Exciton dynamics in different aromatic hydrocarbon systems

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The exciton dispersion is examined in the case of four selected prototypical molecular solids (pentacene, tetracene, picene, chrysene). The model parameters are determined by the nonlinear fits to the experimental dispersion data obtained by inelastic electron scattering. Within the picture that relies on Frenkel-type excitons we obtain that theoretical dispersion curves along different directions in the Brillouin zone are in good agreement with the experimental data, suggesting that the influence of charge-transfer excitons on exciton dispersion of the analyzed organic solids is not as large as proposed. In reciprocal space directions where Davydov splitting is observed we employ the upgraded version of Hamiltonian used in Materials 11, 2219 (2018).

I. INTRODUCTION

Organic semiconductors have been in the focus of both theoretical and experimental studies for decades. This comprehensive research has been motivated by the wide field of their application in novel (opto)electronic devices [1–5]. Besides, it has been observed that some of them, picene for example, exhibit the transition into the superconducting state at rather high transition temperatures [6]. Therefore, the microscopic properties of aromatic hydrocarbons, in particular their exciton dynamics, present the subject of great interest.

Electron energy-loss spectroscopy is an experimental technique that has been recently widely used for direct measurements of the exciton band structure in aromatic hydrocarbons [7–13]. These experiments inspired significant theoretical work based on the first principles, i.e. starting from many-body electron-hole Hamiltonians [14–18]. In these papers it is suggested that exciton dispersion in the organic molecular solids known as phenacenes (picene, chrysene) can be understood within the Frenkel-exciton picture, whereas the contribution of charge-transfer CT excitons are completely ignored, the pentacene excitons in two-level systems and their predominant nearest neighbour interaction, the basic Hamiltonian is given by

\[ H = H_0 + \Delta \sum_n P_n^+ P_n - \frac{X}{2} \sum_{n,\lambda} P_n^+ P_{n+\lambda} \]

where \(P_n^+\) and \(P_n\) represent standard Pauli operators on the site \(n\), whereas parameters \(X\) and \(Y\) respectively describe hopping and interactions of excitons [21, 22]. In a two-level system it is possible to find exact mapping between Pauli Hamiltonian (1) and anisotropic (XXX) Heisenberg Hamiltonian in external field [19]

\[ H = -\frac{I_x}{2} \sum_{n,\lambda} S_n^{-} S_{n+\lambda}^+ - \frac{I_z}{2} \sum_{n,\lambda} S_n^z S_{n+\lambda}^z - \mu \mathcal{H} \sum_n S_n^z. \]

Parameters \(I_x, I_z, \mu \mathcal{H}\) are the exchange integral components, \(\mathcal{H}\) represents external field, while vectors \(\{\lambda\}\) connect nearest neighboring sites. Correspondence between model parameters

\[ I_x = Y, \quad I_z = X, \quad \mu \mathcal{H} = \Delta - \frac{I_z^2}{2} \]

is justified due to the isomorphism of paulion Hilbert space \(\mathcal{H}_p\) and spin Hilbert space \(\mathcal{H}_s\). This procedure, which is purely theoretical, is motivated by the fact that the literature referring to spin systems and the theoretical tools therein developed are significantly richer [23–31].

Note also that, in case of aromatic hydrocarbons analyzed in this paper, the set of neighboring sites connected with hopping integrals splits into three subsets

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determined by the lattice structure and values of hopping parameters.

We shall now focus on the structure of the polycyclic aromatic hydrocarbon systems studied in this paper. Due to the molecular structure differences, tetracene and pentacene belong to the so-called acenes family, while picene and chrysene represent the examples of phenacenes. The former two crystallize in triclinic and the latter two in monoclinic crystal system. However, since the carrier mobility along $c^*$ is significantly smaller in comparison to the in-plane one [32], these structures can be treated as quasi-two-dimensional. The lattice parameters relevant for the further calculations are given in Table I.

