Dynamics of the Excitonic Coupling in Organic Crystals

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We show that the excitonic coupling in molecular crystals undergoes a very large fluctuation at room temperature as a result of the combined thermal motions of the nuclei. This observation dramatically affects the description of exciton transport in organic crystals and any other phenomenon (like singlet fission or exciton dissociation) that originates from an exciton in a molecular crystal or thin film. This unexpected result is due to the predominance of the short-range excitonic coupling mechanisms (exchange, overlap, and charge-transfer mediated) over the Coulombic excitonic coupling for molecules in van der Waals contact. To quantify this effect we develop a procedure to evaluate accurately the short-range excitonic coupling (via a diabatization scheme) along a molecular dynamics trajectory of the representative molecular crystals of anthracene and tetracene.

Exciton transport in molecular aggregates, including crystals and thin films, is governed by the excitonic coupling J between the excited states localized on the molecular units [1,2]. Two limiting transport regimes (coherent and incoherent) are generally evoked to describe the exciton transport in organic crystals [2]. In the coherent regime, the excitonic coupling is much larger than the exciton-phonon coupling and the exciton wave function is delocalized over the aggregate [1]. In the opposite (incoherent) regime, the exciton coupling between adjacent molecules is much weaker than exciton-phonon coupling, and the exciton wave function, localized on a molecular unit, diffuses via a series of exciton hopping events between the neighboring molecules. In both limits it is often assumed that J is a constant, i.e., not dependent on time or, equivalently, on the nuclear displacement (Condon approximation) [2]. However, a fundamental characteristic of the molecular crystals is that they are held together by weak noncovalent intermolecular interactions and therefore possess a large number of low frequency intermolecular vibrations that cause a relatively large displacement of one molecule with respect to their neighbors [3]. The motion of the molecules around their equilibrium position (dynamic disorder) is known to cause very large fluctuations in the transfer integral between orbitals localized on different molecules [4,5] and may as well give rise to large time fluctuations of the excitonic coupling J. The inclusion of the dynamic disorder for the transfer integral proved to be crucial to understand many aspects of charge transport in molecular solids including its temperature dependence, charge localization, and Hall effect [5,6]. Crucially, the characteristic time scale for the fluctuations determines the transport mechanism. The limit of J fluctuations that are faster than any other time scale is studied in the classical Haken-Strobl-Reineker model [7,8], while the limit of J

fluctuations slower than any other time scale is a special case of exciton transport in a statically disordered medium [9]. Away from these two limits it is very difficult to develop analytical theories that incorporate the effect of phonons on the excitonic coupling (nonlocal exciton-phonon coupling).

In this Letter, we assess the magnitude and time scale of the fluctuation of the excitonic coupling due to nuclear thermal motions. To do so, we adopt a combined molecular dynamic (MD) and quantum chemical (QC) approach, and we derive a general diabatization scheme to compute excitonic couplings, in which both short- and long-range effects are accounted for. We present the results for the two archetype anthracene and tetracene molecular crystals, which have been widely studied in the context of organic electronics. In this work we will focus mainly on the case of anthracene because the nature of its lowest-energy excitations [Frenkel type (FE)] is simpler than in the case of tetracene where the lowest-energy excitons are described by a significant mixture of FE excited states and charge-transfer (CT) excited states [10].

The excitonic coupling J can be decomposed into different short-range (exchange, charge-transfer mediated, and overlap) and long-range (Coulombic) contributions [11,12]. The Coulombic contribution is the only contribution effective when the molecules are not in contact and this is the contribution most often evaluated in the literature [13,14], for example if one is interested in Förster excitation energy transfer [13]. In our case however, we obviously need to consider short-range excitonic interaction as well since we are interested in the excitonic coupling between pairs of molecules at van der Waals distance. To estimate the excitonic coupling between adjacent molecules, we have derived a simple and general approximation based on the orthogonal transformation of the

adiabatic states (eigenstates of the total Hamiltonian) to diabatic (noninteracting) states in a two-level dimer system model (see the Supplemental Material [15]). The diabatic states $\{\psi_1^D, \psi_2^D\}$ are related to the adiabatic ones $\{\psi_1^A, \psi_2^A\}$ by means of a unitary transformation matrix ($\mathbf{C} = \{C_{ij}\}$), which defines the relation between the diabatic and adiabatic Hamiltonian matrix ($\mathbf{H}^D$ and $\mathbf{H}^A$) as

