

## Interpretation of the Ultrafast Photoinduced Processes in Pentacene Thin Films

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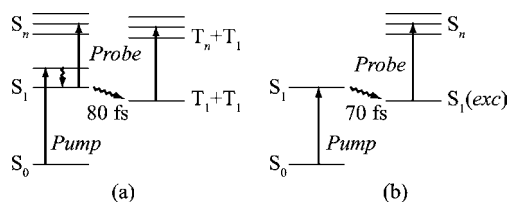
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**Abstract:** Ambiguity remains in the models explaining the photoinduced dynamics in pentacene thin films as observed in pump–probe experiments. One model advocates exciton fission as governing the evolution of the initially excited species, whereas the other advocates the formation of an excimeric species subsequent to excitation. On the basis of calculations by a combined quantum mechanics and molecular mechanics (QM/MM) method and general considerations regarding the excited states of pentacene we propose an alternative, where the initially excited species instead undergoes internal conversion to a doubly excited exciton. The conjecture is supported by the observed photophysical properties of pentacene from both static as well as time-resolved experiments.

### 1. Introduction

Thin films of organic molecular solids have been used to realize a great variety of (opto)electronic devices.<sup>1–3</sup> This is in part due to the plethora of intriguing phenomena and remarkable properties exhibited by these systems such as localization of charge carriers, neutral excitations in form of excitons, energy transport by exciton diffusion, exciton–exciton interactions, anisotropy of optical and electrical parameters, etc.<sup>4–9</sup> Understanding the governing principles of these processes and properties is crucial for device performance, whence the study of the fate of primarily singlet excitons formed by photoexcitation is essential.<sup>10</sup>

Due to its formation of well-ordered thin films and high charge-carrier mobility, pentacene has been the focus of much research.<sup>3</sup> However, deliberations are still ongoing for the correct



**Figure 1.** Models for pentacene thin film dynamics based on pump–probe experiments. (a) Subsequent to excitation internal conversion populates the lowest singlet exciton. In 80 fs the singlet exciton undergoes a fission process yielding two triplet excitons.<sup>12</sup> (b) Subsequent to excitation the system relaxes to an excimer geometry by rotation of the unit cell molecules in 70 fs.<sup>13</sup>

description of the excited states of crystalline pentacene.<sup>11</sup> Furthermore, the photoinduced dynamics in pentacene thin films, i.e. the evolution of the initially excited singlet exciton, has been explained in terms of two contradictory models based on the results of two similar pump–probe experiments.<sup>12–15</sup> One model advocates that the evolution of the excited species is governed by the process of exciton fission, whereby one singlet exciton decays into two spatially separated triplet excitons in 80 fs,<sup>12</sup> cf. Figure 1a. In this interpretation it is the  $S_n \leftarrow S_1$  transitions that are probed at very short time delays, whereas  $T_n \leftarrow T_1$  transitions are probed after the fission process populates the

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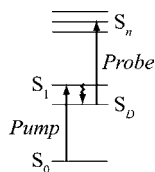
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**Figure 2.** New model that is in line with the photophysical properties of pentacene and the pump–probe experiments. Subsequent to excitation internal conversion leaves the system in the doubly excited singlet exciton. Consequently,  $S_n \leftarrow S_D$  transitions are probed.

triplet manifold. The other model advocates that an excimer-like species is formed on the singlet exciton potential energy surface in 70 fs, whereby  $S_n \leftarrow S_1(exc)$  transitions are probed,<sup>13</sup> where the suffix *exc* denotes the relaxed excimer structure, cf. Figure 1b. The picosecond dynamics following the excimer formation until the return of the species to the ground state after  $\sim 1$  ns has been determined in a model that extends the model presented in Figure 1b. The extended model, however, retains the features of the simpler model specifically the excitation to  $S_1$  and subsequent relaxation to  $S_1(exc)$ .<sup>15</sup>

The disambiguation of the photoinduced dynamics is the main focus of this paper. The interest is thus focused on the electronic excitations of the pentacene molecular crystal, the so-called excitons. As the excitons can qualitatively be distinguished in terms of the excitations of the unit cell dimer, the excited states of this dimer are presented, and these will continuously serve as reference points throughout. Furthermore, the electronic configurations of a model system describing these dimer states are introduced, which present the possibility of not only singly excited but also doubly excited states. A particular singlet state of the latter type, the triplet coupled doubly excited state and the corresponding exciton of the crystal, will later be proposed to play an important role in the photoinduced dynamics.

The discussion of the excimer model also takes as its starting point the excited states of the pentacene dimer calculated by linear response density functional theory (DFT).<sup>16,17</sup> However, to be able to account for the crystalline environment of one unit cell dimer a combined quantum mechanics and molecular mechanics method (QM/MM)<sup>18–20</sup> is employed. This method not only represents the discrete environment by point charges but also by atom-centered polarizabilities. The possibility of excimer formation in the lowest excited state can hereby be investigated. The fission model is discussed based on general considerations regarding triplet excitons as well as the results of the pump–probe experiments on pentacene thin films presented in the literature.<sup>12,13,15</sup>

Neither the excimer nor the fission model can be reconciled with the results and arguments presented. Therefore, it is proposed that the doubly excited exciton  $S_D$  is the lowest excited species in the singlet spin manifold consequently leading to an interpretation in terms of a new model explaining the photoinduced dynamics, cf. Figure 2. In this interpretation the short fs time scale found in the experiments corresponds to internal

conversion from the initially excited species to the doubly excited exciton, which thus plays a prominent role. The new model can be reconciled with the observed photophysical properties of pentacene from both static as well as time-resolved experiments.

