## Decomposition of hexafluoropropylene oxide in a strong IR field

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Multiphoton dissociation (MPD) of hexafluoropropylene oxide (HFPO) under focused  $CO_2$ -laser radiation was studied. A high-energy channel of HFPO decomposition was revealed. The dependences of the MPD yield and the ratio between various channels of HFPO decomposition on the laser radiation frequency in the range from 967.7 to 1090.0 cm<sup>-1</sup>, the incident radiation energy, and the initial pressure of HFPO were obtained. A considerable contribution of thermal decomposition of HFPO occurring outside of the irradiated zone to the total yield of its decomposition was established. An explanation for the pressure dependence of the yield of HFPO decomposition was suggested.

Key words: multiphoton dissociation, hexafluoropropylene oxide, carbenes, thermal decomposition, MPD spectrum.

The mechanism and kinetics of decomposition of hexafluoropropylene oxide (HFPO) are well studied under various conditions.<sup>1-5</sup> The following reactions are the main stages of pyrolysis of HFPO, and they occur under all of the experimental conditions used:

$$C_3F_6O \longrightarrow CF_3CFO + :CF_2,$$
 (1a)  
2 :CF<sub>2</sub>  $\longrightarrow C_2F_4.$ 

The previous study of HFPO decomposition under the conditions of IR laser initiation showed that only these two reactions occur both with sensitized laser pyrolysis of HFPO<sup>6</sup> and its multiphoton dissociation (MPD) in low-energy IR fields ( $<1 \text{ J cm}^{-2}$ ).<sup>7</sup>

A molecule of HFPO can theoretically decompose via other routes, in particular, by forming trifluoromethylfluorocarbene<sup>1</sup>:

$$C_3F_6O \longrightarrow CF_2O + :CFCF_3$$
, (1b)

However, reaction (1b) was not experimentally observed. It has been mentioned<sup>1,8</sup> that the contribution of the supposed reaction (1b) to the total yield of HFPO decomposition cannot exceed 0.01 % when the pyrolysis of HFPO is carried out under static conditions ( $T \approx 500$ K). In addition, it has been established<sup>9</sup> for flow pyrolysis of various perfluoroolefin oxides (T = 700-1000 K) that all perfluoroolefin oxides with a terminal CF<sub>2</sub> group decompose only *via* the elimination of :CF<sub>2</sub>.

It is evident that the activation energy of the supposed reaction (1b) of HFPO decomposition is considerably higher than that of reaction (1a) ( $E_a(1a) \approx 36$  kcal mol<sup>-1</sup>, see Refs. 1 and 6). MPD of HFPO has previously been

performed<sup>7</sup> at the density of the IR laser radiation energy  $\Phi = 0.05-0.5$  J cm<sup>-2</sup> to give relatively high yields of MPD; however, this radiation density was not sufficient to perform reaction (1b). Therefore, the purpose of this work is to reveal the high-energy channel of HFPO decomposition under the conditions of its MPD, using focused IR laser radiation.

## Experimental

A TEA-CO<sub>2</sub>-laser\* ( $\tau_{1/2} = 130$  ns) with retuning of the generation frequency in the 10- and 9- $\mu$ m ranges was used as a source of IR laser radiation. The reaction of HFPO decomposition was carried out in an IR spectrophotometric cell (47 mm in diameter and 100 mm in length) or in a cell of stainless steel (15 mm in diameter and 82 mm in length) with windows of BaF<sub>2</sub>. The cell was attached to the system for chromatographic analysis (the use of reaction cells different in structure exerted no effect on the distribution of the obtained products of HFPO decomposition). IR radiation of the CO2laser passed through a diaphragm 8 mm in diameter and was focused by a lens of NaCl (10-cm focal length) to the center of the cell. The energy density in the focal plane was estimated as 18 to 40 J cm<sup>-2</sup>, when the incident radiation energy  $E_0$  was 200 mJ. For the multipulse mode the pulse frequency was 0.15 Hz.

Reaction products after irradiation were analyzed on a chromatograph (model 3700, flame-ionization detector, column with Poropak S stationary phase). A Specord 75 IR spectrophotometer was used for IR spectral analysis.

In order to estimate contributions of various reactions of HFPO decomposition, the consumption of HFPO and accumulation of perfluorinated acyl fluorides  $CF_3CFO$  and  $CF_2O$  were simultaneously followed by the change in the IR

\* TEA is transversally excited atmospheric.

