Ultrafast photoinduced energy and charge transfer

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After presenting the basic theoretical models of excitation energy transfer and charge transfer, I describe some of the novel experimental methods used to probe them. Finally, I discuss recent results concerning ultrafast energy and charge transfer in biological systems, in chemical systems and in photovoltaics based on sensitized transition metal oxides.

1 Introduction

Photoinduced energy and charge transfer are at the heart of how nature functions and are the basis of an impressive number of applications, both present and to come. Photosynthesis is one of the most obvious examples as it embodies a wide range of energy and charge transfer events, as shown in Fig. 1.

![Image of photosynthetic unit]

**Fig. 1** The integral membrane proteins forming the photosynthetic unit and the processes triggered by light: light absorption and excitation energy transfer (black wavy arrows), electron transfer (blue arrows), proton transfer (red arrows), and ATPase (black arrows). Reproduced from ref. 1 with permission.
Light absorption excites the light harvesting complexes (LHI and LHII), which undergo excitation energy transfer (EET) to the reaction centre (RC). This then drives electron transfer (ET) between the cytochromes c$_2$ and the RC, and the bc$_1$ complex. Proton transfer (PT) ensues, which triggers the ATPase. In this sequence of events, the charge (electron and proton) transfers are not directly triggered by the absorption of light. However, there are numerous examples of light-induced charge transfer processes in Nature. For example, the blue copper protein involved in electron transport in plant photosynthesis can directly undergo photoinduced charge transfer by excitation in the visible region.\textsuperscript{2,3} Another class of system that plays a central role in converting light into the driving force for biological functions, such as ion transport and signal transduction, and is indispensable to the activity of organisms, is represented by the visual proteins.\textsuperscript{4–8} Upon absorption of light, the embedded chromophores undergo, e.g., proton/electron/energy transfers in addition to isomerization, typically on extremely short timescales (100s femtoseconds). These subtle changes in the chromophore trigger a sequence of events involving higher-order structural changes in the protein exterior, leading to the final outcome of a long-lived signaling state that triggers biological functions.

Tracking the flow of energy and charge in natural systems is crucial for understanding how Nature works, but it is also the basis for an impressive variety of present and potential applications in solar energy conversion, photocatalysis, sensors and optoelectronic devices. In photovoltaics, interfacial charge transport implies a photoexcited sensitizer: a dye molecule, a semi-conducting or metallic nanoparticle, and more recently, bulk semi-conductors (such as perovskites), which transfer electrons to an electron conducting substrate material (usually a transition metal oxide, TMO), thus generating electrical current. These sensitized systems have been the focus of intense research over the past three decades.\textsuperscript{9–11} TMOs are also important in photocatalytic applications.\textsuperscript{12–14} Finally, charge and energy transfers are being explored in molecular assemblies (donor–bridge–acceptor, J-/H-aggregates, etc.) with special emphasis on artificial photosynthesis.\textsuperscript{15–20} These assemblies are common in biology and the most obvious example is DNA.

There are innumerable examples of ultrafast intramolecular charge transfer in molecules, in particular transition metal-based molecular complexes, that are the basis for several phenomena, such as electronic and spin dynamics, structural dynamics, and heat dissipation.\textsuperscript{21–28} We will not deal with these in this article. Rather we focus on the study of intermolecular energy and electron transfer between a donor (D) and an acceptor (A) species that may or may not be linked by chemical bonds.

The study of these intermolecular processes has benefited from an impressive improvement in methodologies, both experimental and theoretical, over the past two decades, which I will briefly review bearing in mind that the experimental tools do not necessarily probe EET and ET in the same way, nor with the same observables. I will then present some case studies on biological systems and on sensitized TMOs.

## 2 Modelling excitation energy transfer

EET is the basis for fluorescence resonance energy transfer (FRET), which has become a common tool for the investigation of protein dynamics.\textsuperscript{29,30} Förster's
elegant derivation\textsuperscript{31} begins with a Golden rule expression for the FRET transition rate. Förster theory\textsuperscript{32,33} has been used to model EET by a quantum-mechanical coupling between the electronic transitions of a donor (D) and acceptor (A). The EET rate for a weak dipole–dipole interaction is given by:

\[
k_{\text{EET}} = \frac{1}{\tau_{\text{EET}}} = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6 = 8.79 \times 10^{23} \frac{Q_D}{\tau_D n^2} \frac{\kappa^2}{J} \]

where \( \tau_{\text{EET}} \) is the D lifetime quenched by EET, \( Q_D \) is the quantum yield of the D fluorescence (in the absence of A), \( \kappa^2 \) is the orientation factor, \( \tau_D \) is the pure radiative lifetime of the D fluorescence, \( n \) is the refractive index of the medium or solvent, and \( r \) is the distance between the centres of the two molecules or two dipoles (point dipole approximation) in Å. \( R_0 \) is the classical Förster distance. \( J \) is the overlap integral of the donor fluorescence and acceptor absorption. The orientation factor \( \kappa^2 \) is a function of \( R, \mu_D \) and \( \mu_A \):

\[
\kappa^2 = \left( \mu_D \mu_A \right) - 3 \left( \mu_D R \right) \left( \mu_A R \right)^2
\]

where \( R \) is the unit vector for the D–A centre-to-centre distance, \( \mu_D \) is the unit vector of the D dipole and \( \mu_A \) is the unit vector of the A dipole.

