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New Spectroscopic Methods in Gas-Phase Chemical Kinetics

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The possibilities provided by the application of advances in laser technology to the solution of problems in gas-phase chemical kinetics have been analysed. The basic principles of various laser methods for producing and recording active chemical species have been described. Examples of the use of lasers to study the reactions of radicals and excited species, in the diagnostics of complex chemical processes, and to carry out selective laser-chemical reactions have been examined.
The bibliography contains 110 references.

CONTENTS

I. Introduction 231
II. Methods of laser spectroscopy 232
III. The use of lasers in gas-phase chemical kinetics 235

I. INTRODUCTION

Particular attention has been paid to different problems at various stages of the development of gas-phase chemical kinetics, depending on the state of the theory, practical requirements, and available methods of study. In recent years, a qualitative leap has been made in physicochemical methods of study. The production of lasers, particularly tunable lasers, has made it possible to develop effective methods both for studying a chemical reaction and for influencing it. These methodological possibilities have not only raised studies in traditional directions to a qualitatively higher level but have also defined new and promising problems in gas-phase chemical kinetics.

From the beginning of the development of gas-phase chemical kinetics, two main directions have existed: the study of the general regular features of the course of complex chemical reactions and the study of the elementary steps. The study of complex chemical reactions has shown that most of them consist of a set of elementary steps involving extremely reactive intermediate species — radicals. The general regular kinetic features of radical, chain, and chain branched reactions have been established. These general regular features have been demonstrated for oxidation, halogenation, and cracking reactions. A fundamental contribution to the development of this field was made by Semenov's general theory of chain reactions.[1,2]

The course of a chemical reaction is influenced considerably not only by the active species but also by the energy liberated in the exothermic elementary stages. Allowance for the liberated energy has led to the establishment of the regular features of the non-isothermal course of a reaction. A theory of thermal self-ignition has been developed.[2,3] In these theories, however, it has been assumed that the energy is liberated as heat, and that it can be characterised by a single temperature for all degrees of freedom.

Analysis of all the established regular features has shown that the study of complex chemical reactions cannot be restricted to kinetic measurements of the concentrations of stable species, but must include the recording of the radicals driving the reaction chain and the quantitative study of elementary reactions. The need for quantitative data on elementary reactions is increasing continuously, due to the increasing demands of practice, which requires increasingly reliable quantitative information on the mechanisms of chemical processes.

At the present time there are comparatively simple and general theoretical approaches for calculating the rate constants of elementary reactions taking place under the conditions of Maxwell–Boltzmann energy distribution for the species. These are the transition state method for direct bimolecular reactions and the statistical theory of unimolecular reactions (RRKM theory) and bimolecular reactions, which essentially uses the ideas of the transition state method. These theories give explicit expressions for reaction rate constants in terms of the parameters of the potential energy surfaces.[4-6] The accuracy with which these parameters are known is quite inadequate, however, so that the experimental determination of the rate constants of elementary reactions remains an important problem in gas-phase chemical kinetics.

The subsequent development of the theory of gas-phase chemical kinetics is related to the fact that different forms of the energy of molecules (translational, rotational, vibrational, and electronic excitation energy) are not equivalent from the viewpoint of overcoming the activation barrier. A large number of studies have shown that the breakdown of the Maxwell–Boltzmann distribution of the energy with respect to different degrees of freedom of the reacting species may have a significant influence on the course of a reaction. One clear example of this is provided by the discovery of the class of reactions with energy branching.[7-9] In reactions of this class, vibrationally excited products are formed in the elementary stages of chain propagation. These vibrationally excited species take part in chain branching in different ways. Many complex chemical processes must probably now be analysed with allowance for their energetic non-equilibrium character. The breakdown of the Maxwell–Boltzmann distribution may be brought about not only by a chemical reaction but also by physical methods, for example in plasmochemical and photochemical processes. The production of chemical lasers[10,11] has shown that chemical reactions can be used successfully to convert chemical energy into the energy of coherent optical radiation.

Simple allowance for the reactions of atoms and radicals is insufficient for the kinetic analysis of energetically non-equilibrium processes. It is necessary to know the rate constants of the microscopic processes involving reagents and products in definite quantum states. In this sense it can be said that gas-phase chemical kinetics has now reached the quantum level. Calculations on elementary reactions of this type generally require a detailed analysis of the dynamics of the process, which is not carried out when the transition state method and statistical theory are used.[4-6]

In principle, if quantum effects are insignificant (and this is fairly often the case), the solution of the corresponding problem for a given potential surface is possible using present-day computing methods, even if tens of atoms are involved in the process of chemical rearrangement. As noted above, however, there are practically no data on potential surfaces. Thus the development of theoretical ideas requires

experimental data on the energy distribution in the reaction products, on the intermolecular processes involved in the transfer of different forms of energy, on the intramolecular processes of the transfer of excitation, and on the reactions of species in definite quantum states.

Progress in laser technology has increased sharply the possibilities provided by photochemistry. In laser photochemistry there is extensive discussion of the question of whether selective chemical transformations can be carried out by organising a non-equilibrium state of definite character. An example of selective laser photochemical processes is provided by the separation of isotopes under the influence of laser radiation.[12] The study of the more general principles of selective laser photochemistry is now being carried out in three directions.

1. The selective rupture of molecular bonds in definite positions, and not according to statistical laws. For this it is necessary to develop a method for exciting "local modes" by a powerful short pulse so effectively that they undergo rupture before the energy acquired by the molecule in the pulse is able to undergo statistical redistribution.

2. The carrying out of endothermic reactions at low temperatures by the transfer to the reacting species of that form of energy which is most effective for overcoming the activation barrier.

3. Elementary processes of a new type, which have been called "chemical radiation collisions"[13] are now being discussed. In these new processes, reacting species and photons take part in reactions simultaneously. It should be emphasised that these are not the reactions of reagents excited by light, but reactions in which the powerful electromagnetic field of a light wave changes the potential surface of a system, and hence the probability of the reaction and the reaction channel. The development of studies in this direction is restricted by the need to use very powerful sources of monochromatic radiation.

In the establishment of gas-phase chemical kinetics, most attention has been paid to purely scientific questions, whereas at the present time, fundamental studies are closely related to practical requirements. For example, the study of chemical processes in the atmosphere is related to such practical problems as the preservation of the ozone layer and the purity of the troposphere (smog, acid rain, etc.). The problem of organising economic combustion processes which do not contaminate the environment can now be solved using the details of the chemical mechanism of combustion with allowance for non-equilibrium and hydrodynamic factors. To optimise the operation of the active media in various gas lasers, it is necessary to know the quantitative characteristics of the elementary processes involving the excited species. The search for new active media for chemical lasers is closely related to the study of the energy distribution of reaction products.

Moreover, the organisation of energetically non-equilibrium processes in which the energy is used in the form most effective for overcoming activation barriers may provide a promising route for the development of new processes for chemical technology.

II. METHODS OF LASER SPECTROSCOPY

The present section examines methods for producing and recording labile species (atoms, radicals, excited species). The examination will be restricted to existing methods based on developments in laser technology.

1. Methods of Recording Labile Species

Laser spectroscopy is now widely used for analytical purposes (see the published review[14]). Only those methods which are used in gas-phase chemical kinetics will be examined here.

