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Photo-induced electron transfer: general discussion

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Terry Frankcombe, Gregory Gate, Oliver Gessner, Naomi Ginsberg,
Christopher Grieco, Michael Haggmark, Sharon Hammes-Schiffer,
Vanessa Huxter, Michael Kellogg, Nadia Korovina, Yumin Lee,
Johannes Mahl, Karen Morenz, Jennifer Ogilvie, Thomas A. A. Oliver, 
Tom Penfold, Petter Persson,  Benjamin Schwartz, Minjung Son, 
Vasilios Stavros, Collin Steen,  Mark Thompson, Michael Wasielewski,
Emily Weiss and Jack Woolley

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Nadia Korovina opened discussion of the paper by David N. Beratan: Does the excited state energy of the bridge affect the coupling between the donor and the acceptor? How does the rate of energy transfer through the bridge scale with respect to the bridge energy?

David N. Beratan replied: With Dexter energy transfer reactions, as with electron-transfer reactions, the donor–acceptor coupling and the transfer rate are expected to grow as the states of the bridge become nearly resonant with the donor and acceptor states. In the case of Dexter energy transfer, it is the excitation energy of the bridge states compared to those of the donor/acceptor species that should be considered. The exponential distance decay constant, typically called beta, will become smaller as the bridge electronic transitions approach resonance with the donor and acceptor transitions. Interestingly, we have found that the nature of the mediating virtual states changes as the bridge exciton state energies become closer to being resonant with the donor and acceptor exciton energies. For large excitation energy gaps with the bridge states, charge-transfer virtual states dominate the Dexter coupling. However, as the bridge virtual states approach resonance with the donor and acceptor states, virtual exciton states enter the Dexter mediation. We have described this transition in the Dexter coupling mechanism in ref. 1. Of course, as coupling to the bridge becomes very large, the two-state quantum dynamics formulation and the Fermi's golden rule rate treatment will fail.

1 S. S. Skourtis, C. Liu, P. Antoniou, A. M. Virshup, and D. N. Beratan, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 8115–8120.

Tom Oliver commented: I believe that your model is purely electronic and does not include any vibrational degrees of freedom. Is this a strictly valid approximation, and how would your model change if these were included in your model?

David N. Beratan answered: There are two families of vibronic effect to consider: those arising from the donor and acceptor chromophores and those arising from the bridge. Our studies assume bridge electronic excited states are far off of resonance with the electronic transitions of the donor and acceptor species. In this regime, neglect of vibronic effects that could arise from the bridge is justified since bridge mixing is so weak. As bridge electronic transitions become closer to degenerate with the donor and acceptor transitions, the bridge, donor, and acceptor states will be more strongly mixed and bridge vibronic effect could become quite rich and significant. This is analogous to typical considerations in electron transfer reactions where bridge motion could produce inelastic transport as well as non-Condon effects on the bridge-mediated couplings. In our current treatment of Dexter interactions, we have assumed a Condon approximation and have not explored the (donor and acceptor) nuclear coordinate dependence of the Dexter couplings.

Tom Penfold remarked: You mentioned that for Ru and Os complexes, the picture of distinct singlet and triplet states breaks down. Do you have an idea at what point it becomes important to consider the breakdown of spin-classification? For example, at what point can triplet energy transfer be driven by a Förster mechanism arising from a mixing of singlet character into the triplet state?

David N. Beratan responded: The balance between the Förster and Dexter mechanisms depends on the extent of spin-orbit mixing among the spin states, the magnitude of the transition dipole moments for the donor and acceptor chromophores, and the strong distance dependence of the Dexter coupling. In the Ru-metal organic framework structures that are doped with Os exciton traps,¹ weak transition dipole moments tend to disfavor Förster transfer and produce a greater role for Dexter transfer than might be expected from the admixture of singlet and triplet character in the excited states (the Dexter rate is independent of the transition dipoles of the donor and acceptor chromophores). As such, one expects that the relative balance of Förster and Dexter contributions to be distance dependent (the Förster component will have a small 'prefactor' due to the transition dipole effect, but will have a much softer distance decay than the Dexter component). It would be interesting to develop systems in which the donor-acceptor distance could be varied over a wide range; in such a case with mixed spin states one might expect to find exponential distance dependence (Dexter mechanism transfer) at shorter distances and $1/R^6$ dependence at longer distances. Studies that access a wide range of transfer distances could probably be carried out in disordered glasses, where there is a long history of studying both exciton and electron transfer reactions (see classic studies of Inokuti, Hirayama, Hopfield, and Miller²⁻⁴).

1 J. Lin, X. Hu, P. Zhang, A. Van Rynbach, D. N. Beratan, C. A. Kent, B. P. Mehl, J. M. Papanikolas, T. J. Meyer, Thomas, W. Lin, S. S. Skourtis and M. Constantinou, *J. Phys. Chem. C*, 2013, **117**, 22250–22259.

2 M. Inokuti and F. Hirayama, *J. Chem. Phys.*, 1965, **43**, 1978–1989.

3 D. G. Thomas, J. J. Hopfield and W. M. Augustyniak, *Phys. Rev.*, 1965, **140**, A202–A220.

4 J. V. Beitz and J. R. Miller, *J. Chem. Phys.*, 1979, **71**, 4579.

Emily Weiss asked: How does one think about triplet energy transfer from a donor for which the eigenstates are not pure singlets and triplets (due, say, to spin-orbit coupling) to an acceptor in which the eigenstates are pure singlets and triplets?

David N. Beratan responded: Please see the answer to the previous question for a discussion of this issue in the context of Ru and Os excitation energy transfer. For chromophores that include transition metals, the spin orbit interaction mixes the spin states and one can expect a mixture of both Förster and Dexter mechanisms to become available, with the balance among them set by the strength of the relevant transition dipole matrix elements (Förster component) and the Dexter couplings. The dominance of one mechanism over another is expected to depend on distance; it would be very interesting to look at distance dependent quenching in such systems to identify the crossover point between the Förster and Dexter mechanisms.

Petter Persson commented: In the scheme for alternative Dexter energy transfer pathways in Donor-Bridge-Acceptor (D-B-A) systems that you show in Fig. 2 of your paper (DOI: 10.1039/c9fd00007k) and explore throughout the paper you distinguish clearly between one-particle and two-particle interactions. Can you elaborate any further on any significant trends that you have observed for the energy transfer processes in terms of state energies and coupling elements relating to the fundamentally different nature of the (virtual) states involved in the two different types of pathways as either 'charge-transfer' or 'excitonic' in nature, respectively? Do you think that the difference in the nature of these states could manifest itself in terms of different sensitivity to factors that could be varied experimentally such as a surrounding solvent polarity (or similar), and could this potentially be used to perform controlled energy transfer experiments on relevant molecular systems in which the relative contributions for the different types of pathways to the net energy transfer could be significantly influenced?

David N. Beratan replied: The clearest observation is that bridges with electronic transitions closer to resonance to the donor and acceptor electronic transitions will tend to favor mediation *via* excitonic virtual states, while bridges with higher energy electronic transitions will favor charge-transfer state mediation. This means that the latter mediation mechanism will more closely resemble the mechanism suggested by Closs, Fleming and co-workers^{1,2} cited in our paper (where the Dexter coupling is approximated by a product of electron and hole superexchange interactions), while the former case will be more complex. This is described in greater detail in ref. 3. An exciting challenge is to design chemically bridged donor acceptor systems in which electron, hole, and Dexter energy transfer can all be studied so that these mechanistic interrelationships can be probed in detail.

1 Closs, Fleming and co-workers.

2 S. S. Skourtis, C. Liu, P. Antoniou, A. M. Virshup, and D. N. Beratan, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 8115–8120.

Jeffrey Cina commented: As illustrated in Fig. 2 of your paper (DOI: 10.1039/c9fd00007k), the donor-bridge-acceptor systems you are considering exhibit multiple electronic pathways between donor-excited and acceptor-excited states

mediated by Dexter transfer. While the initial and final adiabatic electronic states are the same in all these pathways, the different pathways consist of distinct sequences of electron and hole propagations. Using the analogy of what occurs in a multiple slit experiment, you predict that these pathways can interfere quantum mechanically at the level of amplitudes, and that the sum of these transfer amplitudes must be summed before squaring to obtain the transfer probability. My question is whether the differing response of the 'environment' of the electronic system, comprising internal and external nuclear degrees of freedom, and possibly the local dielectric response of the surroundings, might provide a form of 'which-path' information, which tends to 'observe' through which of these multiple 'slits' the excitation is transferred? Could these effects perhaps be tuned by varying solvents, isotopes, *etc.* to control the net extent of interference between the multiple pathways?

