Translated from *Uspekhi Khimii*, 47, 967-991 (1978) U.D.C. 541.14

Infrared Photochemistry

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The characteristics of chemical reactions under the influence of infrared radiation and the conditions under which they occur in the absence of equilibrium between the vibrational and other degrees of freedom of the reacting species are examined. Studies on isotopically selective reactions, on the role of various types of energy (namely vibrational and translational energy), and on the overcoming of the activation barrier in chemical reactions are analysed.
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I. INTRODUCTION

The vigorous development of laser techniques in recent years has greatly extended the scope of photochemistry. The application of lasers with ultrashort (picoseconds) pulses made it possible to investigate ultrafast processes which previously had not been susceptible to direct experimental investigation. High radiation densities (megawatts and gigawatts per square centimetre) made it possible to achieve readily multiquantum processes. The highly monochromatic nature of laser radiation has led to selective photochemical reactions (including reactions selective with respect to isotopes).

Whereas in the visible and ultraviolet regions (i.e. in the regions of electronic transitions) the appearance of lasers significantly extended the scope of photochemistry, in the infrared region (i.e. in the region of vibrational transitions) photochemical research has become in general possible only after lasers became available. Until then there had been no sources of infrared radiation with a sufficiently high intensity to be capable of generating in a single, not necessarily very narrow, part of the spectrum excited species at a higher rate than in thermal equilibration processes. Infrared spectroscopy existed but not infrared photochemistry. One can point to only one study of the pre-laser period[1] whose author investigated the *cis–trans* isomerisation of nitrous acid in a low-temperature matrix (at 20 K) under the influence of infrared radiation isolated by filters from the emission spectrum of a heated body.

Numerous studies have now been published on infrared laser photochemistry. Some of them have been analysed in review articles on the chemical action of laser emissions[2-16] and the laser method for isotope separation[17-21] as well as a number of popular articles[22-25]. Most of the reviews have dealt with processes occurring under the influence of laser radiation over the entire spectral range and comparatively little attention has been devoted to the infrared region. Only brief reviews have been devoted to problems of infrared laser photochemistry[5,13].

We shall now formulate the fundamental distinctive features of infrared photochemistry, i.e. the photochemistry of vibrationally excited molecules, in relation to the photochemistry in the ultraviolet and visible regions, i.e. the photochemistry of electronically excited states.

The primary step in photochemical processes under the influence of ultraviolet and visible radiation is the formation of electronically excited species, which then usually decompose or isomerise. The large electronic excitation quanta make the contribution of the thermal reaction pathway insignificant compared with the photochemical pathway. When an infrared quantum is absorbed, vibrationally excited species are formed in the ground electronic state. Owing to the smallness of the infrared quanta, the population of the corresponding vibrationally excited state corresponding to thermal equilibrium is not as a rule negligibly small compared with the population induced by the radiation. For this reason, one of the distinctive features of infrared photochemistry is methodological difficulties associated with the competition between the photochemical and thermal reaction pathways. These difficulties are eliminated mainly by reducing the pressure and temperature. A decrease of pressure retards the deactivation of excited molecules, which is determined by vibrational relaxation in collisions with other species, while a decrease of temperature diminishes the thermal population of the vibrationally excited states. Thus infrared photochemistry is mainly the photochemistry of low pressures and temperatures.

Chemical reactions under the influence of ultraviolet and visible radiation are determined as a rule by the reactivity of the excited state formed in the primary light absorption step. In the infrared region this situation is rarely encountered. It is prevented by intramolecular vibrational energy transfer between different vibrational degrees of freedom, which is very rapid in complex molecules. For this reason, chemical reactions under the influence of infrared radiation may be determined by the reactivity of not only the directly excited bond but also of others. Furthermore, in the infrared region intermolecular energy transfer also plays a relatively major role. As a result, other more reactive species react instead of the molecule excited by infrared radiation; thus infrared photosensitisation must be a fairly common phenomenon.

One of the characteristics of infrared photochemistry is associated with the fact that the reactivity of vibrationally excited molecules increases sharply with increase in the amount of vibrational energy. For a fairly large amount of energy, other processes, such as the dissociation and ionisation of the molecule, also become possible. Multiquantum processes, i.e. processes involving highly excited states, therefore play an extremely important role in the infrared region.

Finally we may note that in the infrared region the quantum yields are usually low, whereas in electronic excitation they frequently approach unity. This is associated primarily with the relatively high rates of deactivation processes compared with the rate of reaction. On the other hand the faster multiquantum processes, such as multiquantum dissociation processes, show quantum yields much less than unity by virtue of the very nature of the process.

In the light of the characteristics of infrared photochemistry formulated above, one may specify three types of chemical reactions, with different degrees of complexity, under the influence of infrared radiation. Firstly, these are reactions under conditions where there is no equilibrium between the vibrational and translational degrees of freedom. One of the main scientific problems in these investigations involves the study of chemical reactions under non-equilibrium conditions, which is very important not only for laser photochemistry but also for plasma chemistry, chemical combustion, and other problems of practical importance. Whereas it is evident that in unimolecular decomposition reactions the vibrational energy is in fact responsible for overcoming the activation barrier, in bimolecular and other reactions the problem is more complex. One of the tasks in infrared laser photochemistry is the elucidation of the role of various types of energy (particularly vibrational energy) in the overcoming of the activation barrier in chemical reactions. A practical aspect of the studies under consideration is a more economical utilisation of the energy required to carry out the chemical reactions. In this case the energy is consumed in "heating" only the vibrational degrees of freedom of the reacting species and not of the entire substance. The high efficiency of modern infrared lasers (particularly the CO_2 laser) permits one to hope that they may be used in practice to achieve processes of this kind.

The second task—the selective involvement in the reaction of molecules having similar chemical properties, particularly isotopic molecules—is more complex. The high rates of exchange of vibrational energy between them make it possible to carry out such processes only in gases at low pressures or in the condensed phase at low temperatures under the conditions of matrix isolation of the excited molecules. Still greater difficulties arise in the solution of the third problem—the achievement of reactions via a selected pathway by "exciting" the corresponding vibrations as a result of the absorption of infrared radiation. Rapid intramolecular transfer of vibrational energy between different degrees of freedom in complex molecules prevents this.

Most studies on infrared laser photochemistry refer to processes in gases at low pressures. They can be divided into two groups. The first involves the study of the dissociation of polyatomic molecules as a result of multiphoton excitation by the action of powerful and short radiation pulses of infrared lasers (particularly the CO_2 laser) and the second involves the study of reactions with atoms and free radicals of molecules whose degree of vibrational excitation is comparatively low. Furthermore, there have been numerous studies where chemical reactions under the influence of infrared laser radiation were due to equilibrium thermal heating. These are mainly processes in gases at comparatively high pressures (tens and hundreds of mmHg) under the influence of continuous laser radiation. The number of studies on chemical reactions in the condensed phase or on solid surfaces has been much smaller owing to the high rates of relaxation of vibrational energy in liquids and solids.

Accordingly, in Section II we examine the competition between the thermal and photochemical mechanisms of reactions under the influence of infrared radiation and analysed studies at high pressures. Strictly speaking, a considerable proportion of these studies cannot be regarded as photochemical (or "laser-chemical"), but laser heating leads to characteristic features in the kinetics compared with the equilibrium heating by the wall. For this reason, the inclusion of these studies in the present review appears useful. Section III is devoted to the reactions of weakly excited molecules with atoms and free radicals. Section IV deals with the results of studies on the selective dissociation of polyatomic molecules under the influence of the pulsed radiation of infrared lasers. The rates of transformation of vibrational energy into translational and rotational energy and the rates of transfer of vibrational energy between different molecules and different vibrational degrees of freedom of one molecule are very important in all reactions involving vibrationally excited species. Numerous experimental and theoretical studies on this problem are now available in the literature and their analysis requires a special review. For this reason, we confine ourselves to an examination of relaxation processes in molecules whose reactions under the influence of infrared radiation have been investigated in greatest detail (Section V). Section VI is devoted to reactions in the condensed phase and on the surface.

The review does not deal with chemical reactions occurring on evaporation of condensed substances and following electrical breakdown in gases under the influence of infrared radiation. Nor do we consider processes involving multistage dissociation and ionisation, where the infrared laser radiation is used solely in the first stage, and processes associated with a change in properties of vibrationally excited molecules other than their reactivity.