Laser absorption spectroscopy (LAS). In classical spectroscopy, the absorption method is used successfully, and more frequently than other methods. It is sufficient, for example, to mention the achievements of kinetic spectroscopy combined with flash photolysis.[15] One of the main problems in absorption methods is to increase their sensitivity with a high spectral resolution. Classical light sources generally have insufficient power in a narrow spectral range, and this restricts the sensitivity of classical absorption spectroscopy.

The use of a laser as a light source in the absorption method makes it possible to increase sharply both the sensitivity of the method and the spectral resolution. This is related to the fact that laser radiation is highly monochromatic, directed, and intense. Lasers are now used in both the infrared and visible ranges. Thus a spectrometer has been developed, based on tunable semiconducting lasers, with a working spectral range of 4–20.5 μm and a spectral resolution of $\sim 10^{-3}$ cm^{-1}.[16] Typical parameters of the absorption method (and other methods) are given in Table 1.

Table 1. Comparative characteristics of laser spectroscopic methods.

Parameter	Methods				
	LAS	IRLS	LMR	FP	CARS
Time resolution, s	10^{-6}	10^{-6}	10^{-2}—10^{-3}	10^{-8}—10^{-9}	10^{-8}
Spatial resolution	1 mm	1 mm	1 mm	10^{-6} cm^{-3}	10^{-5}-10^{-6} cm^{-3}
Sensitivity, cm^{-3}	10^{12}—10^{13}	10^{8}—10^{10}	10^{8}—10^{10}	10^{6}—10^{10}	10^{13}—10^{14}
Spectral resolution, cm^{-1}	0.03	0.03	10^{-2}—10^{-4}	10^{-3}	10^{-2}—10^{-3}
Spectral range, μm	0.2—10	0.4—1.2 and 2.7—3.0	4.0—2000	0.2—1.0	infrared range

Laser magnetic resonance (LMR). The physical principles of LMR are similar to those of EPR. The energy of the laser quantum is chosen to be close to the energy gas (ΔE) between two levels of the fine structure in the case of atoms and two rotational or vibrational-rotational levels in the case of radicals. Resonance between ΔE and the energy of the light quantum is achieved using an external magnetic field. The radiation sources used are gas lasers in the sub-millimetre range (H_2O lasers, lasers with optical pumping) and in the infrared range (CO_2 and CO lasers).

The first laser magnetic resonance spectrometer (LMRS) in the sub-millimetre range was developed in the USA in 1970,[17] and the first LMRS operating in the infrared range, based on a CO_2 laser, was developed in 1975 in the Institute of Chemical Physics of the Academy of Sciences of the USSR.[18]

The high sensitivity of magnetic resonance methods is due primarily to the use of magnetic modulation and a synchronous detection system. A second factor increasing the sensitivity is the positioning of the reaction vessel inside the laser resonator. A theoretical analysis of in-resonator absorption in LMR has been carried out,[19] and the theory has been verified

experimentally.[20] It was found that there is an optimum value of the frequency of magnetic modulation (which is close to the frequency corresponding to the characteristic vibrational relaxation of the laser) at which there is a marked increase in the effective length of the optical path. The fact that this optimum frequency is close to the frequency of modulation of standard EPR spectrometers enabled Gershenzon and coworkers[21] to develop a new class of combined EPR–LMR spectrometers, based on standard radio-spectrometers. In this spectrometer, the gas specimen is present simultaneously in the resonator of the EPR spectrometer and in the resonator of the CO_2 laser. The parameters of the LMR method when used under continuous conditions are given in Table 1.

The possible use of LMR with a resolution of ~4 μs was recently demonstrated.[22] The relatively high sensitivity (~10^{11} SiH_3 radicals per cm^3) was achieved by signal accumulation.[22]

In-resonator laser spectroscopy (IRLS). IRLS was proposed by Soviet workers in 1970.[23] The method is based on the influence of the substance being studied on the parameters of laser radiation. In IRLS, the substance being studied, for example a gas with species having narrow absorption lines in the lasing band, is placed in the resonator of a laser with a broad amplification contour. The parameters of the active medium of the laser are selected in such a way that the amplification of the light intensity in it compensates the losses at the mirrors, but does not compensate the losses associated with the absorption being studied (these losses are distinguished by their frequency dependence). The losses at the mirrors correspond to broader bands, compared with the narrow absorption lines of the substance being studied.

The problems related to the analysis of the necessary conditions for obtaining high sensitivity have been described.[24] In IRLS it is possible to use media in which the width of the uniform lasing contour is much greater than the width of the absorption line in gases. It has been shown theoretically and experimentally that the intensity of lasing at the frequency of the absorption line will be described by the equation:

$$I = I_0 \exp\left(-\sigma n \frac{l}{L} ct\right)$$

where n is the concentration of the substance being studied; σ the photon absorption cross-section; c the velocity of light; l the length of the cell; L the length of the resonator; t the lasing time; and I_0 the intensity of the radiation at the start of lasing, which is assumed to be independent of the frequency. The intensity of lasing at other frequencies, not coinciding with the absorption lines, is practically independent of time.

This equation shows that the method is analogous to the absorption method; the optical path length is $(l/L)ct$. For a lasing time of 10^{-3} s and $l/L = 0.3$, the optical path length is 10^5 m. This long optical path length can be achieved with a reaction vessel with small geometric dimensions. At the same time, the brightness of the light source remains high, and it is possible to use spectrographs with a high spectral resolution.

The active media used in IRLS include glasses doped with neodymium, solutions of organic dyes, and alkali metal halide crystals with colour centres.

Laser induced fluorescence (LIF). The LIF method involves the laser excitation of the electronically excited states of atoms and molecules and the subsequent observation of fluorescence from these states. The intensity of the fluorescence in most cases is proportional to the population of the state excited by the light, and this makes it possible to measure the concentration of molecules in this state. The excitation sources used include pulse and continuous lasers, most frequently dye lasers. The fluorescence is usually observed in a direction at right angles to the line of propagation of the laser radiation. The applicability of the method is restricted by the need for a fairly high fluorescence yield. This last requirement, because of the existence of non-radiative deactivation of electronically excited states, restricts the possibilities provided by the method at fairly high pressures. In those cases where the LIF method is applicable, however, it is very effective. This is related to the fact that the method shows high time and spatial resolution and unique sensitivity. The high spatial resolution makes it possible to carry out a local analysis in a very small volume. Theoretically, this volume may amount to λ^3, where λ is the wavelength; in practice, a volume of ~10^3 μm^3 is easily achieved. The time resolution of the method is related to the duration of the pulse (reaching 10^{-12} s).

The highest sensitivity can be achieved using continuous lasers for the excitation; it is often possible to realise saturation conditions, that is conditions in which the species being studied exists for equal times in the excited and ground states. In this case, even a single atom can emit a large number of photons in one second, and this makes it possible to record single atoms.[25] The use of continuous lasers, however, has some disadvantages, such as the relatively small spectral range of operation (400–900 nm) and the low time resolution. For a number of problems, therefore, it is more appropriate to use pulse lasers (particularly in the ultraviolet range) in the LIF method.

