

## ORGANIC SEMICONDUCTORS

# The birth of an exciton

The photons that make up visible light are indivisible. But certain organic materials can use singlet fission to divide the energy from one photon equally between two molecules. Experiments now reveal the molecular dynamics behind this phenomenon.

Troy Van Voorhis

When organic semiconductors are used in photovoltaics, they have the surprising ability to produce quantum efficiencies greater than 100%. Certain organic materials are capable of carrying out a process known as singlet fission, in which each absorbed photon creates one spin-singlet excited state that subsequently splits into two spin-triplet excited states on neighbouring molecules. Singlet fission thus allows two charge carriers to be generated from each photon. So far, researchers have struggled to understand this unusual effect. But now, writing in *Nature Physics*, Andrew J. Musser and co-workers<sup>1</sup> report ultrafast spectroscopic measurements that track the evolution of molecular vibrations during singlet fission. Their findings provide important clues about the mechanism of rapid fission.

At first glance, singlet fission seems to violate the laws of quantum mechanics. We learn as students that light is composed

of packets of energy (photons) that are indivisible. How then do we explain the fact that in some organic materials a single visible photon is absorbed but two molecules are excited?

The trick here is that the photon does not excite both molecules. The photon excites one molecule to a transient excited state that has singlet overall spin. This transient singlet state then decays to two spin-triplet states on neighbouring molecules. The triplets individually have less than half the energy of the singlet, so energy is conserved.

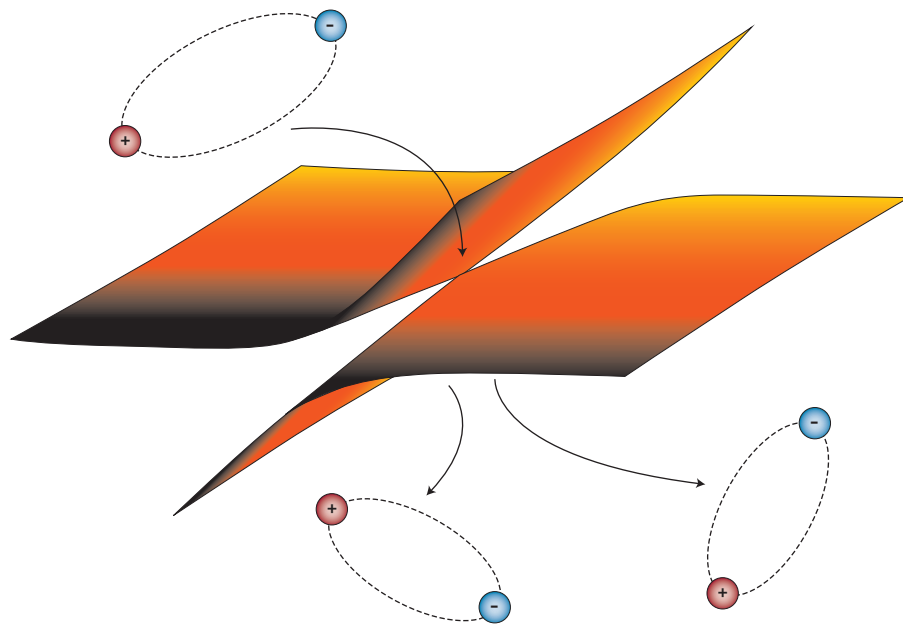
The somewhat surprising thing about singlet fission is that it can be extremely fast — as quick as 70 fs in pentacene crystals<sup>2</sup>. As a result, fission can be very efficient, and this has been shown to lead to exceptionally high quantum efficiencies in certain organic photovoltaics<sup>3</sup>. But researchers are then left with a puzzle: why is fission so fast? What is the mechanism that allows this unusual process to be so efficient?

Different groups have proposed varying mechanisms for fission: the reaction could proceed coherently, through a conical intersection, or even through incoherent transitions. In each case, the critical question is how the molecular vibrations evolve during fission. Are there collective motions or specific modes that govern the reaction? Musser *et al.*<sup>1</sup> used ultrafast vibrational spectroscopy to address this question in a pentacene derivative. In the first set of experiments, a 10 fs ‘pump’ pulse excited the transient singlet state and a broadband ‘probe’ interrogated the vibrational dynamics after a time delay. Spectrally resolving this signal gave the authors information about the frequencies of vibrational modes that were present in the excited state.

These pump–probe measurements were then supplemented by pump–probe–dump measurements in which some of the final triplet excitons were removed from the system by excitation to a higher-lying state, destroying any vibrational coherence. Comparing the vibrational spectra of both the initial singlet and the final triplets revealed that vibrational coherence was maintained throughout fission. That is to say, vibrations that were initially excited in the singlet state maintained their phase relationship with one another as the electronic state divided itself between two molecules.

The implication of these results is that fission cannot proceed through an abrupt, incoherent change in the electronic state. Suppose the contrary is true — that fission does occur through a stochastic change in the electronic state. Then consider two molecules (A and B) that undergo fission at two different times. After fission, the phase of the molecular vibrations of A would be uncorrelated with the phase of the molecular vibrations of B because they were initiated at a different time. Averaging over millions of molecules (as is done in a spectroscopic measurement) would then lead to no observable oscillation in the ensemble and no spectroscopic signal.

