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Chemical reactions take place over an amazingly rapid time-scale, measured in millionths of a billionth of a second (a femtosecond). On time-scales of this duration, atoms and molecules come together, exchange energy and transfer atoms in the very act of transforming one substance into another. The emergence during the last ten years of laser devices that emit bursts of light just a few femtoseconds long can, however, enable scientists to record a series of 'snapshots' in real time of the entire temporal development of chemical reactions, and to understand their dynamical evolution during the critical moments when bonds are broken and made. This article reviews the application of femtosecond lasers to the study of the dynamics of chemical reactions, and attempts to show how a close synergy between calculations and experiment enables the forces that control the conversion of reactants into products to be understood in terms of fundamental quantum theory. This is illustrated through consideration of a hierarchy of problems, starting with photochemistry in gases, catalytic processes at metal surfaces, and ending with processes in the condensed phase. A speculative conclusion forecasts developments in new laser techniques, highlighting how the exploitation of ever shorter laser pulses would permit the study and possible manipulation of the nuclear and electronic effects that lie at the conceptual heart of chemistry.

Keywords: femtosecond lasers; ultrafast spectroscopy; wave-packet dynamics

1. Experiment and theory of reaction transition states

In 1 s light travels about three-quarters of the distance between the Moon and the Earth. By comparison, in 1 fs (10^{-15} s) light manages to get about halfway across the diameter of a human hair. The femtosecond time-scale represents the fundamental temporal limit for reactive processes in chemistry, since it is over this time-scale that atoms and molecules collide and exchange energy and matter during the course of converting reagents into products. For an elementary reaction of the type

$$\mathrm{A} + \mathrm{BC} \rightarrow [\mathrm{A}\cdots\mathrm{B}\cdots\mathrm{C}]^{\ddagger} \rightarrow \mathrm{AB} + \mathrm{C},$$

where A, B and C denote different atoms, the entire trip along the reaction path from reactants A + BC to products AB + C covers a distance of *ca.* 10 Å (1 Å (angstrom) = 10^{-10} m), and takes between 1 and 10 ps (1 ps = 10^{-12} s) to complete, while the time-scale for the vibrations of molecules is between some 10 and 100 times shorter. $[\mathrm{A}\cdots\mathrm{B}\cdots\mathrm{C}]^{\ddagger}$ represents the transition states of the reaction, which are the critical, short-lived configurations intermediate between starting reactants and final products (Zewail 1996; Polanyi & Zewail 1995) where molecular bonds are broken and formed.

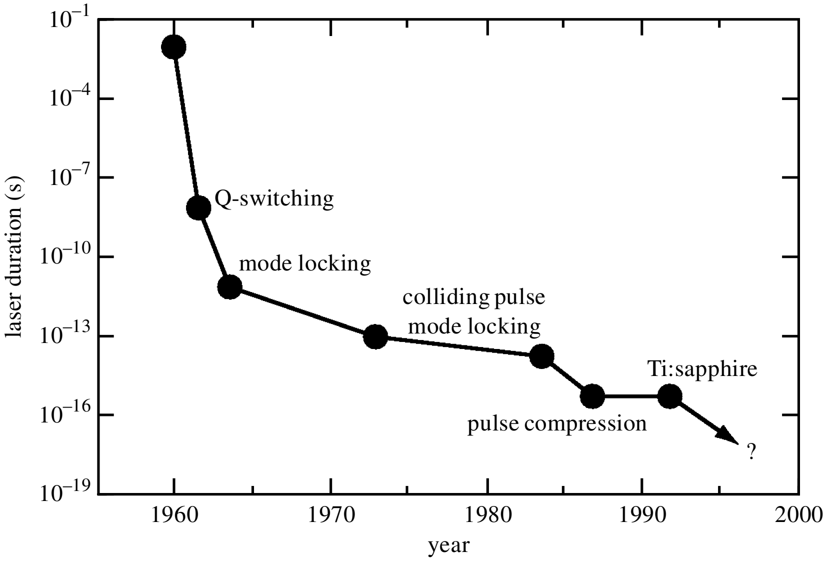

Figure 1. A graph of laser pulse width against year, showing the advance towards ever shorter pulse durations since the invention of the laser in 1960. Note the sudden discontinuities in the graph, as the introduction of new technology (Q-switching, mode-locking) decisively shortens the minimum achievable pulse width.

To carry out a spectroscopy, that is the structural and dynamical determination, of reactive events in transition states as they happen necessitates the application of laser pulses with durations of tens, or at most hundreds, of femtoseconds to resolve in time the motions of transition states. Spectroscopy on the femtosecond time-scale enables a chemical reaction to be viewed in real time at all stages along its trajectory, and is supremely well-suited to probing the ultrafast dynamics of a reaction in the gas phase, at solid surfaces, and in well-characterized solvent environments that mimic the condensed phase.

This paper aims to illustrate the kinds of research problems in ultrafast reaction dynamics that are the subject of current attention, and is organized as follows. The remainder of this section describes the operational approach to studies of chemical reactions using femtosecond lasers, with emphasis on those characteristics that are important in considerations of the interaction of ultrafast laser light with molecules. Recent examples of its application are discussed in § 2, along with attempts to illustrate the close interplay between theory and experiment that is invariably required to extract maximum dynamical information about reactions. A brief, speculative prognosis of future developments is offered in § 3.

(*a*) *Femtosecond lasers*

Figure 1 shows how, since its invention, the pulse width or duration of laser radiation has decreased from *ca.* 10 ms (10×10^{-3} s) in 1960 to 4.5 fs by 1997. Sub-100 fs laser pulses were realized for the first time from a colliding-pulse mode-locked (CPM) dye laser in the early 1980s at AT&T Bell Laboratories by Shank and co-workers (Fork *et al.* 1981); by 1987, these researchers had succeeded in producing record-breaking pulses as short as 6 fs through the application of optical pulse compression techniques to the output from a CPM dye laser (Fork *et al*. 1987). In the decade since 1987, there has only been a slight improvement in the minimum possible pulse width—the world record is currently held by Wiersma's group at the University of Gröningen in The Netherlands (Baltuska *et al*. 1997)—but there have been major developments in the ease of generating and characterizing ultrashort laser pulses, leading to frenetic research activity in the study of ultrafast processes.

The major technical driving force behind this progress was the discovery by Sibbett and co-workers (Spence *et al*. 1991) of the self mode-locking mechanism in transition-metal-doped solid-state laser materials, the first of which was sapphire impregnated with titanium. Self mode-locking is induced through the intensity-dependent non-linear refractive index of the laser medium, and results in the propagation of pulses with high peak powers and ultrashort durations in a single, 'locked' mode, or standing wave pattern. Operating with high average powers (*ca.* 500–1000 mW), at high repetition rates with pulse durations usually between 10 and 100 fs and continuously tunable in wavelength from 670 to 1070 nm, the self mode-locked Ti:sapphire laser is the most versatile of the new generation of solid-state ultrafast lasers (others are the chromium-doped colquiriite minerals). The energy source to drive a Ti:sapphire laser is provided by either a diode laser or an argon-ion laser, both of which lase at the green wavelengths where the Ti^{3+} ion is strongly absorbing. Figure 2*a* shows a photograph of a Ti:sapphire laser. As it is not the purpose of this article to describe the physics that underpins the operation of Ti:sapphire lasers, the interested reader is referred elsewhere for further information (Sibbett *et al*. 1998; Kapteyn & Murnane 1999). Instead, in the next few paragraphs, we highlight aspects of their operation, other than that they deliver ultrashort pulses of light, which are of particular importance for studies in photochemistry.

A fundamental consequence of the short duration of femtosecond laser pulses is that they are not truly monochromatic. This is usually considered one of the identifying characteristics of laser radiation, but it is only true for laser radiation with pulse durations of 1 ns (10^{-9} s) or longer. Because the duration of a femtosecond pulse is so precisely known, the time–energy uncertainty principle of quantum mechanics imposes an inherent imprecision in its frequency, or colour. Femtosecond pulses must also be coherent, that is the peaks of the waves at different frequencies must come into periodic alignment to construct the overall pulse shape and intensity. The result is that femtosecond laser pulses are built from a range of frequencies: the shorter the pulse, the greater the number of frequencies that it supports, and vice versa. On interacting with an ultrashort laser pulse, a molecule is excited not to a single energy level, but is, compared with the time-scale of its vibrational motions, simultaneously and instantaneously excited to a cluster of energy levels by the broadband laser emission. This coherent preparation of a superposition of molecular energy levels provides the trigger that brings about an ultrafast, impulsive motion of the molecule, leading to reaction.

