Chemical reaction dynamics in liquid solutions

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Abstract

The dynamics of bimolecular chemical reactions can be examined in liquid solutions using infra-red absorption spectroscopy with picosecond time resolution. On such short timescales, the transient absorption spectra reveal vibrational mode and quantum-state specific energy disposal, followed by vibrational relaxation as the energy is dissipated to the surrounding solvent. Comparison with energy disposal measurements for gas-phase reactions under single-collision conditions offers direct insights into the modification of the energy landscape and the nuclear dynamics in the presence of the solvent. The reactions of CN radicals with organic molecules in chlorinated solvents exemplify the dynamical information that can be obtained. The potential to extend such experiments to a range of reactions and solvents is discussed.

TOC graphic

Key words
Reaction dynamics; condensed phase; liquids; ultrafast infra-red spectroscopy.
Collisional encounters that transform reagent atoms, radicals or molecules to the products of a chemical reaction may be complete in tens or hundreds of femtoseconds, yet careful observation of the outcomes of these encounters can be used to reconstruct a detailed picture of the process of chemical change.\textsuperscript{1,2} Isolated collisions can be observed in experiments that employ molecular beam methods under high vacuum conditions, and, in combination with laser-based probes, electronic, vibrational, rotational and translational energy content of the products can be resolved, as well as preferred directions of scattering and of orientation of rotational or electronic angular momenta.\textsuperscript{2,3} In favourable cases, such as for the reaction $\text{F} + \text{CD}_4 \rightarrow \text{DF} + \text{CD}_3$, methods such as velocity map imaging (VMI) reveal correlations between the vibrational energy content of both products, and indeed whether specific vibrational modes of the products are excited. Moreover, VMI experiments can simultaneously map out the differential cross sections that quantify the angular scattering distributions for products in selected quantum states.\textsuperscript{3,4} The outcomes of such experiments can be interpreted both qualitatively and quantitatively in terms of the kinematics of the reaction, locations and angular dependence of energy barriers on a potential energy surface (PES), the shapes of transition states (TS) and of the PES in the pre- and post-TS regions, crossings between PESs, and the nuclear dynamics on the PES.\textsuperscript{1,2} Here, theoretical and experimental studies of fundamental chemical reaction mechanisms meet, and critical comparisons can be drawn between the outcomes of quasi-classical trajectory (QCT) or quantum mechanical (QM) scattering calculations and experimental data. These comparisons rigorously test the quality of computed PESs and expose subtle dynamical behaviour such as quantum scattering resonances, tunnelling, and non-adiabatic dynamics.\textsuperscript{2}

The value of studying isolated collisions is now well established, yet reaction within a liquid medium is of considerable importance for synthesis, environmental chemistry, and chemical
biology, and the very short (~100 fs) intervals between collisions with solvent molecules might result in chemical reaction dynamics that are far removed from those under the rarefied conditions of gas-phase studies. Not only might the solvent modify the energy landscape of a reaction and exert physical constraints on the motions of the reacting species, but coupling of the motions of the reactants to the solvent bath may leach any excess energy from the reagents, for example through solvent friction, and may therefore damp the motions of the products, leading to rapid thermalization of all degrees of freedom. The solvent can therefore mask many of the signatures of the chemical dynamics, such as vibrational, rotational and translational energy release, that have been so successfully exploited in gas-phase, small cluster and gas-surface scattering studies to learn about fundamental reaction mechanisms. Some of these signatures can persist in bulk liquids on timescales that are accessible to modern laser spectroscopy methods, however, and this Perspective illustrates how the nascent vibrational energy content of the products of chemical reactions in solution, and any vibrational mode specificity of the release of that energy, can be exploited to learn about solvent modifications of reaction pathways.