David N. Beratan answered: The diagram shown in Fig. 2 of DOI: 10.1039/c9fd00007k elaborates the electronic coupling pathways that exist during the fleeting existence of the transition state for the energy transfer reaction. In the cases studied in our paper, the virtual states that mediate the Dexter coupling are far out of energy resonance with the initial and final states. As such, on the timescale of the transition state (fs) and the electronic dynamics, the nuclei are essentially frozen and the coupling pathways interfere coherently. In the simpler case of single-electron transfer, orbital symmetry effects are known to exert large effects on the transport kinetics, and this influence is a manifestation of the coherent interference among tunneling pathways.^{1,2}

As a result of the coherent interference of coupling pathways in bridge-mediated Dexter energy transfer, one could create 'which way' experiments. Indeed, we have developed this concept and studied it in the context of coherent vibrationally-perturbed electron-transfer reactions. These concepts and designs map very directly onto Dexter energy transfer experiments, as suggested. We have explicitly considered using vibrational markers (based on isotopic and weakly perturbing chemical substitution) to reveal the path taken by an electron, and thus to change the nature of the quantum interferences and the electron transfer kinetics. We believe that multi-slit and 'which way' experiments at the molecular scale provide a rich area for further study. Please see: ref. 3-6 for more detail. Prof. Julia A. Weinstein at the University of Sheffield is also pursuing important studies in a similar spirit.

1 S. S. Skourtis and D. N. Beratan, *Adv. Chem. Phys.*, 1999, **106**, 377–452.

2 S. S. Skourtis, C. Liu, P. Antoniou, A. M. Virshup and D. N. Beratan, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 8115–8120.

3 S. S. Skourtis, D. H. Waldeck and D. N. Beratan, *J. Phys. Chem. B*, 2004, **108**, 15511–15518.

4 D. Xiao, S. S. Skourtis, I. V. Rubtsov and D. N. Beratan, *Nano Lett.*, 2009, **9**, 1818–1823.

5 Z. Lin, C. M. Lawrence, D. Xiao, V. V. Kireev, S. S. Skourtis, J. L. Sessler, D. N. Beratan and I. V. Rubtsov, *J. Am. Chem. Soc.*, 2009, **131**, 18060–18062.

6 Z. Ma, Z. Lin, C. M. Lawrence, I. V. Rubtsov, P. Antoniou, S. S. Skourtis, P. Zhang and D. N. Beratan, *Chem. Sci.*, 2018, **9**, 6395–6405.

Jon Bender asked: Within this theoretical framework, is it possible to explore systems in which the acceptor and bridges are of the same identity in order to explore differences in triplet exciton transfer/transport in different packing motifs, *i.e.* brick-and-mortar (two bridges) compared to face-to-face slip stacking (one bridge)? Studies such as these could be beneficial for establishing design guidelines for crystals with enhanced triplet exciton transport.

David N. Beratan responded: In fact, we have explored multi-step Dexter hopping among degenerate sites in the following study, including structures that differ in 3D architecture.¹ In addition, Fig. 9 of our Faraday Discussions paper in the present volume (DOI: 10.1039/c9fd00007k) shows how shifting the naphthalene–naphthalene stacking influences the Dexter couplings. When donor and bridge species interact very strongly, there are additional issues of how delocalized (trapped) the initially prepared donor exciton state will be, as this characteristic will influence the subsequent dynamics.

1 J. Lin, X. Hu, P. Zhang, A. Van Rynbach, D. N. Beratan, C. A. Kent, B. P. Mehl, J. M. Papanikolas, T. J. Meyer, T. W. Lin, S. S. Skourtis and M. Constantinou, *J. Phys. Chem. C*, 2013, **117**, 22250–22259.

Karen Morenz commented: I was really interested in the role of the molecular orientations or positions in the constructive and destructive interference you see here, but unfortunately in real life I can not just arbitrarily slide my molecules along exactly as far as I want to, so what experiment would you suggest to experimentally verify this?

David N. Beratan answered: Similar issues of molecular orientation, distance, bridge structure, and quantum interference arise in the field of electron transfer photochemistry (see, *e.g.* ref. 1). As the theoretical studies of Dexter energy transfer mature, and the nature of the quantum interferences are better understood, we hope to target specific covalently bonded or self-assembled structures for study. Such structures can “look in” geometries of specific interest.

1 V. Balzani, *Electron Transfer in Chemistry*, vols. I–V, Wiley-VCH, 2001.

Karen Morenz asked: You mentioned that perhaps one could build some rigid covalently bonded structures in order to hold the molecules in a particular orientation—are you planning to do some calculations on such a system so that we could compare experimental observations to that, or how would we connect the current work to an experiment on such a system?

David N. Beratan answered: Considerable attention has been placed on building rigid covalently bonded structures in which to study the distance and bridge-structure dependence of Dexter energy transfer rates.^{1,2} As we come to understand how the Dexter pathways interfere with each other and how the couplings scale with the number of parallel bridge pathways, we hope to suggest some compelling new molecular designs.

1 G. L. Closs, P. Piotrowiak, J. M. Macinnis and G. R. Fleming, *J. Am. Chem. Soc.*, 1988, **110**, 2652–2653.

2 S. Speiser, *Chem. Rev.*, 1996, **96**, 1953–1976.

Stephen Bradforth opened a discussion of the paper by Michael R. Wasieleski: Your results present interesting evidence for quantum coherence in electron transfer pathways. Can the temperature dependence of the rate ratios presented be connected to a simple theory of how quickly the bath should damp out the coherence?

Michael Wasielewski answered: Yes, the connection to theory can be found in ref. 1. In the context of this theory, we are operating in the large free energy drop, low temperature limit, where damping is modest. This also correlates with our own work.²

1 A. J. Leggett *et al.*, *Rev. Mod. Phys.*, 1987, **59**, 1–85.

2 D. D. Powell *et al.*, *J. Phys. Chem. B*, 2017, **121**, 7190–7203.

Benjamin Schwartz asked: To better understand the fluctuations that could be destroying coherence in the multi-pathway electron transfer, would it be possible to build a similar molecule that does not do photoinduced charge transfer so that detailed spectroscopy could be performed on the NDI acceptors? In this way, it might be possible to get a handle on the nature of all the fluctuations and coupling in the system, which could lead to a better understanding of the interference that contributes to the overall photoinduced charge transfer.

Michael Wasielewski replied: This is a matter of timescales. We have examined an NDI-NDI cyclophane in which one of the NDI molecules is reduced with a single electron. On an EPR timescale this electron is rapidly hopping between the two NDIs, but on an electronic timescale, it is not. However, this experiment does not properly answer the question because there is a counterion that actually determines how fast the electron can hop between the two NDIs. In other words, it is difficult to generate a radical anion that can probe the environment on a fast enough timescale in the presence of other ancillary effects interfering.

Minjung Son commented: The DMA-An and NDI moieties are the only donor-acceptor pair for charge transfer considered in this work, for both 1NDI and 2NDI. In the case of 2NDI, however, could there be symmetry-breaking charge transfer between the two NDIs (such as reported in ref. 1 and 2) that might interfere with the signal observed here? Have you considered this possibility at all?

1 E. Vauthey, *ChemPhysChem*, 2012, **13**, 2001–2011.

2 N. Banerji *et al.*, *J. Phys. Chem. A*, 2009, **113**, 8202–8212.

Michael Wasielewski replied: We do not excite NDI, so that symmetry-breaking charge separation is not an option.

Tom Oliver queried: If you directly photoexcite the localised excited states of 1NDI or 2NDI instead of the charge-transfer state, does this change the observed charge separation dynamics?

Michael Wasielewski responded: No, energy transfer from excited NDI to the DMA-An CT state is faster than we can measure.

Jahan Dawlaty asked: Is it possible to photoexcite the split state? The gap is probably somewhere in the mid IR, and it seems reasonable that it should be optically allowed. Therefore it should be possible to study it with a UV-vis pump and mid-IR probe experiment.

Michael Wasielewski replied: The gap between the states is about 1450 cm^{-1} , so it should be possible to see a mid-IR transition provided that other vibrational features do not overlap severely.

Jon Bender said: Do you observe any solvent dependence of the 2-NDI excited state dynamics at room temperature?

Michael Wasielewski replied: We have not performed an extensive survey of solvents.

Jennifer Ogilvie addressed Michael Wasielewski and David N. Beratan: In your paper (DOI: 10.1039/c8fd00218e) you mention the use of selective vibrational labels to probe quantum interference effects. This is perhaps a question to both you and David N. Beratan. Can you please elaborate on how such labels could be used? Might they provide ‘which way’ information or would their use destroy interference effects by making the pathways distinguishable?