A typical Ti:sapphire oscillator can achieve a peak power of some 0.8 W, but this is not high enough to obtain adequate signal-to-noise ratio in experiments where the number of molecules that absorb light is low. To overcome this limitation, the peak power of a femtosecond laser can be dramatically increased by the process of chirped-pulse amplification (Perry & Mourou 1994), which is an optical copy of a radar technique developed to enhance the detection of aircraft. In this approach, the weakly intense pulses available from a femtosecond laser are first stretched in

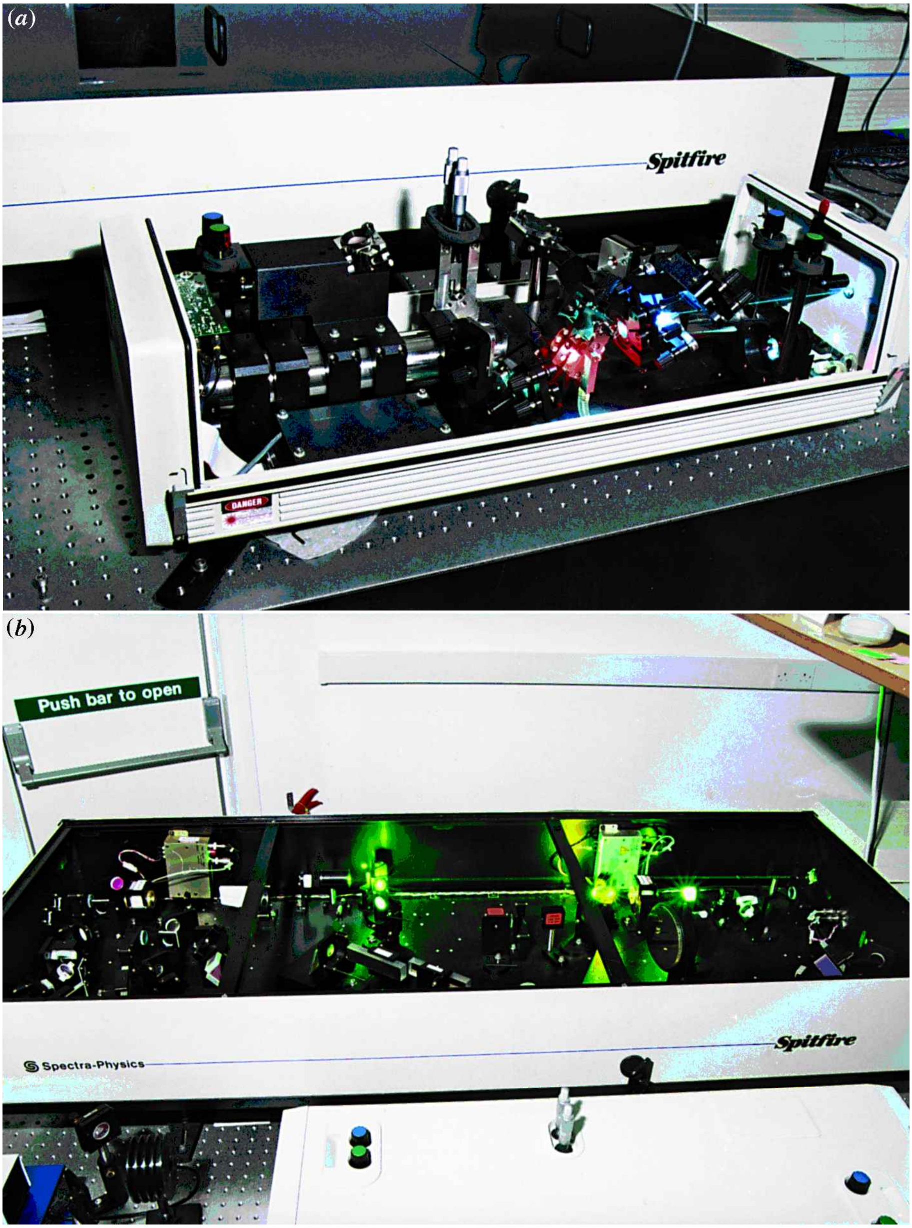

Figure 2. Photograph (*a*) shows a *Tsunami* Ti:sapphire laser manufactured by Spectra-Physics Lasers Inc. To increase the output power from such a device, the pulses must be amplified by a million times. Photograph (*b*) shows a chirped pulse amplifier manufactured by Positive Light Inc.

time to between 10 and 100 ps, then amplified by about a million times in one or more further Ti:sapphire laser crystals, and finally recompressed to femtosecond durations; the purpose of the temporal stretching and compressing manoeuvre is to avoid damage to optical components that would otherwise be rendered by very intense ultrashort pulses. Figure 2*b* shows a view of a chirped-pulse amplifier for the generation of sub-100 fs laser pulses with peak intensities of *ca.* $1.5 \times 10^{12}\ \mathrm{W\,cm^{-2}}$.

The second requirement for real-time investigations of chemical reaction dynamics is one of wide wavelength coverage. The capacity for wavelength tuning is an essential ingredient for photochemical studies due to the different energy gaps that separate the quantum levels of molecules: vibrational resonances are excited with infrared light for example, while electronic states that correspond to different arrangements of the molecular electrons are reached by light in the visible and ultraviolet spectrum. The high output power of chirped-pulse amplified femtosecond lasers render them ideal for synchronous pumping of a device called an optical parametric amplifier (OPA). By analogy with an industrial chemical manufacturing plant, an OPA can be thought of as a photon cracker in which a single, high-intensity photon (from a Ti:sapphire laser) is split by a nonlinear optical interaction in a birefringent crystal, such as β-barium borate, into two daughter components (called the 'signal' and 'idler' photons) of lower intensity and frequencies in the near infrared. When coupled with other nonlinear frequency conversion schemes such as harmonic generation and difference-frequency mixing, an OPA offers continuous tunability across the wide spectral range from 200 nm ($1\ \mathrm{nm} = 10^{-9}\ \mathrm{m}$) in the ultraviolet to 10 μm ($1\ \mu\mathrm{m} = 10^{-6}\ \mathrm{m}$) and beyond in the infrared.

An important point is that these advances have been complemented by the concomitant development of innovative pulse-characterization techniques (Trebino & Kane 1993), such that all the features of femtosecond optical pulses—their energy, shape, duration and phase—can be subject to quantitative *in situ* scrutiny in the course of experiments. Taken together, these advances mean that femtosecond lasers can be applied to study a whole range of ultrafast processes, from the various stages of high-energy plasma formation through chemical reaction dynamics to the critical, individual events of photosynthesis.

(*b*) *Femtosecond pump–probe spectroscopy*

The dynamics of chemical reactions are revealed most intimately using what are known as pump–probe techniques. For reactions in the gas phase, this approach was pioneered by the group of Zewail and co-workers at the California Institute of Technology (Zewail 1996; Zhong & Zewail 1998), and is most conveniently illustrated through an application: the dissociation of IBr is chosen here, which may be represented by the simple equation

$$\mathrm{IBr}^* \rightarrow [\mathrm{I}\cdots\mathrm{Br}]^{\ddagger} \rightarrow \mathrm{I}+\mathrm{Br},\ \ \mathrm{I}+\mathrm{Br}^*.$$

Figure 3 shows that the dissociative process is governed by two interacting potential energy curves, which enable the molecule to separate along a reaction coordinate that yields ground-state atoms ($\mathrm{I}+\mathrm{Br}$) or along one that leads to excited bromine ($\mathrm{I}+\mathrm{Br}^*$). The same figure also illustrates how femtosecond laser pulses configured in a pump–probe sequence can be applied to monitor the time evolution of the $[\mathrm{I}\cdots\mathrm{Br}]^{\ddagger}$ transition states (Vrakking *et al.* 1996). The IBr molecule in the gas phase initially resides in its electronic ground state. This state can be characterized by a potential energy curve, labelled V_0 in figure 3, which is a quantitative representation of the force field that acts on the molecule at equilibrium. (In general, we should talk of a potential energy hypersurface, containing as many dimensions as there are degrees