II. COMPETITION BETWEEN THE THERMAL AND PHOTOCHEMICAL MECHANISM OF REACTIONS UNDER THE INFLUENCE OF INFRARED RADIATION

Irradiation of a substance by infrared light is inevitably accompanied by equilibrium thermal heating owing to vibrational-translational ($V-T$) relaxation. The problem therefore arises of the cause of the chemical reaction under the influence of infrared radiation: equilibrium thermal heating or the involvement of more reactive vibrationally excited species generated by the laser radiation.

The competition between the thermal and photochemical mechanisms of the transformation of the given substance under the influence of pulsed laser radiation has been examined in a study [26] where the criteria for the selection of the duration of the laser pulse and its intensity where the reaction proceeds via a non-thermal pathway were

formulated. Analysis of the thermal and radiation-induced populations of the excited states when the substance is acted upon by continuous laser radiation [27,28] led to the conclusion that there is a critical pressure above which the radiation-induced population cannot exceed the thermal population whatever the power of the laser emission. This critical pressure depends on the size of the infrared quantum, temperature, thermal conductivity of the mixture, the rate of $V-T$ relaxation, and the ratio of the diameters of the reaction vessel and the laser beam. For processes under the influence of the emission of the CO_2 laser at room temperature and for molecules of moderate complexity, the critical pressure does not exceed 1 mmHg.

The thermal and radiation-induced populations of vibrationally excited states have been analysed [26-28] in terms of a two-level approximation, i.e. without taking into account the vibrational–vibrational ($V-V$) relation processes. In reality these processes lead to a redistribution of vibrational energy among different degrees of freedom of the excited molecules. Since the rate of $V-V$ relaxation usually greatly exceeds the rate of $V-T$ relaxation, the energy undergoes equilibrium distribution among the vibrational degrees of freedom, which may be characterised by the vibrational temperature (different from the translational temperature). The criteria governing the "discrepancy" between the vibrational and translational temperatures and the possibility of carrying out chemical reactions under such conditions have been examined [29-31]. However, this analysis was carried out without taking into account the equilibrium thermal heating due to the infrared radiation. We may note that a complicating factor in the consideration of complex molecules is the high probability of $V-T$ relaxation from high vibrational levels. A general theoretical treatment of the distribution of excited species with respect to different vibrational states is not available in the literature for this case.

The first observations of chemical reactions under the influence of infrared laser emissions were made by French investigators [32-35], who recorded the glow of ammonia, ethylene, ethyl chloride, and their decomposition products under the influence of the emission from a continuous CO_2 laser on the gases at a pressure of several hundred mmHg. The authors themselves attributed the observed chemical reactions to equilibrium thermal heating. Subsequently a number of studies were made on the laser pyrolysis of ethylene [36-39], ammonia [40,41], and other compounds which effectively absorb the radiation generated by the CO_2 laser [42-51]. Analysis of the secondary infrared emission spectra under such conditions shows that they are caused by the heating of the gases in the region of laser irradiation [52-54]. The study of the bimolecular reactions of PF_5 with SO_2 [55] and of SF_6 with H_2 and O_2 [56] under the influence of the radiation from the CO_2 laser operating under quasi-continuous conditions (with pulses lasting $10^{-2}-10^{-3}$ s) showed that they also proceed via the thermal mechanism.

However, the authors of a number of studies dealing with chemical reactions under the influence of infrared laser radiation under conditions similar to those described above (i.e. at pressures of tens and hundreds of mmHg) hold a different view and attribute the reactions under these conditions to the non-equilibrium population of highly vibrationally excited states of the molecules irradiated by infrared light. These are the reactions of tetrafluorohydrazine with nitrogen oxides, hydrogen, methane, etc. [57-66], the bromination of pentafluorobenzene [67], the reaction of HBr with carboranes [68,69], the decomposition of Freons [70,72], the interaction of diborane with isobutene [73] and hydrogen sulphide [74], the interaction of boron trichloride with tetrachloroethylene [75] and trimethylboron [76], and the pyrolysis of acetylene [77].

One of the principal arguments of the authors of the majority of these studies in support of a non-thermal mechanism of the chemical reactions is higher rates and differences in the composition of the products of chemical reactions under the influence of infrared radiation compared with reactions under the conditions of ordinary heating to the corresponding temperatures. However, the difficulties in the direct measurements of the temperature rise induced by the laser radiation make it necessary to estimate the temperature by calculation, which hinders the comparison of the results corresponding to laser and thermal initiation of the reactions.

Another argument is the observation of threshold phenomena, i.e. a sharp dependence of the reaction rates on the intensity of the laser radiation when the latter is above a threshold value and the virtually complete absence of reactions below the threshold. According to the authors, the presence of the threshold may show that the rate of reaction is determined by the concentration of highly excited species with an energy much higher than the energy of the absorbed quantum. The probability of their formation in $V-V$ relaxation processes depends strongly on the intensity of the infrared radiation, the dependence being described by a power function. If the equilibrium temperature rise due to the infrared radiation is insignificant, the occurrence of threshold phenomena is indeed a serious argument in support of a photochemical process mechanism. However, the occurrence of an equilibrium temperature rise in the irradiated volume may lead to the same behaviour both in consequence of the pronounced exponential temperature dependence of the rates of the majority of chemical reactions and as a result of the initiation of thermal or chain explosion, so that experiments of this kind require careful analysis.

A number of studies have been devoted to detailed analysis of threshold phenomena in reactions under the influence of infrared radiation [60-63]. One should note that in most instances threshold phenomena have been observed in exothermic reactions. The given substance undergoes virtually complete conversion on irradiation with a single pulse despite the fact that only part of the reactor volume is irradiated. Evidently the pulse of infrared radiation initiates the reaction in the irradiated volume, after which it is propagated throughout the reactor. The explosive decomposition of ethyl iodide under the influence of the radiation of a continuous CO_2 laser has been explained [78] within the framework of the theory of thermal explosion initiated by the laser radiation. In the thermally neutral decomposition of monosilane [61] threshold phenomena have been observed less distinctly and the latter can also be accounted for within the framework of a thermal reaction mechanism: the exponential dependence of the rate of reaction on temperature (the temperature increases with increasing radiation intensity) can simulate effectively threshold phenomena. Thus the threshold phenomena cannot themselves serve as an unambiguous demonstration of a photochemical mechanism of reactions under the influence of infrared radiation.

At first sight non-ambiguous evidence for a non-thermal reaction mechanism at high temperatures was obtained in a study [70] where the decomposition of Freon (CF_2Cl_2) was investigated at a pressure of 100 mmHg under the influence of the radiation of a continuous CO_2 laser. We shall consider this study in greater detail. It involves the investigation

of the decomposition of Freon mixed with SF_6. The infrared absorption bands of CF_2Cl_2 and SF_6 are separated by 17 cm^{-1}. When the laser is tuned to a frequency of 948 cm^{-1}, corresponding to the absorption maximum of SF_6, Freon does not absorb the infrared radiation and, conversely, when the laser is tuned to ν_{max} = 931 cm^{-1} for CF_2Cl_2, SF_6 does not absorb. The SF_6 and CF_2Cl_2 pressures (4.4 and 100 mmHg respectively) were chosen so that the absorption of the infrared radiation by the mixture was the same in the above two experiments, which should have led to identical temperature distributions. If the reaction mechanism is thermal, the nature of the transformations should be independent of whether SF_6 or CF_2Cl_2 absorbs. It was shown experimentally that, when the laser is tuned to the SF_6 absorption, frequency the reaction does not occur (SF_6 is itself stable up to very high temperatures), whereas, on tuning the laser to the absorption frequency of CF_2Cl_2, the latter decomposes. The authors[70] conclude that the decomposition of Freon is due to its vibrational excitation and not to the temperature rise.

Although this conclusion is outwardly self-evident, detailed analysis has shown[43] that it is not unambiguous. In these experiments the absorption coefficients on which the calculation of the SF_6 and CF_2Cl_2 pressures necessary to equalise the absorptions was based were determined at room temperature with the aid of a low-power CO_2 laser. On passing to more powerful infrared radiation, where the gas is appreciably heated, the infrared absorption spectra change owing to the appearance of "hot" bands. Furthermore, it is easy to show[43] that the SF_6 absorption maximum undergoes a bathochromic shift under these conditions. This leads to a greater temperature rise in the mixture when the laser is tuned to 931 cm^{-1}, which is sufficient for the decomposition of Freon by a thermal mechanism. The results of the above study[70] as well as those of other investigations of chemical reactions under the influence of infrared radiation at high pressures have been analysed in detail[43] and it has been concluded that the evidence for a non-thermal mechanism of the laser-chemical reactions under these conditions is not sufficiently established.