Despite the success of the Förster theory for predicting EET rates and assessing conformational equilibrium configurations, in particular via the well-known amino-acid spectroscopic ruler tryptophan (Trp), used in FRET studies of protein dynamics, there are several situations where it fails. These have nicely been evaluated in several recent reviews.\textsuperscript{34,35} Specifically, the theory is formulated under the assumption that the electronic coupling between D and A is very weak.\textsuperscript{36} It also assumes that the D and A sizes are much smaller than \( R_{DA} \), so that the point-dipole approximation can be used. Indeed, deviations from the \((1/R_{DA})^6\) distance dependence of the EET rate usually occur at closer D–A separations when the point-dipole approximation fails. The latter works well for quantifying the optical spectroscopy of allowed transitions because the wavelength of light is long compared to the size of a molecule and therefore its oscillating electric field averages over details of the molecular wave function. This does not apply for close lying chromophores. Indeed, as two molecules are brought together, the Coulomb interaction of electrons and nuclei in one molecule with those in the other increases. Thus, the eigenstates of the isolated molecules are no longer eigenstates of the full Hamiltonian. This gives rise to excitonic couplings, \textit{i.e.} interactions between excited states localized on different molecules.

Depending on the strength of the intermolecular interaction, it is still useful to think of the system as two interacting molecules rather than as a super-molecule. To do so, one expands the full Hamiltonian in the basis of the molecular states and the off-diagonal elements of that expansion are the couplings. The latter contain short- and long-range contributions. The former include exchange, overlap of donor and acceptor wave functions, and exciton transfer mediated by charge-transfer states.\textsuperscript{37,38} Because they depend on the spatial overlap of the D and A wave functions, short-range terms decrease exponentially with distance. Beljonne \textit{et al.}\textsuperscript{39} and Kenny and Kassal\textsuperscript{19} have presented the hierarchy of methods that can accurately describe EET: point-dipole approximation, extended dipole, transition charges from electrostatic potentials, transition monopole
Another deviation of the \((1/R)^6\) dependence of Förster theory is the case when electronic couplings can be mediated by molecular bridges between D to A, and when screening of the electronic couplings by the environment can also change the distance dependence.\textsuperscript{45} Dexter EET can be viewed as double charge transfer: an electron D–A transfer and a hole A–D transfer.\textsuperscript{46} In the case of several chromophores either with bonded or non-bonded interactions, the process is described as an exciton moving an electron–hole pair through the assembly of chromophores. This case is being investigated in a paper by Bai \textit{et al.} (DOI: 10.1039/c9fd00007k) in this issue, which looks at interferences between different Dexter pathways.

The importance of a proper description of the couplings and rates in the strong coupling case pertains to the debate about the electronic coherence between chromophores, which is treated by Siwiak-Jaszek and Olaya-Castro, Lishchuk \textit{et al.}, Richter and Fingerhut, and Wu \textit{et al.} (DOI: 10.1039/c9fd00006b, DOI: 10.1039/c8fd00241j, DOI: 10.1039/c8fd00189h, and DOI: 10.1039/c8fd00190a, respectively) in this issue and to which we will come back later.

### 3 Modelling electron transfer

ET is described by an extraordinarily robust theory.\textsuperscript{47} The non-adiabatic rate \(k_{\text{ET}}\) for electron transfer between a donor D and an acceptor A is given by:

\[
k_{\text{ET}} = \frac{1}{\tau_{\text{ET}}} = \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi\lambda k_B T}} H_{12}^2 \exp\left(\frac{-(\Delta G_0^0 + \lambda)^2}{4\lambda k_B T}\right)
\]

where \(\tau_{\text{ET}}\) is the lifetime of the D quenched by ET, \(\Delta G_0\) is the change in free energy of the reaction (also called the driving force), \(\lambda\) is the reorganization energy and \(H_{12}\) is the adiabatic electronic coupling between the initial and final electronic states. This expression applies provided nuclear motion is treated classically, a reasonable approximation in the high temperature limit, and if the electronic coupling between the ET states is weak, typically below a few tens of cm\(^{-1}\).\textsuperscript{48} Goldsmith \textit{et al.} (DOI: 10.1039/c8fd00240a) present in this issue a nice discussion of Marcus theory applied to the case of photoinduced proton-coupled-electron-transfer.

In the case of ET in biological systems, Beratan and co-workers proposed a relatively simple and successful way of estimating the electronic coupling between donor and acceptor.\textsuperscript{49-53} This so-called pathway model assumes that ET is mediated over different pathways, by consecutive interactions between atoms connecting the donor and the acceptor. The ET events described therein assume migration of only one electron. The electronic coupling equation for ET (tunnelling through a structure-less one-dimensional barrier between localized vibronic states) in a protein is given by:

\[
h_{12} = A \prod_j \varepsilon^C_j \prod_j \varepsilon^H_j \prod_k \varepsilon^S_k
\]

where \(A\) is the pre-factor. Segments of the pathway are characterized as covalent (C), hydrogen-bonded (H), or through-space (S), depending on whether the bonds
share a common atom (C), are linked by a hydrogen bond (H), or are in van der Waals contact (S). In through-bond ET, the backscattering between bonds and all (variable) side groups are neglected. Through space decay assumes for simplicity that the noncovalent contact through which the electron tunnels is composed of only two orbitals, one on each backbone chain. Assuming two identical orbitals, the transfer matrix element connecting them is on the order of $V_b S_{12}$, where $V_b$ is the orbital energy and $S_{12}$ is the orbital overlap.\(^{54}\)

Work with proteins has shown that ET rates depend exponentially on $R_{DA}$; a decay factor of 1.1 Å\(^{-1}\) describes most systems.\(^{55}\) This steep distance dependence limits single-step excited-state ET reactions to distances under 20 Å (Fig. 2), but multistep reactions can transport charges over distances of 30 Å or more.\(^{56}\)

The above discussion dealt with ET in biosystems, but ET at molecule/solid or film/solid interfaces is central to the function of sensitized solar cells, involving molecular dyes,\(^{11,57-59}\) metallic or semiconductor nanoparticles\(^{60}\) or solid state sensitizers such as organic–inorganic perovskites.\(^{61,62}\) It also plays a crucial role in charge separation in organic photovoltaics (Voss et al., DOI: 10.1039/c8fd00210j).\(^{63}\) ET at the molecular/solid interface is also crucial in the function of photocatalytic reactions,\(^{12,64,65}\) molecular electronics,\(^{66}\) photo-electrolysis,\(^{67}\) and photography.\(^{68,69}\) In many of these systems, the ET is extremely fast (few femtoseconds)\(^{70-73}\) such that it cannot be described by a simple rate description, and quantum-chemical methods are needed, often with time-domain modelling. These methods have been presented in detail in several review papers and will not be repeated here.\(^{74-78}\) Rather, we will focus on novel experimental approaches to probing such interfacial charge transfer phenomena and how they deliver further insight into the charge behaviour subsequent to the transfer.