For exothermic reactions with early barriers, it is well-known that under isolated, gas-phase conditions, the chemical dynamics will tend to channel energy into the vibrational motion of the reaction products. Hochstrasser and co-workers recognized that transient infra-red absorption spectroscopy on the picosecond timescale could be employed to search for similar behaviour in reactions in solution, making use of the anharmonic shifts of vibrational hot bands from the fundamental frequencies to identify vibrationally excited, nascent reaction products. Ultraviolet photolysis of ICN in solution in CDCl$_3$ revealed that ~20% of the DCN products of the reaction of CN radicals with CDCl$_3$ were formed with one quantum of excitation of the C–D stretching mode, but for equivalent experiments in CHCl$_3$, only
vibrationally ground state HCN was observed.\textsuperscript{7,11} These reactions are known to produce highly vibrationally excited products under isolated collision conditions,\textsuperscript{12,13,14,15,16} and the conclusion was drawn that the solvent modifies the reaction energy landscape to suppress vibrational energy release. In more recent investigations, Crim and co-workers observed both the rates of removal of CN radicals and production of HCN in reactions with various organic species in a range of chlorinated solvents, using, respectively, transient visible and IR absorption spectroscopy.\textsuperscript{17,18} One intriguing outcome of this work was that the CN radicals were removed more quickly than the apparent rate of formation of HCN, although importantly (for reasons discussed below) the IR probe monitored vibrationally ground state HCN products. With supporting evidence from electronic structure calculations, Crim and co-workers proposed an intermediate role for complexes of the CN radicals with the chlorinated solvents that decoupled the loss of the CN absorption feature from the growth of the HCN IR absorption band.

Both Hochstrasser\textsuperscript{10} and Crim\textsuperscript{19,20} also carried out studies of reactions of Cl atoms with various organic molecules in liquid solutions. These reactions to produce HCl are considerably less exothermic than the equivalent H (and D) atom abstraction reactions of CN radicals and, with a few exceptions, are known not to favour production of vibrationally excited HCl under gas-phase conditions.\textsuperscript{21} No vibrational excitation of HCl was reported for the solution-phase reactions. The first observation of a modest fraction of vibrationally excited DCN from the CN + CDCl\textsubscript{3} reaction remained a tantalizing result,\textsuperscript{11} however, and encouraged us to consider further investigation of reaction dynamics in solution.\textsuperscript{22} We exploited recent developments in IR laser and detector technology that permit use of broadband IR pulses in conjunction with IR-sensitive array detectors to capture spectra over \textasciitilde500 cm\textsuperscript{-1} bandwidth with picosecond time resolution.\textsuperscript{23} The reactions of CN radicals with
organic molecules to form HCN and DCN were attractive choices for these experiments for several reasons: (i) they are exothermic by ~120 kJ mol$^{-1}$ and therefore release sufficient energy to be able to produce products with substantial vibrational excitation; (ii) the vibrational motions, well described in a normal mode picture for HCN as the C≡N stretch ($\nu_1$), the bend ($\nu_2$) and the C–H stretch ($\nu_3$), are all IR-active,$^{24,25}$ so that mode-specific energy release might be observed; and (iii) as noted above, selected reactions have been extensively investigated under gas-phase conditions, so comparisons with condensed phase data should provide insights into the modification of the energy landscape and nuclear dynamics by the solvent.

Much of the remainder of this article presents an overview of the outcomes of a series of investigations of CN radical reactions with cyclohexane, tetramethylsilane (TMS) and tetrahydrofuran (THF), using the chlorinated solvents chloroform (CHCl$_3$ and CDCl$_3$), and dichloromethane (DCM, CH$_2$Cl$_2$ and CD$_2$Cl$_2$). A number of factors dictate the choices of organic co-reagent and solvent, ranging from the purely practical considerations of miscibility of samples, solubility of ICN, and the need to avoid overlap of strong solvent bands in the IR with the vibrational bands of HCN and DCN, to the systematic investigation of dynamics of abstraction of primary and secondary H atoms (for TMS and cyclohexane respectively). A by-product of these experiments is that data are also obtained for the dynamics of the reactions of the CN radicals with the chlorinated solvents, the formation of complexes of CN radicals with the solvent, and geminate recombination of I atoms and CN radicals to form the isomer INC of the originally photolysed ICN.$^{22}$
Figure 1 shows transient IR spectra of HCN formed following UV photolysis of ICN (0.14 M) in a 1.0 M solution of cyclohexane in DCM, with assignment of spectral features. The major part of the observed signals derives from the reaction of CN radicals with cyclohexane, with a <30 % contribution from CN reactions with the solvent (which can be subtracted in data analysis). The spectra were obtained in the C–H stretching region, and the band at 3263 cm$^{-1}$ is assigned to the fundamental absorption of this vibrational mode, denoted as $3_0^1$ (i.e., $v_3 = 0 \rightarrow v_3 = 1$, with $v_3$ specifying the number of quanta of the C–H stretching mode) on the basis of FTIR spectra of static samples of HCN in solution in DCM. In what follows, the notation HCN($v_1v_2v_3$) indicates HCN products with specific numbers of quanta of excitation of the three vibrational modes. Several points are evident from such spectra. Firstly, HCN is observed to form not only in its vibrational ground state, HCN(000), but also with up to 2 quanta of excitation in the bending mode and one quantum of excitation in the C-H stretching modes, HCN(0n1) (with $n \leq 2$). Secondly, the vibrationally excited products are formed at earlier times than the HCN(000), and the growth of the latter products at longer times suggests a substantial fraction forms by vibrational relaxation, instead of directly by the chemical reaction. Measurements in the C≡N stretching region confirm this general picture, with comparably slow growth of signal on the $1_0^1$ band (at 2094 cm$^{-1}$), but spectral congestion in this region and overlapping absorptions from features assigned to INC (at 2065 cm$^{-1}$) and CN–solvent complexes (at 2037 cm$^{-1}$) prevent as definitive an analysis of bands arising from vibrationally excited HCN.22

