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Laser snapshots of molecular motions

Gareth Roberts

*Department of Chemistry, University of Cambridge, Lensfield Road,
Cambridge CB2 1EW, UK*

1.1 Introduction

The molecular motions that drive the conversion of energy and matter in
physics, chemistry and biology take place over an amazingly rapid time,
measured in millionths of a billionth of a second (a femtosecond (fs)). On
time scales of this duration, atoms and molecules come together, exchange
energy and transfer atoms in the very act of transforming one material into
another. To map out such processes as they happen necessitates the appli-
cation of laser pulses with durations of tens, or at most hundreds, of fem-
toseconds to take 'snapshots' of the changes in real time.

This chapter discusses the application of femtosecond lasers to the
study of the dynamics of molecular motion, and attempts to portray how
a synergic combination of theory and experiment enables the interaction
of matter with extremely short bursts of light, and the ultrafast processes
that subsequently occur, to be understood in terms of fundamental
quantum theory. This is illustrated through consideration of a hierarchy of
laser-induced events in molecules in the gas phase and in clusters. A spec-
ulative conclusion forecasts developments in new laser techniques, high-
lighting how the exploitation of ever shorter laser pulses would permit the
study and possible manipulation of the nuclear and electronic dynamics in
molecules.

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1.2 The interaction of intense femtosecond laser light with molecules

The interaction of femtosecond laser light with atoms and molecules is completely different to that involving longer laser pulses. This arises from the ultrashort duration of femtosecond laser pulses, which is faster than the characteristic dynamical time scales of atomic motion, and their ultra-high intensity, which initiates a whole range of unprecedented phenomena. What exactly happens when an intense, ultrafast laser beam irradiates a sample of molecules depends crucially on the intensity of the laser, which determines the number of photons supplied to an individual molecule and can contort the allowed energy levels of the molecule; also important is the frequency of the laser, which, together with the intensity, affords optical access to different molecular energy states. The detailed physics of the light–matter interaction will of course also depend on the structure of the irradiated molecule, but whatever its identity, certain general features of the excitation of atoms and molecules by ultrafast laser photons have emerged from pioneering studies by research groups throughout the world.

First to respond to the laser field are the lighter electrons, which do so on a time scale of attoseconds (a thousandth of a femtosecond): depending upon the intensity of the incident light, the one or more photons absorbed by the molecule either promote an electron to a high-lying energy state of the molecule, or the electron is removed from the molecule altogether, leaving a positively charged ion; at very high intensities multiple electron excitation and ionisation through various mechanisms can occur. Over a far longer time scale of tens or hundreds of femtoseconds, the positions of the atomic nuclei within the molecule rearrange to accommodate the new electrostatic interactions suddenly generated as a result of the new electronic state occupancy prepared by the ultrafast laser pulse: the nuclear motions may involve vibrations and rotations of the molecule, or the molecule may fall apart if the nacent forces acting on the atoms are too great to maintain the initial structural configuration. In addition, at high incident intensities, the electric field associated with the laser beam distorts the electrostatic forces that bind the electrons and nuclei in a molecule to such an extent that the characteristic energy levels of the molecule are modified during the ultrashort duration of the laser pulse.

Each of the above phenomena is the subject of intensive research pro-

grammes in its own right. Figure 1.1 offers a simplified portrayal of some of these events, showing the ionisation of an electron from the warped potential energy structure an atom by an intense laser pulse, the path subsequently followed by the electron in repsonse to the oscillating electric field of the laser pulse, and the emission of a high-frequency harmonic photon which occurs when the electron scatters off the ion core (high-harmonic emission can be exploited to generate attosecond laser pulses, discussed in Section 1.4.1). A similar series of events, with due alteration of the details, occurs in molecules exposed to intense laser light.

