

Multiple Photon Infrared Laser Photophysics and Photochemistry. IV

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This paper is the fourth in series of reviews on multiple photon IR laser photophysics and photochemistry. Unimolecular reactions of MP excited molecules and the isotopic selectivity of MP dissociation are considered.

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7. UNIMOLECULAR REACTIONS OF MOLECULES EXCITED BY IR LASER RADIATION

The strong excitation of molecules under IR laser radiation has made possible certain novel processes in which irreversible changes of the original substance take place. Excited molecules with large amounts of vibrational energy may undergo different transformations even without collisions. Such transformations are called unimolecular reactions. Among these are the processes of dissociation, isomerization, dissociative ionization, etc. We are going to discuss in this chapter two unimolecular processes, particularly the dissociation and the isomerization of molecules as a result of their MP excitation.

Even in the first works,^{1,2} where the effect of collisionless IR photoexcitation of polyatomic molecules was studied, it was found that molecules could dissociate under the action of IR pulses. The effect of MP dissociation turned out after much work to be nearly universal. Polyatomic molecules with little exception are all able to dissociate when the laser radiation frequency is tuned to the frequency of a vibration active in the IR spectrum. Moreover, it is possible to realize selective action on a single molecular component of a gas mixture. All this gave high promise to the practical value of the effect since it was much simpler to chemically bind the radicals formed in photodissociation than to attempt a high-rate (i.e., before selectivity loss) chemical reaction of the molecule itself even if it is highly vibrationally excited. As a result, one of the most effective methods of laser isotope separation is based on the effect of MP molecular dissociation (see Chapter 8), and laser chemical synthesis is under successful development (see Chapter 9).

The basic processes following MP molecular dissociation are interpreted qualitatively in most cases rather simply. When excited highly enough a molecule resonantly absorbs laser radiation and, when its energy exceeds the dissociation energy of the weakest bond, it undergoes decomposition. The dissociation rate is highly dependent on the excess molecular energy over the dissociation limit and grows rather fast which restricts the possibility of strong molecular over-excitation relative to the dissociation limit. But the products formed during a laser pulse can in some cases absorb energy and dissociate in their turn. The spectral properties of the process of MP dissociation must evidently be in qualitative agreement with the absorption spectra of

molecules in a strong IR field considered in the foregoing chapters since a molecule can dissociate only after absorbing a large enough number of quanta.

Experimental dependences of dissociation yield on laser pulse fluence and its frequency (or on the frequencies in two-frequency experiments) are discussed in Section 7.1. These dependences are closely related to the absorbed energy, and in the discussion the data on MP absorption is used.

The questions concerned with experimental study of dissociation products and their energy distribution are discussed in Section 7.2. The qualitative interpretation of these experiments is usually based on the statistical theory of unimolecular reactions.

In Section 7.3 we consider one more possibility of unimolecular transformation of vibrationally excited molecules, that is the process of isomerization.

In the end of this chapter, in Section 7.4, we think it useful to consider the questions connected with collisional processes. The influence of collisions on molecular phototransformations may be very essential. Their inclusion is often necessary for the correct interpretation of the data obtained in an experiment.

7.1. Characteristics of IR multiple photon dissociation

Dissociation in a sufficiently strong IR field has been observed in a large number of polyatomic molecules with the laser radiation frequency tuned to the absorption band active in IR absorption. For some molecules this effect also took place as the excitation was done through the overtones or combination modes. Table 7.1 list(s) molecules in which the effect of MP dissociation has been observed.

The basic parameters which characterize quantitatively the process of MP dissociation are dissociation yield β and its quantum efficiency $\varphi = \beta D / \bar{\epsilon}$ ($\bar{\epsilon}$ is the average value of absorbed energy, D is the bond breaking energy). The dissociation yield is defined as a fraction of molecules dissociating per laser pulse on the gas volume under irradiation. In many works consideration has been given to the dependence of β and φ on laser radiation frequency Ω , pulse energy fluence Φ , energy absorbed by a molecule $\bar{\epsilon}$, etc. The effect of MP dissociation for the molecules acted upon with two successive IR pulses of different

TABLE 7.1
The molecules, for which the effect of MP dissociation has been observed

<i>4-atomics:</i>	SeF ₆ ¹⁴³
BCl ₃ ^{2,87,105-108}	MoF ₆ ¹⁴⁴
D ₂ CO ¹⁰⁹	UF ₆ ¹⁴⁵⁻¹⁴⁷
H ₂ CO ¹¹⁰	CH ₃ NO ₂ ^{6,25,148}
HDCO ¹⁰⁹⁻¹¹¹	CH ₃ NH ₂ ^{6,43,127}
DN ₃ ¹¹²	CH ₃ ONO ¹⁴⁹
HN ₃ ¹¹²	CH ₂ CHCN ^{60,102}
<i>5-atomics:</i>	<i>8-atomics:</i>
SiF ₄ ^{1,8,12,106,113}	C ₂ H ₅ F ¹⁵⁰
OsO ₄ ^{7,10,30,35,58,63,114-117}	C ₂ H ₅ Cl ^{151,153}
CrO ₂ Cl ₂ ^{9,63,65}	CH ₃ CHF ₂ ^{18,52}
CF ₃ I ^{29,32,49,91,93,118}	CH ₂ FCH ₂ Cl ¹⁵²
CF ₃ Br ^{49,78,119,120}	CH ₃ BrCH ₂ F ¹⁵⁰
CF ₃ Cl ^{49,120,121}	CH ₃ CF ₃ ^{150,153}
CF ₃ D ^{103,122}	CH ₃ CCl ₃ ^{49,153}
CF ₂ Br ₂ ^{40,41,106}	CH ₃ CClF ₂ ^{49,153}
CF ₂ Cl ₂ ^{38-41,49,106,113,123}	CF ₃ CF ₃ ¹⁵⁴
CF ₂ HCl ^{49,55,77,174}	CF ₃ CDCl ₂ ¹⁷³
CF ₂ H ₂ ⁴⁹	CF ₃ CClF ₂ ⁴⁹⁷
CCl ₄ ^{124,169,175}	CF ₂ S ₂ CF ₂ ¹⁵⁵
CCl ₃ F ^{40,49}	CHClCHBCl ₂ ¹⁵⁶
CCl ₂ HF ⁴⁹	<i>9-atomics:</i>
HCOOH ¹²⁵	SF ₅ NH ₂ ¹⁵⁷
<i>6-atomics:</i>	C ₂ H ₅ CH ¹⁵⁸
N ₂ F ₄ ^{49,126}	C ₂ H ₅ NC ¹⁵⁹
N ₂ H ₄ ¹²⁷	C ₂ H ₅ OH ¹⁵⁸
CH ₃ OH ^{6,85,100,128}	CH ₃ OCH ₃ ¹⁶⁰
CH ₃ CN ^{6,25,101}	C ₃ H ₆ ¹³²
CH ₃ NC ⁶⁹	<i>10 and more-atomics:</i>
C ₂ H ₄ ^{6,11,94,129}	C ₂ H ₅ NH ₂ ¹⁵⁸
CH ₂ CHF ^{17,18}	CF ₃ COCF ₃ ^{161,162}
CH ₂ CHCl ^{27,130,131}	C ₃ H ₇ Br ¹⁶³
CH ₂ CF ₂ ^{18,25}	C ₃ F ₇ I ¹⁶⁴
CH ₂ CCl ₂ ¹³¹	C ₆ F ₅ H ¹⁶⁵
CHClCF ₂ ^{49,131}	S ₂ F ₁₀ ⁹⁸
CHClCHCl ^{68,131,132}	C ₃ H ₆ O ₃ ¹⁶⁶
CHClCCl ₂ ⁴⁹	C ₂ H ₅ OCHCH ₂ ¹⁶³
CF ₂ CFCI ^{6,42,80,133,134}	CH ₃ OCH ₂ CHCH ₂ ¹⁶³
CF ₃ CN ¹³⁵	CH ₃ COOC ₂ H ₅ ¹⁶³
<i>7-atomics:</i>	(CF ₃) ₃ CBr ²⁹
SF ₆ ^{3,5,12,15-21,31,33-36,44,}	U(OCH ₃) ₆ ¹⁶⁷
47-49,84,88,89,97-99,136-141	UO ₂ (hfacac) ₂ ·THF ¹⁶⁸
SF ₅ Cl ^{95,142}	

frequencies has also been studied. The characteristics of the process considered below have been taken from a large number of specific typical cases. When choosing cases we took into consideration the completeness of the studies of a particular molecule. The SF₆ molecule is beyond competition here since it has been studied in several dozens of works. The molecules OsO₄, CF₃I, SiF₄ have been also covered completely enough. In some cases, however, we shall be using the results on some molecules studied in single works.

Let us begin with a short review of the basic methods of study of molecular photodissociation by IR radiation.

7.1.1. Experimental methods of IR multiple photon dissociation investigation

The simplest method of measuring the dissociation yield β is to measure the decrease of initial substance amount in the cell after irradiation by recording, for example, IR absorption spectra.³ In this case the change in the linear absorption coefficient κ is related to β by

$$\kappa = \kappa_0(1 - \beta\Gamma)^n \quad (7.1)$$

or at small yields ($\beta\Gamma \ll 1$) by

$$\kappa = \kappa_0 \exp(-n\beta\Gamma)$$

where κ_0 is the absorption coefficient before irradiation, n is the number of irradiation pulses, Γ is the ratio of the exposed volume to the total volume of the cell.

The determination of the dissociation yield directly from the consumption of the primary species correctly reflects the result of IR pulse action only in the cases when we may neglect the reverse process of fragment recombination. The search for a suitable radical acceptor for each molecule is an independent problem and, as a rule, acceptors are usually found. This point will be studied in more detail in Section 7.4. Nevertheless, even though it is very simple to measure dissociation yields by monitoring the primary species, much attention has been given to the development of other direct and indirect methods which allow the elimination of secondary processes.

The most universal of these methods is based on a molecular beam technique.^{4,5} In this technique (see Figure 7.1) the laser beam crosses the molecular beam and dissociates the molecules. Even if the

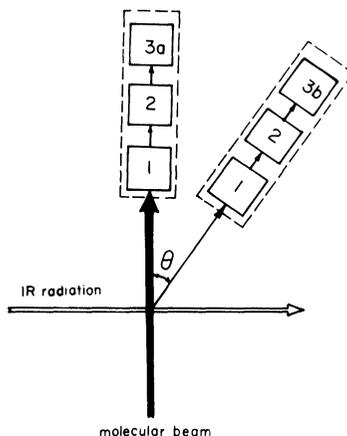


FIGURE 7.1 Schematic diagram of the molecular beam method for observing the effect of MP dissociation. (a) The dissociation yield is measured from the decrease of molecular density in the beam. (b) Angular distribution of radicals is measured. Diagram elements: (1) ionization chamber, (2) quadrupole mass filter, (3a) ion-counting system,⁹⁷ (3b) multiplier.⁵

molecular energy exceeds the dissociation energy just by one IR photon the radicals formed must have an energy that would be much higher than the translational energy of a molecule in the beam. A part of this energy is transferred to translational degrees of freedom, and by virtue of conservation laws the radicals must acquire a momentum component in a transverse direction. Thus, the radicals can be spatially separated from the molecules. Dissociation yield can be measured both from the decrease of number of molecules in the beam itself and by recording the radicals leaving the beam. Detection is carried out with an ionization mass spectrometer which enables the arising fragments to be identified. An important advantage of the method is that it is possible to measure the angular distribution of radicals by changing the angle between the beam direction and the mass spectrometer axis. From the angular distribution function we can determine the translational energy distribution of the fragments.⁴

The methods dependent on detection of the visible luminescence which often follows MP dissociation are less universal but nevertheless in some cases are very effective (see Chapter 1 and below Section 7.2). It should be noted that it is just because of this phenomenon that the

effect of collisionless MP dissociation was revealed in the very first works.^{1,2} The luminescence source may be radicals if they are formed in the electronically excited state.^{1,6} In a number of cases⁷⁻⁹ luminescence is from the molecules themselves. Visible luminescence is convenient for measurements since it can be easily detected. By studying the luminescence quenching on the walls (time-of-flight spectroscopy) it is possible in some cases to determine the mass of emitting particles.¹⁰ Before using visible luminescence to measure the dissociation yield, however, their direct proportional dependence must be determined. In some cases, for example in Refs. 11 and 12, it has been proven that this requirement is fulfilled.

When it is known that in the process of MP dissociation radicals with line absorption spectra in the visible or near UV regions are formed, they can be recorded using the laser induced fluorescence (LIF) method.^{13,61} The typical scheme of the LIF experiment is shown in the Figure 7.2. In this method excitation of the radicals from the ground state is performed by a tunable dye laser, and the fluorescence of electronically-excited radicals thus induced is measured. An important advantage of this method is its high sensitivity which enables radical concentrations from 10^8 to 10^9 cm^{-3} to be detected.

One more possibility of studying the process of MP dissociation is connected with recording the chemiluminescence signal. This method

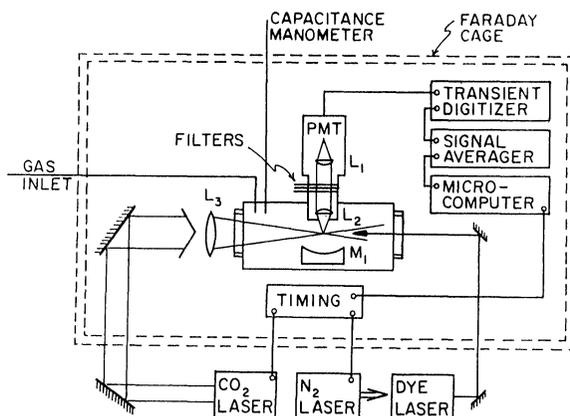


FIGURE 7.2 Scheme of experiment to detect radicals by the method of laser induced fluorescence. L_1 , L_2 , L_3 and M_3 are lenses and a mirror. (From Ref. 61.)

was used¹⁴ when the isotopic selectivity of MP dissociation was first discovered. In this work the mixture $\text{BCl}_3 + \text{O}_2$ was irradiated and the chemiluminescence of BO^* radicals in the visible region was observed. A modification of this method was used^{15,16} to detect F atoms. They were recorded by the IR fluorescence of the vibrationally-excited HF^* molecules formed by the fast reaction $\text{F} + \text{H}_2 \rightarrow \text{HF}^* + \text{H}$.

An interesting study has been^{17,18} the MP dissociation of mixed halogenated ethanes and ethylenes. In this case, by unimolecular dissociation, vibrationally-excited HF^* molecules are formed which allow them to be detected by IR fluorescence.

All the above-listed methods were used to demonstrate molecular photodissociation as well as to measure the dependence of dissociation yield β on laser pulse energy fluence Φ and laser radiation frequency Ω . The molecular beam method and the laser induced fluorescence method have obtained in some cases direct information on dissociation products and their energy distribution. These results will be discussed in the succeeding sections.

In conclusion it should be noted that the probing of radicals with Raman scattering may turn out to be one more promising method for studying the process of MP dissociation. In this case it would be possible to measure both the radical concentration and their internal energy.⁹⁶

7.1.2. Dependence of MP dissociation yield and quantum efficiency on laser pulse energy fluence and absorbed energy

Dissociation threshold. Even in the first works,^{1,2} on MP molecular dissociation, where the visible luminescence of molecules in strong IR fields was studied, particular attention was concentrated on a fast dependence of luminescence signal on laser pulse intensity. This property was treated, as usual, as the presence of a threshold for the effect observed.

The threshold properties of the effect of MP dissociation were first studied in detail¹⁹ for the SF_6 molecule. The results of this work have been discussed already in Chapter 4 (see Section 4.4.1).

The threshold properties of MP dissociation were also studied in other works both for the SF_6 molecule and other molecules. Some results are presented in Table 7.2. It should be noted, however, that the data presented are conventional in character and the very concept

TABLE 7.2
Threshold values of fluence for MP dissociation of some molecules

Molecule	Φ_{th}^a , $\text{J} \cdot \text{cm}^{-2}$	References and comments
BCl_3	20	2, 105
SiF_4	4.5	for ν_3 mode excitation, 113
	15	for $\nu_1 + 2\nu_2 - \nu_4$ excitation, 1
N_2H_4	0.1	127
OsO_4	<0.2	The threshold is dependent on laser frequency, 30
SF_6	0.5–5	5, 18, 19, 47, 84, 113, 136–138. The threshold is dependent on laser frequency, 137, 138
SF_5Cl	0.7	95
SF_5NF_2	< 10^{-2}	157
S_2F_{10}	< 10^{-2}	98
CF_3D	<10	103
CF_3Br	<1.0	119
CF_3I	<0.3	32
CCl_4	{ 1.2	for ν_3 mode excitation, 169
	{ 120	for $\nu_1 + \nu_2 + \nu_4$ excitation, 169
CH_3CN	60	The threshold is dependent on radiation intensity $I_{\text{th}} \approx 10^9 \text{ W cm}^{-2}$, 25
CH_3OH	11	100
C_2H_4	10–20	170
$\text{C}_2\text{H}_3\text{F}$	2	18
$\text{C}_2\text{H}_3\text{Cl}$	20–40	130
CF_3COCF_3	0.7	162

^a The threshold was estimated when its value was not given by authors.

of a threshold depends on the sensitivity of the method we use to detect the dissociation products. Some appropriate studies have shown that near the threshold the dependence $\beta = \beta(\Phi)$ is steep but continuous. The value of β drops quickly to 10^{-4} – 10^{-5} with an insignificant decrease of Φ in a region below “the threshold” which is understood as the existence of some threshold for MP dissociation. Even though the term “dissociation threshold” is used, one should keep in mind its conventional nature.

Some differences in determining the threshold value, particularly for SF_6 , may be caused by different experimental conditions. For example, it has been demonstrated [7.20, 7.21] the necessity of a correct determination of the spatial energy distribution across the laser beam. The geometric factor is of particular importance when the laser radiation is focused.^{22–24}

We have discussed earlier in Chapter 4 (see Section 4.4.1) the physical nature of the MP dissociation threshold. In most cases the

threshold of MP dissociation is caused by excitation of the molecules through the region of vibrational quasi-continuum. The energy distribution function formed as a result of this excitation has a sharp exponential tail in the region of high energies. The position of this tail becomes higher as the laser pulse fluence increases, and the dissociation threshold is apparently related physically to the value of Φ_{th} when the distribution tail reaches the dissociation limit. Such an explanation of threshold is generally used for molecules whose quasi-continuum limit is low enough, and therefore they dissociate at rather moderate pulse energy fluences (1 to 10^2 J/cm²).

MP dissociation for molecules which call for high energy fluences ($\geq 10^2$ J/cm²) is not so unambiguous. It has been pointed out that radiation intensity is essential in MP dissociation of vinyl chloride, ethyl vinyl ether and acetone nitrile.²⁵⁻²⁷

Dependence of β and φ on laser energy fluence and absorbed energy. As the energy fluence exceeds the threshold the dissociation yield increases rapidly. When the value of β becomes significant, more than approximately fifteen per cent, the increase of the dependence slows down and saturation begins. Usually as the energy fluence is increased by about an order as compared to its threshold value the saturation of the dependence becomes appreciable. Some characteristic examples of such dependences are given in Figure 7.3.

MP dissociation is apparently an extension of the effect of molecular MP excitation with IR radiation considered in detail in the foregoing chapters. Among other things it has been shown there that in the process of MP excitation two molecular ensembles are often formed: molecules excited to the quasi-continuum with their fraction q and molecules left on the lower levels. So the character of the dependence of β on Φ (Figure 7.3) is affected by two factors: variation of the fraction of excited molecules q and variation of the average energy of excited molecules $\bar{\epsilon}_q$.

Physically it is more justified to describe the process of molecular dissociation with the value of quantum dissociation efficiency $\varphi = \beta(D/\bar{\epsilon})$ that, as noted in Chapter 6, is independent of the q factor. The dependence of φ on Φ for the CF₃I molecule is given in Figure 4.10. In essence, the quantum efficiency of MP dissociation shows what part of the energy absorbed in the gas is consumed to break the molecular bonds. For CF₃I, for example, the dissociation yield being

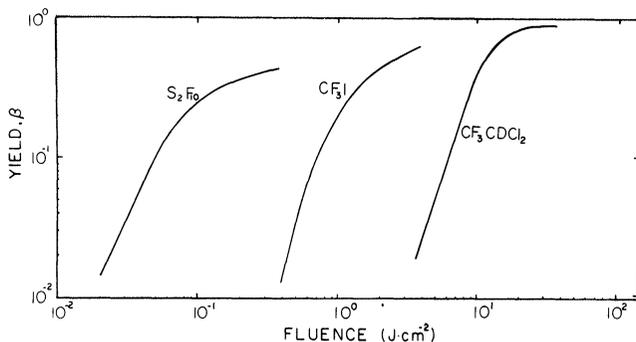


FIGURE 7.3 Characteristic dependences $\beta = \beta(\Phi)$ for different molecules (no account taken of the possible recombination). (From Refs. 98, 32, 173.)

unity, $\varphi \approx 0.9$. The fact that φ differs from unity is caused by overexcitation of the molecules beyond the dissociation limit. In the case of CF_3I the value of overexcitation $\bar{\epsilon}_q - D \approx 1700 \text{ cm}^{-1}$. The overexcitation level is determined by the ratio of the rate of laser excitation of the molecules and the rate of their dissociation. As it follows from the RRKM theory, for small (five or six-atom) molecules the dissociation rate becomes rather high even with a small excess (0.1–0.2 D) over the dissociation limit. Therefore, at the typical laser pulse duration $\tau_p \approx 10^{-7} \text{ s}$ no further molecular overexcitation takes place. The situation is different for large molecules (over 10–12 atoms). Much higher overexcitation is possible here. In the experiments with $(\text{CF}_3)_3\text{CI}$, for example, $\bar{\epsilon}_q \approx 2 D$ was observed. So the value of φ for these molecules cannot be higher than 0.5.

An intimate relation between dissociation yield and absorbed energy has been found.²⁸ In this work it was assumed that in the process of MP excitation a Boltzmann distribution is formed, its average energy determined by the energy absorbed by the molecules. It was also assumed that dissociation would take place only for the molecules having energy above the dissociation limit. Although in this work the gas temperature was not calculated quite correctly, the experimental and calculated curves for SF_6 are in qualitative agreement. A similar approach within the limits of such a thermal model has been used in.^{29,21} The dissociation yield here is calculated in the form

$$\beta = Z_{\text{vib}}^{-1} \int_D^{\infty} \rho(E) e^{-E/kT} dE \quad (7.2)$$

where Z_{vib} is the vibrational statistical sum and $\rho(E)$ is the vibrational state density. Correct calculation of temperature from the values of absorbed energy as well as inclusion of additional absorption by SF_5 radicals formed in the dissociation of SF_6 made it possible to consider²¹ quantitative (within 50%) agreement between the calculated and measured values of dissociation yield. As one would expect, the maximum inconsistency occurs with $\beta \ll 1$ when the Boltzmann distribution tail must give (Figure 6.13) an excessive value of the yield.

Such agreement is due to the fact that, even though the energy distribution function formed in the process of MP excitation is not the Boltzmann one (see Chapter 6), its difference from the Boltzmann function for *excited* molecules is not cardinal. Therefore, in estimations we may use a simple thermal model. In this case, however, we should take into account one important factor, that is, a possibility of the separation of the molecules into two ensembles. Here account must be taken only of the excited molecules, and expression (7.2) can be used only for them. Otherwise the error may be as great as several orders. This can be clearly seen from Figure 6.12 when the calculated data within the frameworks of thermal model (curve 3) is compared with the experimental ones in two cases when the measured parameters are averaged over all molecules (curve 1) or are concerned only with the upper ensemble (curve 2).

7.1.3. Dependence of dissociation yield on IR laser frequency

The relationship between the effects of MP dissociation and absorption vividly manifests itself in the similarity of the spectral dependences of dissociation yield and absorbed energy. Figure 7.4a shows the dependence of dissociation yield on laser radiation frequency as the SF_6 molecule is excited within the limits of the ν_3 band.¹⁹ The maximum of this dependence like that of the corresponding dependence of absorbed energy (see Figure 4.4a) is shifted towards the long-wave edge of the spectrum, and the spectral curves, as a whole, are very alike. More striking consistency of the spectral characteristics of the two effects follows from the spectral dependence of the dissociation yield of OsO_4 molecules³⁰ presented in Figure 7.4l. The structure observed is consistent with the structure in the MP absorption spectrum of this molecule (see Figure 4.4b).

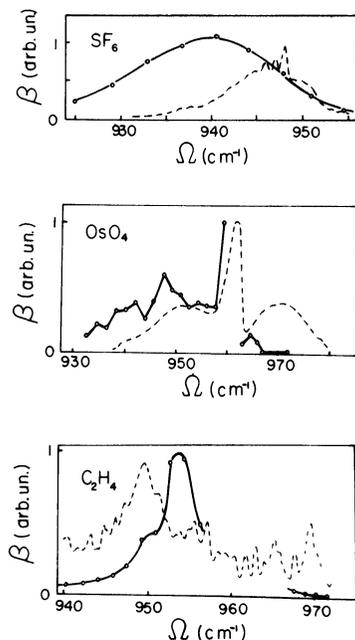


FIGURE 7.4 Dependence of the dissociation yield β on the radiation frequency for some molecules. (a) SF_6 ,¹⁹ (b) OsO_4 ,³⁰ (c) C_2H_4 .¹¹ The corresponding spectra of linear absorption are shown with dashed curves.

The deformation of the MP excitation spectrum caused by changes in the excitation conditions usually brings about corresponding changes in the spectral characteristics of MP dissociation. This may be illustrated by experiments with gas cooling. The narrowing of the MP excitation spectrum caused by the temperature drop brings about a corresponding decrease in the width of dissociation yield spectral curve.³¹ (See Chapter 8 about the influence of gas temperature on dissociation yield.)

It should be pointed out, however, that the consistency between the spectral dependences of absorbed energy and dissociation yield is empirical by nature. There are disparities, and the characteristic example for this is C_2H_4 . In the MP dissociation spectrum of this molecule (see Figure 7.4c) there is only one maximum manifesting itself clearly, whereas there are three maxima in the MP absorption spectrum.¹¹

Localization of the MP dissociation spectrum near the linear absorption spectrum of the corresponding vibration of the molecule under excitation (see Figure 7.4a, b, c) makes possible selective dissociation of molecules in a mixture, for example containing a certain isotope. Although the MP dissociation spectrum, like the MP absorption spectrum, is usually wider than the linear absorption spectrum, its width in many cases, nevertheless, is smaller than the isotope shift between the absorption bands of different isotopic molecules. The isotopic selectivity of MP dissociation has found wide application in isotope separation and in other selective processes. The data on this point are given in Chapters 8 and 9.

Let us discuss one more aspect of the relationship between the characteristics of MP dissociation and the exciting radiation frequency. The dependence of dissociation yield on laser radiation frequency causes the dependence $\beta = \beta(\Phi)$ to change with changes in Ω . This can be clearly seen from Figure 7.5a which presents the dependences of β on Φ as SF_6 is excited at two different CO_2 laser lines. A natural question arises whether the dependence of dissociation yield on absorbed energy changes as the radiation frequency varies. In other words, whether the dissociation yield depends only on absorbed energy or with the same $\bar{\epsilon}$, it also depends on radiation frequency. This question has been studied.²¹ Figure 7.5b gives the values of MP dissociation yield for SF_6 varying with the value of absorbed energy

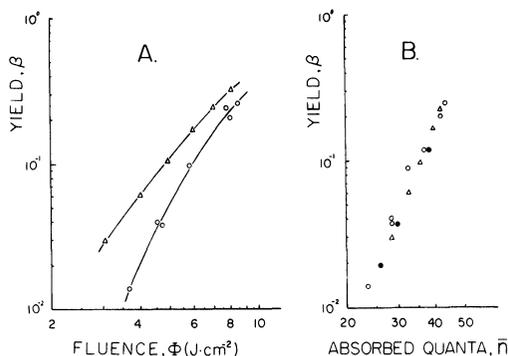


FIGURE 7.5 MP dissociation of SF_6 .² (a) Dependence of β on Φ at the $P(16)$ and $P(24)$ lines of CO_2 laser. (b) Dependence of β on the number of absorbed quanta for the $P(16)$, $P(24)$ and $P(28)$ lines of CO_2 laser. \circ $P(26)$; Δ $P(24)$; \bullet $P(28)$.

during excitation at three different CO₂ laser frequencies. It may be seen that the values of β at all three lines coincide for the same values of the number of absorbed quanta n within the experimental limits.

