$$W = W_0 = \frac{4\sqrt{1-\beta^2}}{3T_0}\left(\frac{H}{H_0}\right)^3 (1-q^2)^{7/2},$$

so that, when $\gamma_0 \to 0$ and $\beta = 0$, we have the result given in[12].

Assuming that $q \ll 1$, $\delta < 1$, we find from (11) that

$$W = W_0 + W_1,$$

$$W_1 = \frac{B}{5}\frac{H}{H_0}q^2(1+\nu\delta)^5.$$

For fields $H \sim 10\,000$ G and $\gamma_0 \sim 0.01$, we have $W_0 \sim 10^{-11}$ sec^{-1}, $W_1 \sim 10^{-5}$ sec^{-1}. Thus, the presence of a plane wave reduces the electron spin-flip time by five or six orders of magnitude, but this time remains very long ($\sim 10^5$ sec) so that the $n=1$, $\zeta = -\varepsilon g$ state remains stable against transition to the $n=0$ state.

In the other limiting case, when $1 - q^2 \ll 1$, we find from (11) that, when $\delta < 1$,

$$W = B\frac{H}{H_0}\frac{35\sqrt{3}}{72}(1-q^2)^{-1/2}\left(1+\frac{192\sqrt{3}}{175}\nu\delta\sqrt{1-q^2}\right),$$

i.e., the $n=1$, $\zeta = -\varepsilon g$ state is no longer stable in the presence of a strong wave.

Thus, when the wave is present, there is a range of levels $\Delta n \sim \delta^{-1}$ ($\delta < 1$) for $t > T_{c1}$ which is filled with electrons but, if the electron spin is antiparallel to the field, the lowest level is $n=0$; when the electron spin is parallel to the field, the lowest level is $n=1$.

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Mechanism of isotopically selective dissociation of SF6 molecules by CO2 laser radiation

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An experimental study is reported of the selective multiphoton dissociation of SF_6 in a strong infrared laser field. The frequency characteristics of the rate of dissociation and of the enrichment coefficient, the threshold charcteristics of the dissociation process, the quantum yield, and the effect of collisions on the rate and selectivity of SF_6 dissociation have all been determined. The mechanism of selective dissociation of the SF_6 molecule by a strong infrared laser field is discussed. A new method is proposed for the selective dissociation of molecules by a two-frequency infrared laser field.

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1. INTRODUCTION

The phenomenon of isotopically selective dissociation of polyatomic molecules by strong CO_2 laser pulses has recently been discovered (BCl_3,[1] SF_6,[2] OsO_4,[3] etc.). This discovery was preceded by studies of the visible and ultraviolet luminescence of molecular gases (C_2F_3Cl, SiF_4, BCl_3, etc.) under the action of a focused CO_2 laser pulse.[4-6] The desire to understand the nature of this emission and to demonstrate that it can appear as a result of the resonance interaction between a strong infrared field and a molecule, without the necessary participation of collisions with other molecules, has led to systematic studies of luminescence in isotopic mixtures of molecules[1] and to the discovery of the above phenomenon. Subsequent experiments have shown that, on the one hand, luminescence does not necessarily occur during the primary dissociation process but is frequently the result of secondary processes (see, for example, the experiments with trans-dichloroethylene[7])

and, on the other hand, the participation of collisions between highly excited molecules after the end of a short laser pulse may increase the dissociation yield without violating the isotopic selectivity (see, for example, the experiments with BCl_3[8]). The entire set of processes taking place under the action of a strong infrared laser pulse is, therefore, a complicated and interesting phenomenon requiring very careful investigation. It has attracted considerable attention not only because selective dissociation is of practical importance for the separation of isotopes but also because of many of its nontrivial features (multiphoton excitation of high vibrational levels with energies of 1–2 eV in fields with intensities of only 10^7 W/cm^2,[3] isotopically selective dissociation produced by influencing weak composite vibrations of molecules,[9] difference between the primary infrared photolysis products and the usual ultraviolet photolysis products[10]) which are difficult to explain within the framework of the existing and relatively primitive ideas on the interaction between multilevel molecular systems and a quasiresonance field.

The most complete investigation of isotopically selective dissociation of a polyatomic molecule in a strong infrared field was reported in the case of the SF_6 molecule in our previous paper.[11] Direct measurements of the variation in the isotopic composition of SF_6 were used to investigate the accumulation of vibrational energy by the molecule in the infrared field of the laser, the dependence of the enrichment coefficient on the incident radiation power and initial gas pressure, and the enrichment kinetics. However, many of the questions that are of fundamental importance for the understanding of selective multiphoton dissociation of molecules in a strong infrared laser field were not considered in[11]. They include the resonance and threshold characteristics of selective multiphoton dissociation, isotopic selectivity in the dissociation products, and influence of particle collisions on the rate and selectivity of dissociation.