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**Table 1.** Extinction coefficients for the main characteristic absorption bands of HFPO and products of its decomposition

Compound	v/cm <sup>−1</sup>	ε·10 <sup>19</sup> /cm <sup>2</sup>	
$C_3F_6O$	1020	7.8±0.35	
$\tilde{C_3F_6O}$	1554	$2.68 \pm 0.07$	
CF <sub>3</sub> CF0	1896	3.11±0.08	
$CF_2O$	1954	4.55±0.15	

spectrum of the reaction mixture depending on the number of laser pulses. The frequencies corresponding to the maxima of the absorption bands were selected from the total IR spectrum:  $C_3F_6O$  1020 and 1554 cm<sup>-1</sup> (see Refs. 6 and 8), CF<sub>3</sub>CFO 1896 cm<sup>-1</sup> (see Refs. 10 and 11), and CF<sub>2</sub>O 1954 cm<sup>-1</sup> (see Refs. 11 and 12). The experimentally determined extinction coefficients presented in Table 1 were used for calculation of amounts of HFPO and perfluorinated acyl fluorides. Since the reaction between O<sub>2</sub> and :CF<sub>2</sub> can result in the formation of CF<sub>2</sub>O,<sup>1</sup> the experimental procedure resulted in the absence of O<sub>2</sub> traces in the reaction system.

In the experiments on HFPO decomposition with focused laser radiation in the excitation frequency range  $\omega_L = 967.7 \text{ cm}^{-1}$  (10R8) to 1090.0 cm<sup>-1</sup> (9R40), the pressure of HFPO was 0.6 to 5 Torr. The yield of MPD of HFPO in the reaction cell per laser pulse (f) was calculated from the equation 13,14:

$$p(C_3F_6O)/p_0(C_3F_6O) = (1-f)^n,$$
 (2)

where  $p_0$  and p are the pressures of the reagent before and after irradiation, n is the number of pulses. In each experiment, a decrease of C<sub>3</sub>F<sub>6</sub>O was directly found from the change in the absorption of IR radiation at 1020 and 1554 cm<sup>-1</sup> and from the pressures of perfluorinated acyl fluorides formed according to the equation of mass balance:

$$p_0(C_3F_6O) = p(C_3F_6O) + p(CF_3CFO) + p(CF_2O),$$
 (3)

which should be fulfilled, because these fluorides formed via different channels of HFPO decomposition do not enter secondary reactions under the conditions of our experiment. The yields of MPD of HFPO f determined by these methods were averaged for each experiment. The errors of determination of f values from Eq. (2) were  $\leq 15$  %.

Assuming that the total yield of MPD of HFPO via the high-energy  $(f_2)$  and low-energy  $(f_1)$  channels are unchanged from pulse to pulse, when yields of HFPO decomposition are small, we used the following expression for determination of the  $f_2/f_1$  ratio:

$$f_2/f_1 = p(\mathrm{CF}_2\mathrm{O})/p(\mathrm{CF}_3\mathrm{CFO}). \tag{4}$$

For some frequencies of laser excitation, the dependences of f and  $f_2/f_1$  on the initial pressure of HFPO and the energy of incident radiation  $E_0$ , which was varied by attenuators of Ge and BaF<sub>2</sub>, were found. The numerical values of  $E_0$  were corrected, taking into account the absorption of IR radiation by the lens and windows of the working cells.

## **Results and Discussion**

It is found in the experiments on MPD of HFPO without focusing the laser radiation that the IR spectrum

of the reaction mixture after HFPO decomposition (up to 70 %) does not qualitatively differ from the IR spectrum of the products of complete thermal decomposition of HFPO upon sensitized laser pyrolysis,<sup>6</sup> i.e., it contains only absorption bands related to tetrafluoroethylene (TFE) and CF<sub>3</sub>CFO. However, when focused laser radiation is used, a new absorption band at 1955-1925 cm<sup>-1</sup>, which can be assigned to the stretching vibration of C=O in the CF2O molecule  $(1957-1929 \text{ cm}^{-1})$ , on the basis of literature data,<sup>11</sup> appears in the IR spectrum of the products of MPD of HFPO. In order to experimentally prove that the absorption band at v = 1955 - 1925 cm<sup>-1</sup> belongs to the CF<sub>2</sub>O molecule, the following experiments were carried out: ozone, which rapidly reacts with TFE,15 was added to the reaction mixture containing only SF<sub>6</sub>, CF<sub>3</sub>CFO, and TFE after the complete decomposition of HFPO upon SF<sub>6</sub>-sensitized laser pyrolysis:

$$C_2F_4 + O_3 \longrightarrow 2 CF_2O + 1/2 O_2$$

This also results in the appearance of the absorption band at 1955-1925 cm<sup>-1</sup> in the IR spectrum.