Thus, in the case of SF₆ the dissociation yield is actually determined only by the value of absorbed energy, at least when excitation takes place within the linear absorption band ν_3 . This fact enabled the authors²¹ to conclude that the vibrational distribution function, too, does not apparently depend on excitation frequency and is fully determined by the average energy of the excited molecules $\bar{\epsilon}$. A similar assumption on the universal character of the distribution function in the MP excitation of CF₃I had been made before.³² It is consistent with the experimental measurement of the MP dissociation parameters of this molecule.

It is quite possible that in MP excitation of molecules, at least at not very large shifts from the center of the linear absorption band of the vibration chosen, the form of the vibrational distribution function really depends a little on radiation frequency. The data available is not enough, however, for unambiguous conclusions. In measurements of dissociation yield the results may be affected by the collisional equilibration towards a Boltzmann description of the distribution function caused by collisions after MP excitation and before a major number of excited molecules has dissociated. The question on the universality of the distribution function remains to be solved. Only direct measurements of the form of the function of vibrational distribution of excited molecules can apparently provide the answer.

7.1.4. MP dissociation in two-frequency IR field

According to the presently accepted theory, there are two main stages in the process of MP excitation: (1) excitation through the lower vibrational levels and (2) subsequent absorption of energy in the vibrational quasi-continuum. This is confirmed by experiments on two-frequency irradiation of molecules. The first experiment of this kind was published in 1976.³³ The idea of two-frequency irradiation is that the function of the radiation for the first and second stages of the process may be different and can be divided. First the molecule is acted upon by the first pulse with a Ω_1 frequency within the absorption band. The second pulse with a different frequency Ω_2 provides subsequent excitation of the molecules in the quasi-

continuum. This frequency can be even brought out beyond the MP absorption contour observed for one-frequency irradiation.

The first work³³ revealed such an important property of the effect of two-frequency dissociation as the absence of a threshold for the energy fluence of the first pulse. The dependence $\beta(\Phi_1)$ measured³⁴ is shown in Figure 7.6. The SF_6 molecule was excited at the frequency $\Omega_1 = 942.4 \text{ cm}^{-1}$, that corresponded approximately to the maximum of multiphoton IR absorption, and $\Omega_2 = 954.5 \text{ cm}^{-1}$. The energy fluence of the second pulse was constant $\Phi_2 = 7.5 \text{ J/cm}^2$. It may be seen that

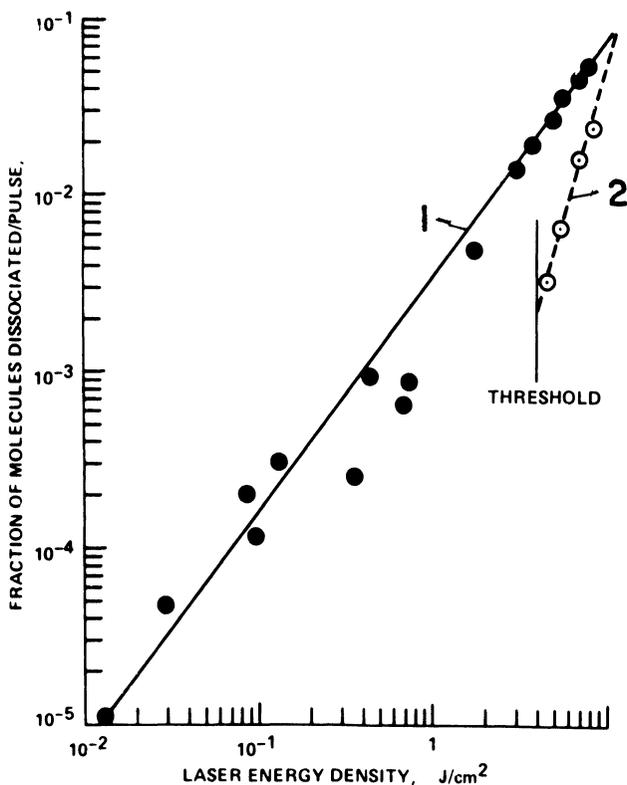


FIGURE 7.6 Two-frequency MP dissociation of SF_6 molecules.³⁴ Dependence $\beta = \beta(\Phi_1)$ with excitation performed by the first field at the frequency $\Omega_1 = 942.4 \text{ cm}^{-1}$ in the presence of the second field at $\Omega_2 = 945.5 \text{ cm}^{-1}$ with the second pulse fluence $\Phi_2 = 7.5 \text{ J/cm}^2$ (curve 1). The dependence $\beta = \beta(\Phi_2)$ in the absence of the second pulse (curve 2) is given for comparison.

the dissociation yield increases almost linearly as Φ_1 increases. This dependence differs greatly from that dependence measured in the absence of the second pulse which has a threshold character. This result shows once again that the interpretation that the threshold property of the MP dissociation effect is related to molecular excitation in the vibrational quasi-continuum is correct.

The studies of the frequency dependences $\beta = \beta(\Omega_1, \Omega_2)^{33,12,35}$ have shown that the resonant character of MP dissociation is basically related to the passage through the lower vibrational levels. As far as the transitions in the vibrational quasi-continuum are concerned, their character is also resonant, although it is much weaker. This conclusion follows from measuring the dependence $\beta = \beta(\Omega_2)$ with $\Omega_1 = \text{const}$ in experiments on such molecules as OsO_4 ,³⁵ SiF_4 ,¹² SF_6 .^{12,34,36} In all these cases the spectral dependence $\beta = \beta(\Omega_2)$ is shifted considerably to the red spectral region (see Figure 6.7). The results obtained enable us to conclude that the vibrational quasi-continuum in the vicinity of the normal vibration under consideration is a wide resonance shifted towards the low-frequency region because of vibration anharmonicity. The spectral properties of the quasi-continuum are discussed in more detail in Chapter 6.

Optimizing conditions for molecular excitation in the quasi-continuum, as one laser pulse is divided into two pulses and one of them is shifted towards the long-wave region, has two important consequences. First, the MP dissociation threshold is reduced. This can be seen from comparing the dependences $\beta = \beta(\Phi_2)$ for different frequencies Ω_2 of the second pulse presented in Figure 7.7. Second, the use of two-frequency excitation above the dissociation threshold may result in a considerable (about an order and more) increase in yield β with the total energy of two pulses being constant. The value of this increase in β depends on the second pulse frequency Ω_2 , which can be clearly seen from Figures 6.7 and 7.7, and on radiation energy fluence when Ω_1 and Ω_2 are fixed. The latter follows from the data presented in Figure 7.8. The dependence of the dissociation yield of SF_6 on energy fluence Φ_2 here is given for several fixed values of Φ_1 . It may be seen that even a small addition of radiation at the Ω_1 frequency causes an appreciable increase in yield as compared to one-frequency excitation. If we reconstruct curves 2, 3 and 4 in Figure 7.8 as the function of the total energy fluence in both fields $\Phi_1 + \Phi_2$ they fall on the same curve (the dashed one). If we compare the latter

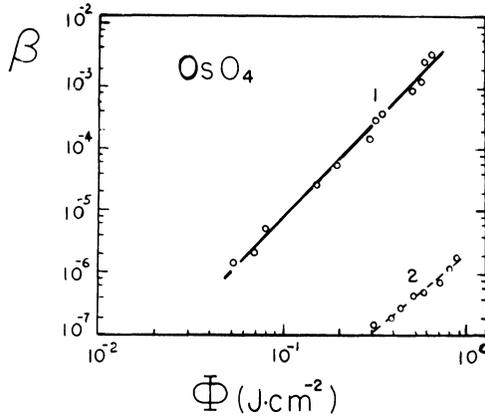


FIGURE 7.7 Two-frequency MP dissociation of OsO_4 molecules.³⁵ The dependences $\beta = \beta(\Phi_2)$ for two different frequencies of the second field: $\Omega_2 = 929.02 \text{ cm}^{-1}$ (curve 1) and $\Omega_2 = 966.25 \text{ cm}^{-1}$ (curve 2). In the both cases $\Omega_1 = 954.55 \text{ cm}^{-1}$, $\Phi_2 = 0.2 \text{ J/cm}^2$.

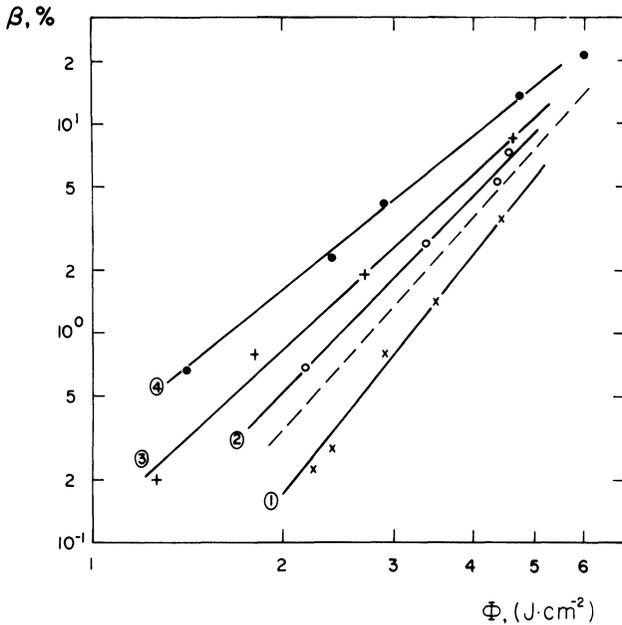


FIGURE 7.8 Dependence of the dissociation yield of SF_6 on fluence $\Phi = \Phi_1 + \Phi_2$ (dashed line) and $\Phi = \Phi_2$ (solid lines) with $\Phi_1 = 0$ (1); 0.23 (2), 0.57 (3) and 1.1 (4) J/cm^2 .⁹⁹

with curve 1 we can determine the pure gain obtained from dividing the energy of the Φ_2 field into two parts. In the region of low energy fluence ($\sim 2 \text{ J/cm}^2$) the gain in the two-frequency method, no matter in which way the field is divided, comes to about 100%. As the energy fluence increases the gain becomes decreased.

Besides the possibility of increasing the dissociation yield, the two-frequency method has one more property important in practice. When the energy fluence of the first pulse which is responsible for resonant excitation of molecules through the lower levels is reduced this causes the MP excitation spectrum to get narrower (see Chapter 5) and, as a result, the dissociation selectivity of the desired molecules to increase. This property of two-frequency dissociation has found application in laser isotope separation (see Chapter 8).

7.2. Products of IR multiple photon dissociation and their energy distribution

In this section we are going to consider the products formed by the process of molecular MP dissociation as well as their energy distribution. We can use several methods to determine the primary dissociation products. In some cases they can be found from the final stable dissociation products if we know the secondary chemical reactions. In most cases, however, indirect determination of primary fragments cannot replace the direct diagnostic methods. The largest progress can be achieved with the use of the molecular beam technique as well as the laser induced fluorescence of radicals technique. These methods enable us not only to identify directly the primary dissociation fragments but they also give important information on the form of the energy distribution of these products.

In discussing the results stated in this section we shall widely use the statistical theory of unimolecular reactions (RRKM). This theory forms the basis for understanding the process of dissociation of the vibrationally excited molecules as a result of their interaction with the IR radiation. All necessary information from the RRKM theory can be found in Section 2.4.

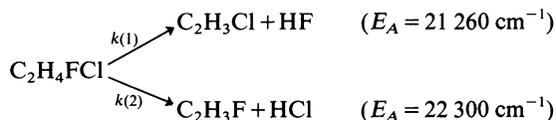
7.2.1. MP dissociation channels and primary fragments

Table 7.3 presents data on products of molecular MP dissociation by IR radiation. This data was obtained in some cases from indirect

considerations but in most cases the products formed were detected using direct diagnostic methods.

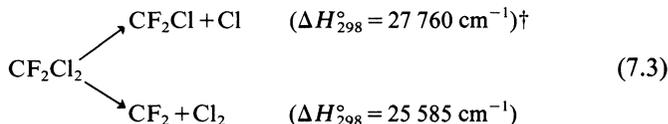
In the second column of Table 7.3 there are main dissociation channels observed in the process of MP excitation of molecules. The data presented shows that the resulting products, as a rule, correspond to the breaking of the weakest molecular bond.

In molecules with two close dissociation channels dissociation is possible by both channels. This can be illustrated with the C_2H_4FCI molecule which has the following dissociation channels.



(E_A is the activation energy). The dissociation rates ratio estimated³⁷ according to the RRKM theory is in good agreement with the concentration ratio of C_2H_3F and C_2H_3Cl measured experimentally. It should be noted that the relative contribution of different channels may depend on the radiation intensity since the dependences of the dissociation rate constants $k(1)$ and $k(2)$ on molecular excitation level may be different.

In the presence of two close dissociation channels one of which is followed by elimination of atoms and the other one by elimination of molecules the first channel often turns out to be more probable even if energetically less advantageous. We can illustrate this with the CF_2Cl_2 molecule which has the following dissociation channels



In this case the dissociation probability by the first channel is about an order higher than by the second one.³⁸⁻⁴⁰ Dissociation by this energetically "disadvantageous" channel has been also observed in MP excitation of CF_2Br_2 ,⁴¹ CF_2CFCl ⁴³ and CH_3NH_2 .⁴³ For the first

† In many cases the value of dissociation energy is determined from the thermal effect of reaction, i.e., from the difference ΔH° in enthalpies of formation of primary and final products. The values ΔH_0° and ΔH_{298}° are given for zero and room temperatures respectively. When there is no barrier for the reverse reaction $\Delta H_0^\circ = D$.

TABLE 7.3
Primary fragments of MP dissociation for some molecules

Molecule	Main channel of MP dissociation	References	Comments
NH ₃	NH ₂ + H	13	
N ₂ H ₄	2NH ₂	127	
N ₂ F ₄	2NF ₂	40, 49, 126	
SF ₆	SF ₅ + F	15, 16, 46, 48	SF ₅ $\xrightarrow{nh\Omega}$ SF ₄ + F ^{45,48}
SF ₅ Cl	SF ₅ + Cl	142	SF ₅ $\xrightarrow{nh\Omega}$ SF ₄ + F (?) ¹⁴²
SF ₅ NF ₂	SF ₅ + NF ₂	157	
S ₂ F ₁₀	2SF ₅	98	
CHFCl ₂	CFCI + HCl	49, 50	
CF ₂ HCl	CF ₂ + HCl	49, 50, 55, 171	Other channels: CFCI + HF, CHCl + F ₂ , CHF + ClF—less than 1% of the main channel
CF ₃ D	CF ₂ + DF	103	
CF ₃ Cl	CF ₃ + Cl	40, 49	CF ₃ $\xrightarrow{nh\Omega}$ CF ₂ + F
CF ₃ Br	CF ₃ + Br	40, 49	
CF ₃ I	CF ₃ + I	40, 49, 93	
CF ₂ Cl ₂	CF ₂ Cl + Cl	38, 40, 49	The other channel CF ₂ + Cl ₂ ⁴¹
CF ₂ Br ₂	CF ₂ Br + Br	40, 49	The other channel CF ₂ + Br ₂ ⁴¹
CFCI ₃	CFCI ₃ + Cl	40, 49	CFCI ₂ $\xrightarrow{nh\Omega}$ CFCI + Cl ⁴⁰
C ₂ H ₄	H ₂ CC + H ₂ (?)	129, 170	H ₂ CC $\xrightarrow{nh\Omega}$ C ₂ + H ₂ ¹²⁹ Visible luminescence of C ₂ radical ^{6,129}
CH ₂ CHF	C ₂ H ₂ + HF	56	
CH ₂ CHCl	C ₂ H ₂ + HCl	30	
CH ₂ CF ₂	C ₂ HE + HF	52, 56	
CHClCCl ₂	C ₂ HCl ₂ + Cl	49	
CF ₂ CFCI	→ CF ₂ + CFCI	42	Visible luminescence of C ₂ radical ⁶
	↳ C ₂ F ₃ + Cl	133	

TABLE 7.3 (continued)

CF ₃ CN	CF ₃ + CN	135	
CH ₂ DCH ₂ Cl	$\begin{cases} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{HCl} \\ \rightarrow \text{C}_2\text{H}_4 + \text{DCl} \end{cases}$	172	$\text{C}_2\text{H}_3\text{D} \xrightarrow{nh\Omega} \text{C}_2\text{H}_2 + \text{HD}^{172}$ $\text{C}_2\text{HD} + \text{H}_2$
CH ₂ FCH ₂ Cl	$\begin{cases} \rightarrow \text{C}_2\text{H}_3\text{F} + \text{HCl} \\ \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{HF} \end{cases}$	37	$\text{C}_2\text{H}_4 \xrightarrow{nh\Omega} \text{C}_2\text{H}_2 + \text{H}_2^{172}$ $\text{C}_2\text{H}_3\text{Cl} \xrightarrow{nh\Omega} \text{C}_2\text{H}_2 + \text{HCl}^{37}$
CH ₂ FCH ₃	C ₂ H ₄ + HF	56	
CHF ₂ CH ₃	C ₂ H ₃ F + HF	56	
CH ₃ CF ₂ Cl	C ₂ H ₂ F ₂ + HCl	49	
CH ₃ CCl ₃	C ₂ H ₂ Cl ₂ + HCl	49	
CF ₃ CF ₂ Cl	$\begin{cases} \rightarrow \text{C}_2\text{F}_5 + \text{Cl} \\ \rightarrow \text{CF}_3 + \text{CF}_2\text{Cl} \end{cases}$	49	
C ₃ H ₇ Br	C ₃ H ₆ + HBr	163	
CH ₃ OH	$\begin{cases} \rightarrow \text{CH}_3 + \text{OH} \\ \rightarrow \text{CH}_2\text{OH} + \text{H} (?) \end{cases}$	100 85	Visible luminescence of OH and CH radicals ^{6,85}
CH ₃ CN	CH ₃ + CN	25, 101	Visible luminescence of CH and C ₂ radicals ⁶

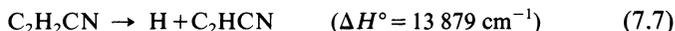
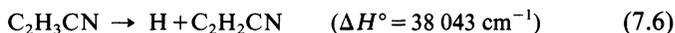
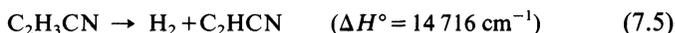
two molecules the dissociation by this channel is preferential. The most probable cause of this effect consists in the presence of a potential barrier for the "advantageous" channel. Indeed, in all these cases the "advantageous" channel is associated with elimination of molecules and rearrangement of molecular bonds. It is well known (see Section 2.4) that for such a process there may be a barrier the height of which E_A for the direct reaction to a greater or lesser degree exceeds the value of H for this process. Also, E_A may exceed the dissociation energy of the next channel and so the dissociation here may be more effective than by the first channel. We shall return to this point in the next section where we consider experimental proof of the presence of a barrier for CF₂Cl₂ based on measuring the vibrational energy in the CF₂ radical.⁴¹

Much research has been directed on the MP dissociation products of the SF₆ molecule. Energetically the most advantageous dissociation channel is the reaction



arbitrary units. At a relatively small excess of laser pulse energy fluence ($\Phi = 4 \text{ J/cm}^2$) over its threshold value the ratio observed for all angles was $[\text{SF}_3^+]/[\text{SF}_2^+] \approx 4$ within the limits of experimental error, which corresponded to the SF_5 radical. When the fluence is increased ($\Phi = 10 \text{ J/cm}^2$) the ratio $[\text{SF}_3^+]/[\text{SF}_2^+]$ in the region of large angles decreases considerably. The authors of the experiments believe that this fact is explained by the second stage of MP dissociation as a result of which the SP_5 radicals formed by reaction (7.4) further dissociate under the action of the radiation.

The case of SF_6 is quite typical. The process in which successive breaking of two and even more bonds takes place can be observed rather frequently. The polyatomic products formed at the first stage of MP dissociation can go on absorbing the radiation particularly when they are vibrationally excited. Such successive dissociation can last as long as the laser pulse, and so long as the fragments can absorb energy. Successive dissociation of a molecule and the resulting fragments is responsible for the birth of such diatomic radicals as C_2 , CH , and CN in the MP dissociation of some hydrocarbons. For illustration, we may present the sequence of the basic processes resulting in simultaneous formation of the C_2 and CN radicals in MP dissociation of $\text{C}_2\text{H}_3\text{CN}$ ⁵¹



The radical C_2HCN formed by (7.5) and (or) (7.6, 7.7) is subjected to further dissociation



The authors⁵¹ note that, despite a great difference in the values of ΔH° in reactions (7.5) and (7.6), the latter can occur since reaction (7.5) has an activation barrier $E_A \approx 28\,000 \text{ cm}^{-1}$.

It is also of interest to clarify the temporal behavior of the reaction radicals in time. We may point out conventionally two processes. The first of them is connected with MP dissociation during a laser pulse, and the main contribution to this process is given by those molecular

states excited over the dissociation limit the decay rate of which $k(E_{\text{vib}})$ exceeds the reverse duration of laser pulse $k(E_{\text{vib}})$. The research using the LIF method that provides rather high time resolution shows that in some cases this process is dominant (see Figure 7.10). The second process is connected with the dissociation of the molecules excited by a laser pulse to the states which lie comparatively not high above the dissociation limit so that their dissociation rate is less than τ_p^{-1} . Thus, the contribution of these two processes depends on the level of molecular excitation over the dissociation limit $E_{\text{vib}} - D$ and the relation between τ_p and $k(E_{\text{vib}})$. The possibility of experimental separation of these two processes was demonstrated⁵² where the MP dissociation of the $\text{C}_2\text{H}_4\text{F}_2$ molecule was studied by recording with time resolution the IR fluorescence of the resultant HF molecules. As a result, estimates were obtained for the decay times of the levels contributing to dissociation during a laser pulse and after its action, along with the relative contributions of the two processes. This experiment in its essence was similar to experiments on the direct study of the energy distribution of the fragments. Such experiments are discussed in the next section. It should be noted that recording of MP dissociation products of molecular ions with time has been achieved.^{53,54}

The cases considered show to what extent the effects arising in molecular dissociation changes as a result of their MP excitation with varied IR radiation. Nevertheless, with all this variety all the results obtained so far are consistent with the statistical model the main assumption of which is fast redistribution of vibrational energy over all molecular modes. There have been so far no reliable experiments which would be indicative of an observation of mode-selective dissoci-

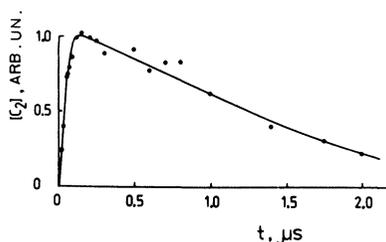


FIGURE 7.10 MP dissociation of C_2H_4 molecules.¹²⁹ The dependence of the concentration of C_2 radicals formed in the process of MP dissociation on time. (The decrease of the signal is connected with the radical flight from the zone of probing.)

ation in MP excitation of molecules.† And conversely, the available results are in agreement with the hypothesis on stochasticity of vibrational motion for highly excited molecules.

7.2.2. Energy distribution of MP dissociation products

Molecules excited as they absorb IR radiation dissociate if their energy E_{vib} exceeds the dissociation energy D . In this case the energy excess $\Delta E = E_{\text{vib}} - D$ is distributed between different degrees of freedom of the resulting fragments. Before considering the particular distributions of this energy we are going to review briefly what is predicted by the RRKM theory on the value of the energy ΔE . The estimations done in Chapter 4 (see Section 4.4.2) show that for typical experimental conditions with the laser pulse duration $\tau_p \approx 10^{-7}$ s the real excitation over the dissociation limit doesn't exceed $\Delta E \leq (0.1-0.3) D$ when the number of atoms in the molecule is ≤ 7 .

The results of experiments with molecular beams agree with these estimations. In the SF_6 molecule,⁴⁸ for example, it was concluded that the value of excess over the dissociation limit, with the CO_2 laser radiation fluence $\Phi = (4-10) \text{ J/cm}^2$, ranged from 6 to 10 quanta. For molecules with a smaller number of atoms the overexcitation is lower which also agrees with the conclusions of the RRKM theory. For the CF_3Br molecule at the same values of Φ the maximum excess over the dissociation limit comes to three quanta.

Now consider how the energy excess ΔE is distributed over the degrees of freedom of fragments. Let us begin with the translational degrees.

Translational energy distribution. According to the RRKM theory, the probability of conversion of the excessive molecular energy $E_{\text{vib}} - D$ equal to E_{TRANS} will be transformed into translational energy is described by the distribution function

$$g(E_{\text{TRANS}}) = \text{const.} \frac{d}{dE_{\text{TRANS}}} R(E_{\text{vib}} - D - E_{\text{TRANS}}) \quad (7.10)$$

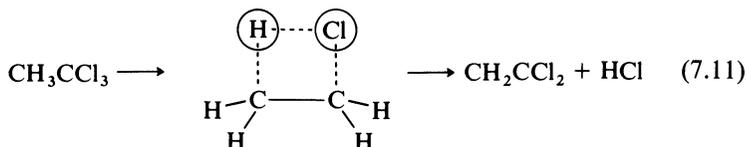
where R is the number of activated complex states in the energy range between D and $E_{\text{vib}} - E_{\text{TRANS}}$. Since the density of activated complex

† We are not considering here a special case of "site-selective" excitation of large molecules (see Section 6.1.2).

states dR/dE grows quickly with increasing energy the maximum of the distribution function $g(E_{\text{TRANS}})$ corresponds to the zero value of recoil energy.

The conclusions of the RRKM theory are in good agreement with the results of experiments in molecular beams when the molecular dissociation is a simple two-center reaction. The measured angular and velocity distributions of dissociation fragments of SF_6 , $\text{C}_2\text{F}_5\text{Cl}$, N_2F_4 and a number of halogenated methanes^{40,48} are consistent with the calculated functions. This enables us to estimate the level of molecular excitation over the dissociation limit. The characteristic feature of these distributions is the presence of a maximum at zero recoil energy. (For angular distribution this corresponds to the zero value of angle θ (see Figure 7.9).) At two-center bond breaking only a small part of excess energy ΔE (less than 20–30%) is converted to the translational energy of fragments. In MP dissociation of SF_6 (reaction (7.4)) of the total overexcitation energy $\Delta E \approx 9000 \text{ cm}^{-1}$ only about 1000 cm^{-1} is converted to translational energy. The rest of the energy remains in the vibrational and rotational degrees of freedom of the SF_5 radical.

The presence of a barrier along the reaction coordinate as often exists for three- or four-center molecular decay, changes the behavior of the recoil energy distribution. The maximum of this distribution can be observed, for example, at some non-zero finite value of energy. The experiments with CHF_2Cl , CHFCl_2 , CH_3CCl_3 , $\text{CH}_3\text{CF}_2\text{Cl}$ ⁵⁰ where elimination of the HCl molecule was observed show that, besides the possible transfer of a part of excess energy ΔE ,† a considerable part (up to 20%) of potential energy of reverse reaction barrier is directly transferred to translational degrees of freedom. In the four-center dissociation of the CH_3CCl_3 molecule⁵⁰



the reverse reaction barrier equals $14\,680 \text{ cm}^{-1}$ and thus the fragments acquire considerable translational energy $\bar{E}_{\text{TRANS}} \approx 2800 \text{ cm}^{-1}$.

† We mean here an excess over the direct reaction barrier.

The formation of a barrier is a result of the interaction of the fragments even after they have formed critical reactive configurations. Therefore it is impossible to predict correctly how the energy is distributed over all degrees of freedom of fragments without additional assumptions on the form of the potential surfaces along the reaction coordinate. The value of E_{TRANS} calculated with the use of the RRKM theory⁵⁰ within the frameworks of statistical distribution over degrees of freedom may differ considerably from the experimental value; in the case of CH_3CCl_3 it is smaller by four times.

