A Correlated Electron View of Singlet Fission

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## CONSPECTUS

Singlet fission occurs when a single exciton splits into multiple electron-hole pairs, and could dramatically increase the efficiency of organic solar cells by converting high energy photons into multiple charge carriers. Scientists might exploit singlet fission to its full potential by first understanding the underlying mechanism of this quantum mechanical process. The pursuit of this fundamental mechanism has recently benefited from the development and application of new correlated wave function methods. These methods—called restricted active space spin flip— can capture the most important electron interactions in molecular materials, such as acene crystals, at low compu-

Intermolecular Motion Drives Fission

tational cost. It is unrealistic to use previous wave function methods due to the excessive computational cost involved in simulating realistic molecular structures at a meaningful level of electron correlation.

In this Account, we describe how we use these techniques to compute single exciton and multiple exciton excited states in tetracene and pentacene crystals in order to understand how a single exciton generated from photon absorption undergoes fission to generate two triplets. Our studies indicate that an adiabatic charge transfer intermediate is unlikely to contribute significantly to the fission process because it lies too high in energy. Instead, we propose a new mechanism that involves the direct coupling of an optically allowed single exciton to an optically dark multiexciton. This coupling is facilitated by intermolecular motion of two acene monomers that drives nonadiabatic population transfer between the two states. This transfer occurs in the limit of near degeneracies between adiabatic states where the Born–Oppenheimer approximation of fixed nuclei is no longer valid. Existing theories for singlet fission have not considered this type of coupling between states and, therefore, cannot describe this mechanism.

The direct mechanism through intermolecular motion describes many experimentally observed characteristics of these materials, such as the ultrafast time scale of photobleaching and triplet generation during singlet fission in pentacene. We believe this newly discovered mechanism provides fundamental insight to guide the creation of new solar materials that exhibit high efficiencies through multiple charge generation.
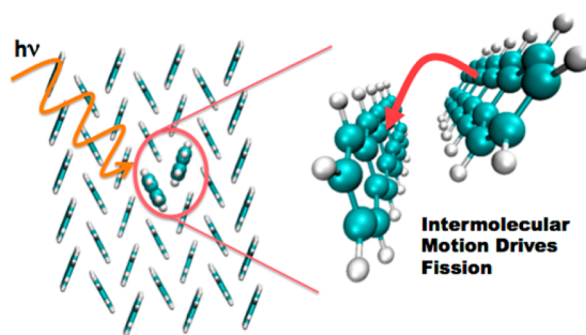
Introduction

Singlet fission (SF) has attracted considerable interest based on its potential to increase the efficiency of photovoltaic materials.[1] SF is the spin-allowed conversion of a photo-excited single exciton into two (singlet-coupled) triplet excitons. Although SF was first observed decades ago in anthracene, tetracene, and rubrene crystals,[2–5] quantum mechanical (QM) calculations of the multiexciton (ME) states

in these materials have until recently been intractable. Consequently, the only known fundamental criterion for SF was the energetic requirement that the bright single exciton (SE) state must have around twice the energy of the triplet (T1) $E_{SE} \geq 2E_{T1}$.[6] However, QM methods have recently advanced to where ME states can be calculated in realistic molecular models[7,8] to enable the identification of specific coupling coordinates for efficient SF. Our ab initio

studies have suggested that SF in tetracene and pentacene occurs through nonadiabatic coupling of SE to ME states mediated by intermolecular motion (see Figures 1 and 2).

Previously, the general mechanism of SF had been described in terms of sequential single electron hops between monomers.[9,10] In this perspective, electrons are often localized on individual molecules such that the quantum states are approximated as weakly interacting single electron configurations. However, electrons in close proximity may be highly correlated and thus their wave functions can differ substantially from these approximate states. When correlation effects are included, the short-range interactions among the π electrons in acene crystals result in strong correlations that can dominate each states' characteristics.
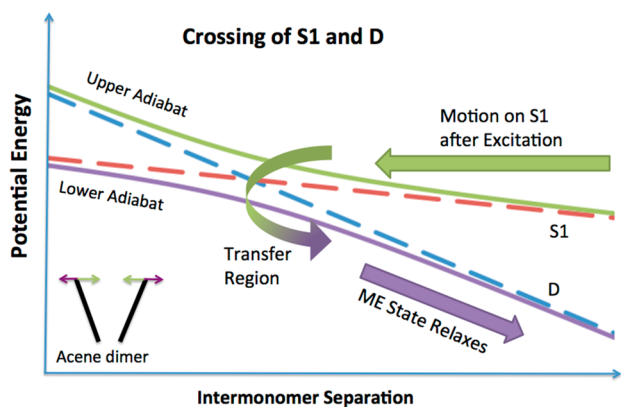

