Solvent Effects on Ultrafast Photochemical Pathways

Ravi Kumar Venkatraman† and Andrew J. Orr-Ewing*

School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, United Kingdom

Conspectus

Photochemical reactions are increasingly being used for chemical and materials synthesis, for example in photoredox catalysis, and generally involve photoexcitation of molecular chromophores dissolved in a liquid solvent. The choice of solvent influences the outcomes of the photochemistry because solute-solvent interactions modify the energies of, and crossings between, electronic states of the chromophores, and they affect the evolving structures of the photoexcited molecules. Ultrafast laser spectroscopy methods with femtosecond to picosecond time resolution can resolve the dynamics of these photoexcited molecules as they undergo structural and electronic changes, relax back to the ground state, dissipate their excess internal energy to the surrounding solvent, or undergo photochemical reactions. In this account, we illustrate how experimental studies using ultrafast lasers can reveal the influences that different solvents or co-solutes exert on the photo-induced non-adiabatic dynamics of internal conversion and intersystem crossing in non-radiative relaxation pathways. Although the environment surrounding a solute molecule is rapidly changing, with fluctuations in the coordination to neighbouring solvent molecules occurring on femtosecond or picosecond timescales, we show that it is possible to photoexcite selectively only those molecular chromophores transiently experiencing specific solute-solvent interactions such as intermolecular hydrogen bonding.
The effects of different solvation environments on the photodynamics are illustrated using four selected examples of photochemical processes in which the solvent has a marked effect on the outcomes. We first consider two aromatic carbonyl compounds, benzophenone and acetophenone which are known to undergo fast intersystem crossing to populate the first excited triplet state on timescales of a few picoseconds. We show that the non-adiabatic excited-state dynamics are modified by transient hydrogen bonding of the carbonyl group to a protic solvent, or by coordination to a metal cation co-solute. We then examine how different solvents modify the competition between two alternative relaxation pathways in a photoexcited UVA-sunscreen molecule, diethylamino hydroxybenzoyl hexyl benzoate (DHHB). This relaxation back to the ground electronic state is an essential part of the effective operation of the sunscreen compound, but the dynamics are sensitive to the surrounding environment. Finally, we consider how solvents of different polarity affect the energies and lifetimes of excited states with locally excited or charge-transfer character in heterocyclic organic compounds used as excited-state electron donors for photoredox catalysis. With these and other examples, we seek to develop a molecular level understanding of how the choice of solution environment might be used to control the outcomes of photochemical reactions.
KEY REFERENCES


- Robertson, P.A; Bishop, H.M.; Orr-Ewing, A.J. Tuning the Excited-State Dynamics of Acetophenone Using Metal Ions in Solution, *J. Phys. Chem. Lett.* 2021, 12, 5473 - 5478.\(^2\) *The excited electronic states of acetophenone are stabilized or destabilized by metal-ion coordination, depending on their orbital character, with consequences for the states reached by photoexcitation, and the subsequent ultrafast dynamics of internal conversion and intersystem crossing.*

- Kao, M.H.; Venkatraman, R.K.; Sneha, M.; Wilton, M.; Orr-Ewing, A.J. Influence of the Solvent Environment on the Ultrafast Relaxation Pathways of a Sunscreen Molecule Diethylamino Hydroxybenzoyl Hexyl Benzoate, *J. Phys. Chem. A,* 2021, 125, 636 - 645.\(^3\) *Ultraviolet photoexcitation of the chosen sunscreen molecule populates the \(S_1\) excited state, which can undergo two competing relaxation pathways to dissipate its excess energy. The balance of this competition is strongly affected by the properties of the solvent.*

- Bhattacherjee, A.; Sneha, M.; Lewis-Borrell, L.; Amoruso, G.; Oliver, T. A. A.; Tyler, J.; Clark, I. P.; Orr-Ewing, A. J. Singlet and Triplet Contributions to the Excited-State
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Ultrafast spectroscopy unravel the photochemical dynamics of three classes of organic photoredox catalysts. The photocatalytic activity involves both singlet and triplet excited states, with the balance affected by the structure of the photocatalyst and the choice of solvent.