In the present paper, we report the results of investigations into: 1) the frequency characteristics of the rate of dissociation of SF_6 molecules and the enrichment coefficient in dissociation products; 2) the dependence of the dissociation rate on the infrared laser intensity, i.e., the threshold characteristics of the selective dissociation process in SF_6; 3) the dissociation quantum yield, i.e., the energy of infrared radiation necessary to dissociate one molecule, and 4) the influence of particle collisions on the rate and selectivity of dissociation of SF_6.

The experimental results reported here, taken together with the data published in[11], provide a relatively complete physical picture of the selective dissociation of SF_6 in a strong resonance infrared laser field. This picture is discussed in the present paper.

2. EXPERIMENTAL SETUP AND METHOD

The experimental setup was described in[11]. We used a pulsed CO_2 laser with a transverse discharge at atmospheric pressure and a dispersive cavity. The maximum generated energy was ~3 J for a pulse length

of ~90 nsec. The width of the generated spectrum was 0.035 cm^{-1}. The pulse modulation depth due to mode locking with a period of ~10 nsec was not more than 25% of the total pulse amplitude.

The SF_6 was illuminated in a stainless steel vessel (10 mm in diameter and 120 mm long) with KBr windows. The laser radiation was focused on the vessel by an NaCl lens with a focal length of 10 cm. The CO_2 laser radiation was focused in the vessel whenever the incident radiation power was held constant. When the dependence of selective dissociation on the incident power was measured, this geometry was methodologically incorrect because of effects associated with the field inhomogeneity which was difficult to take into account in the calculations. The rate of dissociation as a function of the laser power was, therefore, investigated in a collimated beam (unless indicated otherwise). The laser radiation was collimated by an NaCl lens with a focal length of 100 cm. The vessel containing the SF_6 gas was placed in the region before the focus.

The SF_6 gas consumption in the vessel after irradiation was determined from the infrared absorption spectrum of SF_6 which was measured with the IKS-24 spectrophotometer before and after irradiation. The isotopic analysis of the products obtained after irradiation was performed on the MI-1309 mass spectrometer.

The isotopic selectivity of the dissociation of SF_6 molecules by infrared laser radiation was determined not by examining the residual gas, as in our previous paper,[11] but by examining one of the products formed after dissociation (SOF_2). This is a more direct method of determining the selectivity, since it yields immediately the initial selectivity of the process which, for a small amount of dissociated gas, is independent of the consumption of SF_6 in the vessel due to illumination.[11] The determination of the initial selectivity from the analysis of isotopic composition of the residual gas, on the other hand, is difficult in practice because of the uncertainty in the measured degree of dissociation of the gas obtained from infrared absorption, which always amounts to a few percent.

3. RESONANCE CHARACTERISTICS OF THE DISSOCIATION PROCESS

The dependence of the rate of selective dissociation of SF_6 molecules on the CO_2 laser frequency is shown in Fig. 1 (solid curve in the lower part of the figure). The rate of dissociation W was obtained from the expression $N/N_0 = e^{-Wn}$, where N_0 and N are the concentrations of SF_6 molecules in the vessel before and after irradiation, and n is the number of laser pulses. The energy per pulse was held constant at 0.8 J for all the laser lines used in this experiment. The measurements were performed with SF_6 pressure in the vessel equal to 0.2 Torr. It is clear that the maximum dissociation rate is shifted relative to the linear absorption band maximum by 7 ± 0.5 cm^{-1}. This is in agreement with the shift of the $v = 1$ level of the ν_3 vibrational mode due to anharmonic effects,[12] so that the maximum dissociation rate is observed when the radiation frequency is in
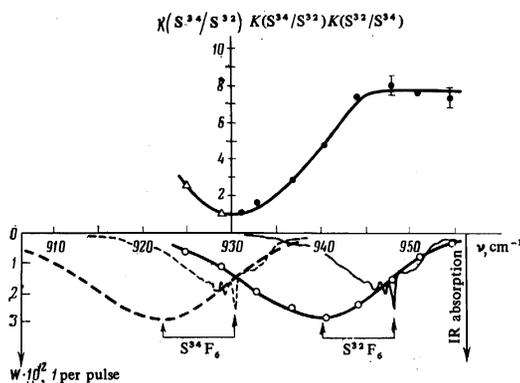
FIG. 1. Enrichment coefficients (top curve) of the reaction product SOF_2 [$\triangle$—$K(S^{34}/S^{32})$, $\bullet$—$K(S^{32}/S^{34})$] and dissociation rates (solid curve, lower figure) for the $S^{32}F_6$ molecules as functions of the frequency of the exciting laser radiation. Broken curve in lower figure shows, for comparison, the analogous curve for $S^{34}F_6$. The SF_6 pressure was 0.2 Torr. The mean intensity in the cell was 30 MW/cm^2 (focused beam, $f=10$ cm). The lower figure also shows the infrared absorption bands associated with the ν_3 vibration of the $S^{32}F_6$ and $S^{34}F_6$ molecules, taken from[21].

