer character,which is in stark contrast and fundamentally different to the description as Frenkel excitons. Furthermore, a recent experimental determination of the exciton dispersion in pentacene along some reciprocal lattice directions using electron energy-loss spectroscopy (EELS or inelastic electron scattering) provided strong evidence that this dispersion cannot be modelled using a simple tight-binding approach [18,19], also questioning the picture of Frenkel excitons in pentacene as the lowest lying singlet excitations.

In this contribution we report on the dependence of the spectral weight of the lowest lying singlet exciton on

---

[a] e-mail: `m.knupfer@ifw-dresden.de`

the direction of the momentum transfer, $\mathbf{q}$, (i.e. the polarization) and on the absolute value of $\mathbf{q}$ using EELS. This method provides access to for instance optically forbidden excitations [20], or can enable to determine the size of the wave function [21,22] or the dispersion [23,24] of an excitation. We show that the spectral weight of the energetically lowest lying singlet excitons in pentacene strongly varies as a function of the momentum. These variations are compared to expectations based on the description of these excitations as Frenkel excitons, and we demonstrate that such a description cannot account for the observed momentum dependencies.

2 Experimental

Pentacene single crystals with a high quality and typical crystal dimensions of 5–15 mm length, 2–5 mm width, and 0.05–0.25 mm thickness were obtained via a directional sublimation of two or three times purified pentacene (Fluka). The crystal growth was carried out at temperatures between 280 °C and 220 °C in closed, evacuated pyrex ampoules and a horizontal two-zone furnace was used. The growth procedure lasted about four to six weeks.

The EELS studies require thin, single crystalline pentacene films (thickness ∼100 nm) which were cut from the largest, flat surface of a single crystal platelet with an ultramicrotome using a diamond knife. The cut films were attached to standard electron microscopy grids [25] and then transferred into the EELS spectrometer [26]. The films were charaterized in-situ using electron diffraction and these diffraction measurements clearly demonstrated that the films are single crystalline [18,19]. Furthermore, the diffraction experiments were used to orient the momentum transfer parallel to selected reciprocal lattice directions (we use the crystallographic data according to Ref. [27]).

The EELS measurements were carried out using a 170 keV spectrometer thoroughly discussed in a previous publication [26]. At this high primary beam energy only singlet excitations are possible [26]. The energy and momentum resolution were 180 meV and 0.03 Å^{-1}, respectively. The EELS signal, i.e. the loss function $\mathrm{Im}(-1/\epsilon(\mathbf{q},\omega))$, which is proportional to the dynamic structure factor $S(\mathbf{q},\omega)$, was determined for various momentum transfers, $\mathbf{q}$, parallel to the directions of the corresponding reciprocal lattice vectors. In order to compare the spectral weight of the lowest lying excitations we normalized the data according to the sum rule for the loss functions [26].

3 Results and discussion

The loss function of pentacene is characterized by a feature starting at about 1.6–1.7 eV excitation energy, which is due to the energetically lowest lying electronic excitations in this material. The transport energy gap of pentacene is larger than the onset of the electronic excitations (or the optical onset) [28,29] which demonstrates that these lowest lying excitations are excitons with a binding energy of at least 0.2 eV. In Figure 1 we show the loss function of pentacene for absolute values of the momentum transfer, q of 0.1 Å^{-1} and for $\mathbf{q}$ parallel to different reciprocal lattice directions within the $\mathbf{a}^*$,$\mathbf{b}^*$ plane. At such a small absolute value of momentum transfer, these data are comparable to those from optical techniques.

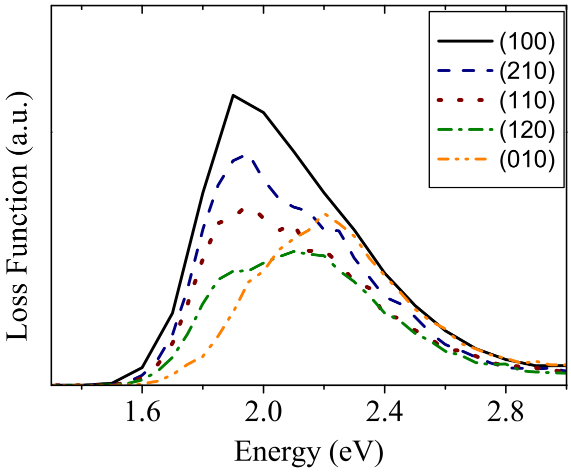

Fig. 1. (Color online) The loss function of pentacene for momentum transfers parallel to the different direction in reciprocal space within the $\mathbf{a}^*$, $\mathbf{b}^*$ plane (see labels (hk0)). The absolute value of momentum transfer is 0.1 Å^{-1}, consequently these data are comparable to those from optical studies with a light polarization vector in the direction of the corresponding $\mathbf{q}$ vector.