FIGURE 1. Electronic and nuclear coupling that leads to population transfer from the bright to dark state in pentacene. The system is initially excited to the upper adiabat which has bright (S1) character. It undergoes motion to the vicinity of the conical intersection, where the character of the upper adiabat changes from bright to dark (multiexciton; ME). This leads to significant probability of nonadiabatic transitions to the lower adiabat, as indicated by exit on the lower dark (ME) adiabat.

A more adaptable basis consists of interacting electrons occupying orbitals. This type of basis underlies most ab initio wave functions and therefore can provide a fundamental description of the SE and ME states involved in SF. In its simplest form, the lowest energy antisymmetrized wave function constructed by filling a set of molecular orbitals (MOs) with electrons yields Hartree–Fock (HF) theory. This ab initio method is a good zero-order representation of ground states. Additional electronic configurations can be constructed by exciting electrons from occupied orbitals into unfilled orbitals. Superposing these configurations is the basis of configuration interaction (CI) theories, which can describe adiabatic ground or excited states including strong electron correlations.

First principles methods such as CI describe electron correlation without detailed prior knowledge of the state's character. No assumptions of energy, localization, charge transfer character, or degree of electron excitation of excited states are required beforehand. However, all tractable ab initio methods involve approximations, and those approximations must be appropriate for the target system (e.g., HF is not appropriate for strongly correlated states). Subject to appropriate approximations, molecular ground and excited states emerge as correlated solutions to systems of interacting electrons within ab initio theory. In the first part of this Account, we will describe electronic structure methods that are appropriate to calculate SE and ME states.

Even if their electronic structure approximations are appropriate, ab initio methods still rely on a more basic assumption: the Born–Oppenheimer approximation (BOA). The BOA assumes that the wave function can be well-described by decoupling the nuclear and electronic degrees
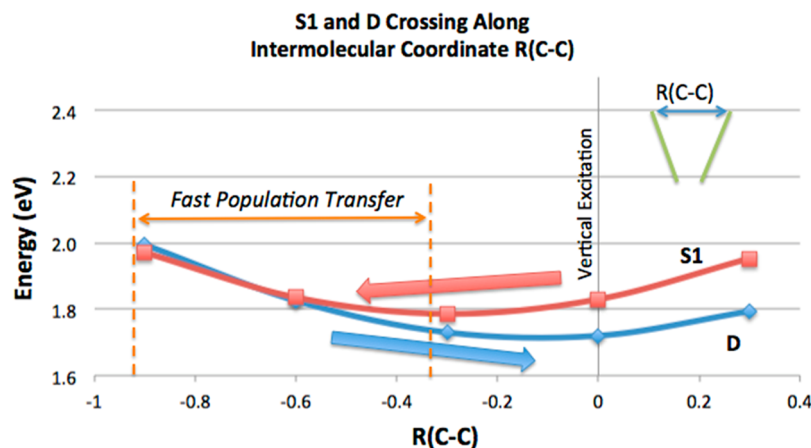

FIGURE 2. Potential energy surface showing calculated crossing of single exciton (SE) state S1 with ME state D in a model of crystalline pentacene. Population transfer from S1 to D predominantly occurs in the region of near-degeneracy, where the character of the adiabatic states changes rapidly from bright (SE) to dark (ME) and vice versa.

of freedom and calculating the electronic wave function as a function of fixed nuclear position. This approximation is excellent whenever the various BO electronic states (known as adiabats) are well separated in energy. However, the BOA breaks down when coupling between two near-degenerate adiabatic states occurs via nuclear motion, as a consequence of the neglected nonadiabatic coupling. As we discuss in detail below, nonadiabatic coupling is critical to rapid SF in pentacene, because intermolecular nuclear motion facilitates population transfer from the bright optically allowed excited state to the nearly degenerate dark ME state. Our ab initio approach avoids undue assumptions about the character and couplings between states through direct QM computation of these properties.