FIG. 3. Enrichment coefficient $K(S^{32}/S^{34})$ of the dissociation product SOF_2 as a function of the initial SF_6 pressure. The laser $P(16)$ line was generated at 947.7 cm^{-1}, and the average intensity in the cell was 90 MW/cm^2 (focused beam, $f=10$ cm).

resonance with the $v=1 \rightarrow v=2$ transition of the ν_3 vibration.

The dependence of the dissociation rate on the laser radiation frequency clearly shows that, when SF_6 gas containing a mixture of isotopes ($S^{32}F_6$ and $S^{34}F_6$) is irradiated, there is no selectivity, i.e., $K(S^{32}/S^{34})=1$, at the radiation frequency at which the rates of dissociation of the two isotopes are equal. To verify this, we recorded the frequency dependence of the enrichment coefficient $K(S^{32}/S^{34})$ for the dissociation products. As noted in[111], one of the dissociation products is SOF_2. The upper curve in Fig. 1 shows the results of these measurements. It is clear that, at high frequencies, when the dissociation rate of $S^{32}F_6$ is much greater than $S^{34}F_6$, the enrichment coefficient is a constant but, as the laser frequency approaches the center of the $S^{34}F_6$ absorption band, the rate falls to unity, indicating the absence of isotopic enrichment when the mixture of isotopes is illuminated at the frequency ~930 cm^{-1}. Further reduction in the frequency of the laser radiation was found to be accompanied by an increase in the enrichment of the mixture with the S^{34} isotope.
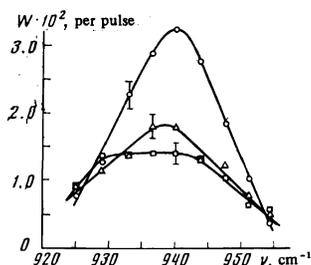
If we suppose that the shape of the frequency dependence of the dissociation rate of $S^{34}F_6$ (dashed curve in the lower part of Fig. 1) is precisely the same as the analogous result for $S^{32}F_6$, and there is merely an overall shift by an amount equal to the isotopic shift, then the point of intersection of these curves (normalized to unity) corresponds to the frequency at which there should be no enrichment. In reality, the laser radiation frequency at which enrichment is absent is shifted by 1 cm^{-1} toward higher frequencies relative to the point of intersection of the resonance characteristics of the dissociation rates.

We have also investigated the change in the frequency dependence $W(\nu)$ of the dissociation rate of SF_6 under the influence of buffer gases. These results are shown in Fig. 2. The buffer gas was argon. It is clear from Fig. 2 that the shape of the frequency dependence of the dissociation rate shifts toward lower frequencies when the partial pressure of argon is increased and the SF_6 pressure is held constant, and there is a simultaneous reduction in the absolute value of the dissociation rate. It is important to note that, at both ends of the $W(\nu)$ curve, the absolute value of the dissociation rate undergoes practically no change. When the argon pressure is 20 Torr, the resonance curve for the dissociation rate of SF_6 is flat at the center and looks like the result of the superposition of a resonance curve with the same frequency at maximum on a narrower resonance curve with the same amplitude but shifted toward lower frequencies by about 10 cm^{-1}.

Reduction in the SF_6 pressure down to 0.06 Torr did not lead to a shift of the maximum dissociation rate.

4. SELECTIVITY OF DISSOCIATION PROCESS

The limiting value of the enrichment coefficient of the dissociation products (see Fig. 1) in the absence of loss of selectivity in reactions involving primary dissociation products is measured by the ratio of the dissociation rates at a given laser frequency for molecules of different isotopic composition. In reality, there may be different channels for the loss of selectivity, which may lead to a reduction in the limiting value of the enrichment coefficient.

Figure 3 shows the enrichment coefficient $K(S^{32}/S^{34})$

FIG. 2. Effect of buffer gas (Ar) on the frequency dependence of the dissociation rate of the SF_6 molecules. Initial pressure of SF_6 in a cell—0.2 Torr, Ar pressure: o—0 Torr, $\triangle$—2 Torr, $\square$—20 Torr.
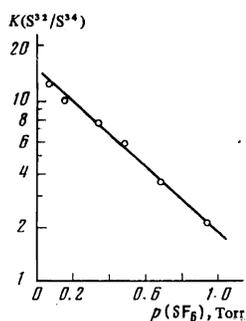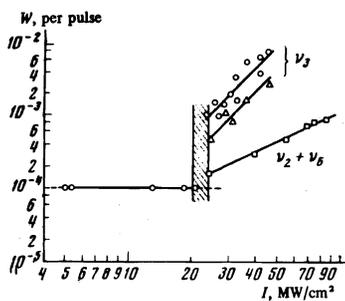
FIG. 4. Dissociation rate of SF_6 molecules as a function of laser intensity. The irradiation was carried out in the ν_3 absorption band at 947.7 cm^{-1} [o—P(16) line], 951.2 cm^{-1} [Δ—P(12) line], and at the composite vibration $\nu_2+\nu_6$ at 984.4 cm^{-1} [R(34)]. Measurements at the main frequency ν_3 were performed in an unfocused beam, whereas those at the composite frequency were carried out in a focused beam. SF_6 pressure 0.2 Torr. The ratio of the logarithmic scales along the abscissa and ordinate axes is 3 : 1.