The development of non-linear optics has made it possible to move far into the short-wave range of the spectrum using powerful pulse lasers and frequency-doubling crystals. A spectral range to 200 nm is now easily achieved. Lasing at much shorter wavelengths of the spectrum has also been described. For example, the production of non-tunable radiation in the region of 39 nm has been reported.[26]

Active Raman spectroscopy (ARS or CARS). This method is based on the fact that in a field of sufficiently intense light rays with frequencies ω_1 and ω_2 satisfying the condition $\Omega = \omega_1 - \omega_2$ (Ω is the frequency of the molecular vibrations), build-up of molecular vibrations with frequency Ω takes place. As a result, the light ray with frequency ω_1 begins to be scattered on the excited vibrations with the appearance of radiation at the anti-Stokes frequency ($\omega_a = \omega_1 + \Omega = \omega_2 + 2\Omega$). The sensitivity of the method depends on the intensity of the radiation at the frequency ω_a. To obtain sufficiently intense radiation at the frequency ω_a it is necessary that definite relationships between the wave vectors of the light rays with frequencies ω_1 and ω_2 be satisfied. This condition is most frequently satisfied by using collinearly propagating light rays with frequencies of ω_1 and ω_2. Although this configuration is easily realised, it lowers the spatial resolution of the method. There are however methods which make it possible to obtain high sensitivity together with good spatial resolution by this method. CARS has been described in detail.[27] The CARS method most frequently uses the second harmonic of a YAG:Nd^{3+} laser (frequency ω_1) and a tunable laser based on dye solutions (frequency ω_2).

2. Comparison of the Methods

The possibilities of using laser spectroscopy to solve problems in gas-phase chemical kinetics are determined by the following parameters: sensitivity, time resolution (which

characterises the speed of the method), spectral resolution (which makes it possible to record species in definite quantum states), spatial resolution (which shows the possibility of local analysis), and the spectral range of action of the method (which characterises the universality of the method). These characteristics of the methods show that a particular method is preferred for the solution of each problem. The parameters of the methods described above are given in Table 1. It should be emphasised that the figures given in Table 1 are not the best values, but typical values achieved in many studies. The sensitivity depends not only on the method but also on the absorption cross-section of the species being recorded. Since the values of the cross-sections are different for different molecules, the sensitivity of the methods is represented by a fairly wide range of values in Table 1.

Table 1 shows that the absorption method, and also the IRLS and LMR methods, do not make it possible to carry out a local analysis. In those cases where the reaction medium shows symmetry with respect to one of the axes, these methods can be used to analyse the distribution of the concentration of the species in space. A volume local analysis can be carried out only by LIF and ARS methods. These methods also have the highest time resolution. The LIF method has the highest sensitivity, although it is not very general, since the radiative channel for the relaxation of the excitation is often very weak. The ARS method, however, is fairly universal. The use of a tunable laser in this method makes it possible to select any frequency difference $\omega_1 - \omega_2$, so that ARS can be used to record any species in which there is an active Raman transition. A disadvantage of the ARS method is the relatively low sensitivity.

The absorption method and the LMR method are also fairly universal, since they cover the infrared range, in which the vibrational frequencies of many species lie. LMR can record only paramagnetic species, whereas the absorption method can record all species. The sensitivity of the LMR method is much higher, however. The combination of LMR and EPR in a single instrument increases the possibilities provided by LMR, since the measurement of the absolute concentrations by the LMR method can be carried out using EPR, for which a method for measuring absolute concentrations already exists. The LMR method, and also the absorption method using continuous lasers, have relatively low time resolution. Pulse versions of LMR and the absorption method have recently appeared, which make it possible to obtain a time resolution of $\sim 10^{-6}$ s.[16-22] One of the disadvantages of working in the infrared range is the sharp decrease in sensitivity in studies at high pressures, because of pressure broadening of the absorption lines. IRLS makes it possible to work with a high sensitivity at higher pressures. This method also has a fairly high time resolution. IRLS makes it possible to record with a high sensitivity not only absorption, but also the amplification of light when there is inversion of the population of the energy levels in the medium being studied. A disadvantage of the IRLS method is the restriction of the spectral range of applicability in the ultraviolet (to 350 nm).

Comparison of the parameters of the method described shows that the methods supplement one another. The parameters given in Table 1 for these methods show the type of problem for which it is appropriate to use a particular method. Thus ARS should be most widely used to probe flames. In combustion processes, the concentrations of even the labile species are generally relatively high, so that a high sensitivity is not required. For the solution of these problems, primary importance is also acquired by the characteristics of the ARS method, since it is universal, and permits local analysis. For the study of reactions involving radicals, laser spectroscopy in the infrared range is most widely used. It is convenient to use LMR to record radicals. LMR combined with EPR is particularly promising for the study of the kinetics of the reactions between two radicals.

For the study of processes involving very short-lived species, it is appropriate to use pulse methods such as IRLS and LIF, which give the required time resolution. Because of its unique sensitivity, it is also appropriate to use LIF to obtain information on the primary distribution of energy in an elementary chemical experiment.

Specific examples of the use of these methods will be described below.

3. Methods for Producing Labile Species

To study various processes involving labile species, it is necessary to have methods for obtaining them. The present examination will be restricted to laser methods for producing radicals and excited species. The most widely encountered method for obtaining radicals is by flash photolysis. The combination of this method with classical kinetic spectroscopy made it possible to begin the quantitative study of reactions involving radicals. In the classical version of the method, however, it was usually necessary to use a high energy flash to produce the photolysis; the light was not monochromatic. As a result of absorption, part of the light energy was used up in the dissociation of the molecule, and part was liberated in various degrees of freedom of the molecules and their fragments. The existence of excited species of different types and the non-isothermal conditions under which the reaction took place, often made quantitative studies difficult.

The use of the more sensitive methods of laser spectroscopy to record radicals makes it possible to lower considerably the energy of the radiation producing the photolysis. The replacement of the light source by a laser source makes it possible to use monochromatic radiation for the photolysis, and hence to obtain radicals (and other species) with a definite energy content. Another advantage of the use of lasers for the production of radicals and excited species is the possibility of producing the necessary concentration of labile species in a local volume in very short time intervals. If the labile species are recorded in a local volume with very short delay times between the irradiating and probing pulses, even lower irradiation pulse energies are required to produce a detectable concentration of labile species.

The simplest method fairly frequently used to obtain excited species is by direct one-photon optical excitation. This method is most frequently used in the infrared range for the selective excitation of the lower vibrational states of molecules.[28-30] For medium absorption cross-sections $\sigma = 10^{-18}$–10^{-20} cm^2 and existing laser powers, it is fairly easy to achieve saturation conditions, that is to transfer half of the irradiated molecules from the ground to the excited state. An analgous technique can be used to excite the electronic states of molecules in the visible and ultraviolet ranges. The possibilities in this case (from the viewpoint of the ease of obtaining high concentrations of excited species) do not differ greatly from the conditions in the infrared range.