## 2. Computational Methods

**2.1. Calculations on the Pentacene Dimer.** The structure of pentacene was geometry optimized at the B3LYP/6-31G(d) level of theory in Gaussian 03.<sup>21</sup> A pentacene dimer was constrained to  $D_{2h}$  symmetry. The intermolecular distance was scanned, and the two lowest excitation energies belonging to each irreducible representation of the  $D_{2h}$  point group were calculated using linear response DFT with the exchange–correlation functional CAM-B3LYP<sup>22,23</sup> and the 6-31++G(d) basis set for separations in the interval from 2.80–10.00 Å in the Dalton Quantum Chemistry Program (QCP).<sup>24</sup> The step size ranged from 0.02 Å in the interval from 3.00–4.20 Å to 0.10 Å in the intervals from 2.80–3.00 Å and 4.20–6.00 Å and finally to 1.00 Å in the interval from 6.00–10.00 Å. CAM-B3LYP was chosen as B3LYP exhibit problems in dimer calculations,<sup>25</sup> and CAM-B3LYP has been shown to outperform B3LYP in these cases.<sup>26</sup> Linear response DFT is also known to yield too low excitation energies for charge-transfer states, however, CAM-B3LYP has been shown to consistently correct these errors and yield excitation energies in very good agreement with the results obtained in correlated calculations as well as with experimental data.<sup>22,23,27–30</sup>

**2.2. QM/MM Calculations.** The crystal structure of the thin film polymorph of pentacene on a TOPAS substrate was obtained as a cif file from the Supporting Information of ref 31. The combined DFT and MM calculations were performed using a local implementation of the QM/MM code<sup>20</sup> in the Dalton QCP. The partial charges for the MM region were calculated in Gaussian 03<sup>21</sup> at the B3LYP/aug-cc-pVTZ level of theory according to the CHELPG scheme<sup>32</sup> and distributed to reproduce the molecular dipole moment. Distributed polarizabilities centered on each atom in the MM region were calculated in MOLCAS<sup>33</sup> by the LoProp method<sup>34</sup> at the B3LYP/aug-cc-pVDZ level of theory. The energy contributions due to the van der Waals forces and short-range repulsion were taken into account using a Lennard-Jones 6–12 potential with the parameters  $\sigma_H = 2.42$  Å,  $\epsilon_H = 0.12552$  kJ/mol,

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$\sigma_c = 3.55 \text{ \AA}$ , and  $\epsilon_c = 0.29288 \text{ kJ/mol}$ .<sup>35</sup> These parameters were also assumed to be appropriate for the excited states. The QM region consisted of a unit cell pair of molecules, while the MM region was taken as the nearest neighbor molecules in the *ab*-plane of the crystal resulting in eight molecules in the MM region, see section 4.3. For all configurations the six lowest excitation energies were calculated using linear response DFT/MM with CAM-B3LYP and the 6-31++G(d) basis set.

### 3. Electron Configurations of Dimer States

To facilitate our discussion a brief description of the pertinent electronic states and configurations is given. As molecular crystals are held together by weak van der Waals forces, the electronic excited states of the crystal are readily derived from those of the free molecules.<sup>9</sup> Thus, a qualitative distinction between the excited states of the crystal can be obtained by looking at the excited states of a dimer as crystalline pentacene has two molecules in the unit cell. The zero-order wave functions of the excited states of a symmetric dimer of pentacene composed of two monomers denoted by *M* are given by linear combinations of product functions.<sup>36</sup> This gives rise to the so-called exciton and charge resonance states:

$$\text{Singlet exciton resonance: } {}^1M^*{}^1M \pm {}^1M^1M^* \quad (1)$$

$$\text{Singlet charge resonance: } {}^2M^{+2}M^- \pm {}^2M^{-2}M^+ \quad (2)$$

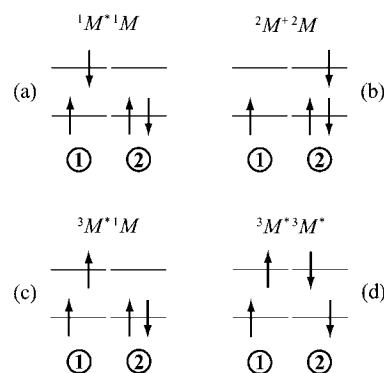
Here  ${}^1M^*$  indicates the lowest excited singlet of the monomer and  ${}^2M^-$  and  ${}^2M^+$  indicate the monomer anion and cation respectively. The exchange of the excitation energy between the two molecules of the dimer evident in the exciton resonance states in eq 1 gives rise to the so-called resonance interaction energy. This resonance interaction splits the plus and minus combinations of the exciton resonance states in two Davydov components differing in energy. One also has triplet exciton resonance states originating from the lowest triplet state of the monomer  ${}^3M^*$ :

$$\text{Triplet exciton resonance: } {}^3M^*{}^1M \pm {}^1M^3M^* \quad (3)$$

Configurations where both monomers are excited are also possible. In weakly interacting molecules spin-forbidden excitations on each molecule can interact and lead to new spin-forbidden and -allowed excitations in the dimer.<sup>37</sup> The coupling between the two systems can give rise to the doubly excited state in eq 4, which couples a triplet on each monomer into a total singlet spin configuration in the dimer.

$$\text{Singlet doubly excited: } {}^3M^*{}^3M^* \quad (4)$$

In certain cases, such as the case of pentacene, the lowest triplet energetically lies below half the energy of the lowest excited singlet. Therefore, the triplet coupled, doubly excited singlet state has to be considered as the energy of this state,  ${}^3M^*{}^3M^*$ , could be comparable to that of the singly excited configurations,  ${}^1M^*{}^1M \pm {}^1M^1M^*$ . When adopting a two-level two-electron model the components of the functions given in



**Figure 3.** Nonspin-adapted configurations of the components of the functions given in eqs 1–4. Configurations illustrate components of the (a) exciton resonance, (b) charge resonance, (c) triplet exciton resonance, and (d) doubly excited functions. (1) and (2) distinguish the two molecules of the dimer.

eqs 1–4 can be described by the nonspin-adapted configurations of Figure 3.<sup>36,38</sup>

In the crystal the excitations localized on the dimer in one unit cell will be delocalized over the crystal due to the regular lattice structure. The singlet and triplet exciton resonance states of the dimer,  ${}^1M^*{}^1M + {}^1M^1M^*$  and  ${}^3M^*{}^1M + {}^1M^3M^*$ , will thus become the excitons denoted by  $S_1$  and  $T_1$ , whereas the doubly excited state  ${}^3M^*{}^3M^*$  will become the doubly excited exciton  $S_D$ .