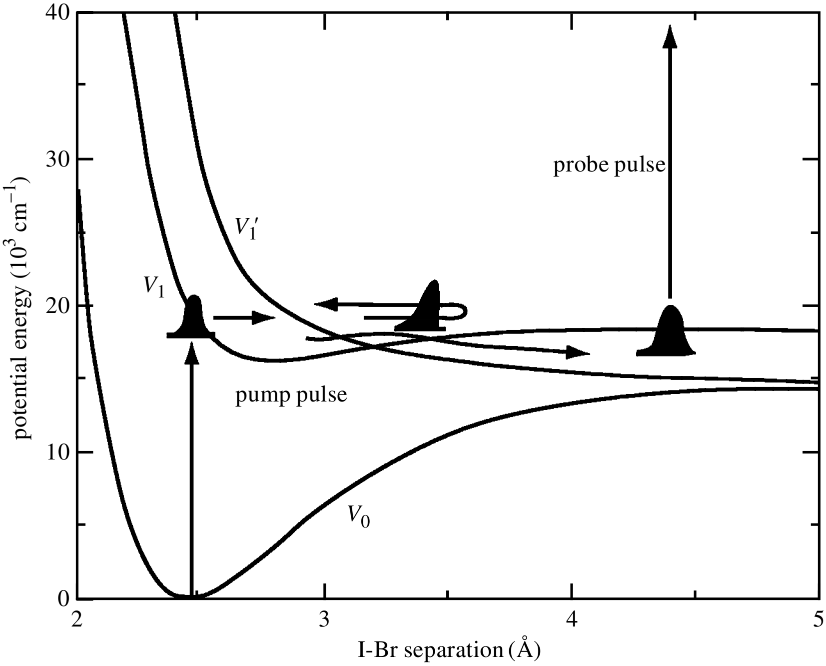

Figure 3. The concept of femtosecond spectroscopy of chemical reactions can be described in terms of optical transitions excited by ultrafast laser pulses between the potential energy curves that represent different energy states of a molecule, here shown for IBr. An initial pump laser excites a vertical transition from the potential curve of the lowest (ground) electronic state V_0 of the molecule to an excited state. The break-up of IBr to form I + Br is described by quantum theory by a wave packet that either oscillates between the extremes of V_1, or crosses over onto the steeply repulsive potential V_1' leading to dissociation. These motions are monitored in the time domain by simultaneous absorption of two photons from a probe laser pulse, which ionizes the dissociating molecule.

of freedom available to the molecule, but, for ease of representation, the number of dimensions is here restricted to the interatomic separation, and so the hypersurface reduces to a curve of potential energy versus I–Br distance.) An initial, ultrafast (less than or equal to 90 fs) 'pump' pulse promotes IBr to the potential energy curve V_1 of a higher energy state, where the electrostatic nuclear and electronic forces within the excited IBr* molecule initially act to force the I and Br atoms apart. V_1 contains a minimum, however, so the nascent $[\mathrm{I}\cdots\mathrm{Br}]^{\ddagger}$ transition states formed as the atoms begin to separate remain trapped in the excited state unless they can cross over onto the repulsive potential V_1', which intersects the bound curve at an extended I–Br bond length. Quantum theory does in fact allow such a curve crossing to occur, with a probability that depends on, amongst other things, the velocity of the escaping atoms, the exact shape of the intersecting potentials at their crossing point, and the spacing of vibrational quantum levels available to the excited molecule in its quasi-bound state.

From a theoretical perspective (Hussain & Roberts 1999), the object that is initially created in the excited state is a coherent superposition of all the wave functions that are encompassed by the broad frequency spread of the pump laser pulse. This superposition state, or wave packet, spreads and executes either periodic vibrational motion as it oscillates between the inner and outer turning points of the bound potential, or dissociates to form separated atoms, as indicated by the trajectories shown in figure 3. The time evolution of the wave packet over the intersecting potentials V_1 and V_1' is monitored by its interaction with a second ultrashort 'probe' pulse, which ionizes the molecule by simultaneous absorption of two photons, leading to removal of an electron from the highest-lying level of the molecule; the ionized IBr^{*+} is then detected in a mass spectrometer (Vrakking *et al*. 1996).

The key experimental requirement in this and all other pump–probe measurements is the ability to deliver two very short optical pulses to the sample separately spaced by a controllable and accurately known difference in time. This is achieved in the laboratory by routing one of the pulses via an interferometric translation stage, which can vary the path length between pump and probe pulses prior to the sample with a precision of a fraction of 1 µm (a distance of 1 µm is equivalent to *ca.* 3.33 fs in time). The experiment consists of measuring the number of ionized IBr^{*+} molecules excited by pump and probe pulses as a function of the delay time between the two (see figure 4), since this is directly proportional to the probability of locating the extended $[\mathrm{I}\cdots\mathrm{Br}]^{\ddagger}$ transition states over different coordinates of the potential energy curves V_1 and V_1'; the probe pulse can be thought of as projecting onto the potentials a detection 'window', the width of which is determined by the spectral breadth, and hence duration, of the pulse, through which the dynamics of the dissociating molecule can be observed (Bersohn & Zewail 1988).

Figure 4*a*, *b* shows examples of the ionization signals that are recorded as a function of pump–probe time delay: the decrease in signal intensity with increasing pump–probe time delay monitors the loss of initial IBr* to form separated I and Br over the potential V_1'; and the oscillations superimposed upon the decay reflect the quantized nature of vibrational motion of the quasi-bound $[\mathrm{I}\cdots\mathrm{Br}]^{\ddagger}$ transition states within the bound V_1 curve. A series of experiments in which the pump wavelength is varied reveals that at some energies the oscillations predominate for times beyond 10 ps, while at other energies the decay of population by curve crossing wins out within 400 fs or so.

These results can be accounted for quantitatively by theoretical quantum dynamics simulations of the motion of the wave packet $|\Psi(\mathrm{t})\rangle$ over the repulsive potential. These are carried out by numerical integration of the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial|\Psi(\mathrm{t})\rangle}{\partial t} = H|\Psi(\mathrm{t})\rangle,$$

which governs the deterministic time-evolution of $|\Psi(\mathrm{t})\rangle$ over the repulsive potential. H is the Hamiltonian operator, which conveys all the kinetic and potential energy information in mathematical form necessary to propagate $|\Psi(\mathrm{t})\rangle$ according to the laws of quantum theory. Also included in the Hamiltonian operator is a mathematical description of how the pump and probe laser photons interact with a molecule in its different electronic states. This allows, for example, the IBr ionization intensity to be computed from the temporal behaviour of $|\Psi(\mathrm{t})\rangle$ (Hussain & Roberts 1999). Figure 4*c* displays a calculated pump–probe ionization trace that corresponds to the same initial conditions of figure 4*a*. A mathematical analysis of these data using the technique of Fourier transformation reveals the vibrational frequencies of IBr* that survive for picosecond durations, or not: information such as