1. Introduction

Solvent plays a decisive role in the outcomes of various fundamental chemical and biological processes, with influence over the rates, mechanisms, and thermochemistry of chemical reactions,5–9 the photochemistry of excited states of solute molecules,10 and the structure-functional properties of biomolecules.11 Solvents can influence the chemical behaviour of solutes through their bulk properties such as polarity and viscosity, but also at the microscopic level of explicit solute-solvent interactions. These various solvation effects are broadly classified into non-specific (e.g., Coulombic and van der Waals) interactions and specific (e.g., hydrogen bonding, hydrophobic, aromatic) interactions.6,12,13

The choice of solvent will influence various chemical and biological phenomena,14 but in this account, we limit our discussion to studies of photoinduced processes, activated by absorption of ultraviolet (UV) or visible light by a solute chromophore. The initial events that follow photoexcitation to an electronically excited state can involve non-adiabatic pathways such as internal conversion (IC) or intersystem crossing (ISC), isomerization, electron transfer, energy transfer, reaction (with the solvent or a co-solute), intramolecular charge transfer, and proton-coupled electron transfer (PCET). Recent advances in cutting-edge ultrafast spectroscopy and computational chemistry techniques are enhancing our understanding of the importance of
crossings between electronically excited states, especially the vital role of seams of conical intersections, in controlling these ultrafast non-adiabatic processes.\textsuperscript{15-17}

Studies of ultrafast changes in the structure and electronic properties of isolated, photoexcited molecules in the gas phase\textsuperscript{18-22} serve as an initial model for understanding the non-adiabatic dynamics of these molecules in more complex environments such as a liquid solution or protein, but the interactions with the surrounding environment will change the photochemical dynamics in numerous ways.\textsuperscript{23,24} A variety of ultrafast spectroscopy and diffraction techniques are therefore being developed to explore photochemical dynamics in condensed phases.\textsuperscript{25,26} The intricacies of a liquid medium will differ for standard organic solvents, aqueous solutions, or multi-component, cellular-like environments. For example, the outcomes of an organic photocatalysis reaction will depend on choice of solvent, while modern cell-imaging techniques exploit the ways in which different biochemical environments alter the emission of fluorescent dyes.\textsuperscript{27}

When a chromophore is dissolved in a liquid, the fluctuating solvent environment alters the electronic properties of the solute, which in turn causes structural changes. Similarly, the solute shapes the surrounding solvent structure.\textsuperscript{28} Static (equilibrium) solvation effects are observed in the differential solvation of a chromophore in its ground and excited electronic states, manifesting as solvent-polarity dependent changes in band positions, intensities, and widths in steady-state electronic absorption spectra. This solvatochromism also arises in luminescence and vibrational spectroscopy.\textsuperscript{12,13} However, ultrafast spectroscopy can be used to probe the dynamic (non-equilibrium) aspects of solvation and solvent shaping, giving both solute and solvent perspectives. Figure 1 provides an example for a fluorescent chromophore. Upon photo-absorption to an excited electronic state, the associated charge redistribution within the
chromophore is faster than the timescale for the surrounding solvent molecules to respond. After photoexcitation, the solvent molecules reorganize spatially and orientationally to stabilize the new electron-density distribution of the chromophore. The resulting dynamic Stokes shift observed in time-resolved fluorescence experiments has been widely used to study the timescales for these solvation dynamics.²⁹

**Figure 1.** Schematic illustration of potential energy landscapes involving solvation dynamics. The solvent molecule dipole orientations around the chromophore remain the same on the timescale of photoexcitation, but subsequently reorganize in response to the new charge distribution of the chromophore, leading to solvent relaxation indicated by a solvation coordinate. The vibrational coordinate captures the internal vibrational motions of the chromophore. Emission from the solvent-relaxed state appears to longer wavelength (i.e., Stokes shifted) than the absorption band.
Figure 2 shows typical timescales for the photoinduced dynamics of a chromophore and the surrounding solvent. The initial phase of the solvation dynamics involves the collective, librational (inertial) motion of solvent molecules in the vicinity of the chromophore, typically on sub-picosecond timescales. It is followed by a slower orientational and translational diffusive motion of the solvent molecules on timescales ranging from a few picoseconds to sub-nanosecond. Numerous elementary photophysical and photochemical processes occur on similar timescales to the solvation dynamics; therefore, the solvent and reaction coordinates are tightly entangled.

Figure 2. Timescales for various important photophysical, photochemical, and solvation dynamical processes in solution. IVR denotes intramolecular vibrational energy redistribution.

Hydrogen bonding is a specific solute-solvent interaction that has attracted numerous investigations because of the properties it bestows to liquids such as water, as well as its fundamental importance in regulating molecular and supramolecular structures. While hydrogen-bond binding energies (4 – 40 kJ mol\(^{-1}\)) are much smaller than those of covalent bonds, the making and breaking of H-bonds can result in ultrafast structural fluctuations. These
fluctuations perturb the molecular structures of chromophores on similar timescales, shifting and inhomogeneously broadening spectral lineshapes.\textsuperscript{13,32} In liquid solutions, the timescales of hydrogen bond (or other solvent-solute) fluctuations can range from tens of femtosecond to a few picoseconds, and ultrafast infrared spectroscopy has been extensively used to understand the hydrogen bond dynamics of water in various chemical environments.\textsuperscript{33} Ultrafast two-dimensional infrared (2DIR) spectroscopy can correlate the vibrational signatures of molecules in changing solvent environments, with 2DIR lineshape analysis providing structural and dynamic information on vibrational coupling, solvent dynamics, and exchange between hydrogen and non-hydrogen bonded conformations.\textsuperscript{34–37} The complementary method of two-dimensional electronic spectroscopy (2DES) reveals information on excited-state solvation dynamics and environmental interactions.\textsuperscript{38,39}