![Fig. 2] Electron transfer rate ($k_{ET}$) and Förster resonance energy transfer rate ($k_{FRET}$), as a function of donor–acceptor separations ($R_{DA}$) and Förster radii ($R_{Förster}$). Shorter $R_{DA}$ and $R_{Förster}$ tend to favor ET. However, beyond 20 Å FRET is expected to be dominant. Reproduced from ref. 79 with permission from the American Association for the Advancement of Science, copyright (2013).
4 Novel experimental tools

With the advent of ultrafast (fs–ps) spectroscopy at the end of the 1980s, it became possible to track in “real-time” EET and ET processes in biological and chemical systems and at interfaces, using pump–probe techniques. Vibrational coherences generated by ultrafast EET and ET have also been reported in various systems and a nice discussion of such processes and of the debates around them are presented in the paper by Wu et al. (DOI: 10.1039/c8fd00190a) of this issue. In general, ultrafast pump–probe spectroscopy identifies these coherences from an a priori knowledge of frequencies and modes, but electronic coherences that would be characterised by similar frequencies as the vibrational ones makes the two difficult to distinguish. Furthermore, interrogating EET or ET in (bio)chemical systems or at interfaces requires spectroscopic probes that can clearly distinguish the donor from the acceptor. The constant development of methods over the past two decades has offered more specific ways of tracking these phenomena. Here we mainly focus on the novel tools by briefly recalling their main features.

(A) X-ray spectroscopy

Probing on ultrafast time scales oxidation state changes that occur in the D–A pair upon ET processes can best be achieved with element-specificity using time-resolved X-ray absorption (XAS) or emission (XES) spectroscopy. These methods are universal markers of the oxidation and spin states of the atoms. XAS probes the unoccupied density of the valence states, while XES probes the occupied density of states. Both are therefore particularly sensitive to the electron density in and occupancy of the valence orbitals, whose changes result in shifts of a specific core–shell edge absorption or emission. The absorption edge represents the ionization threshold of a given core electron. At energies higher that the edge, XAS contains modulations due to the scattering of the generated photoelectron onto the neighbour atoms, giving rise to the X-ray near-edge absorption structure (XANES) and extended X-ray absorption fine structure (EXAFS) features, which reflect the local geometry around the selected atom. In a time-domain experiment, such features may change due to structural rearrangements. XES is in addition an ideal marker of the spin state of the system under investigation. Thus, XAS and XES contain specific information about the electronic, spin and geometric structure of the elements constituting the system. In summary, because of their element-specificity and sensitivity to electron density, X-ray spectroscopies can, in principle, distinguish the donor from the acceptor in ET and EET processes.

The methodology for time resolved X-ray spectroscopy was first demonstrated in the hard X-ray range in the case of photoinduced intramolecular ET in transition metal complexes, and it was expanded to other types of ET processes: charge-transfer-to-solvent, interfacial ET, and hole and electron trapping in TiO2 (ref. 115 and 118) and ZnO. Expanding the use of time-resolved XAS or XES to the soft X-rays allows the investigation of light elements, since the K-edges of elements such as C, N, O, etc. are found in the 300–600 eV region. This was achieved in closed cells by Huse and co-workers, but novel liquid sample delivery schemes under vacuum, are now opening the field.
In addition to the above X-ray spectroscopies, we should also mention another core-level spectroscopy: X-ray photoelectron spectroscopy (XPS), which allows element-selective detection along with the absolute binding energies of given orbitals.\textsuperscript{126–129} While its extension to solutions has been achieved for some years now\textsuperscript{122,129–133} it has mostly been used for studies of ET (or electron injection) of sensitized systems, for which they are actually an ideal tool.\textsuperscript{134–137}

(B) Deep-ultraviolet spectroscopy

Amino-acid residues in proteins and the nucleobases of DNA and RNA all have their absorption bands below 300 nm in the deep-ultraviolet (deep-UV) region. In addition, most large band-gap semi-conductors, such as TMOs or transition metal nitrides, that are of great importance in photovoltaics and photocatalysis, have their band gaps lying below 380 nm, some actually closer to 300 nm. There is therefore need for a tool that can excite and probe in this spectral region. While pumping in the deep-UV is not an issue using the third harmonic of the Ti:Sa laser, probing over large spectral windows in the deep-UV region was achieved by scanning the probe wavelength,\textsuperscript{4,138} prior to the advent of achromatic doubling,\textsuperscript{139} which allows the generation of a white light continuum in this spectral range.\textsuperscript{140} This was exploited\textsuperscript{141–143} to generate a probe continuum from 250 to 380 nm. When used with a tuneable monochromatic pump pulse over the same range, 2D deep- to near-UV TA experiments (see next section) can be performed, which enable the detection of hitherto novel ultrafast intramolecular processes in molecules,\textsuperscript{144} and intermolecules ones in haemoproteins (see below).\textsuperscript{145,146}

Ultrafast deep-UV TA together with UV fluorescence up-conversion spectroscopy\textsuperscript{147–155} and deep-UV Raman spectroscopy\textsuperscript{8,156,157} represent an ideal toolbox for the identification of ET and EET involving amino-acid residues and nucleobases of biosystems. The multidimensional extension of these spectroscopies is a powerful addition to the toolbox.