### 4. The Excimer Model

In this section we assess the plausibility of the excimer model based on the findings from linear response DFT and DFT/MM calculations.

**4.1. Crystal Excimers.** The formation of excimers in crystals has for example been observed for pyrene and  $\alpha$ -perylene based on the spectral features of the fluorescence.<sup>39–41</sup> The crystal structures of these species have the molecules arranged in parallel,<sup>42</sup> and the molecular arrangement is thus predisposed for the formation of excimers. In contrast, excimer formation has not been observed for  $\beta$ -perylene,<sup>40</sup> the crystal of which has the molecules arranged in a herringbone motif similar to that found for pentacene. Disregarding the case of very high defect concentration and high pressure this is a general observation for molecules adopting the two different arrangements in the crystal.<sup>42</sup> It should thus not be expected that excimer formation occurs in crystalline pentacene

**4.2. The  $D_{2h}$  Pentacene Dimer.** The excimer model used in explaining the observed photoinduced dynamics implies that a bound dimer exists between two pentacene molecules in the excited state, which is dissociative to a certain extent in the ground state. A simple indication of the plausibility of this assumption can be found by considering the excited states of a pentacene dimer having  $D_{2h}$  symmetry as a function of the interplanar separation. The lowest two states of the dimer are exciton resonance states originating from the lowest excited state of the monomer, cf. eq 1 and Figure 4. At large separation the energy of these states converge to the energy of the excited

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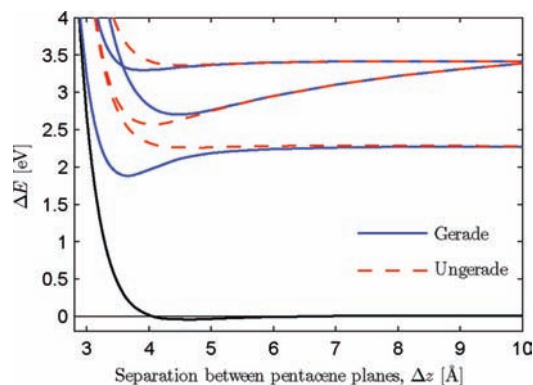
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**Figure 4.** Ground state and six lowest excited singlet states as a function of interplanar separation in a  $D_{2h}$  pentacene dimer. Energies are relative to the ground-state energy of the dimer at infinite separation between the two molecules.

state of the monomer. At higher energies two charge resonance states are identified by their increasing energy with separation. These states could be expected to be slightly too low in energy due to the imprecise long-range behavior of the CAM-B3LYP functional;<sup>22</sup> however, as discussed in section 2.1 CAM-B3LYP consistently yields very good excitation energies to charge-transfer states. Moreover, it is the lowest excited states, which are of interest.

From Figure 4 it can be seen that an excimer is formed in the lowest exciton resonance state at an interplanar distance of 3.66 Å. The excimer is stabilized by 0.26 eV with respect to the energy of the lowest excited state at an interplanar distance of 4.70 Å, where the minimum in the ground state is found. Furthermore, the excimer is stabilized by 0.39 eV with respect to dissociation in the lowest excited state. The rather large equilibrium distance in the ground state is most likely related to the known deficiency of DFT to describe the long-range electron correlation effect of dispersion due to the locality or semilocality of the exchange-correlation functionals employed.<sup>43–46</sup> Grimme has suggested an empirical correction to DFT, yielding the so-called DFT-D method, where an empirical potential of the form  $C_6 \cdot R^{-6}$  is added to the DFT energy.<sup>47,48</sup> The parametrization of the empirical potential requires the determination of an exchange-correlation functional dependent parameter  $s_6$ , which has been found for several standard functionals<sup>48,49</sup> such as B3LYP,<sup>50</sup> TPSS,<sup>51</sup> BLYP,<sup>52,53</sup> PBE,<sup>54</sup> and BH-LYP.<sup>52,53,55</sup> However, it is not known if the parametrization of the empirical potential is useful in the context of functionals including Coulomb attenuated operators such as CAM-B3LYP, the investigation of which is outside the scope of this paper. Furthermore, it could be expected that a reparametrization of the potential would be necessary, and an optimization of

parameters not only with respect to equilibrium structures and binding energies but full potential energy surfaces due to the distance dependence on the inclusion of exact-exchange. Nevertheless, optimizing the value of  $s_6$  from single-point CAM-B3LYP/TZV2P<sup>56</sup> calculations on the MP2 equilibrium structures of the sandwich, parallel-displaced and T-shaped benzene dimers from ref 57 with respect to the MP2/CCSD(T) binding energies<sup>57</sup> yields a value of 0.61 for  $s_6$ . Employing the dispersion correction of Grimme with this value of  $s_6$  for the pentacene dimer yields a more reasonable ground-state equilibrium distance of 3.74 Å. The optimal value of  $s_6$  is, however, seen to be substantially different for the superficial sandwich and parallel-displaced benzene dimers than the T-shaped benzene dimer substantiating the hesitations put forward. Importantly, the conclusions drawn from the dimer calculations with respect to the plausibility of excimer formation are not affected by the inclusion of a correction for dispersion, what will also be found for the QM/MM calculations, thus, no further corrections for dispersion will be employed.

The observation that a minimum is found in the lowest excited state seems to support the assumption of excimer formation in the crystal. Although the excited states of the unit cell dimer will only be slightly perturbed in the crystal, the surrounding molecules act as a cage inhibiting larger structural rearrangements. Thus, the resonance interaction between the two molecules that is responsible for the stabilization of the excited state with respect to the ground state must overcome the energetic penalty imposed by the environment. The QM/MM scheme is able to take this effect of the environment into account in a computationally feasible manner.