Figure 1 reveals that the loss function is considerably anisotropic in the $\mathbf{a}^*$, $\mathbf{b}^*$ plane. The lowest lying excitation at around 1.8 eV, which is strongest for $\mathbf{q} \parallel \mathbf{a}^*$ continuously decreases in spectral weight upon turning the momentum vector to the $\mathbf{b}^*$ direction. At higher energies, the data exhibit much less anisotropy. These results are in good agreement with those from optical studies of pentacene single crystals [14,30–32]. As mentioned in the introduction, this anisotropy has been explained by the existence of two Davydov components in pentacene, in correspondence to other organic molecular crystals. Starting from a local approach, and describing the lowest lying exciton as the lowest Davydov component related to a Frenkel exciton, one would predict a particular momentum dependence of the spectral weight for momentum vectors parallel to the reciprocal lattice vectors $\mathbf{a}^*$ and $\mathbf{b}^*$. In general, EELS probes collective, longitudinal excitations [33], and thus the excitation dipoles of different molecules oscillate parallel to each other. Furthermore, the momentum of the excitation provides a description of the phase or wave length of these dipoles. Consequently, at a momentum corresponding to a wave length λ with $q = 2\pi/\lambda = a^*$ or b^*, the excitation dipole components of the two inequivalent molecules in the unit cell parallel to the direction in question (giving rise to the Davydov splitting) would have opposite phase, in other words, the spectral weight should be minimal (zero) while it is maximal at small q and vice

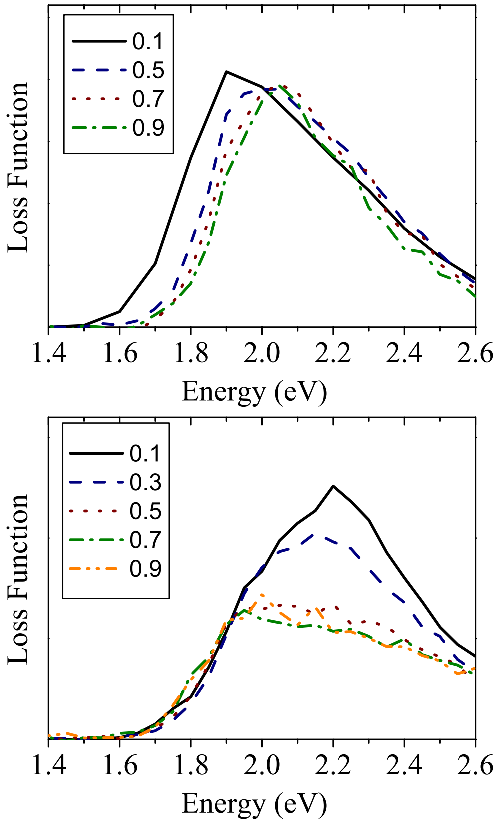

Fig. 2. (Color online) Momentum dependence of the loss function for different momentum transfers given in Å^{-1}. The upper panel shows the evolution of the loss function for momentum vectors $\mathbf{q}$ parallel to the $\mathbf{a}^*$ reciprocal lattice direction. The lower panel depicts the loss function for momentum vectors $\mathbf{q}$ parallel to the $\mathbf{b}^*$ reciprocal lattice direction. The curves are labelled by the absolute value of the momentum transfer, q, in Å^{-1}.

versa. Thus, upon increasing q the intensity of the lowest lying feature for $\mathbf{q} \parallel \mathbf{a}^*$ should result in an intensity decrease until the excitation has vanished at $q = a^*$, while for $\mathbf{q} \parallel \mathbf{b}^*$ the intensity should reach its maximum at $q = b^*$. This now can be tested going to higher momentum transfers in our EELS experiment.

