Dynamics of Chemical and Photochemical Reactions in Solution

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Introduction

Liquid solvents provide an essential medium for many biologically, environmentally and industrially important chemical processes. Much of the chemistry of life takes places in an aqueous environment, whereas chemical synthesis underpinning the manufacture of pharmaceuticals relies on a variety of organic solvents. The solvent influences the thermodynamic properties of the reaction, and favourable solvation of reaction intermediates can accelerate reaction rates by reducing the heights of energy barriers along reaction pathways. At the microscopic scale, solvent-solute interactions fluctuate on ultrafast (femtosecond) timescales, and the precise consequences of these interactions on reaction mechanisms remain uncertain.

We seek to understand better the role played by solvents at a molecular level in both unimolecular and bimolecular reactions. One aspect of our work examines the competing unimolecular pathways of fragmentation, isomerization and energy dissipation in molecules that are energetically excited by absorption of ultraviolet radiation. Another explores how labile free radical species interact with solvent and co-solute molecules during the course of bimolecular reactive encounters. Experimental studies performed with the ULTRA femtosecond laser system use transient electronic absorption (TEA) and transient vibrational absorption (TVA) spectroscopies in the ultraviolet (UV)/visible and infrared (IR) spectral regions respectively to observe short-lived reaction intermediates. The interpretation of these time-resolved spectroscopic measurements is guided by computation of the potential energy surfaces controlling the chemical reactions, and simulations of motions of the reacting molecules that incorporate the effects of a surrounding solvent. The advances resulting from our ULTRA investigations are summarized in three feature articles [1-3]. The following sections highlight recent examples.

Unimolecular Photodissociation Dynamics

Our previous studies of $(n/\pi)\sigma^*$-state mediated photo-dissociation dynamics of heteroatom containing molecules [3] demonstrated the extent to which detailed information obtained regarding the decay dynamics of photoexcited molecules in the *gas phase* was able to inform our knowledge and understanding of the corresponding processes in *solution*. Such studies have recently been extended to probe the UV-induced ring-opening reactions of heterocyclic α-carbonyl systems [4,5] – systems which should show the same $(n/\pi)\sigma^*$ behaviour, but which are difficult to investigate in the gas phase. This class of heterocyclic molecule is well-suited to study by TVA, since ring-opening results in the formation of a ketene which has an intense and characteristic antisymmetric stretching vibrational band at ~2125 cm^{-1}. Two closely related systems which have been studied using ULTRA are α-pyrone and benzo-α-pyrone (henceforth called coumarin). Structurally, these molecules only differ from each other by the presence of the adjoining fused benzene ring in coumarin – as shown in the insets in figure 1. Figure 1(a) displays TVA spectra obtained by pumping a 20 mM solution of α-pyrone in CH$_3$CN at 266 nm and setting the

broadband probe to cover the 1500–1800 cm^{-1} range. Four bleach features are present, centred around 1545, 1625, 1715, and 1735 cm^{-1}. As the pump/probe time delay is increased, the intensity of these features is seen to decrease, indicating a repopulation of the ground electronic state following the initial UV excitation. The incomplete bleach recovery – asymptotically reaching ~55% – shows that a significant fraction of the initially excited population evolves to form photoproducts. Evidence for such product formation is provided by the growth of absorption features located at 1560, 1595, and 1665 cm^{-1}.
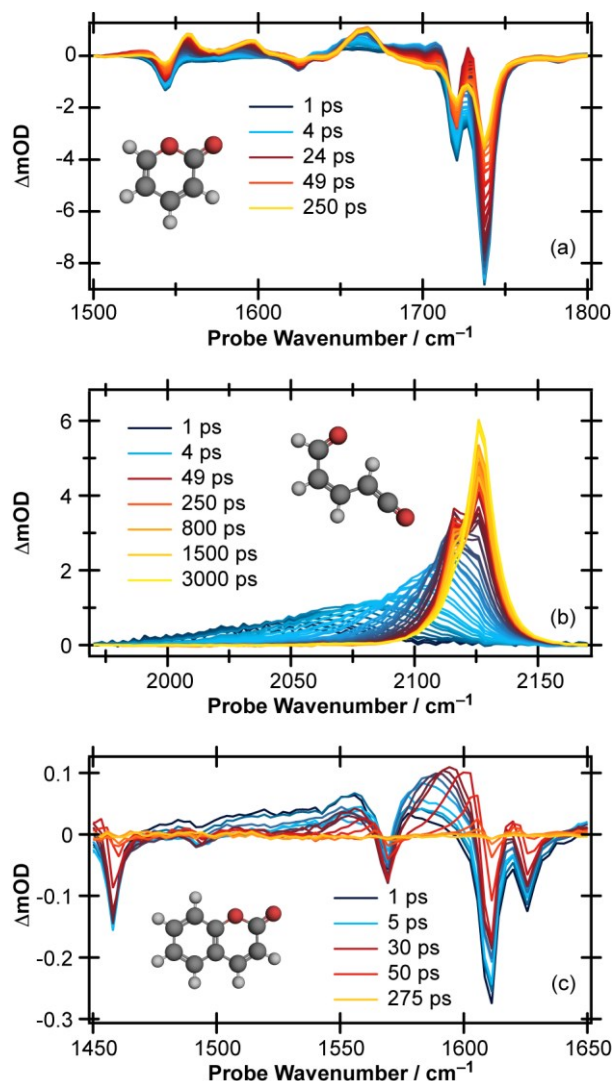