for SOF_2 as a function of SF_6 pressure in the vessel. It is clear that, in this particular interval of pressures, the enrichment coefficient decreases exponentially with increasing SF_6 pressure, and the maximum enrichment coefficient in the reaction products at the lowest SF_6 pressure (0.05 Torr) is only 12. The ratio of dissociation rates for different isotopic molecules, $W(S^{32}F_6)/W(S^{34}F_6)$, at the given frequency is ~ 200, which is much greater than the measured value. The loss of selectivity may be due to several reasons, including vibrational-vibrational exchange between molecules of different isotopic composition during the presence of the pump pulse, isotopically nonselective excitation of molecules up to the dissociation limit due to post-pulse $V-V$ exchange, and nonselective reactions between radicals and molecules that are either unexcited or excited by $V-V$ exchange. Let us briefly consider these three sources of loss of selectivity.

1) It is clear from Fig. 3 that the enrichment coefficient of the reaction products falls by a factor of e when the pressure is reduced by 0.55 Torr. It follows from this that the $S^{32}F_6$ molecule succeeds in exchanging vibrational energy with the $S^{34}F_6$ molecule during the pulse (total pulse length is 180 nsec at the base). As a result of this rapid exchange, the $S^{34}F_6$ molecule which has received energy as a result of $V-V$ exchange succeeds in interacting with the radiation field and dissociates. We note that $V-V$ exchange occurs despite the fact that the mixture contains only about 4.2% of $S^{34}F_6$ and that only a small fraction of the $S^{32}F_6$ particles interacts with the radiation field. This shows that the cross section for $V-V$ exchange in the case of molecules in a highly excited vibrational state should be much greater than for molecules with $v=1$, for which the time between gas-kinetic collisions at a pressure of 0.5 Torr is about 160 nsec.

2) The second channel for loss of selectivity begins to operate after the end of the laser pulse, and the rate of loss of selectivity is determined by the ratio of the probabilities of vibrational-vibrational and vibrational-translational exchange. If the rate of $V-V$ exchange at

a given SF_6 pressure is independent of the buffer-gas pressure, the rate of $V-T$ relaxation can be substantially increased by adding the necessary buffer gas. We chose the ammonia molecule for this purpose. It accelerates the effective time of $V-T$ relaxation in SF_6 and has an exceedingly short relaxation time (τ_{V-T} = 1.4 μsec · Torr^{-1} [13]) as compared with the relaxation time in SF_6 (τ_{V-T} = 150 μsec · Torr^{-1} [14]). The 0–1 transition of the ν_2 (NH_3) vibration is at resonance (ΔE ~ 15 cm^{-1}) with ν_3 (SF_6) and, consequently, we have the possibility of an efficient transfer of vibrational energy from SF_6 to NH_3 and beyond into heat. Under the above conditions, the enrichment coefficient of the reaction products rose from 8 for pure SF_6 (at 0.2 Torr) to 12, indicating that there was a loss of selectivity after the laser pulse and that it might be possible to remove it. Unfortunately, the dissociation rate of SF_6 falls rapidly when NH_3 is added to the vessel. This is due to the very effective $V-V$ exchange, and it has not been possible to achieve a substantial increase in the pressure of the added NH_3.[1] An analogous effect is produced by adding oxygen at a pressure of 20 Torr.

3) The third channel of loss of selectivity is provided by chemical reactions. Here, it is important to note that we do not know the complete sequence of radical reactions leading to the formation[2] of the SOF_2 and SO_2F_4 molecules found among the reaction products. The fact that the enrichment is much smaller in SO_2F_4 than in SOF_2 suggests that a nonselective chemical reaction is taking place. It is difficult, at present, to establish the fraction of these reactions that is superimposed on the mass peaks due to the SO_2F_4 ion fragments because of the presence of a large background.

We draw attention to the fact that the addition of other "acceptor" radicals such as H_2, O_2, and NH_3 does not influence the composition of the resulting products. This leads us to the suggestion that the dissociation of SF_6 involves the formation not of fluorine atoms but, more likely, the F_2 and SF_4 molecules which heterogeneously react with hydroxyl groups on the vessel walls. When a glass vessel is replaced by a stainless steel container, this results in the appearance of some new products which can be seen in the mass spectrum but do not appear in the case of a glass container. These new products have not as yet been identified. The fact that the dissociation of SF_6 in the infrared field involves the separation of the F_2 molecule is not surprising if we recall that the molecules absorb more energy than is required for dissociation.[11]