In Figure 2 we show the evolution of the loss function for increasing momentum along $\mathbf{a}^*$ and $\mathbf{b}^*$. The upper panel of Figure 2 reveals the loss function for momentum transfers $\mathbf{q}$ parallel to the $\mathbf{a}^*$ reciprocal lattice direction, while the lower panel shows the corresponding data for $\mathbf{q} \parallel \mathbf{b}^*$. The curves are labelled according to the absolute value of momentum transfer in Å^{-1}. For $\mathbf{q} \parallel \mathbf{a}^*$, the data clearly reveal a continuous shift to higher energies upon increasing momentum transfer, as has been discussed in detail recently [18,19]. Importantly, the momentum dependent changes as seen in Figure 2 are inconsistent with an intensity decrease for larger momenta, contrary to the expectation for the lower Davydov component outlined above.

The results for $\mathbf{q} \parallel \mathbf{b}^*$ exhibit surprising variation of the spectral shape as a function of momentum. While for energies below 2 eV the loss function hardly changes, there is a significant and unexpected decrease of spectral weight of the broad structure centered at about 2.2 eV when going to larger momentum up to about 0.5 Å^{-1}. For $q > 0.5$ Å^{-1}, the data are barely momentum dependent at all. Consequently, we do not observe the appearance of an excitation feature below 2 eV which could be associated with the above mentioned lower Davydov component. In addition, different from $\mathbf{q} \parallel \mathbf{a}^*$ there is virtually no dispersion along $\mathbf{b}^*$. The strong intensity decrease at higher energies indicates that the electronic excitations responsible for this behavior are dipole allowed. If we assumed that this excitation vanishes at about 0.5 Å^{-1}, the momentum dependent decrease of its spectral weight would correspond to an extension of the excited state wave function of about 15 Å, much larger than a unit cell dimension in the $\mathbf{a}$, $\mathbf{b}$ plane of pentacene. Thus, this excitation most likely has a strong charge transfer character. Previous studies have indeed discussed the excitations above 2 eV in terms of charge transfer excitations/excitons [14,34].

Coming back to the excitations at energies below 2 eV, our results demonstrate that the spectral weight of the lowest lying excitons do not follow the expectation from a simple Frenkel-type picture. Thus, they point to a modification or extension of this approach. This is in line with our recent analysis of the dispersion of these excitons within the $\mathbf{a}^*$, $\mathbf{b}^*$ plane of pentacene which has shown that this dispersion cannot be modelled within a tight-binding approach based upon next nearest neighbor interactions [18]. Interestingly, recent calculations [15–17] predict a charge distribution of the lowest lying singlet exciton which is predominantly of charge transfer type. A comparison of their results to our ones above reveals a qualitative agreement of the polarization dependence [35]. Moreover, these calculations also predict excitations of electronic origin at energies above 2 eV which could give rise to the observed momentum dependent spectral weight. Furthermore, calculations of the electronic polarization in pentacene single crystals report interaction energies of cation-anion pairs, which represent charge transfer electron-hole pairs, of the order of 0.6–0.7 eV [36]. In consideration of the transport energy gap, which is a measure for uncorrelated, unbound electron-hole pairs and which is reported to be 2.2–2.6 eV [28,29], one would also expect charge transfer excitons at energies below 2 eV.

4 Summary

To summarize, we have presented an experimental study of the low lying electronic excitation in pentacene single crystals using electron energy-loss spectroscopy. Our results demonstrate that the spectral weight of the singlet excitons in pentacene is strongly dependent on the direction as well as the absolute value of the momentum. This cannot be fully modelled using Frenkel-type excitons only. These results therefore ask for a reconsideration of the theoretical, microscopic picture for the excitons in pentacene, and probably also in other organic molecular solids.

We are grateful to R. Hübel, R. Schönfelder and S. Leger for technical assistance.