From careful measurements of such processs, it is possible to develop quantitative models to describe the molecular dynamical response to impulsive laser excitation. These enable the fundamental interaction of intense, ultrafast laser light with molecules to be understood from first
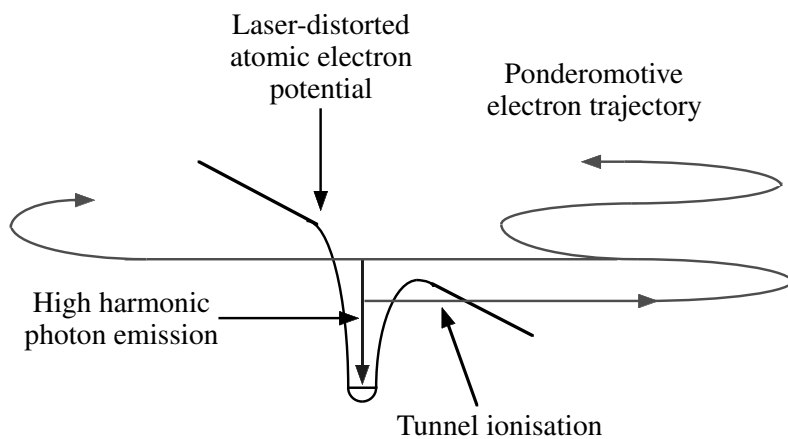

Figure 1.1. A sequence of events following the interaction of an intense, ultrafast laser pulse with an atom. The potential energy structure of the electron, which would otherwise be symmetric either side of a minimum, thereby confining the electron to the vicinity of the atomic nucleus, is distorted by the incident laser radiation. The electron first escapes (ionises) from the atom by tunnelling through the barrier on the side of lower potential energy and then executes an oscillatory trajectory determined by its kinetic (or ponderomotive) energy in the electric field of the laser pulse. If the electron follows a trajectory that brings it back close to the nucleus of the ionised atom, emission of a high-frequency photon can occur as the negatively charged electron is accelerated by the positively charged ion. This high-frequency photon is found to be an exact harmonic (overtone) of the laser frequency originally absorbed by the atom.

principles in terms of the wave description of matter and light due to quantum theory.

Following a description of femtosecond lasers, the remainder of this chapter concentrates on the nuclear dynamics of molecules exposed to ultrafast laser radiation rather than electronic effects, in order to try to understand how molecules fragment and collide on a femtosecond time scale. Of special interest in molecular physics are the critical, intermediate stages of the overall time evolution, where the rapidly changing forces within ephemeral molecular configurations govern the flow of energy and matter.

1.3 Femtosecond lasers

To carry out a spectroscopy, that is the structural and dynamical determination, of elementary processes in real time at a molecular level necessitates the application of laser pulses with durations of tens, or at most hundreds, of femtoseconds to resolve in time the molecular motions. Sub-100 fs laser pulses were realised for the first time from a colliding-pulse mode-locked dye laser in the early 1980s at AT&T Bell Laboratories by Shank and coworkers: by 1987 these researchers had succeeded in producing record-breaking pulses as short as 6 fs by optical pulse compression of the output of mode-locked dye laser. In the decade since 1987 there has only been a slight improvement in the minimum possible pulse width, but there have been truly major developments in the ease of generating and characterising ultrashort laser pulses.

The major technical driving force behind this progress was the discovery by Sibbett and coworkers in 1990 of a new category of ultrafast laser operation in solid-state materials, the most important of which is sapphire impregnated with titanium (others are the chromium-doped colquiriite minerals). These devices rely upon the intensity dependence of the refractive index of the gain medium to generate powerful, ultrashort laser pulses in a single 'locked' mode: a photograph of a commercial titanium:sapphire laser is shown in Figure 1.2.