Michael Wasielewski responded: This would depend, of course, on how great a perturbation the change would be. For example, it may be possible to substitute a single deuterium atom at a C–H bond of one NDI of the two, which would have a small effect on the electronic symmetry. Observation of the C–D vibrations would be required. Whether this perturbation is sufficiently small would need to be determined experimentally.

David N. Beratan replied: In our most optimistic scenario, vibrational labels could indeed provide ‘which way’ information. This pathway manipulation, although a manifestation of purely coherent quantum dynamics, could have profound implications for electron transfer kinetics and yields. For example, imagine that the electron transfer process is symmetry forbidden in the absence of the vibronic effect described above. The process that excites (or de-excites) a localized vibrational mode would turn on the electron transfer process by eliminating destructive interference between the pathways. We have described these effects in some detail in previous work.^{1,2} A complexity is that the key experiments may need to be carried out at very low temperatures to avoid thermal fluctuations that could also lower symmetry and turn on otherwise ‘forbidden’ processes. Experimental efforts aimed at realizing vibrationally perturbed electron transfer have most likely manipulated the reaction coordinate motion, rather than strongly perturbing the electronic dynamics.³ Synthetic, spectroscopic, and theoretical collaborations are underway to refine the molecular designs in order to realize the novel double-slit quantum dynamics at the nanoscale that has been predicted by theory. We have not fully extended the double-slit concepts to Dexter exciton transfer, but the coherent bridge-mediated nature of the Dexter coupling suggests that entirely analogous physics should be accessible.

1 S. S. Skourtis, D. H. Waldeck and D. N. Beratan, *J. Phys. Chem. B*, 2004, **108**, 15511–15518.

2 D. Xiao, S. S. Skourtis, I. V. Rubtsov, and D. N. Beratan, *Nano Lett.*, 2009, **9**, 1818–1823.

3 Z. Ma, Z. Lin, C. M. Lawrence I. V. Rubtsov, P. Antoniou, S. S. Skourtis, P. Zhang and D. N. Beratan, *Chem. Sci.*, 2018, **9**, 6395–6405.

Tom Oliver asked: Instead of using an electric field to bias electron transfer to a specific NDI acceptor, could you place the molecule inside an asymmetric protein, and in analogy with photosynthetic reaction centres,¹ make the electron transfer directional without changing the chemical structure of electron donors/acceptors?

1 M. A. Steffen, *Science*, 1994, **264**, 810.

Michael Wasielewski responded: In principle, yes, provided an appropriate protein could be found with a large enough binding site to accommodate 2NDI.

Oliver Gessner questioned: Could you provide an intuitive, physical picture for the significant increase in charge transfer (CT) rates due to quantum interference between the two CT pathways beyond mathematical expressions? Parallels to the famous double-slit analogue seem obvious at first glance but, in the case of CT, questions arise about how to translate the fundamental ideas of local signal enhancements into rate enhancements. Is there 'a price to pay' for the increased CT rate, for example, in terms of the amount of charge that may be transferred within a given time interval? Could the basic concepts, principally, be extended 'indefinitely', *i.e.*, scaled to an arbitrarily large number of interference pathways with correspondingly increasing CT rates (neglecting practical issues associated with chemical synthesis)?

Michael Wasielewski replied: The result of using more than two slits (interfering pathways) can be described as a sum of two-slit experiments (Born's rule) as has been recently validated by experiment.¹ We would expect a rate increase limited by the time resolution of the experiment (and in the limit by relativistic effects). Also it is likely that dephasing will be faster with more sites since there are more system-bath interactions, so the experiment becomes far more challenging. However, there should be no effect on the overall yield of electron transfer.

1 J. P. Cotter, *et al.*, *Sci. Adv.*, 2017, **3**, e1602478.

Nadia Korovina remarked: The quantum interference effect that results in a $>2\times$ increase in charge transfer when two cofacial acceptor compounds are attached to the donor is due to substantial orbital overlap of the two acceptor chromophores. If the two acceptors were attached to the donor in such a way that the orbital overlap was minimized between them, would the increase in the rate of charge transfer be exactly two upon addition of the second acceptor? Do you have any experimental evidence of this?

Michael Wasielewski answered: We expect that the quantum interference effect would diminish as the electronic coupling between the two acceptors also decreases. While there is no experimental evidence, we have examined this case in ref. 1.

1 D. D. Powell, M. R. Wasielewski and M. A. Ratner, *J. Phys. Chem. B*, 2017, **121**, 7190–7203.

Jon Bender asked: Can you imagine a scenario in which rigid or alkyl functional groups containing cyano Stark effect probes at the imide positions of NDIs within your NDI dimer could be sensitive enough to changes in the individual NDI moiety charge states/density while being able to resolve changes in the electric

field about each NDI monomer individually? Such a scenario may prove to be a fruitful test of your experimental interpretation.

Michael Wasielewski answered: Addition of CN or other functional groups having characteristic vibrations would have to be done on each NDI to maintain symmetry. We are currently exploring whether the vibrations of the carbonyl groups of NDI can offer similar information.

Vasilios Stavros remarked: From your TA spectra of 1- and 2-NDI, do you see any evidence of vibrational cooling from the spectral narrowing of, say, the ground state bleach signature?

Michael Wasielewski answered: No, there is no significant evidence of vibrational cooling in these systems on the timescale of our measurements.

Vanessa Huxter opened discussion of the paper by Benjamin J. Schwartz: Although it may be difficult to achieve experimentally, could you comment on the possibility of controlling disorder as a function of dopant choice to modify the ratio of trapped to free polarons.

Benjamin Schwartz answered: This is a very interesting question and one that we are still actively pursuing. Our main conclusion in this paper is that disorder in the distribution of dopant counterions leads to increased polaron trapping and thus poorer carrier mobility. We have been working on controlling this disorder in two different ways. In ref. 14 of our paper (DOI: 10.1039/c8fd00210j), we describe work in which we take advantage of our sequential doping method to control the crystallinity of P3HT doped with F4TCNQ. We find that, as expected, more crystalline P3HT has less disorder and thus higher carrier mobilities, but this is primarily because there are more places to put the dopant counterions far from the polarons on the polymer backbone rather than because crystallinity allows for greater polaron delocalization. With this in mind, in ref. 50 of the paper we used dodecaborane cluster-based dopants to isolate the counterion from the polaron. Even though these large dopants completely destroyed crystallinity in our doped P3HT films, the carrier mobilities we observed were higher than in our much more crystalline films doped with F4TCNQ, verifying that controlling the interactions between the polaron and counterion is more important than controlling crystallinity when it comes to increasing the ratio of free to trapped polarons. We are continuing to work with new dopant/polymer combinations in order to better understand all the interactions between polymer crystallinity, counterion proximity to the polaron and the general nature of disorder in determining carrier mobility.

Tom Oliver said: In your paper you illustrate that only specific polaron transitions are optically bright. What are the selection rules for polaron absorptions?

Benjamin Schwartz responded: Based on Fig. 2b in our paper (DOI: 10.1039/c8fd00210j), the standard picture of polaron optical transitions is that P1 and P2 are optically allowed while the P3 and P3' transitions are forbidden by symmetry. However, if the polaron has a significant degree of two-dimensional delocalization, as illustrated in Fig. 2d of our paper, then the P3 and P3'

transitions become more optically allowed (and possibly non-degenerate) while the P2 transition loses oscillator strength. Since polarons in P3HT have a partial 2-D character, this means that P1, P2, P3 and P3' generally can all be observed. There is an excellent discussion of polaron optical selection rules in ref. 18 of our paper.

Tom Oliver asked: Would I be right in saying that the symmetry of the polymer itself then dictates the selection rules and allowed polaron absorptions?

Benjamin Schwartz answered: Yes; most conjugated polymers can be roughly classified as having electronic states of Ag and Bu symmetry, and this is what gives rise to the basic selection rules for polaronic optical transitions.

Tom Oliver asked: Due to polaron formation in your doped P3HT films, do you observe any infrared active vibrational (IRAV) modes?¹ And are the IRAV modes similarly modulated by the presence of bipolarons?