Distribution over vibrational and rotational degrees of freedom. The basic results have been obtained using the laser induced fluorescence method. The possibility of its application in measuring vibrational and rotational distribution is obvious enough and consists in probing different vibrational-rotational states in the electronic absorption spectra of dissociation products with a tunable laser. The typical results of this kind of experiment for C_2 radicals is shown in Figure 7.11. Knowing the values of Frank–Condon factors, it is possible to determine the population ratio for any pair of vibrational-rotational levels from the ratio of fluorescence signals and, as a result, to obtain information on the distribution function.

The distribution of vibrational energy in the CF_2 radical formed by MP dissociation of CF_2Cl_2 , CF_2Br_2 and CF_2HCl was studied^{41,55} and it was shown that the distribution of vibrational energy in the CF_2 radical for these three molecules is Boltzmann-like. For illustration, we will consider the CF_2Cl_2 molecule. In Section 7.2.1 it has been

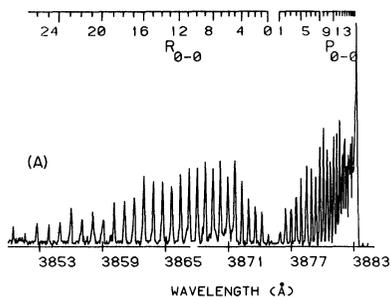


FIGURE 7.11 Spectrum of laser-induced fluorescence of the C_2 radical during MP dissociation of $\text{C}_2\text{H}_3\text{CN}$. The signal is observed at the transition $\text{B} \rightarrow \text{X} (0, 1)$ with the dye laser radiation scanned along the band $\text{X} \rightarrow \text{B} (0, 0)$.

already noted that the preferential role of the channel of elimination of the Cl atom, as compared to that of the Cl₂ molecule, is apparently caused by the presence of a barrier for the second reaction. In this case one would expect that the dissociation of CF₂Cl₂ into the CF₂ radical and the Cl₂ molecule mainly occurs near the barrier top. The measurements of the vibrational distribution in the CF₂ radical⁴¹ fully support these conclusions. It was found that as the laser pulse energy fluence varied from 1.5 to 6 J/cm² the vibrational temperature ($T = 1050 \pm 100$ K) remained almost constant even though the radical yield changed by about an order. Based on these results⁴¹ it was concluded that molecular dissociation actually comes about mainly near the top of the barrier the height of which is estimated by them to be 6900 cm⁻¹.

Measurements have been taken of the rotational energy distribution in the radicals formed by MP dissociation with no variations from the Boltzmann rotational distribution observed. The results are presented in Table 7.4, where the rotational temperatures of the radicals investigated are given as well as their vibrational temperatures for the cases when they were measured in parallel. It may be seen that in most cases the vibrational and rotational temperatures differ greatly. For the CF₂ radical formed by MP dissociation of CF₂CClF the temperatures differ even in different vibrational modes. The experiments with CF₂CClF enable us to conclude that the rotational distribution as well as the average translational energy[†] of the dissociation products of this molecule do not correlate with their vibrational energy.

The results presented in Table 7.4 demonstrate vividly the potential of the fluorescence method. The results, particularly the Boltzmann type distribution as well as the difference between vibrational and rotational temperatures, have not however been interpreted yet.

Interesting results were obtained⁵⁶ when the energy distribution of the vibrationally excited HF molecules formed as a result of their elimination from CH₂CHF, CH₃CH₂F, CH₃CHF₂, CH₂CF₂ was studied observing their IR fluorescence spectra. For these molecules, too, the rotational distribution of fragments was Boltzmann-like. Study

† The translational energy of the fragments may be determined from the measurements of their velocities at which they leave the region of probing (see e.g., Figure 7.10 and the caption to it). It is important that this method gives an opportunity to determine the translational energies for particular quantum states of the fragments. Some results of this kind of experiments are presented in Table 7.4.

TABLE 7.4
 Energy distribution of MP dissociation fragments

Molecule	Fragment	Laser pulse energy fluence, J/cm ²	Vibrational temperature, K	Rotational temperature, K	Average translational energy, ^a kcal/mol	Refs.
CF ₂ Cl ₂	CF ₂	1.5-6	1050 ± 100	550		41, 55
CF ₂ Br ₂	CF ₂	1.5-6	790 ± 70	450		55
CF ₂ HCl	CF ₂	2.4-26	1160 ± 100	2000		55
CH ₃ OH	{OH	150		1250 ± 400		100
	{CH	150		1200 ± 400	100	
CH ₃ CN	CN	300	425	664	101	
C ₂ H ₃ CN	{C ₂	10-80		700 ± 200	1.1 ± 0.3	51, 102
	{CN	10-80		1000 ± 200		51
CF ₂ CFCl	{CFCl	50	1550 ± 300 (ν ₂)	400	0.3	42
	{CF ₂	50	1860 ± 250 (ν ₂)		0.4	42
			1100 (ν ₁ , ν ₃)			

^a Measured in center-of-mass system.

of the vibrational distribution, however, shows that it cannot be adequately described only by the temperature of the corresponding Boltzmann distribution. The results of the measurements show that from 16% to 31% (depending on the molecule) of potential energy of the reverse reaction barrier is directly spent on vibrational excitation of HF. This is about one order higher than the result calculated by the RRKM theory on the assumption of statistical energy distribution.

These results as well as the results of translational energy distribution considered before show once again that in the presence of a potential barrier we cannot calculate correctly the energy distribution of the fragments without knowing the potential surface along the reaction coordinate. At the same time the available data shows that the character of the energy distribution over different degrees of freedom of the fragments apparently depends only slightly on laser IR excitation parameters and is governed predominantly by the level of molecular excitation. This makes possible wide application of IR multiphoton molecular excitation in combination with proper diagnostic methods of radical determination in studying the process of unimolecular dissociation of highly excited molecules and the potential surface structure of these molecules.

7.2.3. Visible luminescence in the case of MP IR excitation of molecules

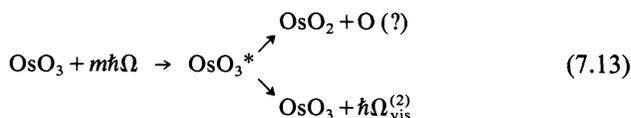
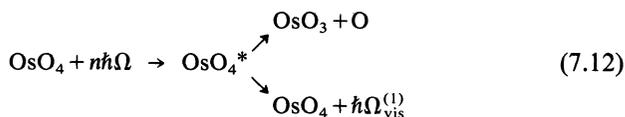
We considered above the characteristics of the dissociation of molecules resulting from their MP excitation followed by the formation of fragments in the ground electronic state. But in MP excitation of some molecules it was possible to observe visible luminescence which was associated with the luminescence of electronically excited radicals (see column 4 in Table 7.3). As a matter of fact, the effect of collisionless molecular dissociation by IR radiation was disclosed by detecting visible luminescence in experiments with SiF_4 ¹ and BCl_3 .² Nevertheless, the mechanism of the formation of electronically excited fragments has remained until recently probably the least understood point in the entire problem of MP excitation and dissociation of molecules.

Recent studies have clarified this point to some extent. The origination of the visible luminescence is apparently caused by a nonadiabatic coupling of the ground electronic state with the excited electronic term when the energy of the latter is lower than the dissociation limit from the ground term (see the end of Section 2.7). This effect is often called inverse electronic relaxation (IER).⁵⁷ It results from a breakdown of the Born–Oppenheimer approximation within which the vibrational states for different electronic terms are not interacting. Interaction, however, causes the real eigenvalues of the molecules to be an isoenergetic state superposition of the ground and excited electronic terms. In multiple photon IR excitation of such states their one-photon decay to the ground state becomes possible, with a quantum of visible radiation emitted.

One of the main predictions of the IER theory⁵⁷ is a considerable increase in the luminescence lifetime τ_0^l as compared to the typical time of dipole-allowed transition τ_1^{ad} in an adiabatic approximation. This increase depends (see Section 2.128) on the ratio of vibrational state densities in the ground and excited electronic states and may be as high as several orders. So, long luminescence, in a range from several tens of microsecond to milliseconds (for OsO_4 $\tau_0^l \approx 1.5 \cdot 10^{-3} \text{ s}$ ⁵⁸), is a characteristic feature which in many cases has made it possible to ascertain the relation of this luminescence to the IER effect.

Long-lived luminescence was observed in IR multiple photon excitation of tetramethyldioxetane;⁵⁹ $\text{S}_2\text{C}_2\text{F}_4$;⁶⁰ C_2H_4 , C_3H_8 , $\text{C}_2\text{H}_3\text{Cl}$, $\text{C}_2\text{H}_3\text{CHO}$;^{61–62} OsO_4 ;⁷ CrO_2Cl_2 .⁹

Rather well studied is visible luminescence arising in MP excitation of OsO_4 . It follows from the results^{7,58,63} that the most probable mechanism of luminescence is as follows



The highly vibrationally excited OsO_4^* molecules formed by MP excitation can emit a visible radiation quantum or dissociate to form OsO_3 (7.12). The latter, when absorbing then the IR radiation, can be highly excited and emit another visible radiation quantum as a result of one more process of IER (7.13).

Processes (7.12) and (7.13) in OsO_4 are separated on the laser radiation energy fluence scale (Figure 7.12). With $\Phi < 3 \text{ J/cm}^2$ the main contribution to the luminescence signal is made by the luminescence of the OsO_4 molecule itself (reaction (7.12)). With $\Phi > 3 \text{ J/cm}^2$ luminescence “quenching” arises which is caused by decreasing concentration of OsO_4^* because of their dissociation. With $\Phi > 4 \text{ J/cm}^2$ a new type of luminescence arises which is apparently connected with luminescence of the OsO_3^* radical according to reaction (7.13). Further increase in laser radiation energy causes the luminescence signal, with $\Phi > 10 \text{ J/cm}^2$, to decrease again, because of dissociation of the OsO_3 radical this time.

The dependence of the luminescence signal on Φ in MP excitation of CrO_2Cl_2 (curve 2, Figure 7.12) is a little different in character but from the results⁶³⁻⁶⁵ it follows that in this case, too, the luminescence source is the CrO_2Cl_2 molecule itself, as well as CrO_2Cl radicals, and then probably CrO .

The fact that visible luminescence is associated with the intermediate products of MP dissociation has been established in time-of-flight experiments⁶² for C_2H_4 ($\tau_0' \approx 8 \mu\text{s}$), C_2HCl_3 ($\tau_0' \approx 40 \mu\text{s}$), $\text{C}_2\text{H}_3\text{CN}$ ($\tau_0' \approx 22 \mu\text{s}$). In the last case the luminescence source is the C_2HCN or C_2CN radicals formed by reactions (7.6), (7.7) or (7.8).

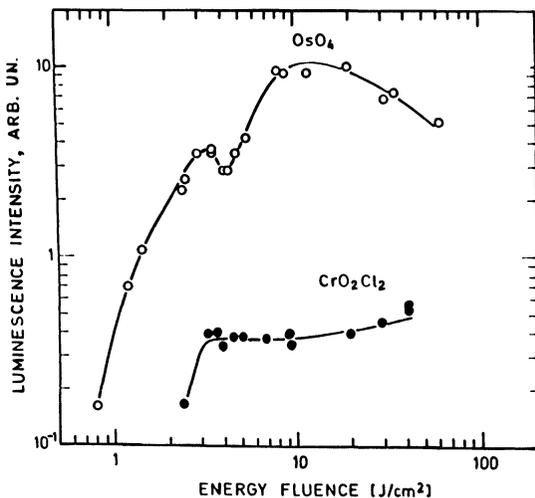


FIGURE 7.12 Dependence of the luminescence signal intensity on the CO_2 pulse fluence in the process of MP dissociation of OsO_4 and CrO_2Cl_2 .⁶³

In conclusion of this short section we must note that studies into visible luminescence in MP excitation are actually far from complete. It is only recently that inverse electron relaxation has been accepted. This effect is the most probable physical mechanism of the formation of electronically excited fragments. This conclusion can be apparently applied to the results of early experiments. The IER effect still requires further research. Specifically, the measured values of luminescence life time τ_0^l are only in qualitative agreement with those predicted theoretically. The difference may be rather significant. For example, the measured luminescence life time of the CrO_2Cl_2 molecule $\tau_0^l \approx 160 \mu\text{s}$ ⁶⁵ which is much larger than $\tau_1^{ad} \sim 1 \mu\text{s}$ but almost two orders less than the calculated value. The role of different channels of quenching, including that from IR fluorescence, remains to be seen. Future studies will probably enable us to understand better this interesting effect.

7.3. Isomerization of multiple photon excited molecules

Besides the processes related to fragmentation of polyatomic molecules, there is one more unimolecular photoprocess, that is, the

isomerization of molecules following their excitation. Photoisomerization of electronically excited molecules is a well known effect.⁶⁶ This process is of great importance in photobiology, for example in the molecular mechanism of vision (photoisomerization of rhodopsin molecules). One may expect that strong vibrational excitation of a polyatomic molecule by an intense IR field can also cause rearrangement of atoms and (or) bonds stably. It is interesting, in principle, to observe such a process in a strong IR field since it allows another probe of the effect of multiphoton absorption of IR radiation by molecules when the excited levels are lower than the level essential for molecular dissociation. It may also be important to achieve the selective isomerization of molecules in a strong IR field for widening the scope of isotope separation by IR laser radiation for the following reasons. First, isomerization gives a stable molecule with no need for chemical scavenging of dissociation fragments. It is also beneficial for the conservation of selectivity from secondary photochemical processes. Second, the isomerization energy may be much lower than the dissociation energy which allows the isomerization process to be performed with lower consumption of energy. On the other hand, because of a comparatively low energy barrier the process of isomerization is more sensitive to thermal heating than the process of dissociation.

There is one more factor which distinguishes dissociation from isomerization. In the first case the energy stored by the molecule is spent to break one of the molecular bonds, and this process is rather fast. In the second case the molecule with its energy being higher than the potential barrier (Figure 7.13) is able to change its structure. But, unlike the process of dissociation, the molecule can for a long time oscillate between two isomeric forms in the ground electronic state. To stabilize the molecule in one of the forms we should take away a part of the energy. Since the rate of radiative transition in the IR range is small ($\tau = 10^{-3} - 10^{-2}$ s) stabilization of the molecule in most cases results from vibrational deexcitation during collisions. So the effect of collisions on the characteristics of isomerization in MP excitation is expected to be stronger than in case of dissociation.

Particular emphasis has been given so far to molecular dissociation, whereas there is a much smaller body of work concerning isomerization. In the first work⁶⁷ consideration was given to isomerization of *trans*-2-butene by CO₂ laser pulses. In addition to dissociation of

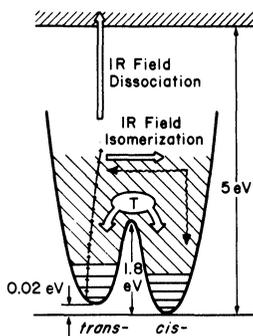


FIGURE 7.13 Dissociation and isomerization resulting from MP excitation of molecules. Example of $C_2H_2Cl_2$.

trans-2-butene, the formation of *cis*-2-butene was observed in the same work, that is, the processes of dissociation and isomerization occurred approximately with the same rate.

The effect of *trans-cis*-isomerization in MP excitation of $C_2H_2Cl_2$ molecules has been studied⁶⁸ in detail. Particular emphasis was placed upon a search for experimental conditions under which the threshold for isomerization would be much lower than for dissociation. In the molecule concerned, however, this aim was not attained, and after comprehensive studies the experimental conditions were found under which the isomerization rate was several times higher than the dissociation rate. It was also proved that the isomerization of the $C_2H_2Cl_2$ molecule was nonthermal. Some molecules have been found that under intense IR radiation only isomeric transformations occur without the formation of any other products. They are CH_3NC ,⁶⁹ and deuterated 1,5-hexadiene⁷⁰ for which the possibility of isotope-selective isomerization was proved. The isomeric transformation⁷¹⁻⁷² of hexafluorocyclobutene to hexafluorobutadiene has been observed, and the separation of the carbon isotopes was observed through such isomerization.⁷²

7.3.1. Experimental results for various molecules

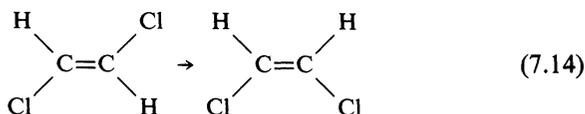
We will consider below the basic experimental results on molecular isomerization by CO_2 laser pulses.

2-butene. In the experiments⁶⁷ with *trans*- and *cis*-isomers of 2-butene, they were irradiated with focused CO_2 laser pulses. Both isomers absorb the CO_2 laser radiation, the absorption factor of the

trans-isomer is 11.5 times larger. The activation energy of *cis-trans*-isomerization is estimated to be about 20 quanta of CO₂ laser radiation. In the experiments pure *trans*- and pure *cis*-isomers as well as their mixture were irradiated. When irradiated the *trans*-isomer gives the following products: methane, ethylene, propane, *cis*-2-butene and butadiene. The product distribution and the relative conversion rates depended slightly both on the pressure of parent molecules and the pressure of inert gases. The same final products were produced from irradiating the *cis*-isomer, and the formation of *trans*-isomer was observed. But the rate of formation of *trans*-isomer was five times lower than in the previous experiments. When the equimolar mixture of the both isomers was irradiated at a total pressure of 4 Torr 15% enrichment of the mixture with *cis*-isomer was obtained. This result is considered by the authors to be basic proof of the nonthermal nature of isomerization.

The results obtained may also be explained, however, by preferential dissociation of *trans*-2-butene due to MP absorption.

Dichlorethylene. The isomerization of *trans*-dichlorethylene⁶⁸ to the *cis*-form under the action of CO₂ laser pulses has been considered:



The energy barrier of *trans-cis*-isomerization (Figure 7.13) equals 1.8 eV. The energy of the C=C bond breaking in the C₂H₂Cl₂ molecule equals 5.0 eV. The CO₂ laser radiation excited the *trans*-C₂H₂Cl₂ molecule whose absorption band ν_6 lies in the region of 10.6 μ . The initial content of *cis*-isomer varied from 10 to 40% and the total pressure from 0.4 to 1.0 Torr.

As the energy fluence was over 50 J/cm² there were three processes observed at the same time: (1) reaction of *trans-cis*-isomerization of C₂H₂Cl₂; (2) dissociation of *trans*-C₂H₂Cl₂ yielding fragments in the ground electronic state and acetylene, the main end product; (3) dissociation yielding electronically-excited radicals CH* and C₂*. Figure 7.14 shows the dependence of the relative concentrations of *trans*- and *cis*-C₂H₂Cl₂ on the number of irradiation pulses. Even though at the beginning of irradiation the amount of *cis*-isomer increases, the process of *trans-cis*-transformation does not continue to the end. After attaining its maximum concentration of about 0.5

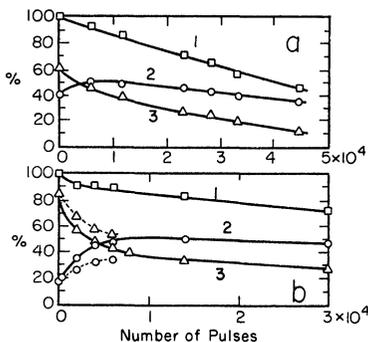


FIGURE 7.14 Dependence of the content of *cis*- and *trans*-isomers of $C_2H_2Cl_2$ on the number of irradiation pulses. (1) *cis* + *trans*, (2) *cis*, (3) *trans*. (a) $\Omega = 934.9 \text{ cm}^{-1}$, $\Phi = 100 \text{ J/cm}^2$, $p = 0.4 \text{ Torr}$. (b) $\Omega = 980.9 \text{ cm}^{-1}$, $\Phi = 250 \text{ J/cm}^2$, $p = 1.0 \text{ Torr}$. The addition of 44 Torr Xe is shown with a dashed line.⁶⁸

the amount of *cis*-isomer in the mixture begins to drop gradually. But the *cis-trans* concentration ratio in the mixture increases continuously and at the end of irradiation may range from 2 to 3 with the initial ratio being 0.67 (Figure 7.14a) and 0.18 (Figure 7.14b). The mixture was being enriched with *cis*-isomer all the time. The curves presented also illustrate the dependence of the total number of dissociated molecules on the number of pulses. It may be seen that it is mainly the *trans*- $C_2H_2Cl_2$ molecules that dissociate.

To determine how the laser pulse tail affects the processes concerned some experiments were carried out with a "shortened" laser pulse without a tail (the duration of such a pulse was 250 ns with respect to base and 60 ns with respect to half-height). It was found that neither fluorescence nor isomerization were observed at the same intensity of IR field, but only dissociation giving unexcited products took place. When a pulse with a long tail is used all three processes occur in the same energy range. They all stop when the energy fluence drops below 50 to 100 J/cm^2 .

Experiments with buffer gases are important for distinguishing the applicable isomerization mechanism for a particular chemical system. Adding a buffer gas produces several effects. First, a buffer gas affects rotational, vibrational and translational relaxation thus acting on the process of MP excitation. Second, as stressed above, adding a buffer gas must have a strong effect on the stabilization rate of molecules in one of the isomeric forms. It also increases the heat capacity of the

gas mixture. All other experimental conditions being equal, this causes the maximum temperature to decrease and thus suppresses thermal processes. In this case it is only buffer gas heat capacity that is of importance. In the experiments with dichlorethylene the role of different buffer gases (Xe, He, H₂, N₂) was studied with the following results:

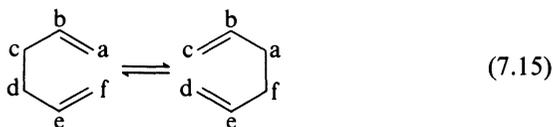
(1) With the addition of a buffer gas the absorbed energy increases. Adding 33 Torr of Xe increases the absorbed energy by more than 10 times which almost completely compensates for the increase of heat capacity. It is clear that in this case the buffer gas cannot suppress thermal processes.

(2) Buffer gases partially suppress the process of isomerization. Measurements show that the suppression effect varies for different gases at the same heat capacity. It also varies for different "buffer gas-dichlorethylene" mixtures with the same heat capacity.

(3) Buffer gas does not have a pronounced effect on the dissociation yield (see Figure 7.13).

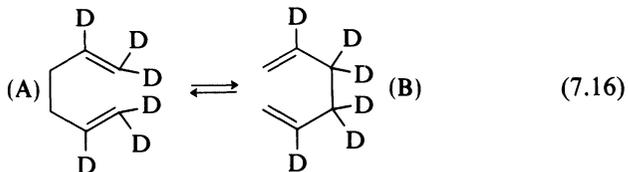
(4) At low pressures of C₂H₂Cl₂ (0.3 Torr) all buffer gases increase the yield of electronically excited dissociation products almost by an order of magnitude.

1,5-hexadiene. The Cope rearrangement in 1,5-hexadiene by CO₂ laser radiation⁷⁰ was studied:



Into certain points of this molecules deuterium was substituted for hydrogen. The initial and final products are chemically the same; they have a zeropoint energy difference and differ in their vibrational spectra. This allows selective excitation of one of the forms. The activation energy of reaction (7.15) $E_A = 12\,000\text{ cm}^{-1}$.

One example of the isomerization reaction of deuterated compounds⁷⁰ is



The (A) compound: 1,5-hexadiene-1,1,2,5,6,6-*d*₆ was synthesized (the

left part of (7.16)). The Cope rearrangement must give birth to the (B) compound: 1,5-hexadiene-2,3,3,4,4,5- d_6 . Heating the initial (A) compound gave a mixture of the (A) and (B) compounds with their concentration ratio of 0.9. The (A) compound is quite transparent at 10.8 μ whereas the (B) compound features strong absorption at this wavelength ($\kappa = 5.8 \cdot 10^{-3} \text{ cm}^{-1} \text{ Torr}^{-1}$). After the mixture was irradiated by CO_2 laser pulses at 10.8 μ the (B) compound disappeared without formation of any dissociation products. In the mixture only the (A) compound remained. The selectivity factor of the isomerization reaction was much higher than unity, and it decreased with increasing pressure. The same results were obtained in case of other deuterated 1,5-hexadiene molecules. These apparently were the first experiments in which the isomerization reaction observed had a rate much higher than the rate of dissociation reaction.

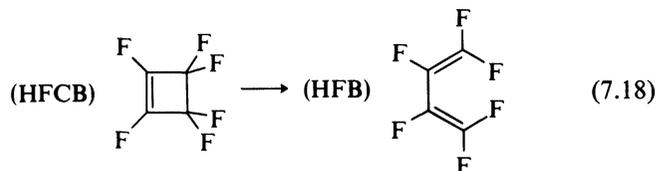
Methylisocyanide. The isomerization reaction of methylisocyanide⁶⁹ by CO_2 laser radiation to acetonitrile has been studied:



The reaction barrier (7.17) equals 12 500 cm^{-1} .⁶⁹ Isomerization of methylisocyanide was observed irradiated with CO_2 laser pulses in the region of 10.6 μ where the ν_4 vibration of CH_3NC lay. It was found that, with the radiation intensity over 70 MW/cm^2 , isomerization of the molecules occurred simultaneously with their dissociation, the latter followed by luminescence of the electronically excited radicals CN^* and C_2^* . When the CO_2 laser radiation intensity is lower only isomerization takes place. No direct dissociation products of CH_3NC were observed.

Experiments at different pressures of CH_3NC show that the isomerization yield increases as the gas pressure grows. It should be noted that isomerization of methylisocyanide was also observed at low gas pressures, up to 10^{-2} Torr.

Hexafluorocyclobutene. The transformation of hexafluorocyclobutene (HFCB)^{71,72} to hexafluorobutadiene (HFB) under CO_2 laser pulses has been studied



The reaction barrier (7.18) equals $16\,400\text{ cm}^{-1}$ and that of the reverse reaction of HFB cyclization $12\,200\text{ cm}^{-1}$.

In irradiating 0.5 Torr of pure HFCB⁷¹ the formation of HFB molecules was observed. With focused radiation the process of isomerization was also followed by the dissociation of the compound under exposure. The isomerization in a non-focused laser beam was the basic reaction but the maximum transformation of HFCB to HFB obtained under such conditions was no higher than 60% which⁷¹ was due to the equilibrium established during the process of irradiation between the direct reaction (7.18) and the reverse reaction of cyclization.

Adding a buffer gas (He) radically changes the course of the reaction. Although at the very beginning of irradiation the isomerization yield of reaction (7.18) decreases, the reverse reaction is suppressed to a greater degree. At a helium pressure of 16 Torr, the reverse reaction was suppressed fully. As a result, the isomerization yield in each pulse during the entire time of irradiation was constant. Therefore, in the presence of the buffer gas it was possible to practically fully convert HFCB to HFB under the action of CO₂ laser pulses.

Carbon isotope separation⁷² has been performed using reaction (7.18). By choosing a proper frequency of CO₂ laser radiation it was possible to establish preferential conditions of reaction (7.18) for the molecules containing only ¹²C or also ¹³C atoms. As a result, the HFB molecules were enriched with the ¹²C or ¹³C isotopes respectively. At the 10.64 μ wavelength, for example, the resulting HFB molecules were enriched with the ¹³C isotope. With the initial pressure of HFCB 0.5 Torr and the He pressure 16 Torr, the isomerization yield of the HFCB molecules containing ¹³C was $\beta_{13} = 6.4 \cdot 10^{-4}$ and was 12.8 times higher than the isomerization yield β_{12} of the molecules containing *only* ¹²C.

As the HFCB molecules were irradiated at 10.3 μ, preferential isomerization of the molecules containing only ¹²C was observed and consequently the HFB molecules were enriched with the ¹²C isotope.

It is worthy of notice that the isotopically selective isomerization of HFCB took place only at a comparatively low pressure of these molecules (0.5 to 1.0 Torr) and with the addition of a buffer gas. In the absence of a buffer it was impossible to achieve isotopically selective isomerization.

7.3.2. Mechanisms of IR laser-induced isomerization

There are several potential mechanisms which may be responsible for molecular isomerization in a strong IR field (see Figure 7.13).