5. DEPENDENCE OF THE DISSOCIATION RATE ON LASER INTENSITY AND ON COLLISIONS

Figure 4 shows the dissociation rate of SF_6 molecules as a function of the laser power at a number of frequencies. We emphasize that all the experiments were carried out in an unfocused beam, which enabled us to avoid the effect of the strong field inhomogeneity produced when the radiation was focused in the vessel. It is clear that a well-defined dissociation threshold appears at about 23 MW/cm^2. When the power was reduced by 8%, no appreciable dissociation could be de-

tected even though the number of laser pulses was sub-
stantially increased in order to increase the sensitivity.
After the threshold, the rate of dissociation increased
as I^3 and the threshold remained the same at different
frequencies [for the $P(12)$ and $P(16)$ lines]. Moreover,
it was found that the dissociation threshold was the same
when the composite $\nu_2 + \nu_6$ vibration was pumped although
the dissociation rate was then lower by a factor of 10. [9]

Figure 5 shows the quantum yield of the selective dis-
sociation of SF_6 by high-intensity infrared radiation as
a function of the incident intensity. As can be seen, the
relationship is linear in this range of values. It follows
that, for a maximum laser power of about 2×10^8 W/cm^2,
about 125 photons of CO_2 laser radiation are necessary
for the selective dissociation of one SF_6 molecule, i.e.,
roughly 12 eV of infrared energy.

We have also investigated the effect of collisions on
the rate of dissociation of SF_6 by infrared laser radia-
tion. Figure 6 shows the rate of dissociation as a func-
tion of SF_6 pressure and the pressure of different buffer
gases. It is clear that, in this range of pressures, the
dissociation rate decreases exponentially with increas-
ing pressure of both SF_6 and the buffer gas, i.e., in
accordance with the formula $W = W_0 \exp(-p/p_0)$, where
p_0 is the characteristic pressure at which the dissocia-
tion rate falls by a factor of e. For the SF_6 gas (Fig.
6a), the pressure $p_0(SF_6)$ is 0.55 Torr. The influence
of buffer gases on the rate of dissociation of SF_6 mole-
cules by high-power infrared radiation is also clear
from the data listed below:

Buffer gas:	Ar	O$_2$	C$_2$H$_4$	NH$_3$
$p_{0\,buff}/p_0(SF_6)$:	16.4	9.0	2.7	0.91

The fact that the pressures at which the dissociation
rate and the enrichment coefficient fall by a factor of e
are equal (see Figs. 3 and 6a) indicates that the main
reason for the reduction in the dissociation rate with in-
creasing pressure is $V-V$ exchange. This is confirmed
by the effect of buffer gases on the rate of dissociation.
In actual fact, the C_2H_4 and NH_3 molecules, which have
vibrational frequencies close to $\nu_3(SF_6)$, reduce the dis-
sociation rate to a greater extent than, for example, O_2.
The effect of argon on the dissociation rate of SF_6 in-
dicates that strong $V-T$ relaxation will also reduce the
dissociation probability.
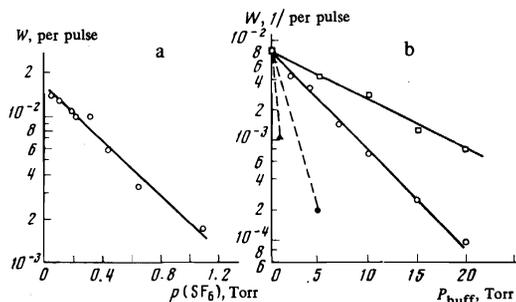
FIG. 6. Dissociation rate of SF_6 molecules as a function of
their pressure (a) and buffer-gas pressure (b): □—Ar, ○—
O_2, ●—C_2H_4, ▲—NH_3. Irradiation frequency 947.7 cm^{-1} [$P(16)$
line]; intensity 46 MW/cm^2 (a) and 25 MW/cm^2 (b); SF_6 pres-
sure 0.2 Torr (b).

6. DISCUSSION OF THE MECHANISM RESPONSIBLE FOR SELECTIVE DISSOCIATION

The experimental results reported in[10,11] and in the
present paper raise a number of important questions
which should be answered by the model involving reso-
nance multiphoton absorption of infrared radiation by
the vibrations of a polyatomic molecule. They are:

1. Why is it that the anharmonic barrier is unimpor-
tant even at the relatively moderate power densities of
about 10^7 W/cm^2 for both strong and very weak molecu-
lar vibrations?

2. Why can a molecule absorb energy from the in-
frared field which is much greater than its dissociation
energy?

3. Why is it that several molecular bonds can be
broken at the same time?

The following model of the process, briefly men-
tioned in[5], was discussed in our previous papers[11,15]
and has recently been reviewed in detail in[16,17]. This
model is based on a combination of two phenomena,
namely, resonance excitation of the first few vibration-
al levels, in which anharmonism is overcome by broad-
ening in the strong field, and the presence of a con-
tinuum of vibrational levels beginning with a certain vi-
brational state v_i. Suppose that the resonance excita-
tion is produced along the sequence of transitions $v = 0$
$\to v = 1 \to \dots \to v = v_i$, so that, when the laser radiation
frequency ν has its optimum value, the detuning due to
anharmonism will be, respectively, $\frac{1}{2}(v_i - 1)\Delta\nu_{anh}, \dots,$
$\frac{1}{2}(v_i - 1)\Delta\nu_{anh}$. However, when the broadening of the
transition by the strong field

$$\Delta\nu_{br} = \mu_{v,\,v+1}\mathscr{E}/hc \qquad (1)$$

is of the same order as the maximum shift due to an-
harmonism, $\frac{1}{2}(v_i - 1)\Delta\nu_{anh}$, the molecular system re-
mains in resonance with the field right up to the excita-
tion of v_i. The radiation intensity necessary to excite
the level v_i by this "brute force" method is given by