1 A. J. Heeger, *Rev. Mod. Phys.*, 1988, **60**, 781.

Benjamin Schwartz responded: We do observe IRAV bands associated with our polarons, which result from the fact that the backbone of the polymer is reorganized in the presence of the positively-charged polaron (in other words, a P3HT radical cation has different vibrations than a neutral P3HT chain). These bands occur at energies lower than 0.5 eV (wavelengths redder than 2400 nm), so we were unable to probe their dynamics in the experiments presented in our paper. We have studied them with steady-state spectroscopy in previous work, however, because the ratio of the intensity of the IRAV bands to the P1 optical transition provides a nice handle on the degree of polaron trapping and localization; see ref. 14 and 50 of our paper (DOI: 10.1039/c8fd00210j) for more details.

Christopher Grieco queried: In this study was the P3HT regio-regular or regio-random in chemical structure? If it is regio-regular, the polymer should form both amorphous and crystalline domains in thin films. The crystalline structure is typically lamellar, in which multiple chains pack together through pi-stacking. It has been reported in the past that 'delocalized polarons' can form in these crystalline domains, in which the (hole) polaron delocalizes through space across multiple polymer chains. These species have absorption bands that are distinct from those of localized polarons. In literature that I am most familiar with (*e.g.* that of Z. Valy Vardeny and coworkers), the absorption bands associated with localized polarons are designated as 'P', and those associated with delocalized polarons are designated as 'DP' (for example, see Fig. 4 and 6 in ref. 1). Why don't you observe 'DP' bands in your spectra?

1 Jiang *et al.*, *Adv. Funct. Mater.*, 2002, **12**, 587–597.

Benjamin Schwartz answered: The P3HT studied in this work is >98% regioregular, purchased commercially from Rieke Metals. Thus, as you point out, our films are semicrystalline, with a crystalline morphology that has the lamellar stacking edge-on to the substrate and the pi-stacking direction in the plane of the

film (see, *e.g.*, ref. 14 in our paper (DOI: 10.1039/c8fd00210j) for a more detailed structural analysis of our P3HT films doped with F4TCNQ by the sequential processing method that we also use in this paper). Indeed, it is whether or not the dopant counterion is located in a crystallite, where it sits in the lamellar regions relatively far from the polaron on the polymer backbone, or in the amorphous regions where it can be much closer to the positive charge, that determines whether or not the polaron is free (delocalized in your language) or trapped. The whole point of our paper is that ultrafast transient absorption can be used as a type of action spectroscopy to detangle the optical transitions of free and trapped polarons, whose absorption spectra strongly overlap in the P1 region. Thus, we do observe free polarons and trapped polarons with different spectra in our experiments, and what we observe is well aligned with the theory we developed in ref. 14 of the paper. The 'DP' band you refer to from the work of Vardeny and co-workers is at a much lower energy (0.1–0.2 eV) than the P1 transition we probe in our paper (0.4–0.7 eV); unfortunately we do not have access to ultrafast pulses in this energy range, so we were not able to probe this band in our samples.

Laura Estergreen remarked: Referring to the UV-vis spectrum that was presented (ref. 3 in DOI: 10.1039/c8fd00210j), as the dopant concentration is increased from 0.001 to 1 mg mL⁻¹, there is a nice isosbestic point right around 2.0 eV. However, at 1 mg mL⁻¹ it appears to deviate. Why is that? Will this impact the transient absorption features and interpretation, as, in the paper, the primary dopant concentrations compared are 1 and 5.5 mg mL⁻¹?

Benjamin Schwartz responded: We believe that this is a direct reflection of the fact that the F4TCNQ sits primarily in the P3HT crystallites at lower doping concentrations but resides in the amorphous P3HT regions at higher doping concentrations. The spectrum of P3HT is well known to depend on its degree of crystallinity, with enhanced vibronic structure on the red edge of the absorption as the degree of order increases. At low and mid-doping concentrations, this vibronic structure is clearly present in the residual neutral P3HT absorption, indicating that there are still undoped crystalline regions remaining in the film. Since only the crystalline P3HT spectrum is bleached at these concentrations, there is a nice isosbestic point, as you point out. At the highest doping concentration, however, the F4TCNQ dopant has filled the crystalline regions, and the residual P3HT absorption that remains no longer has any pronounced vibronic structure and thus is more reflective of amorphous material. Since the amorphous P3HT has a different spectrum than the crystalline P3HT, the fact that the bleached P3HT spectrum changes with doping concentration is what causes the loss of the isosbestic point at high doping concentrations.

Tom Oliver commented: P3HT is commonly used in bulk heterojunction thin films in conjunction with C60 electron acceptors, which obviously changes the thin film composition and morphology compared to F4TCNQ doped P3HT. Do you anticipate this would alter the polaron and bipolaron formation?

Benjamin Schwartz answered: The P3HT samples in our paper are doped in their electronic ground state, as F4TCNQ is a strong enough oxidizing agent to pull an electron directly out of the P3HT valence band. Thus, our situation is

different from that in bulk heterojunction solar cells, where polarons on the polymer are created by photoinduced charge transfer to fullerenes from the excited state. Since the bandgap transition of P3HT is largely suppressed when the material is doped (because electrons have been removed from the valence band), there wouldn't be an easy way to create excitons to do photoinduced charge transfer to fullerenes if fullerenes and F4TCNQ were somehow present in the same P3HT film.

Tom Oliver returned to the discussion of the paper by Michael Wasielewski: How can we retrieve more information (*e.g.* phase) about the superposition of charge-transfer states formed upon coherent charge-separation in Mike Wasielewski's 2NDI molecule? Would a mid-infrared laser probe pulse resonant with the energy splitting between the two acceptor states (A_+ and A_-) be sufficient? Or could transient X-ray experiments provide additional key information?

Michael Wasielewski replied: I do not think that the application of a mid-infrared pulse or the X-ray experiment would provide the phase information. Use of 2D electronic/vibronic spectroscopy would be more informative. We are currently pursuing these experiments.

Oliver Gessner responded: While a mid-IR experiment would probe the existence of a certain energy level spacing, which would be the acceptor state energy splitting here, X-rays would principally be able to provide a local probe of the valence electron dynamics from the perspective of specific reporter atoms. To probe differences between the charge transfer pathways with X-rays, however, one would need to be able to distinguish them, *i.e.*, one would need different X-ray absorption or emission energies, which would require some kind of elemental labeling of the different channels. This would imply, however, that the two pathways would not be strictly equivalent anymore. In this case, one may speculate whether reporter atoms with very similar valence electronic structures and chemical characteristics but different X-ray transitions may be used as 'minimally invasive' probes.

Naomi Ginsberg answered: Perhaps a technique such as time resolved scanning tunneling microscopy would be most useful because it is able to directly map the wavefunction of the molecule.

David N. Beratan responded: If a coherent superposition of N identical acceptor species is formed as the product, one expects $1/N$ of an electron to be located on each of the acceptor units. As such, spectroscopic probes that are diagnostic of the net electron charge on an individual acceptor would be useful. Probes of the acceptor species superposition states are also potentially accessible, although such superposition states would need to be probed on ultrafast time-scales before medium polarization traps a full electron on one of the many accessible A sites. Delocalizing charge coherently over many acceptors in the product state will reduce the reorganization energy for electron transfer. The reorganization energies for transfer to a coherent superposition of acceptor states is expected to scale inversely with the number of participating acceptors participating in the coherent state. This scaling of reorganization energy with N should

have kinetic consequences and, given a family of homologous species with different N values with intervalence (charge transfer) transitions, one could look for the signatures of this expected reorganization energy scaling with N in the energies of charge transfer bands.

Johannes Mahl asked: In the example of donor and acceptor connected with two bridge molecules: while any probe of which of the two bridges the charge took on its way from donor to acceptor will collapse the quantum mechanical wave function, could you think of other characteristics of charge transfer that can be accessed, using a less invasive/more indirect probe technique, while preserving the system's quantum mechanical properties?

Michael Wasielewski replied: Multi-dimensional electronic/vibronic spectroscopy should be able to reveal the presence of coherences that result from the two electron transfer pathways.

Naomi Ginsberg addressed Michael Wasielewski and David N. Beratan: I wonder if there might be a way to do a form of quantum non-demolition measurement to be able to measure the wavefunction amplitude in the different branches of your molecular interferometer. The phase of the wavefunction would presumably be oscillating at optical frequencies. Could one couple to a different degree of freedom, *e.g.* using a spin label and a nitrogen vacancy?