As regards the differences in the composition of the products of laser-chemical reactions at high pressures, it has been shown[43] that they can be due to the exclusion of heterogeneous processes, because the reactor walls remain cold on laser heating. A number of studies involving the pyrolysis of ethane[44,45], formic acid[46], formaldehyde[47], methanol[48], and other compounds as well as the interaction of boron trichloride with acetylene[49], the bromination of pentafluorobenzene[50,67], and other reactions[51] have been devoted to the problem of the characteristic features of chemical reactions on laser heating[43-51]. Since not all substances absorb infrared radiation, they are frequently sensitised by compounds which absorb effectively the radiation of the CO_2 laser, mainly SF_6. In the majority of investigations it is emphasised that laser heating makes it possible to carry out reactions under rigorously homogeneous conditions. This permits the determination of the rate constants and activation energies for the reactions, which under the conditions of ordinary heating are complicated by heterogeneous side reactions[43, 46-48,50].

The exclusion of heterogeneous processes in the laser heating of gases at high pressures is apparently one of the main factors responsible for the unusual products of the chemical reactions. (The formation of mercaptoboranes[74], the reactions of tetrafluorohydrazine[57,58,64], the alkylation of diborane[73], etc.) Thus analysis of the experimental data for gas-phase reactions at pressures of tens and hundreds of mmHg under the influence of continuous and quasi-continuous (with pulses lasting 10^{-3}–10^{-2} s) laser irradiation shows that under these conditions chemical reactions take place mainly via a thermal mechanism. Laser heating can then lead to an alteration of the mechanisms of complex chemical reactions owing to the exclusion of heterogeneous processes. This can be used both for preparative purposes and for the investigation of quantitative kinetic relations governing the homogeneous stages of complex chemical reactions.

In order to avoid the influence of thermal heating on the rate of chemical reactions in systems acted upon by the radiation of continuous infrared lasers, it is necessary to carry out the processes at low pressures[27,28]. This has been confirmed experimentally by a study[79] in which the influence of the radiation of a continuous CO_2 laser on the induction period in the chain decomposition of chlorine dioxide was studied. At pressures more than 1 mmHg the induction period was shortened, i.e. the reaction was accelerated, due to the equilibrium thermal heating as a result of the absorption of the infrared radiation. However, at pressures below 1 mmHg, the induction period for the decomposition of ClO_2 increased under the influence of the laser radiation, which was explained by the acceleration of the $ClO + ClO_2 \rightarrow Cl_2O_3$ elementary stage owing to the vibrational excitation of the ClO_2 molecule; this leads to an increase of the induction period.

Low pressures limit the range of reactions susceptible to such investigations. It is necessary that the reaction should occur at a sufficient rate at low pressures (below 1 mmHg). The activation energy for such a reaction must be fairly low. Among molecular reactions satisfying this requirement, mention may be made of the decomposition of limonene at low pressures[42] and the decomposition of H_3BPF_3 under the influence of the radiation of a continuous CO_2 laser[80,81]. When the latter reaction was carried out at pressures in the range 10^{-3}–10^{-2} mmHg, the authors were able to observe isotopic selectivity with respect to both hydrogen and boron.

III. REACTIONS OF VIBRATIONALLY EXCITED MOLECULES WITH ATOMS AND FREE RADICALS

Reactions with low activation energies are convenient for the investigation of infrared photochemistry for two reasons. Firstly, their high rates make it possible to carry them out at low pressures, which permits investigations under conditions uncomplicated by equilibrium thermal heating. Secondly, for low activation energies, comparable with the energies of the infrared quantum, it is possible to ensure conditions where only vibrationally excited molecules, formed in the primary radiation absorption step, are involved in the reaction and the role of higher vibrationally excited states, arising in $V-V$ relaxation processes, is insignificant. One can then expect a high process selectivity owing to the differences between the infrared absorption spectra of the excited molecules.

The most common processes with low activation energies are those of atoms and free radicals with molecules. One of the problems in the study of the influence of infrared radiation on these reactions is that of the role of vibrational energy in overcoming the activation barrier. Here it is necessary to distinguish two situations. At very low concentrations of the absorbing gas, where the $V-V$

relaxation is slower than that $V-T$ relaxation and the reaction, it is possible to obtain information about the reactivities of individual excited states. At higher concentrations (which are nevertheless sufficiently low to rule out equilibrium thermal heating), where equilibrium is established between all the vibrational degrees of freedom and one can postulate vibrational heating, one may investigate the influence of vibrational temperature on the reaction at a fixed translational temperature.

A promising practical application of these studies involves chemical reactions which are selective with respect to isotopes. The isotopic selectivity may be not only the aim of the investigation but can also serve as a test of the reactivity of the excited isotopic molecule. In view of the high rates of exchange of vibrational energy between the isotopic molecules, the concentrations over which such processes are possible will be fairly low.

One of the first studies which demonstrated experimentally the increase of reactivity under the conditions of laser infrared excitation was that of Brooks and coworkers[82]. They recorded an increase by two orders of magnitude of the cross-section of the $K + HCl \rightarrow KCl + H$ reaction in a molecular beam on excitation of HCl by the radiation of a chemical HCl laser. The study of the role of translational energy in this reaction showed[83] that the reaction cross-section increases only by a factor of five for a corresponding increase in translational energy.

The rate of reaction of a vibrationally excited HCl molecule ($v = 1$), generated by a chemical HCl laser, with hydrogen and oxygen atoms has been measured[84,85]. The infrared fluorescence of HCl ($v = 1$) was recorded and at the same time measurements were made of the concentrations of H and O atoms. The study of the simultaneous decrease of fluorescence intensity yields the sum of the rate constants for relaxation by atoms, namely $O + HCl\ (v = 1) \rightarrow O + HCl\ (v = 0)$, and for the reaction $O + HCl\ (v = 1) \rightarrow OH + Cl$, while the measurement of the decrease in the concentration of atoms makes it possible to determine the reaction rate constant. The overall rates of disappearance of vibrationally excited HCl molecules ($v = 1$) have been measured[84] and it has been shown that, following interaction with hydrogen atoms, the rate of the reaction $H + HCl\ (v = 1) \rightarrow H_2 + Cl$ is negligibly small compared with the rate of relaxation, whereas following interaction with oxygen atoms its contribution is appreciable. Detailed measurements have shown[85] that the rate of reaction of HCl ($v = 1$) with oxygen atoms is lower by a factor of 20 than the rate of relaxation and that the reaction rate constant is $(1.1 \pm 0.3) \times 10^{11}$ cm^3 mole^{-1} s^{-1}. This made it possible to calculate the ratio of the rate constants for the reaction of oxygen atoms with an HCl molecule in the first vibrationally excited and ground states, which amounts to 300 ± 100. It is noteworthy that in this instance the HCl excitation energy (8.2 kcal mole^{-1}) greatly exceeds the activation energy for the reaction with oxygen atoms (4.5 kcal mole^{-1}), so that the maximum expected increase of the rate constant for a vibrationally excited molecule (at 300 K) is by a factor $\exp(4500/RT) = 1.8 \times 10^4$. The measured increase of the rate constant (by a factor of 300) shows that in this reaction the vibrational energy is not fully utilised to overcome the activation barrier.

The measurement of the rate constants for the reactions of vibrationally excited species is greatly simplified if one of the reaction products is also an excited species. In this case it is possible to use the highly sensitive and rapid technique involving the recording of its luminescence. The reactions of vibrationally excited ozone molecules with NO and SO have been studied[86-93]. They lead to the formation of electronically excited NO_2 (in the $^2B_1$ and $^2B_2$ states) and SO_2 ($^1B_1$) molecules, the luminescence of which was recorded. The vibrational excitation of ozone was achieved by means of the radiation of a continuous CO_2 laser which was modulated by a chopper. The luminescence signal of the electronically excited reaction products was also found to be modulated. At the same time the decrease in signal intensity is determined by the sum of the rate constants for relaxation and the reaction and the degree of modulation is determined by the rate constant for the reaction of the vibrationally excited molecules. The rate constants for the reactions of the vibrationally excited ozone molecules with NO and SO measured under these conditions exceed the corresponding values for the non-excited ozone molecules by factors of 5.6 and 2.5. Such low factors can probably be accounted for by the markedly exothermic nature of these reactions. It is not clear whether the acceleration of the reactions should be attributed to the reactivity of the excited state of the ozone molecule (ν_3 antisymmetric stretching vibration) or to the redistribution of the absorbed energy over all the vibrational states of O_3 under the conditions of these experiments.

