Introduction

Since the age of alchemy and the search for the philosopher’s stone, man has looked for ways of controlling the transformation of matter. Today, chemists seek to control the outcome of chemical reactions, to suppress unwanted side products and to synthesize new molecules. In this book we will see how this long-standing dream has been partially achieved through the application of lasers in chemistry and how sometimes we can even teach lasers to be as skilful as chemists!

1.1 Basic concepts in laser chemistry

The laser has revolutionized many branches of science and technology, and this revolution is seen very clearly in chemistry, where the laser has now become one of the essential tools of chemistry.

Chemistry is a scientific discipline that studies matter and its transformation, and it is precisely in these two areas that lasers and laser technology play such a crucial role. As illustrated in Figure 1.1, the laser is a powerful tool which can be used to characterize matter by measuring both its properties and composition. Furthermore, the use of laser radiation can be a powerful method to induce or probe the transformation of matter in real time, on the femtosecond ($10^{-15}$ s) time-scale.

The links between the laser and chemistry

The links between the laser and chemistry are manifold, as shown schematically in Figure 1.2.

First, we have the so-called chemical lasers. This link goes directly from chemistry to lasers, i.e. a chemical reaction provides the energy to pump a laser. An example of this type of laser is the HF chemical laser, in which fluorine atoms, produced in a discharge, react with H$_2$ to produce a population inversion in the ro-vibronic states of the product HF:

$$\text{F} + \text{H}_2 \rightarrow \text{HF}^\ddagger + \text{H}$$

The excited HF$^\ddagger$ then produces intense, line-tuneable laser output in the infrared (IR).

Another example is the excimer laser, where ion-molecule and excited state reactions produce a population inversion; e.g. in the KrF laser, an electric discharge through a mixture of Kr and F$_2$, diluted in He, produces Kr$^+$ ions, Rydberg-excited Kr$^*$, and F atoms, which subsequently react, yielding excited-state KrF$^2$. Since the ground-state potential is repulsive (i.e. the ground state is unbound) the molecule
dissociates immediately after emitting a photon and population inversion is ensured. Excimer lasers are nowadays widely used in the car industry for welding, in research laboratories for fundamental and applied science, and in ophthalmology for eye surgery, to name the most common applications.

These are just two examples where the energy from a chemical reaction is transformed into coherent radiation that is subsequently employed in various applications.

A second link involves the use of lasers as ‘analytical’ tools, for sample analysis and characterization. In this wide field of analytical applications, lasers have been used to probe a variety of systems of chemical interest. Both stable species and nascent radicals produced by fast chemical reactions can be monitored with high sensitivity. As we shall see in later chapters, the special properties of laser radiation have opened up many new possibilities in analytical chemistry.

The third link between lasers and chemistry is the initiation and control of chemical change in a given system. The initiation of chemical processes by laser radiation has become a powerful area, not only in modern photochemistry, but also for technological applications. An example within this category is the multiphoton dissociation of SF₆ (sulphur hexafluoride) by IR laser radiation; this provides a means by which the two isotopomers $^{32}$SF₆ and $^{34}$SF₆ can be separated.

A further example is the control of chemical reactions using the methods of coherent control; this approach lies at the cutting edge of current research in laser chemistry, and we will discuss this topic in some detail in Chapter 19.

**The laser: a ‘magical’ tool in analytical chemistry**

Undoubtedly, lasers have become a sort of a ‘magical’ tool in analytical chemistry. So, why is this? We
could answer in a variety of ways, but perhaps the easiest way is to address the specific properties that characterize laser radiation. Briefly, the properties that distinguish lasers from ordinary light sources are:

- they are brighter;
- they are tuneable and highly monochromatic;
- they are highly directional;
- they allow polarization control;
- they are temporally and spatially coherent;
- they can probe molecules on the femtosecond ($10^{-15}$ s) time-scale.

The brightness of a laser not only implies a better signal-to-noise ratio, but more importantly the capability of probing and recording trace concentrations of transient species, reaction intermediates, photodissociation fragments, etc. In fundamental research, all methods for probing reactions require single-collision conditions; under these conditions, the high laser power makes up for the low particle density. In addition, powerful lasers open up new dimensions in non-linear phenomena, i.e. two-photon or multiphoton processes leading to dissociation and/or ionization.