Ion solvation plays an important role in many biological systems, as well as technological applications such as energy storage and electrocatalysis.\textsuperscript{40,41} Ions modulate the solute structure by direct interaction or indirect modulation of the solvent around the solute.\textsuperscript{40} However, the influence of dissolved ions on the photochemistry of organic chromophores remains poorly explored. The coordination of charged species is expected to change the energies and crossings between excited states of the organic solute molecules, with consequences for the outcomes of the ultrafast non-adiabatic photochemical dynamics.

Several theoretical approaches have been successfully employed to simulate the non-adiabatic quantum dynamics of isolated chromophores,\textsuperscript{15,42,43} and to treat solvated chromophores using an implicit (continuum) solvent model.\textsuperscript{44} Treatment of the non-equilibrium dynamics using explicit models of the solvent-chromophore interactions remains a challenge, but progress is being
made,\textsuperscript{45,46} and will benefit from precise experimental identification of environment-dependent ultrafast dynamics following chromophore photoexcitation.

This account illustrates the influence of both static and dynamic aspects of solvation on the photochemistry of model organic chromophores. One challenge is to pick specific solvation environments from the ensemble distribution resulting from fluctuating solute-solvent interactions.\textsuperscript{47} In section 2, we demonstrate solvation-state selective photoexcitation of benzophenone (Bzp) in different hydrogen bonding environments, revealing the impacts of transient hydrogen bonds to solvent or co-solute molecules on ISC rates and H-atom abstraction reactions. Like Bzp, acetophenone (Acp) is a chromophore found in organic photocatalysts and photosensitizers, but as section 3 shows, its photochemical dynamics are sensitive to coordination with metal ions in solution. Section 4 describes how photoexcited diethylamino hydroxybenzoyl hexyl benzoate (DHHB), a widely used sunscreen compound, displays competing ultrafast relaxation pathways initiated by either excited-state hydrogen transfer (ESHT) or C-C bond torsional dynamics, with the balance influenced by the chosen solvent. Finally, section 5 addresses how the choice of solvent affects the performance of organic chromophores designed for use in photoredox catalysis. These four chosen systems serve to illustrate how transient solvent-solute or solute-co-solute interactions can profoundly alter the ultrafast dynamical pathways in photoexcited organic molecules.

2. Influence of Solvation Dynamics on the Photochemistry of Benzophenone

Benzophenone serves as a prototypical molecular system for understanding the fundamental photochemistry of aromatic ketones.\textsuperscript{48} Its high quantum yield for intersystem crossing has attracted considerable fundamental study and led to a variety of applications.\textsuperscript{48} Nevertheless, the
mechanism for population of the lowest triplet excited state ($T_1$) after $n\rightarrow\pi^*$ photoexcitation to the $S_1$ state remained unresolved until recent experimental and theoretical studies.\textsuperscript{49,50}

Solvatochromic studies of Bzp revealed the possibility of selective photoexcitation of Bzp molecules in different solvation states using the longest wavelength absorption band corresponding to the $n\rightarrow\pi^*$ transition centered on the carbonyl group.\textsuperscript{13} Bzp in methanol solution has solvation environments distinguishable by steady-state IR or Raman spectroscopy, with the solvated Bzp having either a hydrogen-bonded carbonyl (HBC) or remaining uncoordinated (a “dangling” carbonyl, DC). Resonance Raman studies indicated that absorptions at the long-wavelength red-edge ($\lambda_{ex} = 380$ nm) or to the shorter wavelength side ($\lambda_{ex} = 340$ nm) of the $n\rightarrow\pi^*$ band correspond to selective photoexcitation of the DC or HBC forms of Bzp, respectively.\textsuperscript{50}
Figure 3. (a) The electronic absorption spectra of benzophenone (with inset structure) in methanol (CH$_3$OH) and deuterated methanol (CD$_3$OD) solutions. (b) Time-resolved electronic absorption spectra of benzophenone in methanol excited at 340 nm, with the inset color key indicating the time delays used. (c) Global analysis gives the plotted kinetic traces for S$_1$, T$_2$ and T$_1$ state absorptions following 380-nm and 340-nm excitation. (d) Schematic representation of the indirect ISC mechanisms at the two excitation wavelengths. Adapted with permission from J. Phys. Chem. Lett., 2018, 9, 1642. Copyright 2018 American Chemical Society.