Figure 1: Transient vibrational spectra of (a) and (b) 20 mM α-pyrone/CH$_3$CN, and (c) 5 mM coumarin/CD$_3$CN

The ring-opened nature of the photoproducts is clearly demonstrated in fig. 1(b), in which the probe laser has been moved to cover the 1970-2170 cm^{-1} range. At early pump/probe

time delays we observe a broad (~125 cm^{-1}) transient feature centered around 2060 cm^{-1}, which narrows and blue-shifts on a ps timescale. Such behaviour is characteristic of vibrational cooling. Two peaks are clearly identifiable at late times, centered around 2115 and 2125 cm^{-1} respectively, suggesting that more than one product conformer is formed during the UV-induced ring-opening process. The intensity of the 2115 cm^{-1} feature is seen to decrease at late times, while the 2125 cm^{-1} peak continues to grow, an observation which suggests that a secondary (thermally driven) isomerization reaction is occurring.

The photophysics demonstrated by α-pyrone contrast sharply with those shown by coumarin. Fig 1(c) displays the TVA spectra obtained by probing the 1450-1650 cm^{-1} range for a 5mM solution of coumarin/CD$_3$CN. As in α-pyrone, several bleach features are present, which decrease in intensity as the pump/probe time increases. Unlike α-pyrone, a near-complete bleach recovery is observed, indicating that there is very little photoproduct formation following photoexcitation of coumarin at 266 nm. Complementary *ab-initio* calculations performed in Bristol and at Hokkaido University [6] suggest that the energetically-accessible conical intersections linking the ground and electronically-excited manifolds in both molecules are nearly identical, possessing a ring-opened α-pyrone sub-unit in both cases. The finding that such apparently similar potential energy landscapes can result in such strikingly different product branching ratios in the cases of α-pyrone and coumarin serves to highlight the complex interplay between the various factors controlling UV-induced relaxation pathways in heterocyclic molecules.

Bimolecular Reaction Dynamics

Reactions of CN radicals, F-atoms and Cl-atoms in organic solvents serve as model systems for our studies of the flow of excess energy released by exothermic chemical reactions into the reaction products and the surrounding solvent bath [1,2,7,8]. These reactions are chosen because detailed prior study in the gas phase provides a reference against which we can compare the solution-phase dynamics to identify solvent-induced modifications to reaction mechanisms. The reactive radicals associate with solvent molecules on timescales of a few picoseconds and distinct spectroscopic signatures of the resulting radical-solvent complexes permit their production and loss rates to be monitored by TEA spectroscopy. TVA spectroscopy reports on the formation of reaction products, short-lived vibrational excitation of these products before excess internal energy dissipates to the solvent, and restructuring of the solvent to accommodate the newly formed species. The combination of these two transient spectroscopy techniques builds a comprehensive picture of a chemical reaction in solution on ultrafast timescales.

The level of detail now accessible is illustrated by the exothermic reaction of CN radicals with acetone ($\Delta_r H = -135$ kJ mol^{-1}) to make HCN and 2-oxo-propyl [9]:

$$CN + CH_3C(O)CH_3 \rightarrow HCN + CH_3C(O)CH_2$$
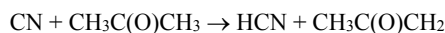
Reaction is initiated in a solution of ICN and acetone in deuterated chloroform by excitation of the ICN with a 50-fs duration pulse of UV radiation of wavelength 266 nm. ICN bonds break in less than 60 fs, releasing CN radicals which have a distinctive sharp absorption band centred at 389 nm that can be observed by TEA spectroscopy. Figure 2 illustrates this spectral band, and its rapid conversion into a broader absorption feature centred to lower wavelength that is attributed to CN solvated by CDCl$_3$. This equilibration of the CN radicals occurs with a time constant of 2 ps. Binding of a CN radical to an acetone molecule is energetically preferred over CN-CDCl$_3$ binding, and ligand exchange therefore occurs over several hundred picoseconds, giving rise to a further absorption band

peaking below 400 nm and evident in Figure 2 at time delays approaching 1750 ps. These TEA measurements characterize the labile CN radicals and their solvent interactions, but the decay of the intensity of the TEA bands shows that the radicals are reacting with the acetone and chloroform.
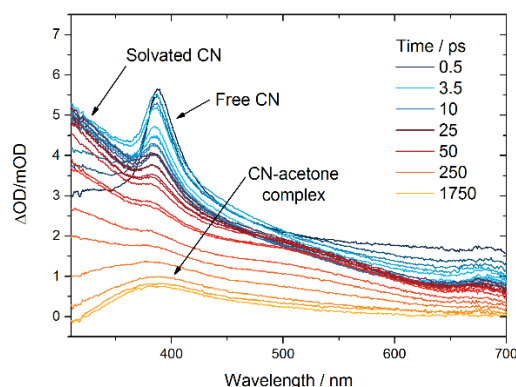

Figure 2: Transient electronic absorption spectra of ICN / 1.0 M acetone / CDCl$_3$ solutions and band assignments.