(1) Multiphoton excitation of the high-lying vibrational levels of a molecule with the result that the molecules acquire energy exceeding the isomerization barrier. If the stored energy is localized at the degree of freedom responsible for isomerization the structural form of the molecule is subjected to changes. This mechanism employs molecular excitation only within the ground electronic state.

(2) Excitation of the electronic state of the molecule due to vibrational energy transfer, i.e., the $V \rightarrow E$ process, with subsequent rearrangement of the molecule in the excited electronic state. In this case the isomerization mechanism is a usual one (see Ref. 66), the only difference consisting in a new way of electronic state excitation.

(3) Selective dissociation of the molecular isomeric form due to MP excitation. The mixture can be enriched with one of the isomers by dissociating the other one. In this case the molecular concentration of the unexcited isomer (for example, *cis*-C₂H₂Cl₂) may also increase due to recombination of the radicals formed by dissociation of *trans*-C₂H₂Cl₂ resulting in all possible isomeric forms. This mechanism causes one isomer to burn out and the others to accumulate.

(4) Thermal isomerization due to an increase of temperature in the region under irradiation after the absorbed energy is thermalized. Such a process is nonselective, and a strong IR field is necessary only to provide a high level of absorbed energy.

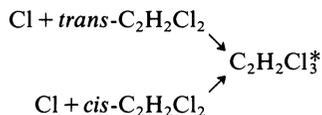
In all the above experiments on molecular isomerization by IR radiation-pulses the thermal mechanism has been eliminated. The most direct proof of the nonthermal nature of the mechanism is observation of the considerable enrichment of the mixture with one of the isomers to levels exceeding their equilibrium concentration. In the experiments with C₂H₂Cl₂, for example, the ratio between the initial and final ratios of *trans*- and *cis*-forms was 10. By varying the radiation frequency it was possible to reverse the ratio (from the initial one—0.18 to the final one—2).

Observation of isotopic selectivity in isomerization of HFCB molecules is also direct proof of the nonthermal mechanism of isomerization. The simple estimations of the temperature conditions after the pulse action in these experiments also reject thermal isomerization. In the experiments with C₂H₂Cl₂, for example, the temperature

in the zone under irradiation was no higher than 650 K. The thermal isomerization time at this temperature⁶⁶ is about 10^3 s, and the characteristic time of its cooling down was 10^{-4} to 10^{-5} s. This excludes the possibility of any essential contribution of the thermal mechanism of $C_2H_2Cl_2$ isomerization. This conclusion can be also applied to other molecules.

It is difficult to choose between the other selective mechanisms 1° to 3° . In the experiments with 1,5-hexadiene⁷⁰ the absence of appreciable dissociation enables us to turn down recombination-dissociation mechanism 3° . This also applies to the experiments with methyl-isocyanide⁶⁹ and hexafluorocyclobutene⁷¹⁻⁷² where, at least under some experimental conditions, only isomerization reaction took place. It is difficult, however, to make an unambiguous choice between possible mechanisms 1° and 2° without additional experiments which would define the nature of the molecular states excited by CO_2 laser radiation. It is particularly important to measure the average level of excitation of the molecules interacting with the radiation.

In the experiments⁶⁸ with dichlorethylene the threshold energy (or power) for the processes of dissociation, isomerization and luminescence was the same. This points to the fact that the contribution of mechanisms 2° and 3° may be essential. In case of $C_2H_2Cl_2$ one more rather specific isomerization channel is possible. If the dissociation of these molecules gives birth to atomic chlorine, which is quite probable since the C_2 and CH radicals are identified from the luminescence spectra,⁶⁸ the atoms of chlorine in this case can induce a chain reaction through the formation of vibrationally excited radicals $C_2H_2Cl_3^*$:⁷³



The $C_2H_2Cl_3^*$ radicals quickly dissociate to *trans*- or *cis*-dichlorethylene with detachment of the Cl atom which continues the chain. As the experiments show,⁷⁴ the length of this chain may be very significant (about 10^3). Thus, even at small amounts of resultant Cl the contribution of this process may be great.

Once again we want to stress the necessity of fast stabilization of molecules in one of the isomeric forms after they have acquired energy higher than the isomerization barrier in the process of MP excitation.

This has been vividly demonstrated by experiments on isomerization of HFCB.⁷² The isotopic selectivity of this process was observed only with adding a buffer gas. The collisions with the buffer gas enable the excited molecules to give away the energy excess and prevent V-V exchange with other molecules thus preserving laser excitation selectivity.

7.4. Role of collisional processes in IR multiple photon dissociation

The results of studying the excitation and dissociation of molecules by IR radiation discussed in the foregoing sections have been obtained on the assumption that the effect of collisions on the process of excitation may be neglected. In most cases this was achieved by choosing a rather low gas pressure so that the laser pulse duration could be shorter than the time between two successive gas-kinetic collisions $\tau_p < \tau_{\text{coll}}$. The stringency of this condition is discussed below. When this condition is not fulfilled collisions can affect the character of excitation of molecules in the IR field and their subsequent dissociation.

Studying the role of collisional processes is important from several standpoints. First, it allows obtaining additional important information on the mechanism of excitation and dissociation of an isolated molecule. Secondly, experiments of this kind are of special interest to us since they make it possible to study the relaxation processes in highly vibrationally excited molecules.

The experimental results below show how the collisions of molecules both between themselves and with buffer gases affect the dissociation yield. Information on secondary chemical processes following molecular dissociation and the effect they can produce on the measurement of MP dissociation parameters will also be discussed.

Questions concerning the effect of collisions on the selectivity of MP excitation and dissociation are considered in Chapter 8.

7.4.1. Collisions with a buffer gas

The collisions of the excited molecules with the buffer gas may give rise to several relaxation processes whose effect on MP excitation and dissociation of molecules is schematically shown in Figure 5.18. First, the rotational state of the molecule in the ground or excited vibrational

state can be changed. The effect of rotational relaxation at the initial stage of MP excitation was considered in detail in Section 5.3.1. We will just recall that this process cannot change substantially the molecular energy but it can involve new molecules into the process of MP excitation populating the resonant states devastated by the field. This, of course, brings about an increase in dissociation yield if a small fraction of molecules q takes place originally in MP excitation (see Figure 5.18). The characteristic pressures, at which the rotational relaxation caused by collisions with a small (few-atom) buffer gas begins to have an effect on the process of MP excitation, range approximately from 0.1 to 1 Torr at $\tau_p \approx 10^{-7}$ s.

Secondly, during collisions with the buffer gas the vibrational state of the molecule can be changed. As a result, the energy is transferred to other degrees of freedom (vibrational, rotational, translational) of the molecule itself or the buffer gas. Therefore, as opposed to rotational relaxation, the $V-V$ and $V-T/R$ processes decrease the vibrational energy of excited molecules and hence the dissociation yield. The influence of rotational and $V-T/R$ relaxation on the MP dissociation process is rather well seen from Figure 7.15, where the dependence of CF_3D dissociation yield on Ar pressure is presented. Initial growth of β with increasing Ar pressure is caused by new molecules involved in the process of MP excitation due to rotational relaxation.¹⁰³ Subsequent decrease in β is a result of CF_3D deexcitation due to $V-T/R$ relaxation. It must be said that the effect of molecular deexcitation takes place both during a laser pulse and after it. The latter should be always kept in mind since the fulfillment of the condition of collisionless MP excitation $\tau_p < \tau_{\text{coll}}$ does not guarantee the collisionless character of the entire process of MP dissociation.

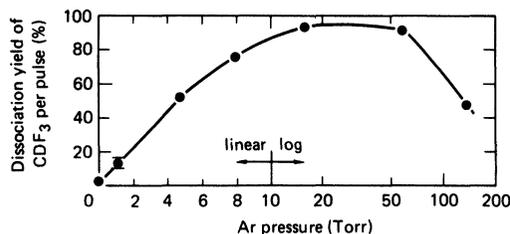


FIGURE 7.15 Dependence of the dissociation yield of CF_3D on Ar pressure. The pressure of CF_3D is $6.5 \cdot 10^{-2}$ Torr. $\Phi = 25 \text{ J/cm}^2$.¹⁰³

The real contribution of each of the relaxation processes listed† depends on many factor. It is determined by the parameters of the molecule under excitation, the conditions of its excitation, the type of buffer gas and its pressure.

The role of rotational relaxation was considered in Section 5.3, and so in this section we are going to dwell on the contribution of vibrational deexcitation caused by the $V-T$ process. In Section 2.5.6 it was noted that the typical value of $V-T$ relaxation rate $k_{V-T} \approx 10^3-10^5 \text{ s}^{-1} \text{ Torr}^{-1}$. This value of k_{V-T} , however, corresponds to small excitation levels of molecules when the relaxing system slightly deviates from equilibrium. At strong excitation of molecules, when they are in the quasi-continuum the $V-T$ process cannot be described only by the rate constant k_{V-T} because it also begins to depend on molecular energy.⁷⁵ In describing the relaxation of highly excited molecules it is more convenient to apply another parameter, that is, the average energy $\langle \Delta E \rangle$ transferred in one gas-kinetic collision. The value $\langle \Delta E \rangle$ depends on the type of colliding partners, and in case of highly excited molecules it usually varies between 150 and 1000 cm^{-1} .⁷⁶ As the number of atoms in a buffer gas molecule increases the $\langle \Delta E \rangle$ value tends to increase. For example, in case of deexcitation of cycloheptatriene with C_2F_6 molecules the $\langle \Delta E \rangle$ value comes to 1700 cm^{-1} .⁷⁶

Let us estimate now the pressure at which $V-T$ relaxation must affect the MP excitation of molecules in the quasi-continuum. It is obvious that this takes place when the rate of energy outflow caused by the $V-T$ process is comparable with the rate of its inflow dE/dt into the molecule by MP absorption, i.e., when

$$\frac{dE}{dt} \approx \langle \Delta E \rangle Z_0 p \quad (7.19)$$

where Z_0 is the frequency of gas-kinetic collisions, p is the buffer gas pressure. Usually $Z_0 \approx 107 \text{ s}^{-1} \text{ Torr}^{-1}$. For rough estimation we take $dE/dt = D/\tau_p$. From (7.19) it is easily obtained that for $D = (20-40) \cdot 10^4 \text{ cm}^{-1}$ and $\tau_p = (1-2) \cdot 10^{-7} \text{ s}$ the buffer gas pressure at which the vibrational deexcitation becomes essential ranges from ten to several hundreds of Torr. The experimental results agree with this estimate.

† Collisions may also disturb the coherence of MP excitation if it takes place. See Chapter 5.

For illustration, let us consider the effect of vibrational deexcitation on the process of MP excitation and dissociation of SF₆ that has been quite studied in detail. Figure 7.16 shows the dependence of the dissociation yield β of SF₆ on the pressure of some buffer gases. Ar and such molecular gases as O₂, C₂H₄ and NH₃ were used as buffers. It may be seen that in the pressure range under study for all gases there is an exponential decrease of β with increasing pressure. The rate of this decrease can be characterized, for example, by the value $P_{\text{buf}}(1/e)$, i.e., by the pressure at which β drops by e times. As seen from Figure 7.16, the value $P_{\text{buf}}(1/e)$ depends on the type of buffer gas. A stronger dependence on the pressure of NH₃ and C₂H₄, as compared to O₂ and Ar, is explained by resonant energy transfer in the first case brought about by the V-V process since the NH₃ and C₂H₄ molecules have vibrations close in frequency to the ν_3 vibration of the SF₆ molecule. A decrease in dissociation yield with the addition of a buffer gas was observed in all experiments of this kind. Even though at first there is an increase of β caused by the effect of rotational relaxation, the effect of vibrational deexcitation, starting from some pressure, becomes dominant (see Figure 7.15). As in SF₆, in most cases the decrease in β is exponential or almost exponential. The difference lies only in the value $P_{\text{buf}}(1/e)$. For example, SF₆ (Figure 7.16) in the presence of Ar $P_{\text{buf}}(1/e) \approx 12\text{--}15$ Torr, for CF₂HCl mixed with Ar $P_{\text{buf}}(1/e) \approx 200$ Torr⁷⁷ and for CF₃Br with N₂ $P_{\text{buf}}(1/e) \approx 400$ Torr.⁷⁸

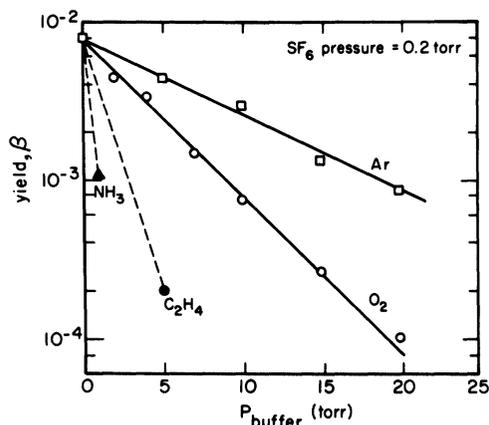


FIGURE 7.16 Dependence of the dissociation yield of SF₆ on the buffer gas pressure.¹⁹

Such a difference is evidently caused by different values of the $\langle \Delta E \rangle$ parameter as well as by different excitation rates of these molecules. The latter can be clearly seen in experiments with SF_6 mixed with Ar. The results presented in Figure 7.16 are obtained with $\Phi = 2.5 \text{ J/cm}^2$, i.e., with a small excess of dissociation limit. The increase of radiation energy fluence up to $\Phi = 5.1 \text{ J/cm}^2$ increases $P_{\text{buf}}(1/e)$ almost by 2.5 times, approximately up to 40 Torr.⁷⁹ Comparing the experimental dependence $\beta = \beta(p_{\text{buf}})$ with those calculated by the model it is possible to find a number of excitation parameters including the value of $\langle \Delta E \rangle$. In the case of CF_2CFCl mixed with Ar⁸⁰ such comparison gives $\langle \Delta E \rangle \approx 900 \text{ cm}^{-1}$ which is consistent with typical values of this parameter.

At a very high pressure of buffer gas, when the inequality $dE/dt \ll Z_0 \langle \Delta E \rangle p$ is fulfilled, high MP excitation of molecules becomes impossible. The absorbed energy is transferred “instantaneously” to the buffer gas, and in this case a purely two-level excitation scheme can be realized. This effect for SF_6 has been observed with $I \approx 10^7 \text{ W/cm}^2$ and helium pressure 20–40 atm.⁸¹

The collisions of the molecules with a buffer affect not only their MP excitation during a laser pulse. The deexcitation after the pulse is over may also be an essential factor. This process is especially important for large molecules characterized by a long time of unimolecular dissociation $\tau_{\text{diss}} \gg \tau_p$. So their deexcitation after the pulse is over is a decisive factor. To confirm this conclusion Figure 7.17 shows the dependence of the dissociation yield β for CF_3Br and $(\text{CF}_3)_3\text{CBr}$ on the I_2 pressure.⁸² These molecules have almost the same energies of breaking of the C—Br bond ($D \approx 25\,000 \text{ cm}^{-1}$). In the experiment with the CF_3Br molecule the average absorbed energy was

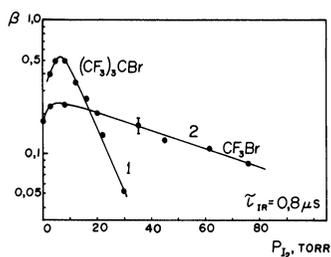


FIGURE 7.17 Dependence of the dissociation yield of $(\text{CF}_3)_3\text{CBr}$ (curve 1) and CF_3Br (curve 2) on I_2 pressure.⁸² $\tau_p = 8 \cdot 10^{-7} \text{ s}$. The initial increase in curves 1 and 2 is connected with recombination suppression.

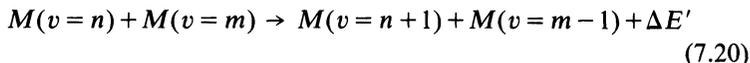
$\bar{\epsilon} \leq D$ and the dissociation basically occurred within a laser pulse. The situation differed for the $(\text{CF}_3)_3\text{CBr}$ molecule when considerable overexcitation took place. The molecules dissociated in a longer time. With $E_{\text{vib}} - D = 4 \cdot 10^4 \text{ cm}^{-1}$, for example, $\tau_{\text{diss}} = 10^{-4} \text{ s}$, and therefore the main contribution to deexcitation is given by collisions after MP excitation. Because of this the dependence of β on buffer gas pressure for these molecules is much steeper despite the MP excitation rate being almost twice as much for $(\text{CF}_3)_3\text{CBr}$. The value of $P_{\text{buf}}(1/e)$ in this case is almost an order less than that for CF_3Br .

The results of a great number of experiments show that the collisions between the excited molecules and the buffer gas can importantly affect the process of MP dissociation. There are two types of dependence of β on buffer gas pressure (Figure 5.18). When the radiation interacts with almost all the molecules and $q = 1$ (SF_6 , CF_3I) the role of rotational relaxation is modest, and the addition of the buffer gas only causes β to decrease due to vibrational deactivation. When $q \ll 1$, with addition of the buffer gas β increases at first due to rotational relaxation, and only then vibrational deactivation begins to manifest itself.

In conclusion it should be noted that, with a buffer gas added, there may be also a decrease in total heating of the gas after the absorbed energy is thermalized. This, in its turn, can have influence on the course of secondary chemical reactions (see Section 7.4.3).

7.4.2. Collisions between excited molecules

When the excited molecules collide with each other we can observe, of course, the same processes which take place as they collide with the buffer gas (rotational relaxation and vibrational energy deactivation). Furthermore, a resonant process of $V-V$ exchange can take place



This process, unlike the case of collisions with the buffer gas, does not bring about a decrease in the average vibrational energy of molecules since the defect of energy $\Delta E'$ is usually small. Exchange (7.20), however, can affect the process of molecular excitation, particularly at its initial stage, when the radiation intensity, for example, does not suffice to excite the molecules to the quasi-continuum. In this case the molecules can reach the quasi-continuum limit due to

energy exchange by scheme (7.20), and then they can be effectively excited by IR radiation. Such a process was applied⁸³ to explain experiments on dissociation of SiH₄ molecules by pulsed IR radiation. In the case of SiH₄ the dissociation threshold increased as the gas pressure was decreased. It was impossible to cause dissociation of SiH₄ under collisionless conditions with the radiation energy fluence up to $\Phi = 150 \text{ J/cm}^2$. As a result of *V-V* exchange at the first stage of excitation the dissociation yield of SiH₄ significantly depends on its pressure and increases as the latter rises. The same situation takes place in the dissociation of CH₃CN molecules²⁵ in the collisional regime.

For a lot of molecules the dissociation yield is independent of their own pressure. Thorough measurements for SF₆^{84,2} when the recombination was suppressed show that the dissociation yield does not depend on the pressure in the range from 0.06 to 3.75 Torr. The same results were obtained⁸⁵ for CH₃OH with the pressure increased up to 10 Torr. This can be explained if the fraction of molecules excited to the quasi-continuum $q \approx 1$ so that the *V-V* exchange with the cold ensemble is negligible.

But even when all the molecules are in the hot ensemble their relaxation from the nonstationary distribution to the Boltzmann one may change the number of molecules over the dissociation limit and, as a result, change the dissociation yield. This process becomes particularly significant after the laser pulse. As early as in the very first works on MP dissociation of SiF₄¹ and BCl₃² the collisional "phase" of dissociation was explained by collisions of highly excited molecules.

Another important consequence of resonant *V-V* exchange is the loss of selectivity of MP excitation and dissociation. *V-V* exchange leads to energy transfer from the excited molecules, for example with a particular isotope, to the nonexcited molecules with a different isotope. As a result, these molecules reach the quasi-continuum and then may be excited up to the dissociation limit by IR radiation. The influence of *V-V* exchange on the selectivity of MP dissociation will be discussed in detail in Chapter 8.

7.4.3. Secondary chemical reactions

The fragments of MP dissociation in most cases are atoms and radicals. These fragments are not chemically stable, therefore subsequent col-

lisions lead to the formation of the final stable molecules.† In some cases these stable molecules may be the initial substance. To suppress this recombination an additional reagent acting as a scavenger of the radicals formed by dissociation is usually introduced into the gas under irradiation.

In some cases recombination is a dominant process, for example in dissociation of BCl_3 ,⁸⁷ and the expenditure of the gas occurs only in the presence of a scavenger. In other cases the contribution of recombination is not so great, and the addition of a scavenger brings about only some increase of the measured dissociation yield. The role of recombination is determined by the ratio of rates of competing processes—recombination and reactions giving rise to products differing from the original substance. So, by adding a sufficient amount of scavenger it is always possible, in principle, to completely suppress recombination.

The role of secondary chemical processes has been studied in more detail in experiments on dissociation of SF_6 . The decrease of SF_6 in the cell under irradiation was observed both in the presence and the absence of scavenger. The latter made it possible to conclude⁸⁸ that the dissociation of SF_6 was irreversible. The subsequent experiments,⁸⁹ however, show that in the cell containing only SF_6 , after irradiation, the content of SF_6 will return with time. With a scavenger added into the cell, such chemical reduction does not occur. Analysis of the end products of dissociation of pure SF_6 shows⁸³ that they are SOF_2 , SOF_4 and SO_2F_2 oxifluorides. These compounds are formed by the reactions of SF_5 and SF_4 arising in dissociation of SF_6 with the water adsorbed on the cell walls. Thus, the measured dissociation yield of SF_6 may materially depend on the condition of the cell walls. It has been shown⁸⁰ that in irradiating pure SF_6 , with the cell walls thoroughly cleaned, there was no expenditure of SF_6 observed. Under the same conditions but with addition of H_2 as a scavenger the dissociation yield was $\beta = 0.15$. These experiments point to the fact that the fragments formed by dissociation of SF_6 are unstable and when there is no scavenger their full recombination to the original molecule is possible.

† The formation of ions was also observed in this type of secondary reactions of MP dissociation fragments (Section 7.8.6).

When a scavenger is added to the gas it should be taken into account that the scavenger can simultaneously act as neutral buffer gases and in a proper way affect both the process of molecular excitation and their subsequent dissociation. The introduction of a scavenger, in particular, can bring about partial deexcitation of excited molecules as illustrated by experiments with CF_3I .^{91,92} The dissociation of this molecule by CO_2 laser radiation is followed by detachment of the iodine atom.⁹¹ Subsequent reactions cause some part of radicals, around 40%,⁹¹ in the absence of scavenger to turn to original CF_3I as a result of recombination. The rest form the final product C_2F_6 . The addition of the O_2 as a scavenger increases the dissociation yield as is shown by curve 1 in Figure 7.18. But at the same time the addition of O_2 leads to deactivation of CF_3I which leads to the subsequent decrease of β . This is confirmed by the results of the experiment with the neutral buffer gas N_2 where a monotonous decrease of β can be observed at once (curve 2, Figure 7.18). The experiment with CF_3I allowed taking into account the contribution of deactivation and determining the primary value of β . These results show that in experiments with scavengers it is always possible to determine their influence on excitation and subsequent dissociation of molecules.

It is well known that the rate of many chemical reactions is greatly affected by the temperature of the medium. This, accordingly, must affect the character of secondary chemical processes. In the above-considered case of CF_3I , for example, the reduction in initial gas temperature caused displacement of the equilibrium towards recombination.⁹² The gas heating, after the laser pulse has passed, which is determined by the value of absorbed energy may result in thermal dissociation of some compounds. For example, it has been concluded³⁹

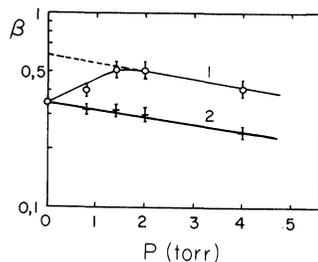


FIGURE 7.18 Dependence of the dissociation yield of CF_3I on the pressure of O_2 (curve 1) and N_2 (curve 2).⁹²

that in dissociation of CF_2Cl_2 a part of CF_2 radicals can be formed by thermal dissociation of CF_2Cl another primary fragment.

Studies into secondary chemical reactions and analysis of their end products with the addition of different scavengers enable in some cases drawing a conclusion on primary products of molecular dissociation. We can refer particularly to experiments with CH_3OH ,⁸⁵ C_2H_4 ,⁹⁴ SF_5Cl ,⁹⁵ etc. In Ref. 39 such studies made it possible to estimate the contribution of each of the two dissociation channels for the CF_2Cl_2 molecule—detachment of the chlorine atom or molecule.

It should be noted that the understanding of secondary chemical processes is important not only for estimating the true primary characteristics of MP dissociation. The study of these processes has another important aspect. With proper choice of scavengers and excitation conditions it is possible to control chemical processes and produce wanted end products. This is important for the practical application of the effect of MP dissociation and particularly for isotope separation and chemical synthesis.

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8. ISOTOPIC SELECTIVITY OF MULTIPLE PHOTON DISSOCIATION OF MOLECULES

This chapter is concerned with one of the most important and beautiful properties of multiple photon dissociation of molecules, that is, its selectivity. As applied to the process of MP dissociation, the concept of selectivity can be considered in two aspects. One can speak of the selective excitation of a specific vibrational mode (or modes) and the breaking of the bond corresponding to that mode. The realization of such a type of selectivity was discussed in the foregoing chapters as well as in Chapter 9. The data available shows that the prospective in this case is rather limited. The second type of selectivity is selective excitation and dissociation of a specified sort of molecules in their mixture including the mixture of different isotopes. In the latter case irradiation of isotopic mixtures of molecules produced the most striking results which open up wide possibilities for different applications of the process of MP dissociation. It is just this property of isotopic selectivity that is the subject of the present chapter.

The very first experiments^{1,2} demonstrated the possibility of molecular dissociation by IR radiation for a time shorter than the characteristic times of all known collisional processes. This raised the hope for providing the selectivity of MP dissociation. However at that time it was not evident at all that the excitation was "soft" enough to obtain selectivity under such collisionless conditions. It was not clear whether the difference of the frequencies of the vibrational transition under excitation, say, within the limits of several dozens of cm^{-1} , is sufficient for selective dissociation of specified molecules. The positive answer to this question was given by experiments with molecules containing different isotopes.

The isotopic selectivity of MP dissociation was first shown in experiments with the $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$ molecules.³ In this case the isotope shift in the frequency of the vibration being excited was 39 cm^{-1} . A great number of subsequent experiments with different molecules showed that the case of the BCl_3 molecule was not unique and that the selectivity of MP dissociation was its characteristic property and resulted from the very mechanism of vibrational excitation of molecules by laser radiation. In the experiments on separation of the uranium isotopes ^{235}U and ^{238}U ⁴ isotopic selectivity of dissociation was observed when the isotope shift in the excited state was just 0.7 cm^{-1} .

Laser isotope separation is one of the most important potential applications of the selective molecular MP dissociation. Therefore, the great majority of experiments dealing with the study of the kinetics of enrichment, the dependence of selectivity on the conditions of excitation, have been carried out with different isotopic molecules but the results obtained hold true for mixtures of any other species.

Multiple photon excitation and dissociation of a two-component mixture, for example a mixture of two isotopes, have a number of very essential specific features as compared to the case of a one-component medium. The study of the isotopic selectivity of MP dissociation has revealed the means of obtaining maximum selectivity of MP excitation and dissociation. These studies make it possible to gain some insight into the very process of multiphoton excitation of molecules including subsequent evolution of highly excited molecules. A brilliant example of this is the very discovery of the effect of isotopic selectivity of MP dissociation that was the final and convincing proof for the possibility of collisionless excitation and dissociation of molecules by IR radiation.

Many experiments on isotopic selectivity of MP molecular dissociation have thus been far performed. These experiments have covered many isotopes, from light ones (hydrogen, deuterium) to heavy ones (osmium, uranium) contained in very different molecules. Table 8.1 presents the basic results. It gives the isotopes and compounds used in the experiments as well as the values obtained for the parameters of selectivity.

The results of studies carried out for the isotopic selectivity of molecular MP dissociation are discussed below in more detail. Special consideration is given to the factors which determine the degree of selectivity of this process and to the possibilities of its increase. We are going to begin with defining the parameters describing the selectivity and their experimental measurement.