The analysis of time-dependent band intensities can be made quantitative using a kinetic model that incorporates rate coefficients for formation of nascent HCN in specific vibrational levels, and collisional relaxation, which is taken to occur in steps of a single vibrational
quantum. Integration of the rate equations gives time dependent populations of the vibrational levels, and spectral band intensities then depend on the difference in population of levels connected by an IR transition.\textsuperscript{22} This method provides an excellent description of the experimental observations, as exemplified in figure 2 by the fit to a representative data set for the CN + TMS reaction in CDCl\textsubscript{3}. The values of the resultant rate coefficients for the reactive processes are indicative of the nascent HCN(\textit{v}_1\textit{v}_2\textit{v}_3) populations. The fits neglect intramolecular vibrational redistribution (IVR), and can be refined to separate the vibrational relaxation of HCN at early times, within the initial solvent cage and in close proximity to the radical co-product, from HCN relaxation after diffusion into the bulk solvent.

The broad conclusion from analysis of data for CN reactions with cyclohexane, TMS, CH\textsubscript{2}Cl\textsubscript{2} and CHCl\textsubscript{3} in various chlorinated solvents is that most of the HCN is formed vibrationally excited, with activity in the bending and C–H stretching modes. The direct branching of the reaction to HCN(000) is small, and the majority of this product forms through vibrational relaxation of internally excited nascent reaction products. This conclusion provides an alternative explanation for the differences in rates of loss of CN and production of HCN reported by Crim and co-workers:\textsuperscript{17,18} because their observations in the IR were of HCN(000) formation, the measurements were of the rates of vibrational relaxation of nascent HCN molecules, instead of the rates of production of HCN through the bimolecular reaction. Indeed, their reported time profiles for build-up of HCN are in excellent accord with our quantum-state specific measurements of HCN(000). Very similar conclusions can be drawn for DCN, although the extent and character of the vibrational excitation of the nascent products differs from HCN.
The extent of vibrational excitation of the HCN / DCN is remarkable for a reaction carried out in a liquid environment, and demonstrates that, despite the fast timescale for collisions with solvent molecules, the solvent friction is not sufficient to damp the nuclear dynamics associated with an early reaction barrier that result in C–H (or C–D) stretching excitation. QCT calculations of isolated CN + RH reactions indicate that the source of bending excitation of the products is a flat angular dependence to the PES in the vicinity of the transition state, so the dynamics can take the reaction through configurations with N≡C—H angles that deviate considerably from the 180° lowest energy geometry. The same behaviour clearly persists in solution, at least for the chlorinated solvents studied, and the evidence from experiment and theory is that the properties of the TS are not significantly altered by the solvent. It would therefore appear that the understanding of this class of reactions, derived from gas-phase experiments and scattering calculations for isolated molecules, can be usefully applied to the reaction dynamics in the liquid phase. More sophisticated calculations of the reaction dynamics that incorporate interactions with the solvent support this view. The potential of mean force is barely changed by the presence of solvent in the critical region around the TS, and trajectories sample very similar reaction pathways to those for the gas phase, as illustrated in figure 3.

