

Multiple Photon IR Laser Photophysics and Photochemistry. V

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This paper ends the series of reviews on multiple photon IR laser photophysics and photochemistry. The applications of IR MP processes in fundamental chemical studies and chemical technology are considered.

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9. MULTIPLE PHOTON IR LASER PHOTOCHEMISTRY

The previous chapters 7 and 8 were concerned with the application of IR MP photochemical methods to unimolecular dissociation and isotope separation. Successful studies in these fields have formed a basis for the applications of IR MP processes in chemistry considered in this chapter.

9.1. Methods of IR laser photochemistry

Resonant multiple-photon excitation of molecular vibrations in an intense IR field can be used for several different approaches to laser chemistry based on the strong vibrational excitation of molecules.

9.1.1. Degree of vibrational nonequilibrium

All the applications of IR MP vibrational excitation for laser-induced chemical reactions can be classified in a simplified way according to the relation between the characteristic times of the vibrational energy relaxation in the excited mode of the molecule interacting with the IR field:

$$\tau_{VV'}^{im} \ll \tau_{VV'} \ll \tau_{VT} \quad (9.1)$$

where $\tau_{VV'}^{im}$ is the time of intramolecular transfer of vibrational energy between various vibrational modes of excited molecule, $\tau_{VV'}$ is the time of intermolecular transfer of vibrational energy between different molecules in a mixture (for example, different isotopic molecules), τ_{VT} is the time of molecular vibrational energy relaxation to translational degrees of freedom and is the time required for full thermal equilibration in a molecular mixture. The first process is intramolecular and can take place even without collisions; the last two processes occur with the participation of collisions, and $\tau_{VV'}$ and τ_{VT} thus depend on specific conditions of experiment—the types and the pressures of the molecular components of the mixture and the buffer gas.

The rate of vibrational excitation of a molecule of MP absorption W depends on laser intensity and vibrational transition cross-sections. From the inequality (9.1) it is possible, in principle, to establish four different relations between the MP excitation rate W and the energy relaxation rate of excited vibrational mode, and respectively four quite

different approaches in IR MP laser photochemistry depending on the degree of vibrational excitation nonequilibrium in a molecule and its mixture. They are considered below.

1°. Under the condition

$$W \gg 1/\tau_{VV}^{im} \quad (9.2)$$

it is possible to realize mode (bond)—selective excitation of molecules without equilibrium even of the molecule that interacts with the intense IR field. In this case a certain mode or functional group of a polyatomic molecule has a higher vibrational temperature than the rest of the modes or functional groups. In this situation mode (bond)—selective IR photochemistry can be achieved. Success, however, can be attained apparently with the use of ultrashort (picosecond) laser pulses and with a proper choice of targets (for example, big molecules with spatially separated functional groups (see Chapter 6, Section 6.1.2). This is confirmed in particular by successful experiments on selective excitation of chromophore with ultrashort UV pulses.^{1,2} Unfortunately, the development of mode (or bond)—selective IR photochemistry is still inhibited because of the absence of suitable technique for generation of ultrashort IR laser pulses.

2°. Under a more moderate condition for MP vibrational excitation rate

$$1/\tau_{VV}^{im} \gg W \gg 1/\tau_{VV} \quad (9.3)$$

it is possible to achieve excitation selective with respect to molecules of different sorts when there is no vibrational equilibrium between the molecules in the mixture but the molecules interacting with the IR field have intramolecular vibrational equilibrium. In this case the molecules in resonance with the IR field acquire a higher vibrational temperature than the rest of the molecules but the translational temperature of all the molecules in the mixture remains unchanged from the initial. This type of molecule-selective IR photochemistry is the most extensively developed field of IR MP photochemistry started in 1974 in experiments on laser isotope separation. Almost all the experiments described here relates to this case.

3°. Under a much more moderate condition

$$1/\tau_{VV} \gg W \gg \tau_{VT} \quad (9.4)$$

vibrational equilibrium is established between all the components in

the mixture (molecules, radicals) but the vibrational excitation has not relaxed to heat yet. This is possible only if there is no molecular component with very fast vibrational-translational relaxation in the mixture. The difference between the vibrational and translational temperatures in the mixture permits nonselective vibrational chemistry during the time $\leq \tau_{VT}$ with the reactions with the least energy barrier taking place. This is the case, in particular, with the use of sensitizers for indirect activation of molecules through the transfer of vibrational energy from the chemically passive sensitizer molecule that absorbs laser radiation well. This method is applied with success in studies of the kinetics of bimolecular reactions as well as in laser-radical chemical synthesis (see Section 9.3).

4°. Finally, under the last condition

$$W \ll 1/\tau_{VT} \quad (9.5)$$

there is equilibrium thermal excitation of all the molecules in the volume of the reactor when there is no heat transfer to the reactor's walls. In this case the vibrational and translational temperatures of all the molecules in the mixture are equal or approximately equal due to relaxation of vibrational excitation by collisions to heat and one can speak of pulsed thermal homogeneous heating of molecular gas. However this approach of IR thermal chemistry is of particular interest, for example, when it is necessary to heat quickly the bulk of a reactor's contents without heating of its walls. (see Section 9.5).

9.1.2 Types of nonequilibrium IR photochemical reactions

Let us consider the possible types of chemical reactions taking place in the process of IR MP initiation. The IR photochemical process is schematically shown in Figure 9.1. The details of the photochemical

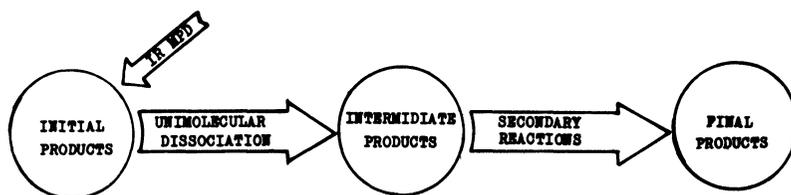


FIGURE 9.1 Simplified scheme of photochemical process initiated by high-power pulsed IR laser radiation.

process, of course, will greatly depend both on the degree of nonequilibrium attained in IR MP excitation of molecules and on the composition of initial products. For example, the mechanism of secondary reactions and the composition of final products must in many respects depend on the presence of other chemically active compounds in the mixture with the MP excited molecules which would be able to react with the primary products of IR MP dissociation. Let us restrict our consideration to the types of IR photochemical reactions in one- and two-component molecular gases. The number of components in this case corresponds to the number of only chemically active compounds in the gas mixture and does not include the buffer gas or the sensitizer gas.

(a) *One-component molecular gas*

1°. Reaction of unimolecular decay



This primary photochemical process has been considered for many molecules in Chapter 7 and so it is not discussed here.

2°. Reaction of successive decay



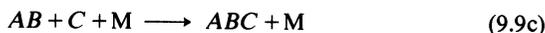
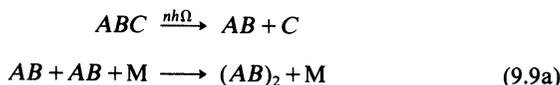
This reaction brings about fragmentation of primary product and will be considered in Sections 9.2.1 and 9.3.2.

3°. Competition of decay channels



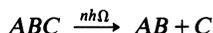
The effect of gas pressure and radiation parameters on the competitive channels of some reactions are considered in Section 9.2.1.

4°. Chemical reactions of primary IR MP dissociation products



These reactions proceed without a significant activation barrier and are a nonthermal channel of secondary photochemical reactions leading to final products (see Section 9.3).

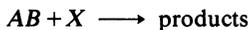
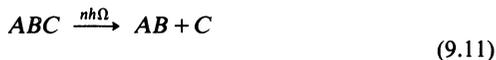
5°. Chemical reactions of radicals with the initial molecule:



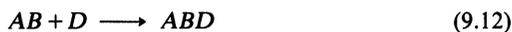
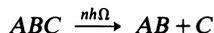
Reactions (9.10a) and (9.10b) have an activation barrier and are a thermal channel of secondary photochemical reactions (see Section 9.2.1).

(b) *Two-component molecular mixture*

6°. Directed reaction of the radical, i.e., product of selective IR MP dissociation of the *ABC* molecule, with the scavenger *X*



7°. Chain reaction initiated by the process of IR MP dissociation



Case (9.12) corresponds to the addition of a radical to a double-bond molecule. Example of such a reaction yielding telomers will be considered in Section 9.3.2.

9.2. Photochemical reactions in one-component molecular gases

With thermal initiation of reactions of polyatomic molecules, as a rule, the amount of various final products is often large and the yield of the desirable product is small. This is caused by the great number of different chemical reactions occurring in a molecular gas when under thermodynamic equilibrium the initial, intermediate and final products have one and the same enhanced temperature.

Quite a different situation occurs with IR MP initiation of radical reactions. In this case free radicals are formed under extremely non-

equilibrium and nonstationary conditions with the temperatures of the initial, intermediate and final products are essentially different. The products of laser-radical chemical reactions may thereby differ greatly from the products of their corresponding thermal reactions since under nonstationary conditions, besides thermodynamic factors, temporal factors must also be essential.

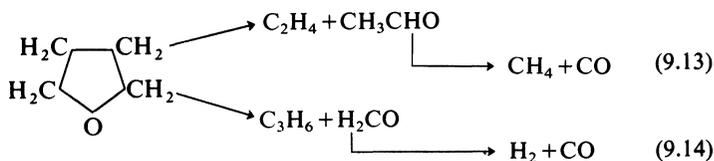
9.2.1. Products at IR MP initiation of chemical reactions

In this section we shall consider reactions of types 1° to 5° listed in Section 9.1.2 using for example some specific IR radical reactions in one-component molecular gases. Here we are interested mainly in the difference in reaction mechanisms in cases of, highly nonequilibrium (collisionless) and equilibrium (thermal) initiation, i.e., in cases 2°, 3° and 4° considered in Section 9.1.1. Each case (from 2° to 4°) is controlled by the rate of vibrational energy introduction into different components (molecules, radicals) which is determined by the laser pulse parameters and the rate of collisional relaxation of excitation.

(a) Influence of collisions

The study of the IR MP dissociation of tetrahydrofuran molecules $C_4H_8O^3$ illustrates clearly the difference in the branching ratio between the reaction channels of a polyatomic molecule for cases of collisionless and collisional (thermal) initiation.

In accordance with Ref. 4, the thermal decay of tetrahydrofuran (THF) with $T = 550^\circ C$ and $p = 200$ Torr occurs according to the following scheme:



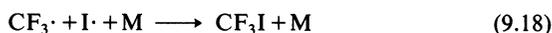
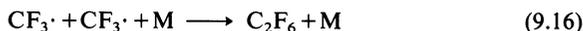
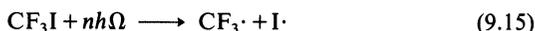
In the final products in this case the concentration ratio $[C_2H_4]/[C_3H_6] = 3.75:1$, that is, channel (9.13) is dominant. In the IR MP dissociation of THF the ratio $[C_2H_4]/[C_3H_6]$ depends on pressure. As p_{THF} increases from 0.3 to 12 Torr, the value of $[C_2H_4]/[C_3H_6]$ rises from 1 to 3.75, that is, to a value corresponding to that of thermal initiation.

According to Ref. 3, the dissociation of THF to C_3H_6 and H_2CO is preceded by an intermediate sequence of reactions with participation of radicals, that is, the products of primary dissociation of THF. At the same time the formation of C_2H_4 and CH_3CHO is preceded by reactions taking place as biradicals collide with heated initial molecules of THF. Thus, according to Refs. 3 and 4, channel (9.13) is purely thermal.

The pressure variation at IR MP dissociation of THF causes the ratio $[CH_4]/[C_2H_4]$ to change, too, which reflects the change of the role of successive dissociation in channel (9.13). As p_{THF} varies from 2 to 10 Torr, the value of $[CH_4]/[C_2H_4]$ increases from 3×10^{-2} to 0.6. The increase in THF pressure from 0.1 to 10 Torr corresponds to the change-over from highly non-equilibrium to thermal (collisional) initiation of reaction. Indeed, at low pressures, according to Ref. 3, the composition of final products is close to that observed in UV photolysis of THF. At the same time, at sufficiently high pressures it is close to the thermal one.

Let us consider the second case—the IR MP dissociation of CF_3I molecules.⁵ As the CO_2 laser energy fluence increases, the MP dissociation yield β increases at first and then, with $\Phi > 4 J/cm^2$, it becomes saturated (Figure 9.2). The value of saturation level in this case depends on the pressure of CF_3I .

At sufficiently a low pressure, $p_{CF_3I} = 0.2$ Torr, the maximum primary dissociation yield of CF_3I $\beta^{prim} = 1$, that is, with $\Phi > 4 J/cm^2$ in the region under irradiation 100% CF_3I molecules dissociate during one pulse (see also Refs. 6–8). According to Ref. 9, the reaction scheme looks thus



The final products are C_2F_6 (9.16), I_2 (9.17) and CF_3I (9.18). The presence of a recombination channel (9.18) according to Ref. 9 is responsible for the reduction of dissociation yield $\beta_{max}^{obs} \approx 0.7$.