Direct one-photon optical excitation can also be used to obtain excited species in higher vibrational levels. It is possible to use initial excitation of the molecule into an electronically excited state by a quantum of visible or ultraviolet light and subsequent internal conversion of the molecule from the excited electronic state into high vibrational levels of the ground state.[31] Another method involves the direct excitation by a quantum of visible light of the higher overtones of the vibrational transitions of a molecule. In spite of the fact that the cross-section of this process is small, the high power of the laser source makes it possible in a number of cases to

produce an appreciable concentration of molecules in states excited to high vibrational levels.[32,33]

The high power of laser radiation makes it possible to use multiphoton processes of different types to produce excited species. These processes include, for example, Raman scattering, in particular stimulated Raman scattering (SRS). In a number of cases it is possible to obtain up to 10^{16} photons at the Stokes frequency after one laser pulse. Since each photon at the Stokes frequency corresponds to one excited molecule, it can readily be seen that SRS can be used to obtain appreciable concentrations of excited species. It is particularly fortunate that when Raman scattering is used, it is possible to excite the levels of molecules corresponding to transitions which are inactive in the infrared spectrum and which therefore cannot be excited by direct optical excitation, for example the totally symmetric vibration (in particular, it is possible to excite the homonuclear diatomic molecules H_2, N_2, etc.).

Excited species are often produced by SRS under pre-threshold conditions at low pressures of the mixture being studied. Laser radiation with two frequencies in the visible range ω_1 and ω_2 is directed on to the object being studied, and the frequency difference corresponds to the frequency of the vibrational transition of the molecule being studied. The radiation of frequency ω_1 is usually the powerful radiation of a non-tunable laser (for example the second harmonic of a YAG : Nd^{3+} laser), and the radiation of frequency ω_2 is obtained by SRS in a high-pressure cell filled with the substance being studied. The use as the source of the radiation ω_2 of the frequency-tunable radiation of a dye laser (two-frequency coherent excitation (TCE) method[34] is promising. The multiphoton infrared excitation of molecules has been widely used.[35,36]

Methods for obtaining species excited to definite levels of internal degrees of freedom have not yet been considered. In a number of cases, however, laser methods also make it possible to obtain molecules with a velocity vector of definite magnitude and direction. If a molecule for which the line contour is determined by Doppler broadening is excited using a laser whose spectral width is appreciably smaller than the width of the absorption line, then only molecules moving at a definite velocity in the direction of the laser beam will be excited. For example, if the laser frequency corresponds to the frequency of the centre of the absorption line, only the molecules "at rest" will be excited.[37] Laser methods also make it possible to excite orientated molecules in definite fashion. Use is made of the polarisation of the laser beam, that is the fact that when radiation interacts with matter, selective excitation is undergone by those molecules for which the transition moment is parallel to the light polarisation vector. It is thus possible to study the reactions of molecules oriented in definite fashion and to investigate the influence of steric factors on the course of a reaction. Some examples will be given later.

III. THE USE OF LASERS IN GAS-PHASE CHEMICAL KINETICS

In this section, an attempt will be made, using specific examples, to demonstrate the possibilities provided by the use of lasers to solve problems in gas-phase chemical kinetics.

1. Elementary Reactions Involving Radicals

The modern development of the theory of chemical transformations, and the increasing demands being made by the chemical industry, require increasingly reliable and accurate quantitative data on the rate constants of elementary reactions. In addition, an important field of study has appeared, namely the chemistry of the atmosphere, in which traditional macro-kinetic methods are probably generally inapplicable, and the modelling of chemical processes by a set of elementary reactions is of decisive importance. Most gas-phase reactions involve the participation of atoms and radicals. The greatest experimental difficulties are encountered when recording polyatomic radicals. Table 2 gives examples of elementary processes of several types involving polyatomic radicals: a) reactions of radicals with stable molecules; b) reactions between radicals; c) processes involving the heterogeneous destruction of radicals. The examination has been restricted to several examples of reactions involving radicals consisting of three or more atoms.

Table 2. Some elementary reactions of radicals, studied by laser spectroscopy.

Radical	Reagent	Method
NH_2	NO [38—40]; O_2 [41, 42]; O_3 [43, 44]; C_2H_4, C_2H_2 [40]; HO_2; NH_2 [45]; CH_3 [46]	IRLS [38, 42, 43, 45]; LAS [41]; LIF [39, 40, 44, 46]
CHF	O_2, NO [47]	LIF [47]
HCO	O_2 [48, 49]; NO [48, 50]; H [51]; HCO [52]	IRLS [48-52]
HNO	NO, HNO [53]	IRLS [53]
PH_2	O_2 [54], PH_2 [55]	IRLS [54, 55]
HO_2	NO [56]; HO_2, O, Cl, OH [57,58]; ClO[59]; H[60]	LMR [56-60]
NF_2	NF_2 [61]; O, N, F, H [62]	LMR [61, 62]
CH_3O	O [63]	LIF [63]
$C_6H_5CH_2$	O_2, Cl_2 [64]	LIF [64]
NH_2	surface of quartz reaction vessel	IRLS [38]; LIF [40]
HO_2	ditto	LMR [65]

Note. Numbers in square brackets denote references (Ed. of Translation).

The high reactivity of radicals makes it difficult to obtain them in sufficiently high concentrations. Moreover, if it is nevertheless possible to create high concentrations of radicals, the study of the reaction of a radical with a molecule is always made difficult by the existence of quadratic reactions involving the interaction between radicals. Thus one of the basic features required of modern methods for studying elementary reactions is a high sensitivity. It can be seen from Table 2 that it is because of the low sensitivity of the CARS method that it is not usually employed for the quantitative study of elementary reactions. All the other methods discussed earlier are used to study elementary reactions.

An attempt will now be made to discuss the advantages and disadvantages of each method in relation to the problem being discussed in the present section. LMR is attractive primarily because of its universality and the possibility of recording (particularly for LMR using lasers in the sub-millimetre region of the spectrum) many paramagnetic species involved in an elementary reaction. In addition, the possibility of obtaining the EPR and LMR spectra simultaneously using combined LMR–EPR spectrometers facilitates the task of determining absolute concentrations in the study of the reactions of radicals, when the concentrations of the reacting species are comparable.

In a study[62] of the reaction $O + NF_2$ using a combined LMR–EPR spectrometer, [O], [NF_2], and [F] were recorded. This made it possible to obtain the rate constant of this reaction and to determine the main channel by which it takes place

$$O + NF_2 \rightarrow FNO + F$$

The following reversible reaction has been studied:[56]

$$HO_2 + NO \rightleftarrows OH + NO_2$$

This work[56] is of interest from the methodological viewpoint, since the concentrations of the species OH, HO_2, and NO_2 were measured. This made it possible to study the temperature dependence of the rates of both the forward and back reactions.

A disadvantage of the LMR method is its low time resolution. For this reason, LMR is combined with flow methods. When sufficiently rapid gas streams are used, the effective time resolution can be brought to ~10^{-3} s. Nevertheless, in the study of a reaction under flow conditions, side processes of different kinds, for example heterogeneous processes, may be superimposed on the reaction being studied. It was noted above than an LMR method with a high time resolution has been developed.[22]

The IRLS and LIF methods have a fairly high time resolution (see Table 1). They can therefore be used in static systems with the flash production of radicals. The use of these methods, because of their high time resolution, makes it possible to avoid the influence of heterogeneous processes, that is to study a reaction in a time which is shorter than the diffusion time of the active species to the walls of the reaction vessel. An example is provided by the use of IRLS to study the reactions of PH_2 radicals.[54,55] Another important advantage of IRLS in the visible wavelength range is that it can be used at high pressures in the system. This makes it possible, for example, to measure the rate constants of fairly slow reactions. IRLS, combined with flash photolysis, has been used[42] to study the destruction of NH_2 radicals, formed by the photolysis of NH_3, in the presence of O_2. The total pressure in the system reached 570 mmHg, and in principle could have been even higher. This made it possible to estimate the rate constant of the reaction $NH_2 + O_2 \xrightarrow{k_1}$ products; $k_1 < 3 \times 10^{-18}$ $cm^3\ s^{-1}$. IRLS has also been used[66] to estimate the rate constant of an even slower reaction: $HNO + O_2 \xrightarrow{k_2}$ products; $k_2 < 8 \times 10^{-20}$ $cm^3\ s^{-1}$.