Laser radiation is monochromatic and in many cases it also is tuneable; these two characteristics together provide the basis for high-resolution laser spectroscopy. The interaction between laser radiation and molecules can be very selective (individual quantum states can be selected), permitting chemists to investigate whether energy in a particular type of molecular motion or excitation can influence its reactivity. Photochemical processes can be carried out with sufficient control that one can separate isotopes, or even write fine lines (of molecular dimensions) on surfaces.

The output of most lasers can be, or is, polarized. The polarization character of the laser field interacting with the chemical reaction partners is indispensable when investigating stereodynamic effects. For example, by changing the plane of polarization of the laser radiation used to excite a reagent, the symmetry of the collision geometry can be altered and, consequently, the outcome of a chemical reaction may change (see the brief examples below in the ‘Stereodynamical aspects’ section).

Temporal coherence allows laser pulses to be tailored, providing the chemist with the opportunity to observe rapid changes down to the femtosecond time-scale. Using the technique of femtosecond excitation and probing, we now have the capability to study ultrafast reactions in real time.

The coherent character of laser radiation is reflected in the photon distribution function, whose phase relation distribution is peaked and very narrow, in contrast to the distribution function from a chaotic light source. Therefore, within a small interaction volume, the spatial and temporal coherence in the laser field results in significant transition probabilities for multiphoton absorption processes, whose occurrence would be nearly insignificant using an incoherent radiation source, even one exhibiting the same overall irradiance as a coherent laser source. This difference in transition probability is crucial for the successful implementation of any method requiring multiphoton absorption, both in general molecular spectroscopy (in monitoring chemical processes) and in techniques exploited in laser analytical chemistry. One such technique is resonance-enhanced multiphoton ionization (REMPI).

One of the major problems in analytical chemistry is the detection and identification of non-volatile compounds at low concentration levels. Mass spectrometry is widely used in the analysis of such compounds, providing an exact mass, and hence species identification. However, successful and unequivocal identification, and quantitative detection, relies on volatilization of the compound into the gas phase prior to injection into the analyser. This constitutes a major problem for thermally labile samples, as they rapidly decompose upon heating. In order to circumvent this difficulty, a wide range of techniques have been developed and applied to the analysis of non-volatile species, including fast atom bombardment (FAB), field desorption (FD), laser desorption (LD), plasma desorption mass spectrometry (PDMS) and secondary-ion mass spectrometry (SIMS). Separating the steps of desorption and ionization can provide an important advantage, as it allows both processes to be
optimized independently. Indeed, laser desorption methods have recently been developed in which the volatilization and ionization steps are separated, providing very high detection sensitivity.

REMPI, coupled with time-of-flight mass spectrometry (TOFMS), is considered to be one of the most powerful methods for trace component analysis in complex mixtures and matrices. The high selectivity of REMPI–TOFMS stems from the combination of the mass-selective detection with the process of resonant ionization; thus, absorption of two or more laser photons through a resonant, intermediate state provides a high level of selectivity, (i.e. laser wavelength-selective ionization). The main advantages of REMPI–TOFMS are its great sensitivity and resolution, high ionization efficiency, the control of molecular fragmentation (by adjusting the laser intensity appropriately), and the possibility of simultaneous analysis of different components present in a given, complex matrix (e.g. non-volatile compounds in biological samples).

Lasers and chemical reactions

Figure 1.3 shows schematically the different regimes where laser techniques can be applied in the study of chemical reactions. Note that we have made a clear distinction between gas- and condensed-phase processes, but only for pedagogical purposes (the technique and fundamental interactions underlying the overall phenomena are frequently the same). For the same reasons, we have separated unimolecular from bimolecular processes in later chapters. We also separately address condensed-phase processes, like surface chemistry, solution reactions, photo-biochemistry, hydrodynamics and etching, in the chapters that follow.

The use of lasers to prepare reactants and/or probe products of chemical reactions

A chemical reaction can be viewed as dynamical motion along the reaction coordinate from reactants to products. Thus, lasers can be used to prepare reagents and to probe products in particular quantum states.