The reaction of O_3 with NO is of interest because the NO molecule can also be vibrationally excited ($v = 1$) by the radiation of the CO laser (1884 cm^{-1}). Such experiments[94] led to an increase of the reaction rate constant by a factor of 5.7 after the vibrational excitation of NO. In this case one may confidently speak of the reactivity of the NO molecule in the first vibrationally excited state.

An analogous method (with excitation by a CO_2 laser) has been used to investigate the reactions of vibrationally excited O_3 with oxygen in the $^1\Delta_g$ state[90] and also to investigate the reactions of atomic oxygen with vibrationally excited C_2H_4 and OCS molecules[95]. In the latter case both direct excitation of the molecules by the radiation of the CO_2 laser and excitation via sensitisers (molecules with high absorption coefficients for the laser radiation, in the present instance CH_3F and CH_2F_2) was achieved.

The use of the rapid luminescence technique for the recording of reaction rates is difficult in reactions leading to the formation of non-excited products. The study of the decrease of the infrared luminescence signal due to a vibrationally excited molecule yields the sum of the rates of reaction and relaxation. The determination of the reaction rate from these data involves considerable experimental difficulties and becomes impossible if the rate of relaxation is much higher than the rate of reaction (see, for example, Refs. 84 and 85). In endothermic reactions, where one may expect a considerable influence of the vibrational excitation, the products are usually non-excited. The most direct way of investigating such reactions involves the direct measurement of the relative increase in reaction rates under the influence of the radiation of continuous lasers. Mass spectrometry is a convenient method for the measurement of reaction rates. Low pressures in the reactor make it possible to connect it via a leak valve to the ion source and to record the change in the concentration of the initial substances and reaction products directly in the course of the process.

This method has been used to investigate the influence of the vibrational excitation of methane on its reaction with atomic chlorine[96]. The methane molecule was excited by the radiation of a continuous He–Ne laser at a wavelength of 3.39 μm, the corresponding frequency being the same as that of the antisymmetric stretching vibration of CH_4. The comparatively low power of the laser (up to 80 MW) nevertheless made it possible to obtain a concentration

of the vibrationally excited molecules higher than the equilibrium value by a factor of several units at room temperature and by several orders of magnitude at 150 K. However, no increase was recorded in the reaction rate under the influence of infrared radiation, within the limits of experimental accuracy. Hence it was concluded that the vibrational energy is relatively ineffective in overcoming the activation barrier in this virtually thermally neutral reaction. The low isotope effect (~3% with respect to bromine) in the analogous CH_3Br chlorination reaction under the influence of the radiation of the CO_2 laser is probably associated with the same factor[97].

The above method has also been applied to the study of the endothermic reaction of bromine atoms with CH_3F.[98,99] The vibrational excitation was achieved by the radiation of a continuous CO_2 laser having a power up to 20 W. An increase in the reaction rate by a factor of several units at CH_3F pressures amounting to tenths and hundredths of mmHg was recorded in these experiments. Special experiments showed that under these conditions the increase in reaction rate is not associated with equilibrium thermal heating but is caused by the superequilibrium concentration of the vibrationally excited molecules generated by the laser radiation. The study of the dependence of the rate of reaction on the power of the laser emission has shown that at low CH_3F pressures it is linear, but, as the pressure rises, the rate increases more rapidly with increase in the power. Hence one may conclude that, under linear conditions, the lowest vibrationally excited states of the CH_3F molecule (with an energy of ~3 kcal mole^{-1}) are responsible for the increase of the reaction rate. An increase in pressure increases the role of higher vibrationally excited states formed when the species initially generated by the laser emission collide with one another; this leads to a more pronounced dependence of the reaction rate on the power. As the pressure in an equimolar mixture of $^{12}CH_3F$ and $^{13}CH_3F$ was reduced to values for which there is insufficient time to establish vibrational equilibrium between the excited and non-excited isotopic molecules (~10^{-2} mmHg), a doubling of the rate of formation of the reaction product containing the carbon isotope present in the CH_3F molecule excited by the laser emission was recorded[99].

The bromination of CH_3F is of interest also because, depending on the wavelength of the light causing the dissociation of the Br_2 molecule into atoms, the latter are formed in both ground ($^2P_{3/2}$) and excited ($^2P_{1/2}$) states with an excitation energy of ~10.5 kcal mole^{-1}. At low pressures the atoms in both states make comparable contributions to the reaction. It has been shown[100] that electronic excitation of the bromine atom reduces the activation energy for its reaction with CH_3F by the excitation energy, with a simultaneous decrease of the preexponential factor by 2.6 orders of magnitude. Photobromination of CH_3F under the influence of ultraviolet light at different wavelengths and study of the influence of infrared radiation on the reaction showed that the vibrational energy is effectively utilised in the endothermic reaction of the bromine atom in its ground state and has no influence whatever on the virtually thermally neutral reaction of the electronically excited bromine atom[101].

It is noteworthy that the low efficiency of the utilisation of the vibrational energy in overcoming the activation barrier in exothermic and thermally neutral reactions is consistent with data on the formation of vibrationally excited species in exothermic reactions. Such processes underlie the operation of chemical lasers and are the converse of those discussed in the present section.

Reactions involving the formation of vibrationally excited species with energies greater than the heats of reaction are at present virtually unknown[102]. It follows from the principle of detailed balancing that in the reverse processes the vibrational energy plays a significant role in overcoming only the endothermic part of the activation barrier, while the remaining energy must be translational or rotational. Theoretical calculations of the rate constants for model interactions of atoms with diatomic molecules[103] also showed that vibrational energy should play a significant role in endothermic reactions and a much smaller role in thermally neutral reactions and, particularly, exothermic reactions, where the barrier must be overcome mainly by translational energy. Analysis of the available experimental data for the reactivity of vibrationally excited molecules[104,105] shows that in the vast majority of instances vibrational energy is not fully utilised in overcoming the activation barrier. The attempts to relate the fraction of the vibrational energy effectively employed in overcoming the activation barrier of the reaction to the size of the barrier, the heat of reaction, or the size of the vibrational quantum[104] have not as yet established any empirical relations. It appears that the number of reliable experimental rate constants for the elementary reactions of vibrationally excited molecules is still insufficient. The most reliable of the available experimental data, obtained by infrared laser photochemical methods, are presented in Table 1.

Table 1. Reactions of vibrationally excited molecules with atoms and free radicals.

Reaction	ΔH, kcal mole^{-1}	E, kcal mole^{-1}	$h\nu$, kcal mole^{-1}	$\left(\frac{k^*}{k}\right)_{calc}$	$\left(\frac{k^*}{k}\right)_{expt}$	Refs.
$HCl^*(v=1)+O \rightarrow OH + Cl$	0.8	4.5	8.2	$1.8\cdot10^4$	300	88
$C_2H_4^* + O \rightarrow CH_3 + CHO$	−30.9	—	3.0	$1.5\cdot10^9$	1.5	95
$OCS^* + O \rightarrow CO + SO$	−53.5	5.8	3.0	$1.5\cdot10^9$	3.0	95
$O_3^*(\nu_{1,2,3}) + SO \rightarrow SO_2(^1B_1) + O_2$	−25	—	3.0	$1.5\cdot10^9$	2.5	88
$O_3^*(\nu_{1,2,3}) + O_2(^1\Delta_g) \rightarrow 2O_2 + O$	1.4	—	3.0	$1.5\cdot10^9$	38	90
$O_3^*(\nu_{1,2,3}) + NO \rightarrow NO_2(^2B_1) + O_2$	−20.0	4.2	3.0	$1.5\cdot10^9$	5.6	90
$O_3^*(\nu_{1,2,3}) + NO \rightarrow NO_2(^2A_1) + O_2$	−48.0	2.3	3.0	40	17.1	90
$NO^*(v=1) + O_3 \rightarrow NO_2(^2B_1) + O_2$	−20.0	4.2	5.4	$1.1\cdot10^9$	5.7	94
$CH_4^*(\nu_3) + Cl \rightarrow HCl + CH_3$	−1.0	3.8	3.7	$3\cdot10^5$ (150 K)	<30	96
$CH_4^*(\nu_3) + Cl \rightarrow HCl + CH_3$	−1.0	3.8	8.6	$2\cdot10^5$ (150 K)	$<10^3$	96
$CH_2F^*(\nu_{2,6}) + Br(^2P_{3/2}) \rightarrow HBr + CH_2F$	12.0	14.6	3.0	56 (373 K)	30	98
$CH_2F^*(\nu_{2,6}) + Br(^2P_{1/2}) \rightarrow HBr + CH_2F$	1.5	4.5	3.0	56 (373 K)	1	101

Note. $(k^*/k)_{calc} = \exp(h\nu/RT)$ for $h\nu < E$ and $\exp(E/RT)$ for $h\nu > E$, ΔH is the heat of reaction, and E and $h\nu$ are respectively the activation and excitation energies.

