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Multiple Photon IR Dissociation of $(\text{CF}_3)_3\text{CBr}$ and Synthesis of $(\text{CF}_3)_3\text{Cl}$ in Laser-Radical Chemical Reactions

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CO_2 -laser induced multiple photon excitation and dissociation of the molecule $(\text{CF}_3)_3\text{CBr}$ in the environment of I_2 has been studied experimentally and theoretically. The synthesis of the $(\text{CF}_3)_3\text{Cl}$ molecule in laser-radical chemical reactions with high yield has been demonstrated.

I. INTRODUCTION

Multiple photon (MP) dissociation of molecules under powerful IR laser radiation^{1,2} is becoming a simple and universal tool for fast production of high concentrations of various free radicals. These radicals can be used for selective synthesis of molecular compounds in radical gas-phase chemical reactions. In MP dissociation of molecules the free radicals are generated under highly nonequilibrium conditions. The products of laser-radical chemical reactions may differ greatly from the products of their corresponding thermal radical reactions because under nonstationary conditions the temporal factors may be also essential besides the thermodynamic ones. IR laser-radical chemical synthesis of such molecules as BCl_2H , SF_5NF_2 , CF_3Br and CF_3I has been studied in several works.³⁻⁶ It is shown

in these works that there is a substantial difference in the composition of products of IR laser-radical reaction and the same reactions performed under thermal initiation.

It is clear that in case of the selective highly effective process of IR laser-radical chemical synthesis, the optimal situation is achieved when the laser radiation energy is spent only to produce desired radicals and is not expended for undesired secondary radicals. In case of MP dissociation of relatively simple molecules, for example BCl_3 , CF_3Br and CF_3I , used for production of radicals in the above mentioned works, this situation actually takes place which is caused by two factors. First, the free radicals resulting from MP dissociation of these molecules have no strong absorption bands coinciding with the excited bands of the original molecules. Second, these radicals are rather simple which also impedes their further MP excitation and dissociation.

However, as shown by the experiments on MP dissociation of a great number of molecules,² dissociation gives birth to several different radicals. First of all this is possible when the radical resulting from the primary act of MP dissociation can effectively absorb the radiation which excites the original molecule. In many cases, especially with complex molecules or at sufficiently high energy densities of laser radiation, this causes further fragmentation of the molecules. A classical example of such successive dissociation is the MP dissociation of the SF_6 molecules forming the radicals SF_5 and then SF_4 .⁷ Besides, situations can take place when in a molecule with similar dissociation energies in different channels the rates of its dissociation in these channels become comparable in magnitude. This leads to competition of different dissociation channels and gives birth to different fragments.⁸ It is evident that the processes of fragmentation for selective laser-radical chemical synthesis are undesirable. Therefore, a condition of MP dissociation should be chosen in order to eliminate these processes.

This work deals with IR MP excitation and dissociation of the 14-atom molecule $(\text{CF}_3)_3\text{CBr}$ in the environment of iodine for the purpose of synthesis of the $(\text{CF}_3)_3\text{CI}$ molecule in an IR laser-radical chemical reaction. In MP dissociation of the $(\text{CF}_3)_3\text{CBr}$ molecule the undesirable fragmentation may be rather essential which materially decreases the efficiency of synthesis of $(\text{CF}_3)_3\text{CI}$. But, as our studies show, the right choice of conditions of MP excitation allows a fairly high dissociation yield of $(\text{CF}_3)_3\text{CBr}$ and at the same time a low level of undesirable fragmentation to be provided. In this way it makes the process of synthesis of $(\text{CF}_3)_3\text{CI}$ sufficiently

effective. A simple theoretical model of MP dissociation of $(\text{CF}_3)_3\text{CBr}$ enables us to explain quite satisfactorily the experimental data.

2. EXPERIMENTAL SETUP

MP excitation and dissociation of the $(\text{CF}_3)_3\text{CBr}$ molecule was carried out with a TEA CO_2 laser (Figure 1) with selection of vibrational-rotational lines. The lines were selected by turning the diffraction grating. With the use of a plane and a concave mirrors the radiation was directed into the cell. The radius of curvature of the mirror was chosen so that the caustic was longer than the cell. Directly before the cell a diaphragm ($d = 3\text{--}5$ mm) was placed transmitting only the central part of the beam. In this manner we could produce a beam rather uniform in section and length. Attenuators made of CaF_2 were used to change the pulse energy. A part of radiation was reflected with a plane-parallel plate made of NaCl to the

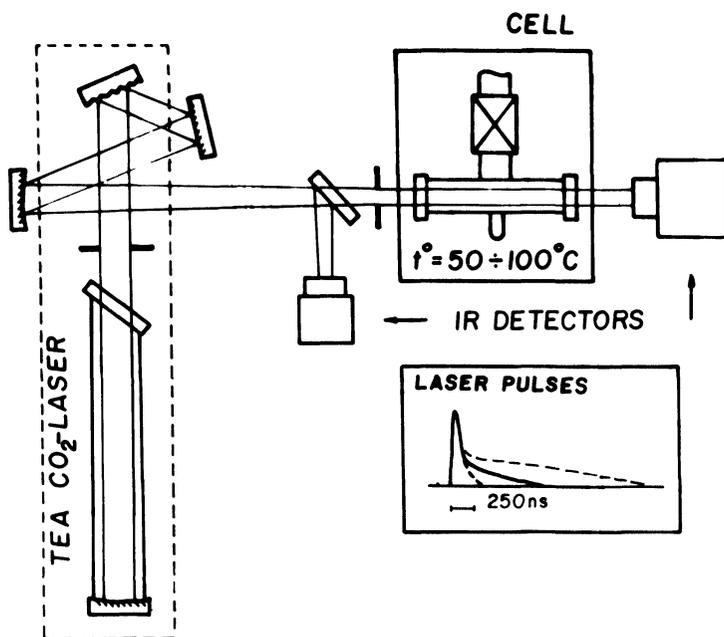


FIGURE 1 Experimental setup.