A good example of the first category is the enhancement of a chemical reaction following vibrational excitation of a reagent. The first experiment showing that vibrational excitation can enhance the cross-section of a chemical reaction was reported for the crossed-beam reaction

$$K + HCl \rightarrow KCl + H$$

Figure 1.3 How lasers can be employed to pump, influence and probe chemical reactions
An HCl chemical laser was employed to resonantly excite the \( v'' = 1 \) level of the HCl reactant. It was estimated that, following vibrational excitation of HCl, the KCl yield was enhanced by about two orders of magnitude.

On the other hand, lasers can also be used to probe reaction products. A representative example is that of reactions of the type

\[
M(M = \text{Mg, Ca}) + X_2(X = \text{F, Cl}) \rightarrow \text{MX}^+ + X
\]

in which the nascent \( \text{MX}^+ \) can be probed by laser-induced fluorescence (LIF). Indeed, rotational and vibrational product state distributions have been determined for this type of reaction from the analysis of such LIF spectra. The reaction is known to occur via electron transfer from the metal atom to the dihalogen. The negative ion \( X_2^- \) so formed rapidly dissociates under the Coulombic attraction of the \( M^+ \) ion. LIF analysis of the nascent CaCl versus MgCl product indicates that whereas CaCl is formed vibrationally excited, MgCl is only rotationally excited. This difference can be explained by the difference in the range at which the electron jump takes place. Whereas in the Ca reactions the jump occurs at long range such that energy is channelled into the Ca—X coordinate (i.e. as CaCl vibrational energy), in the Mg reaction the electron jump distance is shorter, such that there is no possibility for vibrational excitation of the product and most of the energy appears in rotational excitation of the MgCl. This is, therefore, a clear example in which laser probing of the nascent reaction product helps to unravel the reaction mechanism and dynamics at a detailed molecular level.

Probing product state distributions by multiphoton ionization is one of the most sensitive methods for the analysis of both bimolecular and photofragmentation dynamics. For example, by using REMPI one can measure the rotational state distribution in the \( \text{N}_2 \) fragment produced in the photofragmentation of \( \text{N}_2\text{O} \); it was found that the maximum in the rotational state population is near \( J \approx 70 \). This reveals that although the ground electronic state is linear, the excited state is bent and thus the recoil from the O atom results in rotational excitation of the \( \text{N}_2 \) molecule.

It is often possible to use lasers to pump and probe a chemical reaction simultaneously. In other words, it is possible to use one laser to prepare a reactant in a specific quantum state and a second laser to probe the product. A good example is the reaction

\[
\text{Ca}^*(4s4p^1P_1) + \text{H}_2 \rightarrow \text{CaH}(X^2\Sigma^+) + \text{H}
\]

which is exothermic by \( 1267 \text{ cm}^{-1} \). On the other hand, the ground-state reaction

\[
\text{Ca}(4s^2) + \text{H}_2 \rightarrow \text{CaH}(X^2\Sigma^+) + \text{H}
\]

is endothermic by \( 22390 \text{ cm}^{-1} \). Therefore, two lasers were needed to investigate the reaction dynamics in this case: a pump laser operating at \( \lambda_{\text{exc}} = 422.7 \text{ nm} \) was used to prepare Ca atoms in the \( ^1P_1 \) state and a probe laser was used to excite LIF from the CaH via the \( B^2\Sigma^+ - X^2\Sigma^+ \) transition (in the wavelength range of 620–640 nm). The \( (0, 1) \) and \( (1, 2) \) transitions were monitored and analysis of the rotational line intensities gave the product rotational distribution (given the Hönig–London factors, the rotational line intensities for the \( v = 0 \) and \( v = 1 \) levels could be determined). Furthermore, by summing up the rotational lines for each level, and by making use of the Franck–Condon factors, the CaH vibrational distribution could be deduced.

**Laser-assisted chemical reactions**

Laser assisted chemical reactions are defined as reactions in which the product yield is enhanced by exciting the transition state (i.e. the reactants are not excited). A classical example for a photon-mediated atom–diatom reaction is that of

\[
\text{K} + \text{NaCl} \rightarrow [\text{KCl} \cdot \cdot \cdot \text{Na}]^\neq + h\nu \rightarrow \text{KCl} + \text{Na}^*
\]

Excited Na* is observed when the laser photon is selected to excite the \([\text{KCl} \cdot \cdot \cdot \text{Na}]^\neq\) transition state: the excitation photon does not have the correct (resonant) energy to excite either K or NaCl (see the conceptual diagram in Figure 1.4).