Spectral decomposition of ultrafast transient electronic absorption spectra obtained with 340 and 380 nm excitation, examples of which are shown in Figure 3, reveals excited-state
absorption (ESA) bands corresponding to three contributing excited-state species: (i) the $S_1$ state prepared directly by UV absorption; (ii) the $T_2(^3\pi\pi^*)$ state, populated by ISC from $S_1$; and (iii) the long-lived $T_1(^3n\pi^*)$ state populated after IC from $T_2$ followed by vibrational energy transfer to the solvent. For 340-nm excitation, the $S_1$ state population decays to $T_2$ with an ISC time constant $\tau_{\text{ISC}} = 1.7$ ps, from which subsequent relaxation to $T_1$ and vibrational cooling occurs with an $\sim 11$ ps time constant. In contrast, with 380-nm excitation, $T_2$ population grows within the instrument response function ($\tau_{\text{ISC}} < 0.2$ ps) and decays to the $T_1$ state, again with an $\sim 11$ ps time constant. In aprotic dipolar and non-polar solvents, the relaxation time constants are independent of excitation wavelength, and are similar to those for 380-nm excitation in methanol solution. Comparison of the early time kinetics obtained in CD$_3$OD ($\tau_{\text{ISC}} = 2.5$ ps) and CH$_3$OH ($\tau_{\text{ISC}} = 1.7$ ps) solvents reveals the role of fluctuating hydrogen bonding in populating the $T_2(^3\pi\pi^*)$ state. The $S_1(^1n\pi^*)$ and $T_2(^3\pi\pi^*)$ states exhibit hydrogen bond weakening and strengthening, respectively, which is to say the $S_1$ state is destabilized in energy and the $T_2$ state is stabilized by intermolecular H-bonds to methanol. The consequent breaking of the near degeneracy of the $S_1$ and $T_2$ states of Bzp induced by accepting an H-bond is proposed to slow the ISC rate, which becomes more favorable again when the transient H-bond breaks. Hydrogen bond reorganization on few-picosecond timescales therefore influences the rate of ISC from the $S_1(^1n\pi^*)$ to $T_2(^3\pi\pi^*)$ states.
Figure 4. Time-resolved vibrational absorption spectra of: (a) Benzophenone (Bzp) in dichloromethane, with similar ISC dynamics to those shown in Figure 3; (b) Bzp and phenol in dichloromethane showing the H-atom transfer from phenol to Bzp(T₁). All spectra were obtained after 320-nm excitation. The inset color keys indicate spectra obtained at various time delays. Adapted with permission from *J. Am. Chem. Soc.* 2019, 141, 15222. Copyright 2019 American Chemical Society.

Benzophenone in its T₁ state is well-known to abstract an H-atom from compounds such as phenol. Solvatochromic studies of ground-state Bzp in dichloromethane solutions with different concentrations of added phenol indicated the possibility of sub-ensemble photoexcitation of Bzp molecules either hydrogen-bonded or non-hydrogen bonded to phenol by choice of UV excitation wavelength. Comparison of ultrafast time-resolved absorption spectroscopy data such as those in Figure 4 again shows population of the T₁(3ππ*) state occurs via the intermediate T₂(3ππ*) state. Furthermore, IR absorption bands assigned to Bzp ketyl radicals and to phenoxy radicals (Figure 4(b)), both formed by H-atom transfer from phenol to Bzp (T₁), grow over time.
Selective photoexcitation of hydrogen-bonded Bzp-phenol complexes shows bi-exponential radical growth with time-constants of ~20 and ~800 ps. In contrast, selective excitation of Bzp non-hydrogen-bonded to phenol reveals mono-exponential growth of the two radical products with a time constant of ~800 ps. In both cases, the radical formation over the longer timescale is attributed to diffusional bimolecular reaction. In comparison, the faster component of radical formation, observed only for excitation of hydrogen-bonded Bzp-phenol pairs, is attributed to reaction in the static limit within the pre-formed complexes. This interpretation of photochemical reactions between specific geminate pairs comprising a Bzp molecule and a phenol molecule in its first solvation shell is supported by 2DIR spectroscopy and molecular dynamics simulation studies of mixed Bzp and phenol solutions in dichloromethane.\(^1\) The reaction rate in the static limit is faster by a factor of 40 than the diffusive rate because the hydrogen-bonded Bzp-phenol supramolecular complexes are preconfigured for reaction once Bzp reaches its T\(_1\) state.