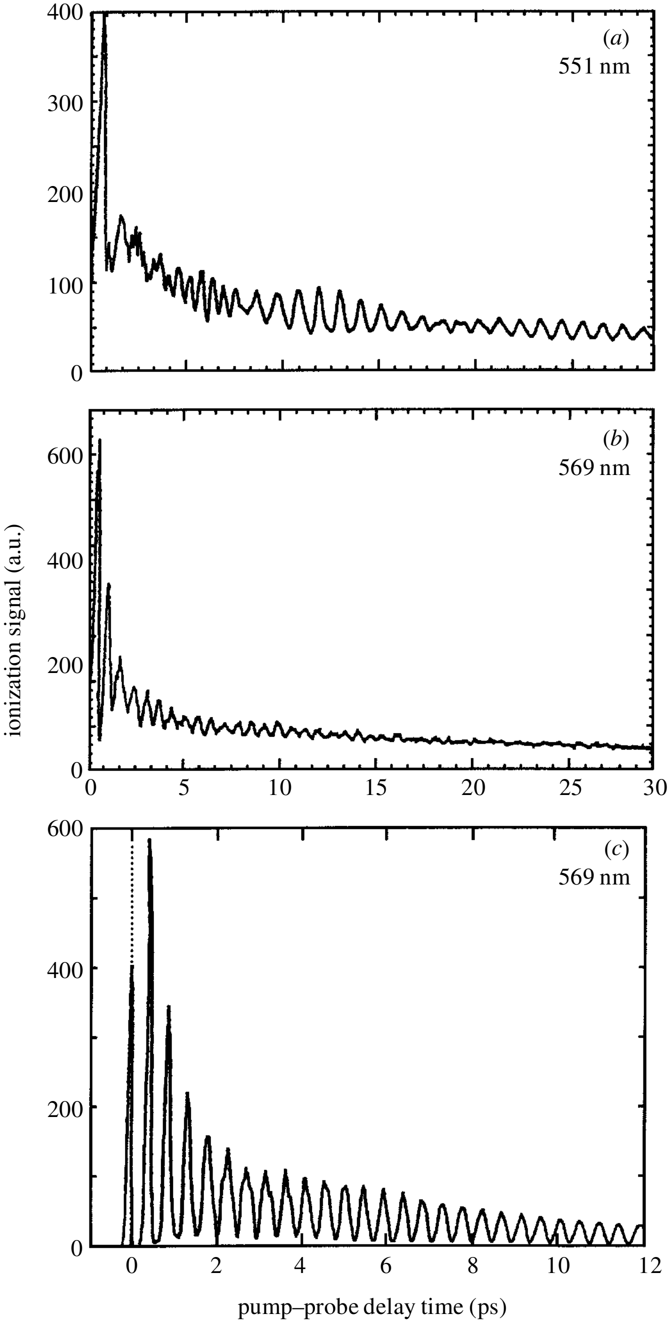

Figure 4. Experimental and theoretical femtosecond spectroscopy of IBr dissociation. Experimental ionization signals ((*a*) and (*b*)) as a function of pump–probe time delay for different pump wavelengths, showing how the time required for decay of the initially excited molecule varies dramatically according to the initial vibrational energy that is deposited in the molecule by the pump pulse. A calculated real-time ionization trace, which attempts to mimic the experimental result shown in (*a*), is shown in (*c*).

this gives insight into the coupling of the quantized vibrational motion of $[\mathrm{I} \cdots \mathrm{Br}]^{\ddagger}$ to the dissociation coordinate at different energies, and enables the nature of the forces that act on the molecule during dissociation to be quantitatively understood.

2. Chemical applications of femtosecond spectroscopy

(a) *Bimolecular gas-phase reactions*

In nature, chemical transformations that proceed by unimolecular decomposition of a single bond are relatively fewer in number compared with reactions that involve collisions between two reactant molecules. Unfortunately, femtosecond spectroscopy is not so readily predisposed to the study of bimolecular reactions by the pump–probe approach. The reason for this is that, typically, the time between collisional events in the gas phase is of the order of nanoseconds. So, with laser pulses of sub-100 fs duration, there is only about one chance in 10 000 of the pump pulse interacting with the colliding molecules at the instant when the reactive collision is taking place; in other words, it is not possible to perform an accurate determination of the zero of time.

An ingenious method to circumvent this problem was first devised by Zewail and co-workers (Scherer *et al*. 1990). These workers took advantage of the vibrational and rotational cooling properties and collision-free conditions of the supersonic expansion of a jet of gas in a high-vacuum chamber—known as a molecular beam—to couple reactant molecules closely together in a weakly bound unreactive state called a van der Waals complex prior to femtosecond laser initiation of the reactive trajectory. The reaction selected for study by these workers was

$$\mathrm{H} + \mathrm{CO_2} \rightarrow [\mathrm{HO} \cdots \mathrm{CO}]^{\ddagger} \rightarrow \mathrm{OH} + \mathrm{CO},$$

in which the reactants were prepared in an $\mathrm{HI} \cdots \mathrm{CO_2}$ complex. A cartoon representation of the experiment performed by Zewail's group and one of their many results are shown in figure 5*a*, *b*. The wavelength of the 100 fs pump pulse is selected to trigger the reaction by cleaving the H–I bond; this liberates the H atom, which translates towards $\mathrm{CO_2}$ and, over the course of *ca.* 10 ps, subsequently reacts to generate OH and CO. Product formation is monitored by the detection of fluorescence from OH induced by the time-delayed probe pulse. In this example, the reaction takes a long time to complete because $\mathrm{H} + \mathrm{CO_2}$ initially combine to form a metastable $[\mathrm{HO} \cdots \mathrm{CO}]^{\ddagger}$ intermediate, which survives long enough to rotate and redistribute energy amongst its available modes until such time as sufficient vibrational motion with the correct energy and phase is localized within the HO–CO bond. When this point is reached, bond rupture occurs and the diatomic products spin away from each other.

The use of molecular beams to lock reactants together within femtosecond striking distance is not the only way to perform ultrafast spectroscopy of bimolecular reactions, however. In a collaboration with research groups at the Max-Planck Institut für Quantenoptik in Garching, Germany, our research group has begun a joint experimental and theoretical investigation of collisions between excited sodium atoms, Na*, and molecular hydrogen, in which the outermost electron of the sodium is promoted to the excited state to yield a highly energized atomic reactant. Schematic potential

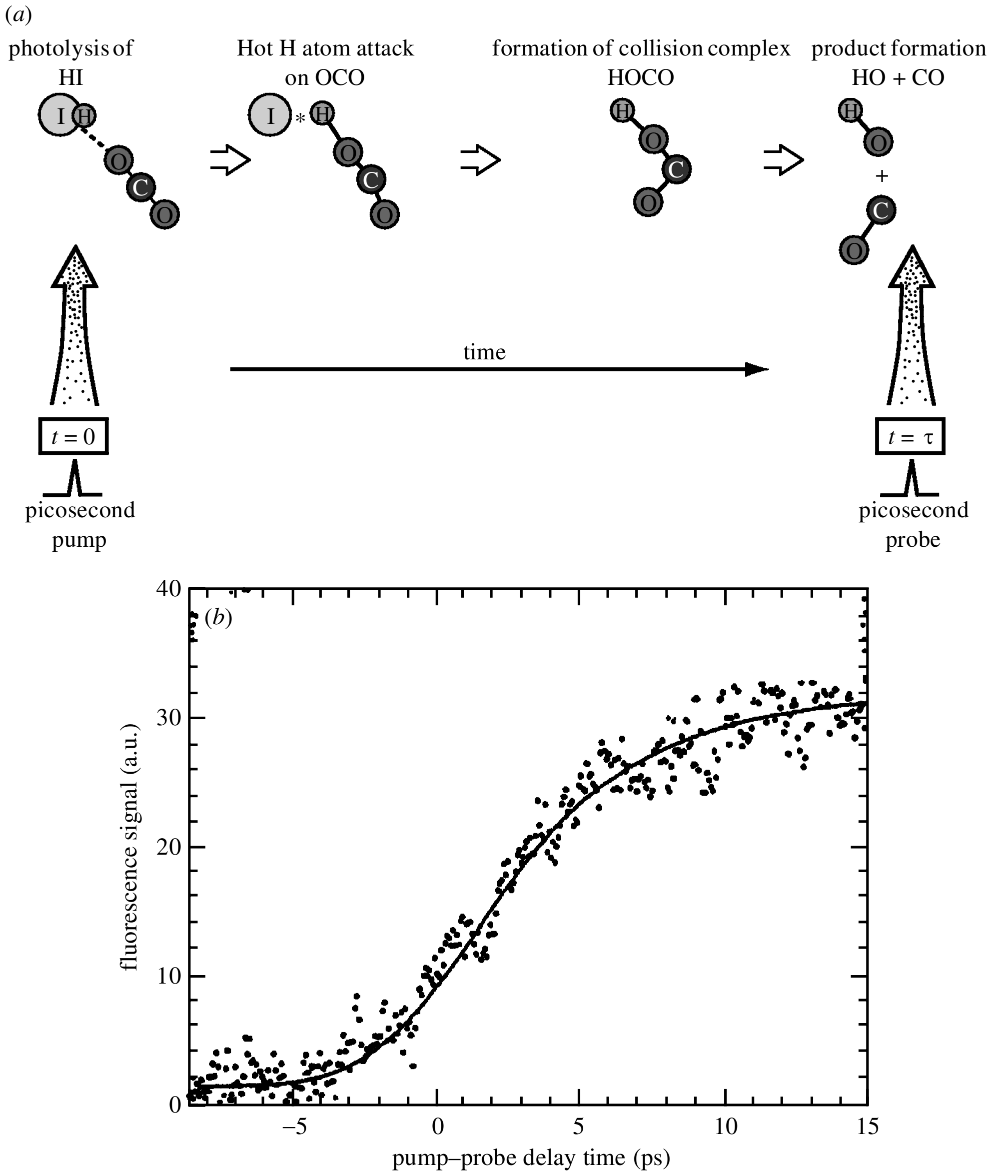

Figure 5. Femtosecond spectroscopy of bimolecular reactions. Pump and probe pulses initiate and monitor the progress of the reaction: $H + CO_2 \rightarrow [HO \cdots CO]^{\ddagger} \rightarrow OH + CO$ (*a*). The build-up of OH product is recorded via the intensity of fluorescence excited by the probe laser as a function of pump–probe time delay, an example of which is shown in (*b*).