IR detector to control the input energy. A calorimeter was used to calibrate it and measure the output energy. The laser pulse was standard in form with its leading spike duration of about 200 ns and a tail duration 0.2 μ s. The effective pulse duration τ is determined by the ratio of energy in its front and tail. It was varied by changing the content of nitrogen in the gas mixture. The pulse shape was determined for each mixture with a "photon-drag" detector. The experiments on MP dissociation and synthesis made use of stainless-steel cells 12.2 cm long, with their internal diameter of 1.4 cm and windows of NaCl. Some iodine crystals were placed in a small appendix of the cell. The cell was located in a thermostat; the temperature variation in the thermostat allowed the pressure of vapor in the cell volume to change. The composition of reaction products in the cell was controlled mainly with an IR spectrometer as well as a mass spectrometer. MP absorption in $(\text{CF}_3)_3\text{CBr}$ was measured per one pass in cells of 100 cm and 12.2 cm and also with the use of an optical-acoustic detector.⁹

3. MULTIPLE PHOTON ABSORPTION OF $(\text{CF}_3)_3\text{CBr}$

The $(\text{CF}_3)_3\text{CBr}$ molecule has two relatively weak absorption bands like ν_{cc_3} ¹⁰ in the region of action of CO_2 laser: $\nu_6 = 934 \text{ cm}^{-1}$ and $\nu_{21} = 963 \text{ cm}^{-1}$. The spectra of linear IR absorption for $(\text{CF}_3)_3\text{CBr}$ and $(\text{CF}_3)_3\text{CI}$ at 295 K are given in Figure 2.

Figure 3 shows a section of the spectrum of the IR laser radiation energy $\bar{\epsilon}$ absorbed in $(\text{CF}_3)_3\text{CBr}$ varying with frequency, for a radiation energy fluence $\phi = 0.32 \text{ J/cm}^2$. The value of $\bar{\epsilon}$ is measured with the optoacoustic method. There is a conventional shift to the long-wave side in the MP absorption spectrum relative to the linear spectrum⁹ which is conditioned by vibration anharmonicity.

The dependence of absorbed energy $\bar{\epsilon}$ on radiation energy density (Figure 4) was measured both in pure $(\text{CF}_3)_3\text{CBr}$ and in its mixture with iodine for varying duration of IR pulse. The dependence $\bar{\epsilon}(\phi)$ observed is nearly linear. The cross-section of MP absorption slightly decreases with an increase in ϕ which can be usually observed in complex molecules with a low boundary of quasi-continuum, for example in S_2F_{10} .¹¹ In pure $(\text{CF}_3)_3\text{CBr}$ with $\phi < 3 \text{ J/cm}^2$ the increase of $\bar{\epsilon}$ somewhat slows down which seems to be connected with dissociation of a part of molecules during a radiation pulse. As may be seen from Figure 4, the absorbed energy in the presence of 12 Torr iodine is much higher than in pure $(\text{CF}_3)_3\text{CBr}$. This may be

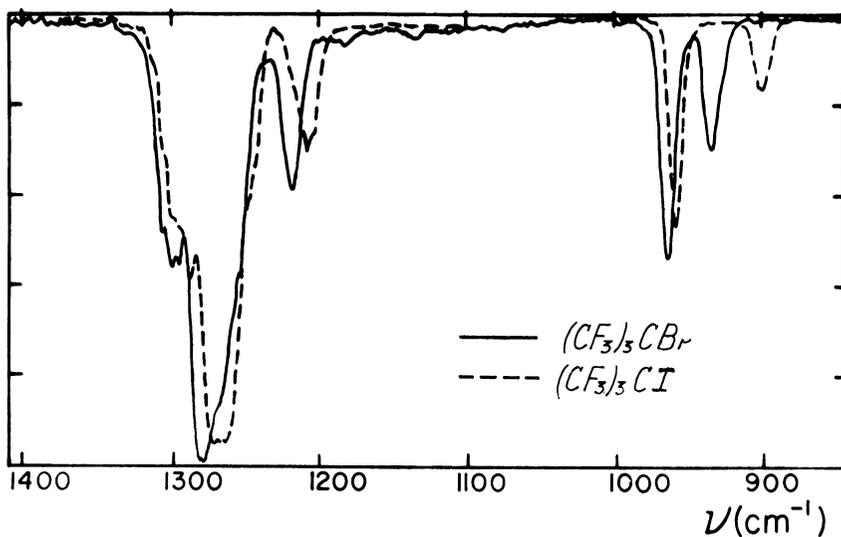


FIGURE 2 Linear IR absorption spectra of $(CF_3)_3CBr$ (1) and $(CF_3)_3CI$ (2) molecules. $P = 1$ Torr; cell length = 12.2 cm.

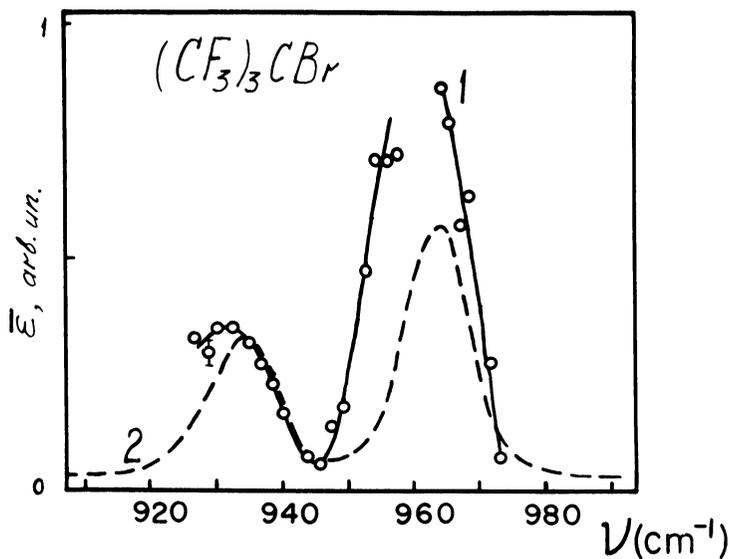


FIGURE 3 1—MP absorption spectrum of $(CF_3)_3CBr$ molecule. $P = 0.6$ Torr, $\phi = 0.32$ J/cm^2 . 2—Linear IR absorption spectrum.