Ab Initio Tools

Under the BOA, the careful choice of electronic structure method can lead to proper descriptions of adiabatic excited states. The first criterion for an appropriate method is that it must properly describe the physical character of the states (qualitative correctness). For instance, a SE has the character of an electron−hole pair, while a charge transfer state appears as a spatially separated electron−hole pair. Furthermore, the oscillator strengths of each photoexcitation should differentiate between strongly and weakly allowed transitions. Moreover, a double exciton, which is significantly more difficult to calculate than a single exciton, must have the character of two correlated electron−hole pairs. If the monomers are well-separated, the double exciton exists as two distinct excitons, each localized on a monomer. At short dimer separations, the multiexciton character is more difficult to describe due to its complex electronic correlations that require many-body theories to fully capture.

A second important criterion is quantitative correctness, which means predicting the ordering of states,[11] and ideally, excitation energies (e.g., within 0.1 eV). This can only be met by very expensive theories such as multireference CI that cannot be applied to large systems. We generally utilize methods that reliably capture the physical character, and are aware when these methods do not fully achieve quantitative accuracy.

Information about the excited states of interest from experiment or benchmark theories on monomers can help alleviate this problem. For instance, if a particular excitation energy is known, an energy shift can correct the error. This is especially useful when developing a potential energy surface (PES) using an approximate theory that does not predict

excitation energies with benchmark accuracy. This energy shift formally converts adiabatic states into diabatic states, where PESs can intersect without an avoided crossing. Fortunately, the off-diagonal diabatic Hamiltonian matrix element can be computed and used to correct this issue as well as estimate population transfer rates.[8] We employed this approach using high accuracy monomer excitation energies from simulation[7] and experimental energies.[8]

Configuration interaction singles (CIS) is the simplest theory for computing excited states.[12] It describes excitons as superpositions of single electron excitations from occupied to empty orbitals and provides a convenient method to describe single electron−hole pair states. Time-dependent DFT (TD-DFT)[12] is the DFT analog of CIS and has become the most popular approach for describing excited states of large molecules due to its low cost to accuracy ratio. When CIS or TD-DFT are combined with appropriate analysis tools such as Natural Transition Orbitals,[13] the precise character of SE states can be visualized as electron−hole pairs. This is useful in differentiating between molecular and charge transfer excitons, or in determining the extent of exciton delocalization over multiple monomers.[8]

By design, CIS and TD-DFT cannot capture ME states that are dominated by multiple-electron excitations because these methods are restricted to single excitations. The most common method that can capture ME states is Complete-Active-Space Self-Consistent Field (CASSCF). CASSCF fulfills the qualitative correctness criterion for SE and ME states and frequently provides correct state ordering. CASSCF is in principle useful for studies of SF, but in practice it is prohibitively expensive to apply to systems (without symmetry) with more than ∼20 non-hydrogen atoms.

Therefore, new theories were applied to calculate ME states in the acenes. Restricted active space spin flip (RAS-SF)[14,15] proves to be one such useful method. RAS-SF requires one specification beyond standard ab initio quantum chemical methods: the number of electrons that are potentially strongly correlated. For example, if two electrons are strongly correlated, an initial ROHF calculation is performed on the high spin triplet state of the biradicaloid system, giving two singly occupied orbitals. From this reference, spin-flip CI describes states by flipping one up spin to down spin. This includes the closed shell ground state and singlet SE states (see Scheme 1). If the spin-flipping excitations are limited to singles, the result is spin-flip CIS (SF-CIS).[16]

RAS-SF[14,15] extends the SF-CIS approach to any number of spin flips from any high spin reference, and also ensures that exact spin-eigenstates are obtained. This is accomplished

SCHEME 1. Single Spin-Flips from a Triplet Reference to Yield Ground and SE States
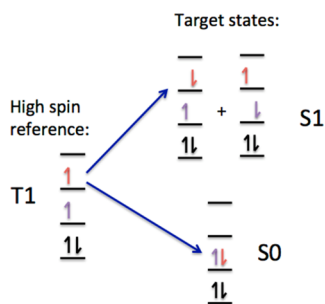
by forming the RAS-SF wave function as a superposition of all possible configurations of $2n$ electrons in the $2n$ active orbitals, as well as permitting single excitations into and out of the active space. The natural spin-flip reference for describing the outcome of SF (an overall singlet-coupled pair of triplets that represents two electron−hole pairs), is a high spin quintet (four parallel spins). Two spin flips from the quintet are necessary to obtain SE and ME states, yielding the ground state, triplet and singlet SEs, as well as the dark ME state. RAS-2SF is orders of magnitude faster than CASSCF, yet yields states that agree well with CASSCF in energy and character.[8]