energy curves for the $Na^* + H_2$ system are displayed in figure 5*c*. The $Na^* + H_2$ system serves as a paradigm for chemical reaction and energy transfer in bimolecular collisions, since, as can be seen from figure 5*c*, the reagents can either react to form $NaH + H$ products or can transfer the initial excitation energy of the sodium atom to the intact H_2 molecule, resulting in the emergence of a deactivated sodium atom, Na, and vibrationally excited hydrogen on the ground-state potential. The trajectory

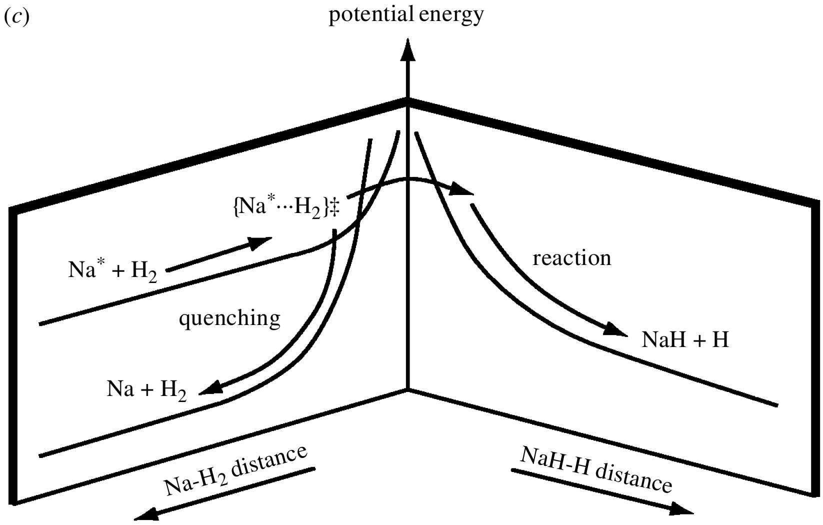

Figure 5. (*Cont.*) (*c*) The potential energy curves that govern collision between excited Na^* atoms and H_2; these show that the $Na^* + H_2$ collision can proceed along two possible exit channels, leading either to reactive formation of $NaH + H$ or to $Na + H_2$ by energy transfer. (Adapted from Motzkus *et al.* (1996) and Scherer *et al.* (1990).)

of the bimolecular collision again proceeds via one or more curve crossings between potential energy surfaces, representing the different forces that act upon $Na^* + H_2$, $Na + H_2$ and $NaH + H$.

Recent research has concentrated on the mechanism of collisional deactivation via electronic-to-vibrational energy transfer, represented by

$$Na^* + H_2 \rightarrow [Na^* \cdots H_2]^\ddagger \rightarrow Na + H_2^*.$$

Experiments in Garching and at the California Institute of Technology aim to track the appearance of ground-state sodium atoms after the $[Na^* \cdots H_2]^\ddagger$ transition state has crossed onto the potential surface that leads asymptotically to $Na + H_2^*$ (Motzkus *et al.* 1996). The problem of defining a starting point in time from which to follow the bimolecular event is overcome in this work by initiating the approach trajectory with a 20 fs pump laser pulse that prepares Na^* atoms in a high-pressure atmosphere of hydrogen, thereby reducing the time between collisions to below 1 ps. The energy quenching process is monitored via the simultaneous absorption of three 20 fs probe photons, and the re-emission of a fourth by the $[Na^* \cdots H_2]^\ddagger$ complex as it breaks apart. This coherent scattering spectroscopy is extremely sensitive and enables the deactivated sodium atoms to be probed as a function of time as they emerge from the curve crossing. Such measurements are supported by theoretical calculations of the wave packet motion over the intersecting potential energy curves (Ben-Nun *et al.* 1997; Martínez *et al.* 1997; Aicken & Roberts 2000), which reveal that the $[Na^* \cdots H_2]^\ddagger$ transition state formed from reactants persists for durations of up to 1200 fs before it fragments, during which time the excitation energy of the Na^* atom is quenched by repeated transfers of population from the excited-state potential to the ground state. The collision is said to be 'sticky', as the $Na^* + H_2$ collide, bounce off one another, and exchange energy and population over a time-scale that is long compared with the oscillation period of H_2 vibrations (*ca.* 8 fs).

(b) Gas-surface reactions

In a different approach to overcome the problem of defining the start of a bimolecular collision, several research groups, including our own, are attempting to study reactions between molecules weakly attached to the surface of a metal instead. In this proposal, the metal surface serves to pre-align molecules in a spatially favourable starting geometry prior to initiation of the reaction by a femtosecond laser pulse, in much the same way that a weakly bound van der Waals complex anchors reactants in spatial proximity in a molecular beam. The method additionally offers the opportunity to examine how the metal surface can act to catalyse a reaction.

When a laser beam irradiates a metal surface covered by a film of molecules, it does not, in general, interact with the molecules themselves, but instead penetrates the molecular overlayer to create a short-lived hot electron gas within the lattice structure of the metal. This process is schematically portrayed in figure 6 for the reaction of CO with O_2 to give CO_2 on a surface of platinum. The exact nature of the laser–metal interaction depends critically upon the duration of the incident laser pulses. With nanosecond laser pulses, for example, the hot electrons collide and exchange energy with the metal atoms such that the electronic and atomic motions within the lattice are always in equilibrium during the laser pulse, and surface processes, including reactions, proceed at the thermal energy of the lattice. However, the time-scale for electron–lattice equilibration is *ca.* 2 ps, so if sub-100 fs laser pulses are used, the electron motions at the surface are about a million times faster than the atomic vibrations within the lattice, leading to totally new reactive effects on a femtosecond time-scale driven by the transient hot electrons of the metal. In this temporal regime, the laser pulse heats up the electron gas to an enormous temperature, typically *ca.* 5000 K, at a heating rate of some 10^{16} K s^{-1}. An example of the temporal separation of thermal disequilibria is displayed in figure 7, which shows the velocity distribution of toluene desorbed from a platinum surface by laser pulses of 200 fs and 2 ps duration (Arnolds *et al.* 2000).

Each feature in the velocity profiles can be accounted for by a statistical distribution of toluene translational energies characterized by a specific temperature, as shown in the diagram. For low multilayer surface coverages of toluene, the velocity profiles show prompt and thermal maxima for both laser durations. Computer modelling of the velocity distributions suggests that the prompt peak corresponds to the maximum lattice temperature achieved by laser excitation, while the lower temperature of the thermal peak results from the detection of molecules that have given up part of their initial, high translational energy through collisions with other toluene molecules. At the higher coverage of ten layers of toluene attached to the surface, the prompt maximum of ejected molecules brought about by 200 fs duration laser pulses is much hotter: in this case, computer modelling indicates that the increase is due to ejection of molecules from the topmost layer attached to the surface by rapidly excited electrons from the platinum that have penetrated through the lower layers. For 2 ps laser pulses, the velocity profile shows the appearance of a new sub-thermal peak: at the present time it is thought that this might be due to a ‘phase explosion’, in which the entire molecular overlayer is heated so quickly that the whole overlayer leaves the metal surface during the laser pulse and fragments to form single molecules and clusters. It is not clear, but intriguing nevertheless, why a feature due to sub-thermal toluene detachment cannot be observed in the velocity profile recorded with 200 fs laser pulses.