Instead of the abrupt-transition picture, Musser *et al.*<sup>1</sup> noted that the spectroscopic



**Figure 1** | In a conical intersection, molecular motion causes two electronic states to become exactly degenerate. Spectroscopic evidence suggests that in singlet fission, a single exciton (top) splits into two excitons (bottom) by passing through just such an intersection.

dynamics of fission were essentially identical to those expected for a conical intersection (Fig. 1). A conical intersection is a situation where a particular molecular motion causes two electronic states to become exactly degenerate. For physical reasons, these crossings almost always have the topology of a two-dimensional cone, leading to the name<sup>4</sup>. Conical intersections have previously been implicated in a host of photochemical phenomena<sup>5</sup>. Fission is unusual in this context because any conical intersection involves electronic states that are spread out over at least two molecules, as opposed to being localized on a single monomer.

Moving forward, these results provide tantalizing hints as to how the physics of singlet fission is connected to similar phenomena. In both multiple exciton generation in quantum dots<sup>6</sup> and natural photosynthesis<sup>7</sup>, there is evidence that quantum coherence contributes appreciably to the efficiency of energy conversion. In contrast, fission-based photovoltaics apparently achieve high yields while maintaining only classical coherence of the vibrations. The results of Musser *et al.*<sup>1</sup> offer a glimpse of how the intricate ultrafast dynamics of singlet fission manage this efficient transformation.

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## ULTRACOLD ATOMS

# The quantum distillery

Selective evaporation of one component from a mixture is a common process, but in the case of ultracold atomic gases, distillation is more complex.

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**D**istillation is a familiar process, known to chemists and whiskey makers for centuries: a mixture of components, only some of which are desired, are separated by allowing just one component to evaporate from the mixture. The process relies on the different physical properties of the constituents, such as the higher vapour pressure of alcohol compared with water. Though well understood in a classical context, such self-purification has recently been suggested to also occur in quantum many-body states<sup>1</sup>. Here, the different quantum properties of the constituents give rise to the distillation. Under the correct conditions, quantum dynamics may lead to smaller samples with purer quantum states than initially present. As they report in *Nature Physics*, Lin Xia and colleagues<sup>2</sup> have demonstrated a key requirement for such purification: the selective quantum evaporation of atoms in specific states from an ultracold cloud of atoms. The approach they use may help to address general open questions in non-equilibrium quantum dynamics and represents an important step towards new methods for purifying quantum states.

Ultracold atomic gases trapped in optical lattices provide clean systems for studying many-body physics<sup>3</sup>. Initially proposed for the study of equilibrium condensed-matter physics, these dilute atomic clouds are increasingly being used to study quantum dynamics. The interest in dynamics is

twofold: the physics is inherently fascinating and often challenging to understand theoretically, and the dynamics may lead to interesting and useful states. For example, some of the most interesting physics in these cold-atom systems occurs at currently unachieved low temperatures (and entropies) and new cooling schemes are needed. Recently, trapped-atom temperatures low enough to allow the observation of magnetic correlations were reached<sup>4,5</sup> by carefully, and adiabatically, adjusting the electromagnetic potentials confining atoms that were cooled using standard techniques. In contrast, in the proposed quantum distillation, entropy reduction occurs dynamically. Following a sudden quench to remove the trapping potential, atoms are free to move in an optical lattice, with those that leave the initial cloud carrying away the disorder.

For this process to work as a quantum purification scheme one must first demonstrate the ability to identify different components and selectively distil out the unwanted ones. Xia *et al.*<sup>2</sup> demonstrated this effect with a cloud of bosonic atoms trapped in one-dimensional optical lattices. The initial state consisted of a mixture of lattice sites with one or two atoms. A lattice with exactly two atoms per site would be purer (having lower entropy). In an analogy with whiskey, the sites with one atom can be identified with alcohol and the sites with two atoms can be identified with water. In the absence of atom–atom interactions,

atoms can hop from site to site on the lattice and freely move away once the overall trap confinement is removed, independent of the site occupation. However, when two atoms on a site have repulsive interactions, a counter-intuitive effect arises: the paired atoms tend to stick together and their motion through the lattice is inhibited. This effect is due to the inability to conserve energy, because paired sites with higher energy have no simple way to release their energy into two free single atoms.

The different mobility for the doubly occupied sites is just the sort of selectivity needed to distil out singly occupied sites. Although the stickiness of paired atoms<sup>6,7</sup> and the free expansion of bosons<sup>8</sup> and fermions<sup>9</sup> in a lattice has been studied previously, Xia *et al.*<sup>2</sup> have, for the first time, directly measured the transport of atoms in both singly- and doubly-occupied sites. They showed that once the confining trap is removed, the core distribution of two atoms per site does not change, whereas atoms in singly occupied sites spread freely away from the central cloud.

The whiskey analogy is not flawless, as the atoms are not perfectly sticky and paired atoms can dissociate into two mobile, singly occupied sites — like water turning into alcohol and evaporating away. The distillation effect described here is complicated further by the fact that singly occupied sites within the remaining doubly occupied core can get trapped, which limits