Or take for example the simpler situation in which we might ask a 'which way' question in a molecular system like benzene. One could in principle ask whether energy (information) is directed along one side of the ring or the other in order to reach the *para* position. But we are describing a single molecule that has wavefunctions that we can compute, *e.g.* using Huckel theory. The wavefunction is an eigenstate of the whole molecule, as would be the case for the more complex molecular interferometer in question. So to localize the wavefunction amplitude on one side of the benzene molecule one could create a superposition of wavefunctions, but because this is quantum mechanics can we truly talk about different routes around the ring? The closest quantum mechanical analogy I can think of would be a wavepacket of some sort (*i.e.* a superposition of states that enables localisation of the wavefunction). One might consider the creation of a Rydberg atom, which we can think of as having a very high energy state that localises the electronic wavefunction far away from the nucleus. Of course this sort of state is approaching a classical limit in which the electron becomes more particle-like. Is this a good analogy or does it obviate the need for an interferometer?

Michael Wasielewski responded: I think that once the interaction between the two acceptors is negligible relative to system–bath interactions, one is in the single particle limit as you suggest for the Rydberg state, so that the idea of an interferometer becomes moot.

David N. Beratan responded: One is free to pose the 'which way' or pathway interference analysis in the language of eigenstates or of localized orbitals (natural bond orbitals, CC sigma bond, CC pi bonds, *etc.*). The coupling pathway language has roots in Dyson expansions of quantum mechanical amplitudes and

proves very convenient and intuitive in understanding multi-pathway quantum interferences in the tunneling regime (compared to an eigenstate language). Some discussion of these complementary frameworks and the utility of the tunneling pathway framework appear in ref. 1–3.

1 S. S. Skourtis and D. N. Beratan, *Adv. Chem. Phys.*, 1999, **106**, 377–452.

2 S. S. Skourtis, D. H. Waldeck and D. N. Beratan, *J. Phys. Chem. B*, 2004, **108**, 15511–15518.

3 J. N. Onuchic and D. N. Beratan, *J. Am. Chem. Soc.*, 1987, **109**, 6771–6778.

Animesh Datta responded: Quantum mechanical interference is observed when an event can occur by any of several alternate pathways. If an experiment is performed in which it is possible, even in principle, to determine which of the alternate pathways was actually taken, then the interference is lost. Almost never explicitly stated, asking a ‘which way’ question assumes that these alternate pathways are macroscopically distinct and experimentally identifiable. It seems to me that this may be unlikely for ‘different routes around the ring’ of benzene using far-field optical methods. So the ‘different routes around the ring’ may not be macroscopically distinct. But maybe some near-field method can identify these ‘routes’ after which we can start talking of quantum interference in a ‘benzene interferometer’. After that, of course, one needs to identify quantum excitation that will move along these ‘routes’ and make sure they do not encounter anything that distinguishes which of the ‘routes’ was taken. There are ‘quantum erasure’ ideas in quantum optics that can suppress distinguishing aspects, but its unclear to me to what extent they can be transferred to chemical/molecular systems.

Naomi Ginsberg returned to the discussion of the paper by Benjamin J. Schwartz: I wonder if one could use transient reflectivity instead of transient absorption in order to help decouple the presence of the many excited species in the spectrum. There could be areas where examining the real, rather than the imaginary, part of the electronic response aids in discerning one feature from another.

Benjamin Schwartz answered: There would definitely be additional information in adding transient reflectivity experiments, but it is not immediately obvious to me how they could be interpreted. This is because I am not aware that the steady-state index of refraction of doped polarons has ever been measured out in the infrared where the P1 band absorbs, so that even if the transient changes in the real and imaginary parts of the index could be deconvoluted, it would be challenging to understand the information carried in the real part of the index.

David N. Beratan opened the discussion of the paper by Sharon Hammes-Schiffer: Please explain why the high frequency nuclear mode associated with proton transfer does not lead to washing out of the Marcus inverted effect in the proton-coupled electron transfer reaction that was studied.

Sharon Hammes-Schiffer responded: For electron transfer reactions coupled to a vibrational mode, the Marcus inverted region may not be exhibited due to contributions from the excited vibrational states, leading to a plateau as the driving force increases. A similar effect is observed for PCET reactions with harmonic or Morse proton potentials. In these cases, the Marcus inverted region

is not exhibited because of contributions from excited proton vibrational states that are nearly activationless. The excited proton vibrational states contribute significantly because the overlap integral corresponding to the lowest reactant proton vibrational state and an excited product proton vibrational state increases as the quantum number for the product state increases (see Fig. 4A from our paper, DOI: 10.1039/c8fd00240a, where the tails of the product wavefunctions extend further toward the reactant for higher excited vibrational states). Fig. 6A from our paper also illustrates this increase in the overlap integrals up to around the seventh excited state, after which the overlap starts to decrease.

In contrast, PCET reactions can exhibit the Marcus inverted region behavior for asymmetric double well proton potentials. In this case, the excited proton vibrational states become delocalized over both wells, as shown in Fig. 4B from our paper, where the third excited state is already over the barrier and therefore delocalized. The delocalized, oscillatory nature of the highly excited proton vibrational wavefunctions leads to phase cancellation and therefore negligible overlap integrals associated with the lowest reactant and highly excited product proton vibrational states. Fig. 6C from our paper depicts the fast decay of the overlap integral after the first few excited product proton vibrational states. Because the square of the overlap integral is a prefactor for each term in the non-adiabatic PCET rate constant expression (eqn 2 in the paper), the vanishing overlap integral eliminates the contributions from these excited proton vibrational states. In this case, for highly exoergic PCET reactions, the contributions from the pairs of reactant/product vibronic states that are activationless are multiplied by zero. Thus, the mid-level excited product proton vibrational states are the dominant contributors, and because the splittings are also relatively small, these pairs of vibronic states are still in the inverted region in that the driving force is greater than the reorganization energy. In this case, the nuclear mode associated with proton transfer does not lead to washing out of the Marcus inverted effect.

Karen Morenz queried: And so to clarify, would you always see the inverse kinetic isotope effect in a proton coupled energy transfer system like this, or is that something that just happens to be inherent to this particular system?

Sharon Hammes-Schiffer answered: The inverse kinetic isotope effect (KIE) will not always be observed in these types of PCET systems. The rate constants for hydrogen and deuterium are computed by summing over all of the reactant and product vibronic states. The percentage contribution from each reactant/product vibronic state pair is determined by a complex balance among the Boltzmann population for the reactant state, which favors the lowest proton vibrational state, the free energy barrier, and the overlap integral associated with the reactant and product proton vibrational wavefunctions. The relative contributions from the vibronic state pairs are different for hydrogen and deuterium due to differences in the vibrational wavefunctions, as well as the smaller energy level splittings for deuterium. The observation of an inverse KIE will depend on the contributions from the vibronic state pairs for hydrogen and deuterium, which in turn depend on a complex balance among several factors inherent to the specific system. Thus, it is difficult to predict an inverse kinetic isotope effect without computing the full

rate constants for hydrogen and deuterium, although it is more likely to occur for large driving force.

Karen Morenz said: This is another sort of clarification question. I was interested in how you achieve the inverse kinetic isotope effect—I mean, I understand that it comes from the vibrational states of deuterium *vs.* hydrogen but is there something particular about the deuterium vibrational states overlap in the proton coupled energy transfer system that leads to this inverse kinetic isotope effect?

Sharon Hammes-Schiffer replied: The inverse KIE most likely arises from greater vibrational wavefunction overlap integrals for deuterium than for hydrogen for the vibronic state pairs with dominant contributions to the corresponding rate constants.

Michael Ashfold asked: Can you please expand a bit on how I should picture photoinduced proton coupled electron transfer in, for example, a hydrogen bonded phenol-pyridine complex using asymmetric double well potentials like those shown in Fig. 4B of your paper (DOI: 10.1039/c8fd00240a).

Sharon Hammes-Schiffer answered: For a triad composed of anthracene, phenol, and pyridine, photoexcitation to a local excited state of the anthracene may be followed by concerted PCET involving electron transfer from the phenol to the anthracene and proton transfer from the phenol to the pyridine.¹ The resulting charge-separated state can then decay to the ground state by another concerted PCET involving electron transfer from the anthracene to the phenol and proton transfer from the pyridinium to the phenoxyl radical. For this system, the one-dimensional asymmetric double well potentials shown in Fig. 4B of our paper (DOI: 10.1039/c8fd00240a) can be generated by moving the proton from the oxygen of the phenol to the nitrogen of the pyridine with all other nuclei fixed. In practice, the proton coordinate axis is determined by connecting the equilibrium positions of the proton bonded to the oxygen or the nitrogen. In the charge-separated state, the lower-energy minimum is near the nitrogen, whereas in the ground state, the lower-energy minimum is near the phenol. This flipping of the asymmetry of the double well potential can be explained in terms of electrostatic interactions between the electron(s) and the proton; when the electron transfers away from the phenol, the proton is more stable on the nitrogen of the pyridine, but when the electron transfers back to the phenol, the proton is more stable on the oxygen of the phenol. This behavior of electron transfer flipping the asymmetric double well proton potentials, or in some cases shifting of the minima of single well potentials that may exhibit shoulders, is characteristic of PCET reactions in general.