A 2D sketch of all analyzed crystal structures is shown in Fig. 1. In case of phenacenes angle between directions $a$ and $b$ is 90° (gray-scale sketch), whereas for acenes (colored image) direction $b$ is slightly shifted, i.e. close to 90° (see Table I). Therefore, we approximate acenes’ lattice by introducing the additional constraint $a \cdot b = 0$ [8, 19]. For all structures shown in Fig. 1, central motive has three types of neighbors: two neighbors at points $A = \{a, -a\}$ coupled trough exchange integral $I_1$, two neighbors at points $B = \{b, -b\}$ coupled through exchange integral $I_2$ and four neighbors at points $C = \{a+b, a-b, a+b, a-b\}$ coupled via exchange integral $I_3$. As we have already stated, the mapping between paulion and Heisenberg Hamiltonian demands anisotropic exchange interactions. As a consequence, all exchange integrals possess $x$ and $z$ components: $I_\alpha \rightarrow (I_{1\alpha}^x, I_{1\alpha}^z)$, where $\alpha = 1, 2$ or 3.

We have shown that bosonization of the Hamiltonian (2) in Bloch approximation is sufficient to reproduce exciton dispersion in pentacene in Brilloin zone directions where Davydov splitting is not observed [19]. However, in order to reproduce both Davydov components, at each lattice site $n$ we define a set of boson occupation states $\{|N_A\rangle_n \otimes |N_B\rangle_n\}$, where indices A and B refer to different Davydov components. Therefore, we upgrade Bloch Hamiltonian by introducing direct sum

$$\tilde{H} = \tilde{H}_A \oplus \tilde{H}_B.$$  

The corresponding Hamiltonians are then defined by

$$\tilde{H}_A = \tilde{H}_0' + \sum_k E_A(k)B_A^k B_A^k,$$  

$$\tilde{H}_B = \tilde{H}_0' + \sum_k E_B(k)B_B^k B_B^k,$$  

where boson commutation relations read

$$[B_{ik}, B_{jq}^\dagger] = \delta_{ij} \delta_{k,q},$$  

$$[B_{ik}, B_{jq}] = [B_{ik}^\dagger, B_{jq}^\dagger] = 0, \quad i, j = A, B.$$  

Exciton dispersion $E_{A/B}(k)$ is given by

$$E_{A/B}(k) = \Delta_{A/B} - I_{A/B}^x \cos(k \cdot a) - I_{A/B}^z \cos(k \cdot b) - 2I_{3A/B}^x \cos\left(\frac{k \cdot a}{2}\right) \cos\left(\frac{k \cdot b}{2}\right),$$  

where

$$\Delta_A = \Delta_B = \Delta = I_1 + I_2 + 2I_3^x + \mu \mathcal{H}.$$  

Since we have shown earlier [19] that the influence of the exciton-exciton interaction is negligible in whole temperature range, we can use the same exchange integrals to reproduce experimental data obtained at different temperatures, whereas the gap $\Delta$ changes with temperature due to the change of the external field $\mathcal{H}$. Experiments show that in Brillouin zone directions along which Davydov splitting is observed the upper Davydov component presents the mirror-like image of the lower one [10, 12]. Therefore, we impose that the exchange integrals which correspond to different Davydov components are related by $I_{3B}^x = -I_{3A}^x$, $\alpha = 1, 2, 3$. In next Section we shall present our results for exciton dispersion in pentacene and tetracene (IIIA.) and picene and chrysene (IIIB.).

### III. RESULTS AND DISCUSSION

#### A. Pentacene and tetracene

By fitting (8) to experimental data for pentacene taken from [10] we obtain the following set of parameters: $\Delta = 1.915$ eV, $I_{1A}^x = 3.2$ meV, $I_{2A}^x = 2.2$ meV, $I_{3A}^x =$
38.2 meV. Exciton dispersion for this parameter set along different reciprocal \( a^* b^* \) plane directions is shown in Fig. 2, together with the experimental data from \([10]\). As can be seen from Fig. 2, exciton dispersion obtained without taking CT excitons into account is in a good agreement with the experimental data. Let us note that in Fig. 2(a), where Davydov splitting is observed, upper branch (B) is obtained by inverting the sign of the exchange integrals \( I_{\alpha} \) of the lower one (A). Hereafter, we shall use green colour for the lower branches and red for the upper ones. With the same exchange integrals we obtain dispersion at room temperature \( (T = 300 \text{ K}) \), which is shown in Fig. 3 together with the experimental data from \([8]\). Let us emphasize that since we have used a single set of model parameters, the plotted dispersion law displays the unique limit, which at \( T = 20 \text{ K} \) equals \( \Delta - I_{\alpha} - I_{\beta} - 2I_{\gamma} = 1.83881 \text{ eV} \) as \( |k| \to 0 \), while at \( T = 300 \text{ K} \) it amounts to 1.75381 eV due to the difference in the gap value \( \Delta \).