**3. Effects of Coordinated Ions on Acetophenone Photodynamics**

The impacts of hydrogen bonding on benzophenone ISC dynamics described in Section 2 show how sensitive the photochemistry of this aromatic carbonyl chromophore is to interactions with its surroundings. In the multi-component solutions typically used for chemical synthesis, the presence of co-solutes may similarly modify the photochemistry of other organic chromophores through various non-covalent interactions. For example, coordination to metal ions could perturb the energies of excited electronic states, the locations of seams of conical intersections between electronic states through which internal conversions occur, and the ISC pathways. Consequently, the introduction of metal salts to solutions might provide useful strategies to manipulate the photochemistry of organic molecules.
Figure 5. Photodynamics of acetophenone (Acp) in acetonitrile with added Mg$^{2+}$ ions. (a) Changes in the steady-state UV absorption spectra for solutions with increasing Acp:Mg$^{2+}$ ratios shown in the inset color key. (b) Transient absorption spectra obtained after 320-nm photoexcitation of a 1:6 Acp:Mg$^{2+}$ solution in acetonitrile, with time delays shown by the inset color key. Black arrows indicate changes in intensity of the S$_2$ and T$_1$ bands with time. (c) Schematic energy level diagram for the ground and first few excited electronic states of Acp in acetonitrile, with excitations at 280 nm and 320 nm shown by purple and blue arrows. Red arrows indicate pathways for internal conversion, intersystem crossing and vibrational energy
transfer to the solvent. (d) Modification of the photochemical pathways in Acp coordinated to an Mg\(^{2+}\) ion, with stabilization of the \(1\pi\pi^*\) and \(3\pi\pi^*\) states. Adapted with permission from *J. Phys. Chem. Lett.*, 2021, **12**, 5473. Copyright 2021 American Chemical Society.

The acetophenone chromophore provides a useful model system to study the effects of metal ions or Lewis acids on carbonyl photochemical dynamics\(^{55-57}\). Figure 5 shows schematically the electronic states involved in Acp photochemistry and the UV absorption spectrum obtained in acetonitrile. Absorption bands in the UV region are attributed to the weak \(S_0 \rightarrow S_1\) (n→\(\pi^*\)) electronic excitation centred at around 320 nm, and the stronger \(S_0 \rightarrow S_2\) (\(\pi \rightarrow \pi^*\)) excitation which dominates at wavelengths below 300 nm. In isolated, gas-phase Acp, internal conversion from \(S_2\) to \(S_1\) is ultrafast, with a time constant of ~140 fs\(^{58}\). Intersystem crossing from \(S_1\) occurs within a few picoseconds\(^{2,59}\), with the likely pathway being to the \(T_2(3\pi\pi^*)\) state before internal conversion to the \(T_1(3\pi\pi^*)\) state\(^{55}\). In computational and spectroscopic studies of the acetophenone derivative Irgacure-2959, Coote and co-workers\(^{55-57}\) showed that the oriented electrostatic field (OEF) introduced by a covalently bound charged functional group or a non-covalently coordinated metal cation stabilizes the energy of the \(S_2\) state and destabilizes the \(S_1\) state. These types of interaction can reverse the ordering of the \(1\pi\pi^*\) and \(1\pi\pi^*\) states, or the \(3\pi\pi^*\) and \(3\pi\pi^*\) states\(^{60}\). The persistence of such effects when metal ions are added to solutions of Acp in polar organic solvents was recently demonstrated by Robertson *et al.*\(^2\). The most immediate evidence for a lowering of the energy of the \(S_2(1\pi\pi^*)\) state of Acp by Mg\(^{2+}\) ions added to an acetonitrile solution comes from changes in the UV absorption spectrum (Figure 5(a)), with the onset of the \(\pi \rightarrow \pi^*\) band shifting to longer wavelength. However, the consequences for the photochemical dynamics are only revealed when ultrafast spectroscopy is employed, as
exemplified in Figure 5(b). By comparing the transient absorption spectroscopy data obtained when an Acp solution is photoexcited at 320 nm and 280 nm in the absence of metal ions, bands can be identified corresponding to excited state absorptions from the $S_1$ state (400 – 600 nm), the $S_2$ state (550 – 700 nm), and the $T_1$ state (with a band peaking near 400 nm). Following 280-nm excitation, lifetimes for the $S_2 \rightarrow S_1$ internal conversion and for ISC from the $S_1$ state are determined to be $\sim$110 fs and 4.4 ps, respectively. The ESA signature of $S_2$-state population is only observed for the 280-nm excitation measurements because this state is energetically inaccessible when the Acp solution is photoexcited at 320 nm.