(C) Multidimensional spectroscopy

The description of the electronic couplings, the involved electronic states and the transfer rates between donor and acceptor is of the utmost importance to understand ultrafast ET and EET. In pump–probe TA spectroscopy, the pump pulse is narrow-band, while the time-delayed weaker probe pulse is a continuum. The resulting signal is the difference of the probe signal with pump and without pump. Repeating experiments with different pump wavelengths yields a 2D map (an axis for the pump energy and the other for the probe energy) corresponding to a specific time delay. This type of 2D spectroscopy has the great advantage of simplicity, but has limited temporal resolution. 2D TA spectroscopy is thus suitable when the timescales of the processes are not too short and we will present below such a case.

When couplings become stronger the spectral signatures are more complex, and in the case of biosystems congestion makes the disentangling of the various spectral signatures nearly impossible using TA spectroscopy. Only with coherent multidimensional (MD) spectroscopic techniques can one disentangle them. Indeed, MD spectroscopy allows one to excite specific states of the system and then monitor the response coming from the excited states with similar or different energies. Coherent or Fourier Transform (FT) MD spectroscopies thus
provide excitation frequency, detection frequency, and time-resolved spectroscopic data. 2D FT electronic spectroscopy\textsuperscript{158-166} has emerged as a powerful tool to disentangle highly congested spectral regions in a given system and specifically variants of the method such as 2D photon echo (2DPE) measurements, can in principle discriminate between nuclear quantum beats and electronic coherent oscillations,\textsuperscript{161,167} which arise from very strong electronic couplings.\textsuperscript{168,169} The underlying reason for this ability is that the data contain information about electronic coherences as well as populations.\textsuperscript{170}

Another spectroscopy that provides detailed information about the interactions between the electronic and vibrational degrees of freedom in molecular systems is 2D electronic-vibrational (2DEV) spectroscopy, which has been witnessing increasing interest in recent years.\textsuperscript{171-173} In 2DEV, one combines the advantages of infrared vibrational spectroscopy with visible electronic spectroscopy, which allows one to directly correlate the electronic and vibrational degrees of freedom simultaneously.

(D) Circular dichroism (CD)

CD spectroscopy measures the absorption difference between left- and right-circularly polarized light. Although, this typically represents 0.1\% of the total absorption,\textsuperscript{174,175} CD spectroscopy is a common tool in analytical biochemistry. In multichromophoric systems, the CD signal arises from coupling between the dipoles associated to each chromophore. The relative orientation and spatial arrangements of the coupled transition dipoles are encoded in the resulting CD signal, whose derivation is based on the Fermi Golden rule with electric and magnetic dipole interaction. It is proportional to the scalar product of electric and magnetic transition dipole moments.\textsuperscript{176} Therefore, CD spectroscopy probes the same couplings as 2D FT spectroscopy, but with the advantage that the theoretical modelling is, in principle, simpler. However, in the time-domain an additional experimental difficulty arises in that, in addition to the difference between left- and right-circularly polarized light absorption, the difference between pumped and un-pumped CD spectra makes the signals extremely weak, reaching a few tenths of a milliOD at most. Nevertheless, several time-resolved CD set-ups have been developed, but very few in the deep-UV region where the important chromophores of biology absorb.\textsuperscript{177-179} My group has recently implemented such an experiment as an extension of our 2D deep-UV set-up.\textsuperscript{142,143} The CD experiment employs a photoelastic modulator to achieve shot-to-shot polarization switching of a 20 kHz pulse train of broadband fs deep- to near-UV (250–370 nm) pulses. The sequence of alternating left- and right-circularly polarized probe pulses is used in a pump–probe scheme with shot-to-shot dispersive detection, allowing the acquisition of broad-band CD spectra of ground- and excited-state species. A sensitivity of $<2 \times 10^{-5}$ OD ($\approx 0.7\text{ mdeg}$) is achieved.\textsuperscript{180} This set-up allows detecting chirality changes of molecular complexes and assemblies of great relevance to biology, such as DNA.

5 Scientific questions

In the following section, I will dwell on some of the scientific subjects relevant to this Faraday Discussion. This section is by no means exhaustive and it does not
(A) Electron versus excitation energy transfer in proteins

The amino-acid residue tryptophan (Trp) is commonly used as the “molecular ruler” in studies of protein dynamics because it is known to undergo dipole-dipole EET to nearby acceptor chromophores via the FRET process. The strong distance dependence of the FRET rate allows one to extract, from the Trp decay times, information about the protein structure and its changes. Because of its low oxidation potential, Trp is also involved in multistep ET processes in proteins and DNA.56,84,182–188 Excited Trp fluorescence quenching has also been attributed to ET to Cu atoms in azurin.189

Trp fluorescence decay in myoglobins (Mbs) has repeatedly been interpreted as being due to EET to the haem.154,190,191 We recently used 2D deep-UV and visible TA, and ultrafast fluorescence up-conversion, to investigate the decay of Trp fluorescence in Mbs,145,146 and in ferric and ferrous cytochrome c (Cyt c).192,193

Mb has two tryptophan residues: Trp7 and Trp14, which are located at distances of 21.2 Å and 15.2 Å (centre to centre), respectively, from the haem group (Fig. 3). Their fluorescence decay times are, in all forms of Mb (ferric or ferrous, and ligated or deoxy), typically 20–30 ps for Trp14 and 110–140 ps for Trp7, compared to the ~2–3 ns lifetime of Trp in water.