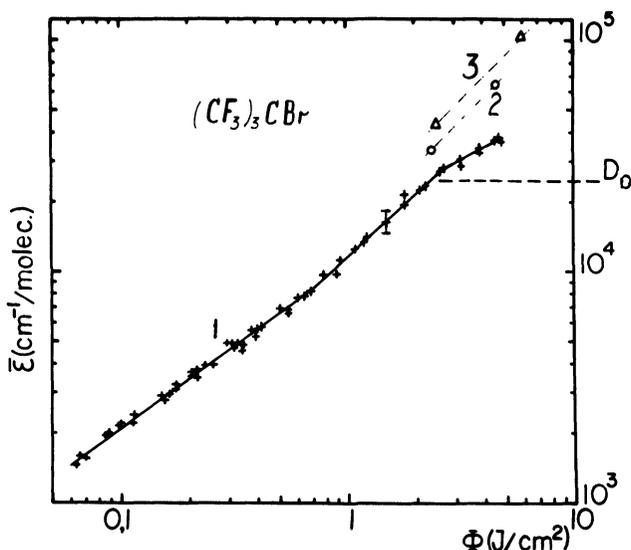


FIGURE 4 Dependence of average absorbed energy on laser energy fluence. 1. $P_{(CF_3)_3CBr} = 0.6$ Torr, $\tau = 100$ ns; 2. $P_{(CF_3)_3CBr} = 2$ Torr, $P_{I_2} = 12.5$ Torr, $\tau = 100$ ns; 3. $P_{(CF_3)_3CBr} = 2$ Torr, $P_{I_2} = 12.5$ Torr, $\tau = 1.5$ μ s $\nu = 934.90$ cm^{-1} .

explained by two causes. First, the effect of rotational relaxation increases the fraction q of molecules involved in the process of MP excitation. Second, there may be an effect of vibrational deactivation produced by the iodine molecules. Indeed, since the cross-section of MP absorption decreases with an increase in excitation level, the processes of V-V exchange and V-T,R relaxation, as the $(CF_3)_3CBr$ molecules collide with I_2 , must cause the value of $\bar{\epsilon}$ to increase.

To study the influence of rotational relaxation on MP excitation of $(CF_3)_3CBr$ we measured the fraction of molecules involved in the process of MP excitation. The value of q was found from the maximum relative increase of $\bar{\epsilon}$ when a buffer gas is added. The value of q turned out to be almost independent of ϕ in the measured range of ϕ from 0.03 to 7 J/cm². The values of q measured near the maximum of linear absorption bands at the pressure of $(CF_3)_3CBr$ $P = 0.14$ Torr and $\tau = 100$ ns were: with $\nu = 967.71$ cm^{-1} , $q = 0.85 \pm 0.1$; and with $\nu = 934.90$ cm^{-1} , $q = 0.7 \pm 0.1$. The values of q measured with $P \geq 0.6$ Torr and with the same frequencies were near unity. This means that the main cause of the increase in absorbed energy, when iodine is added (Figure 4), is a considerable vibrational deactivation of the $(CF_3)_3CBr$ molecules during their

collisions with I_2 . This conclusion is also supported by the results of measurements of the dissociation yield of $(CF_3)_3CBr$ in the atmosphere of iodine.

4. MULTIPLE PHOTON DISSOCIATION OF $(CF_3)_3CBr$ AND SYNTHESIS OF $(CF_3)_3CI$

A considerable fraction of molecules of $(CF_3)_3CBr$ dissociates in one radiation pulse with $\phi > 1-2 \text{ J/cm}^2$. As a result of MP dissociation of $(CF_3)_3CBr$ in the environment of I_2 , the final products contain the desired product $(CF_3)_3CI$ and the secondary product CF_3I . The yield and composition of end products in this case depend greatly on the conditions of excitation. Figure 5 shows how the radiation energy fluence ϕ affects the

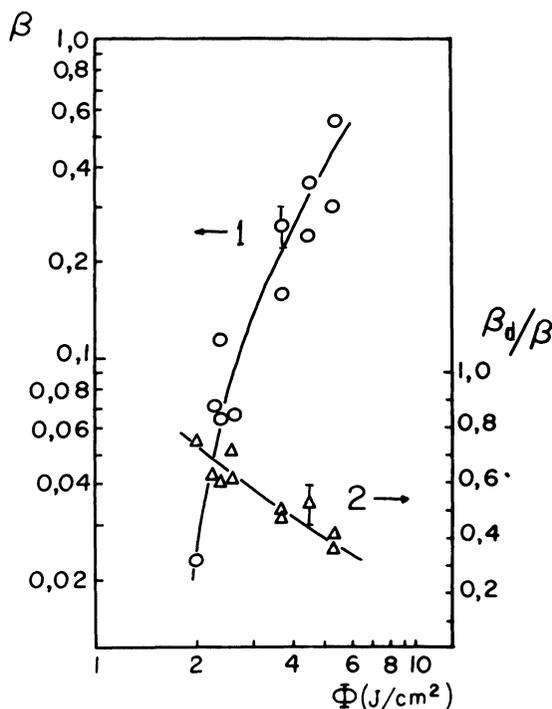


FIGURE 5 Dependence of dissociation yield— β (1), and relative fraction of desired radicals (β_d/β) (2) on the laser energy fluence. $P_{(CF_3)_3CBr} = 0.9 \text{ Torr}$; $P_{I_2} = 12 \text{ Torr}$ ($T = 75^\circ\text{C}$); $\nu = 934.90 \text{ cm}^{-1}$; $\tau = 800 \text{ ns}$.

dissociation yield of β of $(\text{CF}_3)_3\text{CBr}$ as well as the fraction of dissociated molecules β_d/β used for the formation of the desired radical $(\text{CF}_3)_3\text{C}\cdot$ which is essential for synthesis of $(\text{CF}_3)_3\text{CI}$ in the ensuing reaction with I_2 . The value of β increases rapidly with an increase of ϕ . With $\phi = 5.5 \text{ J/cm}^2$ around 50% molecules in the volume under exposure dissociate during one pulse. At the same time the value of β_d/β drops monotonically with an increase in ϕ , and with $\phi = 5.5 \text{ J/cm}^2$ just about 40% dissociated molecules are spent to form the desired radical $(\text{CF}_3)_3\text{C}\cdot$.