State-to-State Transfer Rates

Once a suitable description of individual excited states is available, interactions between these states can be calculated. The exact time evolution of these states could in principle be obtained by solving the time-dependent Schrödinger equation based on the full PES obtained through the electronic structure method, but the cost would be exorbitantly high. Instead, two routes might be followed: (1) ab initio molecular dynamics with state crossing[17] or (2) reduction of the problem to a simplified PES. We have pursued the latter route due to its computational simplicity.

Reduction of the problem to a single critical dimension (vide infra) allows for analytical calculation of the rate of population transfer. Specifically, we utilize Landau−Zener−Stueckelberg (LZS)[18,19] theory to estimate the probability of population transfer along this coordinate. LZS is an extension of the well-known Landau−Zener equation[18] that generalizes the formula for system energies that are equal to or lower than the crossing energy. This extension allows tunneling into the crossing region, and thus provides a more complete description than Landau−Zener theory. A LZS calculation requires two PESs and an estimate of the available total system energy.

Acene Mechanism

Initially, an appropriate model must be chosen that includes not only the level of QM theory, but the number and positions of molecules and their extended environment. Here, we will examine a dimer of acene molecules embedded in the herringbone crystal structure using the RAS-2SF level of theory. The largest model we have employed is a 10-mer of acene molecules, which was used to describe the delocalization of the S1 exciton.[8] While the dimer provides the appropriate basis for describing a ME double triplet, it cannot fully capture the delocalization of the optically allowed SE (which spreads over 6−8 monomers[8]). However, the dimer model efficiently provides a reasonably accurate, although minimal description of the interacting electrons in acene crystals.

Previous computations by two of the authors employed CASSCF to describe the SF process in pentacene.[7] Due to the computational complexity of these techniques CASSCF was applied to a pentacene dimer in a face-to-face geometry where symmetry dramatically reduced the cost. Although a monomer description provided a starting point to describe acene excited states, SF must be represented by at least a dimer model that allows triplets on two different monomers. RAS-SF[14,15] reduced the computational cost of the ab initio calculation of excited states by orders of magnitude, enabling calculation of dimers with no symmetry restrictions.

The efficient computation of SE and ME states in realistic models permits interrogation of the coupling between the nuclear and electronic degrees of freedom. Near a degeneracy, the BOA breaks down and individual adiabatic states become poor descriptions of the system because population transfer between the nearly degenerate states is strongly coupled to nuclear motion. Instead, the system is best described by a time-dependent superposition of the two states.[20] After considering the QM states involved in acene SF, we will describe how the coupling between the SE and the ME state involves a intermolecular vibration that brings these two states into near degeneracy to enable population transfer. This permits us to calculate the rate of ME state formation using LZS theory.

QM States of Acene Dimers

To understand SF, we need to understand the character of states that may participate in this process. The RAS-SF method automatically determines the single and double exciton states of acene dimers, avoiding the need to assume the specific state nature. Single electronic configurations are insufficient
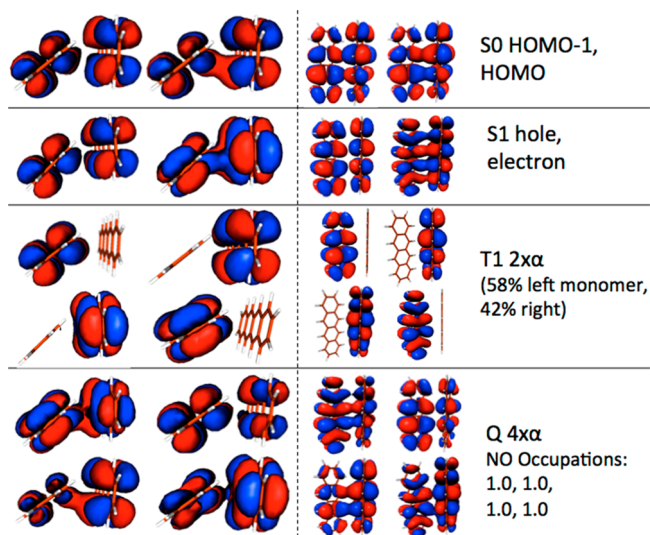
FIGURE 3. Quantum mechanically derived states involved in SF in tetracene, as characterized by key natural orbitals for a model dimer. Two perspective views of each orbital are given: side-on (on left) and front-on (on right). See also Figure 4 for diagrams of the primary configurations for each state. The multiexciton state D is shown in Figure 5.