Theoretical curves in Fig. 2,3 will look like straight lines if we plot \( E(k) \) in wider energy range. This is due to the fact that \( I_{\alpha b} / \Delta \to 0 \). Minor deviations of the theoretical curves from the experimental data are attributed to the presence of other excitations in the system. However, their influence is small in comparison with the Frenkel excitons.

Following analogous procedure, we investigate tetracene, another acenes family hydrocarbon with the larger band gap. Using available experimental data from \([12]\), we obtain the corresponding parameter set. Due to the similarity between pentacene and tetracene structures, we use the same exchange integral component inversion rule to reproduce both Davydov branches. Our results along two different Brillouin zone directions together with the available experimental data are shown in Fig. 4.

As in pentacene case, theoretical curves periodicity follows experimental data. In the vicinity of \( k = 0.8 \text{ Å}^{-1} \) the discrepancy between experimental values and theoretical predictions may originate from the low accuracy with which the measurement was performed in that region \([12]\). Analysis of Fig. 4 shows that the total band width is roughly twice smaller than in pentacene, leading
FIG. 4. Exciton dispersion in tetracene along two different directions in reciprocal lattice. Experimental data at $T = 20$ K are taken from [12]. Theoretical curves are obtained for: $\Delta = 2.405$ eV, $I_{1\alpha} = 5.7$ meV, $I_{2\alpha} = 0.4$ meV, $I_{3\alpha} = 19.8$ meV.

TABLE II. Transport energy gaps ($E_g$) for studied structures vs. calculated optical gaps ($\Delta$) together with the corresponding $|I_x|$ values (at $T = 20$ K)

| Structure  | $E_g$ [eV] | $\Delta$ [eV] | $|I_x|$ [meV] |
|------------|------------|---------------|--------------|
| pentacene  | 2.2 [36, 37] | 1.915 | 38.2 |
| tetracene  | 3.3 [36, 37] | 2.405 | 19.8 |
| picene     | 4.05 [38, 39] | 3.249 | 2.8 |
| chrysene   | 4.2 [39] | 3.4 | 2.8 |

FIG. 5. 3D plot of exciton dispersion in pentacene at $T = 20$ K. Parameter set is the same as in Fig. 2.

FIG. 6. Exciton dispersion in picene along three different directions in reciprocal lattice. Experimental data at $T = 20$ K are taken from [13]. Theoretical curves are obtained for: $\Delta = 3.249$ eV, $I_{1\alpha} = 2.8$ meV, $I_{2\alpha} = 2$ meV, $I_{3\alpha} = 2.8$ meV.

B. Picene and chrysene

Applying the same procedure for the phenacenes picene and chrysene, we obtain the exciton dispersion within the reciprocal $a^*b^*$ plane and compare it to the experimental data from [9, 13] (see Figs. 6, 7). Due to the pronounced similarity between the crystal structures of these molecular solids, we were able to reproduce the experimental data for both hydrocarbons in satisfactory manner with the same exchange integrals set. Comparing the exchange integrals $x$-components with those for acenes, we notice that in case of phenacenes the value of
FIG. 7. Exciton dispersion in chrysene along three different directions in reciprocal lattice. Experimental data at $T = 20\, \text{K}$ are taken from $[13]$. Theoretical curves are obtained for: $\Delta = 3.4\, \text{eV}$, $I_{x1} = 2.8\, \text{meV}$, $I_{x2} = 2\, \text{meV}$, $I_{x3} = 2.8\, \text{meV}$.