1 G. A. Parada, Z. K. Goldsmith, S. Kolmar, B. P. Rimgard, B. Q. Mercado, L. Hammarström, S. Hammes-Schiffer and J. M. Mayer, *Science*, 2019, **364**, 471–475.

Jahan Dawlaty said: As you very nicely showed, the ground state vibrational wavefunction will have vanishing overlap with higher excited states of the acceptor, resulting into the inverted region.

Is it possible to think of a system in which the higher vibrational states of the donor overlaps with higher vibrational states of the acceptor? In that case, the

overlap factor will not go to zero (at least not as quickly). This will involve transfer prior to vibrational cooling in the donor. Basically it can be phrased as, is it possible to imagine cases where transfer occurs prior to vibrational cooling?

Sharon Hammes-Schiffer replied: Our calculations in this paper (DOI: 10.1039/c8fd00240a) assume that vibrational cooling is faster than the PCET reaction, and therefore the reactant state is represented by a Boltzmann distribution among the proton vibrational states. In the non-adiabatic PCET rate constant expression, each term in the summation over reactant and product vibronic states is weighted by the Boltzmann population of the reactant vibronic state. If the system were not at equilibrium prior to PCET, then this rate constant expression would no longer be valid. In this case, we could perform non-adiabatic dynamics simulations to explore the non-equilibrium dynamics of the PCET process. We have developed methods for these types of non-adiabatic dynamics simulations and have applied them to PCET in solution.^{1,2} From the experimental perspective, this situation will occur when photoexcitation leads to non-equilibrium populations of the excited vibrational states, presumably weighted by the Franck–Condon factors, and then the PCET reaction occurs prior to vibrational cooling. If the solvent equilibration were much faster than both vibrational cooling and PCET, then the non-adiabatic PCET rate constant expression presented in the paper would still be valid but would include averaging over the non-equilibrium populations of the vibrational states in certain regimes. Further calculations would be required to determine if these various scenarios could exhibit inverted region behavior.

1 P. Goyal, C. A. Schwerdtfeger, A. V. Soudackov and S. Hammes-Schiffer, *J. Phys. Chem. B*, 2015, **119**, 2758–2768.

2 P. Goyal and S. Hammes-Schiffer, *ACS Energy Lett.*, 2017, **2**, 512–519.

Tom Oliver remarked: In your bidirectional photoinduced PCET study, you observe both an inverted region and inverse kinetic isotope effect as a function of increasing the driving force relative to the reorganisation energy. Do you anticipate this will also occur for photoinduced H-atom transfer reactions where the proton and electron are transferred to a common acceptor?

Sharon Hammes-Schiffer answered: Hydrogen atom transfer (HAT), in which the electron and proton transfer between the same donor and acceptor, is a subset of PCET. In general, PCET encompasses reactions in which the electron and proton transfer between the same or different donors and acceptors and in the same or different directions. My group has published several papers^{1–3} providing diagnostics that distinguish HAT, which is electronically adiabatic but often vibronically non-adiabatic, from the alternative electron-proton transfer (EPT) mechanism, which is typically vibronically and electronically non-adiabatic. Another distinction is that typically EPT reactions involve substantial charge redistribution, while HAT reactions do not involve such charge redistribution. In principle, the inverted region and inverse kinetic isotope effect could be observed in either regime. In practice, we have observed this behavior in theoretical models that are vibronically and electronically non-adiabatic but not yet in models that are vibronically non-adiabatic and electronically adiabatic. Moreover, we do not expect to observe inverted region behavior for fully vibronically adiabatic

reactions, which are defined to occur on the ground vibronic state. However, further exploration is required to fully understand the limits of this behavior.

- 1 J. H. Skone, A. V. Soudackov and S. Hammes-Schiffer, *J. Am. Chem. Soc.*, 2006, **128**, 16655–16663.
- 2 A. Sirjoosingh and S. Hammes-Schiffer, *J. Phys. Chem. A*, 2011, **115**, 2367–2377.
- 3 S. Hammes-Schiffer, *Energy Environ. Sci.*, 2012, **5**, 7696–7703.

Amro Dodin commented: Does this study provide any insight into what properties of the potential energy surfaces lead to the presence or disappearance of the Marcus inverted regime? In particular, is there a specific type of anharmonicity or curvature of the potential that determines this?

Sharon Hammes-Schiffer responded: The experimental accessibility of the Marcus inverted regime depends on a balance of many factors in the rate constant expression. In particular, the rate constant depends on the Boltzmann population of the reactant state, the vibronic coupling (which depends on the electronic coupling and the overlap between the proton vibrational wavefunctions in the electronically non-adiabatic regime), and the free energy barrier (which depends on the reorganization energy, the driving force, and the proton vibrational energy level splittings). For each system, we would need to compute these quantities and use them to calculate the PCET rate constant as a function of driving force. However, one trend that emerged from our calculations on model systems is that the Marcus inverted regime is more likely to be observed for proton potentials that are asymmetric double wells for which the lowest few proton vibrational states are below the barrier, but the remaining vibrational states are above the barrier and therefore are delocalized over both wells. The oscillatory wavefunctions delocalized over both wells typically exhibit negligible overlap with the reactant proton vibrational wavefunction, thereby allowing observation of the inverted region behavior. As shown in our Faraday Discussion paper (DOI: 10.1039/c8fd00240a), the Marcus inverted region behavior is more likely to be observed if this overlap decreases quickly with product state quantum number, as observed for the asymmetric double well proton potentials. For the Morse proton potentials, where this overlap decreases more gradually (*i.e.*, does not become negligible until higher quantum numbers) the inverted region is inaccessible. Thus, the shape of the proton potentials plays a significant role in determining whether or not the Marcus inverted region will be observed. In terms of the physical properties of the system, asymmetric double well proton potentials are common in systems for which the proton transfers across a hydrogen bond but are also found in other types of systems.

Jack Woolley said: The model system that you presented displays an intramolecular hydrogen bond. Could this type of double well potential model situations of intermolecular proton transfer, in particular those between solute and solvent, and if so what sort of additional considerations would you expect to play a role?

Sharon Hammes-Schiffer replied: This PCET theory is also applicable to systems exhibiting intermolecular proton transfer, including proton transfer between the solute and a solvent molecule. My group has computed similar

asymmetric double well potentials or shifted single well potentials for these types of systems. The main additional consideration is the formation of a hydrogen-bonded complex prior to PCET. In this case, the observed rate constant is the product of the equilibrium constant for the formation of this hydrogen-bonded complex and the PCET rate constant. In terms of observing inverted region behavior for such systems, the experimental challenge would be ensuring that the hydrogen-bonded complex remains stable during the photoexcitation, charge separation, and charge recombination processes.

Collin Steen opened discussion of the paper by Mark E. Thompson: Thanks for this very nice contribution. It is exciting to see such a clear dependence of the propensity for symmetry-breaking charge transfer on the environment, specifically solvent polarity. How general is this phenomenon, especially with regard to fluorescence quenching in photosynthetic systems? Do you think there are other factors beyond environmental polarity that need to be considered in more complicated systems such as light-harvesting antenna complexes?

Mark Thompson responded: The polarizability of the medium is also very important. We see SBCT being fast in toluene and benzene and in doped polystyrene thin films. In these cases the media have low or zero polarity, but are polarizable.

Yumin Lee said: Thank you for the great work and presentation. I just wondered that what happens if the dihedral angle changes, for example from π -extension of the rings or using another metal instead of Zn, how can that alter the kinetics regarding charge-transfer? In your insight, do you expect to see the formation of exciton coupling by the angle change could occur and compete with the charge transfer?

Mark Thompson replied: The dihedral angle is very important. If you twist too far away from 90 degrees exciton coupling this will lower the excited energy too low to engage in charge transfer. There are examples of zinc based materials that deviate significantly from 90 degrees and they do not give SBCT states, but non-radiatively decay to the ground state directly from the S_1 .

Graham Fleming asked: Concentration quenching is an almost universal phenomenon with no clear microscopic explanation. Could symmetry breaking charge transfer be the common cause?

Mark Thompson answered: I think that is a great suggestion. This could well be the case, but is hard for us to examine. In the concentration range we need to look for quenching the TA signal will be swamped out. Also, with the rapid tumbling of the molecules in solution, the lifetime of the SBCT state will be very short (and lead to extensive quenching as observed). We will continue to think about this and see if we can design an experiment to test this hypothesis.