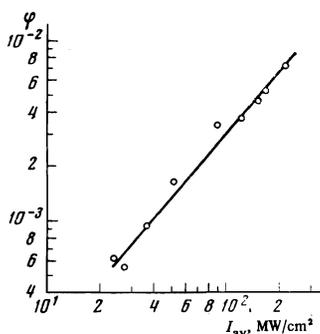$$I \approx \frac{c}{8\pi}\left[\frac{\Delta\nu_{anh}h}{2\mu}(v_i - 1)\right]^2, \qquad (2)$$

FIG. 5. Quantum yield in selective multiphoton dissociation
of SF_6 as a function of laser intensity (focused beam). Radia-
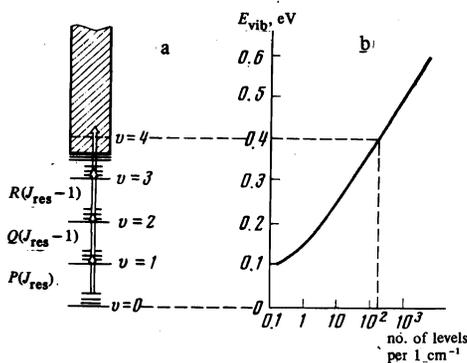tion frequency 940.5 cm^{-1} [$P(24)$] line.

FIG. 7. Vibrational-rotational transitions in the multiphoton dissociation of SF$_6$ by laser radiation (a); the figure also shows the density of vibrational levels as a function of the vibrational energy for the SF$_6$ molecule (b).

where $\bar{\mu}$ is the mean matrix element of the dipole moment of the sequence of vibrational transitions $v = 0 \to v = 1 \to \ldots \to v = v_f$. For example, for $\Delta\nu_{anh}/c = 6$ cm^{-1} and $\bar{\mu} \approx 0.1$ D, the intensity necessary for the excitation of the $v_f = 4$ level in this model of compensation of anharmonism by field broadening is $I \approx 4 \times 10^{10}$ W/cm^2.
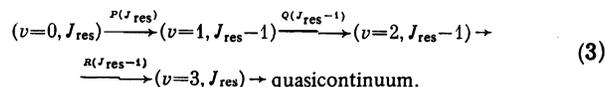
The density of vibrational levels increases rapidly beyond a certain value of the vibrational energy, so that they begin to overlap, forming a near-continuum of weak absorption well below the dissociation limit. Figure 7b shows the density P of vibrational levels as a function of the vibrational energy of the SF$_6$ molecule, calculated from the formulas given in[18]. It is clear that, at energies of $4\hbar\omega$ ($\hbar\omega$ is the quantum of vibrational energy), the level density is 200 per 1 cm^{-1}. The coefficient of absorption in the quasicontinuum is inversely proportional to the increase in the vibrational level density, but the infrared radiation is always in resonance with the quasicontinuum. A sufficiently strong infrared field is, therefore, capable of exciting a molecule that has passed through the intermediate region of anharmonism with a low density of vibrational levels and beyond this, right up to the dissociation limit. Of course, the separation of multiphoton infrared absorption by a polyatomic molecule into two different stages is quite arbitrary since, in the absence of collisions, the molecule interacts coherently with the field during the entire period of time.

The interaction of infrared radiation with the quasicontinuum in which all the vibrations of the polyatomic molecule participate in absorption can, in principle, explain the accumulation of a large amount of energy by the molecule. In actual fact, each vibrational mode can store up an amount of energy of the order of the energy of dissociation of the molecular bond associated with it. The total vibrational energy of all the modes can approach the total energy of dissociation of the molecule into individual fragments. Consequently, all the molecular bonds can, at least in principle, be broken simultaneously. The absorption of infrared radiation in the quasicontinuum due to transitions between highly excited vibrational levels of composite and overtone vibrations should, therefore, provide at least a general answer to questions 2 and 3 above.

However, the compensation of anharmonism by broadening in a strong field will not provide the answer to the first of the above three questions. Firstly, as noted above (see Fig. 4), the selective dissociation of the SF$_6$ molecule will already occur at laser intensities $I \approx 23$ MW/cm^2. At such intensities, the field broadening $\Delta\nu_{br}$ amounts to only 0.4 cm^{-1} ($\mu \approx 0.3$ D[12,19]), which is obviously insufficient to compensate the anharmonism $\Delta\nu_{anh} \approx 6$ cm^{-1}. Secondly, when the strong infrared radiation operates on the weak composite vibrations of the SF$_6$ molecule, the selective dissociation process occurs for the same threshold intensity (see Fig. 4) although for such levels $\Delta\nu_{br} \ll 0.4$ cm^{-1}. Thus, the main difficulty in explaining the collisionless dissociation of molecules in an infrared laser field with intensity of the order of 10^7 W/cm^2 is the precise method whereby anharmonism is overcome in the lower vibrational transitions.