However, pronounced differences are observed when 6 equivalents of Mg(ClO$_4$)$_2$ are added to the Acp solution in acetonitrile. Transient absorption spectroscopy at an excitation wavelength of 320 nm then reveals an ESA band indicative of direct $S_0 \rightarrow S_2$ photoexcitation (Figure 5(b)). This observation, and the shift of the $S_2$ ESA band to shorter wavelength, both support stabilization of the $S_2(1\pi\pi^*)$ state by the OEF of a coordinated Mg$^{2+}$ ion. Moreover, the internal conversion from the $S_2$ to $S_1$ states is slower by a factor of five than for Acp molecules solvated only by acetonitrile. The experimental evidence points to changes to the seam of intersections between the $S_2$ and $S_1$ states resulting from stabilization of the former and destabilization of the latter excited states in the presence of a Mg$^{2+}$ ion. The ISC timescales are also affected by Mg$^{2+}$ coordination, suggesting shifts in the locations of crossings between singlet and triplet state manifolds. Changes to the ESA bands attributed to the longer-lived $T_1$ state may be evidence for switching of the energy ordering of the $3\pi\pi^*$ and $3n\pi^*$ states in the presence of an Mg$^{2+}$ ion. Use of LiCl in place of Mg(ClO$_4$)$_2$ hints at similar consequences of Li$^+$ ion coordination, although the effects are not as pronounced because fewer Acp molecules coordinate with the Li$^+$ ions.
After ISC populates the T₁ state of acetophenone, one known relaxation pathway is Norrish Type-I cleavage of a C-C bond to make radical photoproducts, with a quantum yield that depends on the nuclear dynamics.⁶¹ Because these dynamics, and the timescales for IC and ISC can be manipulated by coordination to metal cations, the addition of metal salts to solutions of acetophenone, and by extrapolation other organic chromophores, may offer opportunities to improve the yields of the desired products of photochemical reactions.


Figure 6. Molecular structures of (a) oxybenzone; (b) DHHB in its enol and (c) keto form. In its ground electronic state, DHHB exists in the enol form but in the first singlet excited electronic state H-atom transfer from the oxygen atom of the -OH group (red) to the central carbonyl group (green) can produce the keto tautomer.
Diethylamino hydroxybenzoyl hexyl benzoate (DHHB) is a UV-A absorber widely used as a sunscreen under the commercial name Uvinul A.\textsuperscript{62} To function effectively as a sunscreen, DHHB must efficiently dissipate the excess energy of an absorbed UV photon, and our studies of the ultrafast photochemistry of this compound show considerable sensitivity of the relaxation pathways to the polarity of the surrounding solvent medium. The molecular structure of DHHB is shown in Figure 6 and resembles that of the UV-B sunscreen oxybenzone. Previous ultrafast spectroscopy studies of photoexcited oxybenzone revealed that its relaxation mechanism is through enol $\rightarrow$ keto tautomerization (via an intramolecular excited-state hydrogen transfer, ESHT) followed by twisting about the central C-C bond to access a conical intersection with the $S_0$ state.\textsuperscript{63} In DHHB, the auxochromic amine and ester groups on an oxybenzone core alter its excited state properties.\textsuperscript{3} Thus, although oxybenzone and DHHB are structurally similar, differences in their $S_1$ state free energy surfaces for keto and enol forms in solution significantly modify the relaxation pathways which are crucial for their sunscreen performance.

Ultrafast transient absorption spectroscopy experiments for photoexcited DHHB solutions in non-polar and polar solvents produce spectra such as those in Figure 7 that reveal its relaxation mechanisms. The competing pathways in DHHB are illustrated schematically in Figure 8 and depend on solvent choice. For example, in a non-polar solvent like cyclohexane, ESHT occurs on timescales of $<200$ fs in the Franck-Condon region of the $S_1$ state, converting the enol to the keto form as the start of the main relaxation pathway. In contrast, in polar solvents (acetonitrile, methanol and dimethyl sulfoxide), disruption of intramolecular hydrogen bonding in the $S_1$ state impedes the ESHT from the initially excited $S_1$ state enol to make the keto tautomer. The stimulated emission observed in the transient spectra is quenched competitively by both this ESHT and torsion about a central C-C bond, with solvent-dependent time constants varying from
300 to 800 fs. The torsional motion towards the twisted minimum energy form of the S\textsubscript{1} enol tautomer brings the DHHB to a conical intersection with the ground state that represents a second relaxation pathway. Because the rates of the C-C torsion and the competitive ESHT both depend on the surrounding environment, the predominant relaxation pathway of the photoexcited DHHB is sensitive to the properties of the solvent. The timescales for decay of the S\textsubscript{1} ESA bands assigned to either the enol or keto forms then range from 7–23 ps depending on the solvent.

**Figure 7.** Transient electronic absorption spectra of diethylamino hydroxybenzoyl hexyl benzoate (DHHB) in (a) methanol (MeOH), (b) acetonitrile (ACN), (c) dimethyl sulfoxide (DMSO), and (d) cyclohexane (CYCH) solutions. The color key identifies spectra obtained at different time delays. Insets display longer time delay spectra corresponding to the triplet states.
Recovery of the ground state bleach observed in transient IR absorption spectra shows that >98% of the photoexcited DHHB relaxes back to the ground state with a time constant of ~12 ps in cyclohexane solvent. A small fraction of the population of the S\(_1\) state in the keto form undergoes intersystem crossing to the T\(_1\) keto state (see Figure 7(d) inset). However, in polar solvents, 95% of the photoexcited DHHB returns to the ground state with a time constant of ~15 ps, with the remaining 5% undergoing ISC from the S\(_1\)-enol to the T\(_1\)-enol states (see Figure 7(a)-(b) insets). A minor competing photoproduct, the trans-enol isomer of DHHB, is formed in these polar solvents by passage through the conical intersection between the S\(_1\) and S\(_0\) states and continuing torsional dynamics in the S\(_0\) state.