Nadia Korovina queried: The spectral signature of your assigned charge transfer state looks very similar to the triplet induced absorption spectrum in

analogous BODIPY compounds. Is there spectroelectrochemical data to confirm the charge transfer assignment?

Mark Thompson answered: The spectrum does not in fact look like the triplet. Our *J. Phys. Chem. C* paper¹ shows both spectroelectrochemical data and the TA spectra of the Zn(dpy)₂ triplet and you can see that the signatures we see in the TA spectra between 0.5 and 900 ps do not match the triplet.

1 C. Trinh, K. Kirlikovali, S. Das, M. E. Ener, H. B. Gray, P. Djurovich, S. E. Bradforth and M. E. Thompson, *J. Phys. Chem. C*, 2014, **118**(38), 21834–21845.

Gregory Gate asked: Why did you also study a Zn dimer, as both dimers appeared to have similar dynamics?

Mark Thompson replied: The coupling between the two chromophores are quite different. One pair is coupled through a C–C bond at the *meso* positions of the two dyes and the other is coupled through a zinc ion. The C–C bond coupling gives rise to a 10× faster rate of charge transfer than the pair coupled through a zinc ion.

Marta Duchi addressed Mark Thompson and Michael Kellogg: Are the observed oscillations in the time-domain transient absorption data a signature of excited state wavepacket dynamics?

Michael Kellogg responded: I do not believe that the oscillations observed in time traces for 2 for the pure solvents are a result of wavepacket motion. There are a few reasons for this. If I plot the time traces for the other CT band at 379 nm, there are no definitive oscillations like there are in the 538 nm band. I would expect to see oscillations for both CT bands, not just one of them. The time traces for the CT only extend out to 20 ps after excitation. If I extend the same CT band out to the entire time window (950 ps), I still see oscillations of the same amplitude which I don't believe are real. Actual oscillations would not live that long. This is for pure solvents. It is important to note that each of the samples for the pure solvents were done on the same day. So, if there was a laser problem like power instability or compression issues, it would likely be the same for all samples. This is why each of the pure solvents seem to have these oscillations. If I plot the CT band for different solvents, say for the CHXTHF mixtures, I do not see any oscillations in the time trace for any wavelength. There is noise in these wavelengths that has the same amplitude as the oscillations in the pure solvents, but they are not a set of periodic oscillations, like the pure solvents. I am not sure what the specific identity of the oscillations are. They are not due to noise because our signal is above the noise floor. I have not repeated these experiments save for ACN and TOL, which I did a few weeks later. And for 538 nm for these new solvents, I do not see these oscillations. Likely, the oscillations were experimental artefacts, but I do not know the origin of them.

Mark Thompson replied: No, the oscillations are not that. They are due to 150 fs time constant for the apparatus. Those oscillation are purely instrumental.

Tom Oliver commented: At the end of your paper (DOI: 10.1039/c8fd00201k) you discuss the relative rate of charge recombination for the two dipyrin structures, and note that rate constants are similar. Given the structural differences between the compounds and presumably different re-organisation energies associated with the respective charge transfer states, would one not expect the recombination rates to be quite different?

Mark Thompson responded: Note that the forward CT is facilitated by the bridging MO at the *meso* carbons of the BODIPY dimer and no such state exists for the Zn(dpy)₂ molecule. Since neither SBCT state has a bridge state and the driving force for the two dimers are the same, we believe that the direct recombination is largely controlled by the hole–electron distances, which are similar in the two complexes. Note that, while we say they are similar, the BODIPY dimer is 50% faster than the Zn(dpy)₂ complex.

Ryan Dill opened the discussion of the paper by Thomas. J. Penfold: In your paper you mention that thioxanthone undergoes a spin-forbidden equilibration with a time constant of 10 picoseconds. Why is it so fast? It contains a sulfur, but I have also seen that xanthone, with no sulfur, has a similar intersystem crossing rate, so the heavy-atom can not be the important factor here. I understand that it is El-Sayed allowed, but it still seems faster than I would have expected.

Tom Penfold responded: The S₁–T₂ spin–orbit coupling in thioxanthone is El-Sayed allowed, and a value of 18 cm⁻¹ is found. However the key aspect here is the fact that these two states are degenerate. The mixing between two states scales as the coupling divided by the energy gap and so the small energy gap helps drive rapid intersystem crossing.

Mark Thompson said: Thioxanthone has a really fast ISC, but is a rarity. For internal conversion to be slow relative to intersystem crossing is even rarer. What are your thoughts on how to slow down internal conversion?

Tom Penfold replied: The ISC of thioxanthone is fast, but similar rates can be achieved in organic molecules exhibiting El-Sayed's allowed spin–orbit coupling. Another well-known example is benzophenone. But as you correctly identify, the challenge in the proposed mechanism is restricting the internal conversion rate. This is slow in thioxanthone because of the large energy gap between the T₁ and T₂ states and consequently for this approach to work, this gap would need to be maintained. A counter challenge, in the context of OLEDs would be that the lower lying T₁ state would act as a non-radiative trap. This would likely cause problems with efficiency and lifetime. To truly establish the ability for this approach to be effective we have to understand how the excited states are formed upon the thioxanthone and if we can control this to avoid T₁ becoming populated. This work is currently underway.

Tom Oliver asked: In Fig. 3 of the paper (DOI: 10.1039/c8fd00201k), the time evolving normalised diabatic state populations of S₁ and T₂ are displayed. There appears to be a small oscillatory component to these dynamics—can you comment on its origin?

Tom Penfold responded: Very small! The timescale of the oscillation is ~ 3 ps which corresponds to ~ 11 cm⁻¹ which is similar to the spin-orbit coupling between the S₁ and T₂ states. I could not expect this to be visible experimentally, and will be largely because the reduced space model will be slightly over-coherent, *i.e.* no bath modes or damping effect of the environment.

Tom Oliver asked: The coupling between the T₂ and T₁ electronic states is very small. Is simply because of the large energy difference between states, or are there additional important factors?

Tom Penfold replied: It is twofold. For thioxanthone the molecule is fairly rigid and therefore any coupling that is activated by vibrational degrees of freedom will be small. In addition, as you say, the gap between the states is very large, which will reduce the effect of any coupling.

Tom Oliver queried: On a more general point, what are the key requirements for efficient triplet-triplet energy transfer? It is apparent the efficiency of such processes are important precursor to enhancing triplet-triplet annihilation up-conversion for solar energy applications.^{1,2}

1 K. A. Phillips *et al.*, *Chem. Eur. J.*, 2018, **24**, 8577–8588.

2 S. Balushev *et al.*, *Phys. Rev. Lett.*, 2005, **97**, 143903.

Tom Penfold responded: Triplet-triplet energy transfer (TTET), as with all transfer mechanisms governed by the Fermi Golden rule are dependent (in the semi-classical limit) on the coupling, the reorganisation energy and the free energy released upon transfer. For the coupling, TTET is a Dexter mechanism and is therefore driven by the exchange interaction. This therefore requires some overlap between the two wavefunctions. This is why the coupling to the T₂ of thioxanthone is smaller as it is a more localised π^* excitation and therefore there is less wavefunction overlap with the T₁ of dichlorobenzene. It is expected that the TTET rates decay exponentially as distances increases, as observed in our work.

Mark Thompson commented: Has the T₂ of thioxanthone been directly sensitized? It would be useful to show that you get highly efficient photoluminescence from the T₂.

Tom Penfold answered: In the experiments performed in ref. 1 and simulated in our present contribution (DOI: 10.1039/c8fd00201k), the dichlorobenzene is photoexcited and used to transfer energy to the triplet states of thioxanthone. For enhanced fluorescence to be observed, the triplet-energy transfer has to pass from the T₁ of dichlorobenzene to the T₂ of thioxanthone. However, as observed experimentally and in our contribution, only a small fraction passes through the T₂ state, instead the T₁ is preferred. This can be understood from calculating the coupling between the states, free energy and reorganisation energy upon population transfer, as shown in the paper.

1 C. Torres Ziegenbein, S. Fröbel, M. Glöß, R. S. Nobuyasu, P. Data, A. Monkman and P. Gilch, *ChemPhysChem*, 2017, **18**(17), 2314–2317.

Jon Bender opened discussion of the paper by Oliver Gessner†: Have you explored changing the steady-state temperature of the copper oxide and underlying substrate to tune their relative thermal conductivities? Or have you explored changing the underlying substrate identity to one with a drastically different thermal conductivity in order to explore the role of the substrate in heat dissipation?