FIGURE 4. Simplified electron configurations that describe ground and excited states involved in SF. The orbitals basis for these configurations are the orbitals for Q in Figure 3. Note that T1 could also be expressed as a single determinant with two alpha or two beta electrons, as T1 has 3-fold spin degeneracy (S = 1). Q has 5-fold spin degeneracy (S = 2).

to describe many of these states due to the intrinsic couplings between these configurations (e.g., as needed to achieve singlet spin multiplicity).

Key natural orbitals (NOs) for the ground state and relevant low-lying excited states of a tetracene dimer are displayed in Figure 3. These orbitals represent the dominant electronic configurations of the various adiabatic states, which are shown as electronic configurations (in the basis of quintet orbitals) in Figure 4 for comparison. The starting point is the ground state, S0, where doubly occupied HOMO and HOMO-1 orbitals are illustrated. No strong correlations are present, and it is well-represented by a MO diagram consisting of a single electron configuration. The HOMO and HOMO-1 of S0 are linear combinations of the separated monomer orbitals.

The photoexcited bright state S1 can be described by $1e^-$ excitation from S0s HOMO to create the SE electron−hole pair. The hole orbital, shown on the left of Figure 3, is similar to the S0 HOMO, and the particle orbital, shown on the right, is similar to the S0 LUMO (not shown). TD-DFT computations on a 10-mer[8] suggest that S1 delocalizes even further such that at least four molecules are required to describe the major components of the exciton. TD-DFT shows that this state has no separation of the electron/hole pair, and predicts an oscillator strength consistent with a strongly allowed optical transition.[8]

The lowest energy triplet, T1, is composed of two electrons that are delocalized across the two monomers, resulting in four

partially occupied orbitals. Each pair of orbitals looks like a localized triplet, but the near degeneracy between the two T1 states in the dimer causes the overall state to delocalize (and is the reason for four significant NOs vs two for S1). As the two monomers separate, the triplet can be fully localized on a single monomer.

The reference quintet state, Q, consists of four singly occupied MOs (SOMOs) in a single electron configuration (i.e., four alpha spins in four orbitals). Each SOMO is occupied by a single alpha electron and is delocalized across the dimer. In principle, an orbital localization could be performed on Q to represent the four SOMOs as two high spin coupled triplets, each localized on a monomer.

Finally, the lowest energy ME singlet state D is shown in Figure 5. In MO terms, the ME state D possesses relatively complex character that requires at least six electronic configurations to describe (Figure 4). Like Q, D involves four (roughly) singly occupied orbitals whose electrons are correlated across the dimer. D is thus primarily a strong spin correlation (SSC),[21] corresponding to the singlet recoupling of the two triplets of Q. However, at the dimer separation in the crystal, the four SOMOs of D are distinct from Q's SOMOs and each has slightly nonunit occupation numbers. Under these conditions, D contains not just the SSC of recoupling the two triplets into a singlet state, but also additional correlations. At large dimer separations, these differences vanish, and D and Q are degenerate.