8.1. Characteristics of isotopically selective MP dissociation

8.1.1. Kinetics of enrichment of a two-component mixture

When a mixture of AB type molecules with different A isotopes is irradiated, there will be preferential dissociation of molecules of that isotopic composition of the absorption band to which the laser radi-

TABLE 8.1
Isotope separation by multiphoton dissociation of molecules

Isotope	Molecule under irradiation	Isotope shift in the resonant mode (cm ⁻¹)	Selectivity (α or K_{pr})	References
1	2	3	4	5
H, D	(CH ₃) ₂ O		4	31
	C ₆ F ₅ H		4.5	61
	HCOOH		24.7 ⁽¹⁾	48
	CH ₃ OH		60 ⁽¹⁾	
	CF ₃ CDCl ₂		1400	36
	CF ₂ HD		3500	21
H, T	CF ₃ D		11 000	21, 64
	CF ₃ T		10	65
¹⁰ B, ¹¹ B	BCl ₃	39	10 ⁽²⁾	3, 54
¹² C, ¹³ C			1.2, ..., 5	9, 16, 66, 34
	HCICCHBCl ₂			62
	CF ₂ Cl ₂	32	1.2, ..., 3.6	23, 67, 34, 50
	(CH ₃) ₂ O	8	1.8	37
	CCl ₄		1, ..., 7.3	18, 68 ⁽⁴⁾ , 42 ⁽⁵⁾ , 69
	CF ₃ I	26	2, ..., 50 ⁽³⁾	30, 8, 25, 31
	CF ₃ Cl		3.3, ..., 108 ⁽³⁾	31
	CF ₃ Br		3.2, ..., 120 ⁽³⁾	31, 52, 53
¹⁴ N, ¹⁵ N	CF ₃ COCF ₃		500	51
	CH ₃ NO ₂	0; 7	1.18; 1.65	6
¹⁶ O, ¹⁸ O	(CH ₃) ₂ O	12	1.6	37
^{28,29,30} Si	SiF ₄	8, 9 (29/28)	1.4 ⁽³⁾	34
^{32, ..., 36} S	SF ₆	17, 4 (32/34)	1, ..., 35	7, 27, 18, 14, 28 ⁽³⁾ , 44 ⁽⁶⁾ , 41 ⁽⁶⁾ , 70, 17, 58, 49, 34, 35
	SF ₅ C		2.3	57
	S ₂ F ₁₀	7 (32/34)	2.4	72
	SF ₃ NF ₂		4.17	73
	CCl ₄		1.15	18
	CF ₂ Cl ₂		1.85	23, 56
	SeF ₆	1.6 ^a	1.05, ..., 2.25	43 ⁽⁵⁾ , 74 ⁽⁴⁾
³⁵ Cl, ³⁷ Cl	MoF ₆	1 ^a	1, ..., 1.4	19
^{74, ..., 82} Se	OsO ₄	0.26 ^a	1, ..., 1.26	40, 38
^{92, ..., 100} Mo	UO ₂	0.7	1.2, ..., 1.9	4
^{184, ..., 192} Os	(hfacac) ₂ · THF			
²³⁵ U, ²³⁸ U	UF ₆		1.2	75 ⁽⁷⁾

^a) Isotopic shift per atomic mass.

(1) Dissociation by HF laser radiation. (2) Measurement in intermediate reaction products. (3) Cooling. (4) Dissociation by NH₃ laser radiation. (5) Two-frequency dissociation by NH₃ and CO₂ lasers. (6) Two-frequency dissociation by CO₂ laser. (7) Two-frequency dissociation by 16 μ laser.

ation frequency is tuned. For simplicity, we shall consider a two-component mixture containing iA and kA isotopes. Let the laser radiation perform preferential dissociation of iAB molecules. It is quite obvious that, as the gas is exposed to radiation, the relative concentration of iAB molecules in the volume will decrease and that of kAB will increase. Thus the residual gas is enriched with the kA isotope. The value of this enrichment increases with exposure time, and it may be quite high with a rather large expenditure of the gas under irradiation.

In the dissociation products, on the contrary, enrichment with the excited iA isotope takes place. The value of enrichment in this case depends on the degree of dissociation selectivity of iAB molecules relative to kAB and drops with irradiation because the kAB molecules dissociate, too, even though with a lower rate than iAB . Thus the value of enrichment of the dissociation products with the iA isotope at large dissociation of the gas exposed will be small.

We shall now, to obtain quantitative relations, consider the kinetics of enrichment in more detail. Let the dissociation yield per pulse in the volume under irradiation be β_i for iAB and β_k for kAB molecules. Since there is preferential dissociation of iAB , $\beta_i > \beta_k$. We can characterize the selectivity of MP dissociation by the parameter

$$\alpha = \frac{\beta_i}{\beta_k} \quad (8.1)$$

In other words, α is the ratio of probabilities of dissociation in one pulse for the two species iAB and kAB in the volume irradiated. Such a definition of selectivity is similar to that used in the conventional methods of isotope separation. In laser isotope separation α also serves as a measure of selectivity for the elementary reaction.

The concentrations of iAB and kAB molecules in the cell N_i and N_k respectively can be written as

$$N_i = N_i^0(1 - \beta_i\Gamma)^2 \quad N_k = N_k^0(1 - \beta_k\Gamma)^n \quad (8.2)$$

where N_i^0 , N_k^0 denote the initial concentrations, n is the number of radiation pulses, Γ is the ratio of the exposed gas volume to the total volume of the cell. Expressions (8.2) are valid when β_i and β_k are independent of gas pressure. This takes place when the dissociation of iAB and kAB molecules results from their purely radiative excitation, particularly at low gas pressures (in more detail see Section 8.5).

In the process of preferential dissociation of iAB molecules the residual gas is enriched with the kA isotope. The value of enrichment is characterized by the enrichment factor in residual gas K_{res}

$$K_{res}(k/i) = \frac{[{}^kAB]_n \cdot [{}^iAB]_0}{[{}^iAB]_n \cdot [{}^kAB]_0} \quad (8.3)$$

where the index 0 relates to the unirradiated mixture and n to the irradiated. Using (8.3) we can obtain

$$K_{res}(k/i) = \frac{(1 - \beta_k \Gamma)^n}{(1 - \beta_i \Gamma)^n} = \frac{(1 - \beta_i \Gamma / \alpha)^n}{(1 - \beta_i \Gamma)^n} \quad (8.4)$$

In the dissociation products enrichment with the iA isotope occurs and the enrichment factor in the dissociation products K_{pr} will be

$$K_{pr}(i/k) = \frac{[{}^iA]_{pr} \cdot [{}^kA]_0}{[{}^kA]_{pr} \cdot [{}^iA]_0} = \frac{\Delta[{}^iAB]}{\Delta[{}^kAB]} \cdot \frac{[{}^iAB]_0}{[{}^kAB]_0} = \frac{1 - (1 - \beta_i \Gamma)^n}{1 - (1 - \beta_k \Gamma)^n} \quad (8.5)$$

With the use of (8.4) and (8.5) we can get the dependence of the enrichment factor in the residual gas and in the dissociation products on the number of pulses as a portion of gas is irradiated in the cell (see Figure 8.1⁵). Accordingly one can see that in the residual gas the value of K_{res} increases with irradiation and, with sufficient exposure, it is possible to get any desired value of K_{res} . In the dissociation products the enrichment factor drops with irradiation. With a small

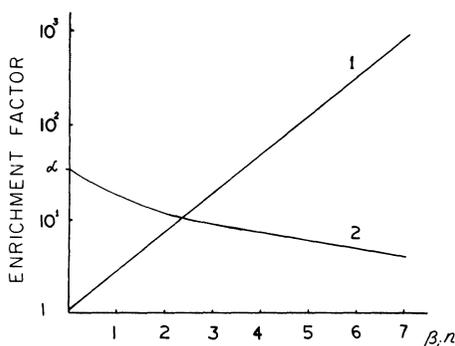


FIGURE 8.1 Dependence of the enrichment factor K on irradiation time (in units of β, n) in exciting the iA isotope. Curve 1 denotes the enrichment in the residual gas, curve 2 in the dissociation products.⁵

expenditure of gas in the cell, i.e., when $\beta_i \Gamma n < 1$, the value of K_{pr} reaches its maximum equal to the selectivity $K_{pr} = \beta_i / \beta_k = \alpha$.

8.1.2. Experimental methods for the measurement of selectivity parameters

K_{pr} and K_{res} are values directly measured in most experiments. By using the values obtained for K_{pr} and K_{res} one can find the value of α . The determination of α is analyzed comprehensively in.⁶

Figure 8.2 schematically shows the process of isotopically selective molecular dissociation and illustrates the available possibilities of the control of selectivity. In most of the experiments the measurements were taken by analyzing the final results of irradiation. In these cases, from (8.4) and (8.5), one needs to know the final content of the isotopes in the gas under irradiation and the dissociation products to evaluate K_{pr} and K_{res} . The simplest way to do this is by IR absorption spectroscopy. This method was first used⁷ for isotopically selective dissociation of SF_6 but it is not always convenient to apply particularly when the isotope concentrations differ greatly.

A more universal method to determine K_{pr} and K_{res} is measuring with the use of a mass spectrometer which provides a required measurement accuracy over a wide concentration range. It should be noted that, from (8.4) and (8.5), the simultaneous mass-spectroscopic measurement of K_{pr} and K_{res} allows measuring the values of β_i and β_k as well. This seems to be the only method at present that enables the value of β_i to be measured when the concentration of the i isotope $x_{0i} \ll 1$.

The K_{pr} and K_{res} values, however, are integral characteristics and depend on gas consumption (see Figure 8.1). The selectivity α is of great physical interest. Strictly speaking, it is the enrichment factor in products under single-shot irradiation. In practice it is not always possible to measure K_{pr} with $n = 1$, especially with $\Gamma \ll 1$, because of the limited sensitivity of the measuring equipment. However at a low gas consumption, as shown above, i.e., with $\beta \Gamma n \ll 1$, $K_{pr} = \alpha$. If the condition of a small consumption is not fulfilled, the value of α can be found, in principle, from relations (8.4) and (8.5).

The value of selectivity obtained in the primary dissociation products has been so far assumed not to decrease in subsequent chemical reactions to yield stable end products but this is not always so. In the

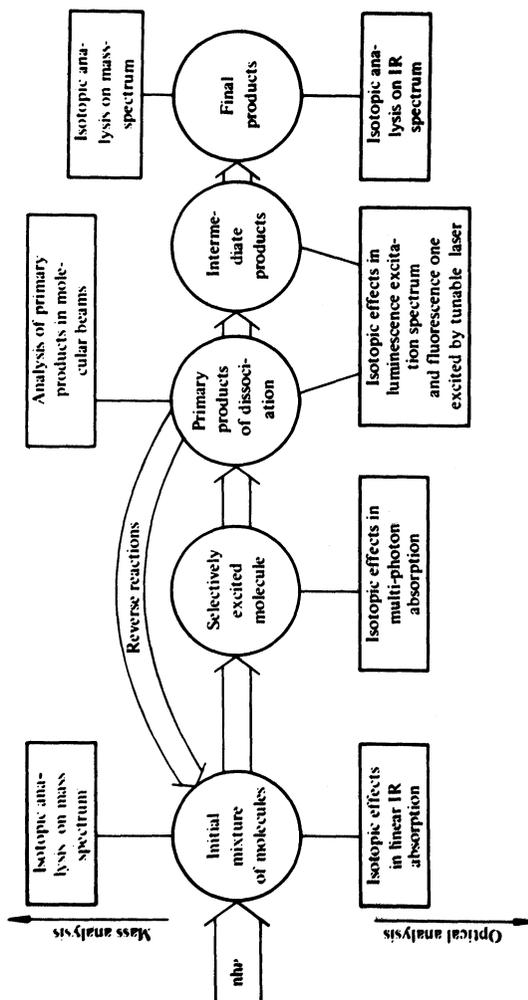


FIGURE 8.2 Scheme of isotope-selective MP molecular dissociation. Methods used to find the selectivity of the process at its different steps.⁶

experiments with BCl_3 ,⁹ it was found that the enrichment factor in the products depended on the types of scavengers used to bind the primary dissociation fragments. This point is discussed below in more detail. We want to note that in this case the actual primary selectivity can be determined in several ways (see Figure 8.2). First, molecular beams can be applied.^{10,11} In this case it is quite possible to measure enrichment immediately in primary dissociation products.

The second possibility of measuring the primary value of α is related to studying isotope effects in the spectrum of primary dissociation fragments or intermediate products of subsequent chemical reactions. We should emphasize here the possibility of analysis of the fluorescence spectra of radicals when they are excited with tunable dye lasers.^{12,13} Furthermore, it is possible to study isotope effects in the chemiluminescence spectra of products at the primary stages of chemical reactions. An example³ of the latter method was the determination of the selectivity of MP dissociation from analyzing the emission spectra of the electronically excited radicals $^{10}\text{BO}^*$ and $^{11}\text{BO}^*$ formed by the dissociation of BCl_3 in the presence of oxygen.

8.2. Resonant properties of selectivity

Studies of MP dissociation show that selectivity results, first of all, from the resonant character of multiple photon excitation. The resonant properties of dissociation, especially the spectra of MP excitation and dissociation of monoisotopic molecules, were considered in the previous chapters. In this section we are going to draw our attention to the results obtained from irradiating a two-component mixture consisting of molecules with different isotopes. Among other things we shall consider the dependence of selectivity on the exciting radiation frequency as well as the effects taking place in MP absorption.

8.2.1. Dependence of MP dissociation selectivity on IR laser frequency

Excitation of fundamental modes. The form of the spectral dependence of dissociation yield obtained for a particular molecule makes it possible to determine the maximum value of selectivity that can be reached in dissociation of molecules with a certain isotope. Indeed, if the dependence of β on the exciting radiation frequency Ω is known for each isotope, it is quite obvious that the ratio of these values at

any value of Ω must yield the greatest possible value of α . Thus, given the MP dissociation spectrum for each of the isotopes, one can determine the spectral dependence of selectivity on the radiation frequency. This conclusion has been supported in a number of experiments.

In the experiments with SF_6 ¹⁴ the enrichment factor of the ^{32}S and ^{34}S isotopes in the products K_{pr} was measured as a function of excitation frequency. The results are presented in Figure 8.3. In the same figure one can see the dependence of the dissociation yield β_{32} measured for $^{32}\text{SF}_6$ molecules. The curve for β_{34} was constructed by transferring the dependence for β by the value of isotope shift $\Delta\nu_{\text{is}}$ under the assumption that the form of the spectral dependence of dissociation yield for $^{32}\text{SF}_6$ and $^{34}\text{SF}_6$ is the same. It may be seen that the value of $K_{\text{pr}}(32/34)$ is maximum in the short-wave spectral range where $\beta_{32} > \beta_{34}$ and preferential dissociation of $^{32}\text{SF}_6$ takes place. With a decrease in Ω the value of $K_{\text{pr}}(32/34)$ is reduced and there is no selectivity ($K_{\text{pr}} = 1$) where the curves for β_{32} and β_{34} intersect. With further decrease in frequency, when β_{34} becomes higher than β_{32} , the products are enriched with the ^{34}S isotope.

The similar dependence of dissociation selectivity on laser radiation frequency was obtained¹⁶ in an experiment with BCl_3 with the natural abundance of boron isotopes $^{10}\text{B} : ^{11}\text{B} = 19 : 81$. The measurements were taken as the laser radiation was focused into a cell with BCl_3 (0.25 Torr)

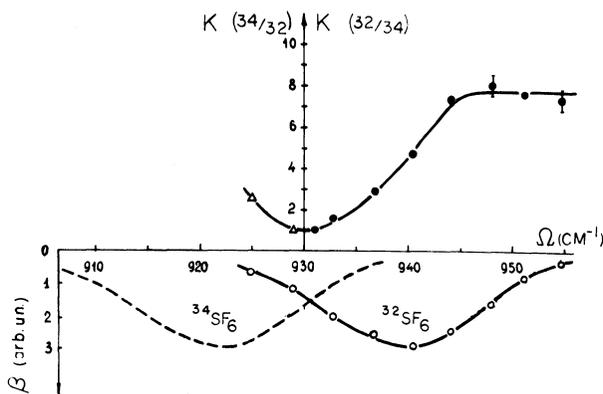


FIGURE 8.3 Spectral dependence of the enrichment factor in the dissociation products of SF_6 at a gas pressure of 0.2 Torr. Below are the spectral curves of dissociation yield for $^{32}\text{SF}_6$ and $^{34}\text{SF}_6$.¹⁴

and air (4 Torr). Oxygen was used to bind the dissociation products of BCl_3 . The results are given in Figure 8.4. It may be seen that the curve of dissociation yield for $^{11}\text{BCl}_3$ is displaced by 17 cm^{-1} from the maximum of its linear absorption. With the isotope shift in the frequency of excited vibration of $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$ $\Delta\nu_{\text{is}} = 39\text{ cm}^{-1}$ one might expect that β_{11} would be equal to β_{10} , i.e., there would be no selectivity at the frequency $\Omega = 956\text{ cm}^{-1}$. The experimental measurements supported this conclusion. Worthy of notice is the asymmetrical form of the dependence $\alpha = \alpha(\Omega)$ —the dissociation selectivity turns out to be higher when the lighter $^{10}\text{BCl}_3$ isotope is excited. This is related¹⁶ to the fact that during a laser pulse the molecules, nevertheless, had time to undergo collisions. As a result of $V-V$ exchange, a fraction of molecules of the unexcited isotope falls within the region with a high density of vibrational states (vibrational quasi-continuum). Now these molecules can absorb laser radiation and dissociate which leads to a decrease in selectivity. The spectral characteristics of the quasi-continuum have such a form that the absorption cross-section in the case of a heavier isotope ($^{11}\text{BCl}_3$) is larger than in the case of

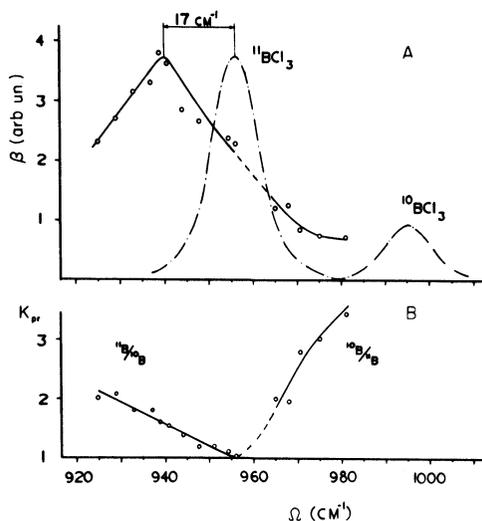


FIGURE 8.4 Dependence of the dissociation yield β (a) and the enrichment factor in products K_{pr} (b) on the laser radiation frequency in the dissociation of BCl_3 .¹⁶ BCl_3 pressure is 0.25 Torr, the pressure of the $\text{O}_2 + \text{N}_2$ is 4 Torr. The dashed line denotes the linear absorption spectrum.

a lighter one ($^{10}\text{BCl}_3$). This results in an asymmetrical form of the dependence $\alpha = \alpha(\Omega)$ (Figure 8.4).

It should be noted that the form of the spectral dependence of dissociation yield may be governed by the energy fluence of exciting radiation Φ . So the form of the spectral dependence of selectivity may be also governed by Φ . It is this circumstance that is related to the experimental fact observed in¹⁷ SF_6 . It was found that at the P(34) line of CO_2 laser with $\Phi > 6 \text{ J/cm}^2$ preferential dissociation of $^{34}\text{SF}_6$ and enrichment with the ^{34}S isotope in the products took place. With $\Phi < 6 \text{ J/cm}^2$, on the contrary, $^{32}\text{SF}_6$ mainly dissociated and the products were enriched with ^{32}S .

Excitation of combination bands. The possibility of selective dissociation during excitation of weak combination molecular vibrations essentially widens the area of application of MP dissociation.

In experiments¹ with SiF_4 to explain the dissociation under CO_2 laser radiation in the 10.6μ region it was suggested that its excitation was through combination vibrational transitions. Other experiments with different molecules confirmed such an assumption.

It was possible,¹⁸ for example, to observe dissociation of SF_6 as the CO_2 laser radiation was tuned to the combination bands $\nu_2 + \nu_6$ and $\nu_2 + \nu_3 - \nu_5$. In the second case the residual SF_6 was enriched with the ^{34}S isotope. It is believed¹⁸ that the value of selectivity during excitation of combination vibrations and overtones may be even higher than during excitation of the fundamental vibration. This can be explained by a smaller value of power broadening in the first case due to a smaller dipole moment of transition.

The isotopic selectivity of dissociation during excitation of combination modes was also demonstrated in experiments with CCl_4 .¹⁸ In these experiments the molecules were irradiated at different CO_2 laser frequencies within the absorption band $\nu_1 + \nu_2 + \nu_4$. Enrichment of the products with both the ^{13}C and ^{37}Cl isotopes could be observed.

The separation of molybdenum isotopes¹⁹ has been achieved with CO_2 laser irradiation of the combination band $\nu_3 + \nu_5$ of the MoF_6 molecule.

Thus, the process of MP molecular dissociation can be isotopically selective acting on weak combination vibrations. Even though during excitation of this vibrations the dissociation yield is smaller than in case of fundamental vibration such a method of excitation can be used in the selective dissociation of molecules. In particular, it can

be used when the excitation of the fundamental vibrations is impossible due to the absence of a proper laser. In this case one can apply the two-frequency method of dissociation with excitation at the first step of an appropriate combination mode.

8.2.2. Selectivity of multiple photon absorption

A characteristic feature of MP dissociation as opposed to other photo-physical processes based on the excitation in one step is that not all molecules having absorbed IR laser photons are able to dissociate. Only those molecules can dissociate which have acquired energy E being higher than the dissociation energy, i.e., $E > D$. Therefore, MP molecular dissociation is characterized by a strong dependence of the dissociation yield β on the average excitation level of molecules. Especially strong dependence is with $\beta \ll 1$ when a small fraction of molecules dissociates at the tail of the energy distribution. In the case of CF_3I , for example, when the energy absorbed per molecule varies between $\bar{\epsilon} = 3000 \text{ cm}^{-1}$ and $\bar{\epsilon} = 7600 \text{ cm}^{-1}$, the dissociation yield changes by more than two orders, i.e., from $\beta = 7 \cdot 10^{-4}$ to $\beta = 10^{-1}$.²⁰ So even when the values of β for each of the isotopes differ greatly, i.e., $\alpha \gg 1$, the difference in the average level of excitation of these molecules may be not so drastic at all. Hence, the parameter α serving as a measure of dissociation selectivity may badly reflect the difference in the excitation level of molecules with different isotopes.

Excitation selectivity. α_{ex} is a measure of the difference in multi-photon absorption of two isotopic molecules. This value can be introduced in a natural way as a ratio of average excitation levels for two species, i.e.,

$$\alpha_{\text{ex}}(i/k) = \frac{\bar{\epsilon}_i}{\bar{\epsilon}_k} \quad (8.6)$$

Since $\bar{\epsilon} = \sigma\Phi$, where σ is the MP excitation cross-section, it follows from (8.6) that

$$\alpha_{\text{ex}} = \frac{\sigma_i}{\sigma_k} \quad (8.7)$$

which agrees with the definition of excitation selectivity.²¹

The α_{ex} value, as well as the α value above, can be determined from the MP excitation spectra for each of the isotopes. In some cases this enables predicting the selectivity in dissociation. On the basis of such

measurements⁶ isotopic selectivity of MP dissociation of $\text{CH}_3^{15}\text{NO}_2$ molecules (see Section 8.2.3) was revealed in the absence of an isotope shift in the linear absorption spectrum, and the possibility of selective excitation²² of $^{238}\text{UF}_6$ molecules in their mixture with $^{235}\text{UF}_6$ by the CF_4 laser has been demonstrated.

It must be noted that both the value of α_{ex} and its dependence on the conditions of excitation (pressure, pulse duration, and so on) have not been so far extensively measured. We can point to the results obtained for different deuterium-containing molecules.²¹ According to the above, α_{ex} turns out to be smaller than α . As the CF_3CDCl_2 and CF_3CHCl_2 molecules were excited under the same experimental conditions, the excitation selectivity was found to be $\alpha_{\text{ex}} = 59$ while $\alpha > 10^3$. Much higher selectivity was reached during excitation of CF_3D . In the presence of CF_3H the value of α_{ex} obtained was 4900 with $\Phi = 1 \text{ J/cm}^2$ and the pulse duration $\tau_p = 2 \text{ ns}$. At smaller values of Φ the value of α_{ex} was higher. It should be noted that the difference between α_{ex} and α for this "small" (as compared to $\text{CF}_3\text{CCl}_2\text{D}$) molecule turned out to be much smaller.

In conclusion it must be said that high values of α_{ex} are essential in a number of applications of isotopically-selective MP dissociation. It is this parameter that in many respects determines the value of energy consumption. Indeed, if there is a mixture of two components "i" and "k" and the content of the excited component "i" is $x_0 \ll 1$, the fraction of total absorbed energy stored in the required component

$$\frac{\Delta E_i}{\Delta E_i + \Delta E_k} = \frac{\bar{\epsilon}_i x_0}{\bar{\epsilon}_i x_0 + (1 - x_0)\bar{\epsilon}_k} = \frac{1}{1 + (1 - x_0)/\alpha_{\text{ex}} x_0} \quad (8.8)$$

From (8.8) it follows that, only when $\alpha_{\text{ex}} = \bar{\epsilon}_i/\bar{\epsilon}_k > 1/x_0$, is the main portion of absorbed energy used for the excitation of the desired molecules.

8.2.3. Selectivity of MP excitation and dissociation for a small isotope shift

We have discussed thus far the results of experiments in which the isotopic selectivity of dissociation was observed in acting on vibrations (fundamental or combination) with an isotope shift in the linear absorption spectrum but isotopic selectivity can be also attained⁶ in the absence of an isotope shift.

Experiments have been carried out with CH_3NO_2 that has two vibrations ν_7 and ν_{13} in the region of the laser. The frequency shift in the ν_7 vibration of $\text{CH}_3^{15}\text{NO}_2$ and $\text{CH}_3^{14}\text{NO}_2$ molecules equals 7 cm^{-1} (see Figure 8.5a). In the linear absorption spectrum of the ν_{13} band there was no isotope shift observed.

However in acting on the ν_{13} vibration with intense radiation ($10^7, \dots, 10^9\text{ W/cm}^2$) the excitation spectrum of $\text{CH}_3^{15}\text{NO}_2$ and $\text{CH}_3^{14}\text{NO}_2$ was found to be deformed in different ways (Figure 8.5b). This difference is equivalent to the appearance of an isotope "shift" of about 5 cm^{-1} . The difference in the spectrum of multiple photon absorption brought about a corresponding difference in the spectral dependence of the dissociation yield of these molecules (Figure 8.5c). The curves from Figure 8.5c were obtained from measuring the luminescence intensity electronically excited dissociation fragments. The maximum difference in the luminescence signal in excitation of two isotopic modifications was $\beta_{15}/\beta_{14} = 2$. As noted above, the difference in the values of dissociation yield makes it possible to anticipate obtaining isotopic selectivity of dissociation in exciting the mixture of these molecules.

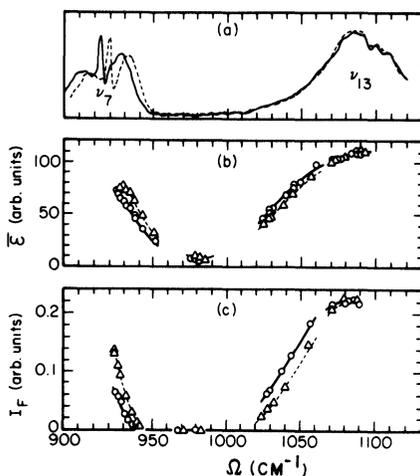


FIGURE 8.5 Isotopic effects for the ν_7 and ν_{13} modes of $\text{CH}_3^{14}\text{NO}_2$ and $\text{CH}_3^{15}\text{NO}_2$.⁶ (a) linear absorption spectrum; (b) MP absorption spectrum, $I = 5 \cdot 10^9\text{ W/cm}^2$; (c) spectral dependence of visible luminescence signal in dissociation of CH_3NO_2 , $I = 5 \cdot 10^9\text{ W/cm}^2$. The dashed line is $\text{CH}_3^{14}\text{NO}_2$, the solid curves are $\text{CH}_3^{15}\text{NO}_2$.