A detailed comparison between the outcomes of condensed phase dynamics measurements described above and of earlier studies of CN radical reaction dynamics with hydrocarbons in the gas phase is desirable if solvent effects on the energy landscape and nuclear dynamics are to be quantified, and the computational predictions confirmed. Classical dynamics simulations for CN + C₆H₁₂ in DCM allow us to model the reaction and analyse the mechanism with very high time resolution, and suggest that at short times, reactions in both the gas phase and solution in DCM are more or less identical. Gas-phase experiments have
not been reported for the particular reactions of CN with cyclohexane or TMS, or for deuterated reactions, however, and some uncertainties remain about the vibrational level populations of HCN from the reactions that have been investigated so far.\textsuperscript{12-16} It is apparent, however, that under isolated collision conditions, the HCN shows similar mode specificity to that observed in solution, but with a greater degree of vibrational excitation, with population of up to 6 quanta of the bend and 2 quanta of the C–H stretch. Some degree of solvent friction is therefore implied by our experiments, resulting in partial – but, importantly, incomplete – damping of the nuclear dynamics that leads to vibrational mode excitation of the HCN in solution. Further work on the gas-phase dynamics is encouraged to enable more complete comparisons, however. The combination of high quality gas-phase data with the types of condensed phase measurements that our transient IR experiments demonstrate to be possible offers a new probe of the molecular level influence of solvent in reactions in bulk liquids.

Of course, not all solvents are alike, and the results described in the preceding paragraphs are specific to chlorinated organic solvents. Some consistency of outcomes for these solvents encourages the expectation that systematic trends might be identified, however, once a sufficient body of data is accumulated. As a first step towards exploring solvent-dependence of the reaction dynamics, we carried out similar measurements for solutions of ICN in THF and d\textsubscript{8}-THF, thereby studying the abstraction of H or D atoms from THF, which also constitutes the solvent environment. THF was selected as a representative polar, but non-chlorinated solvent. For HCN, these experiments were hindered by solvent absorption bands that overlapped the C–H stretching region, but HCN formation could be more cleanly observed in the C≡N stretching region, and DCN bands in both the C–D and C≡N stretching regions were also free from significant solvent interference. INC bands were observed, as for
chlorinated solvents, but the CN band attributed to complexes with the solvent was absent in THF. First inspection of time-resolved HCN spectra identifies a marked difference from the chlorinated solvents: bands associated with HCN(000) rise much more rapidly, and production of HCN(000) is essentially complete within 30 ps. Closer examination of the data, however, reveals an induction period before the growth of the HCN(000) signal, and kinetic analysis suggests initial formation of another product that might be vibrationally excited HCN, or HCN complexed to the radical co-product, with subsequent relaxation to ground-state HCN. This interpretation is strongly supported by classical dynamics calculations in THF, as well as DCN data, which, in the C–D stretching region, show a clear shift of the product absorption feature to higher wavenumber with time, and fits isolate a transient feature that grows in 10 ps and decays within 50 ps, a timescale commensurate with the 50 ps growth of the DCN(000) absorption band. The THF solvent therefore appears to play a more active role in affecting the dynamics of the CN radical reactions, and work is in progress to analyse data for THF / CDCl$_3$ and THF / CD$_2$Cl$_2$ solutions of differing mixing ratios to clarify this role.

Many further such experiments can be envisaged; a variety of solvent types is available for investigation, and studies are not restricted to CN radical reactions. Both Hochstrasser$^{10}$ and Crim$^{19,20}$ explored Cl atom reactions with organic molecules in solution, and we have taken this work further. Crim and co-workers carried out an extensive survey of the kinetics of Cl reactions with various classes of organic co-solute in DCM, and a large body of work has been carried out on the kinetics and dynamics of such reactions in the gas phase.$^{21,26}$ The H-atom abstraction reactions to form HCl are not as exothermic as the equivalent CN radical reactions,$^{21}$ and the propensity for formation of vibrationally excited products is lower. Certain reactions, most notably those to form resonance stabilized radicals, have been shown
to form HCl(v=1) in significant fractions under gas-phase conditions, and we are currently analysing new experimental data for evidence of such behaviour in solution. F atom reactions with hydrocarbons are an attractive target for future condensed phase experiments too, because of the complementary reactive scattering experiments carried out in molecular beam experiments, the propensity to form vibrationally excited products, and associated QM and QCT calculations that reveal a wealth of dynamical behaviour. Planned experiments on the condensed phase reactions must overcome a couple of challenges. The first is to find a clean and efficient photolytic F atom source using a molecule that is sufficiently chemically inert to resist reaction with the solvent and other solutes of choice. The second is that HF and DF bands in solution are significantly shifted to lower wavenumber and remain substantially broader than the HCN bands shown in figure 1. Spectral intensity is thus distributed over a larger number of detector pixels, presenting difficulties of discrimination against background features, and above baseline noise levels.