**4.3. QM/MM Calculations on the Pentacene Dimer in a Crystalline Environment.** The excimer formation in pentacene thin films was proposed by Marciniak et al.<sup>13</sup> to occur by rotation of the unit cell molecules to increase their mutual interaction. In the QM/MM calculations the angle between the molecular planes of the two unit cell molecules constituting the QM region, i.e. the herringbone angle  $\theta$ , was changed employing two different schemes. The molecules were either rotated in an antisymmetric fashion around their respective long molecular axis to obtain values of  $\theta$  in the interval from 0–90°, or only one molecule was rotated to obtain values of  $\theta$  in the interval from 20–70°, cf. Figure 5. In the first scheme the intermolecular distance was also varied by translating the molecules antisymmetrically along the line connecting the centers of the molecules to obtain two-dimensional potential energy surfaces.

Figure 6 shows the ground and four lowest excited states from a QM/MM calculation, where  $\theta$  is varied from 0–90° by use of the antisymmetric rotation scheme without changing the value of  $R$ , cf. Figure 5b. The calculated value of  $\theta \approx 52^\circ$  at the ground-state minimum does not reproduce the value of 59.4° determined experimentally by X-ray diffraction.<sup>31</sup> It is, however, the lowest-intensity Bragg peaks, which are most sensitive to the herringbone angle,  $\theta$ , and thus some uncertainty should be expected on the value of 59.4°, see Supporting Information of ref 31. The discrepancy between experiment and calculation could possibly be due to the neglect of pentacene molecules outside the considered *ab*-plane in the MM region. However, it is observed that the minimum in the lowest excited state is found at the same value of  $\theta$  as that of the ground state. Thus, the

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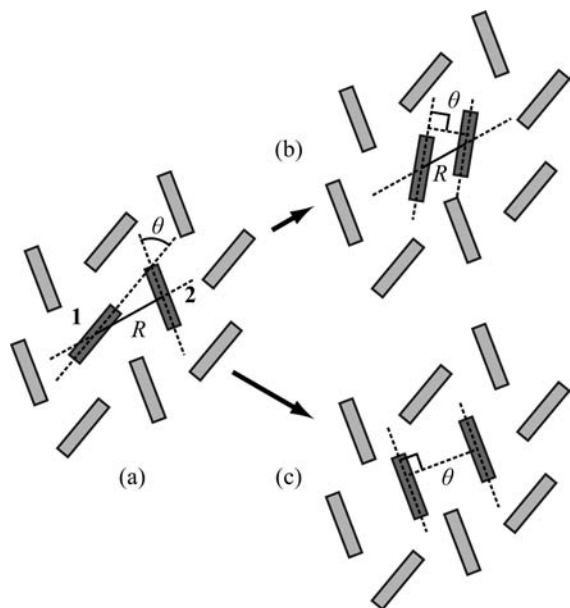
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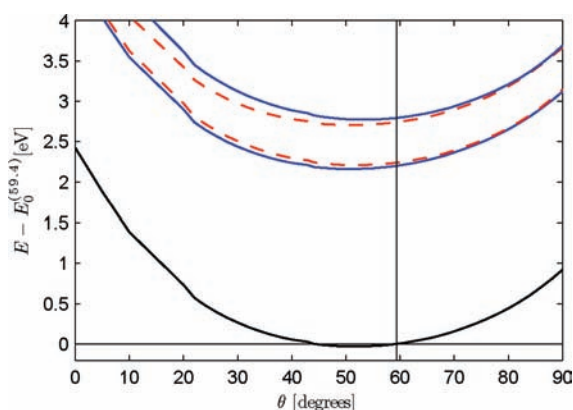
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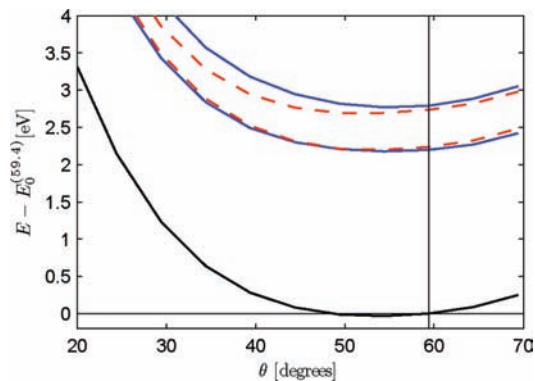


**Figure 5.** Schematic view along the long molecular axis of 10 pentacene molecules in the  $ab$  plane of the thin film polymorph of pentacene.<sup>31</sup> Dark-gray unit cell molecules belong to the QM region, while light-gray molecules belong to the MM region in the QM/MM calculations. (a) Experimentally determined structure with  $\theta = 59.4^\circ$ . (b) Unit cell molecules **1** and **2** rotated antisymmetrically about their respective long molecular axis to decrease  $\theta$  from  $90^\circ$  to  $0^\circ$  and antisymmetrically translated along the line connecting the centers of the molecules to change the intermolecular distance  $R$ . (c) Unit cell molecule **1** rotated about its long molecular axis to decrease  $\theta$  from  $90^\circ$  to  $0^\circ$ .



**Figure 6.** Ground state and four lowest excited singlet states as a function of  $\theta$  for antisymmetric rotation of the unit cell molecules around their respective long molecular axis, cf. Figure 5b. Vertical line indicates the experimental value of  $\theta = 59.4^\circ$ , and energies are relative to the ground-state energy at this angle  $E_0^{(59.4)}$ .

increase in the resonance interaction as  $\theta$  is decreased, as observed from the increased Davydov splitting of the excited states, is not great enough to favor a rotation due to the constraints of the surrounding molecules. Inclusion of the DFT-D correction for dispersion internally in the QM system to the QM/MM energy expression would not be able to move the minimum in the ground state relative to that in the lowest excited state, thus, the conclusion that these are found at the same value of  $\theta$  is unaffected. However, the DFT-D correction could move both minima to a different value of  $\theta$  yielding another possible explanation for the discrepancy in the value of  $\theta$  between experiment and calculation, but this is irrelevant in the context of the current discussion.



**Figure 7.** Ground state and four lowest excited singlet states as a function of  $\theta$  for rotation of molecule **1** of the unit cell around its long molecular axis, cf. Figure 5c. Vertical line indicates the experimental value of  $\theta = 59.4^\circ$ , and energies are relative to the ground-state energy at this angle  $E_0^{(59.4)}$ .