Titanium:sapphire lasers typically deliver pulses with durations between 4.5 and 100 fs, and can achieve a peak power of some 0.8 watts, 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 dra-
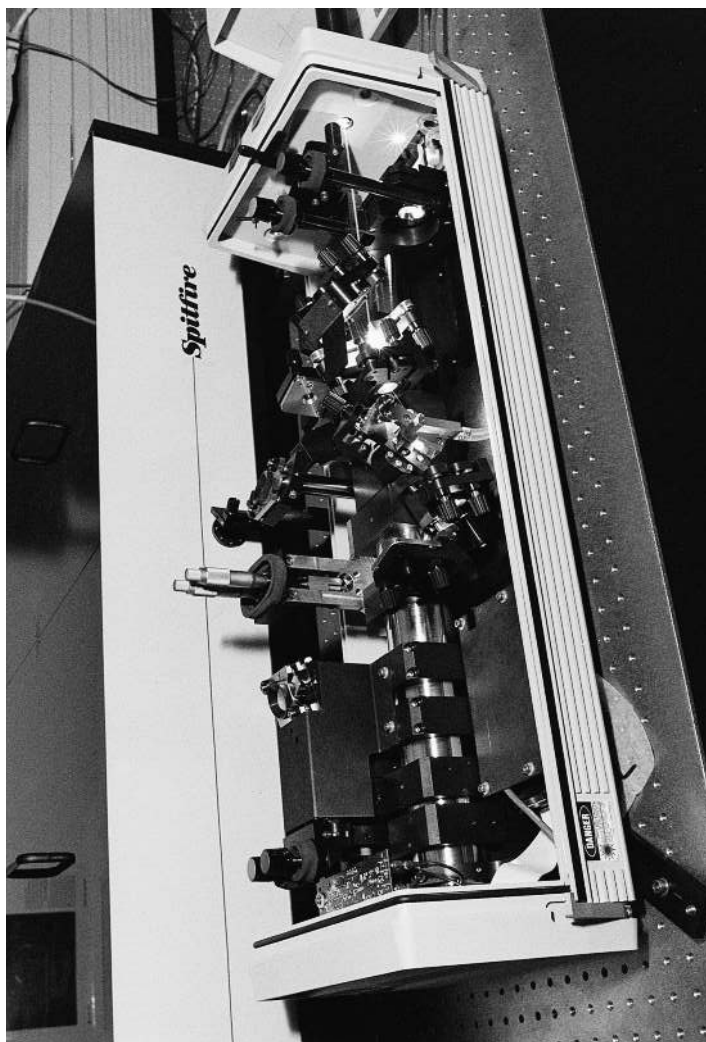
Figure 1.2. Photograph of a *Tsunami* titanium:sapphire laser manufactured by Spectra-Physics Lasers Inc. (Mountain View, California). The lasing transition in Ti:sapphire is between vibrational levels of different electronic states of the Ti^{3+} ion. Mode-locking of the laser is induced by an acousto-optic modulator, which results in the propagation of pulses with high peak powers and femtosecond durations in a single, 'locked' mode, or standing wave pattern. The energy source required to drive a Ti:sapphire laser is provided either by a diode or an argon-ion laser, both of which lase at the green wavelengths where Ti^{3+} is strongly absorbing. When the population of the Ti^{3+} excited state exceeds that of the ground state, laser radiation is emitted at red and near infrared wavelengths between 670 and 1070 nm.

matically increased by the process of chirped-pulse amplification. In this technique, the weakly intense ultrafast pulses are first stretched in time to between 100 and 1000 ps (a picosecond (ps) is 1000 fs), then amplified by about a million times in one or more further Ti:sapphire laser crystals, and finally recompressed to femtosecond durations. A typical peak power achievable with an amplified Ti:sapphire laser today is a hundred billion watts for a laser beam area of one square centimetre (the highest is just over a thousand million billion watts per square centimetre), which contrasts with an incident power of about 0.001 watts received through the iris of a human eye looking directly into the sun. For further details concerning the physics which underpins the operation of ultrafast lasers and their amplification, the interested reader is referred elsewhere for information (see Further reading).

For studies in molecular physics, several characteristics of ultrafast laser pulses are of crucial importance. 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 defining characteristics of laser radiation, but it is only true for laser radiation with pulse durations of a nanosecond (0.000 000 001 s, or a million femtoseconds) 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*.

The second requirement for investigations in ultrafast photophysics is one of wide wavelength coverage. The capacity for wavelength tuning is an essential ingredient in studies of molecular dynamics due to the different energy gaps that separate the quantum levels of molecules: vibrational resonances are excited with infrared light for example, whilst 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 renders them ideal for synchronous pumping of optical parametric devices, whereby photons of light at one frequency are converted through their self-interactions in non-centrosymmetric media into photons at different frequencies. Today, the

application of such schemes offers continuous tunability from the near ultraviolet, through the visible, into the infrared regions of the spectrum.