Our 2D-UV TA studies of ferric Mbs (MbCN and metMb) revealed that Trp14 undergoes both EET and ET to the haem,145 with comparable yields. How coupled EET and ET are in this case is unclear (the issue of coupling is discussed in this issue by M. Richter and B. P. Fingerhut et al. DOI: 10.1039/c8fd00189h). On the other hand, the more distant Trp7 undergoes exclusively EET to the haem. It was also found that the transferred electron ends up on the iron atom, yielding a ferrous porphyrin. Extending the study to the unligated ferrous deoxyMb form, it was found that Trp14-to-haem ET yields a low-valence porphyrin anion.
radical. In order to investigate these processes in ferrous ligated Mbs (MbNO, MbCO), we used IR TA because the dissociation–recombination kinetics of the diatomic ligand, in particular in the case of NO (~10–20 ps and ~150–200 ps), occurs on similar time scales to the decay of the two Trps. The IR probe data yields several new insights into the outcome of the ET, which were not detected in the visible probe experiments. In particular, in MbCN and MbCO the transferred electron density is distributed between the iron and the porphyrin, i.e. it does not fully reduce the Fe atom in the ferric MbCN.

We proposed that the ET proceeds from Trp14 via the leucine 69 (Leu69) and valine 68 (Val68) amino acid residues to the haem. This hypothesis was recently supported by theoretical modelling based on DFT calculations and on the Beratan model.

As already mentioned, ET rates depend exponentially on $R_{DA}$ (Fig. 2). The above results obtained on Trp7 and Trp14 decay in Mbs fully fall within these trends. The more efficient ET, overwhelming the EET for smaller distances would be expected in the case with ferric and ferrous Cytochrome c (Cyt c), since their single Trp59 residue lies ~9 Å from the haem and its centre-of-mass is located almost in the plane of the porphyrin, while its indole plane forms an angle of ~70–80° with the latter (Fig. 4).

We performed ultrafast UV fluorescence up-conversion experiments and TA spectroscopy on both systems, and found that the Trp fluorescence decays on extremely short time scales: 350 fs for ferrous Cyt c, and 770 fs for the ferric form. These values are orders of magnitude shorter than those in Mbs, implying much more efficient ET and/or EET. However, our TA studies did not point to an ET, in particular for ferric Cyt c, where the reduction of the haem would have yielded the ferrous form, as was observed in the case of Trp-to-haem ET in ferric Mbs. The very short Trp decay times hint to a relatively strong interaction with the haem. In the case of bacteriorhodopsin, excitation of retinal yielded a strong response of the nearby Trp residues in the form of a Stark shift. These results had been modelled in terms of an excitonic coupling of retinal with the two nearest lying Trps. We believe that for Cyt c, a similar excitonic coupling occurs at the excitation energy of Trp, due to a resonance with the N bands of the haem. The differences between ferric and ferrous Cyt c may be attributed to the different...

Fig. 4  Scheme of the haem pocket in cytochrome c, with the methionine (Met) and histidine amino-acid residues bound to the Fe atom (red) and the tryptophan near the haem.
relative orientations and distances between the Trp and the haem groups in the two redox states.

The strong coupling case where excitonic pairs are formed as in the above examples, or excitons in larger assemblies of chromophores, e.g. the photosynthetic system (Lishchuk et al., DOI: 10.1039/c8fd00241j; Richter and Fingerhut, DOI: 10.1039/c8fd00189h; Hsieh et al., DOI: 10.1039/c8fd00205c), organic materials (Mroczeck et al., DOI: 10.1039/c8fd00182k), or molecular crystals (Wang et al., DOI: 10.1039/c8fd00157j), is related to the hotly debated issue of electronic vs. vibrational coherences in the photosynthesis, nicely presented by Wu et al. (DOI: 10.1039/c8fd00190a) in this issue. As far as Trps are concerned, an interesting case of strong coupling and its consequences was recently simulated and discussed by Kurian and co-workers in the case of tubulin. Microtubules are biological protein polymers with critical and diverse functions. They share some similarities with photosynthetic antenna complexes, particularly in the ordered arrangement of photoactive molecules with large transition dipole moments, which applies to Trps. While the biological role of photoexcitation of microtubules is still an open question, using positions (in their native configuration), dipole orientations from realistic models (Fig. 5) and a Hamiltonian describing the light–matter interactions, Kurian and co-workers showed that the Trps exhibit a superradiant lowest excitonic state, which represents an excitation fully extended on the chromophore lattice. Furthermore, such a superradiant state

![Fig. 5](image-url)  In microtubules, tubulins form regular networks. Each tubulin contains 8 tryptophans and 34 tyrosines. Upon absorption of deep-UV light, energy transfer occurs along the neuronal microtubules and the exciton propagation extends on the order of dendritic length scales and beyond, according to ref. 197. Reproduced from ref. 197 with permission from Elsevier, copyright 2017.
emerges as a result of super-transfer coupling between the lowest exciton states of the microtubule. These cooperative effects (superradiance and supertransfer) may induce ultra-efficient photoexcitation absorption and could enhance excitonic energy transfer in microtubules over long distances under physiological conditions.

Another system in which excitons are known to occur but whose coherence length, i.e. the number of monomer units it involves, is still a matter of debate is DNA (in single- or double-stranded form). However, in contrast to microtubules, DNA is very flexible and this property is critical for its function as a carrier of genetic information, for binding by transcription factors (TF) and for its organization into chromatin. Therefore, probing DNA conformational dynamics will allow understanding how DNA allostery, modulated by DNA base modifications, affects TF binding. They also directly impact on the coherence length of the excitons and are the origin of the uncertainty on its value. In return, the dynamics of the excitons can report on the conformational evolution of DNA strands (single or double). However, the excited state dynamics of DNA still raise fundamental questions, which are hotly debated. What is the nature of the absorbing state in a single strand? The examination of the absorption spectrum of the monomer and 20-mer (Fig. 6) suggests formation of Frenkel excitons in the 20-mer, which was supported by quantum chemical calculations. However, Nogueira et al. recently argued that the differences between the features of the 20-mer spectrum are due to long-range perturbations of the monomer spectrum.