† Oliver Gessner's paper was presented by Johannes Mahl, Lawrence Berkeley National Laboratory, U. S. A.

Oliver Gessner replied: We have not. However, we do not expect the substrate to play a significant role in this particular experiment for the following reasons. The time-averaged substrate temperature during the pump-probe experiment was monitored with a thermocouple and increased by only a few degrees C compared to the ambient room temperature as a result of the laser exposure. Thus, most of the laser-induced heat from each pump pulse dissipates before the arrival of the next laser pulse, as otherwise a much higher average heating would be observed. Our spatiotemporal temperature modeling is consistent with this finding and strongly indicates that the dissipation of heat is largely accomplished within several hundred nanometers from the surface. Therefore, the impact of the substrate is likely negligible within the precision of this experiment.

Jon Bender said: I am really surprised by the large initial change in temperature that you observe in this system. I have primarily experienced these effects in organic molecular solids personally, which tend to achieve much more modest lattice temperatures. Can you please comment on how this is achieved? Additionally, is it electronic or lattice temperature interested in?

Oliver Gessner replied: Principally, we are interested in both, the electronic and lattice temperatures of the material after photoexcitation. However, as the coupling between electrons and phonons typically occurs within tens of picoseconds or faster, we expect our experiment to be predominantly sensitive to the lattice temperature. The observed temperature jumps are either in reasonable agreement (for 532 nm excitation) or significantly below (for 355 nm excitation) the expected temperature changes, which were calculated using eqn (2) and the experimental laser pulse parameters and material characteristics, as discussed in sections 4 and 5 of the manuscript. We don't know why the experimentally determined temperature jump for 355 nm excitation is much lower than the calculated value but point out that a similar phenomenon was reported by Chen and co-workers in a transient X-ray absorption study of photoexcited hematite (ref. 7 of the paper).

Michael Haggmark said: Your study suggests that the vast majority of the energy is thermalized. Generally speaking, how well characterized are the photodynamics of copper oxide? Another way of asking this, is the quantum yield of fluorescence quite low for powdered copper oxide?

Oliver Gessner replied: The timescales of charge carrier recombination found in the literature are mostly below the temporal resolution of the study presented

here. Born *et al.*¹ observed three timescales in the decay dynamics of CuO nanocrystals following 1.6 eV excitation in an optical pump–probe study. A 330 to 630 fs (pump fluence dependent) decay was attributed to carrier-carrier scattering and exciton-exciton annihilation, a 2 ps decay to carrier-phonon scattering and a 50 ps time constant to trapping and recombination in trap states. Othonos *et al.*¹ observed similar timescales of 0.4 and 2.1 ps in the decay of photo-generated carriers in CuO nanowires.

1 B. Born *et al.*, *ACS Photonics*, 2016, **3**, 2475.

2 A. Othonos *et al.*, *Nanoscale Res. Lett.*, 2011, **6**, 622.

Michael Haggmark remarked: This study nicely followed the thermal effects. Are you planning on studying something with a long-lived excited electronic state as a follow up?

Oliver Gessner responded: A study where both thermal and electronic signatures are present would be an ideal next step for this project. In fact, this was the primary motivation for this Faraday Discussion contribution. However, while the methodology developed within this Faraday Discussion article (DOI: 10.1039/c8fd00236c), in principle, allows to disentangle thermal and electronic effects, it should be noted that, so far, any effort to study photo-induced effects with X-ray spectroscopies on picosecond and longer timescales has found that thermal effects dominated the photo-induced difference spectra (see ref. 7 and 8 of the paper). A promising advantage of acquiring data at multiple pump–probe delays as with the setup used in our study is that thermal and non-thermal effects with similar spectral fingerprints are distinguishable, as long as the timescales of their decay are sufficiently different.

Karen Morenz asked: This is very related to the previous question from Michael Haggmark, and perhaps also a little more off-topic, but I know that a lot of people are really interested in heating and even melting in quantum dots, so could you connect your work up with that situation and tell us how these results can inform us about that sort of system?

Oliver Gessner answered: Time-resolved X-ray absorption may very well be suitable for studying heating and phase transitions in quantum dots, in particular, since the element specificity allows to target the quantum dot and the substrate independently (assuming they consist of different materials). Thus, in addition to the analysis presented here, heterogeneous heat transfer from the quantum dot to the substrate could also be studied by probing two core levels that are exclusively connected to the quantum dot and the substrate, respectively. One may also expect significant changes in the X-ray absorption spectrum upon melting, see *e.g.* data on silicon by Johnson *et al.*,¹ and germanium by Stebel *et al.*²

1 S. L. Johnson *et al.*, *Phys. Rev. Lett.*, 2003, **91**, 157403.

2 L. Stebel *et al.*, *Rev. Sci. Instrum.*, 2011, **82**, 123109.

Benjamin Schwartz remarked: Although your picture of the transient dynamics as resulting from thermal effects makes good sense, I was wondering if it would be possible to independently measure the thermal conductivity of the same

sample using a different ultrafast technique. David Cahill's group at UIUC has developed a method known as time-resolved thermoreflectance, in which a short laser pulse is used to heat a metal placed on one side of the sample, and then the change in reflectivity of the metal is monitored as a function of time, allowing one to extract the thermal conductivity of the material under the metal. In your case, there is already copper metal on the bottom side of the sample, which means it would be straightforward to perform this type of measurement on the exact same sample with a similar excitation pulse but a visible-pulse probe, providing a nice way to examine the thermal effects with two different techniques.

Oliver Gessner responded: This is a very interesting cross-reference to a technique that accesses similar characteristics of the sample as the experimental technique described in our paper. The targets used by Cahill's group consist of well-defined double-layer structures with the sample material deposited on a thin metal foil with thicknesses on the order of 100 nm or less. The metal substrate used in our study is ~ 2 mm thick, which would render a similar experiment unfeasible since the observed dynamics would be entirely dominated by the substrate. However, if a CuO sample could be grown in a better defined way and on a thin film of Cu or other metallic surface, the method presented here could most likely be applied as well as time-domain thermoreflectance measurements.

Terry Frankcombe commented: When I look at the determinations of the temperatures from the experimental data in Fig. 7 of your paper (DOI: 10.1039/c8fd00236c), there seems to be a very large spread. For example, the determined temperatures for long delays in Fig. 7a spread from the low 20s to more than 60 degrees. This is much larger than the spread in temperatures shown in the pre-pump background to the left of time zero. Can you comment on the source of such a large spread of values, and what the uncertainty of each temperature determination should be?

Oliver Gessner answered: The data shown in Fig. 7 of the paper result from the homogeneous fit method, which approximates the Δ trXAS data at every pump-probe delay individually by identifying one steady-state temperature difference spectrum that best fits the Δ trXAS data. Generally, three pump-probe time delay regions may be distinguished, in which different effects dominate the uncertainty of the data: the pre-pump region with $\Delta t \leq 0$, early dynamics with $\Delta t \approx 0$ –50 ns delay, and dynamics at longer delays $\Delta t \geq 50$ ns. In the pre-pump region at nominally negative delays, any laser-induced effect has decayed and the scatter in the inferred temperatures is essentially defined by the reproducibility of the (tr) XAS spectra at room temperature. In the second region, $\Delta t \approx 0$ –50 ns, the temperature uncertainty is relatively small due to the high absolute sample temperatures. In this regime, the XAS spectra are particularly temperature sensitive, *i.e.*, the temperature-induced differences ΔXAS_{temp} per change in temperature ΔT are largest at higher temperatures, as can be seen in Fig. 4. Conversely, this leads to relatively small temperature uncertainties when fitting Δ trXAS data corresponding to higher ΔT . In contrast, the temperature sensitivity of the XAS spectra decreases for low to intermediate temperatures, leading to larger temperature uncertainties for longer delays. Furthermore, for positive delays we cannot exclude potential contributions of laser-induced effects that are

not captured by describing the ΔtrXAS data with $\Delta\text{XAS}_{\text{temp}}$ spectra. We have tried to identify systematic trends beyond the temperature induced effects but were not able to isolate any within the signal-to-noise ratio of the experiment.

It should also be mentioned, that the results of the second (inhomogeneous) fit procedure we applied are subject to much smaller variations since this method simultaneously fits entire temperature profiles and their temporal evolution based on the one-dimensional heat transport model. This global fit routine inherently produces smooth temperature evolution curves as can be seen in Fig. 8 of the paper (DOI: 10.1039/c8fd00236c).

Conflicts of interest

There are no conflicts to declare.