An important point is that these advances have been complemented by the concomitant development of innovative pulse-characterisation procedures such that all the features of femtosecond optical pulses – their energy, shape, duration and phase – can be subject to quantitative *in situ* scrutiny during the course of experiments. Taken together, these resources enable femtosecond lasers to be applied to a whole range of ultrafast processes, from the various stages of plasma formation and nuclear fusion, through molecular fragmentation and collision processes to the crucial, individual events of photosynthesis.

1.4 Femtosecond spectroscopy of molecular dynamics

1.4.1 Ultrafast molecular fragmentation

To determine molecular motions in real time necessitates the application of a time-ordered sequence of (at least) two ultrafast laser pulses to a molecular sample: the first pulse provides the starting trigger to initiate a particular process, the break-up of a molecule, for example; whilst the second pulse, time-delayed with respect to the first, probes the molecular evolution as a function of time. For isolated molecules in the gas phase, this approach was pioneered by the 1999 Nobel Laureate, A. H. Zewail of the California Institute of Technology. The nature of what is involved is most readily appreciated through an application, illustrated here for the photofragmentation of iodine bromide (IBr).

The forces between atoms in a molecule are most conveniently respresented by a surface of potential energy plotted as a function of the interatomic dimensions measured in ångströms (Å) (10Å are equivalent to a millionth of a millimetre). For the IBr molecule in the gas phase, the electronic ground state in which the molecule resides at equilibrium is characterized by a bound potential energy curve, labelled V_0 in Figure 1.3. The dissociative process is governed by two, interacting potential energy curves V_1 and V_1' for different excited states, which enable the molecule to break up along a coordinate leading to ground-state atoms (I + Br) or along a higher energy route which leads to excited bromine (I + Br*). Typical separation velocities are in the range 1500–2500 m s^{-1}. The same figure illustrates how femtosecond laser pulses configured in a pump-probe sequence can be applied to monitor the time-evolution of the photodissociation.
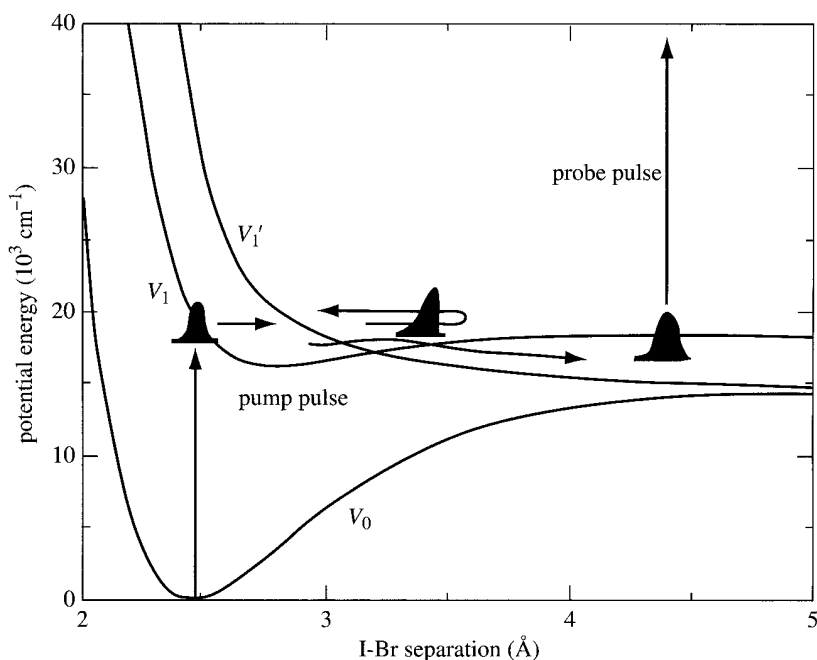
Figure 1.3. Real-time femtosecond spectroscopy of molecules can be described in terms of optical transitions excited by ultrafast laser pulses between potential energy curves which indicate how different energy states of a molecule vary with interatomic distances. The example shown here is for the dissociation of iodine bromide (IBr). An initial pump laser excites a vertical transition from the potential curve of the lowest (ground) electronic state V_0 to an excited state V_1. The fragmentation of IBr to form I + Br is described by quantum theory in terms of a wavepacket which either oscillates between the extremes of V_1 or crosses over onto the steeply repulsive potential V_1' leading to dissociation, as indicated by the two arrows. These motions are monitored in the time domain by simultaneous absorption of two probe-pulse photons which, in this case, ionise the dissociating molecule.