Figure 6 illustrates the dependence of β and β_d/β on the pressure of molecular iodine P_{I_2} controlled by the variations in the temperature of the cell walls. At low P_{I_2} the value of β increases with an increase of P_{I_2} which is due to prevention of recombination of the radicals $(\text{CF}_3)_3\text{C}\cdot$ and $\text{Br}\cdot$. With $P_{\text{I}_2} > 6-8 \text{ Torr}$ the value of β drops rather quickly. This can be evidently explained by deactivation of vibrational excitation of $(\text{CF}_3)_3\text{CBr}$ in collisions with I_2 . At the same time, as P_{I_2} builds up the value of β_d/β increases monotonically. So, an increase in the dissociation yield β at varying radiation energy fluence or I_2 pressure leads to a decrease in the relative yield of desired radicals β_d/β .

The situation is more complicated when the IR radiation frequency varies (Figure 7). On the short-wave side of the spectrum an increase in β also brings about a decrease in β_d/β . But on the long-wave side β_d/β increases

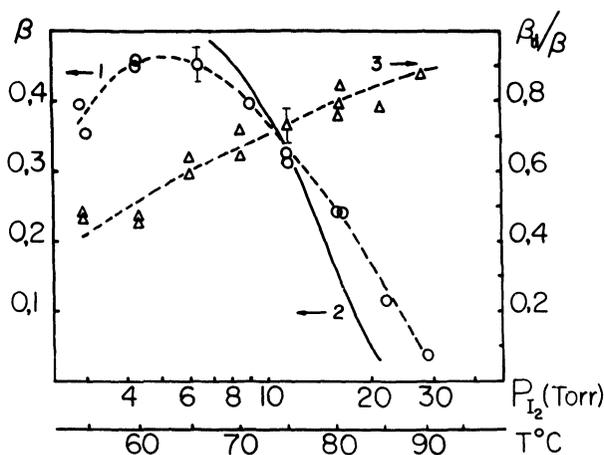


FIGURE 6 Dependences of β (1,2) and β_d/β (3) values on I_2 pressure. $P_{(\text{CF}_3)_3\text{CBr}} = 0.9 \text{ Torr}$, $\phi = 5.5 \text{ J/cm}^2$, $\tau = 800 \text{ ns}$. 1 and 3—experiment, 2—model.

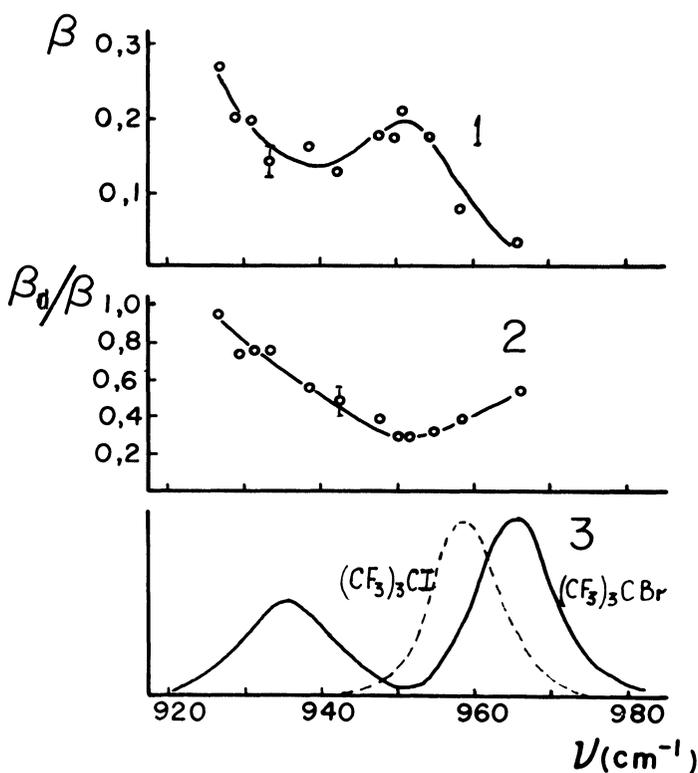


FIGURE 7 Spectral dependences of β (1) and β_d/β (2) values. $P_{(\text{CF}_3)_3\text{CBr}} = 0.9$ Torr; $P_{I_2} = 12$ Torr ($T = 75^\circ\text{C}$); $\phi = 4 \text{ J/cm}^2$. 3—linear IR absorption spectra of $(\text{CF}_3)_3\text{CBr}$ and $(\text{CF}_3)_3\text{CI}$.

simultaneously with an increase in β . This is why on the long-wave side of the spectrum we can realize such optimal conditions for synthesis of $(\text{CF}_3)_3\text{CI}$ as a high dissociation yield and low losses of original substance in the formation of secondary products.

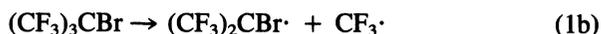
The process of MP dissociation of $(\text{CF}_3)_3\text{CBr}$ is essentially affected by the IR radiation pulse duration. In the table the values of β and β_d/β are given for three different values of IR radiation duration. It may be seen that with decreasing τ , the value of β the same, the value of β_d/β increases considerably, i.e., the process of synthesis of $(\text{CF}_3)_3\text{CI}$ becomes more efficient. In qualitative respect this effect can thus be explained: As the pulse duration is reduced, the fraction of the $(\text{CF}_3)_3\text{C}\cdot$ radicals formed

during an IR radiation pulse and which are able to absorb energy and dissociate, with the $\text{CF}_3\cdot$ group breaking away, is decreased. For quantitative interpretation of the results obtained it is necessary that the dynamics of MP dissociation of $(\text{CF}_3)_3\text{CBr}$ should be considered.

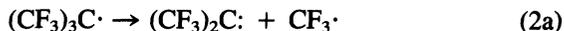
5. INTERPRETATION OF RESULTS

Possible processes of MP excitation and dissociation giving observed products are presented in Figure 8.