The main disadvantage of the IRLS method is its as yet short spectral range of action, which restricts the universality of the method. At the same time, the use of radiation in the infrared range within the framework of this method is now being developed, and this should extend considerably the possibilities provided by the method.

The data in Table 1 show that the LIF method has the highest limiting sensitivity. Although as already noted the requirement of a high fluorescence quantum yield restricts the number of species which can be followed by this method, it is widely used, particularly in other countries, to study the kinetics of chemical reactions. The method has been used to measure the rate constants of a large number of reactions involving both diatomic (OH, SH, CH, C_2, etc.)[67,68] and polyatomic (NH_2, CHF, CH_3O, $C_6H_5CH_2$, etc.) radicals. Some examples of reactions involving polyatomic radicals, which have been studied by LIF are given in Table 2.

LIF based on continuous dye lasers is fairly frequently used to measure reaction rate constants. As in the case of LMR, a flow system is used. An example of studies of this kind is provided by the measurement[40] of the rate constants of the reactions of the NH_2 radical with NO, NO_2, C_2H_2, C_2H_4, allene, etc.

The most promising development from the present viewpoint is the combination of LIF with laser flash photolysis. Thus the reaction $OH + C_2H_4$ has been studied in the temperature range 291–591 K at pressures of 50–600 mmHg.[69] The OH concentration was followed by LIF using a quasi-continuous dye laser, which produced a sequence of lasing pulses with a duration of 8–10 picoseconds and a repeat frequency of 246 MHz. This made it possible to study the kinetics of the destruction of the OH radicals formed in the photolysis of an $N_2O + H_2O$ mixture under the influence of the radiation from an excimer laser based on ArF. The initial OH concentrations measured immediately after the photolysing pulse were 5×10^9–10^{11} cm^{-3}. In this study,[69] LIF was used up to a pressure of 600 mmHg. This was made possible by the sensitivity reserve of the method, in spite of the appreciable quenching of the fluorescence of the radicals at this pressure. LIF has been used[70] to study the reaction† $OH + NO_2 + M \rightarrow HNO_3 + M$ at pressures up to 10 atm.

2. Elementary Processes Involving Excited Species

Elementary processes involving excited species are molecular collisions accompanied either by a change in the energy of the internal degrees of freedom of the colliding species or by chemical transformations. The study of the reactions of species in definite quantum states is closely related to the study of the energy distribution of the products of the elementary reactions. This relationship exists as a consequence of the principle of microscopic reversibility. The present section therefore examines three types of elementary process: a) processes involving the transfer and relaxation of the energy of the internal degrees of freedom in the collisions; b) the reactions of the excited species; and c) the energy distribution of the products of the elementary reactions.

Studies of these processes can make an important contribution to the development of ideas which make it possible to understand the type of reactions in which a particular form of energy is most effective for overcoming the activation barrier. At the same time, the existence of these ideas will probably make it possible to formulate more general regular features for complex energetically non-equilibrium chemical reactions. The study of the reactions of excited species will help in the investigation of the dynamics of the interaction of the species. The rate constants of elementary reactions obtained under Maxwell–Boltzmann distribution conditions in fact carry little information on the dynamics of the interaction of the species. The specification of definite quantum states of the reagents and products makes it possible to detect finer details of the dynamics of collisions and the influence of the characteristics of the potential energy surfaces on the dynamics.

Information on the energy distribution of the reaction products is particularly important. These data make it possible to resolve the question of the possibility of using these reactions as active media for transforming chemical energy into coherent radiant energy. In addition, quantitative data on the behaviour of excited species are necessary for an understanding of specific energetically non-equilibrium processes taking place in chemical lasers, plasmochemical reactors, the upper layers of the atmosphere, etc.

a) Processes involved in the transfer and relaxation of the energy of internal degrees of freedom in collisions

These processes are now being fairly widely studied in both physical and chemical laboratories. The experimental results and theoretical analyses of these processes have been given in detailed monographs.[71,72]

These processes will therefore be dealt with very briefly; the treatment will be restricted to a few types, to demonstrate the possibilities provided by laser technology. Table 3 gives examples of various processes of this kind, with an indication of the methods used to produce and record the excited species.

The first example in Table 3 demonstrates the possibilities provided by laser methods for both the production and recording of excited species. The TCE method used to

†Here, M represents an inert-gas molecule.

produce excited species is very promising. In particular, this method makes it possible to obtain appreciable concentrations of excited species not only in lower but also in higher vibrational excited states. The second example demonstrates the possibility of studying processes of vibrational–vibrational (v–v) exchange for isotopic molecules. LAS, because of its high spectral resolution, makes it possible to record both isotopic species. The last example shows that the processes involved in the transfer and relaxation of vibrational energy are now being studied not only for stable species, but also for radicals.

Table 3. Examples of processes of vibrational relaxation and energy redistribution studied by laser spectroscopy.

No.	Process	Method of excitation	Method of recording	Refs.
1	$CO_2(10^00)+CO_2(01^10) \rightarrow CO_2(11_10)+CO_2(00^00)$	TCE	CARS	[75]
2	$^{12}CH_3F(\nu_3)+{}^{13}CH_3F(0) \rightarrow {}^{12}CH_3F(0)+{}^{13}CH_3F(\nu_3)$	CO_2 laser	LAS	[74]
3	$NH_2(010)+M \rightarrow NH_2(000)+M^{**}$	FP*	IRLS	[75, 76]

*Flash photolysis.
**Here, M represents a molecule of He, Ar, CO, N_2, NH_3, O_2, or C_2H_4.

b) Reactions involving excited species

A large number of studies of reactions involving vibrationally or electronically excited species have now been carried out. The possibilities provided by the use of lasers in this field are illustrated by reactions of three types: the reactions of excited molecules with atoms, the reactions of excited molecules with stable molecules, and reactions involving the isomerisation and decomposition of excited molecules (Table 4).

Table 4. Examples of chemical reactions involving excited species.

No.	Reaction	Method of excitation	Refs.
1	$O+O_3(v) \rightarrow 2O_2$	CO_2 laser	[28]
2	$Br+CH_2F(v) \rightarrow HBr+CH_2F$	CO_2 laser	[29]
3	$Sr+HF(v) \rightarrow SrF+H$	HF laser	[30,77]
4	$NO_2^*+NO_2 \rightarrow 2NO+O_2$	Ar laser	[78,79]
5	$NO_2^*+CO \rightarrow CO_2+NO$	Dye laser	[80]
6	$NO_2^*+C_2F_4 \rightarrow CF_2O+CF_2+NO$	ditto	[79]
7	$O_3(v)+NO \rightarrow NO_2+O_2$	CO_2 laser	[81]
8	$O_3+NO(v) \rightarrow NO_2+O_2$	CO laser	[81]
9	$H_2C{=}CHCH_2NC+h\nu \rightarrow H_2C{=}CHCH_2CN$	Dye laser	[82]

*NO_2^* denotes an electronically excited NO_2 molecule.