References

1. N. Karl, in *Organic Electronic Materials* (Springer, Berlin, 2001), and references therein
2. R.W.I. de Boer, M.E. Gershenson, A.F. Morpurgo, V. Podzorov, Physica Status Solidi A **201**, 1302 (2004), and references therein
3. G. Horowitz, J. Mater. Res. **19**, 1946 (2004), and references therein
4. O.D. Jurchescu, J. Baas, T.T.M. Palstra, Appl. Phys. Lett. **84**, 3061 (2004)
5. S.P. Park, S.S. Kim, J.H. Kim, C.N. Whang, S. Im, Appl. Phys. Lett. **80**, 2872 (2002)
6. C. Voz, J. Puigdollers, I. Martin, D. Munoz, A. Orpella, M. Vetter, A. Alcubilla, Solar Energy Mat. Solar Cells **87**, 567 (2005)
7. M. Obarowska, R. Signerski, J. Godlewski, J. Luminescence **112**, 337 (2005)
8. Y.-Y. Noh, D.-Y. Kim, K. Yase, J. Appl. Phys. **98**, 074505 (2005)
9. E.A. Silinsh, *Organic molecular crystals* (Springer, Berlin, 1980), and references therein
10. M. Pope, C.E. Swenberg, *Electronic processes in organic crystals and polymers* (Oxford University Press, Oxford (1999), and references therein
11. D.P. Craig, S.H. Walmsley, *Excitons in Molecular Crystals* (W.A. Benjamin Inc., New York, 1968)
12. A.S. Davydov, *Theory of Molecular Excitons* (Plenum Press, New York, 1971)
13. J. Frenkel, Phys. Rev. **37**, 1276 (1931)
14. Y.P. Piryatinskii, Sov. Phys. Solid State **31**, 664 (1989)
15. M.L. Tiago, J.E. Northrup, S.G. Louie, Phys. Rev. B **67**, 115212 (2003)
16. K. Hummer, C. Ambrosch-Draxl, Phys. Rev. B **71**, 081202(R) (2005)
17. K. Hummer, C. Ambrosch-Draxl, Phys. Rev. B **72**, 205205 (2005)
18. R. Schuster, M. Knupfer, H. Berger, Phys. Rev. Lett. **98**, 037402 (2007)
19. M. Knupfer, H. Berger, Chem. Phys. **325**, 92 (2006)
20. M. Knupfer, Surf. Sci. Rep. **42**, 1 (2001)
21. M. Knupfer, T. Pichler, M.S. Golden, J. Fink, M. Murgia, R.H. Michel, R. Zamboni, C. Taliani, Phys. Rev. Lett. **83**, 1443 (1999)
22. M. Knupfer, J. Fink, E. Zojer, G. Leising, D. Fichou, Chem. Phys. Lett. **318**, 585 (2000)
23. M. Knupfer, T. Pichler, M.S. Golden, J. Fink, A. Rinzler, R.E. Smalley, Carbon **37**, 733 (1999)
24. M. Knupfer, T. Schwieger, J. Fink, K. Leo, M. Hoffmann, Phys. Rev. B **66**, 035208 (2002)
25. J. Fink, N. Nücker, E. Pellegrin, H. Romberg, M. Alexander, M. Knupfer, J. Electron Spec. Relat. Phenom. **66**, 395 (1994)
26. J. Fink, Adv. Electron. Electron Phys. **75**, 121 (1989)
27. C.C. Mattheus, A.B. Dros, J. Baas, G.T. Oostergetel, A. Meetsma, J.L. de Boer, T.T.M. Palstra, Synth. Met. **138** (2003) 475
28. D.V. Lang, X. Chi, T. Siegrist, A.M. Sergent, A.P. Ramirez, Phys. Rev. Lett. **93**, 086802 (2004)
29. F. Amy, C. Chan, A. Kahn, Org. Electronics **6**, 85 (2005)
30. A.F. Prikhotko, A.F. Skorobogatko, L.I. Tsikora, Optics and Spectroscopy **26**, 524 (1969)
31. D. Faltermeier, B. Gompf, M. Dressel, A.K. Tripathi, J. Pflaum, Phys. Rev. B **74**, 125416 (2006)
32. M. Grobosch, R. Schuster, T. Pichler, M. Knupfer, H. Berger, Phys. Rev. B **74**, 155202 (2006)
33. H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons* (Springer, Heidelberg, 1980), and references therein
34. L. Sebastian, G. Weiser, H. Baessler, Chem. Phys. **61**, 125 (1981)
35. K. Hummer, P. Puschnig, S. Sagmeister, C. Ambrosch-Draxl, Mod. Phys. Lett. B **20**, 261 (2006)
36. E.V. Tsiper, Z.G. Soos, Phys. Rev. B **68**, 085301 (2003)