As entailed from Figure 5b the antisymmetric rotation of the unit cell molecules to a parallel geometry does not lead to a complete overlap of the two unit cell molecules. The rotation of only molecule **1** of the unit cell on the other hand leads to a larger overlap at the parallel geometry, cf. Figure 5c. However, the calculations for this rotation scheme leads to the same conclusions as reached for the antisymmetric rotation as can be inferred from Figure 7.

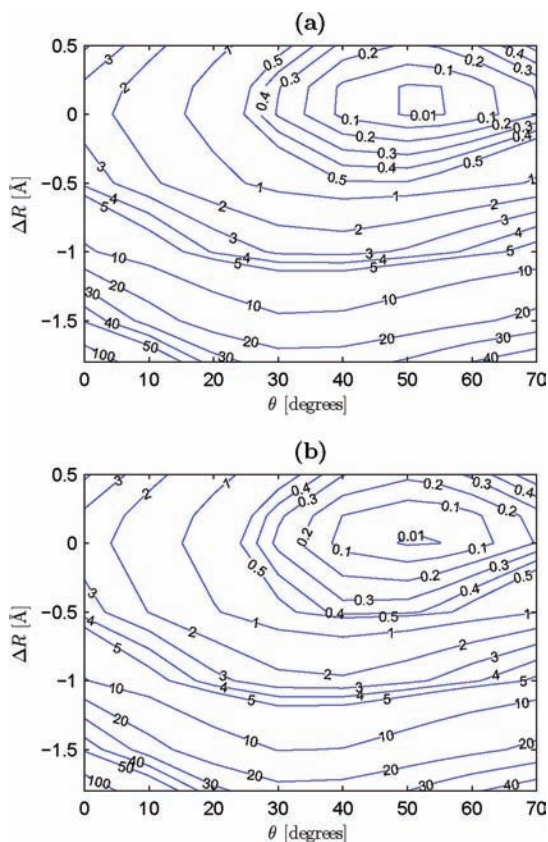
The interaction between the two molecules of the unit cell is affected not only by the angle between the molecular planes but also by the proximity of the two molecules. Figure 8a shows a contour plot of the two-dimensional ground-state potential energy surface as a function of herringbone angle  $\theta$  and relative displacement along the line connecting the centers of the two molecules  $\Delta R$ , where a negative value corresponds to a shortening of the distance relative to  $\Delta R = 0$  for which  $R \approx 4.8$  Å, cf. Figure 5b. The minimum is found around  $\theta \approx 52^\circ$  and  $\Delta R \approx 0.1$  Å. Similarly, Figure 8b shows a contour plot of the lowest excited state. It is observed that the minimum in the lowest excited state is located at the same geometry as that of the ground state; thus, there is no indication of excimer formation. This geometry coincidence of the two minima occurs even though the resonance interaction, as manifested by the Davydov splitting of the two lowest excited states, increases by more than an order of magnitude from the minimum geometry to the parallel geometry at close proximity.

Although the QM/MM scheme employed does not allow for a geometrical relaxation of the environment around the rotated an displaced molecules, the calculations are indicative of the disfavoring of rotation to a parallel excimer geometry. Furthermore, a more global adjustment of the configuration of the molecules of the crystal, we believe, is not feasible on the observed time scale of 70–80 fs. The QM/MM calculations thus substantiate the general observation presented in section 4.1 that excimers are not formed in crystals, where the molecules adopt a herringbone motif.

Further experimental results from the literature regarding the lifetime and the assumed stabilization of the excimer<sup>13,15,58,59</sup> support the conclusion reached from the results of the QM/MM calculations. The dynamics modeled by Marciniak et al. with a detailed kinetic scheme entails a stabilization of the

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**Figure 8.** Contour plots of the (a) ground and (b) lowest excited state as a function of the herringbone angle  $\theta$  and relative displacement along the line connecting the centers of the two molecules  $\Delta R$ . Contour levels in eV are relative to the minimum in the corresponding state.

excimer in pentacene by  $>0.3$  eV.<sup>15</sup> However, in  $\alpha$ -perylene a stabilization of the excimer by only 0.08 eV can be deduced from the observed fluorescence features.<sup>58</sup> As the parallel arrangement of the molecules in  $\alpha$ -perylene, and thereby overlap of  $\pi$ -electron systems, leads to a stronger interaction between the molecules than is the case in crystalline pentacene, it is unlikely that a possible excimer in pentacene should be stabilized to a higher degree than what is observed for  $\alpha$ -perylene. Furthermore, the lifetime of the proposed excimeric species, observed to be  $\sim 1$  ns,<sup>13,15</sup> is much shorter than the lifetime of 90 ns observed for excimers in  $\alpha$ -perylene.<sup>59</sup> On these grounds, we believe the excimer model of the photoinduced dynamics to be unsatisfactory.

## 5. The Fission Model

This section will shortly discuss the spectral features of the photoinduced absorption attributed to absorption from triplet excitons by Jundt et al.<sup>12</sup>

**5.1. Photoinduced Absorption Attributed to Triplet–Triplet Transitions.** The kinetic model put forward by Jundt et al.<sup>12</sup> in explaining the photoinduced dynamics in terms of exciton fission allows the short-time ( $<80$  fs) and long-time photoinduced absorption to be distinguished as  $S_n \leftarrow S_1$  and  $T_n \leftarrow T_1$  transitions respectively. The photoinduced absorption attributed to  $T_n \leftarrow T_1$  transitions by Jundt et al. has its low-energy onset around 1.77 eV (700 nm) and its first peak around 1.88 eV (630 nm). As mentioned by Jundt et al. the  $S_1 \leftarrow S_0$  transition is red-shifted by  $\sim 0.3$  eV on going from pentacene

in a benzene solution<sup>60</sup> to the crystal.<sup>61</sup> On these grounds it is argued that the first allowed triplet–triplet transition in a benzene solution at 2.46 eV (505 nm)<sup>60</sup> should be red-shifted to a similar degree locating the lowest triplet–triplet transition in the crystal at 2.16 eV (574 nm). This, however, corresponds to the highest-energy peak observed by Jundt et al. leaving the lower-energy features to be explained.