Direct experiments on nitrogen isotope separation were performed with the equimolecular mixture of $\text{CH}_3^{15}\text{NO}_2$ and $\text{CH}_3^{14}\text{NO}_2$ irradiated at a frequency of 1025.3 cm^{-1} . The total gas pressure was 0.5 Torr. The measurements show that under these conditions preferential dissociation of $\text{CH}_3^{15}\text{NO}_2$ takes place and the enrichment factor $K_{\text{pr}}(15/14)$ is equal to 1.18 ± 0.08 . The smaller value of K_{pr} , as compared to β_{15}/β_{14} , may be explained by a partial loss of selectivity from $V-V$ exchange and, probably, secondary chemical reactions. With irradiation at 938.7 cm^{-1} , as one might expect from the spectral curves of excitation and dissociation (Figure 8.5b and 8.5c), preferential dissociation of $\text{CH}_3^{14}\text{NO}_2$ was observed. The value of $K_{\text{pr}}(14/15)$ was found to be 1.65 ± 0.15 .

Similar results were obtained in experiments with CF_2Cl_2 ²³ and CF_3Br ,²⁴ where isotopic selectivity of dissociation was also found from excitation of vibrations in the linear spectrum of which the isotope shift did not appear. In case of CF_2Cl_2 the separation of the chlorine isotopes ^{35}Cl and ^{37}Cl was achieved with the selectivity $\alpha = 1.27$ ($\Delta\nu_{\text{is}}(^{35}\text{Cl}-^{37}\text{Cl}) < 0.2\text{ cm}^{-1}$), and in the experiments with CF_3Br it was possible to separate the bromine isotopes ^{79}Br and ^{81}Br with the selectivity $\alpha = 1.04$. In analyzing these results one should take into account the fact that all vibrations including those in which an isotope shift manifests itself take part in the formation of a transition spectrum in the vibrational quasi-continuum. So the spectral characteristics of the quasi-continuum for molecules with different isotopes may somewhat differ. Furthermore, the density of states for the molecule with a heavier isotope must be also somewhat higher. All this can result in slightly different conditions for exciting molecules with different isotopes. It should be noted that at each of the successive transitions this difference may be very small. Nevertheless, it can bring about an appreciable difference in the value of the dissociation yield of two isotopic molecules. This will be illustrated in the following simple example.

Let us consider MP excitation of molecules assuming for simplicity that the excitation cross-section remains constant throughout the sequence of transitions, i.e., $\sigma_{j,j+1} = \sigma_{01} = \text{const}$. In this case the probability of absorption of n quanta by a molecule is given (see Section 3.2.2) by the Poisson distribution $w(n) = (\bar{n})^n \exp(-\bar{n})/n!$, where \bar{n} is the average number of quanta absorbed by a molecular ensemble. In exciting two isotopes the difference in the average excitation level

of these components will depend on the ratio of the transition cross-sections

$$\alpha_{\text{ex}} = \frac{\bar{n}_i}{\bar{n}_k} = \frac{i\sigma_{01}}{k\sigma_{01}} \equiv \alpha_{01}$$

When the difference in cross-sections is small, the excitation selectivity is small, too, i.e., $(\alpha_{01} - 1) \ll 1$. But if the average molecular energy is much smaller than the dissociation energy, i.e., $\bar{n} \ll D/\hbar\Omega$, this small difference in excitation level will cause an appreciable difference in dissociation yield.

If a molecule must absorb n quanta to dissociate, the probability ratio of this process for different isotopes, i.e., the selectivity of MP dissociation, will be $\alpha = (\alpha_{01})^n \cdot \exp[(1 - \alpha_{01})\bar{n}]$. With $(\alpha_{01} - 1)\bar{n} \ll 1$ the selectivity will be $\alpha \approx \alpha_{01}^{n-\bar{n}}$. Thus, the effect can be increased considerably as compared to the simple ratio of absorption cross-sections.

It must be stressed that such accumulation or multiplication of selectivity may take place only with $\beta \ll 1$ when a small fraction of molecules dissociates at the far tail of energy distribution ($n \gg \bar{n}$) which is very sensitive to the position of the distribution function maximum. We have already considered, in fact, this effect in Section 8.22 where the concept of excitation selectivity was introduced. Such multiplication can be alternatively explained by the accumulation of selectivity in a sequence of transitions if they are far from being saturated as actually takes place for the far distribution tail. The experiments with the molecule $\text{UO}_2(\text{hfacac})_2 \cdot \text{THF}^4$ are one of the striking demonstrations for such an effect of selectivity multiplication. The isotope shift in the linear spectrum of the ν_3 vibration of these molecules for the isotopes ^{235}U and ^{238}U comes to $\Delta\nu_{\text{is}} = 0.7 \text{ cm}^{-1}$, the width of the spectrum being 8 cm^{-1} . This molecule has a large number of vibrations and so, when it is under MP excitation in the 10.6μ region, all the transitions including the first one lie in the quasi-continuum, with the cross-section of successive transitions⁴ being almost constant. In this case the selectivity value for molecules having absorbed n photons from the initial state with $\beta \ll 1$ actually comes to $\alpha = (\alpha_{01})^n$,⁴ where α_{01} is the ratio of linear absorption cross-sections for the two isotopes. The comprehensive calculations carried out⁴ within the frameworks of such an approach agree well with the experimentally measured values of α .

8.3. Ultimate spectral selectivity of MP dissociation. Gas temperature effect

Spectral selectivity. The results given in the foregoing section confirm the conclusion that the isotopic selectivity of MP dissociation is related to the resonant properties of MP excitation. The study of the resonant characteristics of molecular excitation and dissociation enable us to conclude that even in the absence of channels of subsequent selectivity loss it must have a finite value. This is due to the fact that each of the isotopic modifications of a molecule has a finite width of the spectral dependence of dissociation yield. The degree of overlapping of these spectral dependences determines the ultimate spectral selectivity of MP dissociation. Such a conclusion is supported, for example, by experiments at low gas pressures when the possibility of selectivity loss resulting from molecular collisions is removed. In this case the experiments (see Section 8.5) show that the selectivity α within a low-pressure range tends to a finite value α_0 . It is quite natural²⁵ to relate this value of α_0 to the ultimate spectral value of selectivity that can be attained with purely radiative excitation.

The present understanding of the process of MP dissociation is that the resonant characteristics comes about mainly during excitation through low-lying vibrational states. Hence, the spectral selectivity of MP dissociation, too, is formed basically at the initial stage of molecular excitation by laser radiation. Very big molecules having a large number of vibrational modes and a low quasi-continuum limit are apparently an exception to this rule. This leads to certain specificity of excitation and formation of selectivity in these molecules (see below).

There is a close relation between the resonance characteristics of MP dissociation and the selectivity of this process, i.e., the action on the spectrum of MP excitation and dissociation of molecules. When the spectrum deformation comes about so that at a fixed frequency the dissociation yield for two isotopes changes in different ways, it evidently causes the selectivity to change. One such mechanism is through variations in the temperature of the gas under irradiation.

Temperature effect. The studies into the spectra of MP molecular dissociation (see Chapter 7) have shown that the form of these curves depends in many respects on the initial state of the molecules being excited. It has been shown²⁶ for example, the large width of the spectral dependence of absorption in SF₆ measured at room temperature

$T = 293$ K is connected with the excitation of molecules from thermally populated low-lying vibrational states. In case of SF_6 with $T = 293$ K only $\approx 30\%$ molecules are in the ground state, and so the contribution of "hot" bands to the formation of the excitation and dissociation spectra is considerable. To narrow the spectral contour of dissociation yield and to increase its selectivity it was proposed²⁷ to use gas cooling, particularly when it flows through the nozzle. That was achieved in a number of subsequent experiments.

Let us consider the case of SF_6 . To enrich the dissociation products with the ^{33}S isotope it is of course necessary to selective dissociate $^{33}\text{SF}_6$. It follows¹⁴ that because of the large width of the spectral contour of dissociation yield and a rather small isotope shift in the frequency of the ν_3 vibration of $^{32}\text{SF}_6$, $^{33}\text{SF}_6$ and $^{34}\text{SF}_6$ it is impossible to gain high dissociation selectivity of $^{33}\text{SF}_6$ at room temperature. The maximum simultaneously expected values of $\alpha(33/32)$ and $\alpha(33/34)$ (from the intersection of the curves in Figure 8.3) come to about 2. Therefore, to obtain high values of separation factor, cooling²⁸ of SF_6 was used. Figure 8.6. shows the spectral dependence of the dissociation yield of $^{32}\text{SF}_6$ with $T = 173$ K. It might be seen that this curve differs significantly from the one measured at $T = 293$ K (see Figure 8.3). Specifically, the width of the contour and the amplitude of its long-wave wing have decreased.

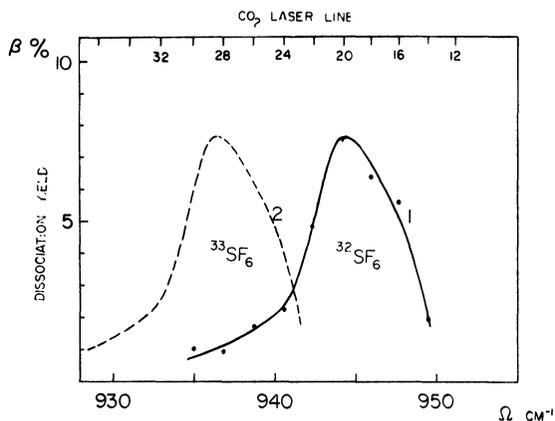


FIGURE 8.6 Spectral dependence of the dissociation yield of $^{32}\text{SF}_6$ (curve 1) at a gas temperature $T = 173$ K; $\Phi = 5.4$ J/cm². Dashed line (2) is the curve for $^{33}\text{SF}_6$.²⁸

The dashed line in Figure 8.6 also shows the dissociation contour for $^{33}\text{SF}_6$ produced by displacing the curve for $^{32}\text{SF}_6$ by 8 cm^{-1} which corresponds to the value of isotope shift. From the intersection of these curves the spectral dependence of $\alpha(33/32)$ was found (Figure 8.7). The experimental dependence of $K_{\text{pr}}(33/32)$ is shown in the same figure. The maximum value of the enrichment factor in the products was $K_{\text{pr}}(33/32) = 5$. The value of selectivity found from relation (8.4) turned out to be equal to $\alpha_{\text{max}}(33/32) = 7$ which was close to its expected value.

Thus, the experiments with SF_6 show that, as expected, gas cooling causes the spectral dependence of the dissociation yield to be narrowed which, in turn, increases the spectral selectivity of molecular dissociation.

In the above case of SF_6 the dissociation contour width (at half height) at room temperature was larger than the isotope shift between the adjacent isotopes, almost twice as large in the experiment (Figure 8.3). Thus it was quite natural that the narrowing of the dissociation contour in gas cooling resulted in a considerable increase in selectivity. A decrease in temperature, however, involves an essential increase of

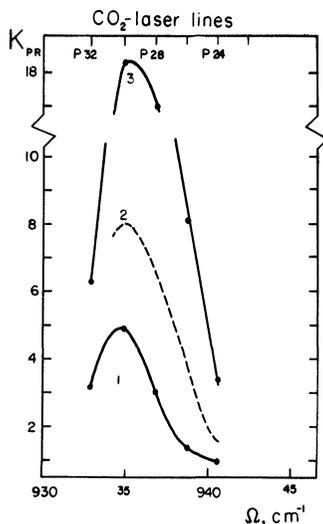


FIGURE 8.7 Enrichment factor K_{pr} in the dissociation products of SF_6 as a function of laser excitation frequency with $T = 173\text{ K}$.²⁸ (1) $K_{\text{pr}}(33/32)$; (2) calculated from the intersection of curves 1 and 2 in Figure 8.6; (3) $K_{\text{pr}}(33/34)$.

α even at large isotope shifts which exceed the dissociation contour width. CF_3I is an example. In this case the isotope shift for $^{12}\text{CF}_3\text{I}$ and $^{13}\text{CF}_3\text{I}$ in the mode⁸ under excitation is $\Delta\nu_{\text{is}} \approx 26 \text{ cm}^{-1}$ which is larger than the dissociation contour width²⁹ $\Delta\nu \approx 17 \text{ cm}^{-1}$. In the first work on CF_3I dissociation³⁰ it was found that in the dissociation of $^{12}\text{CF}_3\text{I}$ the value of $\alpha(12/13)$ increased with gas cooling. More detailed studies into the isotopic selectivity of CF_3I dissociation^{8,25} show that the same effect can be also observed in the dissociation of $^{13}\text{CF}_3\text{I}$. Figure 8.8 shows the dependence of $K_{\text{pr}}(13/12)$ on gas temperature (the content of ^{13}C $x_0 = 0.0108$). The measurements were taken with the CF_3I pressure $p = 1$ Torr when the value of K_{pr} was determined mainly by the spectral selectivity of excitation. It may be seen that the enrichment factor is highly dependent on temperature. As T varies between 370 K and 230 K, the value of $K_{\text{pr}}(13/12)$ increases by 8 times.

The measurements of the spectral dependence of $\alpha(13/12)$ at two different gas temperatures $+22^\circ\text{C}$ and -50°C show³¹ that also in other molecules (CF_3Br , CF_3Cl) the selectivity is higher with gas cooling.

The temperature dependence of selectivity may depend essentially on the conditions of excitation and on the laser radiation frequency in particular. In the above experiments with CF_3I ^{8,25} the $^{13}\text{CF}_3\text{I}$ was excited near the center of the corresponding vibration ν_1 . The strong temperature dependence of α given in Figure 8.8 is caused only by

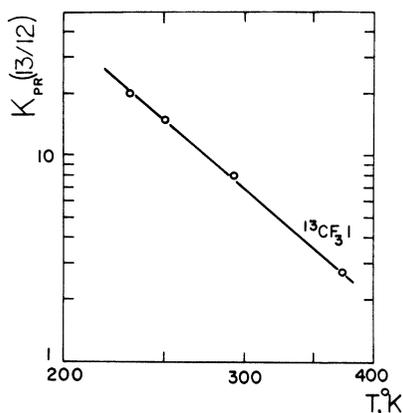


FIGURE 8.8 Enrichment factor in the dissociation products of $^{13}\text{CF}_3\text{I}$ $K_{\text{pr}}(13/12)$ as a function of gas temperature. The pressure of CF_3I is 1 Torr; the content of $^{13}\text{C} - x_0 = 1.08\%$. (On the basis of the data from Refs. 8 and 25.)

the change in the dissociation yield of nonresonant molecules $^{12}\text{CF}_3\text{I}$ while the dissociation yield for $^{13}\text{CF}_3\text{I}$ remains constant. At the same time, in the experiments with the hexafluoroacetone $\text{CF}_3^{12}\text{COCF}_3$ and $\text{CF}_3^{13}\text{COCF}_3$ ³² at decreasing temperature the dissociation yield for both isotopic species decreased. This decrease was slower for $\text{CF}_3^{13}\text{COCF}_3$ in resonance with the field which resulted in an increase in selectivity. As the detuning from the absorption band of the both molecules was increased (to the red side), the dependences $\beta = \beta(T)$ became almost equal which caused α to be independent of T .

The effect of the conditions of excitation on the character of the dependence of α on T is demonstrated more vividly by the experiments with CF_2Cl_2 .³³ Figure 8.9 shows the dependence of the $\alpha(12/13)$ selectivity on temperature with excitation at the lines $P(24)$ (the edge of the R branch of the ν_8 mode (923 cm^{-1}) of $^{12}\text{CF}_2\text{Cl}_2$) and $P(38)$ (around the center of the R branch). It may be seen that at a strong blue shift from the both isotopes ($P(24)$ line) there is even an increase in α as the temperature rises. At the $P(38)$ line α varies slightly with T .

The dependences of MP dissociation selectivity on temperature can be caused by different factors. As noted above, the formation of the

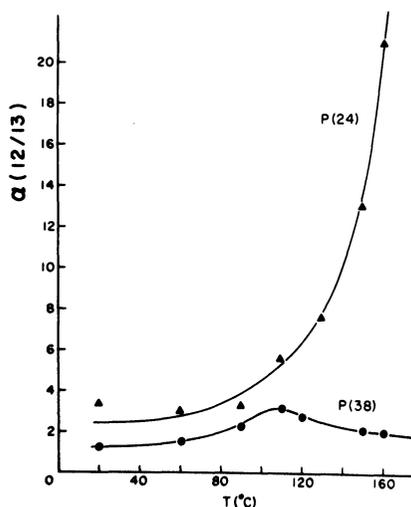


FIGURE 8.9 Dependence of the dissociation selectivity of CF_2Cl_2 $\alpha(12/13)$ on gas temperature at the $P(38)$ and $P(24)$ lines of the $10.6\ \mu$ band of the CO_2 laser.

MP excitation spectrum at lower transitions, and particularly during excitation of molecules with a large shift from the center of the band, is still not clearly understood. We can just present here some qualitative considerations.

Variations in temperature bring about the change in population of both rotational and low-lying vibrational levels. In the first case the variation of the rotational distribution can change the fraction of molecules interacting with the radiation and, as a result, affect the value of dissociation yield and hence selectivity. In the second case, as the vibrational distribution varies, the initial vibrational molecular energy changes. As a consequence, it is easier to excite the molecules to the quasi-continuum since the distance to its "limit" is reduced. It is obvious that this process can also affect selectivity. It is difficult to say which of these factors has a dominant role in the above experiments. It is not improbable that there are some other factors causing α to be dependent on temperature.

The picture is more clear in the excitation of big molecules. In this case the temperature dependence of selectivity is caused mainly by the temperature dependence of the energy gap between the molecular energy content and the dissociation energy limit. The large number of vibrational degrees of freedom in these molecules enables them even at room temperature to store vibrational energy that accounts for a considerable portion, about one half of the dissociation energy. This takes place, for example, in case of $\text{UO}_2(\text{hfacac})_2 \cdot \text{THF}$. Thus even a slight variation in temperature considerably changes the initial molecular energy which is equivalent to the change in position of the dissociation limit. For molecules of such a type $\alpha \approx (\alpha_{01})^n$ (see Section 8.2.3), where n is the number of quanta which must be absorbed for dissociation. It is evident that a decrease in temperature involves an increase in n and hence an increase in selectivity. A more detailed calculation within such a model⁴ with allowance made for the initial vibrational distribution of molecules and the final lifetime relative to dissociation agrees well with experiment.

Thus, the results presented show that gas temperature can essentially affect the selectivity of molecular dissociation. Under certain conditions variation in temperature may serve as an effective means to increase selectivity which is of great importance for a number of applications. In conclusion it should be noted that variation in temperature leads not only to a change of the ultimate spectral selectivity

of MP dissociation but it can also affect the character of the dependence of α on gas pressure. This point will be considered in more detail in Section 8.5.

8.4. Role of laser pulse intensity. Two-frequency MP dissociation

Intensity effects. Studies of MP dissociation show that the resonant characteristics of this process, particularly the form of the spectral dissociation contour, its width and position, depend on laser radiation intensity. This, of course, must cause the selectivity to depend on exciting radiation intensity since its spectral value is governed by the resonant properties of dissociation.

Moreover, several studies on the spectra of multiphoton excitation of molecules by intense IR radiation show that with increasing intensity they are broadened and the structure, if exists, diffuses. Therefore, irrespective of what factors are responsible for these changes—new multiphoton resonances, weak transitions, power broadening, etc.—one should expect that an increase in radiation intensity will bring about a decrease in selectivity.

There is a number of experiments in which the dependence of selectivity on radiation intensity has been studied. The first experiments³⁴ were the dissociation of SF₆ by focusing a laser pulse 1 ns long, with a peak radiation intensity of 10¹³ W/cm². There was no selectivity found. This would be expected since under the conditions of the experiment the power broadening γ_{01} was much larger than the value of isotope shift $\Delta\nu_{is}(32/34) = 17 \text{ cm}^{-1}$.

Of great interest are experiments under much "softer" excitation, at least when $\gamma_{01} < \Delta\nu_{is}$. Here attention must be drawn to the experiments with a different laser pulse shape.³⁵ In this work SF₆ was irradiated in two ways. In the first case the CO₂ laser pulse was smooth in shape and in the second case almost 100% modulation of radiation intensity was observed as a result of self mode locking. The energy in the both cases was constant and so the peak radiation intensity in the second case was higher. The CO₂ laser radiation frequency was tuned to the absorption band of ³²SF₆. The dissociation selectivity of ³²SF₆ with relation to ³³SF₆ was found to be higher by 18% in case of irradiating with a smooth pulse. The isotope shift in this case was $\Delta\nu_{is}(32/33) \approx 8 \text{ cm}^{-1}$. The difference in the enrichment factor relative to ³⁴SF₆, with $\Delta\nu_{is}$ twice as high, could not be observed.

So this experiment shows that an increase in intensity causes the dissociation selectivity to decrease, this effect increasing as the isotope shift is reduced. It is difficult, however, to carry out quantitative interpretation because the measurements were taken at high pressures of SF_6 when an important contribution to α was made by the interisotopic $V-V$ exchange and so purely field effects were considerably reduced.

Quantitative information on the character of the dependence of selectivity on radiation intensity were obtained³⁶ in experiments where a mixture of CF_3CHCl_2 and CF_3CDCl_2 was irradiated at a total pressure of 0.5 Torr with a CO_2 laser tuned to the absorption band of CF_3CDCl_2 whose concentration was 0.5%. Figure 8.10 shows the dependence of the enrichment factor in the products $K_{\text{pr}}(D/H)$ on energy fluence Φ (the pulse duration was 100 ns). It may be seen that the dependence is rather sharp. As Φ was changed by an order of magnitude from 10 J/cm^2 to 100 J/cm^2 , the value of $K_{\text{pr}}(D/H)$ decreased from 1400 to 27. In the same experiment the values of β_H and β_D were measured independently as pure CH_3CHCl_2 or CF_3CDCl_2 were irradiated. Their ratio β_D/β_H agrees well with the

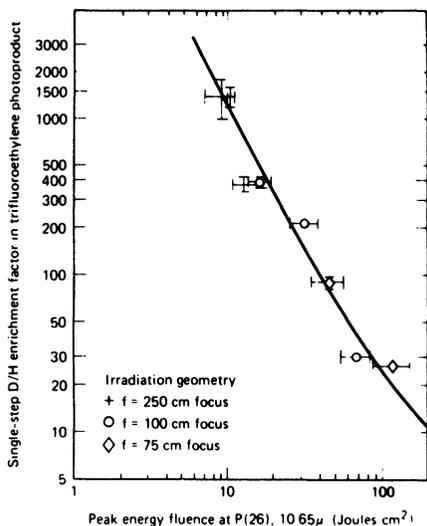


FIGURE 8.10 Enrichment factor in the products $K_{\text{pr}}(D/H)$ as a function of pulse energy fluence in the dissociation of CF_3CDCl_2 .³⁶ The pressure of CF_3CHCl_2 is 0.5 Torr, the content of CF_3CDCl_2 is 0.5%.

measured value of $K_{pr}(D/H)$. This supports the conclusion that the role of interisotopic $V-V$ exchange is small and the curve in Figure 8.10 denotes the dependence of K_{pr} on intensity in "pure" form, i.e. it reflects the character of the dependence of the spectral MP dissociation selectivity of CF_3CDCl_2 on radiation intensity. A decrease in dissociation selectivity has been also observed in experiments with the $(CH_3)_2O$.³⁷

The results of the studies carried out so far into the process of MP molecular dissociation enable us to conclude that the finite value of dissociation selectivity of molecules with a chosen isotope is related to the laser excitation of molecules of a different isotopic composition. An increase in radiation intensity in general causes the excitation of the nondesired isotope to be increased stronger as compared with the desired one and hence the dissociation selectivity is decreased. One of the factors responsible for this may be the power broadening of the transition spectrum. This is not the only cause, however, since in the experiments with CF_3I ^{8,30} appreciable excitation of molecules with a different isotope can be also observed with $\Delta\nu_{is} \gg \gamma_{01}$.

At present there is no reliable theoretical description of MP excitation and dissociation spectra for specific molecules, and so it is difficult to carry out quantitative interpretation of the observed dependences of dissociation selectivity on exciting radiation intensity. At the same time the results obtained point to one more way of increasing spectral selectivity, that is to decrease the laser radiation intensity. Naturally it is desirable not to lose dissociation yield. These two requirements can be met in two-frequency molecular dissociation.

Molecular dissociation in a two-frequency field. In such a method of molecular dissociation the radiation at one frequency performs preliminary isotopically selective excitation of the molecules. It is mainly here that there is spectral selectivity of the MP dissociation. Subsequent excitation and dissociation of the molecules come about as a result of energy absorption from the field at another, usually displaced, frequency. The total radiation energy being the same, the division of the radiation into two pulses with different frequencies can considerably increase the dissociation yield as compared to the case of one-frequency irradiation. At the same time, as the molecules are excited at the first stage, a decrease in radiation intensity causes the dissociation contour to get narrow. Furthermore, it may cause, as in the case of OsO_4 , quite a distinct structure. Such behavior of the excitation

and dissociation spectrum, the formation of a structure in it in particular, enables us to hope for a substantial increase in spectral dissociation selectivity, as compared to the one-frequency method, especially in separating isotopes of heavy elements when the isotope shift in the IR absorption spectrum is small.

This conclusion is confirmed by the experiments with OsO_4 ^{38,39} performed with the natural abundance of osmium isotopes. The dissociation selectivity of OsO_4 in a two-frequency field was studied with the same radiation intensity, 10^7 W/cm^2 , at both frequencies Ω_1 and Ω_2 . The delay between pulses was $\tau \approx 10^{-6} \text{ s}$. The dissociation of OsO_4 was performed at different frequencies of exciting radiation Ω_1 . The frequency of dissociating radiation Ω_2 was constant and corresponded to the $P(20)$ line of the 10.6μ band of CO_2 laser.

Table 8.2 contains the results of mass-spectroscopic analysis of the residual gas OsO_4 during its dissociation in a two-frequency field. The mixture under irradiation comprised 0.2 Torr OsO_4 + 2 Torr OCS. The total dissociation of OsO_4 throughout the irradiation time was $\approx 90\%$. It may be seen that maximum enrichment occurs when the Ω_1 frequency is tuned to the $P(6)$ line. When Ω_1 is tuned to the $P(20)$ line, preferential dissociation of $^{188}\text{OsO}_4$ was observed.

Table 8.2 also gives the results of isotope-selective dissociation of OsO_4 in a one-frequency field.⁴⁰ The total dissociation of OsO_4 in this case was almost the same, that is, 90%. The comparison of the results of irradiation in one- and two-frequency fields shows that in the second case the selectivity is higher. It should be noted that under two-frequency irradiation the OsO_4 molecules had the natural abundance of Os isotopes. Specifically, the concentration ratio of ^{192}Os and ^{187}Os was 41 : 1.64. Under one-frequency irradiation these isotopes had the same abundance, and the maximum enrichment came to $K_{\text{res}}(192/187) = 1.15$. The abundance of the isotopes in the mixture was natural and no enrichment was observed in the residual gas.