A mechanism whereby the effect of anharmonism during the excitation of SF$_6$ molecules by laser radiation can be overcome was put forward in[20] and reduces to the following triple vibrational-rotational resonance (Fig. 7a):

$$(v=0, J_{res}) \xrightarrow{P(J_{res})} (v=1, J_{res}-1) \xrightarrow{Q(J_{res}-1)} (v=2, J_{res}-1) \to$$
$$\xrightarrow{R(J_{res}-1)} (v=3, J_{res}) \to \text{quasicontinuum.} \tag{3}$$

Let us consider the conditions under which this resonance is possible. It is clear from (3) that "rotational" compensation of anharmonism is possible when the widths $\delta\nu_P$, $\delta\nu_R$ of the P and R branches are greater than the shift of the vibrational level due to anharmonism:

$$\Delta\nu_{anh} < \delta\nu_P, \ \delta\nu_R. \tag{4}$$

This condition is satisfied for SF$_6$ (see Table I) and is usually valid for polyatomic molecules. Let ν be the laser radiation frequency so that, for the above three transitions, we have the following set of equations:

$$\begin{aligned} \nu &= \nu_0 - 2BJ & (v=0, J) \to (v=1, J-1), \\ \nu &= \nu_0 - \Delta_{anh} & (v=1, J-1) \to (v=2, J-1), \\ \nu &= \nu_0 - 2\Delta_{anh} + 2BJ & (v=2, J-1) \to (v=3, J), \end{aligned} \tag{5}$$

where ν_0 is the frequency of the vibrational transition $v = 0 \to v = 1$, and B is the rotational constant which is assumed to be the same for all the vibrational levels (the interaction between vibrations and rotations is neglected). The equations given by (5) are satisfied when $2BJ_{res} = \Delta\nu_{anh}$ and, consequently, the triple vibrational-rotational resonance defined by (3) can take place. Because of the broadening of the rotational–vibrational

TABLE I. Parameters of the vibrational-rotational spectrum of SF$_6$ in the ν_3 band.[21,22]

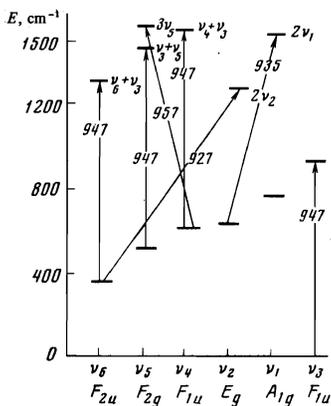| $\delta\nu_P$, cm^{-1}	$\delta\nu_R$, cm^{-1}	B, cm^{-1}	ζ_3	J_{max}
8	6	0.054	0.74	47

FIG. 8. Some allowed dipole transitions in the SF_6 molecule in the region of 950 cm^{-1}.[23]

lines in the infrared laser field, this resonance can occur on a group of rotational sublevels for which

$$|2BJ - \Delta_{anh}| \lesssim \Delta\nu_{br}. \tag{6}$$

The required broadening of the spectral line by the field in the case of the process defined by (3) is relatively moderate, i.e.,

$$\Delta\nu_{br} \gtrsim 2B(1-\zeta) \tag{7}$$

(ζ is the Coriolis interaction constant) and, in the case of SF_6 molecules, amounts to about 0.025 cm^{-1}.

As a result of the "triple resonance," molecules with quantum number J satisfying (6) are found to occupy the $v = 3$ level. When the vibrational level density $P(E)$ of a molecule of energy $E = 4\hbar\omega$ satisfies the condition

$$P^{-1}(4\hbar\omega) < \Delta\nu_{br}, \tag{8}$$

[and this is satisfied by SF_6 (see Fig. 7b)], the molecules can execute direct transitions from the $v = 3$ state to the vibrational "quasicontinuum," and then reach the dissociation limit.

The above model enables us to interpret the experimentally established characteristics of the dissociation of the SF_6 molecule by infrared laser radiation. The resonance properties of the dissociation process are determined by the rotational–vibrational Q-transitions $v = 1 \to v = 2$ with $J = J_{res}$. Consequently, the maximum dissociation rate will coincide with the Q branch of the $v = 1 \to v = 2$ transitions and will be shifted relative to the Q branch for the $v = 0 \to v = 1$ transition by the amount $\Delta\nu_{anh}$ toward lower frequencies in the case of positive anharmonism and toward higher frequencies in the case of negative anharmonism.