At a higher gas pressure, $p_{CF_3I} = 4.4$ Torr, the dissociation yield $\beta_{max}^{obs} \approx 2$ (see Figure 9.2). According to Ref. 5, this result can be

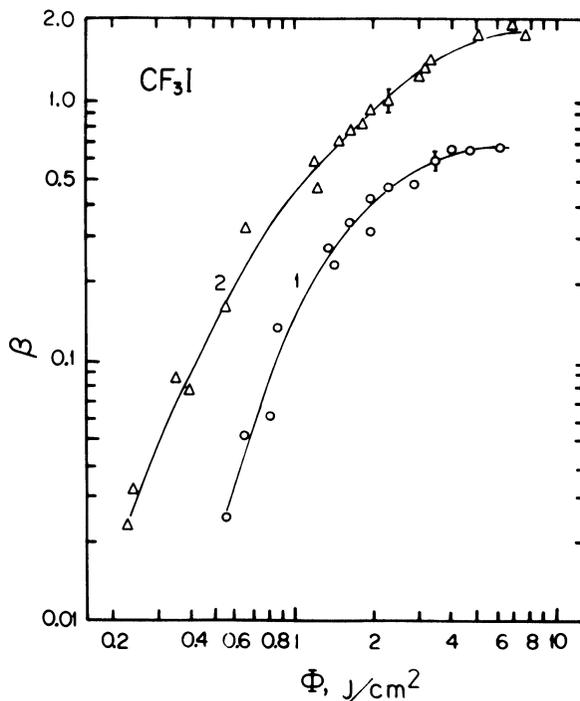
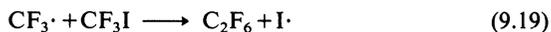


FIGURE 9.2 Dependence of the dissociation yield of the molecule CF_3I on laser energy fluence: 1. $p = 0.2$ Torr; 2. $p = 4.4$ Torr (from Ref. 5).

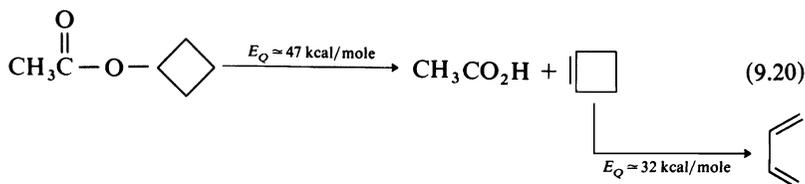
explained in the following way. At a high gas pressure, when the IR MP dissociation of CF_3I occurs under highly collisional conditions, the CF_3 radical formed by reaction (9.15) quickly derives a considerable energy in its collisions with the vibrationally excited CF_3I molecules. This suppresses the formation of the final products because of reaction (9.16) and makes the following thermal reaction channel more probable.¹⁰



The reaction (9.19) can provide the value $\beta_{\text{max}}^{\text{obs}} = 2.5$

The interesting and illustrative case is the IR MP dissociation of cyclobutyl acetate.¹¹ The pyrolysis of this molecule occurs according

to the following scheme



The rate of the second reaction in (9.20) with $T = 100 \text{ K}$ is 10^4 times higher than that of the first one. This means that in the pyrolysis of cyclobutyl acetate the formation of such an intermediate thermally unstable compound as cyclobutene is impossible. Quite a different situation takes place in the IR MP dissociation of cyclobutyl acetate. If at pressures $p > 2 \text{ Torr}$ the cyclobutene yield is negligible, its yield begins rising and becomes considerable as the gas pressure is reduced. In this case the cyclobutene yield is favourably affected by the buffer gas pressure (Figure 9.3). For example, when 1 Torr of CF_4 pressure is added, the relative yield of cyclobutene is increased by four times, the total dissociation yield β varying little in this case. Such a favour-

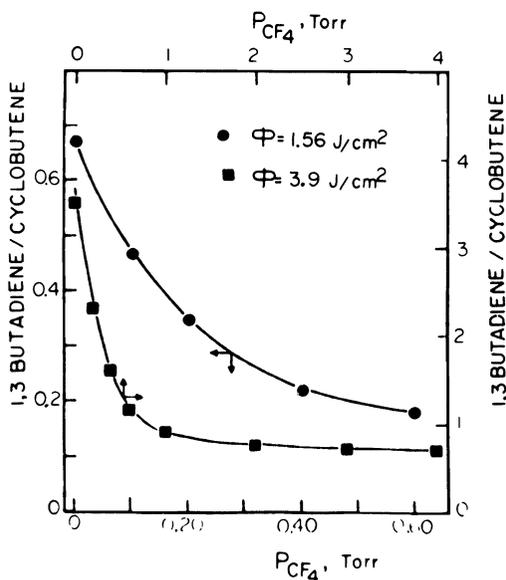


FIGURE 9.3 Dependence of the ratio of reaction yields (9.20) through the different channels on the pressure of buffer gas CF_4 (from Ref. 11).

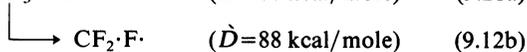
able effect of buffer gas can be explained by cooling the reacting mixture and eliminating thermal reactions producing the 1,3-butadiene.

So, as the above experiments show, the initiation of a reaction under near-collisionless conditions makes it possible to suppress materially thermal reaction channels, to change the ratio of competitive channels and to suppress to a considerable extent the successive reaction channels which lead to molecular fragmentation.

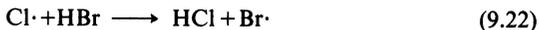
(b) *Influence of laser pulse parameters*

We will next consider the influence of laser pulse parameters on the type of IR photochemical reactions. The reactions, the successive dissociation of such molecules as SF₆,¹² SF₅Cl,¹³ CF₃Cl,¹⁴ CF₃Br,¹⁵ CFCl₃,¹⁶ C₂H₄¹⁷ are the simplest examples.

In the case of CF₃Cl, for example, the successive IR MP dissociation occurs thus



The diagnostics of the Cl and F atoms was carried out in Ref. 14 by observing the IR chemiluminescence signals of the HCl and HF molecules formed in the reactor with a small amount of HBr added



The rate constants of reactions (9.22) and (9.23) are well known which allows reliable measurements of the concentrations of Cl and F atoms. The measurements of IR chemiluminescence intensities show, that with $\Phi=10$ to 100 J/cm^2 the yield ratio of F and Cl atoms in reaction (9.21) is 1:3.5.

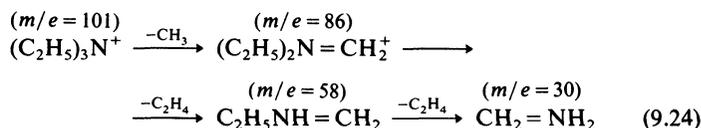
Such a relatively high yield of F atoms and its slow dependence on Φ are surprising at first sight. But it should be taken into account here that the exciting IR radiation frequency $\Omega = 1090.03 \text{ cm}^{-1}$ used Ref. 14 is considerably detuned relative to the absorption band maximum of CF₃Cl ($\nu = 1105 \text{ cm}^{-1}$) and at the same time it is close to the absorption band maximum of the radical CF₃ ($\nu = 1087 \text{ cm}^{-1}$). This factor explains a high relative yield of F atom in reaction (9.21b). Indeed, in the IR MP dissociation of such similar molecules as CF₃Br¹⁵ and CF₃I⁵ excited near their absorption band maxima the relative

yield of F atoms is negligible. So, by choosing the laser pulse frequency one can essentially affect the process of molecular fragmentation.

The influence of the excitation degree and the radiation frequency on the character of fragmentation manifests itself rather distinctly in the case of big molecules. Therefore we are going to consider here the IR MP dissociation of the polyatomic molecular ion $(C_2H_5)_3N^+$.¹⁸ It is much simpler to study the reaction channels for molecular ions than for neutral molecules since, first, the diagnostics of fragments can be done with a mass-spectrometer and, secondly, it is easy to provide observation under collisionless excitation.^{18,19} The application of multi-photon ionization by visible or UV laser radiation allows preparation of the wanted concentration of molecular ions of a definite sort.^{5,20}

The ion $(C_2H_5)_3N^+$ has been formed¹⁸ in the process of three-photon ionization of triethylamine by dye laser radiation with $\lambda = 452$ nm. The fragments of IR MP dissociation were detected with a quadrupole mass-filter.

According to Ref. 18 the successive dissociation of $(C_2H_5)_3N^+$ comes about thus



With an increase of Φ the relative yield of smaller fragments increases, too. The fragment distribution in this case depends not only on laser energy fluence but also on its frequency. At the same energy fluences Φ and at similar dissociation yields (determined by the relative decrease of mass peak $m/e = 101$) the fragment distributions for two frequencies ($\Omega = 1079.85$ cm⁻¹ and $\Omega = 940.55$ cm⁻¹) differ essentially. It is just this factor (9.18) that is responsible for the different absorption of laser radiation at different frequencies by IR MR dissociation fragments.

The ratio of parallel competitive reaction channels can be varied by changing the laser energy fluence and intensity. Indeed, as the molecular excitation rate is increased, it causes the degree of molecular excitation over the dissociation limit to be increased (see below (Ref. 29)). So, if a molecule has two unimolecular dissociation channels similar in energy, the variation of its excitation rate can change its

dissociation rate through two different channels and hence change the ratio of the final products.

The IR MP dissociation of the CF_2Br_2 and CF_2Cl_2 is a very striking example of such a situation²¹ (Figure 9.4). For the CF_2Cl_2 molecules, for example, the unimolecular dissociation is possible through the one of two competitive channels



The use of the radical scavenger Br_2 made it possible (9.21) to determine the ratio of channels (9.25) and (9.26). To see this, in the case of channel (9.25) the molecule CF_2ClBr and in the case of (9.26) CF_2Br_2 are formed. Br_2 is thereby taken in excess to bind all the resultant radicals CF_2Cl and CF_2 . Besides the scavenger method, the radical CF_2 was directly detected²² by the resonant fluorescence technique. As seen from Figure 9.4, the relative fraction of CF_2 radicals for the CF_2Cl_2 and CF_2Br_2 , that is the relative reaction yield through the channel with detachment of a molecule (Cl_2 or Br_2), depends on the total dissociation yield β . Even though channel (9.26) for CF_2Cl_2 is

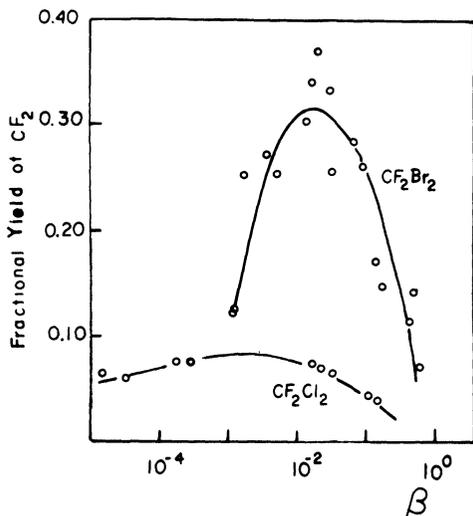


FIGURE 9.4 Dependence of the relative yield of the CF_2 radical on β in the IR MP dissociation of the molecules CF_2Br_2 and CF_2Cl_2 (from Ref. 21).

less endothermic than channel (9.25), there is an activation barrier for the reaction reverse to (9.26) that equals 10 kcal/mol. Therefore the activation barriers for unimolecular dissociation reactions (9.25) and (9.26) are very close, and this results in a competition of these two channels.

In Refs. 23–25 consideration is given to the case of IR MP dissociation of a more complex molecule, ethylvinyl ether. Figure 9.5a pres-

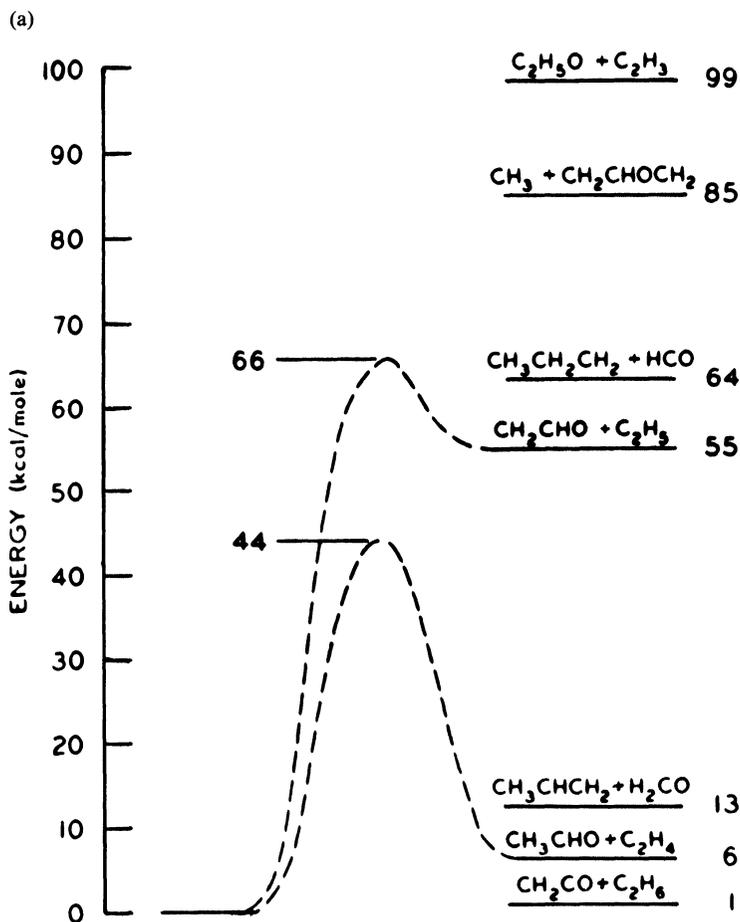


FIGURE 9.5 (a) Some possible dissociation channels for the molecule of ethylvinyl ether (from Ref. 24).