As in the ordinary method of excitation, in the case of two-frequency excitation the MP dissociation selectivity depends on radiation intensity and additionally on the intensity ratio between the first and second fields. This is confirmed by experiments with SF_6 .⁴¹ The SF_6 was excited by the first field at $\Omega_1 = 947.7 \text{ cm}^{-1}$ (the $P(16)$ line of CO_2 laser). The frequency of the second field was $\Omega_2 = 938.8 \text{ cm}^{-1}$ (the $P(28)$ line). The dependences of the enrichment factor in the products $K_{\text{pr}}(32/34)$ on the energy fluence Φ_1 of the first field with $\Phi_2 = \text{const}$

TABLE 8.2
 Enrichment factor in residual gas during one- and two-frequency dissociation of OsO_4 ³⁸⁻⁴⁰

Laser radiation line and frequency		Enrichment factor in residual gas $K_{\text{res}}(i/k)(\pm 0.2)$					
$\Omega_1(\text{cm}^{-1})$	$\Omega_2(\text{cm}^{-1})$	K(192/190)	K(192/189)	K(192/188)	K(192/187)	K(192/186)	
P(2) - 959.4	P(20) - 944.2	1.02	1.00	1.04	1.08	1.07	
P(6) - 956.2	P(20) - 944.2	1.11	1.13	1.24	1.48	1.60	
P(12) - 951.2	P(20) - 944.2	1.05	1.07	1.13	1.14	1.19	
P(20) - 944.2	P(20) - 944.2	1.02	1.02	1.08	1.00	1.01	
R(2) - 963.2	no				1.15		
P(2) - 959.4	no				0.93		

as well as on Φ_2 with $\Phi_1 = \text{const}$ are given respectively in Figure 8.11a and 8.11b. The initial decrease of K_{pr} (Figure 8.11a), as the first field was engaged, was related to interisotopic V-V exchange since the experiment was performed with $p = 0.2$ Torr and the delay between pulses $\varepsilon = 200$ ns when the contribution of this process was already appreciable. A subsequent increase in Φ_1 does not lead to any appreciable changes in selectivity.

The dependence $K_{\text{pr}} = \bar{K}_{\text{pr}}(\Phi_2)$ is quite different at fixed Φ_1 (Figure 8.11b). The dissociation selectivity here rises monotonically as the energy fluence of the second field increases. By the time the Ω_2 pulse arrives there are two groups of excited molecules: the more excited $^{32}\text{SF}_6$ molecules and the less excited $^{34}\text{SF}_6$ molecules. The results obtained show that with increasing Φ_2 the molecules of the first group absorb energy faster than those of the second group.

The application of the two-frequency dissociation technique essentially widens the scope of MP molecular dissociation. Two-frequency irradiation, for example, allows using rather low-power tunable lasers at the first step which will provide the wanted spectral selectivity of excitation. At the second step it is possible to use more powerful lasers which need not be tuned to the vibrational transitions of the molecule being excited.

This can be illustrated by the experiments on isotope separation of carbon and selenium in two-frequency dissociation of CCl_4 ⁴² and SeF_6 ⁴³ respectively. In these experiments selective excitation of molecules with the desired isotope was carried out with a pulsed NH_3 laser tuned to the frequency of one of the fundamental vibrations of CCl_4 or SeF_6 . At the second step a pulsed CO_2 laser was used. Its

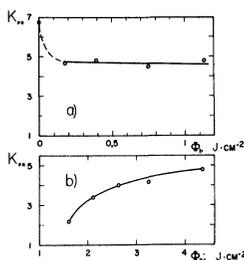


FIGURE 8.11 Enrichment factor $K_{\text{pr}}(32/34)$ of SF_6 as a function of laser energy fluence of the first pulse Φ_1 with $\Phi_2 = 4.4 \text{ J/cm}^2$ (a) and the second pulse Φ_2 with $\Phi_1 = 1 \text{ J/cm}^2$ (b).

radiation was out of resonance with the fundamental frequencies of vibrational transitions of these molecules.

As the experiments with SeF_6 show, the addition of CO_2 laser radiation provides a considerable increase in dissociation yield, by 2.5 times without a reduction in selectivity as compared to irradiation by only a NH_3 laser. This result complies with the concept of the separate functions of the two fields according to which it is the first resonant field that is responsible for the spectral selectivity of excitation.

When using the two-frequency method of dissociation one should remember an important factor. As it has been noted and the direct experiments on two-frequency dissociation of SF_6 show,⁴⁴ the dissociation selectivity materially depends on the delay time between pulses τ . With increasing τ the value of $\alpha(32/34)$ in experiments with SF_6 decreased fast which the authors⁴⁴ attributed to the excitation of $^{34}\text{SF}_6$ between pulses as a result of the process of $V-V$ exchange. Therefore, it is necessary to choose properly the delay time between the two fields in order to eliminate a considerable decrease of the selectivity attained at the first step of radiative excitation.

In conclusion we will mention another version of the two-frequency method of molecular dissociation. It includes the use of UV lasers at the second step as a source of dissociating radiation, with the preliminary multiple photon excitation at the first step by IR radiation. Experiments of this kind were performed with CF_3I .^{45†} The isotope-selective excitation at the first step was performed with CO_2 laser radiation. The excited molecules were dissociated with XeF laser radiation at the 350 nm wavelength. The value of selectivity obtained in these experiments $\alpha(12/13) = 48$ exceeds the values resulting from one-frequency MP dissociation of CF_3I by IR radiation at the same temperature and gas pressure. This points to great potential for the method of double IR-UV molecular photodissociation.

8.5. Effects of collisions on the selectivity of MP dissociation

In discussing the effect of isotopic selectivity of MP dissociation we have so far neglected the effect of collisions. In most cases this is

† These experiments are further development of the method of double IR-UV dissociation discussed in Refs. 46 and 47.

possible in experiments at sufficiently low gas pressures. But very often, particularly in different applications it becomes necessary to excite molecules at gas pressures as high as possible. The study of collisional processes for highly excited molecules is also of independent interest. A large number of research thus deal with the effect of collisions on isotopic selectivity.

An increase in gas pressure leads to a rather great number of collisions taking place during MP dissociation, i.e., in the time in which the basic fraction of dissociating molecules decays.† As a result of these collisions, the vibrational and rotational states of colliding partners change. In the previous chapters it has been shown that the processes of $V-V$, $V-T$ and rotational relaxation may have a pronounced and, under certain conditions, a very significant effect on the process of MP dissociation and the observed dissociation yield. In the case of an excitation of a two-component medium the effect of collisions on selectivity is reduced to the different action of multicomponent collisional processes on MP dissociation. There are very many possibilities of these effects, however.

The existence of several types of relaxation processes, the difference in rates of these processes (see Section 2.5) cause the effect of collisions on selectivity to be highly dependent not only of the conditions of excitation but also of the properties of the molecule being excited and the type of collision partner. All this makes the observed effects varied.

This section presents the essential results obtained in studying the influence of collisions on MP dissociation selectivity. While describing these results we tried to systematize them from the standpoint of the contribution of different relaxation processes so far as the available data allowed. It should be noted, however, that the role of each has not been studied nearly in equal measure. If the action of interisotopic $V-V$ exchange, at least during a radiation pulse, is understood quite sufficiently, this cannot be said about $V-T$ and rotational relaxations.

We are going to begin by describing the results of studies into the effect of the parent gas pressure on selectivity.

8.5.1. Dependence of selectivity on parent gas pressure and relative isotope content

As can be seen from the discussion below, the effect of the pressure of the gas under irradiation on MP dissociation selectivity may

† This time may apparently exceed the exciting pulse duration.

materially depend on the relative concentration x_0 of the isotopic component being excited. Therefore, we shall consider separately the cases of exciting components with high ($(1 - x_0) \ll 1$) and low ($x_0 \ll 1$) contents.

Excitation of a "rich" component ($(1 - x_0) \ll 1$)

The dependence of the MP dissociation selectivity on parent gas pressure in this case has been studied in many experiments for different molecules and isotopes. The characteristic feature of the dependences produced is decreasing selectivity as the gas pressure increases starting, at least, with a certain characteristic pressure. A monotonic decrease in dissociation selectivity with an increase in parent gas pressure has been observed in experiments with SF_6 ,^{14,17} BCl_3 ,^{9,34} CF_2Cl_2 ,³⁴ HCOOH ,⁴⁸ and CF_3I .^{8,30}

Figure 8.12 shows the dependence of $K_{\text{pr}}(32/34)$ attained in the dissociation of $^{32}\text{SF}_6$.¹⁴ As the pressure of SF_6 increases, K_{pr} drops exponentially. The characteristic pressure ρ_0 at which K_{pr} is reduced by e times comes to 0.55 Torr.

In most cases such a decrease in selectivity with increasing gas pressure is attributed to the process of $V-V$ exchange, as a result of which transfer of vibrational energy to unexcited nonresonant isotopic molecules takes place during collisions. This causes the dissociation of these molecules to increase due to two factors. First, the molecules with the undesired isotope excited in $V-V$ exchange are able to dissociate *during a laser pulse*. In more detail this case is considered in Section 8.5.2 where the quantitative relations connecting the α value with the $V-V$ exchange rate constant, gas pressure and laser pulse duration are also presented.

Secondly, the excitation of these molecules by $V-V$ exchange *after a laser pulse* can make a considerable contribution to increasing the

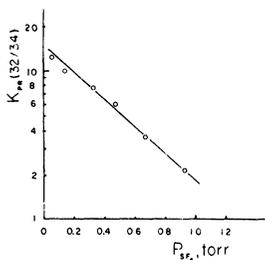


FIGURE 8.12 Enrichment factor $K_{\text{pr}}(32/34)$ as a function of the pressure of SF_6 .¹⁴

undesired isotope dissociation yield. In both cases $V-V$ exchange causes the dissociation selectivity to decrease with increasing pressure.

There is one more factor, in principle, that makes α depend on parent gas pressure. It is the decrease in dissociation yield β of the desired isotope as the pressure rises and, for example, may take place when a considerable contribution to β is made by the dissociation of molecules in long-lived states above the dissociation limit. The energy exchange between the unexcited molecules and the ensemble of highly excited molecules causes the latter to de-excite and both β and α to decrease.

The decrease of β for the desired isotope was pointed to as one of the factors responsible for the decrease of selectivity with increasing pressure.^{14,35} But it should be noted that the $V-V$ exchange with the molecules of the "cold" ensemble brings about the de-excitation and decrease of the dissociation yield for the molecules with the undesired isotope, too. So the sign of selectivity variation depends on the ratio of the contributions of this process to the dissociation yield for two isotopes. Probably, situations are not impossible when such a process may result in an increase in selectivity.

The value of enrichment factor in residual gas, as shown in many experiments,^{9,27,34,49} is also reduced as the gas pressure increases. Such behaviour of K_{res} results from the dependence of this value both on the selectivity α and the dissociation yield β of the molecules with the isotope under excitation (see (8.4)). An increase in pressure involves a decrease in α and, besides, can cause β to decrease, as it has been just noted. It is these two factors that cause the enrichment factor K_{res} to decrease as the gas pressure increases.

Excitation of a "poor" component ($x_0 \ll 1$) In this case the excited molecules with the poor isotope are surrounded by molecules with the rich isotope and actually only collide with them. This may bring about quite definite differences in the dissociation conditions of both components, as compared to the case of the excitation of the rich isotope and, as a result, there is a difference in the behavior of the dependence of α on ρ . The experiments confirm this conclusion.

Figure 8.13a shows the dependence of the enrichment factor K_{pr} in the products on the total gas pressure ρ of CF_3I when $^{13}CF_3I$ with the natural abundance of the ^{13}C isotope $x_0 = 0.0108$ is excited at two temperatures. For comparison, Figure 8.13b presents analogous depen-

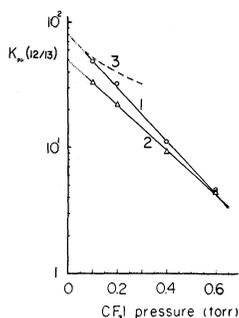


FIGURE 8.13a Enrichment factor in the dissociation products of $^{12}\text{CF}_3\text{I}$ $K_{\text{pr}}(12/13)$ as a function of the total pressure of CF_3I .²⁵ Curves: (1) $T = -45^\circ\text{C}$; (2) $T = +20^\circ\text{C}$; (3) calculations (see Section 8.5.2).

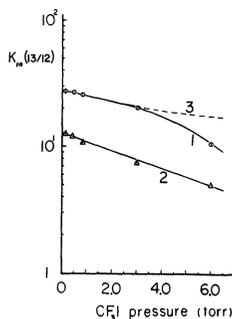


FIGURE 8.13b Enrichment factor in the dissociation products of $^{13}\text{CF}_3\text{I}$ $K_{\text{pr}}(13/12)$ as a function of the total pressure of CF_3I .²⁵ Curves: (1) $T = -45^\circ\text{C}$; (2) $T = +20^\circ\text{C}$; (3) calculations.

dences for the case of excitation of $^{12}\text{CF}_3\text{I}$ under the same experimental conditions. In both cases the value of K_{pr} is decreased as the pressure rises. This decrease can be described, as in the case of SF_6 (see Figure 8.12), by an expression like $K_{\text{pr}} = K_{\text{pr}}^0 \exp(-\rho/\rho_0)$. The values of K_{pr}^0 and ρ_0 are given in Table 8.3. One can clearly see that the dependence of K_{pr} on ρ in the case of $^{13}\text{CF}_3\text{I}$ is much slower. In this case ρ_0 is 53 times higher (the gas temperature $T = -45^\circ\text{C}$) than that of $^{12}\text{CF}_3\text{I}$, and so the value of K_{pr} remains high even at comparatively high gas pressures. ($K_{\text{pr}} = 20$ with $p = 3$ Torr).

A slower dependence of selectivity on gas pressure in exciting molecules with the poor isotope was observed also in the experiments

with the natural mixture of $^{13}\text{CF}_2\text{Cl}_2$ and $^{12}\text{CF}_2\text{Cl}_2$.⁵⁰ High selectivity at high gas pressures was also obtained in the experiments with CF_3CHCl_2 .³⁶ As the deuterated molecule CF_3CDCl_2 ($x_0 = 0.005$) was excited by CO_2 laser pulses 100 ns long, the enrichment factor in the products was $K_{\text{pr}} = 4$ with $p = 25$ Torr.

Such behavior of the dependence of selectivity on pressure at different concentrations of the isotope being excited that seems to be unexpected at first sight has rather a simple physical explanation. As mentioned above, a decrease in selectivity with increasing pressure comes about due to increasing rate of $V-V$ exchange. The probability of the molecule with the undesired isotope acquiring necessary excitation in such a process and dissociating is proportional to the number of collisions with the excited molecules containing the desired isotope and hence to their partial pressures. Thus, dissociation selectivity must be determined by the *partial* pressure of the molecules with the isotope under excitation.⁸ As a result, when the concentration of resonant isotope varies, it leads to changes in the rate of pressure dependence of selectivity. The conditions under which this conclusion is valid (in the case $x_0 \ll 1$) will be considered in Section 8.5.2.

In the case considered above the decrease in selectivity with an increase in the total gas pressure was slow but quite definite. However, there may be an increase in selectivity as the pressure increases. Such an increase in α was observed in the experiments on hexafluoroacetone.⁵¹ Figure 8.14 shows the dependence of dissociation selectivity in exciting $\text{CF}_3^{13}\text{COCF}_3$ with the natural abundance of ^{13}C . As the total gas pressure increases up to 10 Torr, the selectivity is increased by about 5 times. An increase in selectivity with increasing gas pressure was also observed in experiments with CF_3Br .^{52,53} In this case, too, α increased as the component with a low content of ^{13}C , $^{13}\text{CF}_3\text{Br}$, was excited.

An important specific feature that unites these experiments and differentiates them from those considered where α decreases with increasing p is a large detuning from the center of the MP excitation band of the desired isotope. The dependence of α on p shown in Figure 8.14, for example, is obtained with the detuning (to the red side) from the center of the band of $\text{CF}_3^{13}\text{COCF}_3$ being 31 cm^{-1} , its total width $\leq 7\text{ cm}^{-1}$.⁵¹ The detuning from the band of $\text{CF}_3^{12}\text{COCF}_3$ in this case comes to 47 cm^{-1} . The excitation at the far end of the MP absorption band is apparently one of the critical conditions for

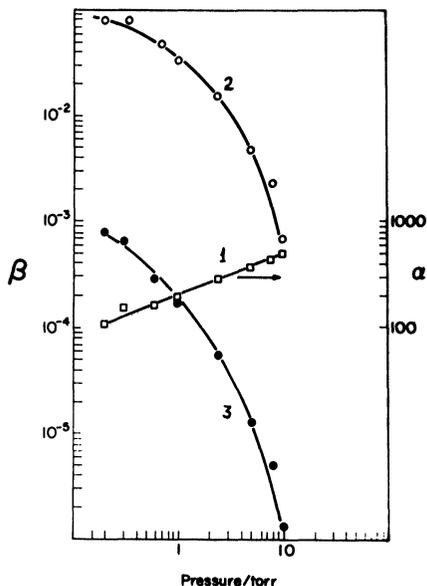


FIGURE 8.14 Isotopically selective MP dissociation of hexafluoroacetone.⁵¹ Excitation of $\text{CF}_3^{13}\text{COCF}_3$. Curve 1 is the selectivity of MP dissociation. Curves 2 and 3 denote the dissociation yields of $\text{CF}_3^{13}\text{COCF}_3$ and $\text{CF}_3^{12}\text{COCF}_3$ respectively.

observing an increase in α . This is confirmed by experiments with $\text{CF}_3\text{Br}^{53}$ (see also Section 8.5.3, Figure 8.16), where is illustrated that the dependence of α on ρ varies with the laser radiation frequency. With excitation at the center of the band the selectivity decreases with increasing gas pressure.

The results will be discussed in more detail below, at the end of Sections 8.5.2 and 8.5.3.

8.5.2. Role of V-V exchange

The results of experiments at different pressures of the gas being irradiated show that the V-V exchange bringing about vibrational excitation and dissociation of molecules with the undesired isotope may have a pronounced effect on the selectivity of MP dissociation. As a result, the measured values of selectivity become, as a rule, smaller than their spectral value.

The process of $V-V$ exchange during MP molecular dissociation may be divided into two stages: exchange during an exciting pulse and after the pulse is over. This division is natural and clearly during the laser pulse there is a source of molecular excitation (the laser) which can compensate for the energy flow from the resonant component caused by a $V-V$ process. This is especially essential in exciting the lesser component. For lack of sufficient data the criterion—at which of the stages the $V-V$ exchange gives the greatest contribution to the decrease of selectivity—has not been formulated exactly yet. Therefore we will restrict ourselves to a general note. It is quite evident that, when a great part of dissociating molecules decays during an exciting pulse, the first stage of $V-V$ exchange is the main cause of any selectivity variation.

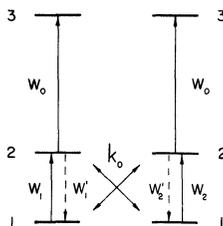
The results are given below of studies into the effect of $V-V$ exchange on the isotopic selectivity of MP dissociation. First we shall consider comprehensively the first stage, that is, the $V-V$ exchange during a laser pulse, and then touch upon its contribution after the laser pulse is over.

Model of $V-V$ exchange during a laser pulse

First we are going to consider the model of $V-V$ exchange developed in Ref. 25 to explain experiments on isotopically selective dissociation of CF_3I molecules. The results obtained, however, are general in character and allow quantitative analysis of the role of $V-V$ exchange during excitation and dissociation of molecules in a strong IR field.

In this model it is assumed that a decrease in spectral selectivity results from the vibrational excitation exchange in collisions of molecules with different isotopes during a laser pulse. As a result of this process, the molecules with the undesired isotope whose vibrational transition frequency is out of resonance with the radiation can acquire sufficient energy for their subsequent excitation and dissociation by laser radiation.

In a real situation the colliding molecules may be in different energy states, and the exchange rate may depend on the excitation level of these molecules. In the model in use the processes of exchange and laser excitation are considered in a simplified manner. The molecules excited to the vibrational quasi-continuum are regarded as one ensemble in state 2 (Figure 8.15). The interaction of these excited molecules with those at lower levels (state 1 in Figure 8.15) is described


 FIGURE 8.15 Model of MP dissociation selectivity loss by V-V exchange.²⁵

by one phenomenological rate constant of V-V exchange k_{vv} . The laser excitation from state 1 to state 2 of molecules with different isotopes occurs at the rates w_1 and w_2 . The rate of excitation to the energy region where molecular dissociation takes place (state 3 in Figure 8.15) will be w_0 . The value of w_0 is considered to be equal for both types of molecules.

Such a model corresponds to the division of the process of molecular excitation into two steps. In the first step the excitation that can be isotopically selective takes place at several lower vibrational levels. In the second step excitation occurs in the vibrational quasi-continuum. The cross-sections of this process in most cases can be considered equal for the both isotopes due to the large spectral width of the quasi-continuum.

The equations describing the model concerned have the form

$$\frac{dm_1}{dt} = -w_1 m_1 + w_1' m_2 - k_{vv} M_2 m_1 + k_{vv} m_2 M_1 \quad (8.9)$$

$$\frac{dm_2}{dt} = -w_0 m_2 + w_1 m_1 - w_1' m_2 - k_{vv} M_1 m_2 + k_{vv} m_1 M_2 \quad (8.10)$$

$$\frac{dM_2}{dt} = -w_0 M_2 + w_2 M_1 - w_2' M_2 - k_{vv} M_2 m_1 + k_{vv} m_2 M_1 \quad (8.11)$$

$$\frac{dM_2}{dt} = -w_2 M_1 + w_2' M_1 - k_{vv} M_1 m_2 + k_{vv} m_1 M_2 \quad (8.12)$$

where m_1 , m_2 and M_1 , M_2 are the populations of states 1 and 2 for molecules with the isotopes m and M respectively. The dissociation

yield for each of the isotopes is determined as

$$\beta_1 = \frac{w_0}{m_1^0} \int_0^{\tau_p} m_2(t) dt \quad \beta_2 = \frac{w_0}{M_1^0} \int_0^{\tau_p} M_2(t) dt \quad (8.13)$$

where τ_p is the pulse duration, m_1^0 and M_1^0 are the initial concentrations of molecules. For the system of equations (8.9) to (8.12) to be solved analytically,²⁵ m_1 and M_1 are assumed to be constant which correspond to low dissociation yields $\beta_1, \beta_2 \ll 1$ and the reverse transitions w_1' and w_2' are disregarded.

As a result, the selectivity of MP dissociation (mainly the molecules with the isotope m are excited) can be expressed as

$$\alpha' = \frac{\beta_1}{\beta_2} = \frac{w_1(3 - w_0\tau_p) - (1 - x_0)(w_1 - w_2)\tau_p k_{vv}\rho}{w_2(3 - w_0\tau_p) + x_0(w_1 - w_2)\tau_p k_{vv}\rho} \quad (8.14)$$

where $p = m_1^0 + M_1^0$ is the total gas pressure, and x_0 is the concentration of molecules with the isotope m . Expression (8.14) is derived with additional assumptions $w_0\tau_p \ll 1$ and $\tau_p k_{vv}\rho \ll 1$. With $p \rightarrow 0$ we get the natural result $\alpha' \rightarrow w_1/w_2 \equiv \alpha'_0$, i.e., the ultimate value of selectivity is determined by the ratio of the laser excitation rates w_1 and w_2 . Finally we have

$$\alpha' = \frac{\alpha'_0(3 - w_0\tau_p) - (1 - x_0)(\alpha'_0 - 1)\tau_p k_{vv}\rho}{(3 - w_0\tau_p) + x_0(\alpha'_0 - 1)\tau_p k_{vv}\rho} \quad (8.15)$$

The slope of the dependence of α on ρ can be expressed as

$$v_1 = \left. \frac{1}{\alpha'_0} \frac{d\alpha'}{d\rho} \right|_{\rho=0} = -\frac{(\alpha'_0 - 1)[1 + x_0(\alpha'_0 - 1)]\tau_p k_{vv}}{\alpha'_0(3 - w_0\tau_p)} \quad (8.16)$$

In much the same manner for excitation of molecules with the other isotope M can we get

$$\alpha'' = \frac{\beta_2}{\beta_1} = \frac{\alpha''_0(3 - w_0\tau_p) - x_0(\alpha''_0 - 1)\tau_p k_{vv}\rho}{(3 - w_0\tau_p) + (1 - x_0)(\alpha''_0 - 1)\tau_p k_{vv}\rho} \quad (8.17)$$

$$v_2 = \left. \frac{1}{\alpha''_0} \frac{d\alpha''}{d\rho} \right|_{\rho=0} = -\frac{(1 - x_0)(\alpha''_0 - 1)\tau_p k_{vv}}{3 - w_0\tau_p} \quad (8.18)$$

where $\alpha''_0 = w_2/w_1$ is the ultimate spectral value of selectivity α'' .

*Comparison with experiment. The case of CF_3I .*²⁵ The first conclusion from the solution of (8.9) to (8.12) is that the character of the depen-

dence of selectivity on pressure may differ substantially when molecules with high and low isotope contents are excited. In the second case, with $x_0 \ll 1$, the dependence of α' on ρ is governed by the value of the $\alpha'_0 x_0$ parameter. With $\alpha'_0 x_0 \gg 1$ the value of selectivity depends on the *partial pressure* of the isotope being excited m (see expression (8.15)) and with $\alpha'_0 x_0 \ll 1$ on the *total gas pressure*. Therefore, at sufficiently high spectral selectivity the dependence of selectivity on gas pressure may be essentially slower when the poor isotope is excited. This conclusion agrees well with experiment (see Figure 8.13a, b). From (8.16) and (8.17) it follows that the ratio of the rates of α dependence on ρ for two isotopes will be

$$\frac{v_2}{v_1} = \frac{(1-x_0)(\alpha''_0-1)\alpha'_0}{[1+x_0(\alpha'_0-1)](\alpha'_0-1)} \quad (8.19)$$

It should be noted that v_2/v_1 depends only on the values of x_0 , α'_0 , α''_0 and is independent of the rates of laser excitation and V-V exchange. With the use of the data from Table 8.3 the value of v_2/v_1 can be calculated from (8.19) and compared with the experimental value.† With $T = -45^\circ\text{C}$ $v_2/v_1 = 62.7$ which is close to the measured value.

The rate constant of vibrational exchange k_{vv} can be determined from (8.16) and (8.18) with the use of the experimental values for the slope of the dependence of K_{pr} on pressure, $K_{pr}^0(13/12)$ and $K_{pr}^0(12/13)$, pulse duration τ_p . The values of k_{vv} obtained for $T = +20^\circ\text{C}$ and $T = -45^\circ\text{C}$ are given in Table 8.3. It should be noted that the values of K_{vv} obtained in *independent* experiments on excitation of both $^{13}\text{CF}_3\text{I}$ and $^{12}\text{CF}_3\text{I}$ are close. The order of magnitude for the

TABLE 8.3
Parameters of isotopically-selective dissociation of $\text{CF}_3\text{I}^{8,25}$

	Excitation of $^{13}\text{CF}_3\text{I}$		Excitation of $^{12}\text{CF}_3\text{I}$	
	+20°C	-45°C	+20°C	-45°C
K_{pr}^0	12.6	28	50	80
ρ_0 (Torr)	6.4 ± 0.1	10.6 ± 0.1	0.24 ± 0.005	0.2 ± 0.005
k_{vv} (s · Torr) ⁻¹	$2.44 \cdot 10^6$	$1.22 \cdot 10^6$	$1.38 \cdot 10^6$	$1.03 \cdot 10^6$

† It was assumed that $\alpha'_0 = K_{pr}^0(13/12)$ and $\alpha''_0 = K_{pr}^0(12/13)$.

obtained values of k_{vv} is $10^6 \text{ s}^{-1} \text{ Torr}^{-1}$, i.e., close to the typical value of the rate constant of $V-V$ exchange in polyatomic molecules (see Section 2.5). The dependence of α on ρ can be calculated with formulas (8.15) and (8.17) with the use of the values of k_{vv} determined above. The results of such calculation for $T = -45^\circ\text{C}$ are shown with a dashed line in Figures 8.13a and 8.13b. The discrepancy between the experimental and calculated values with $\rho > \rho_0$ is caused by two factors. First, it is the simplified consideration of the processes of laser excitation and $V-V$ exchange. The variation in average level of excitation of the undesired isotope in $V-V$ exchange is not allowed for here which must affect the rate of its subsequent laser excitation. Secondly, the contribution of molecular dissociation after the laser pulse is over is not taken into account.