An initial, ultrafast 'pump' pulse promotes IBr to the potential energy curve V_1, where the electrostatic nuclear and electronic forces within the incipient excited IBr* molecule act to force the I and Br atoms apart. V_1 contains a minimum, however, so as the atoms begin to separate the molecule remains trapped in the excited state unless it 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, the object that is initially created in the excited state is a coherent superposition of all the wavefunctions encompassed by the broad frequency spread of the laser. Because the laser pulse is so short in comparison with the characteristic nuclear dynamical time scales of the motion, each excited wavefunction is prepared with a definite phase relation with respect to all the others in the superposition. It is this initial coherence and its rate of dissipation which determine all spectroscopic and collisional properties of the molecule as it evolves over a femtosecond time scale. For IBr, the nascent superposition state, or wavepacket, 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 1.3.

The time evolution of the wavepacket over the intersecting potentials V_1 and V_1' is monitored by its interaction with a second ultrashort 'probe' pulse, which in this case supplies two ultraviolet photons to ionise the molecule by removal of an outer electron. The key experimental requirement in this and all other pump-probe measurements is the ability to deliver the two ultrafast laser 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 the sample with a precision of a fraction of a micrometre (μm) ($1\,\mu$m distance equates to about 3.33 fs in time). The experiment consists of measuring in a mass spectrometer the number of ionised IBr*+ molecules excited by pump and probe pulses as function of the delay time between the two (see Figure 1.3), since this is directly proportional to the probability of locating the extended [I . . . Br] molecule 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.

Figures 1.4(a) and (b) show examples of the ionisation signals that are
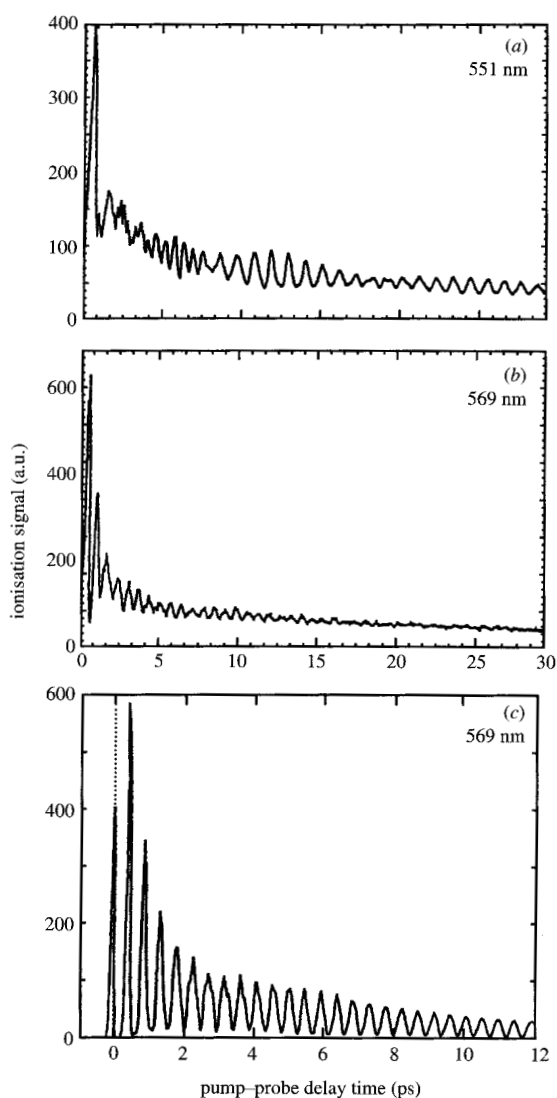
Figure 1.4. Experimental and theoretical femtosecond spectroscopy of IBr dissociation. Experimental ionisation signals as a function of pump-probe time delay for different pump wavelengths given in (a) and (b) show how the time required for decay of the initally excited molecule varies dramatically according to the initial vibrational energy that is deposited in the molecule by the pump laser. The calculated ionisation trace shown in (c) mimics the experimental result shown in (b).