The $(\text{CF}_3)_3\text{CBr}$ molecule can dissociate in one of the two channels:



The resulting radicals can also absorb laser radiation and decompose:

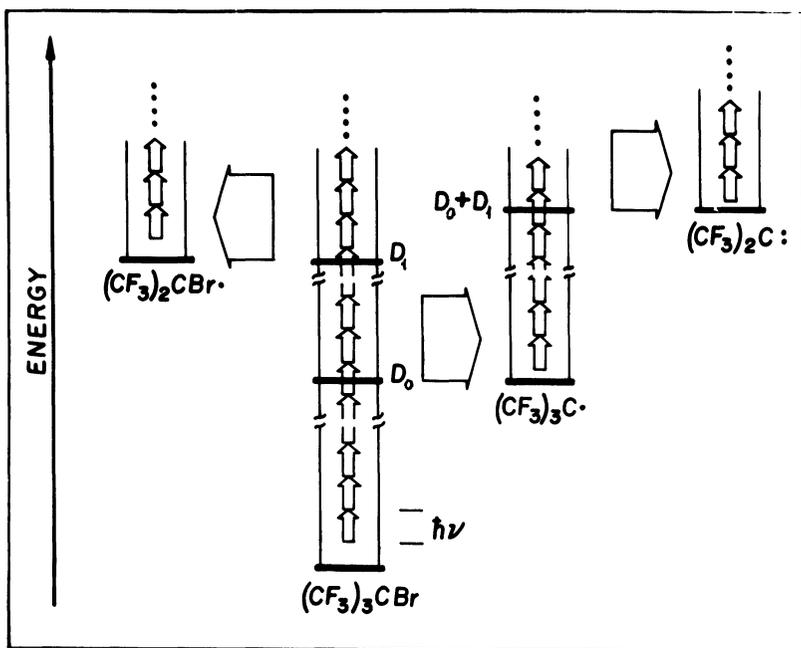


The end products CF_3I and $(\text{CF}_3)_3\text{CI}$ are synthesized then in such reactions



We are not going to consider this stage in detail since the experiments were performed with an excess of I_2 which enables us to disregard the recombination reactions, i.e., reverse reactions (1) and (2). So we merely assume that all formed (and not decomposed then) radicals are bound with iodine.

First of all, it should be pointed out that the $\text{CF}_3\cdot$ radical can be formed in two different channels: 1) immediately in dissociation of $(\text{CF}_3)_3\text{CBr}$ [reaction (1b), "a parallel channel"]; and 2) in dissociation of the $(\text{CF}_3)_3\text{C}\cdot$ radical [reaction (2a), "a successive channel"]. We think that in our case the main contribution is made by the successive channel. If $\text{CF}_3\cdot$ were

FIGURE 8 Possible pathways of $(CF_3)_3CBr$ molecule dissociation.

formed in the parallel channel, the both basic products $(CF_3)_3CI$ and CF_3I would result directly from decomposition of $(CF_3)_3CBr$ [reactions (1a) and (1b)], and then their ratio would be determined exclusively by the excitation level of the original molecule. In this case β_d/β would decrease with increasing energy since at low excitation levels the breakaway of the Br atom is preferential due to a smaller bond energy, and at high excitation the preferential breakaway of $CF_3\cdot$ is conditioned by statistical factors. Since the total expenditure of $(CF_3)_3CBr$ also depends on the level of its excitation, in case of formation of CF_3I in the parallel channel one may expect that the ratio of the products will drop monotonically with increasing β and not depend on other factors. From Figure 7 we can see, however, that with excitation at the frequencies of 930 and 951 cm^{-1} at the same yields $\beta = 0.2$ the product ratios will be radically different: 0.8 and 0.3 respectively. This difference may be explained only if we attribute the main contribution to the formation of $(CF_3)_3CI$ to the successive channel provided that the $(CF_3)_3C\cdot$ radical has a much smaller absorption cross-section in the region of 930 cm^{-1} .

The conclusion on a small contribution of the parallel channel is also supported by calculating the decay rate in reactions (2a) and (1b) with the use of the RRKM theory.¹² Even though the absolute accuracy of these calculations is not large because of nondeterminacy in the choice of activated complex parameters, the relative position of the curves given in Figure 9 allows us to conclude that with the real excitation energies $E \approx 60\,000\text{ cm}^{-1}$ reaction (1b) may be neglected as compared to (1a).

In Figure 9 we can see another peculiarity characteristic of dissociation of large molecules: their decay rate increases rather slowly with increasing

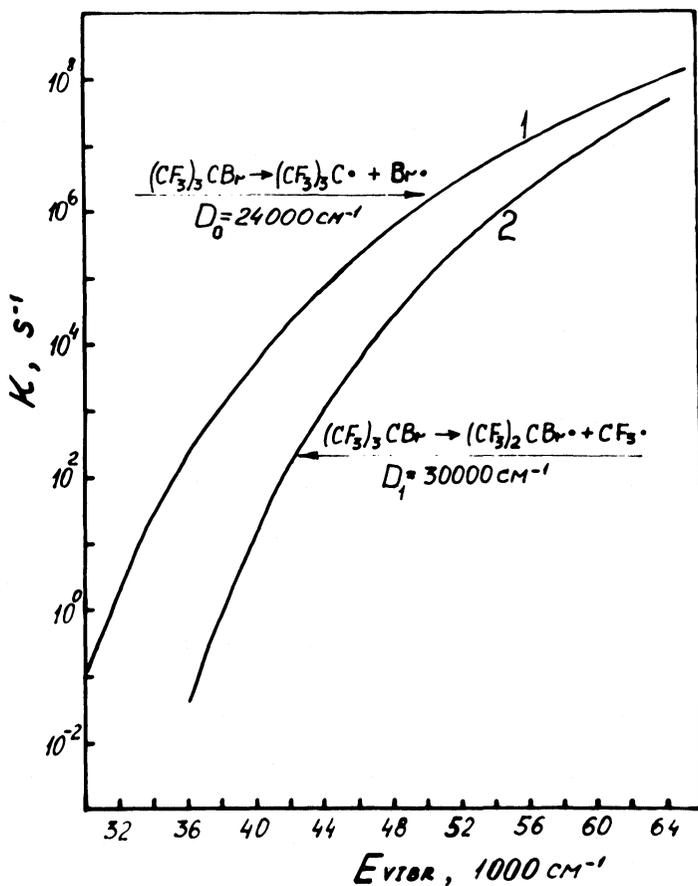
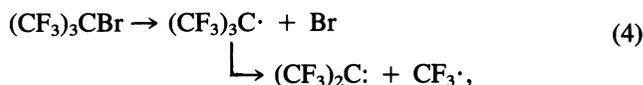