Given these states, some comments on spin degeneracies and decoherence in SF are in order. As D is a singlet (S = 0) state of an acene dimer, it is nondegenerate in the sense of having only a single magnetic sublevel. If the two monomers in state D are separated, D's energy approaches that of Q, which is 5-fold degenerate (S = 2) and becomes the same as localized triplets on each monomer, which are each 3-fold degenerate (S=1). The nine triplet−triplet monomer localized levels may be recoupled into nine spin eigenstates of
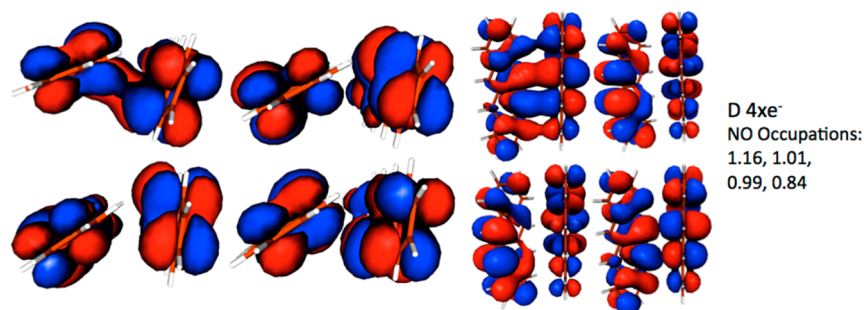
FIGURE 5. Quantum mechanically derived double-exciton state D in tetracene from RAS-2SF: side-on (on left) and front-on (on right). Each orbital in D has a somewhat distinct shape from the corresponding quintet orbitals shown in Figure 3.

the dimer: Q (5-fold degenerate), T (3-fold degenerate), and D (nondegenerate). Decoherence of D is required to yield independent triplet excitations (two T1 levels). This long-distance behavior is clear, and means that writing D as "^{1}TT", which represents the singlet coupling of two monomer triplets, does not entail a single electronic configuration with two spin up electrons on one monomer and two spin down electrons on the other, but a combination of the six configurations shown in Figure 4. The correlation effects between the two triplets at short distance mean that D is slightly lower in energy than its triplet and quintet counterparts.

We do not show the CT states for the dimer because they are higher in energy. TD-DFT calculations of tetracene and pentacene tetramers showed that the lowest energy CT adiabats are approximately 0.3 eV above S1 in both materials,[8] suggesting that they are not involved in SF in the acenes. This corroborates experimental results that measured CT at 0.3 eV or more above S1 in tetracene and pentacene.[22,23]

Intermolecular Coupling for Singlet Fission

The ability to compute excited states at any particular geometry enables the calculation of coupling through the nuclear coordinates. Which nuclear coordinates couple S1 and D to mediate nonadiabatic transition from S1 to D is not obvious because of the many degrees of freedom for large acenes (174 for a tetracene dimer!). However, analysis of the nature of the states proves vital to identifying coupling coordinates. Inspection of the key orbitals displayed in Figures 3 and 5 makes it clear that nuclear motion that changes the $\pi-\pi$ interactions between the two acene monomers strongly affects the key states involved in SF.

This insight led to the first QM characterization of the dark ME state in a pentacene dimer.[7] By necessity, the dimer was restricted to a face-to-face geometry with $D2h$ symmetry to reduce computational cost. The first bright singlet excitation,

S1, and the ME state, D, were calculated as a function of intermonomer separation. The crucial result is that along the intermonomer coordinate, the PESs of S1 and D have different slopes and cross. S1 forms a stable excited state dimer with a shorter intermonomer separation than the ground state, while D is repulsive at all separations. Because the singlet states S1 and D possess different symmetries,[7] their PESs do not involve an avoided crossing, but instead exhibit a symmetry-allowed crossing. Considering their fundamentally different character, it is appropriate to label S1 (bright) and D (dark) as either adiabatic or diabatic states with zero off-diagonal coupling. In this $D2h$ symmetry model, their crossing is well-represented by the dashed lines of Figure 1.

In acene crystals the dimer symmetry is lowered from $D2h$, allowing S1 and D to mix and create a weakly avoided crossing of the bright and dark states. This crossing is represented by the solid lines of Figure 1 and is very close to a conical intersection. Now the diabatic character of the upper and lower adiabatic states changes from one side of the crossing to the other. For instance, the higher adiabat at the ground state geometry corresponds to the bright diabat, while at closer spacings the higher state now has ME (dark) character (see Figures 1 and 2). This suggests that SF results from S1 moving through an intermonomer vibration toward a conical intersection[20] with the ME state D. In this region, rapid, coherent population transfer to D results.