Reaction No.1 was studied in Ref.28. The O_3 molecules were first excited by the radiation from a CO_2 laser (direct one-photon optical excitation (DOOE) into the first vibrational level of the vibrational modes ν_2 (or ν_1) and ν_3. The efficiency of the vibrational energy in overcoming the activation barrier of this exothermic reaction was determined.

Reaction No.2 was studied in Ref.29. DOOE was again used to produce the vibrationally excited species. The experiments showed that under the influence of the radiation of a CO_2 laser with a power of 20 W, the reaction rate increases by factors of several tens or hundreds (the increase is particularly marked at low temperatures). This increase in rate cannot be attributed to the participation in the reaction of only those vibrationally excited states of CH_2F which are excited directly by the laser radiation. This led the authors[29] to suggest that the increase in the rate of reaction is due to the participation in it of higher vibrationally excited states formed in processes of v–v exchange of energy. The authors showed that the vibrational energy is effective in overcoming the activation barrier of this reaction.

The study of the reactions of Sr atoms with the HF molecule in states with $v = 0$ or 1 (reaction No.3 in Table 4) is of considerable interest.[30,77] The reactivity of vibrationally excited HF molecules ($v = 1$) was studied using the so-called beam–gas configuration, that is the beam of Sr atoms from the furnace was directed into a cell containing hydrogen fluoride at a low pressure (~10^{-4} mmHg). The HF molecules were excited into the state with $v = 1$ by DOOE using an HF laser. The kinetics of the reaction were followed by LIF, by recording the reaction product SrF. It was found that the cross-section of this endothermic reaction ($\Delta H = 6.4 \pm 1.6$ kcal mole^{-1}) for HF ($v = 1$) is greater by at least four orders of magnitude than that for HF ($v = 0$).

The authors cited[30] compared their data with the results of a study of the dependence of the cross-section of reaction No.3 on the translational energy of the HF molecules. In this case, crossed molecular beams of Sr and HF were used. The reaction was again followed by LIF, from the product SrF. Comparison of the results of the two experiments showed that vibrational energy is apparently slightly more effective than translational energy in overcoming the activation barrier of the reaction.

Examples of the reaction of excited species with stable molecules are provided by the reactions of excited NO_2^* molecules with NO_2, CO, and C_2F_4.[78–80] In these studies, the NO_2 molecules were excited either by an argon laser or by dye lasers. The reaction $NO_2 + NO_2 \rightarrow 2NO + O_2$ is endothermic, whereas the reaction $NO_2 + CO \rightarrow CO_2 + NO$ is exothermic. Nevertheless, the rate constants of the reactions of the excited molecules NO_2^* with NO_2 and CO show the same dependence on the wavelength of the irradiating light. This fact is difficult to explain if it is assumed that only the vibrational form of the energy is effective in overcoming the activation barrier in these reactions.[79]

Table 4 also gives examples of processes involving the isomerisation of a molecule under the influence of laser radiation. The direction and rate of these reactions depend significantly on processes of intramolecular energy redistribution.

In a polyatomic molecule, even in the absence of collisions, as a result of the strong interaction of different degrees of freedom in a short time, relaxation processes take place, which wipe clean from the "memory" of the molecule those states in which it existed immediately after excitation, and these lead finally to some statistical distribution of the energy in the molecule. This raises the interesting question of whether it is possible to achieve conditions in which a chemical reaction is able to take place before the complete statistical redistribution of the energy. In this case it might be possible to control the directions of reactions by means of laser radiation. Thus one of the principal tasks in laser chemistry involves the investigation of the possibility of carrying out chemical reactions not according to statistical laws under the influence of a laser.

Until recently it was generally accepted that the processes involving the intramolecular redistribution of energy for polyatomic molecules at a sufficiently high level of excitation take place very rapidly (in times $\lesssim 10^{-12}$ s). This assumption was based, for example, on a large amount of experimental data on chemical activation, which are effectively explained by RRKM theory for unimolecular reactions. According to this theory, the energy of vibrational excitation of a molecule is able to undergo complete redistribution within the complex molecule, in times shorter than the characteristic time of the reaction, so that the decomposition obeys the laws of statistics. It has been suggested,[83,84] however, that in some cases the statistical theory (RRKM) effectively explains experiments on chemical activation because of the statistical character of the formation of the excited molecules.

A number of successful attempts have now been made to follow intramolecular processes of energy redistribution. These studies can be divided into two groups. The first group consists of studies of spectra containing bands which are assigned to the high overtones of the vibrations of polyatomic molecules. Highly sensitive methods of laser spectroscopy, IRLS and optico-acoustic spectroscopy, have made it possible to record the spectra of the overtones of the vibrations of a large number of molecules.[85,86] The width of the lines in these spectra is related to the lifetime of the excited state by the uncertainty relation. The recorded spectra generally relate to the overtones of the strongly anharmonic vibrations of C–H and N–H bonds. In most cases, the line width is large (for example 100 cm^{-1} for benzene[85]). This corresponds to lifetimes of the state of ~10^{-13} s. On the other hand, in a number of cases it is possible to observe the spectra of the high overtones of molecules with fairly narrow lines (for example, for NH_3 and C_2H_2 the line width is 0.3 cm^{-1} for excitation energies of ~2 eV).[86] This should apparently indicate a low rate of energy redistribution in this case. The second direction of studies involves the measurement of the rates of different unimolecular reactions of molecules which have been vibrationally excited as a result of the absorption of one quantum of laser radiation, and the comparison of the reaction rate constant obtained[33,82] with RRKM theory.

Table 5.

Reaction	Method of recording	References
$Ca(^1P_1) + HCl \rightarrow CaCl(A^2\Pi) + H$	LIF	[87]
$Ca(^1P_1) + HCl \rightarrow CaCl(B^2\Sigma) + H$	LIF	[87]
$O(^1D) + RH \rightarrow R + OH$	LIF	[88]
$HONO + h\nu \rightarrow OH + NO$	LIF	[37]

The unimolecular isomerisation of allyl isocyanate $H_2C{=}CH{-}CH_2NC$ has been studied.[82] The levels excited corresponded to the overtones of the vibrations of different C–H bonds in the molecule: saturated–alkene ($H_2C{=}$), unsaturated–alkene ($=CH-$), and methylene ($-CH_2-$). The excitation was carried out by placing the substance being studied in the resonator of a dye laser tuned to the wavelength corresponding to the absorption of the overtone being studied. The course of the reaction was followed by measuring the concentration of the reagents by an optico-acoustic method.