$E(k)$ is significantly smaller. This is attributed to the fact that the band gap (and consequently the optical gap) in phenacenes is larger than in acenes (see Table II).

By inspection of Figs. 6, 7 we notice that dispersion in case of phenacenes is more isotropic. Further, the total band width is approximately 10 meV, which is roughly ten times smaller value than for acenes.

Analogous to IIIA, we present the three-dimensional plot of exciton dispersion in picene (Fig. 8).

IV. CONCLUSION

We analyze the exciton dispersion in different molecular solids relying on the correspondence between Pauli (1) and Heisenberg (2) Hamiltonians. Following standard Bloch bosonization procedure we obtain exciton dispersion relation. In order to investigate Davydov splitting phenomenon, we use the upgraded model Hamiltonian introduced in this paper (4). By fitting exchange integrals to the experimental results, we obtain exciton dispersions that possess the same periodicity as experimental data. Analyses of dispersion curves show that in the acenes (pentacene and tetracene) the dispersion is rather anisotropic, contrary to the phenacenes (picene and chrysene) where it is more isotropic and almost constant. As regards the phenacenes, our results corroborate the earlier stated conclusion [9, 13] that the lowest-lying excitations in picene and chrysene are localized Frenkel excitons. However, we obtain that the experimental data for pentacene and tetracene can also be satisfactorily reproduced within the noninteracting exciton picture. Therefore, we suggest that the influence of the CT excitons on exciton dispersion in acenes is not as large as claimed earlier. Further, it can be seen that the dispersion curves along different Brillouin zone directions for given molecular solid tend to the same value as $k \to 0$. This reflects the fact that the single parameter set is used for all $k$-space directions, unlike [8]. Comparative study of analyzed hydrocarbons shows that the magnitudes of the optical gap $\Delta$ and the exchange integral $I^2$ are inversely proportional. Therefore, in phenacenes the carrier mobility is smaller, i.e. the exciton-exciton interaction is weaker than in acenes. However, despite those differences, our calculations based on Frenkel exciton model reproduce the experimental data for all analyzed hydrocarbons in satisfying manner. This suggests that small variations of the exciton dispersion should not be connected with the applicability of the Frenkel exciton model. In order to corroborate this statement, a variety of examples can be found in the magnon dispersion analyses for different magnetic insulators [40–43]. In order to further test our suggested model, additional measurements of exciton dispersion where Davydov splitting is observed are required.

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[1] M. Gershenson, V. Podzorov, and A. Morpurgo, Rev. Mod. Phys. 78, 973 (2006).

[2] P. Peumans, S. Uchida, and S. R. Forrest, in Materials for Sustainable Energy: A Collection of Peer-Re
viewed Research and Review Articles from Nature Publishing Group (World Scientific, 2011) pp. 94–98.

[3] M. A. Baldo, D. O’Brien, Y. You, A. Shoustikov, S. Sibley, M. Thompson, and S. R. Forrest, Nature 395, 151 (1998).

[4] S. R. Forrest, Nature 428, 911 (2004).

[5] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, Nat. Mater. 4, 864 (2011).

[6] R. Mitsuhashi, Y. Suzuki, Y. Yamanari, H. Mitamura, T. Kambe, N. Ikeda, H. Okamoto, A. Fujiwara, M. Yamaji, N. Kawasaki, et al., Nature 464, 76 (2010).

[7] M. Knupfer and H. Berger, Chem. Phys. 325, 92 (2006).

[8] R. Schuster, M. Knupfer, and H. Berger, Phys. Rev. Lett. 98, 037402 (2007).

[9] F. Roth, B. Mahns, B. Büchner, and M. Knupfer, Phys. Rev. B 83, 165436 (2011).

[10] F. Roth, R. Schuster, A. König, M. Knupfer, and H. Berger, J. Chem. Phys. 136, 204708 (2012).

[11] F. Roth, B. Mahns, S. Hampel, M. Nohr, H. Berger, B. Büchner, and M. Knupfer, Eur. Phys. J. B 86, 66 (2013).