Further, the  $T_n \leftarrow T_1$  transitions should in fact be red-shifted to a lesser extent than the  $S_1 \leftarrow S_0$  transition as the Coulombic-integral part of the resonance interaction leading to the Davydov splitting is absent, leaving only smaller orbital-overlap-dependent contributions.<sup>62</sup> Extrapolating values of the Davydov splitting from the smaller acenes to pentacene yields a red-shift due to the resonance interaction of only  $\sim 2$  meV, see Supporting Information. A possible larger red-shift has to be the consequence of a static solvent shift. It is observed that the  $S_0 \leftarrow T_1$  transition of pentacene in a cyclohexane solution at 0.95 eV (1300 nm)<sup>63</sup> is red-shifted by  $\sim 0.1$  to 0.85 eV (1460 nm) in the crystal.<sup>64</sup> Cautiously, this value could be taken as an upper bound for the red-shift of  $T_n \leftarrow T_1$  transitions. Hereby, the features observed in the photoinduced absorption by Jundt et al., i.e. the absorption of the probe, cannot be assigned to  $T_n \leftarrow T_1$  transitions.

**5.2. Observations from Pump–probe Experiments.** Strong arguments against the photoinduced absorption being the result of  $T_n \leftarrow T_1$  transitions come from the advocates of the excimer model.<sup>13,15</sup> The observed lifetime of  $\sim 1$  ns is too short to account for the lifetime of a triplet state.<sup>60</sup> Furthermore, the polarization dependence of a band around 2.30–2.38 eV (540–520 nm), the strength of which increases on a time scale of 1 ps, allows this feature to be assigned to absorption from triplet excitons formed in a second step following the initial 70 fs process.<sup>15</sup> This yields a red-shift of  $\sim 0.1$  eV for triplet–triplet transitions compared to solution perfectly in line with the considerations put forward in the previous section. Furthermore, the subsequent kinetic analysis reveals that the triplet exciton yield is only about 2%. On these grounds we also believe the exciton fission model of the photoinduced dynamics to be unsatisfactory.

## 6. The Doubly Excited Exciton Model

With both previously proposed models believed to be unsatisfactory, a new model is called for. In putting forward a new model for the observed photoinduced dynamics in pentacene thin films, all aspects of the photophysical properties of pentacene have to be considered. This leads to a model where the doubly excited exciton plays a prominent role and which appears to be consistent with the photophysical properties of pentacene observed in both static as well as time-resolved experiments.

**6.1. The Doubly Excited State and Exciton.** The considerations by Jundt et al.<sup>12</sup> leading to the proposition of the fission model are based on the observation of the low triplet/singlet energy ratio in pentacene. Figure 9 illustrates the evolution of

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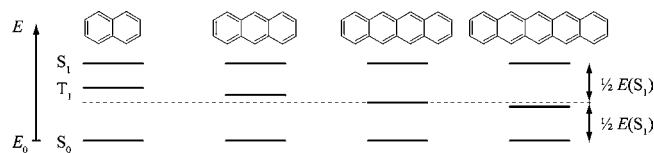
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**Figure 9.** Schematic representation of the energy ratio of the lowest excited triplet and singlet of the polyacenes from naphthalene (left) to pentacene (right). The energy scales have been displaced to level the ground-state energy, while the energy of the excited singlet has been normalized to unity for the individual system. The triplet/singlet energy ratio is observed to drop from  $>0.50$  in naphthalene to  $<0.50$  in pentacene. Energies taken from refs 9, 41 and 73.

the triplet/singlet energy ratio in the polyacenes from naphthalene to pentacene. As the triplet/singlet energy ratio for pentacene is  $<0.50$ , the fission process is energetically allowed; however, the low ratio also has another consequence for the excited states of a pentacene dimer. The doubly excited state described by eq 4 with the electronic configuration given in Figure 3d has in the asymptotic limit of infinite separation between the two molecules an energy equal to twice the energy of the molecular triplet. This energy is lower than the energy of one molecule in the lowest excited singlet state and one molecule in the ground state. The energy is thus lower than the energy of the exciton resonance state given in eq 1 described by the configuration in Figure 3a in the asymptotic limit of infinite separation between the two molecules. One can thus speculate that the lowest excited singlet state of the dimer is not the singlet exciton resonance state given by eq 1 but in fact is the doubly excited state given by eq 4. Likewise, one can speculate that the lowest singlet exciton of the crystal is in fact the doubly excited exciton  $S_D$ . Analogous to the presented case for the pentacene dimer, an exciton model of the excited states of butadiene describes the important contribution to the low-lying doubly excited  ${}^1A_g$  state as having the two ethylene units individually excited to a triplet state, which are coupled to yield an overall singlet.<sup>65</sup> For the case of a pair of molecules, a similar type of situation has been observed in the absorption of the so-called collision pair of  $O_2$  molecules,  $O_2 \cdot O_2$ , where the interaction between two  $O_2$  molecules leads to the one-photon double electronic transition  $a^1\Delta_g + a^1\Delta_g \leftarrow X^3\Sigma_g^- + X^3\Sigma_g^-$  at a wavelength approximately halved compared with the single electronic transition of an isolated  $O_2$  molecule.<sup>66–68</sup> The doubly excited state is not found in the linear response DFT calculations presented in Figure 4, since standard linear response approaches in DFT are not able to correctly describe doubly or higher excited states.<sup>69</sup>

## 6.2. Implications of the Doubly Excited Exciton Model.

**6.2.1. Relation to the Static Photophysical Properties.** Although the computational results in Figure 4 imply that excimer formation could occur in a pentacene dimer in solution, to the best of our knowledge fluorescence from such a state has not been observed. In the symmetric conformation investigated the  $S_0 \leftarrow S_1$  transition is forbidden by symmetry, yielding a possible

explanation for the lack of fluorescence from the excimer; however, this is not different from known excimer-forming systems such as perylene,<sup>25</sup> where weak fluorescence from the excimer state is observed.<sup>70</sup> In contrast to excimer-forming aromatic molecules such as perylene and pyrene, the polyacenes and thereby pentacene are known to form photochemical dimers.<sup>71,72</sup> This tendency to form photochemical dimers yields another possible explanation for the lack of excimer fluorescence, since the dimerization process is believed to occur via the excimer, thereby yielding an efficient channel for fluorescence quenching.<sup>73</sup>