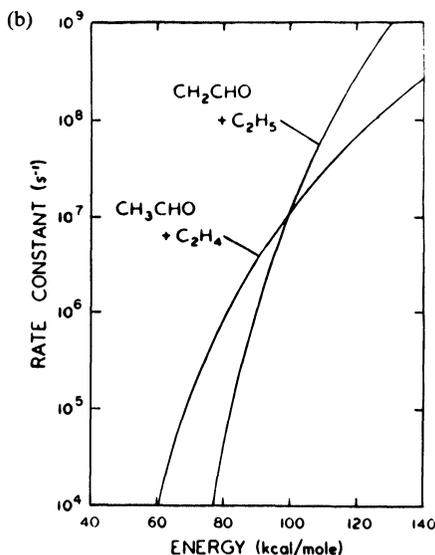
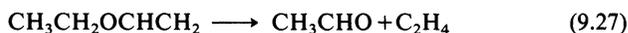


FIGURE 9.5 (b) Dependence of the dissociation rate of ethylvinyl ether on internal energy. The calculation is carried out in accordance with the RRKM theory (from Ref. 24).

ents some potential dissociation channels of this molecule calculated on the basis of the thermochemical results.²⁴ The pyrolysis of ethylvinyl ether with $T = 400\text{--}600$ K produces mainly acetaldehyde and ethylene:



At the same time, in the process of IR MP dissociation of ethylvinyl ether one can also observe a higher-energy radical channel



In this case^{23–25} the ratio of channels (9.27) and (9.28) depends materially on laser pulse parameters. As the exciting IR pulse duration τ_p is decreased²³ (the intensity I is increased) at a fixed energy fluence Φ , the dissociation reaction of ethylvinyl ether shifts to channel (9.28). If with $\tau_p = 2 \mu\text{s}$ ($p = 0.5$ Torr, $\Phi = 0.56\text{--}0.91 \text{ J/cm}^2$) the final products completely correspond to channel (9.27), with $\tau_p = 0.2 \mu\text{s}$ it is channel (9.28) that is dominant.

For more correct measurement of the ratio of unimolecular dissociation channels (9.27) and (9.28) it is necessary to get rid of secondary reactions. The ratio of channels (9.27) and (9.28) has been found

using²⁴ a time-of-flight mass-spectrometer and the technique of intercrossing laser and molecular beams (see Chapter 7). The accurate measurements performed²⁴ for dissociation channels (9.27) and (9.28) have shown that the relative yield of unimolecular dissociation of ethylvinyl ether through channel (9.28) rises with an increase of Φ , and with $\Phi = 0.7, 1.8$ and 12 J/cm^2 it equals respectively 14%, 31% and 43%.

The fact that the relative yield of channel (9.28) rises with an increase of Φ is related to the increase of the degree of molecular excitation. Indeed, channel (9.28) has a preexponential factor $A \approx 10^{15}$, whereas for the low-energy channel it will be $A \approx 10^{11}$. So at sufficiently high levels of excitation over both dissociation limits the rate of dissociation through channel (9.28) may exceed the rate of dissociation through channel (9.27). The dissociation rates calculated with the use of the RRKM theory (Figure 9.5b) confirm these qualitative considerations.

So, the products of IR MP molecular dissociation strongly depend on the conditions of their excitation. If at thermal initiation the channels of chemical reaction and the final products are fully determined by thermodynamics, at nonequilibrium IR MP initiation it is possible, as shown above (and other work,²⁶⁻³³) to control the channels of chemical reactions and make the unusual channels studied under equilibrium conditions more competitive by changing the laser pulse parameters. In this respect the method of IR MP initiation (IR photolysis) is much more effective than the conventional pyrolysis of molecules.

9.2.2. *Nonstationary vibrational overexcitation and new channels of chemical reactions*

All the states of a molecule with vibrational energy E exceeding the lowest dissociation limit are, in principle, chemically unstable. Therefore, the molecule absorbing by IR MP excitation the vibrational energy $E > D_0$ is able to dissociate. For molecules with a comparatively small number of atoms $N < 6-8$ the theory of unimolecular dissociation predicts a very fast increase of the dissociation rate with the increasing value $(E - D_0)$. For such molecules the maximum excitation over the dissociation limit is relatively small $(E^{\text{max}} - D_0) \ll D_0$ (see Section 2.4) in agreement with the results of direct experiments (see Chapter 7). At the same time for sufficiently big molecules with

$N > 10-12$, according to the theory of unimolecular dissociation, the rate of dissociation $K_{\mu m}(E)$ is not high compared to the MP excitation rate even at considerable excitation over the dissociation limit.

In a semiclassical approximation of the RRKM theory ($E^{\max} \gg E_0$, where E_0 is the energy of zero-point molecular vibrations) the following estimation can be obtained³⁴ for the maximal deposition of energy to vibrations E^{\max} :

$$(E^{\max} - D_0)/D_0 = \left[1 - \left(\frac{W}{\bar{\omega}} \right)^{1/(S-1)} \right]^{-1} - E_0/D_0 - 1 \quad (9.29)$$

where W is the rate of vibrational molecular MP excitation, S is the number of vibrational degrees of freedom, $\bar{\omega}$ is the frequency factor (see Chapter 2, Section 2.4, expression (2.86)). The frequency factor $\bar{\omega}$ by order of magnitude is equal to the molecular vibration frequency $10^{13}-10^{14} \text{ s}^{-1}$. IR MP excitation easily provides the excitation rate $W \approx 10^9 \text{ s}^{-1}$. Then, according to (9.29), with $s \gg \ln(\bar{\omega}/W)$ the vibrational excitation of molecule over the dissociation limit D_0 may be as much as twice ($(E^{\max} - D_0)/D_0 \approx 1$).

Above in Chapters 5 and 6, we have already discussed such characteristic features of IR MP excitation of big molecules as a small role of the effect of "rotational bottle neck" as well as a much smaller reduction in MP absorption cross-section with increasing energy fluence Φ . Here we are going to discuss the MP excitation of big molecules in the real continuum of vibrational states and the effects related to their high vibrational overexcitation.

(a) *Strong IR MP absorption*

Let us consider the dependence of the average absorbed energy $\bar{\epsilon}$ on radiation energy fluence Φ for two molecules: a small one— CF_3I ($S = 9$) and a big one— $(\text{CF}_3)_3\text{CI}$ ($S = 36$)³⁵ (Figure 9.6). The value $\bar{\epsilon}$ for the molecule CF_3I is saturated with $\Phi > 4 \text{ J/cm}^2$ and equals $\bar{\epsilon}^{\max} \approx D$. At the same time, for the molecule $(\text{CF}_3)_3\text{CI}$ the value $\bar{\epsilon}$ increases linearly with an increase in Φ and exceeds considerably the value of D_0 .

The given examples of IR MP absorption in CF_3I and $(\text{CF}_3)_3\text{CI}$ are two qualitatively different situations. In the case of CF_3I , when the molecule acquires the energy $E \approx 20\,000 \text{ cm}^{-1}$, the process of IR radiation absorption actually stops. This is explained³⁶, first, by the effective dissociation of CF_3I during the laser pulse and, secondly, by the

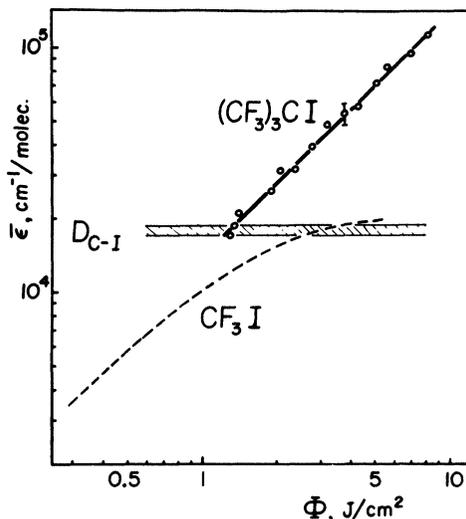
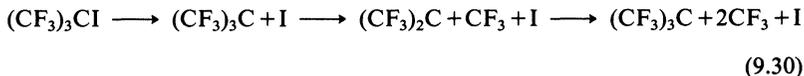


FIGURE 9.6 Dependence of absorbed energy $\bar{\epsilon}$ on laser energy fluence in the IR MP excitation and dissociation of the molecules CF_3I and $(\text{CF}_3)_3\text{CI}$ (from Ref. 35).

small cross-section of absorption by CF_3 radicals on laser frequency ($\Omega = 1079.4 \text{ cm}^{-1}$).

On the contrary, in the IR MP excitation of such a big molecule as $(\text{CF}_3)_3\text{CI}$ its dissociation during a radiation pulse ($\tau_p = 10^{-7} \text{ s}$) takes place only under sufficient overexcitation. The molecule $(\text{CF}_3)_3\text{CI}$ can derive³⁵ the energy $\bar{\epsilon} \approx (1.7-2) D$ in 10^{-6} s and only then begins to dissociate. Furthermore, the radicals $(\text{CF}_3)_3\text{C}$ formed in the primary dissociation of $(\text{CF}_3)_3\text{CI}$ have a considerable excess of energy which enables their further IR MP excitation. Indeed, as it has been shown,²⁵ with an increase of Φ above $1.5-2 \text{ J/cm}^2$ the yield of CF_3 radicals (and their recombination product C_2F_6) rises rapidly. At a sufficiently high value of Φ the molecule $(\text{CF}_3)_3\text{CI}$ successively dissociate to a number of small fragments



that explains such a high value of absorbed energy (Figure 9.6) with $\Phi > 3-4 \text{ J/cm}^2$.

Strong overexcitation and fragmentation have been studied for some big molecules.³⁷⁻³⁹ The effect of fragmentation is, as a rule, undesirable for laser-radical synthesis. However, the effect of strong overexcitation opens up such unusual dissociation channels of vibrationally excited molecules as electronic predissociation and the formation of charged particles which are discussed below.

(b) *Electronic predissociation*

The unimolecular dissociation of the molecule $(\text{CF}_3)_3\text{CI}$ during the laser pulse $\tau_p = 10^{-6}$ s takes place with the vibrational energy being $E = 35\,000\text{--}40\,000\text{ cm}^{-1}$.³⁵ This agrees well with the estimations made with formula (9.29).

At such overexcitation the vibrational energy of molecule E exceeds the energy limit of its first electron term ($E^* \approx 27\,000\text{ cm}^{-1}$) which is repulsive (Figure 9.7a). It is natural to assume that in this case due to a nondiabatic coupling between the electronic and vibrational motions the IR MP overexcitation of the molecules $(\text{CF}_3)_3\text{CI}$ can lead to its electronic predissociation. It is well known that in UV photolysis of many iodides, particularly $(\text{CF}_3)_3\text{CI}$ a considerable fraction of iodine atoms is formed in the excited state $\text{I}^*(^2P_{1/2})$.⁴⁰ So, if the effect of electronic predissociation of vibrationally overexcited molecules $(\text{CF}_3)_3\text{CI}$ actually takes place, the atoms $\text{I}^*(^2P_{1/2})$ luminescent at $\lambda = 1.315\text{ }\mu\text{m}$ must be formed. At the same time, the dissociation of the molecule within the ground electronic state produces iodine atoms in the ground state $\text{I}(^2P_{3/2})$.

The observation⁴¹ of IR luminescence of atomic iodine at the transition $^2P_{1/2} \rightarrow ^2P_{3/2}$ ($\lambda = 1.315\text{ }\mu\text{m}$), as $(\text{CF}_3)_3\text{CI}$ molecules are irradiated by CO_2 laser pulse with the duration $\tau_p = 1\text{ }\mu\text{s}$ and the frequency $\Omega = 949.48\text{ cm}^{-1}$ is direct experimental proof of the effect of electronic predissociation of vibrationally overexcited molecules. The dependence of IR luminescence intensity on laser energy fluence Φ with the pressure of $(\text{CF}_3)_3\text{CI}$ $p = 1$ Torr is illustrated in Figure 9.7b. The IR luminescence signal was registered with a PbS photodetector. For absolute calibration of the IR luminescence signal the intensity of excited iodine atoms UV photolysis of $(\text{CF}_3)_3\text{CI}$ molecules by excimer XeCl laser radiation ($\lambda = 308\text{ nm}$) was carried out. The geometry of irradiation and luminescent light collection were the same as in IR MP photolysis. Then from the known value of quantum yield of I^* atoms (η^{UV}) the absolute sensitivity of detection was measured. The

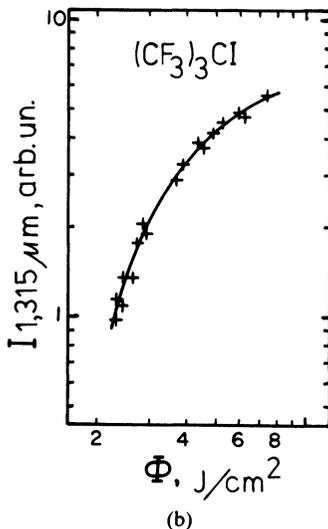
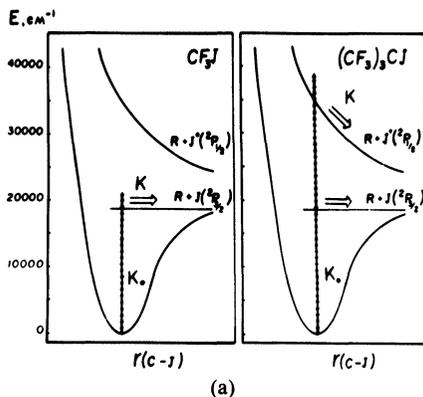


FIGURE 9.7 (a) Unimolecular dissociation channels of the molecules CF_3I and $(\text{CF}_3)_3\text{CI}$ (from Ref. 41); (b) Dependence of luminescence intensity ($\lambda = 1.315 \mu\text{m}$) on laser energy fluence in the IR MP excitation of the $(\text{CF}_3)_3\text{CI}$ molecule (from Ref. 41).