A number of studies on the effect of infrared laser emission on the reactions of atoms with molecules were undertaken specially to achieve chemical reactions selective with respect to isotopes. One of the first attempts to achieve such a process was undertaken by Mayer et al.[106] A mixture of CH_3OH, CD_3OD, and Br_2 at 70 mmHg was exposed to the emission of a continuous HF laser with a power of 90 W, which is selectively absorbed by the CH_3OH molecule, while CD_3OD does not absorb such emission. After irradiation for 1 min, 90% of CH_3OH was converted into CH_2O, while CD_3OD hardly reacted under these conditions. The rate-limiting step of the process is the reaction of the bromine atom with CH_3OH, the activ-

ation energy for which is 6.2 kcal mole^{-1}. Since the energy of the quantum of the HF laser (10.4 kcal mole^{-1}) exceeds the above value, the authors concluded that they observed the reaction of a vibrationally excited CH_3OH molecule with a bromine atom, which thus proceeds without activation energy, in contrast to the non-excited CD_3OD molecule. This leads to a high isotopic selectivity of the given reaction. However, the above conclusion is doubtful, because at the high pressures employed (i.e. for high rates of $V-T$ relaxation) it is difficult to expect appreciable deviations of the populations of the vibrationally excited molecules from the equilibrium values and the results may be accounted for by a kinetic isotope effect. Special experiments on the chlorination of a mixture of CH_4 and CD_4 by the emission of a continuous CO_2 laser, carried out at the same pressures as in the study of Mayer et al.[106], showed[107] that mainly CH_4 molecules are involved in the reaction, although the laser emission is absorbed by the CD_4 molecule. Detailed measurements of the quantum yield of the reaction in a methanol–bromine mixture under the influence of infrared radiation[108] also failed to confirm the conclusions of Mayer et al.[106]

More evident successes in carrying out an isotopically selective reaction were achieved by Arnoldi et al.[109] and Leone et al.[110] By exciting an $H^{35}Cl$ molecule to the second vibrational level using the emission of a pulsed chemical HCl laser[109] and a parametric oscillator[110], it was possible to carry out a $Br + H^{35}Cl \rightarrow HBr + {}^{35}Cl$ reaction selective with respect to chlorine isotopes. However, rapid secondary radical processes precluded an isotopic enrichment of the final reaction product.

The chlorination of CH_3Br [97] (selectivity with respect to bromine isotopes) and the bromination of CH_3F [99] (selectivity with respect to carbon isotopes) are examples of processes in which isotope enrichment was achieved in the final products under the influence of the emission of a continuous CO_2 laser.

IV. SELECTIVE DISSOCIATION OF POLYATOMIC MOLECULES UNDER THE INFLUENCE OF PULSED INFRARED RADIATION

The selective dissociation of molecules (as well as other reactions with high activation energies), requiring the absorption of many infrared photons, initially appeared to be virtually impossible to achieve. Indeed when the infrared laser emission is absorbed, the products are molecules with a low degree of excitation which are incapable of absorbing radiation at the same frequency owing to vibrational anharmonicity. Higher vibrationally excited states may arise on collision of the initially excited molecules with one another, i.e. in a $V-V$ relaxation process. At high emission intensities this can lead to specific reactions, but the selectivity attainable in the primary absorption step must be lost in the course of the $V-V$ processes.

Letokhov and Ambartsumyan observed that the above difficulties may be overcome by employing a powerful pulsed infrared emission. This discovery greatly extended the likely applications of infrared lasers both in carrying out isotopically selective chemical reactions and in the development of vibrational photochemistry.

The first evidence for the possibility of multiphoton absorption was obtained in studies[111,112] where luminescence was observed in the visible and infrared regions of the spectrum, due to the rapid dissociation of NH_3, SiF_4, and CCl_2F_2 molecules under the influence of the focussed emission of a powerful pulsing CO_2 laser. Later analogous results were obtained also in studies of the dissociation of other compounds[113–116]. The study of the luminescence kinetics showed[117–119] that two stages are observed: a rapid stage arising immediately after the pulse of the infrared radiation and a slow stage due to collisions. It has been shown[120–122] that, when many compounds are irradiated by powerful pulses from a CO_2 laser, not only dissociation but also ionisation takes place.

Ambartsumyan et al.[118] showed for the first time that dissociation in the field of the emission from a powerful pulsed CO_2 laser is isotopically selective. The luminescence due to the ^{10}BO and ^{11}BO radicals, formed as a result of the irradiation of BCl_3 having the natural isotope composition in an oxygen atmosphere, was recorded, the enrichment coefficient in the BO intermediate reaching 10 under these conditions. Soon the above method led to isotope enrichment of the final products of the dissociation of SF_6,[123,124] BCl_3,[125] OsO_4,[126] and CCl_4.[127] Subsequently such experiments on the isotopically selective dissociation of polyatomic molecules were reproduced in many laboratories for the same and a number of new systems [128–134] and many experimental and theoretical studies, devoted to the detailed investigation of the mechanism of this phenomenon, were published[135–169].

The fundamental feature of these investigations was the elucidation of the problemof compensating the vibrational anharmoniticity, which must lead to the breakdown of the conditions for the resonance absorption of infrared radiation after the absorption of the first quantum. The initial explanations reduced to the Stark broadening of the frequencies of vibrational transitions in the strong field of the infrared radiation[118–124]. However, calculations showed[169] that this requires a much higher radiation intensity than those for which selective dissociation is observed. Next the hypothesis was put forward that compensation of the anharmonicity is required only for a few of the lowest vibrational transitions (3–4 for molecules such as those of SF_6, BCl_3, etc.), where the vibrational spectrum has a discrete structure, while in higher vibrational transitions the density of the levels increases so much that they form a quasi-continuum[138,141]. Experiments on two-frequency dissociation[138–141], in which molecules were excited by resonance infrared radiation to a few of the initial levels and dissociation was achieved by means of non-resonance infrared radiation absorbed in the quasi-continuum, confirmed this view. According to the proposed hypothesis[138,141], the vibrational anharmonicity in the lowest transitions is compensated as a result of rotational energy; the first, second, and third quanta of infrared radiation are resonance-absorbed by one of the rotational lines of the P-, Q-, and R-branches of the vibrational transition respectively. The dependence of the probability of dissociation on the frequency of the resonance infrared radiation is consistent with this hypothesis.

However, only some of the molecules in specific rotational states are involved in vibrational energy accumulation processes when this mechanism operates. On the other hand, measurements of the number of molecules dissociating under the influence of infrared radiation have shown that in the region of the focus of the light beam virtually all the molecules are dissociated by a single pulse. For this reason, in the latest studies on this problem the anharmonic splitting of overtomes[147], the removal of the degeneracy of the vibrational levels in symmetrical molecules[154,164], and forced transitions between various rotational levels[153] were additionally invoked to account for the compensation of the vibrational anharmonicity in the lowest transitions.

One of the causes of the loss of selectivity (for fairly large isotopic shifts) is $V-V$ relaxation processes, so that a high selectivity in multiphoton dissociation is achieved only at low pressures (below 1 mmHg). Another cause may be secondary radical reactions, lowering the selectivity of the primary dissociation step. For example, it has been shown that the formation of active species such as fluorine atoms in the primary dissociation step may lead to a decrease of selectivity[170,171]. For this reason, the study of the chemical mechanism of the primary dissociation step is of great interest.