It was concluded[82] that the measured rate of isomerisation is slightly greater than that predicted by RRKM theory. Moreover, the reaction rate was found to depend markedly on the type of vibration excited (the highest rate was observed for the excitation of the vibrations of the $=CH-$ group). The results apparently indicate that on laser excitation, the allyl isocyanate molecule undergoes isomerisation more rapidly than the complete statistical redistribution of the energy within the molecule. It should be noted that although the observed deviations from RRKM theory are fairly small, their smallness, as pointed out by the authors cited,[82] may be related to different relaxational collision processes which "mask" the significant role of non-randomised states in the reaction.

c) The energy distribution of the products of elementary reactions

Examples of studies of this type are given in Table 5. As already noted, in the study of reaction No.3 (Table 4) by LIF, the molecules of the product SrF, formed in different quantum states, were recorded. The dependence of the distribution of the SrF molecules with respect to vibrational states on the direction of the polarisation of the radiation of the HF laser exciting the molecule of the HF reagent into the first vibrational level was observed. Thus when the polarisation of the laser beam was perpendicular to the direction of the beam of Sr atoms, the observed distribution of SrF molecules with respect to vibrational degrees of freedom for the reaction Sr + HF ($v = 1$, $J = 1$) corresponded to the following relationship: $v_0 : v_1 : v_2 = 1.00 : 0.63 : 0.29$. If however the polarisation of the laser beam was parallel to the direction of the beam of Sr atoms, the observed distribution was different: $v_0 : v_1 : v_2 = 1.00 : 0.72 : 0.13$. This experimental result agrees with theoretical predictions based on the assumption that the minimum in the reaction path for the reaction of HF with alkaline earth metal atoms corresponds to a bent configuration of the molecule.

It has also been shown[37,88] that laser methods can be used to study the influence of the relative orientation of the molecules of reagents on the energy distribution of the products. The reaction of Ca ($^1P_1$) atoms with the HCl molecule was studied.[88] The Ca atoms were excited into the state $^1P_1$ from the ground state $^1S_0$ using a dye laser with a wavelength of 422.6 nm. The atom beam–gas configuration (pressure ~10^{-4} mmHg) was used. The fluorescence of the CaCl molecules in the states $A^2\Pi$ and $B^2\Sigma$ formed in the course of the reaction was observed. It was found that when the polarisation of the exciting laser beam changed from the parallel (relative to the direction of the beam of Ca atoms) to the perpendicular, the intensity of the fluorescence from the state $B^2\Sigma$ decreased by 16%, and the fluorescence from the state $A^2\Pi$ increased by 7%. Since there were a large number of factors decreasing the selectivity of excitation, the authors cited pointed out that the significant influence of the geometry of the approach on the ratio of the channels by which the reaction takes place is being observed.

There have been a large number of studies of the distribution of the rotational and vibrational energy of OH radicals formed by the reactions of a $O(^1D)$ atom with different hydrogen-containing molecules. Thus the dynamics of the reaction of the $O(^1D)$ atom with saturated hydrocarbons has been studied.[89] Oxygen atoms in the singlet excited state $O(^1D)$ were obtained by the laser photolysis of ozone: $O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$ using the radiation of the fourth harmonic of a YAG : Nd^{3+} laser (duration 7 ns). With a short (20 ns–0.5 μs) delay after the photolysing pulse, the energy distribution of the OH radical reaction product was probed by LIF (a dye laser with a pulse duration of ~10 ns was used).

The distribution of the energy in OH radicals, formed in the course of the reaction, among the vibrational and rotational degrees of freedom was measured. The data on the distribution of the rotational energy are of considerable interest. It was found that the distribution is "bimodal" in character, indicating the existence of two reaction channels. One channel corresponds to a rotational distribution in which only the levels with small quantum numbers J are extensively populated. This channel was interpreted as the direct abstraction of an H atom from the hydrocarbon. The second channel corresponds to a broad distribution, in which levels with high values of J are also extensively populated. The second reaction channel was interpreted by the authors cited as the insertion of an O atom into the hydrocarbon molecule with the formation of an excited alcohol molecule, and its subsequent decomposition. The high value of the surprisal parameter indicates that the decomposition of the alcohol molecule is non-statistical in character. The channel involving the abstraction of an H atom is more characteristic of the higher hydrocarbons C_3H_8 and $C(CH_3)_4$, whereas for CH_4 and C_2H_6 a large contribution is made by the reaction channel involving the formation of the excited alcohol molecule.

Important information on the dynamics of the elementary act can be obtained by using laser methods to study photodissociation processes. In this case, the decomposition of a molecule excited by light is often described as "a half collision", signifying that the study of the decomposition of the excited molecule as it were gives half of the information on the inelastic collision of molecules, which takes place via the formation of the same excited state as the photodissociation.

Laser methods have been used[37] to study the photodissociation of the molecule of *trans*-nitrous acid (HONO). The *trans*-HONO molecule was excited by laser radiation with a wavelength of 369 nm, and it decomposed rapidly to OH and NO. The HONO molecule decomposes so rapidly that the molecule is unable to undergo a significant change in its orientation in the time interval between the absorption of the light quantum and its decomposition. The distribution of the energy of the OH radical reaction product among the different degrees of freedom was studied by LIF. It was found that the Doppler contour of the LIF excitation lines of the OH radical has a split maximum, corresponding to a small fraction of OH molecules having their velocity vector directed at right angles to the direction of the laser beams. Because of the polarisation of the radiation of the photolysing laser, only the molecules orientated in such a way that the dipole moment of the transition was parallel to the direction of the polarisation were excited, so that it can be stated that the OH radicals formed in the photodissociation of HONO move apart chiefly in a plane perpendicular to the transition moment of the HONO molecule. Modelling of the line contour form of the fluorescence excitation spectrum showed that the average rate of divergence of the OH radicals was ~2.58 km s^{-1} (which corresponds to a translational energy of 4720 cm^{-1}). From momentum conservation considerations it was found that the translational degrees of freedom of the OH and NO fragments correspond to 72% of the energy liberated in the photodissociation. The distribution of the OH radicals with respect to the rotational degrees of freedom was studied for different directions of the polarisation of the radiation of the photolysing laser. This established that the axis of rotation of the OH radicals is oriented preferentially in a direction parallel to the transition moment of the HONO molecule. It was established that the effective rotational temperature of the OH radicals is close to room temperature, and that there exists a state of non-equilibrium between the levels of types F_1'' and F_2'' (components of spin–orbit splitting).

The above studies show that extensive and detailed information on the dynamics of the elementary act can be obtained by laser methods.

3. Diagnostics of Complex Chemical Reactions

Until recently, because of the lack of sensitive methods for recording radicals, conclusions about the mechanisms of complex chemical reactions were reached on the basis of macrokinetic measurements of the concentrations of the original reagents and the stable products. The appearance of direct methods for studying elementary reactions has made it possible to confirm conclusions about the mechanism of a complex reaction by experimental data on key elementary stages. This method of investigating a complex mechanism remains basic today. This is because even the methods of laser spectroscopy usually do not have sufficient sensitivity for the diagnostics of slow chemical reactions. For chain branched reactions, however, the diagnostics of unstable intermediate species can be successfully undertaken by the methods described above. Thus LMR has recorded the SiH_3 radical in a rarefield flame of $SiH_4 + O_2$ [89] or $SiH_4 + Cl_2$,[90] and also the HO_2 radical in a rarefied $H_2 + O_2$ flame.[91]

A more general approach to the investigation of the mechanisms of chain branched reactions is possible by carrying them out under conditions of stationary isothermal propagation of the reaction zone.[92–94] The macrokinetic characteristics in this case are given by the measured dependence of the rate of propagation of the reaction zone on the initial conditions. Concentrations of intermediate species sufficient for recording by the methods of laser spectroscopy are formed in the reaction zone. Combined measurements of the concentration profiles of the intermediate species and the rate of propagation of the reaction zone would probably make it possible, in a comparatively small number of experiments, to obtain sufficient information to establish reliably the reaction mechanism.