**Laser-stimulated versus laser-induced chemical reactions**

Chemical reactions can be stimulated or induced by lasers. The former case refers to the situation where
the laser enhances the reaction rate. Thus, when the laser is turned off, the reaction rate diminishes but the process continues. The example given above, namely the reaction $K^+ + HCl \rightarrow KCl + H$, which can be stimulated with a chemical laser by pumping the $v'' = 1$ level of HCl, thus falls into this category.

The situation is different, however, for a laser-induced chemical reaction, e.g. the multiphoton dissociation of $SF_6$, leading to the products $SF_5^+ + F$. When the laser is turned off, photodissociation ceases.

Gas-phase photodissociation can be induced by single- or multi-photon excitation processes. Single-photon dissociation, combined with imaging techniques, has revealed detailed insight into the bond-breaking process. A representative illustration of this type of study is the far-ultraviolet (UV) photolysis of $NO_2$ leading to the products $O(1D) + NO$. From the analysis of the imaging data for $O(1D)$, both the translational and the vibrational distributions in the product fragments have been deduced; these data provide a detailed insight into the dynamics of the dissociation process and clearly show that there is a change in geometry, from bent to linear, on excitation.

Molecular photodissociation can also be achieved by IR multiphoton excitation. A classical example of such processes is that of $SF_6 + nh\nu \rightarrow SF_5 + F$, which can also be applied to produce isotope enrichment in a $^{32}SF_6/^{34}SF_6$ mixture (the mechanism for this process is discussed in some detail in Chapter 18).

**Figure 1.4** Laser-assisted (endothemic) chemical reaction. Note that $h\nu_{pump}$ excites neither reagents nor products.

**Stereodynamical aspects**

The electronic excitation of a reagent can have several effects on a chemical reaction. For example, a higher electronic energy content in a reagent can make a reaction exothermic that would otherwise have been endothermic; as a consequence, enhancement of the reaction yield may ensue. However, laser excitation of a reactant species (atom or molecule) not only increases its internal energy, it also generally modifies its electronic state symmetry. It is well known that symmetry plays an important role in photon-induced transitions (cf. selection rules in electronic, vibrational and rotational spectroscopy), but it can also play an important role in chemical reactivity. Electronic excitation invariably changes the shape and symmetry of the potential energy surface (PES) and it may induce a different reaction mechanism compared with that of the ground state. An example is the change from abstraction to predominantly insertion reactions, seen for oxygen atoms, as one goes from the ground state, $O(3P)$, to the first excited state, $O(1D)$. Here also, we see that energy alone is not sufficient to promote a reaction, as the second excited state of the oxygen atom, $O(1S)$, is far less reactive than the lower energy $O(1D)$ state.

Since the early days of reaction dynamics, the vectorial character of the elementary chemical reaction has been well recognized. Not only are scalar quantities (such as collision energy or total reaction cross-section) important in shaping a reactive collision, but vectorial properties (such as the reagent’s orientation, and orbital or molecular alignment) can also significantly influence the outcome of an elementary chemical reaction.

For example, photodissociation is an anisotropic process. The polarization of the electric field of the photolysis laser defines a spatial axis, to which the vectors describing both the parent molecule and the products can be correlated (see Figure 1.5).

In a full-collision experiment, e.g. in crossed-beam, beam–gas or gas cell arrangements, the reference axis is the relative velocity vector. Conceptually, the vector correlation is identical to that of photodissociation, only now the relative-velocity vector rather than the electric-field vector defines the symmetry. Thus, the reagents’ electronic orbital alignment can influence the product yield of a chemical reaction. Imagine, for
example, the system $A + B_2$, which yields the reaction products $AB + B$. In the case that the $A$ atom is elevated to an excited state, say by a transition $^1S_0 \rightarrow ^1P_1$, the alignment of the $^1P_1$ orbital with respect to the relative-velocity vector can influence the outcome of the reaction $A(^1P_1) + B_2 \rightarrow AB + B$. For the case that the $p$-orbital is parallel to the relative velocity vector, the PES is of so-called $\Sigma$ symmetry and the yield of $AB$ in its excited $\Sigma$ state is enhanced. Conversely, if the $p$-orbital is perpendicular to the relative velocity vector, then the yield of $AB$ in its electronically excited $\Pi$ state is enhanced, as shown pictorially in Figure 1.6.