Pentacene can, however, be distinguished from the smaller polyacenes in one important respect. Irradiation by 4.00 eV (310 nm) UV light of the symmetric photochemical dimer of pentacene dispersed in a poly(methyl methacrylate) (PMMA) host matrix at low temperature (13 K) or high pressure (13 kbar) yields so-called “broken dimers” through photolysis.<sup>72</sup> The resulting two pentacene moieties of the “broken dimer” are unable to move away from each other due to the low temperature or high pressure. In contrast to what is observed in similar experiments for dianthracene<sup>74</sup> and ditetracene,<sup>75</sup> “broken dimers” of dipentacene do not exhibit broad and structureless red-shifted emission similar to excimer emission. Pentacene is thereby set aside from not only other aromatic molecules such as perylene and pyrene but also the smaller polyacenes.

Fluorescence has been observed at low temperature from single crystals, thin films,<sup>76–78</sup> ultrathin films, and clusters of pentacene.<sup>79</sup> Reports of fluorescence from thin films of pentacene<sup>77</sup> have later been suggested to be caused by impurities.<sup>80</sup> A general observation, however, is a lack of fluorescence from solid pentacene.<sup>12,61,80–82</sup> The latter observation is further supported by the absence of stimulated emission in the pump–probe experiments.<sup>13,15</sup> A new model deduced to explain the photoinduced dynamics should take all these photophysical properties into account.

The conjecture regarding the doubly excited state has certain consequences. The doubly excited state belongs to the totally symmetric representation.<sup>36</sup> The crystal structure of pentacene belongs to the  $P1$  space group, the crystallographic point group being  $C_i$  with inversion as its only symmetry element aside from the identity. The transition from the doubly excited state to the ground state is thus forbidden by symmetry in a dimer possessing a center of symmetry as well as in the crystal. Furthermore, in unsymmetric systems the transition from the

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doubly excited state to the ground state should be expected to be associated with a small transition dipole moment. Thus, assuming the conjecture regarding the doubly excited exciton to be correct, the arguments regarding symmetry presented above could explain not only the lacking fluorescence of crystalline pentacene and lacking excimer emission in solution but importantly the lacking red-shifted emission from “broken dimers”, which sets pentacene aside from the smaller polyacenes. Furthermore, the arguments presented could explain the absence of the doubly excited exciton from the absorption spectrum. With this knowledge at hand the scene is set for a new model bringing into line the observed photoinduced dynamics from time-resolved experiments with the doubly excited exciton.

**6.2.2. Relation to the Time-Resolved Experiments.** The proposed kinetic models of Jundt et al.<sup>12</sup> and Marciniak et al.<sup>13,15</sup> are stated to fit well with the experimental data and should still be able to describe any new model proposed. Generally the two models both advocate the population of one level by the exciting pulse and a subsequent depopulation to another level in an ultrafast process on  $\sim 70$ – $80$  fs, which subsequently relaxes to the ground state through different relaxation channels in nanoseconds. In line with this general “model” and assuming the doubly excited exciton  $S_D$  to be the lowest exciton in the singlet spin manifold, the initially excited species will undergo internal conversion to  $S_D$ , cf. Figure 2. Associated with this process is the short time constant of  $\sim 70$ – $80$  fs observed in the experiments. Following this initial process  $S_n \leftarrow S_D$  transitions will be probed. One could speculate that the energy of the doubly excited exciton is slightly lower than the energy of two spatially separated triplet excitons leading to the energy barrier to exciton fission and the resulting low triplet exciton yield deduced by Marciniak et al.<sup>15</sup> The following picosecond dynamics modeled by Marciniak et al. with a detailed kinetic scheme still holds if one replaces their excimeric species with the doubly excited exciton  $S_D$ . The longer time constant of  $\sim 1$  ns can be associated with the lifetime of the doubly excited exciton. In the simpler model of Jundt et al.<sup>12</sup> transitions probed at long time delays are believed to be  $T_n \leftarrow T_1$  transitions; however, these can be reassigned to  $S_n \leftarrow S_D$  transitions. According to the scheme in Figure 2 these should be slightly blue-shifted with respect to the  $S_n \leftarrow S_1$  transitions probed at short-time delays, which is indeed what is observed.<sup>12</sup>

The population of the doubly excited exciton  $S_D$ , which in the notation of the dimer model in section 3 is given by  ${}^3M^{*3}M^{*}$ , opens the possibility of photoinduced absorption to higher doubly excited excitons  $S_{D^*}$ , which couple the lowest triplet of one molecule to a higher excited triplet of the other molecule in a total singlet spin configuration. We can denote this configuration in the dimer model by  ${}^3M^{*3}M^{**}$ , where  ${}^3M^{**}$  indicates some higher excited triplet state of the molecule taken to be the lowest state observed in the triplet–triplet absorption of pentacene in benzene.<sup>60</sup> The  $S_{D^*} \leftarrow S_D$  transition thus should have an energy corresponding to the energy of the lowest triplet–triplet transition of the molecule as it corresponds to the  ${}^3M^{*3}M^{**} \leftarrow {}^3M^{*3}M^{*}$  transition in the dimer and  ${}^3M^{**} \leftarrow {}^3M^{*}$  transition in the molecule. By analogy with the other transitions discussed, the transition between the two doubly excited excitons should also be red-shifted with respect to that in solution. From the discussion in section 5 the red-shift due to the static solvent shift of the triplet–triplet transition in the molecule is  $\sim 0.1$  eV, which would shift the transition between the two doubly excited excitons from the value of the

triplet–triplet transition in solution of 2.46 eV (505 nm) to 2.36 eV (525 nm). In this case, however, the higher doubly excited exciton is split by the resonance interaction, which in the dimer notation yields the two exciton resonance states  ${}^3M^{*3}M^{**} \pm {}^3M^{**3}M^{*}$  and the corresponding excitons  $S_{D^*}^{\pm}$ . In the dimer model the magnitude of the interaction is described by the off-diagonal matrix element between the locally excited configurations:<sup>83</sup>

$$E_{\text{int}} = \langle {}^3M^{*3}M^{**} | \hat{H} | {}^3M^{**3}M^{*} \rangle \quad (5)$$