FIGURE 9 Dependence of monomolecular decay rates of $(\text{CF}_3)_3\text{CBr}$ molecule on their vibrational energy. 1— $(\text{CF}_3)_3\text{C}\cdot + \text{Br}\cdot$ —decay; 2— $(\text{CF}_3)_2\text{CBr}\cdot + \text{CF}_3\cdot$ —decay.

energy with the result that their strong excitation over the dissociation limit becomes possible. The decay rate of $(\text{CF}_3)_3\text{CBr}$, for example, will be only $k_{D_0} = 6.2 \cdot 10^5 \text{ s}^{-1}$ with $E = 2D_0 = 48\,000 \text{ cm}^{-1}$, and even if it is higher than the dissociation limit by three times (i.e., with $E = 3D_1 = 72\,000 \text{ cm}^{-1}$) the decay having a constant $k_{D_0} = 5.3 \cdot 10^8 \text{ s}^{-1}$ may compete with further acquiring of energy (with $\tau = 100 \text{ ns}$ and $\bar{\epsilon} \approx 50\,000 \text{ cm}^{-1}$ the rate of photon absorption equals $5 \cdot 10^8 \text{ s}^{-1}$). So, in a pulsed IR field, rather complex polyatomic molecules can easily acquire energy that exceeds by 2 or 3 times the energy of rupture of the weakest bond. It is a low decay rate of $(\text{CF}_3)_3\text{CBr}$ that causes the value of β to drop quickly as P_{I_2} increases (Figure 5). Indeed, vibrational deactivation of the molecule during its collisions with the buffer gas occurs in a time $\tau + 1/k_{D_0}$. According to the estimates given above, this time for $(\text{CF}_3)_3\text{CBr}$ may exceed considerably the pulse duration. At the same time, in case of such a simple molecule as CF_3Br the decay rate is high enough even if its excitation is a little higher than the dissociation limit and vibrational deactivation occurs in a time of the order of a pulse duration. As a result, the rate of decrease of β with an increase in P_{I_2} is an order lower for the CF_3Br molecule than for $(\text{CF}_3)_3\text{CBr}$.⁶

Taking into consideration the fact that the parallel channel (1b) turns out to be unessential, we want to demonstrate now that the kinetics of formation of the basic $[(\text{CF}_3)_3\text{CI}]$ and secondary $[\text{CF}_3\text{I}]$ products agrees with the following simple scheme



if the assumption is made that the radicals $(\text{CF}_3)_3\text{C}\cdot$ and $\text{CF}_3\cdot$ are completely bound with iodine. The validity of such interpretation is confirmed by calculations within a simple model when the kinetics of formation of each of the radicals is described by an Arrhenius-like expression

$$\begin{aligned}
 \frac{dn_i}{dt} &= n_{i-1} A_{i-1} \exp\left(-\frac{S_{i-1} D_{i-1}}{E_{i-1} + E_{z,i-1}}\right) \\
 &\quad - n_i A_i \exp\left(-\frac{S_i D_i}{E_i + E_{z,i}}\right),
 \end{aligned}
 \tag{5}$$

where n_i ($i = 0, 1, 2$) are the densities of $(\text{CF}_3)_3\text{CBr}$, $(\text{CF}_3)_3\text{C}\cdot$ and $(\text{CF}_3)_2\text{C}\cdot$ respectively; D_i is the energy of rupture of corresponding bonds; $A_{-1} = A_2 = 0$. The expression $\exp(-s_i D_i / (E_i + E_{z,i}))$ is used as the dependence of the dissociation rate on the energy E_i , which is contained in s_i vibrational degrees of freedom of the i -th component in the mixture, $E_{z,i}$ is the corresponding energy of zero-order vibrations. This expression follows from the RRKM theory when we use the quasi-classical expression for state density at Boltzmann distribution of vibrational energy. Dissociation non-equilibrium was allowed for by introducing different vibrational temperatures $T_i = E_i / s_i$ for each component of the mixture. Their variation was described by the equations

$$\begin{aligned}
 s_i n_i \frac{dT_i}{dt} &= \sigma_i n_i I + s_i (T_{i-1} - T_i) n_{i-1} A_{i-1} \exp\left(-\frac{s_{i-1} D_{i-1}}{E_{i-1} + E_{z,i-1}}\right) \\
 &- \left(D_i + \frac{\Delta s_{i+1,i}}{2} T_i\right) n_i A_i \exp\left(-\frac{s_i D_i}{E_i + E_{z,i}}\right) \\
 &+ \sum_{j \neq i} (\sigma v)_{ij} n_i n_j (T_j - T_i) + (\sigma v)_{ib} n_i n_b (T_b - T_i)
 \end{aligned} \tag{6}$$

The first term describes the absorption of laser radiation of intensity I . We use such a simple expression for the rate of energy accumulation because the molecule is assumed to be in the region of quasicontinuum.^{1,2} This assumption is quite substantiated since, as the number of atoms is large, even after absorbing one quantum the molecules turns out to be in a region with a high density of vibrational states. This can be also confirmed by the fact that the value of q observed for $(\text{CF}_3)_3\text{CBr}$ is close to unity. The second term in (6) allows for the arrival of energy to the component “ i ” together with the dissociation products of the component “ $i - 1$,” the third term allows for the energy expended on dissociation. The rest of the terms are conditioned by collisional transfer of energy between the components of the mixture. The last term allows for the presence of a buffer which basically consists of I_2 but, for simplicity, includes both the rest of the components of the mixture not allowed for in (5), (6) and the rotational-

translational degrees of freedom of $(\text{CF}_3)_3\text{CBr}$, $(\text{CF}_3)_3\text{C}\cdot$ and $(\text{CF}_3)_2\text{C}\cdot$. The buffer heating is described by the equation

$$s_b n_b \frac{dT_b}{dt} = - \sum_i \frac{\Delta s_{i+1,i}}{2} (T_i - T_b) n_i A_i \exp\left(-\frac{s_i D_i}{E_i + E_{z,i}}\right) - \sum_i (\sigma\nu)_{ib} n_i n_b (T_b - T_i) \quad (7)$$

The first term, containing $\Delta s_{i+1,i} = s_{i+1} - s_i < 0$, describes the heating of the buffer caused by transfer of some energy during dissociation to rotational-translational degrees of freedom; their corresponding terms are present in (6), too.