The direct correlation observed between the parallel and perpendicular alignments in the centre of mass and the $\Sigma$- and $\Pi$-product channels, in the laboratory frame, is an example of the stereodynamical aspect of chemical reactions that can be precisely investigated by linking them to suitable laser photon fields.

The universality of the laser chemistry

A complete knowledge of chemical reactivity requires a full understanding of single collision events. One of the most powerful tools with which to investigate such events is the molecular beam method. Under molecular beam conditions one can study bimolecular reactions in great detail, using both laser excitation and probing techniques.

The intermediates in many bimolecular reactions exhibit lifetimes of less than a picosecond. Thus, it was only after the development of ultrafast laser pulses (of the order of 100 fs or so) that it has become possible to study the spectroscopy and dynamics of transitions states directly, giving rise to the so-called field of femto-chemistry. This discipline has revolutionized the study of chemical reactions in real time, and one of its most prominent exponents, Ahmed H. Zewail, was awarded the Nobel Prize for Chemistry in 1999 for his pioneering contributions to this field.

Chemical reactivity depends significantly on the state (phase) and degree (size) of aggregation of a particular species. Laser techniques have been developed to study chemical processes in the gas phase, in clusters, in solutions and on surfaces. Thus, clusters, i.e. finite aggregates containing from two up to $10^4$ particles, show unique properties that allow us to investigate the gradual transition from molecular to
condensed-matter systems (see the schematics of the transition from isolated particles through aggregates to solid surfaces in Figure 1.7).

The binding forces in aggregates and clusters are often weak interactions of the van der Waals type. These van der Waals forces are responsible for important phenomena such as deviations from ideal gas behaviour, and the condensation of atoms and molecules into liquid and crystalline states. Such weakly bound van der Waals molecules have become model systems in chemistry. Both the structure and the photodissociation of van der Waals molecules are discussed later in some detail (see the examples in Part 6).

The study of laser-induced chemical reactions in clusters is normally carried out in a molecular beam environment. One of the great advantages of using the molecular beam technique is its capability to generate supercooled van der Waals clusters of virtually any molecule or atom in the periodic table. This method of ‘freezing out’ the high number of excited rotational and vibrational states of molecular species in the beam is a powerful tool, not only to implement high-resolution spectroscopic studies, but also to form all kinds of aggregates and clusters. One of the most widely used methods for cluster formation is the technique of laser vaporization. This powerful method was developed by Smalley in the 1980s and led to the discovery of C\textsubscript{60} and the other fullerenes, which was recognized by the award of the 1996 Nobel Prize in Chemistry to Kroto, Curl and Smalley.

Reactions in solution are very important in chemistry; the solvent plays a crucial role in these processes. For example, trapping reactive species in a ‘solvent cage’ (see the centre part of Figure 1.7 for a schematic of the principle), on the time-scale for reaction, can enhance bond formation. The solvent may also act as a ‘chaperone’, stabilizing energetic species. Studies in solvent environments have only become possible recently, once again aided by the advent of ultrafast lasers, which allowed the investigation of the solvation dynamics in real time.

Processes such as photodissociation of adsorbed molecules or phonon- versus electron-driven surface reactions are topics that are currently attracting great attention. The photodissociation of an adsorbed molecule may occur directly or indirectly. Direct absorption of a photon of sufficient energy can result in a Franck–Condon transition from the ground to an electronically excited repulsive or predissociative state. Indirect photodissociation of adsorbates, involving absorption of photons by the substrate, can take place via two processes. The first one is analogous to the process of sensitized photolysis in gases (i.e. energy is transferred from the initially excited species to another chemical species). The second one, also substrate mediated, implies the photo-transfer of an electron from the substrate to an anti-bonding orbital of the adsorbate, i.e. charge transfer photodissociation. Laser techniques are now revealing some of the fundamental principles involved in these two excitation mechanisms.
State-of-the-art laser chemistry

Probably the most revolutionary development in our knowledge of the nature of the chemical bond and the dynamics of the chemical reactions has been gained by using ultrafast lasers, mostly in the femtosecond time-scale. This area of research is now commonly known as femto-chemistry, and ample coverage is given to it in this book. As we will show in detail later, laser excitation by femtosecond pulses leads to a coherent superposition of excited states. By observing the time evolution of the wave packet that is created, one can record snapshots of molecular photofragmentation and chemical reactions, i.e. the bond-breaking and bond-forming processes can be studied in real time.