**Figure 8.** Schematic potential energy surfaces for the relaxation of UV-photoexcited DHHB. In the S\(_0\) state, the enol form is preferred, but following UV absorption to the S\(_1\) enol, there is competition between excited state H-atom transfer (ESHT) and C-C bond torsion to reach the
twisted minimum energy enol structure on the $S_1$ PES. Passage through a conical intersection and vibrational energy transfer to the solvent then repopulates the $S_0$ enol form, with a small fraction continuing to twist to reach the $S_0$ trans-enol form.

5. **Solvent Effects on the Excited State Dynamics of Dihydrophenazine, Phenoxazine and Phenothiazine Photoredox Catalysts**

The sensitivity of non-adiabatic pathways in photoexcited molecules to the choice of solvent also impacts on the design and performance of photocatalysts constructed from organic chromophores. Various organic dyes are currently being tested as candidate organic photocatalysts (OPCs) for use in synthetic chemistry, CO$_2$ reduction, and polymerization reactions controlled by photoredox catalysis. Custom-designed derivatives of dihydrophenazine, phenoxazine and phenothiazine chromophores have proved effective in atom-transfer radical polymerization (ATRP) strategies for growth of low dispersity polymers, and are strongly reducing from their excited electronic states. Using transient absorption spectroscopy, we have systematically investigated the solvent-dependence of the excited state dynamics and electron transfer reactions of several such OPCs. One example of a dihydrophenazine derivative is shown in Figure 9 and is used here to illustrate how competing photochemical pathways can be strongly affected by interactions with the solvent.

In common with several other classes of OPCs, the N-aryl dihydrophenazine, phenoxazine, and phenothiazine compounds have electronically excited states of both locally excited (LE) and charge-transfer (CT) character, in the latter case with electron density moving to the N-aryl groups. The addition of electron withdrawing groups to the para position of these pendant aromatic rings stabilizes the CT states proposed to be advantageous for subsequent
intermolecular electron transfer reactions to organohalide electron acceptors which serve as radical initiators for the polymerization chemistry.

**Figure 9.** Solvent-dependent photochemical dynamics of a dihydrophenazine organic photocatalyst with the structure in (a). Example time-resolved vibrational absorption spectra of the OPC following 370-nm photoexcitation in (b) DMF and (c) toluene-d₈, showing both excited-state absorption and ground-state bleach features. The inset color keys identify spectra measured at different time delays, and black arrows indicate directions of change of band intensities. Panels (d) and (e) illustrate schematically the different photodynamics occurring in the two solvents, with DMF stabilizing CT-character states more effectively than toluene, and the measured S₁ state lifetimes. Red arrows indicate pathways for internal conversion, intersystem crossing, and vibrational energy transfer to the solvent.
Recent ultrafast transient absorption spectroscopy studies of the excited state photochemistry of the dihydrophenazine, phenoxazine and phenothiazine OPCs, as exemplified in Figure 9, have unraveled the competition between intermolecular electron transfer from the $S_1$ state to an acceptor, intersystem crossing to $T_1$ with subsequent electron transfer, and relaxation by radiative or non-radiative pathways back to the $S_0$ state.\textsuperscript{4,70–72} The balance of these competing photochemical pathways is highly sensitive to the properties of the solvent, with comparative studies in N,N-dimethyl formamide (DMF), dichloromethane (DCM), and toluene showing significant changes to $S_1$ state lifetimes, ISC yields, and electron transfer rate coefficients. For example, the OPC 4,4’-(phenazine-5,10-diyl)dibenzonitrile (Figure 9(a)) has an $S_1$ lifetime of 140 ps in DMF solution, which is too short for it to be a strong fluorescence emitter or to undergo significant ISC to populate the $T_1$ state. In DCM solution, the $S_1$ lifetime increases to 510 ps, and in toluene solution it is 5.7 ns giving a readily observable fluorescence spectrum and a quantum yield for ISC of $\Phi_{ISC} = 0.57$. Despite its short $S_1$ lifetime in DMF, this OPC still functions as an effective photoredox catalyst for controlled ATRP, most likely because suppression of bimolecular electron transfer reactions by non-radiative intramolecular decay of the $S_1$ state regulates the overall density of radical species in the polymerizing solution.