The discovery of multiphoton absorption of intense infrared radiation "without collisions" leads to new interesting possibilities in the study of the unimolecular decomposition of molecules with a large excess of energy. Among these, mention should be made in the first place of the possibility of observing non-statistical unimolecular decomposition of vibrationally excited species and decomposition in states whose energy greatly exceeds the dissociation threshold. Bimolecular reactions involving such highly excited molecules may also be of great interest. At the present time the number of studies published on the mechanisms of reactions of highly vibrationally excited molecules is much smaller than the number of studies on isotopically selective dissociation. Among these, mention should be made of the decomposition of alkyl halides [172], the reactions of methyl halides with halogens [173,174], and the *cis–trans* isomerisation of $C_2H_2Cl_2$ [175] and deuterohexadienes [176]. The dissociation due to vibrational excitation proceeds by no means in all cases via fundamentally new chemical reaction pathways. Thus it has been shown [177] that, when pulsed infrared radiation acts on mixtures of SF_6 with hydrocarbons, the latter react with the fluorine atoms formed on dissociation of SF_6. The chemical reactions of molecules which do not absorb the infrared laser emission are of great interest. In this case the reaction may be achieved as a result of the transfer of vibrational energy from molecules which effectively absorb the infrared emission. An examples of such a process may be the decomposition of 1,2-dihydroxytetramethylethane into two acetone molecules as a result of the transfer of vibrational energy from a CH_3F molecule, excited by the emission of a pulsed CO_2 laser, to a molecule of 1,2-dihydroxytetramethylethane [178].

The processes examined may also be of preparative interest. The synthesis of $BHCl_2$ from BCl_3 and H_2 was achieved [179] on irradiating a mixture of the latter two substances by the pulses of a CO_2 laser. It has been stated [180] that it is likely to be useful to dissociate small amounts of impurities in order to achieve a high degree of purification of the main substance; arsenic trichloride was freed in this way from 1,2-dichloroethane and carbon tetrachloride.

The vast majority of processes considered in this section have been achieved with the aid of the emission from a CO_2 laser. This is the most powerful, economical, and simplest gas laser to operate. It can operate on different lines in the range 9.4–10.6 μm (the use of isotopic modifications of CO_2 such as $^{13}CO_2$ or $^{12}C^{18}O^{16}O$ extends this range to 8.5–10.6 μm). However, not all the molecules which are of theoretical or practical interest have absorption lines in this region. Diatomic homonuclear molecules such as H_2, N_2, O_2, and others cannot be vibrationally excited by infrared radiation at all. The phenomenon of stimulated Raman scattering (SRS) may be used to excite such molecules. When a pulse of laser emission in the ultraviolet, visible, or near infrared range is passed through a cuvette with a gas at a high pressure, then a Stokes component, the energy of the quantum of which is lower than the energy of the initial quantum by the energy of the vibrational quantum of the substance in the cuvette, appears at the exit together with the transmitted emission. The interaction of these two types of emission, having different frequencies, with the same substance in the following cuvette leads to its vibrational excitation.

The idea of using SRS for isotope separation has been suggested [181]. This process was achieved experimentally in the formation of NO by the reaction of N_2 or O_2. [182] The vibrational excitation of N_2 was achieved with the aid of SRS in liquid nitrogen. The absorption coefficient with respect to nitrogen-15 reached 10^2 under these conditions. The same result was also obtained in the excitation of a mixture of N_2 and O_2 in a pulsed electric discharge [183]. The authors [182] explained it by the establishment of different vibrational temperatures of $^{14}N_2$ and $^{15}N_2$ under the conditions of the experiment described. However, in analogous experiments in a discharge tube an enrichment of 21% with respect to nitrogen-15 was attained [184]. In order to resolve this discrepancy, additional studies are necessary.

At the same time, using SRS it is possible to achieve the vibrational excitation of molecules which do not absorb infared radiation. This technique permits an alteration of the laser frequency and its displacement to the regions where sufficiently powerful infrared lasers are not available. Hydrogen-based SRS has been used to dissociate SF_6 in the region of the $\nu_4 + \nu_5$ combination band [185], which made it possible to increase the process selectivity.

V. RELAXATION AND VIBRATIONAL ENERGY TRANSFER PROCESSES

The main processes competing with the reactions of vibrationally excited molecules are the $V-T$ and $V-R$ relaxation processes leading to the loss of vibrational energy and the $V-V$ relaxation processes leading to its redistribution between different molecules and between vibrational degrees of freedom within the same molecule. In most cases the vibrationally excited species react more slowly than they relax, so that the rate of the relaxation processes must be compared with the rate of generation of vibrationally excited species (proportional to the intensity of the infrared radiation and the absorption coefficient) in order to determine the conditions under which a non-equilibrium population of the corresponding excited state is possible. Before lasers became available, the main sources of information about the relaxation of vibrational excitation were experiments in shock tubes and by acoustic methods as well as kinetic spectroscopy. When infrared laser became available, the above possibilities were greatly extended. The problems of the relaxation of vibrational excitation have been described in a number of review articles and monographs [186-190].

The method of infrared luminescence induced by the laser emission, first used to measure the vibrational relaxation of CO_2, [191] and the double resonance method employed for the measurement of the rates of transfer of vibrational energy in SF_6, [192] BCl_3, [193] and CH_3F [194-196] are most widely employed to investigate the relaxation and vibrational energy transfer processes. The first method involves the observation of the time dependence of the luminescence originating from different vibrational levels and arising after the excitation of the molecule by an infrared pulse. In order to record the spectral dependence of the luminescence, different infrared detectors, cooled to low temperatures, are used. The luminescence

originating from different vibrational states is isolated by means of combinations of interference filters. In addition, the filters protect the infrared detector from scattered laser emission, the intensity of which greatly exceeds the luminescence intensity. The recorded signal is usually weak, but the high frequency of the pulses from modern infrared lasers (mainly the CO_2 laser and optical parametric oscillators) makes it possible to use signal accumulation techniques in order to improve the signal to noise ratio.

The double resonance method involves the observation of the changes in the infrared absorption at a fixed frequency when the molecule is excited by an infrared pulse at another frequency. The possibility of using long absorption cells (in contrast to the infrared luminescence method) and hence of reducing the pressure of the gas investigated makes this procedure preferable in the study of rapid processes such as the resonance transfer of vibrational energy between isotopic molecules.

The rates of relaxation processes in a large number of molecules have been investigated in detail with the aid of the above methods. The rate constant for the $V-T$ and $V-V$ relaxation processes for SF_6, BCl_3, HCl, O_3, and CH_3F molecules, the laser-induced chemical reactions of which have been studied in greatest detail, are presented in Table 2. Analysis of the available experimental data shows that the $V-T$ relaxation involving the molecules takes place comparatively slowly and usually requires 10^2-10^5 collisions. The rate-limiting stage of the $V-T$ relaxation is the deactivation of the lowest vibrationally

Table 2. The relaxation and vibrational energy transfer processes for molecules whose reactions under the influence of infrared radiation have been investigated in greatest detail (k is the rate constant and n the number of collisions).