Traditionally, the control of chemical processes is accomplished by well-established procedures, e.g. by changing the temperature or pressure of the reaction mixture, or perhaps by using a catalyst that significantly lower the activation energy for a given reaction channel.

However, since the advent of laser technology, the laser has been suggested as a new tool for controlling chemical reactions. One of the most developed schemes to control chemical reactions is through the excitation of the reagents into specific states, which are then stimulated to evolve into distinct product states. An example of this line of attack has been the development of mode-selective chemistry: for certain reactions, vibrational excitation seems to be more effective than translational excitation of the reagents. However, it has to be noted that the rapid internal vibrational redistribution within bond-excited reagents makes mode selectivity in chemical reactions a challenging task.

For the last decade or so, a new method has been developed to control chemical reactions that it is based on the wave nature of atoms and molecules. The new methodology is called ‘quantum control’, or ‘coherent control’ of chemical reactions, and is based on the coherent excitation of the molecule by a laser. Generally speaking, an ultra-short laser pulse creates a wave packet whose time evolution describes the molecular evolution in the superposition of excited states. Quantum control tries to modify the superposition of such an ensemble of excited states and, therefore, influences the motion of the wave packet in such a manner that highly constructive interference occurs in the desired reaction pathway, and all other reaction pathways experience maximum destructive interference.

The multidisciplinarity of laser chemistry

The rapid developments in new laser techniques and applications have extended the field of laser chemistry into many other scientific fields, such as biology, medicine, and environmental science, as well as into modern technological processes. This ‘natural’ invasion is a result of the multidisciplinary character of modern laser chemistry. Examples of this multidisciplinary character are numerous and are amply covered in later chapters of the book. However, a few examples are outlined here in order to illustrate the key features relevant to laser chemistry better.

We have mentioned earlier that the brightness of laser light provides the ideal conditions for non-linear spectroscopy in atomic and molecular physics and analytical chemistry, but it can also lead to ‘blood-free’ and sterile surgery in medicine and other application in modern biomedicine.

In surgery it is very important to achieve three main effects: vaporization, coagulation and incision. The experience gained through laser chemistry, particularly with laser ablation of solid samples, has enabled the laser beam parameters to be optimized for all three effects. The photoactivation of certain chemicals in vivo can be used in the treatment of cancer. As described in Part 6 of this book, by photoactivating a dye material (given to the patient sometime earlier to the anticipated laser exposure) a photochemical reaction can be initiated that causes the death of malignant cells without destroying adjacent normal cells. This treatment, known as photodynamic therapy, is a clear example of the way in which laser-induced selective chemistry can be used in medicine.

Laser analytical chemistry is perhaps one of the sub-fields that has had the highest impact on other fields and associated technologies. The spectral purity, or monochromaticity, of the laser light, amply exploited in reaction dynamics by preparing specific reagents’ states or probing specific product states, is today used extensively in environmental science, e.g.
for laser remote sensing (light detection and ranging (lidar), differential absorption lidar (DIAL), etc.), or in biology for selective excitation of chromophores in cells or biological tissues. Key examples of these types of multidisciplinary application are amply described in later chapters.

Another illustration of the multidisciplinarity of laser chemistry is the development of modern applications in nanotechnology, where, for example, nanoscale patterning is an emerging laser chemical method. We will see how the concept of localized atomic scattering extends to that of localized atomic reaction: the formation of the new bond created at the surface takes place in an adjacent location to the old bond that is being broken. In Chapter 27 we will then see how this localized atomic reaction development can be used to produce nanoscale patterning, i.e. patterning with exceptionally high spatial resolution.

As mentioned above, the temporal coherence of the laser light has revolutionized the investigation of chemical processes in real time because it has made possible the preparation, and subsequent evolution, of wave packets in molecular and atomic systems. This coherent character of laser light is currently used for quantum control of chemical processes. Although this field is still in its infancy, important scientific and technological applications are expected in the near future and will undoubtedly extend beyond chemistry.