$$\mathbf{H}^D = \mathbf{C}\mathbf{H}^A\mathbf{C}^\dagger. \tag{1}$$

$\mathbf{H}^A$ is the diagonal matrix containing the adiabatic excited state energies of the dimer system, obtained from an electronic structure calculation of the dimer. The off-diagonal element of $\mathbf{H}^D$ is the excitonic coupling J, while the diagonal elements of $\mathbf{H}^D$ are the diabatic energies. With the definitions above, computing the excitonic coupling is equivalent to determining the most convenient unitary transformation matrix that generates the diabatic states from adiabatic ones. The diabatic states should represent the noninteracting excitons localized on different elements of the molecular pair and should be as close as possible to the states that two noninteracting molecules would have. Therefore, we compute the unitary matrix $\mathbf{C}$ that minimizes the difference between the transition dipole moments from the ground state of the diabatic states ($\boldsymbol{\mu}_1^D$ and $\boldsymbol{\mu}_2^D$) and the transition dipole moments from the ground state of two isolated molecules in the same geometry ($\boldsymbol{\mu}_1^{ISO}$ and $\boldsymbol{\mu}_2^{ISO}$). As the unitary transformation $\mathbf{C}$ relates also $\boldsymbol{\mu}_1^D$ and $\boldsymbol{\mu}_2^D$ with the adiabatic transition dipole moments of the molecular dimer $\boldsymbol{\mu}_1^A$ and $\boldsymbol{\mu}_2^A$, $\mathbf{C}$ can be fully determined from the knowledge of $\boldsymbol{\mu}_1^{ISO}$, $\boldsymbol{\mu}_2^{ISO}$, $\boldsymbol{\mu}_1^A$, and $\boldsymbol{\mu}_2^A$, which are easily accessible from electronic structure calculation methods. The search for the best unitary transformation that minimizes the difference between two given matrixes is a standard linear algebra problem [32] whose solution is outlined in the Supplemental Material [15].

The approximation proposed, similar in spirit to other diabatization schemes [33–35], offers a number of advantages with respect to the Förster approximation and also other diabatization methods: (i) it is a general approach and can be used with any electronic structure calculation method, (ii) it captures the physics of the important short-range contributions (exchange, overlap, and charge-transfer mediated terms), (iii) it becomes particularly suitable in the presence of two nonequivalent but identical molecules, (iv) it allows the evaluation of the coupling J where the phase of the diabatic states is locked and the sign of J is consistent along repeated evaluations at different geometries, and (v) the approach can be generalized to compute the coupling between more states. The latter makes the proposed diabatization scheme preferable when additional states (like charge-transfer states) have energy comparable to that of the Frenkel excitons, a situation not investigated here but encountered in some molecular crystals. Properties (iv) and especially (ii) above are

essential for the problem investigated here because one would not expect important fluctuations of the excitonic coupling if these were mainly due to Coulombic terms.

To evaluate the time fluctuation of the excitonic coupling owing to the thermal motions in anthracene and tetracene crystals, we have adopted a combined MD and QC approach [15]. MD simulations of the crystal structures of anthracene and tetracene at a constant temperature of 300 K were carried out. We have considered only the excitonic coupling between neighboring dimers because these have been shown to be sufficient to gain quantitative insight in the excited state properties of the crystal [10,36]. Moreover, excitonic coupling between molecular pairs at longer distances is dominated by the electrostatic term, which is not expected to be sensitive to small thermal fluctuations. For 2050 MD snapshots (separated by 0.05 ps of simulation time) the excitonic couplings for three parallel (A) and three tilted (B) dimers [Fig. 1(b)] were computed by means of time-dependent density functional theory calculations, using the long-range corrected ω B97X-D density functional [37] and the 3-21G* basis sets. For tetracene, only the excitonic couplings for three parallel dimers were evaluated for each MD snapshot (Fig. S2(a) [15]). Figure 1(c) shows the time evolution of the excitonic couplings computed for the two anthracene dimers (A and B) at 300 K and Fig. 1(d) displays the distribution of the excitonic couplings.

The excitonic couplings are approximately normally distributed [Fig. 1(d)]. The parallel dimer presents a mean value for J ($\langle J \rangle$) of -0.035 eV with a standard deviation σ_J of 0.010 eV while for the tilted dimer the $\langle J \rangle$ and σ_J values are -0.007 and 0.022 eV, respectively. It should be stressed that the modulation of the excitonic coupling introduced by the thermal motions of nuclei is of the same order of magnitude as the average excitonic couplings. In the case of tetracene, similar conclusions are attained with $\langle J \rangle$ and σ_J values of -0.030 and -0.013 eV, respectively (see Fig. S2 in the Supplemental Material [15]). Tilted dimers in tetracene have not been discussed because during the dynamics the two lowest FE excited states are significantly mixed with a low-energy CT excited state. In this scenario, not only the coupling between the pure FE excited states should be taken into account but also the coupling between the pure FE excited states with the CT excited state, a separate effect that is beyond the scope of this analysis.