The existence of this absorption band in the IR spectrum of the products of MPD of HFPO testifies that there is another, high-energy channel of HFPO decomposition, which results in the formation of  $CF_2O$  and occurs via the overall reaction

$$C_3F_6O \longrightarrow C_2F_4 + CF_2O, \qquad (5)$$

because the analysis of secondary products of HFPO decomposition detects only TFE, CF<sub>3</sub>CFO, and CF<sub>2</sub>O. Therefore, basing on the results of this work, we can draw no definitive conclusion about the mechanism of the primary stage of HFPO decomposition *via* the highenergy channel. However, the parameters of MPD of HFPO can be determined rather correctly from Eqs. (2)-(4), because acyl fluorides obtained *via* different channels almost do not enter subsequent reactions with perfluorocarbenes under the used conditions.<sup>16</sup>

In order to determine the yield of MPD of HFPO (f), the experimental data were treated on the basis of Eqs. (2) and (3), depending on the number of laser pulses (Fig. 1). It is seen from Fig. 1 that the fraction of HFPO in the reaction mixture (in logarithmic coordinates) linearly depends on the number of pulses nonly up to small n values and, hence, up to a small degree of HFPO decomposition (~20-40 %). The total yield f decreases as the number of pulses increases, and HFPO stops decomposing above some n value. This result is regular. It is known that yields of MPD of various multiatomic molecules, including HFPO, exponentially decrease as the pressure of buffer gases increases, especially for multiatomic gases.7,17,18 In our case, buffer gases for HFPO are fluorinated acyl fluorides and TFE formed due to its MPD, their amount increasing relative to that of HFPO as the latter decomposes with



**Fig. 1.** Characteristic dependences of the fraction of undecomposed HFPO (1) and the ratio of acyl fluorides formed upon MPD of HFPO (2) on the number (n) of laser pulses.  $\omega_L = 1025.3 \text{ cm}^{-1}$ ,  $p_0(C_3F_6O) = 4.5 \text{ Torr}$ ,  $E_0 = 155 \text{ mJ}$ .

increase in the number of pulses, and, thus, the MPD yield f decreases. In addition, under the experimental conditions used, a considerable contribution to the yields of MPD of HFPO is made by the thermal decomposition of HFPO occurring due to heating of the system after the postpulse V-T,R-relaxation of multiphoton-excited HFPO molecules. Then the energy absorbed by HFPO molecules decreases as the reagent is consumed, while the total heat capacity of the system remains approximately unchanged (a decrease in the contribution of HFPO to the heat capacity is compensated by an increase in the contribution of the products of HFPO decomposition). This results in a decrease in the equilibrium temperature achieved due to the V-T,R-relaxation and, hence, in a decrease in the fraction from the thermal decomposition of HFPO.

It has also been found that in the majority of experiments the  $p(CF_2O)/p(CF_3CFO)$  ratio at first remains unchanged and then monotonically increases to approach some limiting value as the number of pulses increases (Fig. 1). The region in which  $p(CF_2O)/p(CF_3CFO)$  is constant approximately corresponds to the region in which the yield of MPD of HFPO per pulse is also constant. Only in this region the ratio of the pressures of acyl fluorides formed characterizes numerically the  $f_2/f_1$  value in accordance with Eq. (4). The subsequent increase in the  $p(CF_2O)/p(CF_3CFO)$  ratio means a relative increase in  $f_2$  compared to  $f_1$ , which agrees with the known data<sup>19</sup> that a decrease in the yield of MPD of the reagent via the low-energy channel of decomposition as the pressure of the buffer gas increases is faster than that via the high-energy channel.