In this picture, the degree of $\pi-\pi$ interaction along the intermonomer separation coordinate is the key electronic-nuclear coupling that facilitates SF in pentacene. To analyze the interaction between S1 and D in a more realistic crystal environment we employed[8] a hybrid QM/molecular mechanics (QM/MM) model. This model described acene dimers with RAS-2SF and the surrounding crystal with the MM3 force field[24] to include lattice strain due to motion of the QM dimer. Several possible intermonomer coordinates

were investigated, and we discovered one that had a particularly large effect on the interacting states. This coordinate, denoted R(C–C), represents relative displacements of the carbon atoms in the top row of each acene monomer from their ground state geometry (i.e., at the initial geometry, R(C–C) is 0 Å). Similar to the face-to-face dimer, S1 relaxes to an excited state dimer from the vertically excited geometry by reducing the intermonomer distance along R(C–C) by 0.3 Å. This relaxation, shown in Figure 2 for pentacene, occurs spontaneously due to the attractive potential of S1. Along the same coordinate R(C–C), D maintains a weakly repulsive potential favoring monomer separation.

The above results show that in a realistic crystal structure, vibrational motion can bring S1 and D into near degeneracy to enable rapid population transfer and internal conversion of the SE state S1 to the ME state D. This explains the key step in the mechanism of SF. Spontaneous motion along R(C–C) after photoexcitation to S1 changes the degree of π–π interaction between the two monomers and brings S1 and D close together. Application of LZS theory leads to the estimate (using the computed electronic coupling value of 40 cm^{-1}) that one vibration along R(C–C) through this region results in a probability of transition to D of 16%.[8] Because the electronic and nuclear degrees of freedom are coupled, higher transition probabilities result from additional nuclear kinetic energy. If the vibrational mode along R(C–C) were excited by one quantum of energy within the harmonic oscillator approximation, the transition probability increases to 26%. This establishes that the rate of SF predicted by motion along the intermolecular vibration is large, and that SF occurs on a sub-ps time scale.

In tetracene, the energetic ordering of S1 and D is reversed from pentacene with D lying ~0.2 eV above S1. Nuclear-electronic coupling still exists along R(C–C), but additional energy is required to access the vicinity of the conical intersection and populate the higher energy state. Predicting the rate of conversion of S1 into D in tetracene requires a careful analysis of the dynamics involved in population transfer from S1 to D that includes the effects of excitation of the R(C–C) vibrational coordinate.

A qualitative summary of the SF mechanism is presented in Figure 1. The interplay between electronic and nuclear degrees of freedom allows S1 and D to couple along an intermolecular vibrational coordinate, resulting in fast SF. This level of detail available through QM simulation enables us to explain many aspects of experiment, as well as to envision new materials that may undergo SF. Our proposed mechanism for SF in the acenes is direct, meaning that it occurs in one step and does not pass through intermediate states. This not only results in faster SF, but also a simplified design criteria: intermolecular coupling of two π systems can form ME states directly from a bright SE without the need for an adiabatic CT intermediate.

Perhaps the most important advance in this methodology is in the treatment of electronic-nuclear coupling. In previous methods,[9,10,25,26] nuclei are assumed to be fixed and therefore conical intersections or avoided crossings are not treated, restricting the dynamical possibilities. Ab initio studies provide a direct description of these important effects while additionally avoiding emphasis on experimentally unrealizable diabatic states. We would like to point out here that diabatic CT states are included in our Hamiltonian, but the diagonalization procedure focuses our discussion onto the adiabatic eigenstates (which are nonarbitrary representations of electronic states). Diabatic CT states may be involved in SF, but they appear to be "virtual states" that provide part of the basis for realizable adiabatic states.

Experiment and Simulation for the Acenes

Many experimental studies of SF, especially in pentacene[27–34] and tetracene,[35–37] have appeared recently. These studies tend to agree rapid, exothermic SF occurs in pentacene, but tetracene undergoes SF with significantly different dynamics.