Process	k, $cm^3\ mole^{-1}\ s^{-1}$	n	Refs.
$SF_6(\nu_6) + SF_6(O) \rightarrow 2SF_6(O) + 363\ cm^{-1}$	$1.5\cdot10^{11}$	$2.2\cdot10^3$	192
	$1.2\cdot10^{11}$	$2.9\cdot10^3$	197
$SF_6(\nu_6) + Ar \rightarrow SF_6(O) + Ar + 363\ cm^{-1}$	$4.0\cdot10^{10}$	$3.4\cdot10^3$	192
$SF_6(\nu_6) + He \rightarrow SF_6(O) + He + 363\ cm^{-1}$	$4.6\cdot10^{11}$	$9\ 1\cdot10^2$	192
$SF_6(\nu_l) + SF_6(\nu_k) \rightleftarrows SF_6(\nu_l) + SF_6(\nu_m) + \Delta E$	$1.3\cdot10^{13}$	12	197
	$1.7\cdot10^{13}$	9	198
$BCl_3(\nu_4) + BCl_3(O) \rightarrow 2BCl_3(O) + 243\ cm^{-1}$	$3.2\cdot10^{12}$	$1.5\cdot10^2$	193
$BCl_3(\nu_4) + Ar \rightarrow BCl_3(O) + Ar + 243\ cm^{-1}$	$8.5\cdot10^{10}$	$2.2\cdot10^3$	193
$BCl_3(\nu_4) + He \rightarrow BCl_3(O) + He + 243\ cm^{-1}$	$2.9\cdot10^{11}$	$1.9\cdot10^3$	193
$BCl_3(\nu_l) + BCl_3(\nu_k) \rightleftarrows BCl_3(\nu_l) + BCl_3(\nu_m) + \Delta E$	$3.7\cdot10^{13}$	13	193
$HCl(v=1) + HCl(v=0) \rightarrow 2HCl(v=0) + 2886\ cm^{-1}$	$1.6\cdot10^{10}$	$7.9\cdot10^3$	199
$HCl(v=1) + He, Ne, Ar \rightarrow HCl(v=0) + He, Ne, Ar + 2886\ cm^{-1}$	$<3.7\cdot10^7$	$>3.3\cdot10^6$	199
$HCl(v=2) + HCl(v=0) \rightleftarrows 2HCl(v=1) - 102\ cm^{-1}$	$1.9\cdot10^{12}$	65	200
$H^{35}Cl(v=1) + H^{37}Cl(v=0) \rightleftarrows H^{35}Cl(v=0) + H^{37}Cl(v=1) + 2\ cm^{-1}$	$2.0\cdot10^{13}$	10	200
$HCl(v=1) + Cl \rightarrow HCl(v=0) + Cl + 2886\ cm^{-1}$	$4.2\cdot10^{12}$	18	201
	$5.3\cdot10^{12}$	15	202
$HCl(v=1) + Br \rightarrow HCl(v=0) + Br + 2886\ cm^{-1}$	$1.6\cdot10^{11}$	$4.6\cdot10^2$	201
$HCl(v=1) + O \rightarrow HCl(v=0) + O + 2886\ cm^{-1}$	$2.2\cdot10^{12}$	33	203
$HCl(v=1) + H \rightarrow HCl(v=0) + H + 2886\ cm^{-1}$	$4.6\cdot10^{12}$	46	204
	$3.9\cdot10^{12}$	57	94
$HCl(v=1) + D \rightarrow HCl(v=0) + D + 2886\ cm^{-1}$	$6.5\cdot10^{12}$	25	204
$O_3(\nu_3) + O_3(O) \rightarrow 2O_3(O) + 1042\ cm^{-1}$	$3.8\cdot10^{10}$	$4.6\cdot10^3$	205
$O_3(\nu_3) + Ar \rightarrow O_3(O) + Ar + 1042\ cm^{-1}$	$5.0\cdot10^9$	$3.0\cdot10^4$	93
	$4.0\cdot10^9$	$3.7\cdot10^4$	89, 205
$O_3(\nu_3) + He \rightarrow O_3(O) + He + 1042\ cm^{-1}$	$3.6\cdot10^{10}$	$8.0\cdot10^3$	89, 93
	$4.0\cdot10^{10}$	$7.2\cdot10^3$	205
$O_3(\nu_3) + O_2 \rightarrow O_3(O) + O_2 + 1042\ cm^{-1}$	$1.5\cdot10^{10}$	$1.1\cdot10^4$	93
	$8.0\cdot10^9$	$2.0\cdot10^4$	89
	$1.2\cdot10^{10}$	$1.4\cdot10^4$	205
	$1.1\cdot10^{10}$	$1.4\cdot10^4$	92
$O_3(\nu_3) + NO_2 \rightarrow O_3(O) + NO_2 + 1042\ cm^{-1}$	$7.5\cdot10^{10}$	$2.4\cdot10^3$	93
$O_3(\nu_1, \nu_3) + O(^3P) \rightarrow \begin{cases} \rightarrow O_3(\nu_2) + O(^3P) + 370\ cm^{-1} \\ \rightarrow 2O_2 \end{cases}$	$(6\div9)\cdot10^{12}$	$10\div15$	206
$O_3(\nu_2) + O(^3P) \rightarrow \begin{cases} \rightarrow O_3(O) + O(^3P) + 700\ cm^{-1} \\ \rightarrow 2O_2 \end{cases}$	$(1\div2)\cdot10^{12}$	$50\div100$	206
$CH_3F(\nu_3) + CH_3F(O) \rightarrow 2CH_3F(O) + 1048\ cm^{-1}$	$1.1\cdot10^{10}$	$1.5\cdot10^4$	207
$CH_3F(\nu_3) + Ar \rightarrow CH_3F(O) + Ar + 1048\ cm^{-1}$	$7.3\cdot10^8$	$2\cdot10^5$	207
$CH_3F(\nu_3) + He \rightarrow CH_3F(O) + He + 1048\ cm^{-1}$	$1.5\cdot10^{10}$	$1.7\cdot10^4$	207
$CH_3F(\nu_3) + CH_3F(\nu_3) \rightleftarrows CH_3F(2\nu_3) + CH_3F(O) + 10\ cm^{-1}$	$2.2\cdot10^{13}$	7	208
$CH_3F(3\nu_3) + CH_3F(O) \rightleftarrows CH_3F(O) + CH_3F(\nu_{1,4}) + 120{,}100\ cm^{-1}$	$2.2\cdot10^{12}$	70	208
$CH_3F(\nu_{1,4}) + CH_3F(O) \rightleftarrows CH_3F(O) + CH_3F(2\nu_{2,5}) + 10\ cm^{-1}$	$>1.7\cdot10^{13}$	<10	208
$CH_3F(2\nu_{2,5}) + CH_3F(O) \rightleftarrows 2CH_3F(\nu_{2,5}) + 10\ cm^{-1}$	$>3.3\cdot10^{12}$	<50	208
$CH_3F(\nu_3) + CH_3F(O) \rightleftarrows CH_3F(O) + CH_3F(\nu_6) - 133\ cm^{-1}$	$1.0\cdot10^{12}$	150	208
$CH_3F(\nu_3) + Ar \rightleftarrows CH_3F(\nu_6) + Ar + 133\ cm^{-1}$	$7.5\cdot10^{10}$	$2.2\cdot10^3$	195
$^{12}CH_3F(\nu_3) + {}^{13}CH_3F(O) \rightleftarrows {}^{13}CH_3F(O) + {}^{13}CH_3F(\nu_3) + 12\ cm^{-1}$	$1.7\cdot10^{13}$	10	196
	$2.8\cdot10^{13}$	6	194
$o\text{-}CH_3F(\nu_3) + n\text{-}CH_3F(O) \rightleftarrows o\text{-}CH_3F(O) + n\text{-}CH_3F(\nu_3)$	$3.5\cdot10^{13}$	5	196

excited state. Hence it follows that the simplest type of non-equilibrium in vibrational excitation may be a "discrepancy" between the vibrational and translational temperatures. This discrepancy may arise at low pressures under the conditions of continuous irradiation or at higher pressures under the conditions of pulsed irradiation. It is noteworthy that the rate of relaxation of the vibrational energy is determined by the deactivation of the lowest vibrational level only under the conditions of comparatively weak optical pumping. $V-T$ relaxation processes involving higher vibrational levels, the rates of which is higher than that of relaxation involving the lowest level, play an appreciable role at high concentrations of vibrationally excited molecules[209].

The $V-V$ relaxation processes are much faster, usually requiring between 10 and 100 collisions. For this reason it is much more difficult to achieve the vibrational "heating" of a specified degree of freedom, particularly since intramolecular vibrational energy transfer processes, occurring over periods shorter than the period between collisions, are possible in complex molecules[210]. The transfer of vibrational energy between isotopic molecules, involving virtually a resonance mechanism, is even faster than the collision processes involved in $V-V$ relaxation. Less than ten collisions are required for this purpose[192-196].

Whereas the $V-T$ relaxation of vibrationally excited molecules by inert gas molecules and atoms is comparatively slow, the rate of the $V-T$ relaxation by free atoms is much higher and approaches the rate of the $V-V$ processes. A large number of direct experimental measurements of the rate constants for these processes have been made in recent years; some of these have been examined in reviews[105,189,211]. The results of some of the latest measurements of the rate constants for the above processes are presented in Table 2. Comparison of the rate constants for the $V-T$ relaxation of vibrationally excited molecules by inert gas molecules and atoms with the constants for relaxation by chemically active atoms showed that the rates of the latter are greater by 2–3 orders of magnitude. This implies that in real reacting systems, where the relative concentrations of atoms may exceed $10^{-3}-10^{-2}$ (for example, in flash photolysis or in processes occurring in an electric discharge), the relaxation of vibrationally excited molecules at such species must be taken into account.