The dependences of the total yield of MPD of HFPO (f) on the energy  $(E_0)$  of incident laser radiation were



**Fig. 2.** MPD yield of HFPO (*f*) depending on the incident radiation energy  $E_0$ .  $p_0(C_3F_6O) = 1.2$  Torr (1-3),  $\omega_L = 982.1$  (1), 985.5 (2), 1029.4 cm<sup>-1</sup> (3);  $p_0(C_3F_6O) = 20$  Torr,  $\omega_L = 1029.4$  cm<sup>-1</sup> (4).

studied for some frequencies of laser excitation. The  $f(E_0)$  dependences for  $\omega_L = 982.1$ , 985.5, and 1029.4 cm<sup>-1</sup> at an initial pressure of HFPO  $p_0(C_3F_6O) = 1.2$  Torr are presented in Fig. 2. It is known<sup>14,19–21</sup> that in the case of focused radiation the yield of MPD can be presented as a power function of the energy  $(E_0)$  of incident laser radiation (Eq. 6).

$$f \sim E_0^{\alpha},\tag{6}$$

In this case, the  $\alpha$  parameter often takes the value of 3/2 (see Ref. 20–22). Such a dependence is obtained in the threshold model based on the assumptions that reagent molecules in the conic irradiated zone, where the value of the radiation density is greater than some threshold value, decompose completely, and decomposition out of this zone is absent.<sup>14,20</sup> According to the more exact model that takes into account the energy distribution in the laser beam and an additional contribution to the decomposition of the reagent due to collision-induced reactions out of the irradiated zone,<sup>21</sup> the  $\alpha$  parameter should be greater than 3/2 at small values of energy  $E_0$  and should approach the value  $\alpha = 3/2$  when  $E_0$  increases.

The  $f(E_0)$  dependence obtained for HFPO qualitatively agrees with this model. The experimental data on the yields of MPD of HFPO for  $\omega_L = 1029.4 \text{ cm}^{-1}$ (Fig. 2) obtained in the maximum range of  $E_0$  show that the  $\alpha$  value monotonically decreases from 2.9 at  $E_0 < 15$ mJ to 1.0 at  $E_0 > 32$  mJ as  $E_0$  increases (see Table 2). However, the  $\alpha$  value not only approaches 3/2, but also takes lower values at relatively small values of  $E_0$ (compared to the data of Refs. 19 and 23). This anomalously low value of  $\alpha$  in the case of MPD of HFPO can be explained in the following way. On the

$\omega_{\rm L}/{\rm cm}^{-1}$	Yield MPD	$p(C_3F_6O)$ /Torr	<i>E</i> <sub>0</sub> /mJ	α
1029.4	f	1.2	11-15	2.88±1.00
1029.4	f	1.2	15-32	$1.40 \pm 0.04$
1029.4	f	1.2	32-136	$1.00 \pm 0.17$
982.1	f	1.2	72-226	$1.42 \pm 0.13$
985.5	Ĵ	1.2	34-181	$1.26 \pm 0.40$
1029.4	f	20.2	162-201	$1.22 \pm 0.28$
1029.4	$f_2$	1.2	15-136	1.50±0.14

**Table 2.** Values of parameter  $\alpha$  in Eq. (6) upon MPD of HFPO

one hand, it is known that the absorption of laser radiation by simple multiatomic molecules (4–7 atoms) does not result in a considerable vibrational overexcitation of the molecules to the energy level higher than the dissociation boundary due to the high rate of their monomolecular decomposition.<sup>24</sup> An HFPO molecule is rather complicated and, as shown previously,<sup>25</sup> can be overexcited to the energy level that is three times higher than the dissociation boundary. In this case, the yields of HFPO decomposition are relatively low, which contradicts the postulate of the threshold model that all molecules of the reagent fallen into the region with the radiation density higher than the threshold one undergo decomposition. Therefore, it is likely that this threshold model, describing the decomposition of reagent molecules, cannot be used in our case. On the other hand, the boundary of HFPO dissociation via reaction (1a)  $(D_1)$  $\approx$  12800 cm<sup>-1</sup>) is very low, and the decomposition of HFPO is observed without focusing laser radiation. Therefore, it can be asserted that the whole irradiated volume is the zone of multiphoton decomposition of HFPO for focused radiation at any  $E_0$  value. It follows from this assertion that the yield of MPD of HFPO (f) depends on  $E_0$  to a lesser extent than it is supposed in theoretical models, 14,21 especially at the values of  $E_0$ when the yield of MPD of HFPO in the irradiated volume is close to unity.