Equations (5)–(7) contain a large number of parameters the values of which are not known now. Since the processing of our results does not enable us to restore unambiguously the full set of parameters we have assigned some rightful, though arbitrary, values to the most of them (see Table I). The energy of rupture of the C—C bond in the radical $(\text{CF}_3)_3\text{C}\cdot - D_0$ and the rate constants of energy transfer to the buffer $(\sigma\nu)_{ib}$ were considered to be varying parameters. The rates $(\sigma\nu)_{ij}$ did not vary since the energy transfer between the dissociating components is unessential due

TABLE I

Experiment			Model			
$\bar{\epsilon}, 1000\text{cm}^{-1}$	β	β_d/β	$\bar{\epsilon}, 1000\text{cm}^{-1}$	β	β_d/β	$(\beta_d/\beta)_{\text{inc}}^*$
		$\tau = 100 \text{ ns}$				
32	0.06	0.88	30	0.044	0.78	0.84
62	0.38	0.73	42	0.33	0.51	0.57
		$\tau = 800 \text{ ns}$				
36	0.07	0.65	42	0.04	0.67	0.68
60	0.38	0.40	60	0.37	0.30	0.31
		$\tau = 1500 \text{ ns}$				
42	0.05	0.60	—	—	—	—
100	0.37	0.33	—	—	—	—

The following parameters were used in calculations:
 $D_0 = 24000 \text{ cm}^{-1}$; $D_1 = 22000 \text{ cm}^{-1}$; $A_0 = 10^{14} \text{ s}^{-1}$; $A_1 = 10^{15} \text{ s}^{-1}$; $S_0 = 36$; $S_1 = 33$; $S_2 = 27$; $P_{12} = 12 \text{ Torr}$; $n_b(\sigma\nu)_{ib} = 5 \cdot 10^7 \text{ s}^{-1}$.

* $\tau_{\text{inc}} = 100 \text{ ns}$.

to a small difference between their temperatures. For simplicity, we considered the cross-sections σ_i to be independent of the excitation level and i ; in this case the set of equations (5)–(7) has a simple integral that expresses the law of conservation of energy

$$\begin{aligned} (s_0 n_0 T_0 + s_b n_b T_b)_{t=0} + n_0 \sigma_0 \int_0^t I(t') dt' \\ = \sum_i s_i n_i T_i + s_b n_b T_b \end{aligned} \quad (8)$$

This equation was actually used to control the accuracy of the computer calculations.

The reaction yield was calculated for the instant $t_{\text{cool}} = 5 \mu\text{s}$ after the pulse began. In most cases the reaction by this moment was already over and its increase did not change essentially the results.

Before turning to the comparison of this model with experiment we should stress that in deducing (5) we used the assumption on Boltzmann (thermal) energy distribution over vibrational degrees of freedom. This assumption in a reaction under high-power pulsed radiation can no doubt be fulfilled just approximately. Moreover, even if the distribution, on the whole, is close to the Boltzmann one, the presence of a chemical reaction will cause the high-energy distribution tail to vary from it. It is known that the main contribution to the reaction at Boltzmann distribution is made by molecules with their energy of the order of $\bar{\epsilon} + D$.¹³ For (5) to be valid, it is necessary that the reaction rate with this energy should be lower than the frequency of collisions. Using the data given in Figure 9, we can see that at a pressure of about 10 Torr these rates become equal with $E \approx 40\,000 \text{ cm}^{-1}$ which with $s = 36$ corresponds to $T = 1100 \text{ cm}^{-1}$. Since in our calculations the temperatures were 800 to 900 cm^{-1} this suggests that the Boltzmann distribution is partially disturbed. Besides, in case of short pulses the rate of laser excitation also becomes sufficiently high which disturbs the Boltzmann distribution. Therefore we should not expect full quantitative agreement of the model with experiment. We are going to use the results of our calculations only for qualitative confirmation of our interpretation of the basic results.

The reaction yield β and the product ratio are calculated in the table. The best agreement was attained with the value of relaxation rate $n_b (\sigma\nu)_{ib} = 5 \cdot 10^7 \text{ cm}^{-1}$ which corresponds to an average loss of energy by a

reacting molecule of approximately 200 cm^{-1} per one gas-kinetic collision with a molecule of I_2 . Figure 6 (curve 2) shows the estimated dependence $\beta(P_{\text{I}_2})$ which approximates the experimental one.

The dependence $\beta(\bar{\epsilon})$ observed turns out to be less sharp than that predicted by our model. The experimental and theoretical dependences can be consistent within this model only due to variations in the energy of rupture of the C—I bond D_0 . But the calculations performed show that satisfactory agreement can be attained only at inadmissible parameters $D_0 = 70\,000 \text{ cm}^{-1}$ and $A_0 = 4.3 \cdot 10^{37} \text{ s}^{-1}$. So, then we used the realistic values $D_0 = 24\,000 \text{ cm}^{-1}$ and $A_0 = 10^{14} \text{ s}^{-1}$ which did not vary. The slow dependence $\beta(\bar{\epsilon})$ observed was interpreted as evidence of an increase in the rate of relaxation processes with increasing molecular energy which was not allowed for within the model concerned.

Here we want to point out a factor which at first sight seems unexpected. To obtain a slower dependence $\beta(\bar{\epsilon})$ we must increase the activation energy D_0 despite the fact that this leads to a sharper dependence of the reaction rate $d\beta/dt \sim \exp[-s_0 D_0 / (\bar{\epsilon} + E_{z,0})]$ on absorbed energy. This result becomes clear if we take into account that D_0 in this case is also the dissociation energy, and the law of conservation of energy calls for a decrease of β with increasing D_0 . In Ref. 14 it is shown that in such a case the dissociation yield varies linearly with absorbed energy $\beta = (\bar{\epsilon} - E_{th})/D_0$ (E_{th} is a threshold energy), and an increase in D_0 here really brings about a slower dependence $\beta(\bar{\epsilon})$.