Another important question that needs to be addressed is; does the initially excited state remain unchanged or does it evolve into other species, i.e. if monomers are excited, do they evolve into excitons delocalized on 2 bases or

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**Fig. 6** Experimental (symbols) absorption spectra in aqueous solution of single base adenosine (Ado) and of 20-mer adenine strands in aqueous solution. The 20-mer spectrum shows a lower energy red wing and a blue shifted maximum. The calculated spectra (solid lines) were derived from quantum chemical calculations described in ref. 201. Reproduced from ref. 201 with permission from the American Chemical Society, copyright 2007.
more? Finally, assuming we have excitons, how do they trap to form what Kohler and co-workers\textsuperscript{199} define as excimers and exciplexes?

Despite a rich literature using a variety of experimental tools (single wavelength deep-UV\textsuperscript{199,200} and broadband visible\textsuperscript{203,204} TA, fluorescence up-conversion,\textsuperscript{147,150,151,205,206} 2D spectroscopy\textsuperscript{207–209} and liquid phase ultrafast photoelectron spectroscopy\textsuperscript{210,211}), many of these questions are still open. The studies by Fiebig and co-workers using a UV-visible (320–500 nm) continuum probe on monomeric and stacked DNA bases of variable number (from dimer to 18-mer) already delivered some rich insight. From the evolution of the signal at 430 nm as a function of the number of bases (Fig. 7), they concluded that the delocalization length of the exciton is between 3 and 4. My group has recently carried out broadband deep-UV (240–360 nm) probe studies upon 266 nm of the adenosine monomer, dimer and 20-mer and 2D deep-UV spectroscopy, which will soon be published. The interesting feature of these studies is that we can also detect the ground state bleach signal of the species, allowing a more complete visualization of the evolution of the photoexcited species.

The advent of coherent 2D UV spectroscopies\textsuperscript{140,208,212–214} should pave the way to finer studies of the dynamics of DNA and, more generally, biological systems.\textsuperscript{209,215–218}

(B) Chemical systems

Chemical reactions in solution often imply an exchange of charges, in particular an ET. This not only concerns the two reactants, which may or may not be linked by a bridge, but also the solvation shell around them is not just a spectator but reacts to the charge exchange, which creates a new field of forces, by rearranging itself in such a way as to minimize the free energy. If in addition the reactant is photoexcited, then intramolecular relaxation processes may occur therein, which

![Fig. 7](image_url)

**Fig. 7** Ratio of the spectral intensity (open circles) between the transient absorption of different strains of adenosine, associated to the exciton (at 435 nm) and to the monomer (at 330 nm), 3 ps after excitation, as a function of the stack length \(n\), according to ref. 204. The fit of the curve shows a \(1/e\) delocalization length of the exciton of \(d \approx 3–4\) bases. The values for the A:T duplexes are connected with a dotted line. Reproduced from ref. 204 with permission from the National Academy of Science, copyright 2007.
can take place on timescales comparable to those of ET and solvation dynamics, making these difficult to disentangle. This is why unambiguous markers of the oxidation state, the solvation dynamics and the intramolecular relaxation are needed. The latter two phenomena have already been dealt with rather well by ultrafast 2D spectroscopies that can disentangle the homogeneous and inhomogeneous contributions to a spectral feature and their evolution with time. The detection of an oxidised or reduced species is more difficult due to the fact that their spectral features are different to those of the neutral form, and conclusions about charge transfer processes rely on an \textit{a priori} knowledge of the system, as was done in ref. 145.

As already mentioned, XAS and XES are universal markers of the oxidation state.\textsuperscript{101} Of course, this is the case when the whole charge density is localised on a given element. This is often the case with metal complexes and several examples exist of ps XAS detection of intramolecular electron transfer in transition metal complexes.\textsuperscript{108–110} The extension of such experiments to ET in molecular dyads has been achieved by Canton \textit{et al.}\textsuperscript{219} who combined XES and X-ray scattering (XRS) with femtosecond resolution and characterized the non-equilibrated electron transfer (ET) dynamics in a bimetallic complex consisting of a light harvesting, ruthenium (Ru)-based complex linked to an optically dark cobalt (Co) complex that acts as an electron sink. The bridge between them mediates the ultrafast ET. This system is characteristic of the wide class of synthetic and natural photocatalysts, for which studies by various methods have barely started: a combination of a UV and IR pump aimed at vibrational control of ET and an IR probe,\textsuperscript{17,220} 2D electronic spectroscopy,\textsuperscript{221} and 2DEV.\textsuperscript{171,173} Canton and co-workers could thus detect the dynamics of electron departure from the donor, the transit time via the bridge, the arrival to the acceptor, and, finally, the formation time of the high spin state in the latter (Fig. 8). This work showed the great advantages of X-ray probes in studies of ultrafast photoinduced ET: (i) the unambiguous identification of the

![Fig. 8](https://example.com/fig8.png)

**Fig. 8** Schematic representation of the results obtained by Canton \textit{et al.}\textsuperscript{219} on the electron transfer in the bimetallic RuCo complex [(bpy)$_2$Ru$^{II}$tpphz$^+$Co$^{III}$bpy)$_2$]$_{5+}$ (with bpy = bipyridine, tpphz = tetrapyridophenazine) using transient optical absorption spectroscopy (TOAS), fs X-ray emission spectroscopy (XES) and X-ray scattering (XDS). Excitation of the Ru complex transfers an electron to the Co-complex via the bridge (red and yellow arrows). The reduction and high spin state of the Co-complex is detected by XES, while its structural rearrangement and solvent relaxation is detected by XDS. Reproduced from ref. 219 with permission.
donor and acceptor; (ii) the detection of the optically silent acceptor; (iii) the identification of its high spin electronic state.