One of the main applications of laser light in chemistry is the induction of chemical processes via stimulated resonant transitions. The rate of excitation for a stimulated transition is proportional to the light intensity. Therefore, the use of intense laser light can provide a very high rate of energy deposition into a molecular system. Typical values can be 1–10 eV during time periods of ~10 ns down to less than 100 fs, i.e. up to 10^{14} eV s^{-1}, which exceeds significantly the system relaxation rate. This means that one can excite atomic or molecular systems without any ‘heating’. These are ideal conditions with which to develop mode-selective or bond-selective chemistry. This has been a long-standing dream in chemistry, whose realization has now become possible, albeit only for certain restricted experimental conditions. On the more practical side, high rates of light energy deposition are now exploited in modern microbiology or in the food industry (e.g. to sterilize solutions and food products).

### 1.2 Organization of the book

The basic questions to be answered in any chemistry experiment, or indeed any theoretical investigation, are why and how chemical reactions (unimolecular or bimolecular) occur. With laser chemistry one hopes to elucidate whether the presence of laser radiation in the reaction zone influences the reaction by its interaction with the reagents or reaction intermediates, or whether it only serves as a probe to establish the presence of a particular species in the entrance, intermediate or exit channels of the reaction. These fundamental objectives, which are germane to the understanding of laser chemistry, are detailed in this textbook, together with a wealth of representative examples.

#### Introduction to lasers, laser spectroscopy, instrumentation and measurement methodology

Conceptually, all laser chemistry experiments are made up of the same general building blocks, as summarized in Figure 1.8.

At the centre of any laser chemistry experiment is the reaction zone, on which normally all interest and instrumental efforts are focused. Specific configurations of the reaction region, and the experimental apparatus used, differ widely; these depend on the nature of the chemical reactants, how they are prepared for interaction and what answers are sought in a particular investigation. Hence, in this chapter, the discussion of specific components (like vacuum chambers, flow systems, particle beam generation, etc.) are largely omitted (further details are given where specific examples are discussed in later chapters).

Around the reaction zone one can identify input and output channels for atoms/molecules and radiation. Broadly speaking, the input channel(s) for atoms and molecules constitute the provision of reagents to the reaction zone. This provision may happen in a variety
of ways, including gas flows, atomic/molecular beam transport or laser ablation, to name the most common procedures encountered in experiments related to the chemical reactions discussed in this book, i.e. reactions mainly in the gas phase. Details of the relevant mechanisms for atom/molecule provision and characteristics of their motion are outlined later in the chapters on unimolecular and bimolecular reactions in Parts 4 and 5.

One can distinguish two main input channels for laser radiation, namely one for the preparation of reagents or reaction intermediates and one for the probing of individual parts or the whole of the reaction, from reagents through intermediates to products. Both channels do not necessarily have to be present. Depending on the nature of the experiment, one channel may be sufficient to provide the required information, e.g. in cases in which a reaction is initiated by laser radiation and its products are probed by non-laser means, or, conversely, where only the products of a chemical process are probed by a laser.

The results of a (laser-induced) chemical process or the probing of a reaction are typically monitored via the detection of photons or particles, or both. The specific signatures of reagent/intermediate/product responses are analysed using suitable ‘filters’ (e.g. spectrometers for wavelength analysis of light, or mass spectrometers for mass and/or energy analysis). The response from the photon and particle detectors following the analyser is ideally linear with incident quanta, to allow for quantitative measurements. Finally, in today’s high-tech world, the signals are processed, accumulated and evaluated using a range of computer-controlled equipment.

As is evident from Figure 1.8, many of the building blocks in a general laser chemistry experiment encompass several optical principles and comprise numerous optical components. These include the transfer and manipulation (intensity, spectral and temporal characteristics) of light beams, significant parts of the laser sources and spectral analysis equipment.

Hence, in order to avoid the reader having to revert frequently to other textbooks, we provide in the first three main sections (Parts 1–3):

1. A brief outline of basic information on the energy levels in atoms and molecules, as well as photon transitions/selection-rules (Chapter 2); a short
summary of how lasers work (Chapter 3) and descriptions of the most common laser sources used in laser chemistry studies (Chapter 4).

2. A detailed outline of those laser-spectroscopic techniques, which are the most common in laser chemistry experiments, including methods based on photon detection (Chapters 6 to 8) and ion detection (Chapter 9).

