Comment on "Coherence and Uncertainty in Nanostructured Organic Photovoltaics"

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In a recent paper[1] the authors make the following claims.

(1) The spatially extended excited-state wave functions can be understood as originating from fundamental quantum uncertainty. During the light-absorption process, the existence of the photon is uncertain, implying a momentum uncertainty equal to the momentum of the photon. As a result, its position, as well as the position of the photo-excitation it creates, is uncertain, as required by Heisenberg's famous equation: $\Delta x \Delta p \geq \hbar/2$. The length scale imposed by the uncertainty principle is $\lambda/4\pi$, which is greater than 20 nm for visible radiation. Thus, the photoexcitation process generates a delocalized coherent superposition of the eigenfunctions of the Schrodinger equation that describes the nanostructured organic photovoltaic blend.

(2) A general means of understanding excited-state delocalization on short time scales is through fundamental quantum uncertainty; the initial photoexcitation is a coherent superposition of eigenfunctions of the Schrodinger equation, having a spatial distribution of $\lambda/4\pi$.

(3) We observed a generality in the charge-generation dynamics of organic bulk heterojunction materials that is unexpected from the perspective of a highly localized initial photoexcitation. The creation of long-range coherent superposition states is a natural consequence of the Heisenberg uncertainty principle, as applied to the photon absorption process. We expect that phenomena of this type are important not only for organic bulk heterojunction solar cells but also for nanostructured materials in general.

The authors have performed pump–probe measurements in various electron donor/acceptor blends and found similar fast transients <50 fs in the different materials studied. This time scale is much faster than the exciton hopping time between donors and acceptors. They then concluded that this process must be universal and looked for a profound explanation based on the foundations of quantum mechanics that is independent of any molecular properties. To that end they erroneously invoked the Heisenberg Principle $\Delta p \Delta x >, \hbar/2$ *for the absorbed photon*. They argued that thanks to Heisenberg, the absorbed photon is delocalized and can cover the entire sample instantaneously, hence the ultrafast charge transfer time scale. They claim that exciton migration is not necessary for charge separation because a delocalized photon creates delocalized excitations. Because photon delocalization is involved, it is a universal mechanism. This argument is false on many fronts.

The pump–probe signal does not depend on any property of individual photons or on the corpuscular nature of light. When strong classical fields are used, the response and the signals depend on the spatial, temporal, and spectral profile of the *electric field*, which is a collective representation of many photons.[2] Diffraction limits the beam size to $\lambda/2$, which happens to agree with "Heisenberg's" estimate.[1] What a single photon does is irrelevant to these measurements. Charge transport must depend on properties of matter (energy levels, density of states, effective size of quasiparticles, couplings) and cannot be universal. After all, real electrons have to move. Thus the desire to demonstrate universal "coherence effects" in photovoltaics is misguided.

There are two types of coherences in many-chromophore systems. The first is related to exciton delocalization (i.e., the eigenstates can spread over few or many chromophores).[3–14] The second is coherence between eigenstates (i.e., when the incoming light prepares a superposition of eigenstates with well-defined phases). Coherence between eigenstates is expected to decay on the time scale of the exciton bandwidth, but coherence within eigenstates, known as exciton delocalization, may persist for longer times. Exciton delocalization and, more generally, carrier delocalization are well understood phenomena. The exciton size can be attributed to the interplay of coupling and disorder. Delocalized excitons can span many chromophores and can thus give rise to fast transients that do not require exciton hopping. These effects depend on details of material properties and are not universal. The Marcus Theory[15] when formulated in the delocalized basis[16] can give rise to fast electron transfer. There is nothing particularly novel or surprising about this.

With classical light, elementary quantum mechanics tells us that, immediately following photoexcitation, molecules are prepared in a superposition of eigenstates with a broad bandwidth. Subsequent dephasing can create eigenstates. All of these depend on the material level structure, the eigenstates of the system, and the dipole matrix elements. The size of the light beam is a factor, for example, for fields shaped on the nanoscale,[17] but this only involves classical optics and has nothing to do with quantum uncertainty.

The cited quantum effects in photosynthesis[18] is another example where the quest for universal principles has triggered extensive activity centered on how biology uses quantum coherence to optimize the charge-separation yield. Phase coherence was found to persist for 0.5 ps in photon echo experiments of the light harvesting antenna complex FMO and other systems. However, despite the original claims, that finding

is not very surprising either: A distinction must be made between interband dephasing of the ground to excited state coherence and intraband dephasing between various exciton states. Intraband dephasing is expected to last longer than interband. Dephasing of interexciton coherence arises from their different coupling to a bath that causes their energy difference to fluctuate. Excited electronic states have typically a very different charge distribution and coupling to a bath than the ground state. However, different exciton states are not that different from each other. The optical coherence between the excited and ground state thus typically has a much faster dephasing than the coherence between excitons. This is well documented in molecules and in semiconductors. Furthermore, there is growing evidence that the coherence is vibrational in nature. This makes it even less surprising and relevant to biological energy transfer. Despite many speculations, there is, so far, no evidence that coherence is essential for the charge separation quantum yield and that it has been optimized by evolution. All effects can be well understood in terms of exciton delocalization and are a twist to an old topic.

In summary, exciton coherence and localization are well established concepts dating back to the 1970s that are constantly being rediscovered and recast with a different terminology, earlier in biological light harvesting and now in photovoltaics. There is nothing particularly surprising in the recent biological or photovoltaic experiments that require paradigm change. However, an interesting issue that may be raised following ref 1 is whether the quantum nature of light and properties of photons can be used to better understand charge and energy migration. This is possible but will require different types of measurements. $\Delta x \Delta p$ of a photon while being absorbed is not an experimental observable. Heisenberg had derived an interesting uncertainty between the electric ΔE and magnetic ΔH field fluctuations in a small volume that could be highly relevant for nanostructures, but this does not involve individual photons.[19]

Chemistry and biology are all about details. Typically, physicists look for universal phenomena that only depend on the fundamental constants of nature. To import such ideas to real systems one must do more sophisticated experiments as is commonly done in the field of quantum information and employ individual photons and quantum light.[20] Even though these are not ambient conditions for solar cells and charge separation, they may be used as a spectroscopic tool for probing the fundamental interactions underlying real classical and biological processes. Examples are photon counting coincidence and statistics and using the unusual spectral and temporal profiles of entangled photons.[21,22] Such experiments could be used to provide new probes for photovoltaics. The development of quantum field spectroscopy is an interesting challenge but totally unrelated to conventional spectroscopy with classical light, such as pump−probe.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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