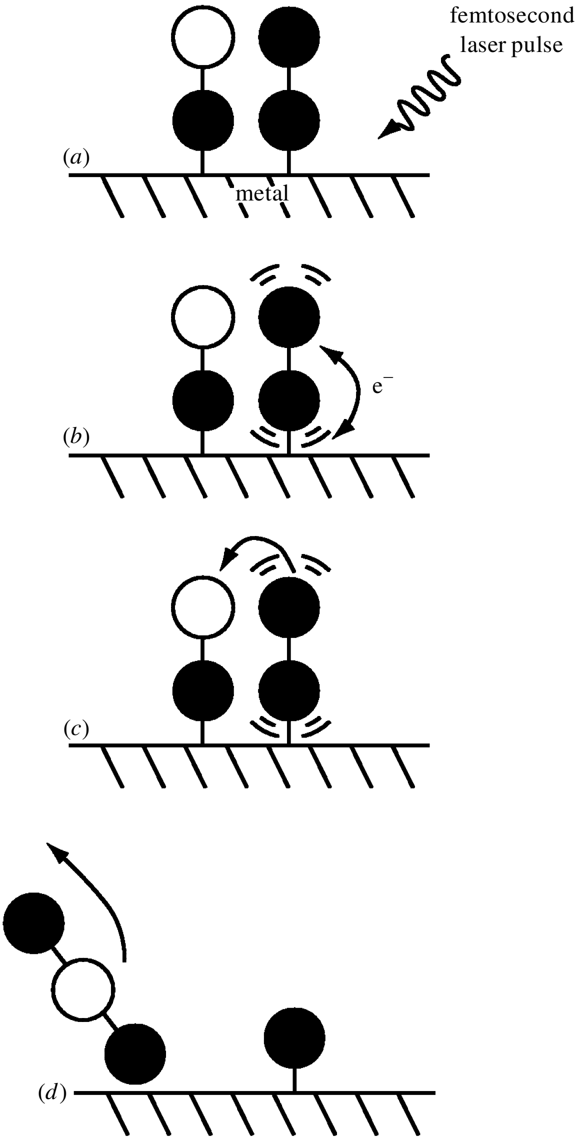

Figure 6. Femtosecond laser-initiated reactions between molecules at a metal surface, epitomized here by the reaction of O_2 with CO on platinum to give CO_2. A very short, intense burst of laser light incident on the metal surface (*a*) initiates multiple scattering between hot electrons (e^-) and O_2 attached to the surface of platinum (*b*). The oxygen molecule thus excited subsequently reacts with CO (*c*) to yield CO_2, which moves into the gas phase (*d*). (Oxygen atoms are shown by filled circles and the carbon atom by open circles.)

On account of the rapid rise in their temperatures during femtosecond laser irradiation, the outermost electrons of the metal induce multiple transitions between the energy states of the molecules attached to the surface throughout the duration of the pulse (Cavanagh *et al.* 1993; Ho 1996). Depending upon the precise chemical identity of the molecules and the metal surface, these repeated excitation events

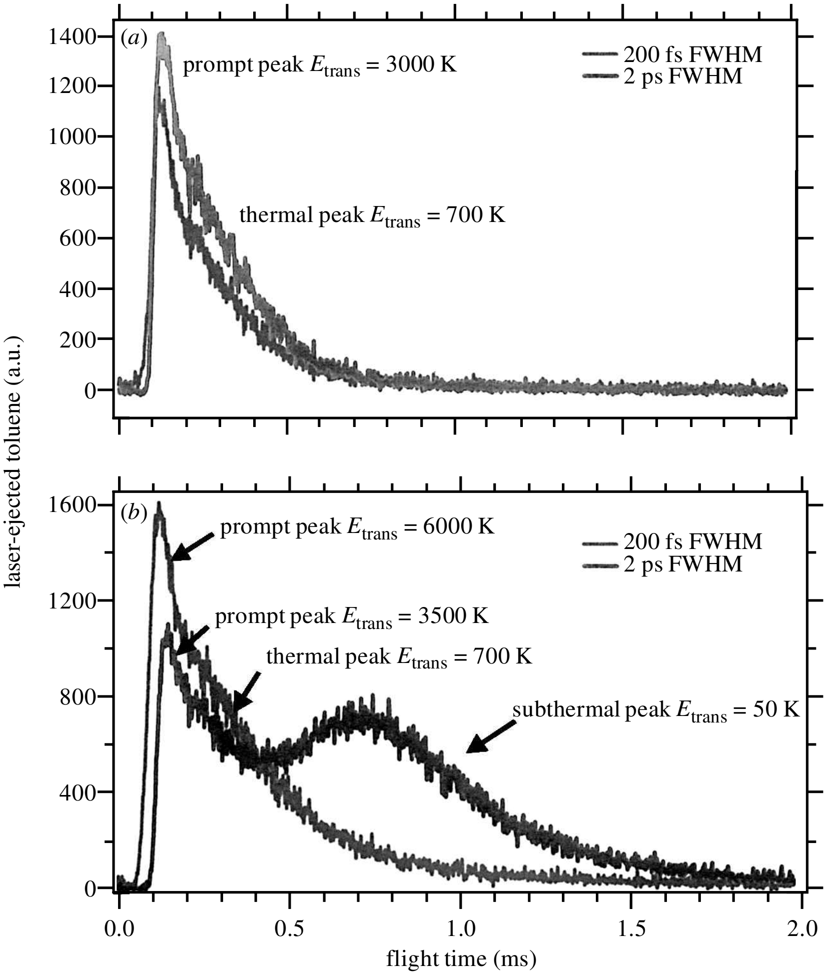

Figure 7. The ejection of toluene molecules into the gas phase from the surface of a platinum crystal at a temperature of 110 K by laser pulses of 200 fs (grey traces) and 2 ps (black traces) duration. The velocity profiles, shown for initial surface coverages of 2 and 10 monolayers (ML), record the yield of gas-phase toluene detected in a mass spectrometer as a function of the flight time it takes molecules to travel a known distance within the spectrometer, and can be described quantitatively by ultrafast laser-initiated and slower, thermal surface detachment mechanisms: each feature is ascribed a temperature as indicated, which corresponds to the degree of molecular translational excitation as toluene is ejected from the platinum into the gas phase (see text).

bring about either ejection of the molecular overlayer into the gas phase, or reaction between different molecules co-adsorbed onto the metal surface. Molecular ionization and vibrational excitation often accompany these processes.

A particular reaction that is of interest to a number of research groups is the platinum-catalysed oxidation of CO by O_2 to yield CO_2, for which a schematic is presented in figure 6*a*–*d*. The reaction can be initiated by irradiating a platinum surface covered in a mixture of CO and O_2 with a frequency-tripled 100 fs Ti:sapphire laser beam at a wavelength of 267 nm in the near ultraviolet (Finlay *et al.* 1997).

The central issues here are, as always, how does the reaction occur, and what is the nature of the reactive transition state? Careful measurements of the yield of desorbed CO_2 using isotopically labelled O_2 and a comparison with thermally induced O_2 dissociation rates point strongly towards a mechanism in which coupling between a sub-100 fs ultraviolet laser pulse and metal electrons brings about excitation of an intact O_2 molecule, which then reacts with CO on the surface to yield products via a $[CO_3^*]^\ddagger$ transition state (Finlay *et al*. 1997):

$$O_2(ad) \rightarrow O_2^*(ad), \qquad O_2^*(ad) + CO(ad) \rightarrow CO_3^*(ad) \rightarrow O(ad) + CO_2(g).$$

To verify this mechanism, or otherwise, pump–probe experiments to monitor the transition-state dynamics are planned by a number of research groups, including our own. In gas-surface studies, the probe wavelength must be chosen with care, since a visible or ultraviolet probe pulse would simply cause additional excitation of the metal electrons subsequent to that deliberately initiated by the pump pulse. Instead, probe-pulse frequencies must be selected in the infrared spectrum at values that resonate with vibrational modes of $CO_3^*(ad)$ in order to enable the motions of the constituent atoms to be monitored in real time.

(*c*) *Solvent effects on reaction dynamics*

In most chemical reactions, the reactant and product molecules are not isolated as they are in the gas phase, or semi-isolated as they are when attached to a metal surface, but rather are in intimate contact with their surroundings. In the solution phase, the immediate environment is the solvent, which can facilitate, lubricate or impair a reaction depending on the nature of the forces that the solvent exerts on the reaction coordinate of the solute and how these change with time along the course of the reaction path. Even a solvent that only weakly perturbs the reactants can profoundly alter the course of a reaction, by physically obstructing the exit path of a departing product for example, or by disturbing the phase coherence of concerted molecular motions or removing excess energy from reactive intermediates or products. When a reaction involves charged molecules in a polar solvent, i.e. one that is able to respond to the presence of localized dipoles and point charges, the forces between solute and solvent become comparable with chemical bond strengths; in this situation the solvent does not merely interrupt and/or redirect the reactive motion of molecules on a potential surface, but changes the topography of the potential.

By applying femtosecond pump–probe techniques to reactions in small solvent clusters in the gas phase, researchers have in the last few years begun to supply answers to fundamental questions about the mechanisms and time-scales of basic photophysical and reactive processes in a solvent at a molecular level. The most important of these concern the fate of the initial laser deposition of energy within a localized solute mode as a result of intramolecular and intermolecular energy redistribution, coherence loss of the nascent wave packet and reaction, and how these effects evolve with increasing numbers of solvent degrees of freedom.