The possibilities provided by kinetic laser spectroscopy in the study of elementary reactions are leading to the development of another approach to the establishment of the mechanisms of complex chemical reactions. The essential feature of this approach is the "construction" of the mechanism of a complex reaction on the basis of a systematic study of the elementary reactions, after which it is tested to find out whether it can explain available data obtained by macrokinetic measurements. This approach has been used[66] to investigate the mechanism of the photo-oxidation of ammonia. This approach is generally very laborious, however.

Even greater difficulties arise in the description of combustion processes. In this case the complex reaction mechanism is influenced by the non-isothermal course of the process and by hydrodynamic factors. It is for this reason that the study of combustion processes requires laser methods which have a high spatial resolution. The CARS and LIF methods are preferred in the diagnostics of combustion processes.

The possibilities provided by the use of these methods to study combustion processes have been reviewed.[95] It may be noted that certain difficulties are also encountered when both CARS and LIF methods are used in the diagnostics of combustion. In the first place, difficulties in the application of these methods are introduced by a whole range of effects of stray light: the luminescence of the flame, the scattering of the laser beam on non-uniformities, the luminescence of aerosol particles under the influence of the laser beam, etc. These phenomena introduce particular difficulties in the application of the LIF method. Another difficulty associated with

its use is the quenching of the fluorescence. Although the high sensitivity of LIF combined with the fairly high concentration of the species also makes it possible to observe fluorescence which has been partly quenched (even by many orders of magnitude of the intensity), the indeterminate nature of the rates of quenching and their possible dependence on the concentrations of various substances in the flame make it difficult to obtain a reliable profile even for the relative concentration of the species being studied in the flame. At the present time, however, the so-called saturated LIF method[96,97] has been developed, in which the study of the dependence of the signal of partly saturated LIF on the power of the exciting laser makes it possible to determine the rate of quenching of the fluorescence and the relative concentration of the material being studied in a given local volume.

The absence of fluorescence quenching, the high universality, and the weaker influence of stray scattering of various kinds (since the observation is carried out in the anti-Stokes region of the spectrum) make the CARS method very convenient for the study of combustion processes. A disadvantage of the method is the existence of a non-resonance scattering signal, which restricts the possibilities provided by the measurement of the concentrations of those species which make up a small fraction of the main gas; at the same time, the improvement of the CARS method suggests that this difficulty will be overcome.[98]

Although absorption methods do not make it possible to measure local concentrations at a given point, they can be used in the study of so-called planar flames. In this case the spatial resolution may be fairly high. Here, it is appropriate to mention the possibilities provided by the use of IRLS, particularly in the version where Raman scattering is used.[99] In this case, in addition to the universality of the IRLS method, there is also the advantage that it is only weakly sensitive to losses which are weakly dependent on frequency, and is not sensitive to stray scattering.

In a large number of recent studies, laser methods have been used to investigate combustion processes. Only some of these will be mentioned. LIF has been used[100] to measure the OH and NH concentration profiles in a stoichiometric $CH_4 + N_2O$ flame. It was also possible to obtain the temperature profiles in this flame. LIF, LAS, and analysis of the products have been used[101] to study the formation of polycyclic aromatic hydrocarbons in rich $CH_4 + O_2$ flames.

The CARS method and other methods using Raman scattering induced by laser radiation are also widely employed in the study of flames. The use of CARS to measure the concentrations of N_2, O_2, H_2, H_2O, CO, CO_2, and CH_4 in a flame has been reported.[95] CARS has also been used to measure the temperature profiles in engines.[102]

4. Laser Chemical Technology

The demands being made of chemical technology are constantly increasing, due largely to various aspects of environmental protection. The question of the creation of a chemical technology without waste is now being considered. Selective laser photochemistry opens up promising routes for achieving this in certain cases. The possibilities provided by the use of laser photochemistry in chemical technology have been reviewed.[103–105]

This question can be examined briefly by considering several examples of selective laser-chemical reactions, given below:

Reaction	Method of excitation	References
$N_2 + O_2 + h\nu \rightarrow 2NO$	SRS	[106]
$2NO_2 + C_2F_4 \xrightarrow{h\nu} CF_2O + 2NO$	argon laser	[79]
$C_2H_4Cl_2 \xrightarrow{h\nu} C_2H_3Cl + HCl$	excimer laser	[107]

The binding of atmospheric nitrogen is an endothermic reaction. It represents the first example of a reaction involving vibrationally excited molecules obtained by laser methods. In Ref.106, vibrationally excited nitrogen molecules were obtained by stimulated Raman scattering.

The oxidation of tetrafluoroethylene by nitrogen dioxide is an example of an exothermic reaction having an activation barrier. Thus at room temperature the dark reaction $NO_2 + C_2F_4$ takes place very slowly and non-selectively to give several products – fluorophosgene, tetrafluoroethylene oxide, perfluoroacetaldehyde, etc. When the isothermal (at 300 K) reaction is carried out under the influence of an argon laser, its rate increases by a factor of several tens, and the reaction takes place selectively to give the single product fluorophosgene.[79] It is possible to carry out this reaction selectively in another direction to give a product of practical importance, namely tetrafluoroethylene oxide. An unsatisfactory feature of this process is the fairly low quantum yield.

The third example is of interest in that laser radiation is used to bring about a chain reaction; in this case, therefore, the quantum yield of the product is very high ($\sim 10^3$). Laser photolysis only brings about chain initiation, and this makes it possible to carry out the reaction at lower temperatures than in thermal initiation. This leads to a decrease in the yield of side products, that is to an increase in the selectivity of the reaction. The advantage of the laser as photolysing source is that it is possible to achieve a high intensity of the monochromatic light which influences only the starting material, and does not bring about photolysis of the products.

Another promising application of lasers in chemical technology is the laser purification of materials.[108] The principles of laser purification are based on the selective action of the laser radiation on the impurities. The essential features of the method reduce to the conversion of the impurity molecules under the influence of radiation into species which can be readily removed from the reaction vessel. The photolysis of the impurities is carried out either by multiphoton dissociation under the influence of lasers in the infrared range or by one-photon dissociation using lasers in the visible or ultraviolet ranges. An example of the use of lasers in the infrared range is provided by a study[109] involving the selective multiphoton dissociation of organic impurities in $AsCl_3$ under the influence of a pulse CO_2 laser.

It should be noted that when multiphoton dissociation is used to purify gases, a larger proportion of the light energy of the laser is used up in heating the main material. In addition, the selectivity of action may be lowered as a result of collision processes at higher gas pressures. It may therefore be assumed that the use of lasers in the visible and ultraviolet ranges should be more promising for the laser purification of gases. The example of the use of an excimer laser to purify synthesis gas (a mixture of CO and H_2) from hydrogen sulphide can be considered. It is well known that, using catalysts, valuable materials can be obtained from synthesis gas; even extremely small quantities of H_2S impurity, however, poison the catalyst. It has been shown[110] that laser purification makes it possible to lower the concentration of sulphur-containing compounds in synthesis gas to below 10^{-7}, which is sufficient for effective operation of the catalyst. The authors cited[110] also carried out preliminary estimates of the economics of laser purification of the gas. They concluded that for an H_2S concentration below 10^{-6}, the use of excimer lasers to purify synthesis gas is economically favourable.

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