The threshold laser intensity for the dissociation process is not connected with the overcoming of anharmonism on the first few vibrational levels. Our measurements of laser energy absorbed by the SF_6 gas as a function of incident intensity show that the absorption reaches saturation for $I_s \approx 30$ kW/cm^2 (SF_6 pressure 0.35 Torr). The experimentally established threshold intensity for the dissociation of SF_6 (~ 23 MW/cm^2) is determined by the saturation of the quasicontinuum and not by the sequence of rotational–vibrational transi-

tions given by (3). Let us estimate the absorption cross section in the quasicontinuum, σ_{cont}, using the following expression for the power necessary to saturate absorption through transitions in the vibrational quasicontinuum:

$$P_{cont} \approx \hbar\omega/\sigma_{cont}\tau_p, \tag{9}$$

where τ_p is the laser pulse length ($\tau_p \ll \tau_{rel}$—the characteristic time for the relaxation of the excitation in the region of the quasicontinuum). Substituting $P_{cont} = P_{thr}$, we find that $\sigma_{cont} \approx 10^{-20}$ cm^2.

The change in the resonance characteristic under the influence of collisions with the buffer gas is probably connected with the appearance of the competing channel

$$(v=1, J_{res}) \xrightarrow{P(J_{res})} (v=2, J_{res}-1) \xrightarrow{Q(J_{res}-1)} (v=3, J_{res}-1) \to \text{quasicontinuum} \tag{10}$$

in addition to (3). This new channel appears after the redistribution of molecules over the rotational states of the first vibrational state, due to the rotational relaxation during the laser pulse, and leads to the appearance of the additional maximum, the position of which coincides with the Q transition of the $v = 2 \to v = 3$ vibration.

We also note that, for the SF_6 molecule with a relatively low quasicontinuum limit (Fig. 7b), the dissociation of a small fraction of molecules occupying the first vibrational level ($\sim 1\%$ at 300 °K) because of the Boltzmann distribution is always possible in accordance with the scheme $v = 1 \to v = 2 \to$ quasicontinuum, provided the separation between the vibrational states is compensated in the region of $3\hbar\omega$.

We note that the rotational compensation of anharmonism will not explain the width of the resonance characteristic $W(\nu)$. This is so because this particular model is a highly simplified version of the actual process. In reality, there can be transitions from high-lying vibrational levels to different composite vibrational states. Some of these transitions are shown in Fig. 8. They provide additional thermal Q branches in the infrared absorption line spectrum of SF_6 (see Fig. 8), and the weaker of them may not appear but provide a considerable contribution to nonlinear absorption in the strong infrared laser field. The process defined by (3) is also insufficient to enable us to explain the dissociation of polyatomic molecules in a strong infrared laser field when the limit of the vibrational quasicontinuum of these molecules exceeds $4\hbar\omega$.

However, the above model does provide a good explanation of many of the experimental results on SF_6 dissociation, and enables us to put forward a new method for the dissociation of molecules in a two-frequency infrared field of a laser. The principle of this method is as follows. Selective excitation of molecules by the triple rotational–vibrational resonance is produced in a sufficiently weak infrared laser field at frequency ν_1 which is in precise resonance with the Q branch of the 1–2 transition, and the subsequent dissociation occurs through the quasicontinuum of vibrational levels by a strong infrared laser field at frequency ν_2 lying outside
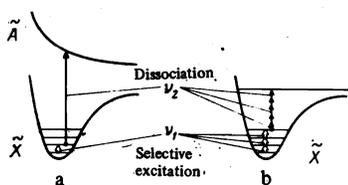
FIG. 9. Comparison of two-step dissociation (a) and two-frequency multiphoton dissociation (b) of molecules by high-power infrared laser radiation.

the absorption band. This two-frequency process is illustrated in Fig. 9b.

The advantage of this method is that the first selecting stage is produced in the infrared laser field which gives rise to only a slight broadening of the absorption line [for example, for SF_6, (7) yields $\Delta\nu_{br} \approx 0.025$ cm^{-1}] and, consequently, does not lead to loss of selectivity due to the overlapping of absorption lines in the case of molecules of different isotopic composition. Subsequent dissociation of the selectively excited molecules can be produced by a strong infrared laser field [$I_2 \gg \hbar\nu_2/\sigma_{cont}\tau_p$ (9)], the frequency of which is sufficiently different from the infrared absorption lines of both isotopic molecules and, consequently, does not produce the broadening of the excitation resonance. This method may turn out to be very useful, especially for molecules with small isotopic shifts in the infrared absorption spectrum. Here, we are essentially dealing with the method of selective step-by-step dissociation of molecules in the two-frequency laser field in which selective excitation is produced by infrared radiation, and the dissociation of the selectively excited molecules is produced by radiation tuned to resonance with the electronic transition (Fig. 9a).[24] The essential difference is that, in the case of polyatomic molecules, the presence of the vibrational quasicontinuum enables us to dissociate selectively-excited molecules by infrared radiation without the use of electronic transitions.

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[1])Effective dissociation of the ammonia molecules has also been observed.

[2])SOF$_2$ can also appear as a result of the following heterogeneous reaction with water molecules sorbed by the walls: $SF_4 + H_2O \rightarrow SOF_2 + 2HF$.

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