Gas-phase clusters comprising a solute molecule surrounded by a relatively small number of solvent species are especially well suited to the study of solute–solvent dynamical interactions, because systems of a desired size and chemical composition can be selected by a mass spectrometer, thereby enabling femtosecond spectroscopy of a reaction in the presence of a precisely known number of solvent molecules. A popular choice for investigation has been the dissociation of molecular halogens encompassed by noble gas atoms, since the weakness of the forces between the halogen solute and atomic solvent in comparison with the molecular bond strength permits ready identification of reactive and energy transfer routes, rendering them amenable to both in-depth experimental and theoretical study.

A recent experimental study by the group of Neumark (at the University of California at Berkeley) on the dissociation of the negatively charged I_2^- ion in the presence of 0, 6 or 20 argon atoms exemplifies marvellously the way in which the issues listed above can be successfully addressed by femtosecond spectroscopy (Greenblatt *et al.* 1997; Parson & Faeder 1997). In these experiments, schematically depicted in figure 8*a*, the dissociation of size-selected $I_2^- \cdot \mathrm{Ar_n}$ clusters is triggered by 100 fs pulses from a Ti:sapphire laser at 780 nm, and followed by a probe pulse at 260 nm, which detaches the excess electron from the negatively charged molecule. Measurements of the kinetic energy distribution of the photoejected electrons (called a photoelectron spectrum) as a function of pump–probe delay time turn out to be an extremely sensitive and direct probe of the rapidly changing local environment of the detached electron, in that they reveal how the chemical binding interactions within a solute and the interactions between solute and solvent evolve during the dissociative escape of the solute atoms.

In the absence of argon solvent, the photoelectron spectrum changes smoothly from a pattern characteristic of I_2^- to one commensurate with I^-, shown in figure 8*b*, on a time-scale of 250 fs after the initial pump pulse, indicating that the dissociation is complete by this time. When the solute is embedded in a cluster of six argon atoms, the transient photoelectron spectra show features similar to that of the bare solute up to 250 fs, but at longer times between 250 and 1200 fs, a lingering interaction between the product I^- and several solvent atoms remains discernible in the spectrum. There is, however, no evidence in figure 8*b* of 'caging' of the dissociation process, that is of its physical prevention. For the largest cluster, $I_2^- \cdot \mathrm{Ar}_{20}$, the photoelectron spectrum evolves in a more complicated fashion: for durations up to 1200 fs, it quantitatively resembles that for the smaller clusters; but at longer times, new features grow, which can be attributed to the recombination of I and I^- to form I_2^- through inelastic collisions with the solvent shell of argon that now more or less completely envelopes the solute. Recombination on one of the excited-state potential curves shown in figure 8*a* leads to an $I_2^- \cdot \mathrm{Ar}_{11}$ product, in which I_2^- is left vibrationally cold on a time-scale of 35 ps; recombination over the ground-state potential involves considerably more energy flow and yields bare I_2^- in its sixth vibrational level, the process taking an amazingly long 200 ps to complete!

Experiments such as these provide an unprecedented level of detail on the dynamics of elementary reactions in a solvated environment, but they still, at least at the present time, require computational simulations of the dynamics in order to map out the motions of the individual atoms over one or more potential surfaces and to elucidate the structures of the reactive transition states that control the flow of energy between solute and solvent over a femtosecond time-scale. For very small clusters, say of a diatomic solute and one or two solvent atoms, with computational facilities available today, it is possible to carry out calculations of the reactive motions in which every degree of freedom is treated by the theory of quantum dynamics. As the number of degrees of freedom increases beyond about four, though, a full quantum dynamical

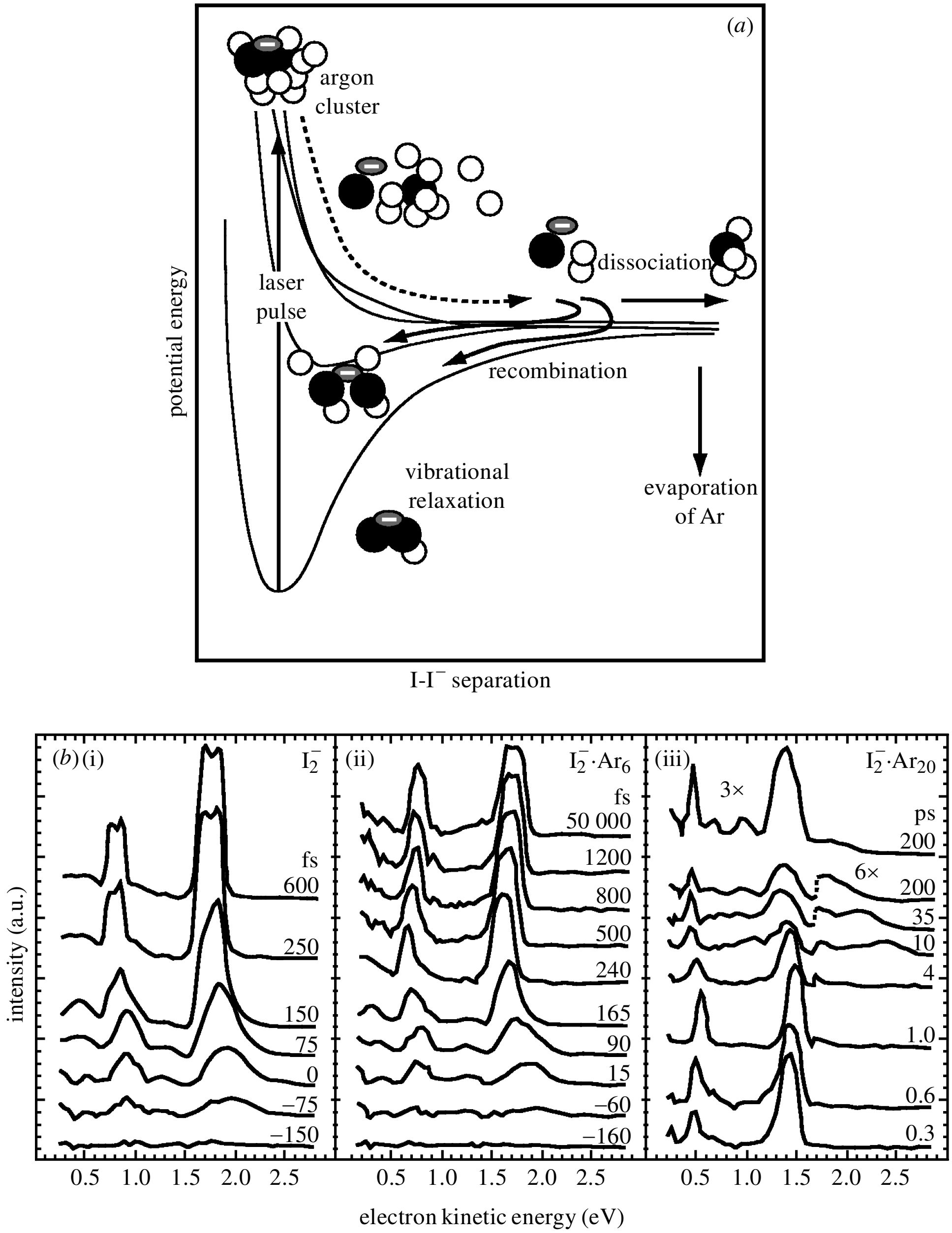

Figure 8. Femtosecond spectroscopy of reactions in clusters. (*a*) An ultrafast pump pulse initiates dissociation of an I_2^- ion (shaded circles) in a cluster of argon atoms (open circles) shown superimposed upon the potential energy curves of I_2^-, dissociation of which is monitored by photodetachment of an electron by an ultraviolet femtosecond probe pulse (not shown). (*b*) Photoelectron spectra as a function of kinetic energy (in electron volts) at various times between pump and probe pulses for I_2^-, $I_2^- \cdot Ar_6$ and $I_2^- \cdot Ar_{20}$, showing the onset of solvent effects beyond 250 fs and their evolution with cluster size. (Adapted from Greenblatt *et al.* (1997) and Parson & Faeder (1997).)