These solvent-dependent effects derive from the sensitivity of the energies of states with CT character to the polarity of the solvent, whereas the LE states are less affected. Consequently, the energy ordering of the excited singlet states and the locations of crossings to triplet states depend on the choice of solvent. In the case of the OPC in Figure 9(a), the electron-withdrawing CN groups in para positions on the N-aryl rings favor an $S_1$ state with CT character, which is further stabilized in DMF or, to a lesser extent in DCM. The degree of solvent stabilization of
this CT state has a profound influence on how quickly $S_1$ population can access non-radiative decay pathways to the $S_0$ state, most likely via one or more conical intersections.

6. Conclusions

The choice of solvent is often critical for the success of synthetic chemical procedures, for reasons ranging from the relatively mundane, such as solubility of reactants or the chemical inertness of the solvent, to more mechanistically important factors. In this latter group are considerations such as solvent-stabilization of transition states or key intermediates, and the effects of solvent-solute interactions on the electronically excited states participating in photochemical reactions. Because of the short-lived nature of transition states, intermediates, and excited states, and the rapid fluctuations in solute-solvent interactions at the molecular level, these types of effect can be hard to resolve.

In this account, we show how ultrafast transient absorption spectroscopy can provide new insights about the role solvent interactions play in controlling photochemical reaction pathways. The examples chosen from our recent work illustrate the effects of solvent choice for a variety of organic molecules ranging from sunscreens to photoredox catalysts and highlight several fundamental processes which might be at play in any photochemical reaction. The effects of changes in the ordering of electronically excited states because of different solvent-solute interactions, or coordination to metal ion co-solutes, are exemplified for the singlet and triplet spin-multiplicity $n\pi^*$ and $\pi\pi^*$ states in aromatic carbonyl compounds. Solvent properties also affect differently the energies of excited states of organic chromophores with locally excited or charge transfer character. In both instances, internal conversion and intersystem crossing rates can be altered, with consequences for excited singlet state lifetimes and triplet state quantum yields. The rates of IC and ISC are governed by dynamical pathways to crossing points such as
conical intersections between electronic states, the locations of these crossings, and the strengths of the interstate couplings. The solvent also plays a role in determining the balance of outcomes between competing ultrafast relaxation pathways, as demonstrated by the branching between ESHT and torsional dynamical pathways for S1-state DHHB in different solvents, both of which lead ultimately to almost complete ground-state recovery. Finally, we show how reaction from photoexcited states depends on the composition of the surrounding solvent shell and the stabilization of excited state energies. The chosen examples include intermolecular hydrogen-atom abstraction and electron transfer reactions.

These and other newly emerging mechanistic insights about the dynamics of photochemical reactions in solution are becoming accessible because of advances in ultrafast spectroscopy methods and in computational calculations of excited state energies and dynamics. A room-temperature solution is highly heterogeneous, with many different types of solute-solvent interactions, and rapid fluctuations constantly interchanging between the various local solvation environments. Nevertheless, it is now possible to make experimental measurements that selectively probe these different instantaneous interactions and reveal how they impact on the photochemistry. In turn, these new capabilities offer possible new strategies for controlling photochemical reaction pathways in solution by careful choice of the solvent, the co-solutes, the excitation wavelength, and other experimental conditions.

ASSOCIATED CONTENT
None.

AUTHOR INFORMATION

* Corresponding Author
ORCID

A.J. Orr-Ewing: 0000-0001-5551-9609
R.K. Venkatraman: 0000-0003-0636-5310

Present Addresses

†Department of Physics and Astronomy, The University of Sheffield, Sheffield S3 7RH, UK and Department of Chemistry, The University of Sheffield, Sheffield S10 2TN, UK

Author Contributions

The manuscript was written through the contributions of both authors. Both authors have given approval to the final version of the manuscript.

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BIOGRAPHIES
Ravi Kumar Venkatraman was awarded his B.Sc. (2007) and M.Sc. (2009) in Chemistry by the University of Madras. He obtained his Ph.D. in Physical Chemistry (2017) from the Indian Institute of Science, and then joined the University of Bristol as a Newton International Fellow (2017-2019). Currently he is a postdoctoral research associate at the University of Sheffield. His research interests include photochemical dynamics in the liquid phase and understanding how solvent influences chemical and biological process using ultrafast spectroscopy and computational techniques.

Andrew Orr-Ewing was awarded his B.A. in Chemistry (1988) and D.Phil. in Physical Chemistry (1991) by the University of Oxford. After two years of postdoctoral research at Stanford University, he moved to the University of Bristol where he is now a Professor. His research interests include chemical and photochemical dynamics in the gas and liquid phases, atmospheric chemistry, and optical properties of aerosol particles. He was elected as a Fellow of the Royal Society in 2017, and a Member of the Academia Europaea in 2018.

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