The model developed in Ref. 15 also correctly predicts the dependence of selectivity on laser pulse duration. The CO_2 laser pulse was standard by shape with a front peak and a "tail". The pulse duration varied due to changes in the energy and duration of the "tail" as N_2 was added to the working mixture of the CO_2 laser. The total pulse energy was kept constant. Since the dissociation yield in this experiments with CF_3I depended only on the laser pulse energy fluence and did not depend on the pulse shape, this enabled introducing the effective pulse duration

$$\tau_{\text{eff}} = y_0\tau_1 + (1 - y_0)\tau_2 \quad (8.20)$$

where τ_1 and τ_2 are the widths (at half height) of the pulse front peak and "tail", y_0 is the fraction of total pulse energy contained in the front peak. In the experiment two types of pulses were used, short τ_s and long T_l . Their effective duration was $\tau_s = 1.85 \cdot 10^{-7} \text{ s}$, $\tau_l = 7.75 \cdot 10^{-7} \text{ s}$.

From expression (8.15) and (8.17) it is possible to estimate the values of α' and α'' for different pulse durations τ_s and τ_l on the assumption that the ultimate spectral selectivity (α'_0 and α''_0) does not depend on τ_p . This assumption is quite reasonable. The experiments on SF_6 ,¹⁷ for example, carried out at a low gas pressure $1.6 \cdot 10^{-2} \text{ Torr}$, when the collisions may be neglected, have shown that selectivity is independent of laser pulse duration. In the estimates the values of k_{vv} presented in Table 8.3 were used. The results obtained for exciting both $^{13}\text{CF}_3\text{I}$ and $^{12}\text{CF}_3\text{I}$ are given in Table 8.4, where the experimentally measured values of K_{pr} (13/12) and k_{pr} (12/13) can be found, too. The com-

TABLE 8.4
 Dependence of CF₃I dissociation selectivity on laser pulse duration²⁵

Excitation of ¹³ CF ₃ I <i>p</i> = 0.8 Torr <i>T</i> = -45°C			Excitation of ¹² CF ₃ I <i>p</i> = 0.2 Torr <i>T</i> = +20°C		
	Experiment	Model	Experiment	Model	
Short pulse	25.2	25.9	21.8	27.3	
Long pulse	17.9	19.8	10.2	11.2	
Ratio (short/long)	1.41	1.31	2.14	2.44	

parison of the results of experiment and calculations shows that the model used agrees well with experiment.

These experiments with different pulse durations demonstrate that V-V exchange during a laser pulse is the main channel of selectivity loss in CF₃I. At the same time these measurements show that, at least under the conditions of experiments with CF₃I, exchange reactions like (8.23) cannot be the main contribution to spectral selectivity loss because the characteristic time of such reactions is several orders longer than the laser pulse duration.

Possibilities of decrease in the role of V-V exchange

The comparison of the model with experiment shows that, even though the model is simplified in character, it correctly describes the action of V-V exchange during an excitation pulse on the isotopic selectivity of MP dissociation. So the conclusions of this model can be used to analyze the possibilities of a decrease in the effect of V-V exchange and an increase in the primary dissociation selectivity.

It follows from the model that in exciting a component with a low content of desired isotope ($x_0 \ll 1$) it is possible to work with a high total gas pressure if *the spectral dissociation selectivity α_0 is high*. The criterion of fulfilling this condition is $\alpha_0 \geq 1/x_0$. In this case the enrichment factor depends on the partial pressure of the desired isotope and so the gas pressure may be sufficiently high. This conclusion has been supported by experiments. In the experiments on CF₃I,^{8,25} the condition $\alpha_0 \approx 1/x_0$ was fulfilled and so high dissociation selectivity of ¹³CF₃I was observed at a high total pressure of CF₃I. In experiments /8.28/ with SF₆ the value of $\alpha_0 x_0$ was small ($\alpha_0 x_0 = 0.06 \ll 1$) due to insufficiently high spectral selectivity of ³³SF₆ dissociation ($\alpha_0 \approx 7$). This factor is apparently responsible for the fast dependence

of α on ρ observed in the experiment, approximately as in exciting $^{32}\text{SF}_6$.

Thus, an increase in spectral excitation selectivity is one of the ways of decreasing the effect of the process of $V-V$ exchange as molecules with a low content of desired isotope dissociate.

One more way of increasing the primary dissociation selectivity consists of reducing the exciting pulse duration. In this case, when the process of $V-V$ exchange during a laser pulse has a dominant role in decreasing the selectivity, a decrease in τ_p causes, of course, the contribution of $V-V$ exchange to the measured value of selectivity to fall. This conclusion was confirmed in experiments on CF_3I where it was demonstrated that a reduction in pulse duration brought about an increase of α in exciting molecules both with the poor and rich isotope $^{13}\text{CF}_3\text{I}$ and $^{12}\text{CF}_3\text{I}$. Therefore, by decreasing the laser pulse duration one can increase the total gas pressure with the dissociation selectivity remaining high. A striking proof of this is the work on hydrogen isotope separation.²¹ Having reduced the laser pulse duration to 2×10^{-9} s a mixture of CF_3D and CF_3H could yield an enrichment factor in the products $K_{\text{pr}}(D/H) = 11\,000$ at a total gas pressure of 100 Torr.

It follows from the above model that during resonant excitation of molecules with a rich isotope the condition

$$\rho_0 \alpha_0'' k_{vv} \tau_p \approx \text{const} \quad (8.21)$$

is fulfilled. This expression, in particular, shows why at a comparatively low rate of $V-V$ exchange $k_{vv} \sim 10^6 \text{ s}^{-1} \text{ Torr}^{-1}$ the selectivity can be decreased considerably at still small values $\rho \tau_p < 1/k_{vv}$. The point is that the whole rate of $V-V$ exchange between two systems (in our case between molecules with different isotopes) is determined not only by the value of k_{vv} but is also proportional to the degree of deviation of these systems from equilibrium with each other, i.e., the value of excitation selectivity. This is responsible for the appearance of α_0 in expression (8.21). (As molecules with a poor isotope are excited, if $\alpha_0 x_0 \gg 1$, expression (8.21) has the same form, but ρ_0 here denotes the partial pressure of the isotope under excitation.)

From (8.21) it follows that by changing the spectral selectivity, for example through gas temperature or frequency tuning of exciting radiation, one can affect the rate of $V-V$ exchange and hence vary the rate of the dependence of α on ρ . It is this factor that decelerates

the dependence of $K_{pr}(12/13)$ on the pressure of CF_3I (Figure 8.13b) as the gas temperature rises. Expression (8.21) makes it possible to optimize the irradiation frequency, gas temperature and pressure in isotopically selective MP dissociation. In some cases we can profitably decrease the spectral selectivity to increase the gas pressure at some required fixed value $\alpha'' < \alpha_0''$.

V-V exchange after the excitation pulse. At this stage *V-V* exchange can also affect the parameters of MP dissociation and particularly its selectivity. In the first experiments on MP dissociation of molecules^{1,2} it was shown that the redistribution of vibrational energy as a result of *V-V* exchange can contribute considerably to the observed dissociation yield forming its so-called collisional phase. The investigation of the isotopic selectivity of this dissociation stage⁵⁴ was actually the first experiment on the influence of collisions on the selectivity of MP dissociation. The experiment was performed with $^{10}BCl_3$ and $^{11}BCl_3$ and its aim was to study the selectivity of formation of the dissociation fragments of these molecules at different instants of time after the CO_2 laser pulse. The results of this work show that selectivity is preserved in the collisional dissociation phase, too, at least during (1-2) τ_{vv} . Later the selectivity of collisional dissociation phase was studied theoretically.⁵⁵ The model calculations carried out show that selectivity may actually take place in this dissociation phase during (0-2) τ_{vv} even though it is reduced in time in this case. The selectivity value here is determined by the difference in excitation level of the two components and their relative concentrations.

The cases considered above are basically concerned with exciting rather few-atomic molecules. As it follows from the RRKM theory (see Section 2.4), these molecules dissociate in 10^{-9} to 10^{-7} s even at low excitation over the dissociation limit (1 or 2 quanta of CO_2 laser). A different situation exists for bigger molecules consisting of eight, nine or more atoms. For these molecules the time of unimolecular decay is increased by 2 or 3 orders and even more. The laser pulse duration being $\sim 10^{-7}$ s, the dissociation of such molecules would occur mainly when the pulse is over. In this situation the *V-V* exchange with cold molecules may cause deexcitation of vibrationally excited molecules and, accordingly, a decrease in dissociation yield. The deexcitation role of *V-V* exchange would apparently show itself most efficiently when the laser excites the poor component. The dependence of the dissociation yield on the pressure of CF_3COCF_3 ⁵¹ from exciting

$\text{CF}_3^{13}\text{COCF}_3$ is characteristic in this sense (see Figure 8.14). The increase of the gas pressure from 0.2 Torr to 10 Torr results in a decrease in yield by about three orders.

It would be of interest to explain the observed increase in selectivity due to a different contribution of the process of deexcitation to the dissociation yield of different components. Indeed, as the research shows, the dissociation yield is determined mainly by the energy stored in a molecule, i.e., it is a function of the average level of molecular excitation $\beta = f(\bar{\epsilon})$. This dependence increases with a decrease in $\bar{\epsilon}$. In exciting the poor component the average energy level of excited molecules after the pulse is over must exceed the corresponding value for the rich component if the selectivity is sufficiently high. According to the above, the decrease in $\bar{\epsilon}$ from $V-V$ exchange with the ensemble of cold molecules must affect more the dissociation yield of the molecules of the rich component. As a result, it must increase the selectivity of MP dissociation as the pressure rises.

It is not impossible that it is just such a mechanism that takes place for CF_4COCF_3 . The data available, however, is not sufficient for a final conclusion especially as an analogous increase in selectivity was observed in the experiments with CF_3Br both with increasing gas pressure /8.52, 8.53/ and with a buffer added.⁵³ In these experiments the effect of $V-V$ exchange after the laser pulse can be neglected.

It is the dependence of the function $\alpha = \alpha(\rho)$ on the excitation radiation frequency⁵³ that can apparently give a key to understanding the causes of such an increase in α . The contribution of rotational relaxation is one of the probable causes of such a dependence. The potential influence of rotational relaxation on the isotopic selectivity of MP dissociation will be considered below.

8.5.3. Collisions with buffer gas. Effect of $V-T$ and rotational relaxation

In parallel with $V-V$ exchange, the processes of $V-T$ and rotational relaxation also take place as a result of collisions.† All the necessary information on these processes is given in Section 2.5. We want to recall that $V-T$ relaxation is related to the transfer of a part of vibrational energy to translational degrees of freedom. This, in

† Collisions also induce phase relaxation but the effect of this process on the isotopic selectivity of MP dissociation has not yet been revealed, and so will not be considered.

particular, leads to vibrational deexcitation of excited molecules especially when they are highly diluted with cold molecules.

Rotational relaxation causes an equilibrium distribution over rotational levels to be reached after a perturbation. Besides a great difference in rate constants, the processes of $V-T$ and rotational relaxation also differ by the fact that the establishment of rotational equilibrium for polyatomic molecules does not significantly change their vibrational energy.

The action of rotational and $V-T$ relaxation is rather often masked by the high-rate resonant $V-V$ exchange, and so the effect of these processes on the isotopic selectivity of MP dissociation can be studied more conveniently with the use of buffer gases. Usually for these purposes one- or two-atom gases are used. This makes it possible to eliminate the effect of $V-V$ exchange and thereby reveal the role of the two other relaxation processes.

After these preliminary notes we are going to proceed to considering the available data.

Experimental results. There have been rather few experiments dealing with the effect of the addition of different gases on selectivity. For example, it has been shown¹⁴ that the addition of 0.5 Torr NH_3 to 0.2 Torr SF_6 increases $K_{\text{pr}}(32/24)$ by one and a half times. The addition of 20 Torr oxygen had the same effect. Such behavior of K_{pr} was explained¹⁴ by a general decrease in the average energy level of molecules due to their deexcitation by the buffer gas.

An increase in dissociation selectivity with increasing pressure of $\text{N}_2 + \text{O}_2$ has been also observed in experiments with BCl_3 .⁹ It must be noted, however, that in this case O_2 also acts as an acceptor and so the measured increase of K_{pr} may be also related to the suppression of nonselective chemical reactions (see below). Some increase in dissociation selectivity was observed during addition of buffer gas in the experiments with CF_2Cl_2 ⁵⁶ and CF_3I .⁸

In experiments on SF_5Cl ⁵⁷ the addition of hydrogen that acted as an acceptor at the same time also brought about a small increase in the value of $\alpha(32/34)$. The addition of nitrogen to 0.25 Torr SF_5Cl reduced the dissociation selectivity from $\alpha(32/34) = 2.33$ with $\rho_{\text{N}_2} = 0$ to 1.33 with $\rho_{\text{N}_2} = 3$ Torr. A decrease in selectivity with increasing pressure of H_2 has been also observed in experiments with SF_6 .³⁵

More detailed studies have been carried out.⁵⁸ In these experiments the total dissociation of $^{32}\text{SF}_6$ and $^{34}\text{SF}_6$ was measured in a cell during

resonant excitation of $^{32}\text{SF}_6$ in the presence of different buffer gases by a CO_2 laser. Some results of these measurements are discussed below.

It is impossible to find the value of α from the data⁵⁸ with the use of expression (8.4) because of the high total dissociation of SF_6 . Nevertheless, this data shows the general qualitative picture of buffer gas influence on selectivity. As small amounts of such monoatomic gases as Ar, Ne and He were added, the dissociation of $^{32}\text{SF}_6$ almost did not change. At the same time there is an increase in the dissociation of $^{34}\text{SF}_6$ which corresponds to a decrease in selectivity of the process of dissociation. With strong dilution of SF_6 with a buffer (1:100) the dissociation of $^{32}\text{SF}_6$ is reduced considerably, the dissociation of $^{34}\text{SF}_6$ changing somewhat less, which corresponds to a further decrease in selectivity as compared to the case of pure SF_6 .

The results are explained⁵⁸ by $V-T$ and rotational relaxation. With addition of small amounts of a buffer the main contribution is by rotational relaxation discussed in more detail below.

With larger addition of buffer gases the variation of α is related to the deexcitation of the molecules excited by the laser radiation as a result of $V-T$ relaxation. As follows from the data,⁵⁸ the lighter the buffer, the higher the deexcitation, which is very characteristic of the $V-T$ process. Nevertheless, it is not impossible that at such pressures, as well, rotational relaxation makes its own contribution.

The results presented show that the effect of buffer gases on selectivity is caused by different processes and so its character may depend on such factors as the type of buffer and its pressure as well as the conditions of laser excitation. The measurements with H_2 directly point to this. The experiments show that with addition of hydrogen the selectivity increases unlike the case of monoatomic gases and the measurements with SF_6 ³⁵ already mentioned above.

Thus, the results presented are contradictory at first glance. In some experiments the addition of a buffer increases the selectivity, in other ones it decreases the selectivity. Other studies⁵³ make things somewhat clearer, and the results will be considered in more detail.

In these experiments⁵³ consideration was given to the effect of gas (buffer and parent) pressure on the MP dissociation selectivity of $^{13}\text{CF}_3\text{Br}$ under different conditions of excitation. The CF_3Br were excited at the $P(12)$ and $P(32)$ lines of the CO_2 laser in the $9.6\ \mu$

region. This corresponds to the excitation of $^{13}\text{CF}_3\text{Br}$ approximately at the center of the ν_1 band ($\nu_1 - 52(P(12)) = 3.7 \text{ cm}^{-1}$) and at its long-wave end ($\nu_1 - 52(P(32)) = 22.2 \text{ cm}^{-1}$). The detunings from the band of $^{12}\text{CF}_3\text{Br}$ were respectively 30 cm^{-1} and 48.5 cm^{-1} . The values of $\alpha(13/12)$ measured at different pressures of the buffer gas N_2 are given in Figure 8.16a. It may be seen that the behavior of the function $\alpha = \alpha(\rho_{\text{N}_2})$ changes radically with radiation frequency. As the excitation frequency is moved towards the center of the band of $^{13}\text{CF}_3\text{Br}$ the selectivity decreases with addition of nitrogen (curve 1) and at the edge of the band it increases (curve 2).

With $\rho < 10$ Torr the dependence of α on the pressure of CF_3Br has the same qualitative character (curves 3 and 4). The difference lies in a faster pressure dependence. The variation in gas temperature also affects the form of the function $\alpha = \alpha(\rho)$ (compare curves 5 and 4).

The results presented as well as the measurements of the dissociation yield for $^{13}\text{CF}_3\text{Br}$ and $^{12}\text{CF}_3\text{Br}$ leads to the conclusion that it is mainly rotational relaxation that is responsible for such behavior of α . The mechanism of its action will be clear from the model below.

*Rotational relaxation model.*⁵³ Let us consider the case of exciting two isotopic components of $N_i (i = 1, 2)$ in the presence of the buffer gas M . In the previous chapters it has been shown that molecules at different rotational levels can interact with the laser radiation in different ways. For simplicity let us assume that the field interacts only with a certain group of levels the equilibrium population of which $n_i^e = f_i N_i$. The excitation from these levels comes about at the rate w_i , and as a result of rotational relaxation they are repopulated with the rate constant k_r . In this case the following relations

$$\begin{aligned} \dot{n}_i &= -w_i n_i + k_r M (f_i N_i - n_i) \\ \dot{N}_i &= -w_i N_i \end{aligned} \quad (8.22)$$

are fulfilled. These equations describe the effect of rotational relaxation in the ground state. A similar approach has been applied with success to describe the effect of a rotational "bottle neck" at single-photon excitation (see Section 3.3). To describe multiple photon excitation, equations (8.22) can be supplemented with an appropriate system of equations describing the subsequent excitation in the quasi-continuum (see Chapter 6). But in our case this is not necessary, and we can use for analysis the reduced system (8.22). This is due to the fact that, as

was shown in experiments on SF₆ and CF₃I (see Chapter 6), the action of rotational relaxation is limited basically to populating the depleted rotational levels in the ground state and it affects only slightly the subsequent excitation of molecules, at least in these two molecules.

The solution of equation (8.22) shows that the value of the contribution of rotational relaxation to dissociation selectivity as well as its sign are governed by the relations between $w_i\tau_\rho$, f_i and $k_rM\tau_\rho$.

Let both components interact effectively with the field, i.e., $w_i\tau_\rho \gg 1$, $i = 1, 2$. This corresponds to the saturation of resonant levels and the formation of deep "holes" in the rotational distribution. It can be shown that in this case α always decreases with addition of a buffer gas.

With only the desired component saturated, α can be increased with increasing pressure. We shall not write out the qualitative relations between $w_i\tau_\rho$, f_i and $k_rM\tau_\rho$ at which an increase in α occurs. These cases are comprehensively discussed in Ref. 53. The general qualitative conclusion is that an increase in α takes place when the relative contribution of rotational relaxation to the MP dissociation yield for the desired component is larger than that for the undesired one. This evidently occurs when the degree of rotational distribution disturbance from equilibrium caused by radiation is smaller for the undesired component. This, for example, can be when the "hole" in the rotational distribution of this component is small. In this case we may even have $f_2 = 1$, i.e., all the molecules interact with the field, although slightly ($w_2\tau_\rho \ll 1$). Rotational relaxation in this case does not contribute to β_2 as it increases β_1 , and hence $\alpha = \beta_1/\beta_2$ if $f_1 < 1$.

Now let $f_1 = 1$ and $w_1\tau_\rho \gg 1$, i.e., conversely all the molecules of the desired component effectively interact with the field. In this case rotational relaxation contributes only to the value of β (if $f_2 < 1$) and hence decreases α . This case apparently took place with SF₆⁵⁸ since with the energy fluence used all the molecules of the desired component, i.e., ³²SF₆, interacted with the field.

Discussion of results. Turning back to the experiments with CF₃Br we should note that the measurements of the MP dissociation yield provide us with a powerful argument in favor of the discussed mechanism of the effect of rotational relaxation. With an addition of a buffer gas one could always observe an increase in β_1 and β_2 . The character of the dependence may be seen from Figure 8.16b which presents the result for β_{13} during excitation at the band edge (curve 1). Similar

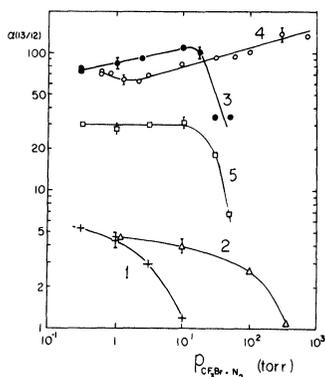


FIGURE 8.16a MP dissociation selectivity α (13/12) of CF_3Br molecules as a function of gas pressure. (1, 2) the pressure of N varies with $\rho_{\text{CF}_3\text{Br}} = 0.3$ Torr; (3, 4, 5) the pressure of CF_3Br varies with $\rho_{\text{N}_2} = 0$; (5) gas temperature $T = 356$ K, the rest of the curves are plotted for $T = 293$ K. (1, 3) excitation at the $P(12)$ line; (2, 4, 5) excitation at the $P(32)$ line. The value of Φ everywhere is 4 J/cm^2 .⁵³

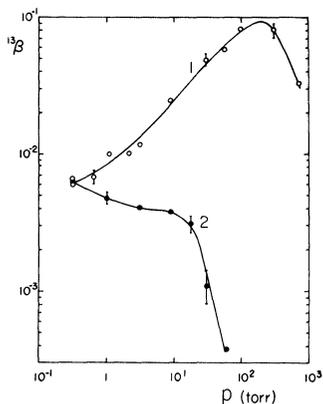


FIGURE 8.16b Dependence of the MP dissociation yield of $^{13}\text{CF}_3\text{Br}$ on the pressure of N_2 (curve 1) and CF_3Br (curve 2) with excitation at the $P(32)$ line.⁵³

dependences can be observed for quite a number of molecules (see Section 7.4.1). They all are caused by the action of rotational relaxation. The contribution of $V-T$ relaxation manifests itself much later. In experiments with CF_3Br the deexcitation caused by this process becomes essential with $\rho_{\text{N}_2} > 100$ Torr. Thus, at lower pressures the

only collisional process that affects the MP dissociation of both components is rotational relaxation.

Another argument in favor of this mechanism is the possibility of changing the form of the dependence $\alpha = \alpha(\rho)$ by changing only the radiation frequency. Such a change apparently brings about a change in the fraction of molecules f_i of both components interacting with the field. As follows from the above model, the ratio between the values of f_i and $w_i\tau_\rho$ is a critical factor which determines the contribution of rotational relaxation and its sign.

The dependence of α on the pressure of CF_3Br in Figure 8.16a is also apparently caused by the similar action of rotational relaxation but the situation is more complicated. As it may be seen from Figure 8.16b, $V-V$ exchange makes a considerable contribution to the process of MP dissociation. The difference in character of curves 1 and 2 is caused by the different mechanisms of deexcitation. $V-V$ exchange with cold $^{12}\text{CF}_3\text{Br}$ molecules is the mechanism in the second case.

The rate constants of the $V-V$ (the parent gas) and $V-T$ (the buffer) processes usually differ by 2 or 3 orders. This is responsible for the difference by 2 orders between the rate of decrease of β_{13} with ρ for curves 1 and 2. With $\rho_{\text{CF}_3\text{Br}} < 10$ Torr (curve 2) rotational relaxation can only partially compensate for the decrease of β_{13} as a result of $V-V$ transfer. At a higher pressure the $V-V$ exchange becomes a dominating factor, and it is responsible for a drastic decrease of α with $\rho_{\text{CF}_3\text{Br}} > 10$ Torr. It is not impossible that it contributes to selectivity at lower pressures as well. The competition between laser excitation and the deexcitation due to the process of $V-V$ exchange, for example, was considered⁵² to be responsible for the increase of α with increasing ρ during excitation at the edge of the $^{13}\text{CF}_3\text{Br}$ band.

Finally, Figure 8.16a shows that a variation in gas temperature also affects the character of the dependence $\alpha = \alpha(\rho)$. This seems to be related to the change of the values of f_i resulting from the variation of initial molecular distribution. However, the factors considered in Section 8.3 can also produce an effect here.

In conclusion we should stress again that the processes of $V-T$ and rotational relaxation act on selectivity only when they make a different contribution to the MP dissociation yield of two isotopic components. As far as rotational relaxation is concerned, its action on selectivity as well as the sign of this action depend on the conditions of excitation.

One of the ways of increasing selectivity due to rotational relaxation is detuning from the center of the excitation band of both components. In this case we can set the conditions when rotational relaxation makes a larger contribution to the dissociation yield of the desired component. The increase in the number of molecules involved in the process of MP excitation caused by rotational relaxation can⁵³ considerably compensate for the decrease in dissociation yield of the desired component caused by the detuning from the center of the band.

8.6. Loss of MP dissociation selectivity in secondary chemical processes

At the end of this chapter we want to consider one more channel of selectivity loss. This may be chemical reactions in which the fragments resulting from molecular dissociation participate. In a number of intermediate reactions the primary dissociation selectivity may be lost to a greater or lesser degree. There are a large number of possibilities of reaction types here but the final result of all of them is that the molecules of the initial substance are involved nonselectively in chemical reactions. They can react with both intermediate and end products of reactions of dissociation fragments. The last possibility has been given particular emphasis.³⁴ In this work the authors studied, among other things, the dependence of α on the number of radiation pulses during dissociation of BCl_3 in mixture with H_2 . The experiments show that the value of α decreases as the gas is irradiated. The authors³⁴ relate this decrease to the accumulation of new products in the cell and their reaction with the original BCl_3 molecules.

The exchange reaction with an atom or a radical group can be considered as one more channel of primary selectivity loss. This can be illustrated by such a reaction



The exchange with the iodine atom by scheme (8.23) during dissociation of CF_3I (the molecule dissociates into CF_3 and I) has even been considered³⁹ as the main channel of selectivity loss. This conclusion, as applied to CF_3I , however, cannot be apparently justified (see Section 8.5.2). In general such reactions, however, can occur and result in a decrease in primary selectivity.

It is important to choose a proper scavenger for binding the resultant dissociation fragments as illustrated⁹ with experiments on BCl_3 . As it

has been already said, the dissociation of BCl_3 is reversible and thus scavengers should be used. In the experiments HBr , O_2 , C_2D_2 , NO and H_2 were used as acceptors. It follows from these experiments that the value of $K_{\text{pr}}(10/11)$ measured from the final results of irradiation essentially depends on the kind of scavenger and hence on the type of intermediate reactions. In case of HBr , for example, the value K_{pr} is two times higher than in case of H_2 .

When O_2 is used as a scavenger, the selectivity may be measured at early stages of the reaction. In Ref. 54 K_{pr} was measured at the first stage, the formation of the BO radical, from the chemiluminescence spectrum.† At this stage $K_{\text{pr}} \approx 10$ which was much higher than the value obtained from the end products of irradiation. This result obviously points to the fact that the decrease in selectivity occurred in the process of chemical formation of end products.

A decrease in selectivity due to secondary chemical reactions was also observed in experiments with pentafluorobenzene.⁶⁰ In isotopically selective dissociation of $\text{C}_6\text{F}_5\text{H}$ and $\text{C}_6\text{F}_5\text{D}$ it was found that the atoms and radicals resulting in the dissociation of these molecules reacted with the original substance and thereby decreased the final selectivity of the entire process. By adding different scavengers it was possible⁶¹ to reduce the contribution of these reactions and, as a result, to increase the measured value of α .

An essential role of secondary chemical processes was disclosed in MP dissociation of *trans*- $\text{ClHC}=\text{CHBCl}_2$ molecules.⁶² It was found that the quantum yield of dissociation was higher than unity. This allowed drawing a conclusion of a great contribution of secondary chain chemical reactions. These reactions reduce the primary selectivity of MP dissociation (for boron isotopes) and give rise to comparatively low values of α in end products.

In conclusion it should be mentioned the possibility of chemical reactions for vibrationally-excited molecules. It has been so far believed that the formation of enriched end products in the presence of scavenger takes place only when the fragments of molecular dissociation react. However, scavengers can react with highly vibrationally-excited molecules too. Such reactions, in principle, can occur and make their contribution to the observed value of selectivity.

† While studying the isotopic effects in the spectra of resulting radicals, it is possible in principle, to follow the value of α at all the stages of the reaction.

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