TVA spectroscopy provides complementary information about the products of the reaction, and Figure 3 shows example spectra obtained in the C=N and the C=O stretching regions. Several species contribute to the TVA spectra, but the focus here is on the product HCN (2097 cm^{-1}) and 2-oxo-propyl (1550 cm^{-1}) bands.
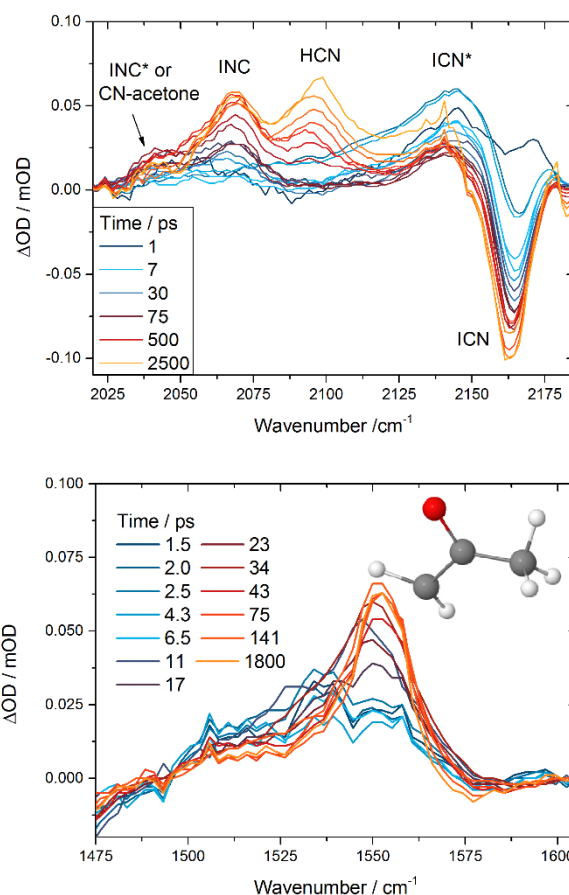

Figure 3: Time-resolved vibrational spectra of ICN / acetone / CDCl$_3$ solutions obtained in the C=N stretching region (upper panel) and C=O region (lower panel).

The HCN band shows a delayed onset followed by growth in intensity. The reciprocal of the time constant for this growth depends linearly on the concentration of acetone in the solution. Analysis of the concentration dependence provides a bimolecular rate coefficient for the reaction of solvent-

complexed CN radicals with acetone of $k = (2.0 \pm 0.9) \times 10^9$ $M^{-1} s^{-1}$. The delayed onset of the growth of the HCN band is a signature of the exothermic reaction favouring vibrational excitation of this reaction product: the vibrational cooling to the ground state that we observe by TVA spectroscopy takes a few tens of picoseconds.

The 2-oxo-propyl band at 1550 cm^{-1} is broad at early time delays but narrows, with intensity shifting to the higher wavenumber side over ~50 ps. This behaviour is indicative of vibrational cooling of internally hot radicals from the chemical reaction. A kinetic analysis shows growth of the vibrationally hot molecules within 2 ps, suggesting that they result from reactions of free CN radicals before they have associated with solvent molecules. The vibrational cooling occurs with a time constant of 34 ps that is controlled by coupling of the motions of the radical to those of the solvent bath. We estimate that ~70% of the energy released by the exothermic reaction of CN radicals with acetone first enters vibrational motions of the HCN and 2-oxo-propyl products before dissipating to the solvent. This dissipation occurs within the first 100 ps after reaction is complete.

The application of TVA and TEA spectroscopy methods allows us to follow in unprecedented detail the ultrafast elementary steps involved in chemical reactions in solution. Many new insights are emerging, as illustrated by the reactions of CN radicals with acetone. Future challenges include extending this work to reactions of ions, and to aqueous environments.

Conclusions

Observation of unimolecular and bimolecular reactions in solution by a combination of time-resolved UV/visible and IR absorption spectroscopies can provide remarkably detailed pictures of the reaction mechanisms. The spectroscopic measurements reveal relaxation of excited states, bond-breaking and bond-forming events, interaction of intermediates and products with the solvent, and dissipation of energy, all of which occur on ultrafast timescales. These insights are leading to a quantitative understanding of how liquid solvents influence the pathways and dynamics of chemical reactions.

Acknowledgements

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