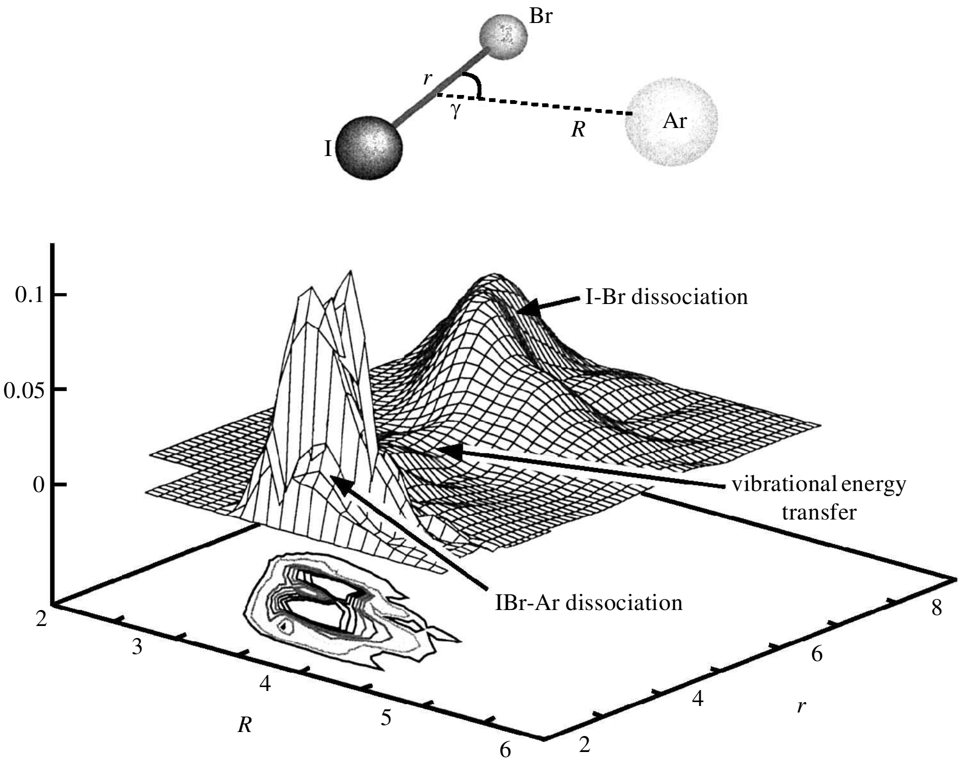

Figure 9. Quantum theory of IBr·Ar dissociation, showing a snapshot of the wave packet states at 840 fs after excitation of the I–Br mode by a 100 fs laser pulse. The wave packet maximum reveals predominant fragmentation of the IBr solute along the r coordinate at short IBr–Ar distances (R coordinate), while a tail of amplitude stretches to longer R coordinates, indicating transfer of vibrational energy from the solute to the solvent, which leads to dissociation of the argon atom initially bound to IBr.

treatment becomes prohibitively expensive in terms of computation time and memory requirements (and money). Theoretical investigations of dynamics in larger clusters thus resort to a mixed quantum-classical approach in which the important degrees of freedom, the reaction coordinate and modes directly coupled to it, are described by quantum dynamics, and the other, less important, degrees of freedom are treated by classical mechanics, which is computationally far less demanding. Understanding how a solvent influences a chemical reaction remains one of the most challenging problems in chemical physics today.

An example of the former type of calculation is shown in figure 9, which portrays a snapshot of the wave packet motion of IBr·Ar initiated by a 100 fs laser pulse (Hussain & Roberts 2000). The early-time (less than or equal to 150 fs) motions of the complex, which is almost T-shaped, comprise a simultaneous lengthening of the I–Br bond and a slower transfer of vibrational energy from the I–Br solute coordinate to the IBr–Ar solvent mode. Just as was found for the isolated IBr molecule (see § 1 *b*), a fraction of the wave packet amplitude along the I–Br direction proceeds to dissociation by curve crossing, while the remainder becomes trapped in the quasi-bound potential well. By 840 fs, bursts of vibrational energy transfer to the solvent degree of freedom give rise to a stream of population heading in the IBr–Ar direction, which eventually leads to expulsion of argon from the complex. To connect this dynamical picture with information available from experiments, calculations have also been carried out of the vibrational spectra of the cluster as a function of time after the femtosecond pump pulse. These show that relaxation of the nascent IBr vibrational content is at first periodic, but, at times longer than *ca.* 150 fs, becomes quasi-continuous as the coherence of the nascent wave packet is lost due to reaction.

3. What next? A speculative look into the future

This may be the millennium issue of *Philosophical Transactions of the Royal Society*, but the author certainly is not going to guess what might happen in chemical reaction dynamics during the next 1000 years! The discussion here is restricted to two significant developments that may be anticipated within the coming years. Ultrafast spectroscopy is very much a science that, by its very nature, is driven by advances in technology, and the awaited developments described here are no exception.

(*a*) *Attosecond laser pulses*

Of course, even when the world's fastest laser pulses are at your disposal, what you really want are pulses that are faster still! Laser pulses with durations in the attosecond (10^{-18} s) regime would open up the possibility of observing the motions of electrons in atoms and molecules on their natural time-scale, and would enable phenomena such as molecular ionization, electron formation and bond breaking to be captured and recorded in real time.

There are a couple of schemes that are being actively pursued to generate laser pulses that are significantly shorter than the shortest available today (4.5 fs). The physics of each scheme is well understood and the technology required to implement them in existence; what is difficult is that the proposals are currently hard to apply in the laboratory. To reach the attosecond regime, laser pulses must be composed of very many different frequencies, as required by the time–energy uncertainty principle, and they must be coherent. A usable source of attosecond pulses must also be intense enough to result in experimentally detectable changes in light absorption or emission, and they must be separated in time by about one-millionth of a second, in order that modern electronic circuitry can record the changes that they induce.

A scheme that has generated considerable optimism so far is that suggested by Corkum and colleagues at the National Research Council in Ottawa, Canada, which takes advantage of the high harmonic frequencies simultaneously generated when a femtosecond Ti:sapphire laser pulse ionizes a gas, helium or neon, in a narrow waveguide to construct the broad spectrum of colours necessary to support attosecond laser emission (Corkum *et al.* 1994; Ivanov *et al.* 1995). These harmonics are much like the overtones of a musical note: they are generated by oscillations of the electrons liberated by ionization in the laser field and are formed coherently, that is with their amplitudes in phase with one another. At the present time, researchers have succeeded in generating up to the 297th harmonic of the original 800 nm light from a 25 fs Ti:sapphire laser in helium by this approach, yielding a harmonic spectrum that extends into the X-ray region as far as 2.7 nm (Chang *et al.* 1997), and current research focuses on exploiting this result to construct a usable source of attosecond pulses. To the best of the author's knowledge, attosecond laser pulses have yet to be characterized definitively in the laboratory, but theoretical work suggests that high-harmonic pulses of less than 1 fs have almost certainly been produced (Christov *et al.* 1998). In addition to providing a possible source of attosecond light, the discovery of high-order harmonic generation also offers the chance to construct coherent, ultrafast X-ray laser devices.

(*b*) *Coherent control of chemical reactions*

When it was invented in 1960, the laser was considered by many to be the ideal tool for control of chemical reactions at the molecular level. The reasoning was that by choosing the frequency of a monochromatic (long pulse duration) laser to match exactly that of a local vibrational mode between atoms in a polyatomic molecule, it ought to be possible to deposit sufficient energy in the mode in question to bring about selective cleavage of the bond, thereby generating a specific product. With the benefit of hindsight, it is clear that the approach failed to take into account the immediate and rapid loss of selectivity due to intramolecular redistribution of energy over a femtosecond time-scale, as described for IBr–Ar in § 2 *c* above, for example. With the advent of femtosecond laser technology, however, the outlook for control of chemical reactions has improved dramatically, at least for photodissociation reactions.

Seven years ago, it was suggested by Judson & Rabitz (1992) that in order to reach a particular choice of final photoproducts, the electric field associated with a laser pulse could be specially designed to fit the forces experienced by a molecule at different points along its reactive trajectory, such that the amplitudes of the different possible reactive pathways always added up coherently along one, specific pathway at successive times after the initial photoabsorption event. Calculation of the optimal laser pulses required by this scheme dictates the use of a so-called 'genetic' computer algorithm to manipulate the electric field pattern of the laser applied to the dissociating molecule at different times until a sought-after product objective is attained.

In order that this proposal can be made to work, what is clearly required is a device that can make rapid changes to the temporal pattern of the electric field of a laser pulse. The recent development of liquid-crystal spatial light modulators to act as pulse shapers could open the gateway to a plethora of experimental realizations of coherent chemical control. In work carried out in Würzburg University by Gerber and co-workers (and published during the preparation of this article), the automated, specific dissociation of two iron-containing organometallic molecules to yield chemically distinct products has, for the first time, successfully demonstrated the application of a genetic algorithm to select the desired products from a photofragmentation reaction (Assion *et al.* 1998). It might be conjectured that these experiments constitute the first steps towards the selective, optical synthesis of chemical substances.

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