VI. REACTIONS OF VIBRATIONALLY EXCITED MOLECULES IN THE CONDENSED PHASE AND ON THE SURFACES

Whereas in the gas phase superequilibrium concentrations of vibrationally excited molecules may be obtained at low temperatures even under the influence of the emission of continuous infrared lasers of comparatively low power (watts per cm^2), on passing to a condensed phase this requires a much greater radiation density—megawatts and gigawatts per cm^2.[31,212] Such radiation densities are attainable only in pulsed lasers. Furthermore, when energy with such a high density is incident on a given substance, considerable heating, leading to its evaporation, is inevitable. For example, it has been shown[213] that the interaction of the radiation from a pulsed CO_2 laser (energy per pulse 1 J, duration of pulse 80 ns) with water and chloroform leads to the formation of a shock wave as a result of the rapid evaporation of the liquid and the increase of pressure over the surface. Such interactions of infrared radiation with a given substance are undoubtedly of chemical interest. An apparatus has been described[214] for the synthesis of organometallic compounds by the interaction between the metals evaporated by the laser beam and the vapours of organic compounds. However, the discussion of processes beginning with a change in the phase state of the relevant substance under the influence of infrared radiation is outside the scope of the present review.

In view of the experimental difficulties mentioned above, the number of studies on the infrared photochemistry of the condensed phase is much smaller than the number of corresponding studies in the gas phase. The effect of the emission of a CO_2 laser on adenosine triphosphate and ammonium pyrophosphate, prepared in the form of potassium bromide discs, has been studied[215]. It was established that, after exposure to the pulsed radiation (with pulses lasting 100 ns), molecular structure are produced with an increased angle between the P–O–P bonds, while quasi-continuous irradiation (with pulses lasting 0.1–1 s) causes the same changes as thermal heating. A displacement of the complex-formation equilibrium under the influence of the pulsed radiation of a CO_2 laser incident on the interface between aqueous and organic uranyl nitrate solutions has been observed[216,217].

The above reactions are most likely to be due to the purely thermal effect of the laser emission, since the $V-T$ relaxation times under these conditions should be short. Experiments at low temperatures, where the rates of the relaxation processes may be greatly reduced, are therefore more promising. For example, a study of the infrared fluorescence of the CO molecule in solid argon and neon matrices at 10–30 K established that, after the excitation of the $^{12}C^{16}O$ molecule to its lowest excited vibrational level by the second harmonic of the radiation from a pulsed CO_2 laser, signals appear due to the fluorescence of $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$ molecules in vibrational states up to $v = 8$.[218] The times during which the corresponding signals increase, determined by the rate of the $V-V$ relaxation of CO, amounted to tens and hundreds of microseconds in these experiments (depending on the degree of dilution of CO by argon or neon), while the times during which the signal intensities decrease, determined by the rate of the $V-T$ relaxation of the vibrationally excited CO molecules at Ar and Ne species and the emission of radiation, amounted to 15–20 ms. The comparatively low rates of relaxation in low-temperature matrices suggest that the effect of infrared laser emissions on such systems may exhibit a high isotopic and stereochemical selectivity. The behaviour of iron tetracarbonyl $Fe(CO)_4$, isolated in a methane matrix at 20 K, has been investigated[219]. $Fe(CO)_4$ was obtained by the ultraviolet irradiation of the matrix containing $Fe(CO)_5$. Heating to 35 K led to the regeneration of the pentacarbonyl; black body infrared emission (Nernst glower) induced the reaction $Fe(CO)_4 + CH_4 \rightarrow [Fe(CO)_4.CH_4]$, which does not occur when the matrix is heated. The influence of the radiation from a continuous CO laser (power 400–650 mW, intensity <1 W cm^{-2}) on $Fe(CO)_4$ enriched in carbon-13 (34%) initiated the same reaction but, depending on the radiation frequency, only isomers with a specific number and distribution of ^{13}CO groups reacted.

Isotopically selective dissociation of SF_6 in a low-temperature matrix under the influence of the pulsed radiation of a CO_2 laser has been observed[220]. Isotopically-selective evaporation of BCl_3, on irradiation by a continuous CO_2 laser of a film obtained by freezing boron trichloride at 77 K on a solid support, has been reported[221].

The study of the role of vibrational excitation in heterogeneous-catalytic reactions is of great interest. Such processes may be investigated at gas pressures which are sufficiently low to enable the vibrationally excited molecules generated by the laser emission in the bulk phase to reach the surface without losing vibrational energy by collisions. The influence of the vibrational excitation of N_2O molecules, due to the radiation from a continuous electric-discharge N_2O laser (with a power up to 90 mW) in the reaction $N_2O + Cu \rightarrow N_2 + CuO$ at pressures of approximately 1 mmHg, has been investigated [222] and it has been established that the probability of the reaction increases as a result of vibrational excitation by a factor of 5×10^3 (from 2.9×10^{-11} to 1.5×10^{-7}). This cannot be explained solely in terms of the reactivity of the vibrationally excited state of the N_2O (001) molecule with an energy of approximately 3 kcal mole^{-1}. An increase of reaction probability by a factor greater than $\exp(h\nu/RT)$, which does not exceed 60 at the experimental temperature (363 K), is impossible under these conditions. It appears that under the given experimental conditions higher vibrationally excited states are also populated, i.e. N_2O undergoes vibrational "heating" to a temperature greatly exceeding the translational temperature. Analogous studies were made in another investigation [223], where the stimulation of the heterogeneous ammonia decomposition reaction on the surface of platinum by the radiation from a CO_2 laser was observed.

Adsorption processes involving vibrationally excited molecules generated by continuous infrared radiation have been investigated in a number of studies [224-226]. The recorded isotope effects in the adsorption of BCl_3 and when the latter is filtered through finely dispersed sodium chloride exceed the equilibrium isotope effects.

Table 3. Characteristics of the infrared lasers used in photochemical research (studies on relaxation are not included).

Type of laser	Range of generation, cm^{-1}	Energy of quantum, kcal mole^{-1}	Power, W	Energy of pulse, J	Duration of pulse, s	Number of published studies
CO_2 *	900—1100	2.6—3.1	to 650	—	—	70
CO_2	900—1100	2.6—3.1	—	to 10	$3 \cdot 10^{-8}$—$1 \cdot 10^{-6}$	66
CO *	1500—2000	4.3—5.7	3,0	—	—	2
N_2O *	900—970	2.6—2.8	0,09	—	—	1
HF *	3500—3800	9.5—11.0	90	—	—	1
HCl	2500—2900	7.2—8.6	—	0.01	10^{-6}—10^{-5}	3
Neodymium	9400	27.0	—	to 10	10^{-3}	1
Neodymium + H_2SRS	1100—1200	3.2—3.5	—	0.5	$2 \cdot 10^{-8}$	1
Ruby + N_2 SRS	2330	6.7	—	0.8—1.4	$3 \cdot 10^{-8}$	1
Parametric $LiNbO_3$ oscillator	2800—18 300	8.2—52.9	—	10^{-5}	10^{-7}	1

*Continuous operating conditions; pulsed conditions were employed in the remaining instances.

In conclusion we may note that the scope for the formulation and interpretation of laser-chemical studies in the condensed phase is significantly restricted by the scarcity of experimental data for vibrational relaxation under these conditions.

VII. CONCLUSION

Numerous experimental studies published in recent years are evidence for the vigorous development of infrared laser photochemistry. A characteristic feature of the initial stage of the development of this research field was a distinctly applied bias of many of the investigations, associated with the prospect of developing new isotope separation methods. The considerable possibilities of infrared lasers in carrying out selective chemical processes were demonstrated and the difficulties and unsolved problems arising in this connection were described. The proportion of studies directed to the solution of fundamental chemical kinetic problems has begun to increase in recent years: the characteristics of reactions under non-equilibrium conditions, the influence of various forms of energy on reactivity, the competition between the reaction and relaxation, and others.

The development of infrared photochemistry will undoubtedly depend on the progress in laser engineering. Analysis of published studies (Table 3) shows that most of them have been carried out with the aid of pulsed and continuous CO_2 lasers. The lack of commercial infrared lasers operating in other frequency ranges restricts the range of systems susceptible to experimental photochemical investigation. This restriction arises not only because the spectra of many molecules lack absorption lines falling within the range of CO_2 lasers but also because of the small energy of the emitted quanta of such lasers, which hinders the competition between the radiation-induced and thermal processes involving the generation of vibrationally excited molecules. Another factor which narrows the range of systems suitable for experimental study is the difficulty of a smooth adjustment of the infrared frequency of lasers. However, these difficulties are not insurmountable, since tunable lasers, covering virtually the entire infrared range (at least in the pulsed version), already exist in physics laboratories. One may hope that the use of this new laser technique will promote the successful development of infrared photochemistry.

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