To analyze in more detail the excitonic coupling dynamics, the Fourier transformation of the autocorrelation function $\langle \delta J(0)\delta J(t) \rangle$ has been computed and is shown in Fig. 2 for the excitonic couplings of anthracene (dimers A and B) and tetracene (dimer A, Fig. S2 [15]) (the deviation from the average excitonic coupling has been defined as $\delta J(t) = J(t) - \langle J(t) \rangle$). Figure 2 clearly reveals that low-frequency vibrations below 75 cm^{-1} for both pairs A and B in anthracene are responsible for the large modulation of the excitonic coupling whereas vibrations

FIG. 2 (color online).   Fourier transform of the autocorrelation function of the excitonic coupling between the first excited states of the neighboring molecules for anthracene dimers A (top) and B (bottom), at 300 K.
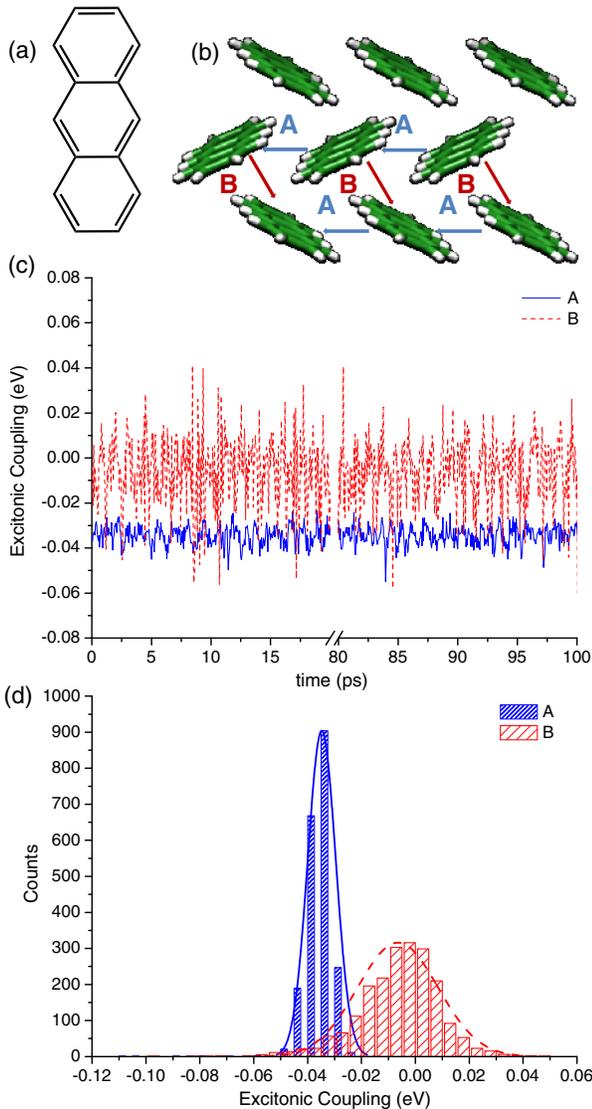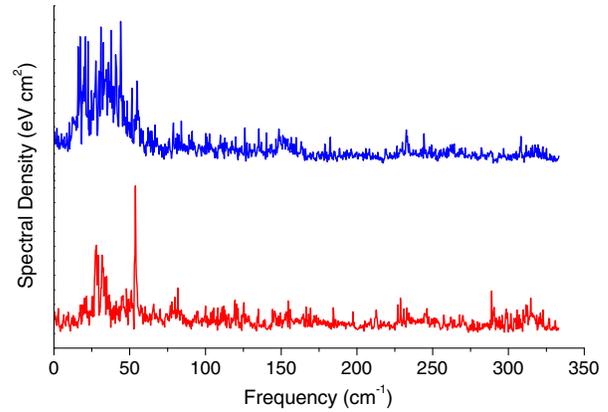
FIG. 1 (color online).   (a) Chemical structure and (b) crystal arrangement for anthracene with the labeling of the nonequivalent nearest neighbors (molecular dimers A and B). (c) Time evolution of the excitonic coupling due to the thermal motions (300 K) for the two anthracene dimers A and B and (d) distribution of the excitonic couplings.