3. An introduction to the basic concepts of optical phenomena and a description of routinely encountered optical components (Chapters 10 to 12). Part 3 concludes with a discussion of common photon and atomic/molecular analysis systems, and the associated detectors (Chapter 13), and a short summary of signal processing and data acquisition, as far as it is relevant to the context of this textbook (Chapter 14).

We have made every possible effort to keep these parts as self-contained as possible; however, reference to additional reading material is given where appropriate or required.

Laser chemistry: unimolecular reactions, bimolecular reactions, cluster and surface reactions

Central to this book is a second three-part set of chapters where a wide range of laser chemistry principles, processes and methodologies are discussed. Numerous examples are provided, which highlight specific aspects of particular principles or measurement techniques. The following themes are discussed.

1. The concepts of laser chemistry are developed along the lines of unimolecular reactions, or, in other words, dissociative processes in the most common sense. The discussion evolves from the photodissociation of diatomic molecules through triatomic species up to larger polyatomic entities (Chapters 15 to 17). Suitable coverage is also given to multiphoton and photoionization processes, which involve the subtle inclusion of intermediate and continuum states (Chapter 18). The part on unimolecular reactions concludes with a discussion of coherent control in chemical processes (Chapter 19).

2. In the segment on bimolecular reactions, the concepts of kinetics and reaction dynamics are developed further; in particular, the ideas of three-dimensional (3D) collision dynamics and technologies (e.g. molecular beam techniques) and the idea of state-to-state reactivity are outlined (Chapters 20 and 21). The preparation of reagents and the probing of reaction products by laser techniques are extensively discussed in Chapters 22 and 23.

3. Although the main focus is on gas-phase reactions, the discussion would be incomplete without including processes that are at the interface between the different phases of matter (the boundaries of chemical processes in the gas, liquid or solid phase are indeed rather fuzzy). This area is addressed in the segment on cluster and surface reactions, evolving from van der Waals and cluster entities (Chapter 24), via elementary reactions in a solvent cage (Chapter 25), to laser-induced processes in adsorbates on surfaces (Chapters 26 and 27).

In these three parts, emphasis is put on the understanding of fundamental principles; however, at the same time, we have made every effort to cover modern trends in the field of laser chemistry, e.g. the increasing importance of femto-chemistry.

Practical applications

The fundamental processes and basic methodologies in laser chemistry, which are the main focus of our discussion, are now emerging from the realm of curiosity-driven investigations into firmly based applications in research laboratories and use in the real world. Because of the rapid advance of laser technology and the maturity of various laser chemical techniques, the range of practical applications is growing exponentially. Hence, this application part can only provide snapshots, with a few selected examples.

In the context of practical applications, laser chemistry reveals its inter- and multi-disciplinarity. The use
of lasers in applications both driving and monitoring chemical processes is found in fields such as the following.

- Environmental studies, particularly of the atmosphere; the primary chemistry of gas-phase reactions, which is a centrepiece of this book, is most evident and readily accessible (see Chapter 28).

- Combustion processes of small (e.g. car engines) and large (e.g. incinerators) scale are the focus of many studies, and instruments based on laser-analytical techniques are now incorporated into process control (see Chapter 29).

- Chemical processes are encountered in the biomedical context, and here the laser has helped to untangle many of the extremely complex reaction chains and study the underlying dynamics in real time (see Chapter 30).

**Worked examples and further material**

Clearly, a textbook without some worked examples and problems that a reader can try to solve, in order to test his or her understanding of the material, would be incomplete. However, the reader will immediately notice, when scanning through the chapters, that there are only a few worked examples, and no question-and-answer sections at the end of a chapter, as is common in many textbooks. This is deliberate and is not an omission. When designing questions and working through numerical examples, we found that a large number of sensible problems needed the input of data arrays, which would not have been easy to incorporate into a written text. Therefore, we have opted for an approach, that provides examples on the web pages associated with the book (the pages are on the Wiley website www.wiley europe.com/college/Telle).

For each chapter we have collated a range of questions and provided data. These will help the reader gain deeper insight into many of the processes we discuss. In addition, we have provided further material in this form of electronic access, specifically on topics that are very much in a state of flux today (e.g. attosecond and free-electron laser sources). This approach permits us to add or delete particular items as they develop or lose mainstream interest. Also, we have provided some additional material in colour; although not essential, colour often makes particular aspects easier to visualize, e.g. graphs, figures and images.