The mechanistic information from QM calculations can elucidate the photophysical properties of pentacene crystals. An observation from pump–probe spectroscopy of pentacene was the rapid photobleaching of the S0 → S1 transition. This generally occurred on a 100 fs time scale,[30–34] precluding any intersystem crossing event. Following disappearance of S1, photoinduced absorption peaks were identified as triplets in the region of >1.3 eV.[33] These long-lived peaks match the location of the T1 → T2 transition we predicted.[7,8] The rapid photobleaching and concomitant rise of triplet absorption on an ultrafast time scale is well-explained by our results. Photoabsorption to the SE excited state S1 is followed by vibrational relaxation along the R(C–C) coordinate toward the SE/ME crossing region. According to LZS theory, ~20% of S1 should transition into D within one-half of a vibration period (~100 fs), which agrees well with pump–probe results and suggests that intermolecular motion drives the coupling of the bright SE state to the dark ME state. Furthermore, the near degeneracy of SE/ME allows a superposition of states to exist at short times after photoexcitation. This superposition was suggested recently,[34] although a detailed description of the dynamics along R(C–C) will be necessary to quantify this aspect of SF in pentacene.

Compared to pentacene, the photophysics of tetracene[35−37] are less well-understood. E_{S1} is thought to lie just below $2E_{T1}$,[6] implying that thermal activation is required for SF. SF also appears to be slower in tetracene compared to pentacene.[35,36] However, because the two triplets lie uphill from the lowest photoexcited state, SF in tetracene will be affected by changes in film morphology or by which excited state is actually populated by photoexcitation. For instance, S1 states near an interface with an acceptor material, substrate, or vacuum or within an amorphous region could have substantially different energies than those in the perfect bulk crystal. Moreover, if S1 is excited in a vibrationally excited state, or if the higher component of the Davydov doublet is excited, SF may occur spontaneously. These considerations depend on the type and polarization of the incoming pump pulse, further complicating SF in tetracene. Pulse shaping experiments[35] showed that selective excitation of a particular intermolecular coupling coordinate could maximize SF, in agreement with our prediction that additional vibrational energy in the R(C−C) mode could yield additional ME population in tetracene. In short, recent experiments on tetracene are not inconsistent with our proposed direct intermolecular coupling mechanism for SF, but more details need to be resolved.

Conclusions and Prospects

The ab initio methods required for the study of SF mechanisms in organic molecules have been described. An analysis of the SE and ME states explains the mechanism of SF in pentacene, and suggests that a similar mechanism is operative in tetracene. The mechanism of SF in pentacene is relatively straightforward: rapid exothermic population transfer from a bright SE into the dark ME mediated by intermolecular motion, which results in photobleaching of S1 and production of multiple triplets. The mechanism in tetracene is less well understood. In tetracene, additional energy above S1 appears needed to populate D, and the source of this energy is unclear (if the invoked triplet energy level in the crystal were inaccurate by just 0.1 eV, this conundrum might be resolved). The energy may come from thermal fluctuations, photoexcitation into a vibrationally excited state, or simply photoexcitation of higher energy optically allowed states than S1. Additional studies will be necessary to clarify this issue. However, the mechanistic knowledge gained from ab initio calculations will likely prove invaluable in unraveling SF mechanisms in these systems.

Given their ability to predict SF mechanisms quantitatively, ab initio methods can now be used to design new SF materials. New molecules that exploit particular $\pi-\pi$ interactions between S1 and D could be especially promising. Beyond the mechanistic insight that could guide the design of materials, direct screening of candidate SF materials is also possible.

BIOGRAPHICAL INFORMATION

Paul M. Zimmerman received a B.S. from the University of California at Berkeley in 2005, and a Ph.D. working with Charles Musgrave at Stanford University in 2010. He then completed a postdoc with Alexis Bell and Martin Head-Gordon at Berkeley. Paul is an assistant professor in Chemistry at the University of Michigan.

Charles B. Musgrave was born in Los Angeles, California on May 6, 1966. He attended University of California Berkeley (B.S. 1988) and Caltech (Ph.D. 1994), where he worked under the supervision of Dr. William A. Goddard, III. He was a postdoctoral fellow at MIT with Dr. Klavs F. Jensen and joined the faculty at Stanford University in 1996. He was a visiting professor at Harvard University in 2004−2005. He joined the University of Colorado at Boulder in Chemical and Biological Engineering in 2008.

Martin Head-Gordon is the Kenneth S. Pitzer Professor of Chemistry at the University of California, Berkeley, where he leads a research group in electronic structure theory. He holds a joint appointment in LBNL's Chemical Sciences Division. Australian by birth, Martin came to the United States in 1984 for graduate school at Carnegie-Mellon University (with John Pople), followed by postdoctoral research at Bell Laboratories (with John Tully).

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