above 200 cm^{-1} seem to hardly contribute to the modulation of J. Since only low-frequency vibrations have a strong impact on the fluctuation of the excitonic coupling, the semiclassical description adopted here for the molecular motions can be considered valid at room temperature. The peaks in the spectral density correspond to low frequency phonon modes with the largest exciton-phonon coupling and they appear in the same spectral region of low frequency modes observed in Raman spectroscopy [38] or computed for similar molecules [39]. The noise in the spectral density could be further reduced by analyzing a trajectory longer than 2050 points, but this was deemed

unnecessary to support the conclusion of this work (the computational cost for the data in Fig. 2 exceeds 1500 cpu hours). The fluctuation of the excitonic couplings is similar (in magnitude and time scale) to the observed fluctuation of the transfer integral between neighboring orbitals of relevance for charge transport [4], and, it is likely caused by short-range excitonic coupling interactions. Indeed, if we include only the Coulombic interaction (see Fig. S3 in Ref. [15]) the exciton coupling fluctuation is much reduced, suggesting that short-range interaction is the main player for the modulation of excitonic couplings in molecular crystals. The importance of these terms for naphthalene dimers at short intermolecular distances was highlighted by Hsu *et al.* [40] in a static calculation. Our dynamic picture provides additional information on the likelihood that certain structures are actually found in the crystal and the sensitivity of the excitonic coupling to molecular geometry (including not only the intermolecular distance but also librations and molecular low frequency modes).

When the thermal motion of the molecules is added the physical picture of exciton transport is deeply modified. First of all, the magnitude of the fluctuations prevents the description in terms of excitonic bands renormalized by the nonlocal exciton-phonon coupling [41]: the perturbation is just as large as the zeroth-order excitonic coupling. Second, the low-frequency phonons that modulate the excitonic coupling have characteristic oscillation periods of the order of 1 ps, which is of the same magnitude as the hopping time (2.5 ps) if such a hopping mechanism is assumed [42,43]. In this limit, it is also not possible to decouple electronic and nuclear motions assuming that the latter are much faster as done for example in the Haken-Strobl-Reineker model [7,8]. Similarly, it is not possible to assume that the fluctuation is slow enough to discuss the transport as an incoherent sequence of hopping events in a disordered landscape [9].

The actual transport mechanism will be influenced by the magnitude of the local exciton-phonon coupling. For large coupling (more common in small molecules), it is possible that a small-exciton polaron is formed and that the transport takes place by hopping with a large time modulation of the coupling between states. In larger molecules, which normally have a smaller local exciton-phonon coupling, the effect can be more dramatic with excitons dynamically localized by the disorder in the off-diagonal matrix element of the Hamiltonian with their dynamics promoted by the same nuclear motions that are responsible for the dynamic localization. Such a limit has been studied with numerical methods in the context of charge transport [5,44–48] and it can be potentially extended to the study of exciton transport. New phenomenological models put forward to study charge transport in the case of dynamically disordered solids [49] can also be used to study the exciton transport and to understand the long-range exciton diffusion experimentally observed in organic semiconductors [50]. Although this work pointed out a similarity between charge and exciton transport in molecular crystals possibly greater than expected, it may be useful to remember that such a similarity is limited by the existence of other excitons (of Frenkel or CT nature) closer to the lowest energy excitonic band that may complicate the picture. Moreover, the fluctuation of the excitonic coupling characterized in this Letter may also help in rationalizing other interesting phenomena currently under investigation, including singlet fission in molecular crystals [51,52] and charge generation in organic photovoltaic devices [53].

To sum up, we have evaluated the role of the thermal motions on the modulation of the excitonic coupling in anthracene and tetracene crystals by means of a combined molecular dynamic and quantum chemical approach. A simple and general diabatization scheme to estimate all components (short and long range) of the excitonic couplings has been derived. The inclusion of short-range excitonic interaction proved crucial to show that the fluctuation of the excitonic coupling introduced by the thermal motion is extremely large and comparable to its average value. Considering the time scale of such fluctuations, phenomena originally discussed for the charge carriers in molecular crystals, like dynamic localization, are therefore also likely for excitons. The main result of this Letter is essential for the proper description of exciton transport in molecular materials and to develop the appropriate theoretical framework to study any phenomena that originate from molecular excitons in the solid state.

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