IR MP dissociation yield of $(\text{CF}_3)_3\text{CI}$ molecules (β) was determined independently. The measurements performed⁴¹ show that with $\Phi = 5 \text{ J/cm}^2$ the yield $\beta = 1$. In this case no less than 10% iodine atoms are formed in the state $^2P_{1/2}$. Thus, the quantum yield of I^* atoms in the process of IR MP overexcitation of $(\text{CF}_3)_3\text{CI}$ by CO_2 laser pulses

with $\Phi = 5 \text{ J/cm}^2$ equals $\eta^{\text{IR}} \approx 0.1$. For comparison, in UV photolysis of these molecules at $\lambda = 308 \text{ nm}$ $\eta^{\text{UV}} = 0.3$ ⁴⁰

Besides detecting I^* atoms with IR luminescence, they were detected⁴¹ with visible luminescence of electronically excited iodine molecules at $\lambda = 580 \text{ nm}$ formed by the secondary chemical reaction



The measurements of the temporal characteristics of this luminescence show that they are quite identical to the corresponding characteristics in UV photolysis.

Similar experiments performed⁴¹ for the CF_3I molecule showed that there is no luminescence signal at $\lambda = 1.315 \mu\text{m}$ and at $\lambda = 580 \text{ nm}$ with $p \leq 1 \text{ Torr}$ (see Ref. 8). This is in agreement with the absence of strong overexcitation in CF_3I . Thus it can be concluded⁴¹ that the electronic predissociation of the $(\text{CF}_3)_3\text{CI}$ molecule results directly from its strong vibrational overexcitation because it is a molecule with a sufficiently big number of atoms and furthermore is possible due to a low rate of unimolecular decay in the ground electronic state.

(c) Formation of charged particles

According to (9.29), the value E^{max} rises with an increase in the number of degrees of freedom S . As a test,³⁴ strong IR MP overexcitation of a polyatomic molecule-anthracene ($\text{C}_{14}\text{H}_{10}$) for which $S = 66$ – was performed. As an estimation (9.29) for this molecule $E^{\text{max}} \approx 4D_0 \approx 19 \text{ eV}$. With such considerable values of vibrational energy, due to a nonadiabatic coupling of electronic and vibrational motions, it seems quite possible to excite high lying electronic states which, among other things, would cause the molecule to be ionized.

A time-of-flight mass-spectrometer was used³⁴ to observe the charged particles formed by IR MP excitation of the molecules. The experiments were carried out with IR laser pulses of two different durations: “short” pulse with $\tau_p = 70 \text{ ns}$, “long” pulse with $\tau_p = 1 \mu\text{s}$. The mass-spectrometer was calibrated against the molecular ion $\text{C}_{14}\text{H}_{10}^+$ formed by two-photon ionization of anthracene vapour by excimer KrF laser radiation ($\lambda = 249 \text{ nm}$, $\tau_p = 20 \text{ ns}$) (see Figure 9.8c). Figure 9.8a shows a characteristic mass-spectrum of positive particles formed as the anthracene molecules are irradiated with $p = 4 \cdot 10^{-6} \text{ Torr}$ by “a short” pulse of CO_2 laser radiation with the energy fluence $\Phi = 55 \text{ J/cm}^2$. The heaviest ion observed in this mass-spectrum

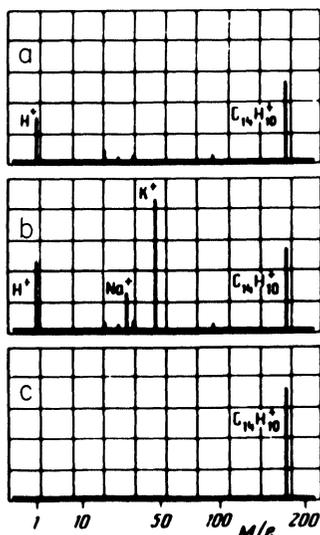


FIGURE 9.8 Mass-spectrum of positive ions formed by irradiating anthracene molecules with: (a) “short” CO₂ laser pulses, $\tau_p \approx 70$ ns; (b) “short” CO₂ laser pulses when some part of radiation is reflected on the surface of the copper electrode in the mass-spectrometer; (c) KrF laser (from Ref. 34).

is C₁₄H₁₀⁺ and the lightest one is the hydrogen ion H⁺. The threshold of ion formation in the case of “short” IR pulse corresponds to the value $\Phi \approx 35$ J/cm². In irradiating anthracene vapour with “long” pulses up to $\Phi = 80$ J/cm² no³⁴ ions were observed.

To clear up the potential role of ion formation on the surface of mass-spectrometer elements under the action of IR radiation, a check experiment³⁴ was performed in which the laser pulse after the chamber was directed onto the surface of the electrode located right under the ionization region. The mass-spectrum in this case showed additional peaks formed which correspond to the ions Na⁺ and K⁺ (Figure 9.8b) desorbed from the brass electrode surface as a result of its heating by the IR radiation pulse. In the case of a similar check experiment with “a long” IR pulse one can observe just the ions Na⁺ and K⁺.

These experiments have shown that in the case of collisionless IR MP excitation of anthracene molecules one can observe their ionization and proton detachment. The fact that the internal energy of molecules exceeds the energy of corresponding reaction channels is a necessary condition for the existence of these processes. Figure 9.9

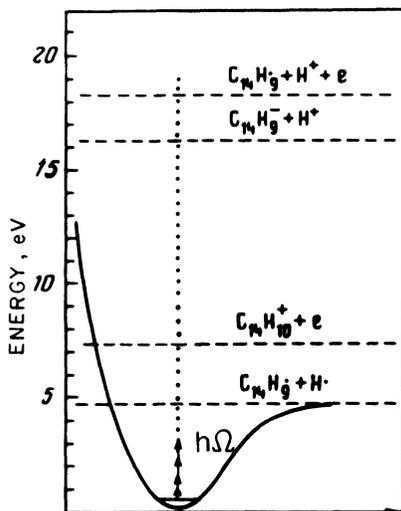


FIGURE 9.9 Thresholds of some possible reactions of the anthracene molecule (from Ref. 34).

shows an energy diagram where one can see thresholds of some potential dissociation reactions of anthracene molecules. The ionization threshold equals 7.4 eV; the thresholds of proton formation in the reactions given in Figure 9.9 equal 16.3 and 18.4 eV. Thus, the observation of proton and electron detachment, as the anthracene molecule is under IR irradiation, points directly to its strong vibrational excitation over the dissociation limit in the ground electronic state. The observed levels of molecular over-excitation as well as the leading role of radiation intensity (and hence the role of excitation rate W) confirm the possibility of vibrational overexcitation of big molecules.

Thus for molecules with a comparatively small number of atoms, for example SF_6 , BCl_3 and others, at typical pulse durations $\tau_p \approx 10^7\text{--}10^{-6}$ s in accordance with the predictions of the RRKM theory and the results of direct observations (see Chapter 7) the maximal vibrational excitation over the dissociation limit is small. In this case the IR MP ionization of small molecules by IR radiation is improbable.

The formation of charged particles in vibrational excitation on neutral molecules is one of the manifestations of a nonadiabatic coupling of electronic and vibrational motions in highly excited

molecules along with the processes of inverse electronic relaxation,⁴² electron detachment from a negative ion⁴³ and the above-discussed electronic predissociation. The strong IR MP overexcitation of molecules provides a new possibility of effective preparation of highly excited vibrational molecular states.

9.3. Photochemical reactions in two-component gas media

Pulsed selective production of high concentrations of definite free radicals in a mixture with a specially chosen reagent enables bimolecular reactions aimed at obtaining the wanted product. This interesting possibility is used at present in chemical kinetics to determine bimolecular reaction rates as well as in chemical technology for highly effective directed synthesis of molecular compounds.

9.3.1. Study of bimolecular reactions

The method of pulsed IR photolysis in combination with mass-spectrometric and spectroscopic diagnostics allows the measurement of absolute rates of chemical reactions under controllable conditions. The method of IR excitation is particularly valuable in measuring the rates of fast gas-phase radical reactions. IR photolysis makes it possible to produce relatively cold radicals and to study the reactions under conditions not possible in thermal generation of radicals (pyrolysis).

The universality of the method of IR photolysis permits studying reactions of various radicals. Contemporary methods of spectroscopic diagnostics make it possible to investigate the reactions of radicals in different quantum states and to determine the quantum state distribution of reaction products.

Below are several specific examples of the application of IR MP excitation and dissociation for studying bimolecular reactions.

(a) Reactions of C_2 radicals.

There was very little information on the reactions of the C_2 radical in a gas phase before the method of IR photolysis because of the absence of suitable methods of C_2 radical generation under controllable conditions and quantum states. At the same time, the reactions of C_2 with different molecules, for example with Q_2 , play a significant part in the processes of burning, airborne pollution, atmospheric chemistry and some other important processes. Therefore, it is

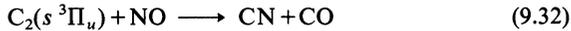
necessary to know the absolute reaction rates of C₂ to model these processes.

In pulsed IR photolysis of C₂H₄ and C₂H₃CN molecules C₂ radicals are formed both in the ground ($X^1\Sigma_g^+$) and in the electronically excited metastable state ($a^2\Pi_u$).^{44,45} The reaction rates of C₂ in these states can be measured directly using laser-induced fluorescence.^{46,47} This method is very handy to investigate the reaction kinetics of radicals from a definite electronically-vibrationally-rotational state since it features a high sensitivity and high spectral and time resolutions.

Another method which allows measuring radical reaction rates consists in measurement of chemiluminescence kinetics⁴⁸ arising in the exothermic reaction of the C₂ radical with a molecule, an atom, or a radical.

Table 9.1 shows the results of measurements of the rate constants for some reactions of the C₂ radical carried out by the methods of laser-induced fluorescence and chemiluminescence. As shown by measurements, these reactions are very fast. The reactions of C₂ with NO, C₂N₃CN and C₂H₄, for example, occur actually during every gas-kinetic collision which shows that there is no geometric barrier for these reactions.

Now consider the distribution of one of the products CN over electronic, vibrational and rotational states for the reaction



In reaction (9.32) the molecule CN can be formed⁴⁵ in one of the three electronic states ($X^2\Sigma^+$), ($B^2\Sigma^+$) or ($A^2\Pi$). The formation of CN in the excited state ($B^2\Sigma^+$) (the lifetime is 6–7 μs) is followed by “violet” chemiluminescence (the transition $B^2\Sigma^+ \rightarrow X^2\Sigma^+$), in the excited state

TABLE 9.1
Rate constants for some reactions of the C₂ radical

Reaction	Rate constant of reaction (cm ³ mol ⁻¹ s ⁻¹)	Reference
C ₂ ($x^1\Sigma_g^+$) + O ₂	3.0 ± 0.2 · 10 ⁻¹²	44
C ₂ ($a^2\Pi_u$) + O ₂	3.0 ± 0.2 · 10 ⁻¹²	44
	3.4 · 10 ⁻¹²	49
C ₂ ($a^3\Pi_u$) + NO	7.5 ± 0.3 · 10 ⁻¹¹	45
C ₂ ($a^3\Pi_u$) + C ₂ H ₃ CN	1.2 ± 0.2 · 10 ⁻¹⁰	45
C ₂ ($a^3\Pi_u$) + C ₂ H ₄	1.7 ± 0.2 · 10 ⁻¹⁰	45

($A^2\Pi$) (the lifetime is 60 ns) by "red" chemiluminescence (the transition $A^2\Pi \rightarrow X^2\Pi$).

First, the measurement of the integral intensities of these bands allows determining the concentration ratio $[CN(A)]/[CN(B)]$ of the molecules CN formed in the states ($A^2\Pi$) and ($B^2\Sigma^+$). According to Ref. 45, the value $[CN(A)]/[CN(B)] \approx 7$. Analysis of these spectra yield relative populations of vibrational levels and a rotational temperature assuming Boltzmann distribution over rotational levels.