[12] F. Roth, M. Nohr, S. Hampel, and M. Knupfer, EPL 112, 37004 (2015).

[13] F. Roth and M. Knupfer, J. Electron Spectrosc. 204, 23 (2015).

[14] P. Cudazzo, M. Gatti, and A. Rubio, Phys. Rev. B 86, 195307 (2012).

[15] P. Cudazzo, M. Gatti, A. Rubio, and F. Sottile, Phys. Rev. B 88, 195152 (2013).

[16] P. Cudazzo, F. Sottile, A. Rubio, and M. Gatti, J. Phys.: Condens. Matter 27, 113204 (2015).

[17] L. Kronik and J. B. Neaton, Annu. Rev. Phys. Chem. 67, 587 (2016).

[18] S. Sharifzadeh, P. Darancet, L. Kronik, and J. B. Neaton, J. Phys. Chem. Lett. 4, 2197 (2013).

[19] S. Gombar, P. Mali, M. Pantić, M. Pavkov-Hrvojević, and S. Radošević, Materials 11, 2219 (2018).

[20] A. S. Davydov, Soviet Physics Uspekhi 7, 145 (1964).

[21] V. Agranovich, Excitations in organic solids (Oxford University Press, 2008).

[22] V. Agranovich and B. Toshich, Sov. Phys. JETP 26, 104 (1968).

[23] S. V. Tyablikov, Methods in the Quantum Theory of Magnetism (Springer, 1967).

[24] P. Frbrich and P. Kuntz, Phys. Rep. 432, 223 (2006).

[25] A. Auerbach, Interacting electrons and quantum magnetism (Springer, 2012).

[26] E. Manousakis, Rev. Mod. Phys. 63, 1 (1991).

[27] W. Nolting and A. Ramakanth, Quantum theory of magnetism (Springer, 2009).

[28] A. W. Sandvik and J. Kurkijärvi, Phys. Rev. B 43, 5950 (1991).

[29] M. R. Pantić, D. V. Kapor, S. M. Radošević, and P. M. Mali, Solid State Commun. 182, 55 (2014).

[30] C. P. Hofmann, Phys. Rev. B 60, 388 (1999).

[31] C. P. Hofmann, Phys. Rev. B 86, 054409 (2012).

[32] V. Stehr, J. Pfister, R. F. Fink, B. Engels, and C. Deibel, Phys. Rev. B 83, 155208 (2011).

[33] J. Cornil, J. P. Calbert, and J. L. Brdas, J. Am. Chem. Soc. 123, 1250 (2001).

[34] D. Holmes, S. Kumaraswamy, A. J. Matzger, and K. P. C. Vollhardt, Chem. Eur. J. 5, 3399 (1999).

[35] F. Roth, B. Mahns, R. Schönfelder, S. Hampel, M. Nohr, B. Büchner, and M. Knupfer, J. Chem. Phys. 137, 114508 (2012).

[36] F. Amy, C. Chan, and A. Kahn, Org. Electron. 6, 85 (2005).

[37] N. Sato, K. Seki, and H. Inokuchi, J. Chem. Soc. Faraday Trans. 77, 1621 (1981).

[38] F. Roth, M. Gatti, P. Cudazzo, M. Grobosch, B. Mahns, B. Büchner, A. Rubio, and M. Knupfer, New J. Phys. 12, 103036 (2010).

[39] N. Sato, H. Inokuchi, and E. A. Silinsh, Chem. Phys. 115, 269 (1987).

[40] A. Läuchli, F. Mila, and K. Penc, Phys. Rev. Lett. 97, 087205 (2006).

[41] L. Passell, O. W. Dietrich, and J. Als-Nielsen, Phys. Rev. B 14, 4907 (1976).

[42] O. W. Dietrich, J. Als-Nielsen, and L. Passell, Phys. Rev. B 14, 4923 (1976).

[43] S. Radošević, M. Pavkov-Hrvojević, M. Pantić, M. Rtonjksi, D. Kapor, and M. Škrinjar, Eur. Phys. J. B 68, 511 (2009).