If we neglect overlap-dependent contributions, this matrix element is equal to the interaction of the two transition dipole moments of the excitations in each monomer,<sup>36,83</sup> which corresponds to the so-called Coulombic-integral contribution mentioned in section 5. In the case of the triplet exciton resonance states and corresponding excitons discussed in section 5, these transition dipole moments are zero as the transitions are spin-forbidden (neglecting spin–orbit coupling), leaving only the neglected overlap-dependent contributions. However, in the case here of the higher doubly excited state the molecular  ${}^3M^{**} \leftarrow {}^3M^{*}$  transition is dipole-allowed and very strong<sup>60</sup> such that the interaction can be calculated in the dipole approximation (in eV) by:<sup>83</sup>

$$E_{\text{int}} = (1.645867 \times 10^2) f \eta \epsilon^{-1} r^{-3} \quad (6)$$

where  $f$  is the oscillator strength of the molecular transition at energy  $\epsilon$  (in eV),  $r$  (in Å) is the distance between the centers of the two molecules, and  $\eta$  is given by:

$$\eta = \vec{e}_1 \cdot \vec{e}_2 - 3(\vec{e}_1 \cdot \vec{e}_{12})(\vec{e}_2 \cdot \vec{e}_{12}) \quad (7)$$

$\vec{e}_1$ ,  $\vec{e}_2$ , and  $\vec{e}_{12}$  are unit vectors along the transition dipole moments of the two molecules and the line through the centers of the two molecules, respectively. Using the experimentally determined values<sup>60</sup> of  $f = 0.7$  and  $\epsilon = 2.46$  eV yields  $E_{\text{int}} = 0.41$  eV. The energy difference between the two exciton resonance states is thus  $2E_{\text{int}} = 0.82$  eV.

Further characteristics of the molecular transitions are relevant when discussing the  $S_{D^*}^{\pm}$  excitons of the crystal. The transition dipole moment of the lowest allowed triplet–triplet transition in pentacene,  ${}^3M^{**} \leftarrow {}^3M^{*}$ , is oriented along the long molecular axis of the molecule.<sup>84</sup> Due to the almost coaxial (long molecular axis) geometry of the two molecules in the unit cell, transition to  $S_{D^*}^+$  will be strongly allowed with a transition dipole moment primarily along the normal to the thin film plane, whereas transition to  $S_{D^*}^-$  will be very weak with a transition dipole moment primarily in the plane of the thin film. The energy of  $S_{D^*}^+$  will be blue-shifted while that of  $S_{D^*}^-$  will be red-shifted due to the in-phase and out-of-phase transition dipole arrangement respectively.<sup>85</sup> In fact, a band is observed in the transient absorption<sup>13,15</sup> around 2.00 eV (620 nm) with the time-dependence and polarization properties corresponding to the  $S_{D^*}^- \leftarrow S_D$  transition. This would imply a red-shift of 0.36 eV for  $S_{D^*}^-$ , which is very close to the value of 0.41 eV found above in the dipole approximation for the dimer model. Similarly,  $S_{D^*}^+$  should be blue-shifted by 0.36 to 2.72 eV (456 nm), and the very strong  $S_{D^*}^+ \leftarrow S_D$  transition would thus not be observable in the experiment<sup>13,15</sup> as the white light continuum generated

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in a sapphire substrate shows a drastic decrease in intensity above 2.48 eV (below 500 nm).<sup>86</sup> Furthermore, if the white light continuum extended above 2.48 eV (below 500 nm) the transition would primarily be observed for a beam incidence angle away from normal incidence. It is important to note that similar to  $S_D$ ,  $S_D^{\pm}$  are not expected to be present in the static absorption spectrum and are thus only relevant in the context of the time-resolved pump–probe experiments.

We believe to have substantiated that the model of the photoinduced dynamics involving the doubly excited exciton  $S_D$  is not only qualitatively in accordance with the observed static photophysical properties of pentacene as well as the time-resolved experiments but also exhibit quantitative agreement with the features observed. Moreover, this model seems to be the only one which consistently exhibit these properties.

## 7. Conclusion

The disentanglement of the photoinduced dynamics in pentacene thin films has been the subject of ambiguity as two contradictory models have been presented in the literature. The formation of an excimer subsequent to excitation has been proposed as one pathway leading from the initially excited species to the return to the ground state. The results of QM/MM calculations, where the crystalline environment is taken into account, however, indicate that the excimer formation by rotation of the unit cell molecules is not plausible. This indication is in line with general observations regarding excimers in organic molecular crystals. Also, general considerations and

predictions regarding the spectral features of triplet excitons leaves the fission model, which advocates singlet exciton fission into triplet excitons as the general pathway, unsatisfactory.

The photophysical properties of pentacene nevertheless opens up the possibility of an alternative model explaining the photoinduced dynamics. The low triplet/singlet energy ratio in pentacene entails the possibility of a doubly excited exciton as the lowest excited species in the singlet spin manifold. With this assumption it can be conjectured that the observed dynamics is indeed due to internal conversion from the initially excited species to the doubly excited exciton and a following decay to the ground state. It is left to further experimental studies to completely prove or disprove the conjecture presented in this paper.

**Acknowledgment.** We greatly acknowledge helpful discussions with Stephan P. A. Sauer. We thank the Danish Center for Scientific Computing (DCSC) for the computational resources. T.S.K., K.B.M., and T.I.S. acknowledge support from the Danish National Research Foundation through the Centre for Molecular Movies, K.V.M. acknowledges support from the Villum Kann Rasmussen Foundation, and J.K. and K.V.M. acknowledge support from The Danish Council for Independent Research for Natural Sciences.

**Supporting Information Available:** Cartesian coordinates of optimized geometry of pentacene, discussion of the red-shift of triplet–triplet transitions in the pentacene crystal, and complete ref 21. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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