The vibrational temperature of $CN(B^2\Sigma^+)$ corresponding to this distribution is $T_{\text{vib}} = 10\,500$ K. The vibrational temperature for $C_2(A^2\Pi)$ measured in the same way is $T_{\text{vib}} = 13\,000$ K. Thus, a combination of pulsed IR photolysis with the technique of laser-induced fluorescence or chemiluminescence gives important information about the ways and rates of chemical radical reactions. This technique has been used in studying the reactions for some free radicals: for example BCl_2 ,⁴⁸ C_3 ,⁴⁵ CN .⁴⁵

(b) *Reactions of fluorine atom*

Atomic fluorine is chemically very active and many of its reactions are very fast. Of great interest for chemical kinetics are reactions of the fluorine atom with molecular hydrogen and deuterium



These reactions have been studied theoretically using both quantum-mechanical and classical methods for calculating trajectories. Experimental studies of these reactions' rates and their reaction product energy distributions have used the methods of IR chemiluminescence and molecular beam scattering as well as the chemical HF and DF lasers. However, despite extensive studies, there remained discrepancies between reaction rates (9.33a) and (9.33b) at room temperature; the Arrhenius parameters of these reactions are also not consistent. The combination of IR photolysis of a fluorine-containing molecule (for example SF_6) in the presence of H_2 or D_2 with measurement of the IR chemiluminescence kinetics of HF or DF gives another very simple and informative method for determining the rate constants of reactions (9.33a) and (9.33b). Table 9.2 presents the results of measurements of the temperature dependences of these constants carried out Refs. 50 and 51 in two temperature intervals. It can be seen that the

TABLE 9.2
 Temperature dependences of the rate constants for the reactions $F + H_2(K_H)$ and $F + D_2(K_D)$

	$T = 190\text{--}373\text{ K}$	Ref.	$T = 295\text{--}765\text{ K}$	Ref.
K_H ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$1.0 \cdot 10^{-10} \exp -(860 \pm 100)/RT$	50	$2.2 \cdot 10^{-10} \exp -(1182 \pm 100)/KT$	51
K_D ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$0.9 \cdot 1 \cdot 10^{-10} \exp -(1100 \pm 100)/RT$	50	$1.1 \cdot 10^{-10} \exp -(1200 \pm 142)/RT$	51

results obtained by different research groups are in satisfactory agreement. This method can be successfully applied to study some other reactions, for example, the reactions of the fluorine atom with HCl, HBr, DBr, HI,⁵² CF₃O.⁵³

(c) *Reactions of fluoroorganic radicals*

One of the experimental methods of chemical kinetics is molecular pyrolysis in a Knudsen cell at low pressures (10^{-3} to 10^{-2} Torr) with a subsequent study of reaction products with time-resolved mass-spectrometry.⁵⁴ IR photolysis⁵⁵⁻⁵⁷ has been substituted for the thermal generation of radicals and the rate constants were measured for a number of reactions of some fluoroorganic radicals: CF₃, C₂F₅, C₃F₇.

In Table 9.3 are given the rate constants of reactions of the CF₃ radical with the molecules Br₂, NOCl, O₃, NO₂⁵⁶ and those of the radicals C₂F₅ and *n*-C₃F₇ with the molecule Br₂.⁵⁸ The fluoroorganic radicals R=CF₃, C₂F₅, *n*-C₃F₇ have been formed by IR photolysis of molecules RI in a Knudsen cell at room temperature. The temperature dependences of radical reaction rate constants can be determined in this method by changing the temperature of the Knudsen cell's walls.

The reactions⁵⁹⁻⁶¹ of methyl, allyl, acetyl and chlorodifluoromethyl radical with the molecules Br₂ and NO₂ were studied with a photoionization mass-spectrometer.

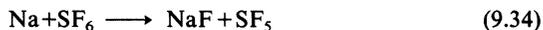
(d) *Reactions of vibrationally excited molecules*

Of considerable interest for chemical kinetics are not only the radicals but also the vibrationally excited molecules produced by IR photolysis. Under collisionless IR excitation only the vibrational energy of molecule is increased, whereas the translational energies do

TABLE 9.3
Rate constants for some reactions of the radicals CF₃,⁵⁶ C₂F₅ and *n*-C₃F₇⁵⁸

Reaction	Rate constant (cm ³ mol ⁻¹ s ⁻¹)
CF ₃ + Br ₂ → CF ₃ Br + Br	(2.8 ± 0.4) · 10 ⁻¹¹
CF ₃ + NOCl → CF ₃ Cl + NO	(1.3 ± 0.2) · 10 ⁻¹¹
CF ₃ + O ₃ → CF ₂ O + O ₂ + F	(2 ± 0.3) · 10 ⁻¹¹
CF ₃ + NO ₂ → CF ₂ O + NO + F	(0.6 ± 0.1) · 10 ⁻¹⁰
C ₂ F ₅ + Br → C ₂ F ₅ Br + Br	(0.75 ± 0.2) · 10 ⁻¹¹
C ₃ F ₇ + Br ₂ → C ₃ F ₇ Br + Br	(1.1 ± 0.3) · 10 ⁻¹¹

not increase. This makes it possible to study the role of different types of molecular energy in overcoming the activation barrier of chemical reaction.^{62,63} The reaction of Na atoms with IR excited SF₆ molecules is an example of such a study. The rates of the reaction⁶²



have been compared at IR and thermal excitation of SF₆, when the vibrational, rotational and translational degrees of freedom have the same temperature. The measurements carried out in the temperature range $T = 380\text{--}440$ K show that reaction (9.34) has an activation barrier $E_a = 3.3$ kcal/mol. In this case the rates of reaction (9.34) for two different types of excitation will be equal at the same stores of vibrational energy. This means that the main role in overcoming the activation barrier of reaction (9.34) is played by the vibrational temperature of the SF₆ molecule; the role of its translational and rotational energy is insignificant.

The examples considered here show that the method of IR MP excitation and dissociation of polyatomic molecules enables even now the obtaining of important information on the rates and mechanisms of the different types of gas-phase reactions. Due to its simplicity, universality and informative ability this method combined with contemporary methods of diagnostics of intermediate species (such as mass-spectroscopic methods, methods of kinetic spectroscopy and particularly laser spectroscopy) is becoming a routine method of chemical kinetics.

9.3.2. Laser radical chemical synthesis

IR MP dissociation of polyatomic molecules makes it possible in a short time ($10^{-6}\text{--}10^{-9}$ s) to obtain high concentrations of various free radicals (see Chapter 7). These radicals can be used not only for research in chemical physics but also for directed synthesis of molecular compounds in subsequent gas-phase radical chemical reactions. Let us consider some examples of such an approach to chemical synthesis.

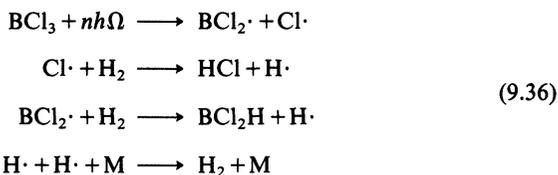
(a) Synthesis of BCl₂H

The chemical reaction of BCl₃ with H₂ irradiated by focused pulses of a TEA CO₂ laser has been studied⁴⁷ in detail. Under thermal conditions of reaction the compounds B₂H₆, highest boranes, chlor-

boranes, HCl and BHCl₂ are formed with a yield of only several percent BHCl₂ in this mixture. Under laser action the nonthermal reaction gives rise to only BHCl₂ and HCl molecules



The reaction brings about an equilibrium with 50% conversion of the initial BCl₃ and H₂. Reaction (9.35) is endothermal by about 0.65 eV, i.e., by an energy of about 6 photons of CO₂ laser. The microscopic reaction, of course, is more complex and proceeds probably thus:



This experiment was performed with the total pressure of the mixture (1 : 1) from 40 to 100 torr. The maximum quantum efficiency of reaction during the single laser pulse $\varphi \approx 0.3$ was observed at a pressure of 80 Torr. This is rather a high quantum efficiency for a reaction controlled by IR field. Under the conditions of the above experiment the effects of collisionless MP excitation and dissociation are not the only ones. This maximum quantum efficiency being at such pressure must indicate that effects where collisions are combined with multiple-photon absorption are manifested. In practice such a combination, as said above, can be the most useful as far as the minimum of energy consumption and the maximum efficiency of the process stimulated by powerful IR radiation are concerned.

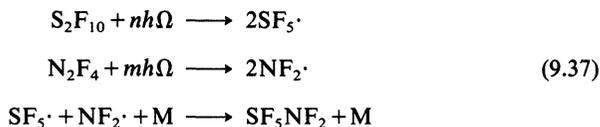
The reaction of BCl₃ and H₂ initiated by laser radiation is a vivid example of a system in which only one channel of reaction has a high probability, the product yield is high and the absorbed photons are fully used. The essential feature here is the appearance of the free radicals BCl₂ and Cl in the molecular mixture whose concentration is determined not by the temperature of the mixture only but by the MP dissociation yield of BCl₃ molecules also.

(b) *Synthesis of SF₅NF₂*

Here we are going to consider an instance of radical chemical synthesis of SF₅NF₂ molecules as the mixture of the molecules S₂F₁₀

and N_2F_4 are acted upon by powerful IR radiation pulses.⁶⁵ The conventional thermal chemical synthesis of SF_5NF_2 is elegantly known rather well and so the aim⁶⁵ was not to develop a new method of synthesis of this compound but to prove the realizability of laser radical-radical reactions as a new way of chemical synthesis.

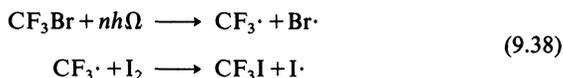
In the conventional laboratory synthesis of SF_5NF_2 the mixture of S_2F_{10} and N_2F_4 is heated at rather high pressures to a temperature of 425 K in a sealed reactor for 10 to 20 hours. With the use of the laser method SF_5NF_2 was photochemically synthesized at a low pressure, room temperature, during a short time. Even one pulse of CO_2 laser with its duration $\tau_p = 10^{-7}$ s produces a considerable amount of product. The CO_2 laser dissociates both of the initial S_2F_{10} and N_2F_4 at once, and the reaction proceeds as follows



Before these experiments it was believed that the S_2F_{10} molecule at thermal heating was an inefficient source of SF_5 radicals but laser IR MP dissociation of this molecule could easily provide high concentrations of SF_5 . This opens up ways for IR laser photochemical synthesis of such nonsynthesized compounds as SF_5COCl and SF_5NO_2 .⁶⁵ Since IR MP dissociation can be isotopically selective, this makes it possible to synthesize chemical compounds labelled with the wanted isotope.

(c) *Synthesis of CF_3I . Combined (thermal + laser IR MP) excitation*

Selective IR MP dissociation of CF_3Br molecules in the presence of the I_2 scavenger is another example of effective IR photochemical synthesis.⁶⁶ This synthesis is a part of the chemical cycle of laser separation of carbon isotopes on a practical scale (see Chapter 8). It has been shown⁶⁶ that there is a possibility of highly effective photochemical conversion of CF_3Br molecules mixed with I_2 to the molecule CF_3I with the pressure of I_2 $P_{I_2} \geq 10$ Torr. The photochemical reaction in this case proceeds according to the scheme



With the CO_2 -laser energy fluence $\Phi > 7-8$ J/cm² the dissociation yield

of CF_3Br may be as high as 100%. In this case the consumption of laser energy to synthesize one molecule of CF_3I just slightly exceeds the dissociation energy of CF_3Br $D_{\text{C-Br}} \approx 2.5$ eV.

The efficiency of IR laser-radical synthesis in many cases can be increased using the method of combined (thermal-IR MP) excitation.⁶⁷ Indeed, it is not necessary at all that all the energy essential to dissociate a molecule should be deposited into it by the IR MP excitation. A considerable part of this energy can be deposited into the molecule through thermal excitation and then the heated molecule can be subjected to IR MP excitation. The conditions of heating and IR MP excitation chosen properly, it is possible to keep the process of molecular dissociation nonequilibrium and selective and thereby increase the wanted product yield.

Preliminary heating of gas may be by the usual means, i.e., by heating the reactor's walls as well as by laser (infrared, for example) radiation or an electric discharge.

The combined type of excitation and synthesis was used⁶⁷ for CF_3I . When CF_3Br is used as an initial compound, preliminary homogeneous heating of the gas can easily be by irradiating the mixture $\text{CF}_3\text{Br} + \text{I}_2$ with CW CO_2 laser radiation absorbed well by the CF_3Br molecule. For example, when CF_3Br is heated to $T = 800$ K, the yield of IR MP dissociation by pulsed CO_2 laser increases from $\beta = 0.04$ to $\beta = 1$ (see Figure 9.10). With $p_{\text{CF}_3\text{Br}} = 1$ Torr and $p_{\text{I}_2} = 10$ Torr almost full conversion of CF_3Br to CF_3I occurs.

When CF_3Cl is used as an initial compound, it is difficult to both direct IR MP excitation of CF_3Cl by pulsed CO_2 laser radiation and its heating by CW CO_2 laser radiation since the absorption band of CF_3Cl ($\nu = 1105$ cm^{-1}) lies at the short-wave side relative to the CO_2 laser spectrum. However, the absorption spectrum of molecules under heating is usually shifted to the long-wavelength side due to vibration anharmonicity. So in the case of CF_3Cl for its effective IR MP dissociation the molecule should be heated to such temperatures when the anharmonic shift exceeds the frequency detuning of laser radiation and absorption band.