This perspective has sought to convey that the study of reaction dynamics, a mature and insightful field for gas-phase and gas-surface collisions and for reactions in clusters, has excellent prospects for successful extension to reactions in bulk liquid solutions. There is much excellent published work on liquid phase dynamics, photochemistry, energy transfer and IVR that has not been reviewed here – the scope is deliberately confined to bimolecular reactions for which the literature for gas-phase dynamics is much richer and more extensive than for the liquid phase. What is evident from our experimental and computational investigations so far is that there is considerable potential to undertake studies of reactions in solution on ultrafast timescales with quantum-state resolution of the energy disposal in the products. Ideas of competition between vibrational and translation energy release, captured in the Polanyi rules for bimolecular collisions, can be explored in solution, and the effects
of solvent friction on the dynamics can be examined. In short, dynamical studies can be carried out that are competitive with gas-phase experiments in terms of their information content. A growing body of work on photodissociation in solution, and the disposal of excess energy to rotational and vibrational degrees of freedom, is providing complementary information for unimolecular dynamics involving both ground and excited electronic states.\textsuperscript{28,29,30} The outcomes of some of these recent photodissociation experiments in solution\textsuperscript{29} and those discussed here for bimolecular reactions, question the interpretation of short-time dynamics in solution using approaches based on linear response theory, and call for computational and simulation methods that incorporate the time-dependent dynamics explicitly, providing fertile ground for the interaction between experiment and theory.

**Biographies**

**Andrew Orr-Ewing** is Professor of Physical Chemistry at the University of Bristol, and has long-standing research interests in chemical reaction dynamics in the gas phase. More recently, this research program has extended to experimental and computational studies of condensed phase reaction mechanisms.

**David Glowacki** is a post-doctoral research associate in the Centre for Computational Chemistry at the University of Bristol, with research interests in reaction kinetics, dynamics, non-equilibrium statistical mechanics and energy transfer. He has recently begun to examine these issues in condensed phase chemistry.

**Rebecca Rose** is a post-doctoral research associate in the Laser Chemistry, Spectroscopy and Dynamics Group at the University of Bristol. She was awarded her doctorate for velocity
map imaging studies of gas-phase reaction dynamics, and is now extending this experience to condensed phase chemical reactions.

Stuart Greaves is a Leverhulme Trust Early Career Fellow at the University of Bristol. His research examines reaction dynamics in the gas phase, at gas-liquid interfaces and in liquid solutions using both experimental and computational methods.

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Figure Captions

**Figure 1:** Time-evolution of the absorption spectrum of HCN products of reaction of CN radicals with cyclohexane (1.0 M) in solution in dichloromethane. The absorption feature labelled A, centered at 3160 cm\(^{-1}\), is attributed to HCN vibrationally excited with one quantum of C–H stretch and up to two quanta of the bending mode. The band labelled C is absorption by HCN from its vibrational ground state, and this fundamental band is centered at 3263 cm\(^{-1}\). The label B indicates absorption bands for bend-excited HCN molecules, which are anharmonically shifted to lower wavenumber than the fundamental band and which are observed most clearly at early times.

**Figure 2:** Time-dependence of integrated intensities of spectral bands assigned to HCN(0\(n\)1) (green), HCN(001) (blue), HCN(0\(n\)0) (red) and HCN(000) (black) (with \(n = 1, 2\)) from the reaction of CN radicals with TMS (1.0 M) in solution in CDCl\(_3\). Circles are experimental data, and the solid lines are the results of fits to the kinetic model summarized in the right-hand box. This model incorporates four reactions to form HCN in the specified vibrational levels and four relaxation processes in which either bending or C–H stretching vibration is quenched by the solvent.

**Figure 3:** Visualizations of the CN + C\(_6\)H\(_{12}\) atomic motions extracted from numerous calculated trajectories at the point where they pass over their gas-phase (left) and liquid DCM solution phase (right) variational abstraction transition states. Grey, red and black lines trace the motions of, respectively, nitrogen, carbon and hydrogen atoms. The two plots demonstrate the similarity of dynamics of reaction at short times in the gaseous and liquid environments. The experimentally measured bend excitation of the HCN can be understood from the large range of H-C≡N angles observed in both sets of trajectories.
References


Figure 1
Figure 2

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Integrated intensity vs Time / ps