Other examples of intermolecular electron transfer processes detected by time-resolved X-ray spectroscopy are those involving charge-transfer-to-solvent states, for which a typical example is aqueous iodide. These states are metastable states of the solute–solvent system and for that reason they exist only in polar solvents. This process requires 2–3 ps to be completed. Further studies using fluorescence up-conversion allowed us to detect the departure of the electron from the CTTS state, since it fluoresces as long as the excited state wave function still has an overlap with the ground state one. These studies showed that the decay of the CTTS states (between 50 and 450 fs) is highly inhomogeneous due to the infinite number of initial configurations of iodide in the labile solvation shell. Another system exhibiting CTTS states, aqueous [Fe(CN)6]3−, which we investigated using time-resolved X-ray spectroscopy, did not yield any ultrafast fluorescence hinting to a possible intramolecular channel for the electron departure.

Finally, I would like to dwell on our recent development of ultrafast broadband (260–360 nm) deep-UV circular dichroism (CD) spectroscopy, which although mainly implemented to tackle biological systems, e.g. DNA, we first demonstrated on a simple model system, ruthenium-trisbipyridine ([Ru(bpy)3]2+) in water undergoing a metal-to-ligand-charge transfer (MLCT) upon photoexcitation. This molecule is chiral in the ground state and the dipoles of the 3 bpy ligands are coupled and have their ligand-centred π−π* bands centred at 292 nm. MLCT excitation transfers an electron to one of the bpy ligands, breaking the chiral character of the molecule. Our experiments exhibited a very clear response of the two enantiomers, paving the way to the study of biological systems. As a start, we investigated thiolated dipeptides as the model units of peptide chains. The coupling of the two thioamide units could not be resolved by achiral 2D-UV spectroscopy, however it gives rise to a pronounced bisignate CD spectrum. The time-resolved CD experiments reveal the weakening of this coupling upon 266 nm excitation, which releases conformational constraints. These results show that direct local probing of fast backbone conformational change via CD is possible. Furthermore, site-selective thio-substitution promises a more detailed probing of conformational dynamics in peptides and proteins.

(C) Photovoltaics and photocatalysis

Transition metal complexes are highly studied candidates for photocatalysis and photovoltaics in so-called dye sensitized solar cells (DSSCs). In DSSCs, the most popular dyes are ruthenium-polypyridine complexes, adsorbed onto a transition metal oxide (TMO) substrate (TiO2 or ZnO). The ruthenium complexes serve as visible light harvesters and upon excitation of their singlet metal-to-ligand-charge-transfer (1MLCT) state, they undergo ultrafast electronic relaxation and intersystem crossing to the 3MLCT state and simultaneously to these, electron injection into the conduction band (CB) of the TMO occurs. This process has been probed using ultrafast spectroscopy in the visible to the THz range.
However, these probes are only sensitive to the free carriers (i.e. the Drude electrons in the CB of the material), cannot detect trapped charges (important for catalysis) and are not material specific (the response of Drude electrons is not specific to the material). In the past decade my group has developed several tools to interrogate the fate of charge carriers (both electrons and holes) in TMOs, in particular upon charge injection.\textsuperscript{73,115,118,119,237,238}

We implemented a picosecond optical pump/XAS probe in the case of ruthenium dye sensitized anatase TiO\(_2\) nanoparticles (NPs) in solution, probing both photooxidation of the dye and the reduction of Ti atoms at defects due to electrons injected into the substrate. We also compared these results to the case of direct band gap excitation of the bare NPs. These were chosen to reproduce the average grain size of mesoporous TiO\(_2\) films used in DSSCs. Previously, Katz et al.\textsuperscript{116,239} had carried out an Fe K-edge absorption study of iron oxide nanoparticles, upon electron injection from adsorbed organic dyes. By comparing their transients with simulated ones, they concluded that the reduced metal sites formed small polarons on a 100 ps time scale. Our ps XAS studies on bare NPs showed that upon deep-UV band gap excitation, the electron gets trapped at defects characterised by pentacoordination of the Ti atoms reducing them from 4\(^+\) to 3\(^+\).\textsuperscript{115} Further, fs XAS studies showed that the electron is trapped in \(~100\) fs, but the structural relaxation of the oxygen cage around it requires a longer time of about 330 fs.\textsuperscript{118,240} This ultrafast electron trapping suggests that the electron barely travels in the lattice and is trapped at or near the unit cell where it was created. Given that in anatase TiO\(_2\) NPs the shell region is defect-rich, we conclude that most of the trapped electrons are found therein. However, it is obvious that not all electrons are trapped. When conducting the experiment on dye-sensitized NPs, the XAS spectral signatures were somewhat different to the bare NP case, which we attributed to the electron being trapped in the outer

![Fig. 9 2D deep-UV TA maps (pump and probe photon energy) of a colloidal solution of anatase TiO\(_2\) NPs at room temperature. The spectral response is displayed at three different time delays between pump and probe: 1 ps, 100 ps, and 500 ps. The time resolution is 150 fs. The signal is dominated by a bleach over the entire probe region, with two bands appearing at 3.85 eV and 4.4 eV, which are not distinguished in the steady-state absorption spectrum. The signal is due to a combination of phase space filling or bleach, which attenuates the absorption, and long-range Coulomb screening, which broadens it. Reproduced from ref. 244 with permission from the American Chemical Society, copyright 2018.](image_url)
surface region of the NPs. We also carried out similar studies on the amorphous and rutile polynorphs of TiO$_2$, yielding the same trends as in anatase.