Homogeneous heating of the mixture $\text{CF}_3\text{Cl} + \text{I}_2$ can be realized by adding into it a molecular gas which absorbs well CO_2 laser radiation, SF_6 for example. The absorption of CW Ir radiation by SF_6 molecules leads to heating of the whole mixture, followed by a shift of the absorption band of CF_3Cl and thereby allows effective IR MP dissoci-

ation of CF_3Cl (see Table 9.4). In this case there cannot be observed any considerable IR MP dissociation of the SF_6 molecule. Thus, the SF_6 molecule acts as a sensitizer that permits a deposition of laser radiation energy to the molecular system but does not participate in photochemical transformations. This fact points to a selectivity of the process of IR MP dissociation even at sufficiently high temperatures.

So, the experiments show that the use of the combined method of excitation makes it possible, first, to increase the IR MP dissociation yield and, second, to widen the class of initial compounds for effective laser-radical chemical synthesis.

(d) *Directed effective synthesis of $(\text{CF}_3)_3\text{CI}$*

An optimal situation for highly effective laser-radical chemical synthesis is when the MP dissociation of the initial molecule takes place yielding only wanted radicals and there is no laser energy consumption to form undesirable radicals. In the above-considered cases of relatively simple molecules BCl_3 and CF_3Br this actually takes place which is connected with two factors. First, the radicals resulting from the MP dissociation of these molecules have not intense absorption bands coinciding with the excited bands of initial molecules. Second, the resultant radicals are relatively simple which also prevents their further MP excitation and dissociation.

According to the experiments on MP dissociation of a large number of molecules, however, in many cases (see Chapter 7 and Section 9.2)

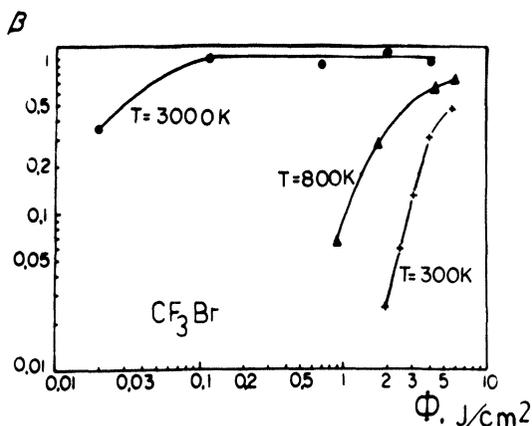


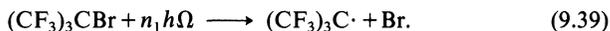
FIGURE 9.10 Dependence of the dissociation yield of the molecule CF_3Br on laser energy fluence at different temperatures (from Ref. 67).

TABLE 9.4
Sensitized IR MP dissociation yield for CF_3Cl molecule
(from Ref. 69)

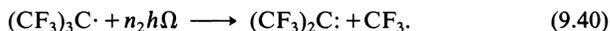
$\text{CF}_3\text{Cl} + \text{SF}_6 + \text{I}_2$ (1 Torr + 0.6 Torr + 10 Torr)	
$T = 290 \text{ K}$	$\beta = 0.005$
$T = 1000 \text{ K}$	$\beta = 0.8$

several different radicals are formed by dissociation. First of all, this is possible only when the radical formed by the primary MP dissociation is also able to absorb the laser radiation which excites the initial molecules. In many cases, particularly with complex molecules, this causes their further fragmentation. Furthermore, when the dissociation energies of different channels for a molecule are close, the rates of its dissociation through these channels become comparable. This leads to a competition of different dissociation channels and the formation of a different fragments (see Section 9.2). It is quite clear that these processes are undesirable in laser-radical chemical synthesis. Therefore, it is necessary to choose such conditions of MP excitation which would allow them to be eliminated.

We shall consider the case of synthesis of a 14-atom molecule, $(\text{CF}_3)_3\text{CI}$, in the MP dissociation of the $(\text{CF}_3)_3\text{CBr}$ molecule mixed with I_2 . In this case⁶⁸ the desired radical $(\text{CF}_3)_3\text{C}$ and the additional radical CF_3 are formed. Figure 9.11 presents some dependences of the dissociation yield β of $(\text{CF}_3)_3\text{CBr}$ on the energy fluence Φ of laser pulse and of the fraction of dissociated molecules β_d/β which leads to the desired radical $(\text{CF}_3)_3\text{C}$ on Φ . As Φ increases, the value β increases rapidly and β_d/β drops. As follows from the frequency dependences presented in Figure 9.12, the maximum values of β and β_d/β are attained as the laser frequency is displaced to the long-wavelength side relative to the line absorption bands presented in Figure 9.12. The detachment of the bromine atom is the product of the primary MP dissociation of $(\text{CF}_3)_3\text{CBr}$



As shown in (9.68), the additional radical CF_3 is formed by successive MP dissociation of the $(\text{CF}_3)_3\text{C}$ radical



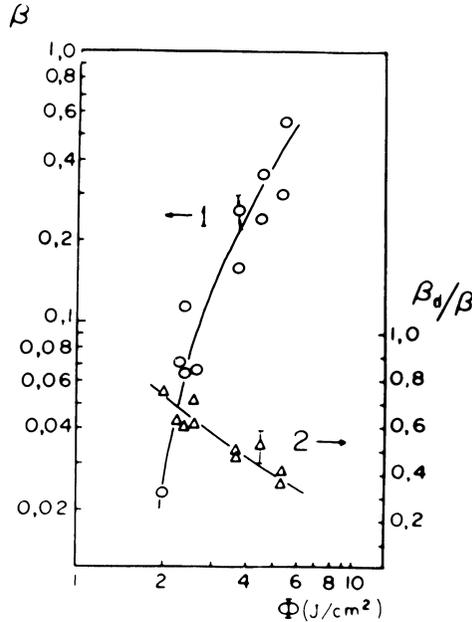


FIGURE 9.11 Dependence of the dissociation yield of the molecule $(\text{CF}_3)_3\text{CBr}$ β (curve 1) and the relative yield of the desired product β_d/β (curve 2) on laser energy fluence (from Ref. 68).

This, in particular, follows from the analysis of the frequency dependences of β and β_d/β (Figure 9.12). Indeed, at the shortwavelength edge of spectrum the conditions for the formation of additional radicals are much better than at the long-wavelength edge. This can be explained by the frequency dependence of dissociation of the desired radical $(\text{CF}_3)_3\text{C}$ which must be shifted to the short wavelength region relatively to the analogical dependence for the molecule $(\text{CF}_3)_3\text{CBr}$.

The conclusion on a small contribution of the parallel channel is also supported by the values of molecular dissociation rates estimated by the RRKM theory. The probability of detachment of the Br atom from $(\text{CF}_3)_3\text{CBr}$ ($D = 24\,000\text{ cm}^{-1}$) is more than an order higher than the probability of detachment of CF_3 from $(\text{CF}_3)_3\text{CBr}$ ($D \approx 30\,000\text{ cm}^{-1}$).

The dependence of β_d/β on the IR laser pulse duration τ_p (Figure 9.13) supports (9.68) the mechanism of successive dissociation. The

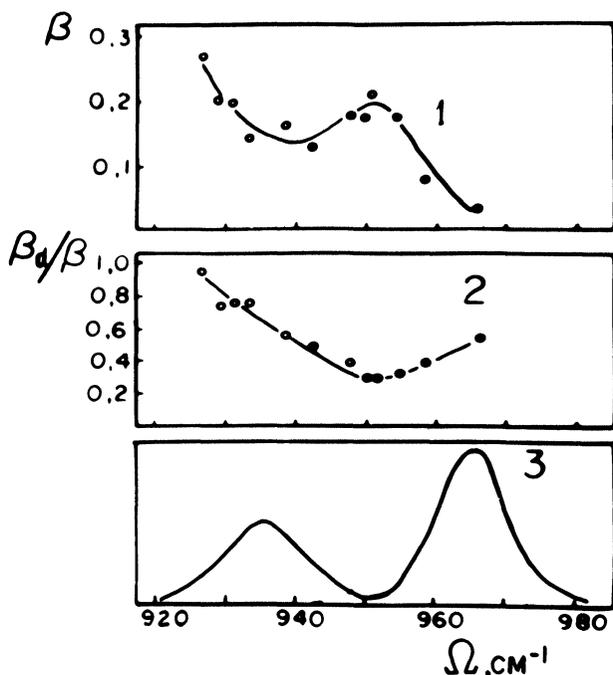


FIGURE 9.12 Dependence of the dissociation yield of the molecule $(\text{CF}_3)_3\text{CBr}$ β (curve 1) and the relative yield of the desired product β_d/β (curve 2) on laser frequency. Curves 3 are the linear absorption spectrum of $(\text{CF}_3)_3\text{CBr}$ (from Ref. 68).

increase of τ_p from 800 ns to 4 μs at a fixed laser energy fluence $\Phi = 3 \text{ J/cm}^2$ causes the value β to be reduced from 0.7 to 0.3. This may be explained by an increase of the fraction of $(\text{CF}_3)_3\text{C}$ radicals formed throughout a laser pulse and being capable of further MP absorption. Thus, when the frequency, duration and energy fluence of laser pulse are chosen properly, this allows setting up conditions under which it is possible to obtain sufficiently a high yield of desired $(\text{CF}_3)_3\text{C}$ radicals and, at the same time, a low yield of additional radicals which is important for highly effective laser-radical synthesis of $(\text{CF}_3)_3\text{CI}$.

(e) *Synthesis of fluor-organic telomers in chain reactions*

In the above-described experiments one atom in a molecule was substituted by another one. Here is a more complex case where big

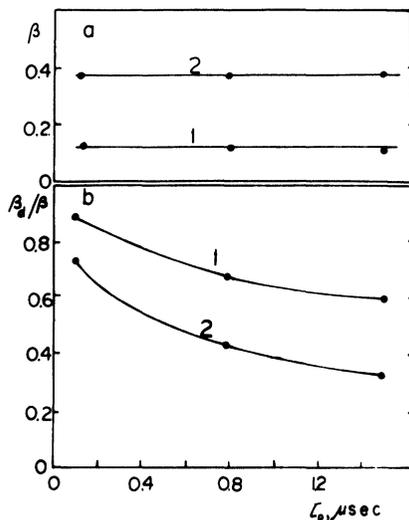
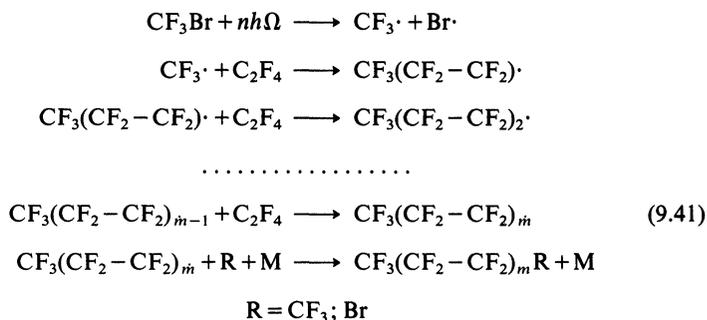


FIGURE 9.13 Dependence of the values β and β_d/β for the molecule $(\text{CF}_3)_3\text{CBr}$ on laser pulse duration τ_p curves 1. $\Phi = 3.0 \text{ J/cm}^2$; curves 2. $\Phi = 5.5 \text{ J/cm}^2$ (from Ref. 68).

polyatomic molecules are synthesized by IR MP dissociation of a simple five-atom molecule. Let us consider the IR MP dissociation of the CF_3Br molecule mixed with C_2F_4 .⁶⁹ In this case one can observe the following chain of chemical reactions



The average chain length \bar{m} changes with the excitation condition and gas mixture parameters. For example, telomers with an average chain length $\bar{m} \approx 10$ are formed under the following conditions: $\Phi = 6 \text{ J/cm}^2$; $\tau_p = 100 \text{ ns}$; $p_{\text{CF}_3\text{Br}} = 1 \text{ Torr}$; $p_{(\text{C}_2\text{F}_4)} = 50 \text{ Torr}$.

So, the above examples illustrate several approaches to gas-phase synthesis of molecular compounds in laser-radical reactions stimulated by the IR MP excitation and dissociation of polyatomic molecules. It must be emphasized that the high degree of directivity of these processes is their essential feature. Below, in Section 9.3.3, there is a simple model presented to explain the high directivity of gas-phase radical reactions stimulated by IR MP laser excitation.

9.3.3. Directivity of MP IR laser-induced radical reactions

Let us consider the simple model^{70,71} of successive dissociation of a polyatomic molecule



The kinetics of this reaction depends on the ratio between the rates of the first (9.42a) and second (9.42b) dissociations and, first of all, on the corresponding bond energies D_{ABC} and D_{AB} . In the case $k_2 \ll k_1 (D_{ABC} < D_{AB})$ there is actually a successive dissociation when with increasing absorbed energy just the first dissociation (9.42a) takes place, and then, when the yield approximates 100%, the second dissociation (9.42b) begins to play a role.

The situation is quite different in the reverse case when the intermediate radical AB is unstable: $k_1 \ll k_2 (D_{ABC} > D_{AB})$. Such a situation is rather typical of polyatomic molecules. Polyatomic radicals are thermally, as a rule, less stable than their initial stable molecular compounds. As the reaction is thermally initiated, the temperatures of all the components are equal (for example, $T_{ABC} = T_{AB}$), and this condition means that it is impossible to produce considerable concentrations of AB . The reactions under collisionless conditions, however, occur in the absence of equilibrium ($T_{AB} < T_{ABC}$) which makes it possible to carry out effective synthesis of the unstable radicals AB (see Section 9.3.2).