Satisfactory agreement with experiment on β_d/β for a long pulse ($\tau = 800 \text{ ns}$) has been obtained with $D_1 = 22\,000 \text{ cm}^{-1}$. This energy turns out to be lower than the energy of the C—C bond ($\sim 30\,000 \text{ cm}^{-1}$), which may be attributed to a less stable structure of the radical $(\text{CF}_3)_3\text{C}\cdot$. In our model, however, the dependence of β_d/β on pulse duration has proved too slight. This is quite clear and again related to the disturbance of the Boltzmann distribution at high energies. Indeed, the use of (5) presupposes that dissociation products are formed at a temperature close to the temperature of the reagent and at this instant their rate of decay is equal to the equilibrium rate with this temperature. Taking into account the fact that the main contribution to dissociation is made by molecules with their energy of about $\bar{\epsilon} + D$ we may conclude that, for this picture to be valid, two-step dissociation must have Boltzmann distribution in the primary molecule up to energies of about $\bar{\epsilon} + 2D_0$ which is hardly probable. In a more realistic model we should allow for the time required for the product of the first stage of decay $[(\text{CF}_3)_3\text{C}\cdot]$ to acquire energy which would be

sufficient for further dissociation. Though it can not consistently be done in our model limited by Boltzmann distributions, we tried to estimate its influence in a simplest model. We assumed that radicals $(CF_3)_3C\cdot$ can dissociate only after some decay τ_{inc} (incubation time) from their formation. So the dissociation rate of $(CF_3)_3C\cdot$ has been calculated by substituting into the right-hand side of (5) the values of concentration of $(CF_3)_3C\cdot$ at the proceeding instant of time $t - \tau_{inc}$. The discrepancy with experiment is much less with $\tau_{inc} = 100$ ns (see Table I).

Thus, the basic distinctive features of the process of laser synthesis can be understood within the simple model developed with reasonable parameters.

6. CONCLUSION

The studies of IR MP excitation and dissociation of a sufficiently complex molecule $(CF_3)_3CBr$ in the environment of iodine with the object of synthesizing the $(CF_3)_3CI$ molecule carried out in this work have shown that, with the frequency and duration of IR radiation properly chosen, the process of synthesis can be effective enough. Specifically, with a pulse duration of CO_2 laser $\tau \approx 100$ ns, frequency $\nu = 931.00$ cm^{-1} , energy fluence $\phi = 5.5$ J/cm^2 , the dissociation yield of $(CF_3)_3CBr$ will be $\beta = 0.7$, and no less than 70% of the dissociated molecules are transformed in this case into $(CF_3)_3CI$. Further increase in the efficiency of the process of laser-radical synthesis of $(CF_3)_3CI$ may be connected with the application of the method of combined (thermal + MP) excitation.⁶ Besides, as it follows from Figure 6 and Table I, if we reduce the frequency and duration of CO_2 laser pulse this may also contribute to the growth of the dissociation yield of $(CF_3)_3CBr$ β and the ratio of yield of the desired product $(CF_3)_3CI$ to dissociation yield β_d/β . But, as a rule, this entails a decrease in the CO_2 laser efficiency and hence the deterioration of the energetics of synthesis.

The theoretical model of MP dissociation of $(CF_3)_3CBr$ developed in this work provides quite satisfactory qualitative interpretation of the experimental data obtained. Despite the use of essential simplifying assumptions (Boltzmann distribution of energy, independence of relaxation rate on energy, etc.) with reasonable choice of the parameters describing dissociation and relaxation, it was possible to reproduce the data on dissociation yield β , relative yield of desired product β_d/β and their dependence of iodine pressure. At the same time the comparison of the exper-

imental and theoretical dependences of the dissociation rate on absorbed energy points to a considerable increase of the relaxation rate with an increase in the molecular energy. The data on the dependence of the product ratio on pulse duration unambiguously suggests that the nonequilibrium dissociation of the $(\text{CF}_3)_3\text{CBr}$ is very essential.

References

1. V. S. Letokhov and A. A. Makarov, *Uspekhi Fiz. Nauk* (Russian), **134**, 45 (1981).
2. V. N. Bagratashvili, V. S. Letokhov, A. A. Makarov and E. A. Ryabov, *Multiple Photon Molecular Processes in IR Laser Field*. Publication of Soviet Institute of Scientific and Technical Information, Moscow, 1980.
3. S. D. Rockwood and J. W. Hudson, *Chem. Phys. Lett.*, **34**, 542 (1975).
4. J. H. Clark, K. M. Leary, T. M. Loree and L. B. Harding, *Advances in Laser Chemistry*, ed. A. Zewail, Springer Series in Chemical Physics, New York, Springer, vol. 3, 74 (1978).
5. G. I. Abdushelishvili et al, *Pis'ma J. Techn. Fiz.* (Russian), **5**, 849 (1979).
6. V. N. Bagratashvili, V. N. Burimov, L. E. Deev, A. V. Zabolotnykh, V. S. Letokhov, G. I. Nazarenko, A. P. Sviridov and V. S. Shaidurov, *Kvantovaya elektronika* (Russian), **9**, 425 (1982).
7. A. K. Petrov, Yu. N. Samsonov, A. V. Baklanov, V. V. Vishin and A. M. Orishitch, *Izvestija AN SSSR* (Russian), **N9**, 2148 (1976).
8. A. B. Baklanov, A. K. Petrov and Yu. N. Molin, *Doklady Ak. Nauk SSSR*, **242**, 6333 (1978) (Russian).
9. V. N. Bagratashvili, I. N. Knyazev, V. S. Letokhov and V. V. Lobko, *Opt. Comm.*, **18**, 525 (1976).
10. H. Bürger and G. Pawelke, *Spectrochim. Acta*, **35A**, 559 and 565 (1979).
11. J. L. Lyman and K. M. Leary, *J. Chem. Phys.*, **69**, 1858 (1978).
12. P. J. Robinson and K. A. Holbrook, *Unimolecular reactions*, Wiley, London ao., 1972.
13. S. W. Benson, *Thermochemical Kinetics*, Wiley, New York-London-Sydney, 1968. Equation (I.50).
14. V. N. Bagratashvili and M. V. Kuzmin, *Khimicheskaya Fizika* (Russian), to be published.