ZnO is another very promising material for photovoltaics and photocatalysis, as well as many other applications. In this material, the Zn atoms have a d$^{10}$ electronic structure, therefore they cannot trap electrons as in TiO$_2$, yet when we carried out ps XAS on ZnO NPs, we found a very pronounced response at the Zn K-edge. At the same time, the ps X-ray emission spectra did not hint (as expected) to a change of electronic structure of the Zn atoms. In fact, their strong K-edge response is due to the fact that the material contains singly (positively) charged oxygen vacancies. Upon photoexcitation, free holes are created, which migrate and get trapped at these vacancies to turn them into doubly charged ones. This process induces a dramatic displacement of the four surrounding Zn atoms, which explains why the Zn K-edge is so strongly affected. Thus, one charge can affect several atoms simultaneously. The additional interesting aspect of this work is that it allows us to detect for the first time selectively the hole in the VB of a TMO. Indeed, the VB is dominated by the oxygen orbitals in all TMOs, and detecting them using XAS or XES implies working in the soft X-ray range at the O K-edge. This requires a solid sample in vacuum, while here we detect them in solution.

As already mentioned, the high contrast achieved by X-ray spectroscopy upon the oxidation state change of a given element implies that for the TMOs only localised charges can unambiguously be detected using X-ray spectroscopy, but not the free ones. A method is needed that can detect the free charges, while being element-specific. 2D deep-UV TA spectroscopy turned out to be an extremely valuable tool for the characterisation of charge carrier dynamics in TMOs. We recently carried out a study of anatase TiO$_2$ NPs, and revealed hitherto unknown features in the TA, as can be seen in Fig. 9. These features are missing in the steady state absorption spectrum but show up here because of the suppression of

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**Fig. 10** Spectral responses of the ruthenium dye sensitizer in solution upon 550 nm excitation (green), the bare NPs of the substrate material (blue) upon above band-gap excitation in the deep-UV region and of the sensitized material upon 550 nm excitation. In the case of the bare TiO$_2$ NPs, the signal is identical to that in Fig. 9. For ZnO NPs, the signal is entirely due to a bleach due to the filling of the conduction band. In the sensitized NPs, the same signatures appear as in the bare case, except for an offset in the case of TiO$_2$, due to the contribution of Drude electrons, and a shift in the case ZnO, which will be discussed elsewhere. Reproduced from ref. 238 with permission from the American Chemical Society, copyright 2017.
scattering in the difference spectra (pumped minus unpumped). Interestingly, the same features are present in the transient reflectivity spectra of single crystals of anatase TiO$_2$, pointing to a bulk like origin. Further analysis using a wide range of experimental (spectroscopic ellipsometry and angle-resolved photoemission) and theory established that the first feature at 3.85 eV is due to a strongly bound exciton (binding energy $\sim$ 150 meV) intermediate between a Frenkel and a Wannier exciton. However, most remarkable is that this exciton is confined to a 2D plane of the 3D lattice. Furthermore, we found that it is robust against defects, temperature and strain.\textsuperscript{243} This finding prompted us to propose the use of excitonic transitions as a substrate-specific probe of electron injection from a sensitizer. Indeed, injecting electrons into the CB should affect the excitonic transitions by reducing the transition probability (phase-space filling) or broadening it by Coulomb screening.

Fig. 10 shows the results obtained for a ruthenium-dye adsorbed on anatase TiO$_2$ NPs and ZnO NPs. In both cases, the response at the energy of the first exciton is very clear and its kinetic behaviour reproduces what was obtained from the detection of Drude electrons using other methods in other spectral ranges (THz, IR and Visible).\textsuperscript{72,245} However the deep-UV detection teaches us something new about what the effect of the Drude electrons is in the CB of the material. Indeed, in TiO$_2$ the excitonic response is mainly due to Coulomb screening, while in ZnO it is due to phase space filling. These responses have implications on the functioning of the material as a photovoltaic device. This work also suggests an avenue for performing 2D visible/deep-UV spectroscopy of charge injection, as it has been suggested that the injection efficiency is excitation energy-dependent.\textsuperscript{246}

6 Outlook

In this article, I have attempted to review a number of recent results we and others have obtained using novel ultrafast spectroscopic tools (X-ray spectroscopy, 2D deep-UV, etc.), casting them in the context of this Faraday Discussion. What, in my humble opinion, emerges are a number of points regarding both methodologies and concepts. These are far from being exhaustive. As far as methodologies are concerned, there is no doubt that the emergence of 2D spectroscopies in their various forms, but more specifically electronic ones, represent a crucial turning point in the study of EET and ET. Extending them to shorter wavelengths is a promising avenue that will yield new insights, especially when they will be implemented as core-level spectroscopies.\textsuperscript{218,247,248} A complement to these is offered by ultrafast circular dichroism spectroscopy, which in the optical domain has the advantage of a relatively simple theoretical modelling. CD spectroscopy offers in addition access to structural information, while working in the optical domain. For biosystems in physiological solutions, this is unique as the only alternative is X-ray solution scattering, which requires heavy simulations for the interpretation of results.

In terms of concepts, there has been no doubt about vibrational coherence in biosystems, and in the case of electronic coherence, these systems exhibit quantum mechanical properties such as delocalization and super-radiance. Excitons are key objects in the capture of light, its transport in neutral form and its conversion to electrical charges. What we are now seeing is that in addition, excitons can serve as probes of conformational dynamics, e.g. in DNA.
Interfacial charge transfer is central to electrochemistry, photocatalysis and to photovoltaics based on sensitized systems and on organic materials. The way it is governed by the nature of the donor and the acceptor is still not rationalised and much needs to be done yet in this respect. Finally, and somewhat related, proton coupled electron transfer, which is essential in enzymatic activities and in artificial synthesis to allow the system to recover, is an area where intense work is needed if any of the proposed schemes for solar energy conversion can “see the light”.

Conflicts of interest

There no conflicts of interest to declare.

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