Below the cases of thermal and IR MP initiation of reactions (9.42a) and (9.42b) are considered.

(a) Thermal initiation

The kinetic equations of successive dissociation reactions (9.42a) and (9.42b) for the thermal case have the form

$$\begin{aligned} d\beta/dt &= k_1(1-\beta) \\ d\beta_{AB}/dt &= k_1(1-\beta) - k_2\beta_{AB} \end{aligned} \quad (9.43)$$

where β and β_{AB} are respectively the primary yield of dissociation reaction (9.42a) and the yield of the wanted product AB in the presence of reaction (9.42b).

The solution of system (9.43) can be presented, as the dependence of the relative yield of wanted product β_{AB}/β on the total yield of reaction β . The value β_{AB}/β can be used to measure the reaction directivity. The solution of (9.43) with $k_1 \neq k_2$ is determined by the expression (9.71):

$$\beta_{AB}/\beta = 1/k_2/k_1 - 1(1-\beta)/\beta[1 - (1-\beta)^{k_2/k_1-1}] \quad (9.44)$$

With $k_2/k_1 \gg 1$ a high relative yield of wanted product is possible only at low yields β . At the same time at considerable values of β the value of β_{AB}/β is very small. In particular, with $\beta = 1/2$ and $k_2/k_1 \gg 1$

$$(\beta_{AB}/\beta)_{1/2} = 1/k_2/k_1 - 1 \ll 1. \quad (9.45)$$

Thus, at thermal initiation of reactions (9.42a) and (9.42b) provided that $k_2 \gg k_1$ it is impossible to reach simultaneously a high reaction yield and a high degree of directivity.

(b) *IR MP initiation of reaction*

Now let these reactions (9.42) be initiated by an IR laser pulse where the highly selective production of AB ($\beta_{AB}/\beta \approx 1$) with a high efficiency of synthesis are possible (i.e., $\beta \approx 1$).⁷¹

The calculation of β_{AB} and β at IR MP excitation is much more complicated than in the case of thermal reaction since in this case the shape of vibrational distribution function is not known a priori. To find it one should solve the system of kinetic equations which is a rather difficult problem usually solved by a computer. But to explain a high directivity of laser-induced reaction it is more convenient to use a simplified model that allows obtaining sufficiently clear results.⁷¹ Moreover, the conclusions drawn on its basis are confirmed by the results of numerical calculations based on a more complete description.⁷⁰

Below there are formulated the basic assumptions of this model, which are not principal, but simplify the calculation in large degree:

(1°) Collisions are not essential during a laser pulse. This, however, does not exclude their influence after the irradiation is over.

(2°) The IR radiation absorption cross-section does not depend on energy. The inclusion of the cross-section reduction usually taking place with an increase of vibrational energy will cause only the reaction directivity to increase.

(3°) The reaction products AB and A absorb radiation with the same cross-section as the initial molecule ABC .

(4°) The molecules ABC , AB and A are polyatomic that allows taking into account only their vibrational energy and neglecting both the translational-rotational and vibrational energies of the B and C molecules.

Assumptions (1°) to (4°) fulfilled, the reaction product ratio can be calculated with the use of a simple model⁷¹ based on the joint distribution function $(JDF)f(E)$. JDF describes simultaneously all the components in the mixture

$$f(E) = f_{ABC}(E) + f_{AB}(E - D_{ABC}) + f_A(E - D_{ABC} - D_{AB}) \quad (9.46)$$

Here $f_i(E)$ ($i = ABC, AB, A$) are the vibrational distribution functions of "active" (i.e., absorbing IR radiation) molecules: D_{ABC} , D_{AB} are the energies of the bonds $AB-C$ and $A-B$ respectively. Thus $f(E)$ depends on the "total" energy of molecules which, apart from vibrational energy, includes the energy of broken bonds, too. Introduction of JDF is convenient since the processes of unimolecular dissociation do not affect $f(E)$: indeed, a decrease in $f_{ABC}(E)$ in the dissociation of ABC is precisely compensated for by increasing $f_{AB}(E - D_{ABC})$.

The $f(E)$ varies only under the action of laser radiation, and by virtue of (2°) and (3°) it looks very simple: the distribution maximum \bar{E} shifts upwards monotonically as the absorbed energy increases.

The joint distribution function $f(E)$ provides a simple method for calculating the absorbed energy but makes it impossible to find directly the reaction yield β and the product ratio β_{AB}/β . For their approximated calculation the following additional assumption can be used:

(5°) The unimolecular dissociation rate increases very rapidly, as the energy is increased, and so it is possible to determine such threshold energy values E_{ABC}^D and E_{AB}^D that with vibrational energy $E < E_{ABC}^D$ the dissociation rate is still small and with $E > E_{ABC}^D$ it exceeds the excitation rate and therefore all the ABC molecules with $E > E_{ABC}^D$ dissociate to AB and C . Similarly to this, E_{AB}^D is a limit at which the dissociation $AB \rightarrow A + B$ occurs.

Figure 9.14 describes the successive dissociation (9.42) by means of $f_i(E)$. Value $E_{ABC}^D \approx D_{ABC}$ and $E_{AB}^D \approx D_{ABC} + D_{AB}$ for relatively small polyatomic molecules which have a very high rate of unimolecular dissociation even when the dissociation limit is exceeded by 2 or 3 vibrational quanta. Thus, according to (5°), to determine the dissociation yield β it is necessary to take a fraction of molecules with their total energy higher than E_{ABC}^D and for β_{AB} with $E_{ABC}^D < E < E_{AB}^D$.

$$\beta = \int_{E_{ABC}^D}^{\infty} f(E) dE \quad (9.47)$$

$$\beta_{ABC} = \int_{E_{ABC}^D}^{E_{AB}^D} f(E) dE \quad (9.48)$$

The results of calculation of the dependence β_{AB}/β on β presented in Figure 9.15 show a principal difference of IR MP excitation from thermal one. Indeed, in the case when the degree of dissociation of the initial molecules ABC is equal to 50% ($\beta = 1/2$) the wanted product AB at thermal initiation has a very low concentration (its yield equals only $(\beta_{AB}/\beta)_{1/2} = 3 \cdot 10^{-3}$). At the same time in a laser-induced reaction with the molecules ABC can be dissociated with high yield ($\beta = 1/2$) and converted to the wanted product almost without losses $(\beta_{ABC}/\beta)_{1/2} = 0.998$.

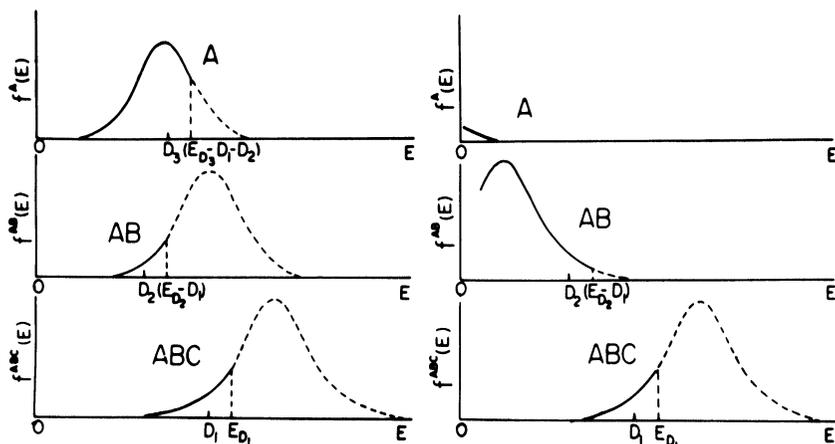


FIGURE 9.14 Vibrational energy distribution function at: (a) thermal initiation of reaction (9.42); (b) IR MP initiation of reaction (9.42) (from Ref. 71).

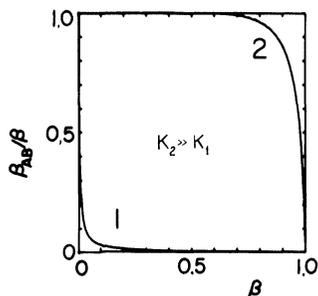


FIGURE 9.15 Dependence of the value β_d/β on β in the case of thermal initiation of reaction (9.42) (curve 1) and in the case of IR MP initiation of reaction (9.42) (curve 2) (from Ref. 71).

(c) *Comparison of thermal and IR MP initiation*

The considered simple model of successive dissociation of molecule demonstrates the increase of reaction directivity as the equilibrium (thermal) initiation is changed by the nonequilibrium IR MP one.

To explain such an enhancement of directivity, let us consider the vibrational energy distributions for the molecules ABC , AB and A formed in these reactions (Figure 9.14). The average energy of the AB molecules at IR MP initiation is much less than at thermal initiation. Indeed, AB molecules are formed by the collisionless dissociation with their energy ($E_{ABC} - D_{ABC}$). Under the conditions of thermal collisional reaction the radicals AB has equilibrium energy due to collisions with hot initial molecules. This occurs with a rate higher than the dissociation rate, and so right after the dissociation of ABC the product AB is "ready" for further thermal dissociation. The vibrational temperatures of all the components in this case are equal $T_{ABC} = T_{AB} = T_A$.

At the same time, in the case of collisionless IR MP dissociation the AB molecules remain cold enough. In this case there will not be further dissociation of AB if the IR MP excitation does not go on up to the value E_{AB}^D . If, nevertheless, some small part dissociates, the average energy of the resulting A product is lower than for the AB molecules. Thus, at IR MP initiation the relation $T_{ABC} > T_{AB} > T_A$ holds true.

Thus, one of the characteristic features of the process of IR MP dissociation of polyatomic molecules is that it is possible to suppress

the successive stages of reaction which at thermal dissociation lead to fragmentation. Such reduction in the number of reaction channels, i.e., an increase in the degree of dissociation directivity is very promising property of IR MP initiated reactions.

9.4. Nonselective IR photochemistry

Under condition (9.4) and, what is more, (9.5) one cannot hope for selective photoprocesses in molecular mixtures. Nevertheless, in these cases, too, the MP excitation of any molecular component in the mixture, despite a fast transfer of vibrational energy to the rest of the molecules, is of particular practical interest. Figure 9.16 illustrates in a simple way some processes in the molecular mixture under conditions (9.4) and (9.5). Let the sensitizer with a high dissociation energy absorb the IR radiation and transfer the excitation to other molecules which have a lower dissociation energy and do not interact

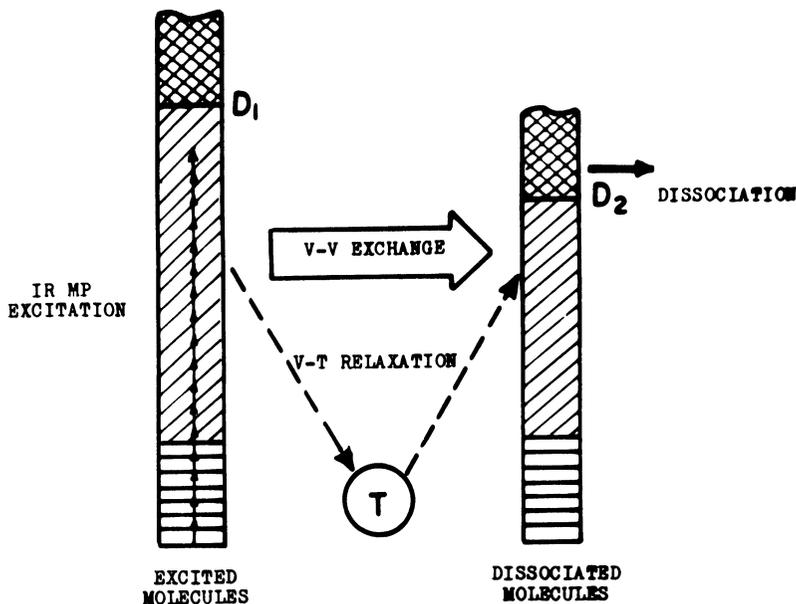


FIGURE 9.16 Processes of V-V' exchange, V-T relaxation and dissociation in molecular mixtures with different dissociation energies in the case of IR MP excitation of the molecule with highest dissociation limit.

with the IR field. The process of $V-T$ relaxation is always present, of course, but at condition $\tau_{V-T} \gg \tau_{V-V}$ for some time there may be a vibrationally excited molecular mixture in which photochemical reactions will take place, particularly a dissociation of the molecules with the lowest energy barrier.

9.4.1. Pulsed pyrolysis of molecules

This method, in particular, allows homogeneous laser-induced pulsed pyrolysis of many molecules not having suitable absorption bands for direct IR MP dissociation. For example, pulsed pyrolysis⁷²⁻⁷⁶ of UF_6 , XeO_4 , 1,2-dichloropropane and some other molecules has been achieved with the thermally stable molecules SF_6 and SiF_4 used as sensitizers. The pyrolysis⁷³ of UF_6 molecules mixed with SF_6 was performed through IR MP excitation of SF_6 by TEA CO_2 laser radiation. The dissociation energy of UF_6 ($D = 68 \pm 3$ kcal/mol) is much lower than that of SF_6 ($D = 92 \pm 3$ kcal/mol). Besides, the mode ν_4 of SF_6 (615 cm^{-1}) is close to the mode ν_3 of UF_6 (625 cm^{-1}) which provides rapid exchange of vibrational energy between SF_6 and UF_6 . So, when the UF_6 molecules collide with highly excited SF_6 molecules, there may be effective vibrational excitation and pyrolysis of UF_6 . Figure 9.17 presents the dependence of the dissociation yield β of UF_6 on the pressure of SF_6 at a fixed total pressure $p_{\text{UF}_6} + p_{\text{SF}_6} = 0.8$ Torr and at a fixed pressure of hydrogen $p_{\text{H}_2} = 0.8$ Torr used as a scavenger of atomic fluoride. The rapid increase of β_{UF_6} observed can be related to the rise of the excitation level of UF_6 as p_{SF_6} increases. Indeed, it may be assumed that the average energy obtained by the UF_6 molecules in their collisions with SF_6 , after vibrational equilibrium is achieved in the system $\text{UF}_6\text{-SF}_6$, is described by the expression

$$\bar{\epsilon}_{\text{UF}_6} \approx \bar{\epsilon}_{\text{SF}_6} \frac{p_{\text{SF}_6}}{p_{\text{SF}_6} + p_{\text{UF}_6}} \quad (9.49)$$

where $\bar{\epsilon}_{\text{SF}_6}$ is the average IR radiation energy absorbed by the SF_6 molecules. So the dependence of β_{UF_6} on $\bar{\epsilon}_{\text{UF}_6}$ is actually reflected in Figure 9.17.

It is apparent that the rate of vibrational energy transfer in collisions must depend on the frequency detuning of the IR active modes of colliding molecules. This manifests itself especially vividly in experiments on isotopic selectivity of the dissociation of SF_3Cl and CF_3I

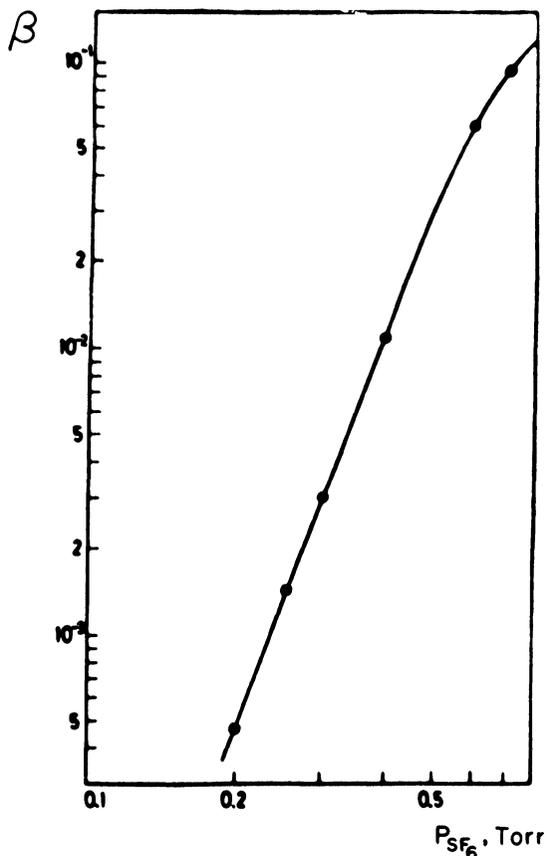


FIGURE 9.17 Dependence of the dissociation yield of UF_6 on the pressure of SF_6 with $p_{\text{SF}_6} + p_{\text{UF}_6} = 0.8$ Torr (from Ref. 73).

molecules sensitized with SF_6 .⁷⁴ Indeed, an isotopical shift of vibrational frequency causes the additional frequency detuning collisional $V-V'$ exchange which results in some dissociation selectivity. For example the isotopic selectivity of sensitized dissociation⁷⁴ was observed for SF_5Cl ($\alpha_{33/32} = 1.57$) and for CF_3I ($\alpha_{13/12} = 1.23$).

In most cases in mixtures of complex molecules there is a channel of $V-T$ relaxation with a high rate and the heating of the whole mixture takes place inevitably including the translational degrees of

freedom. In every case of molecular mixtures it is necessary to study rather complicated pathways of vibrational–vibrational and vibrational–translational energy relaxation (see review Ref. 77). Therefore, authors of experimental works often speculate the difference between the vibrational and translational temperatures of molecules in experiments at high pressures when it is not known to what extent condition (9.5) is fulfilled.

Measurements of the isotopic selectivity of dissociation as a function of pressure give unambiguous information on the extent with which condition (9.4) is fulfilled in a specific experiment. If the excitation rate is high enough, it is possible to irreversibly phototransform molecules in a very short time (less than 10^{-9} s) and hence to use comparatively high pressures (about 1 atm⁷⁸). Similarly, it is experiments in which one can observe the dissociation yield of molecules at high pressures and compare it with the yield under thermal heating that can give information on the extent with which condition (9.5) is fulfilled.

Such an experiment has been carried out⁷⁹ where the dissociation of CF_2HCl molecules was studied under collisional conditions (at a pressure of 60 Torr) under the action of CO_2 laser pulses with power 1.5 MW/cm^2 and duration $\tau_p = 200 \text{ ns}$ at the $9.2 \mu\text{m}$ wavelength. The photodissociation yield with time resolution was measured from the formation of CF_2 radicals in the ground state. The concentration of CF_2 radicals was measured by the method of UV absorption at $\lambda = 249 \text{ nm}$ and concentration of HCl molecules in the vibrational state $\nu = 1$ with their concentration was measured by the method of IR fluorescence at $\lambda = 3.6 \mu\text{m}$. In Figure 9.18 the experimental and calculated yield of CF_2 radicals are compared in the case of full thermal equilibrium. Even at a pressure of 60 Torr, when hundreds of collisions occur during the laser pulse, the vibrational temperature differs from the ambient temperature in the course of the photodissociation reaction. Thus, in this experiment condition (9.5) was not fulfilled yet and the reaction was not only thermal but also photochemical by character.

But, even though the chemical reaction is purely thermal, its photo-initiation in a gas mixture by IR radiation is of practical interest. MP absorption in SF_6 has been used⁸⁰ to ignite fuel-oxygen mixtures.⁸¹ The CO_2 laser pulse has been used to initiate the thermal explosive isomerization⁸¹ of CH_3NC in CH_3CN and to ignite⁸² an $\text{SF}_6/\text{CH}_4/\text{O}_2$ mixture again due to MP absorption in SF_6 .

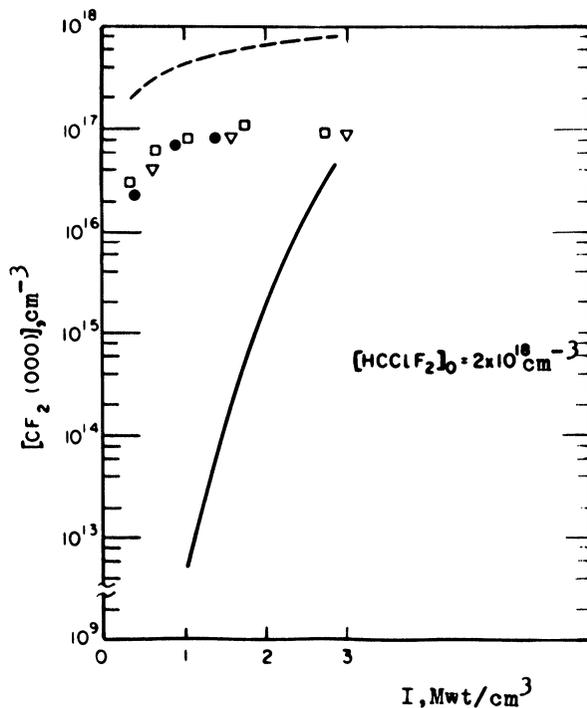


FIGURE 9.18 Comparison of the measured and calculated values of CF_2 radical yield in the IR MP dissociation of the molecule CF_2HCl with $p_{\text{CF}_2\text{HCl}} = 60$ Torr (the calculation is done in the model of thermal excitation (solid curve)) (from Ref. 79).

9.4.2. Study of unimolecular reactions

The method of IR MP excitation can be also applied to determine the parameters of unimolecular reactions under equilibrium conditions.⁸³⁻⁸⁵ Pulsed IR pyrolysis has quite a number of advantages over the method of shock tubes. They are a high rate of heating, the elimination of the role of walls and heterogeneous reactions, and the ability of studying the reactions of hard-volatile compounds. For precise measurements of thermal reaction parameters by the method of IR MP excitation it is necessary, of course, to get rid of all kinds of non-equilibrium in the reaction molecular system. The simplest way of doing it is to activate the molecules not through their direct IR MP excitation but due to transfer of energy to them from a chemically

passive sensitizer that absorbs IR radiation well and also to perform the reaction in presence of few-atom molecular buffer gas acting as a thermostat.⁸⁴

The essence of the method used to determine the Arrhenius parameters of reactions consists in the following.⁸⁵ The gas is heated quickly in a cell by the collisions with the sensitizer under IR MP excitation and then the products and the yield of the reaction are determined with a gas chromatograph. The basic difficulty here is that the temperature in the cell depends on time t and coordinate r , $T = T(t, r)$. This is due to the fact that the laser beam in the cell is nonuniform and the exposed gas is cooled by mixing with the cold unexposed gas.

This problem can be solved. An "internal chemical standard", i.e., a reagent with well-known kinetics and dependence of the reaction rate constant on temperature $k(T)$, is introduced into the gas. In this case it is sufficient just to estimate roughly the time and space profile of temperature $T(t, r)$ in the cell to determine the required parameters. This can be done using a simple gas-kinetic model.^{84,85} It is also possible to use "an internal physical standard", i.e., to measure the IR fluorescence intensity of a heated molecular gas varying with time, which allows a more precise determination of the temperature profile $T(t, r)$ in the gas chamber.

The method of pulsed laser pyrolysis has been used to define the channels and temperature dependences of dissociation of the molecule $\text{CCl}_2\text{HCH}_2\text{Cl}$.⁸⁵ The molecule CH_3CCl_3 was used as "an internal chemical standard". The molecule SiF_4 was used as a sensitizer and "an internal physical standard". It was excited by pulsed CO_2 laser radiation at the frequency $\Omega = 1027.4 \text{ cm}^{-1}$ and the IR fluorescence was detected at $\lambda = 5.0 \mu\text{m}$ which corresponded to the transition $\nu = 2 \rightarrow \nu = 0$ in the excited mode of SiF_4 . The studies carried out (9.85) show that the molecule $\text{CHCl}_2\text{CH}_2\text{Cl}$ has the following dissociation channels

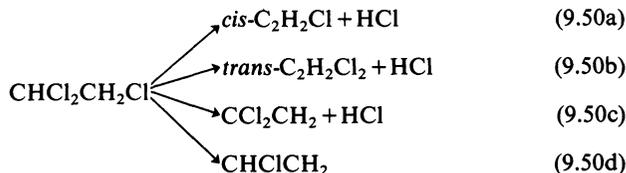


Table 9.5 presents the Arrhenius parameters for reactions (9.50a)–(9.50c) as well as the parameters for the dissociation reaction of the

TABLE 9.5
Arrhenius parameters of chloralkanes dissociation reactions (from Ref. 85)

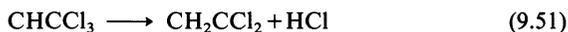
Molecule	$\text{CHCl}_2\text{CH}_2\text{Cl}$ ($T = 1150\text{--}1400\text{ K}$)	CH_3CCl_3 $T = 1130\text{--}1350\text{ K}$
Parameters	<i>Cis</i> $\text{C}_2\text{H}_2\text{Cl} + \text{HCl}$	$\text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$
E_a (kcal/mol)	58.5 ± 2^a $59\text{--}60^b$	60^a 57^b
$\log A(\text{c}^{-1}) $	14.1 ± 0.4^a	23.2^a
	<i>trans</i> $\text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$	$\text{CHClCH}_2\text{Cl} + \text{HCl}$
	59.5 ± 2^a $59\text{--}60^b$	64 ± 4^a —
	13.9 ± 0.4^a	12.8 ± 0.8^a
		$\text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$
		49.5 ± 1.3^a 54.0 C 13.1 ± 0.3^a 14.0^c

^a Pulsed laser pyrolysis.

^b Chemical activation.

^c Thermal reactor, $T = 678\text{--}715\text{ K}$.

“internal chemical standard” CH_3CCl_3



As seen from Table 9.5, the method of pulsed laser pyrolysis provides a very good accuracy in determining the activation energy E_A and the preexponential factor.

Besides the above reactions, the Arrhenius parameters⁸⁴ for a number of molecules such as isobutyl bromide, isopropyl acetate, ethyl acetate, 2,2'-azoisopropane, has been measured with a high accuracy using this method. In this case the parameters measured for 2,2'-azoisopropane disagree materially with the results published before, whereas for the first three molecules they are in good agreement. What is more, the results obtained⁸⁴ give conclusive evidence of the fact that the unimolecular dissociation of 2,2'-azoisopropane occurs through the channel of synchronous detachment of both alkyl groups, which is quite new for the classical problem of azoalkanes dissociation.

In conclusion let us emphasize that the IR MP processes have many potential applications in chemistry. Among them is IR photolysis for electron diffraction study of the structure of free radicals,⁸⁶ selective purification of compounds⁸⁸, and etching of surfaces with the chemically active products of IR MP dissociation.⁸⁷ The universality of the MP molecular processes induced by high-power IR radiation gives hope for wide usage of IR laser photochemistry in fundamental chemical studies and chemical technology.

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