The ratios of the yields of MPD of HFPO in reactions (1a) and (5) were also determined at the excitation frequency  $\omega_{\rm L} = 1029.4 \text{ cm}^{-1}$  for various  $E_0$  values. It turned out that the  $f_2/f_1$  ratio monotonically increases as  $E_0$  increases. The reason for this increase in the contribution of the high-energy channel (5) to the total vield of MPD of HFPO could be the following. In the first approximation the yield of MPD of HFPO in the irradiated volume can be presented as the fraction of HFPO molecules with an energy higher than the dissociation level,<sup>24</sup> which is considerably lower for reaction (1a)  $(D_1)$  than for reaction (5)  $(D_2)$ . Then an increase in  $E_0$  and, hence, a shift of the energy distribution function of HFPO molecules to higher  $E_0$ values results in a situation in which the fraction of molecules with an energy higher than the  $D_1$  level increases slower than the fraction of molecules with the energy higher than a  $D_2$  level. This means that the



**Fig. 3.** Dependence of the total MPD yield of HFPO f(1) and the MPD yield of HFPO *via* the high-energy channel of decomposition  $f_2(2)$  on the incident energy  $E_0$ .  $p_0(C_3F_6O) = 1.2$  Torr,  $\omega_L = 1029.4$  cm<sup>-1</sup>.

contribution of reaction (5) to the overall decomposition of HFPO increases, and the dependence on  $E_0$  is greater for  $f_2$  than for  $f_1$ . Since in the majority of experiments  $f_2/f_1 = 0.05 - 0.15$ , the  $f_1(E_0)$  dependence in the form of Eq. (6) is characterized by approximately the same value of parameter  $\alpha$  as the  $f(E_0)$  dependence. However, due to the experimentally observed increase in the  $f_2/f_1$  value as  $E_0$  increases, the  $f_2(E_0)$  dependence (Fig. 3) is characterized by  $\alpha = 1.50$ , which differs from  $\alpha = 1.00$ obtained for the  $f(E_0)$  dependence in the same range of  $E_0$  (Table 2). Since the  $\alpha$  value determined for the  $f_2(E_0)$  dependence coincides with that predicted by the threshold model,<sup>14,20</sup> the conclusions can be drawn that, first, this model is applicable for description of MPD of HFPO only via the high-energy channel, and, second. HFPO decomposes via reaction (5) only due to MPD, unlike reaction (1a), which allows both MPD of HFPO and its thermal decomposition.

An important purpose of this work was to obtain spectral parameters of MPD of HFPO  $f(\omega_L)$ . For studies with focusing laser excitation, the authors of Refs. 19, 23 and 26 use only several excitation frequencies, which cannot provide complete information in the form of an MPD spectrum. It is of interest, first, to perform MPD of the reagent in a considerably wider frequency range than it is possible without focusing radiation and, second, to compare MPD spectra obtained with focusing and without it.

The decomposition of HFPO with focusing radiation was studied in the range of excitation frequencies  $\omega_L =$ 967.7-1090.0 cm<sup>-1</sup> at the pressure of HFPO  $p_0(C_3F_6O) = 1.2$  Torr and energies  $E_0 = 85-270$  mJ. For correct comparison of the data on the yields of MPD of HFPO at different  $\omega_L$  frequencies, all experi-



**Fig. 4.** Spectra of the MPD yields of HFPO under various conditions of irradiation: (1) focused radiation with  $E_0 = 200$  mJ, (2) unfocused radiation with  $\Phi = 0.3$  J cm<sup>-2</sup>. The region of the spectrum of linear absorption of HFPO (3) is presented for comparison.

mental f values were reduced to the energy  $E_0 = 200 \text{ mJ}$ according to Eq. (6). For all  $\omega_L$  we used the value  $\langle \alpha \rangle = 1.23$  averaged for various excitation frequencies and pressures of HFPO for which the  $\alpha$  parameter is independent within the error of measurements (see Table 2). The  $f(\omega_L)$  dependence is presented in Fig. 4 along with the linear IR spectrum of the absorption of HFPO given for comparison.

Previously,<sup>7</sup> using small-density radiation ( $\Phi = 0.1$ -0.5 J/cm<sup>2</sup>), we observed HFPO decomposition only within the frequency range  $\omega_1 = 985.5 - 1037.4 \text{ cm}^{-1}$ (see Fig. 4), and the yield of MPD of HFPO decreased very rapidly both at the long-wave and short-wave shoulders of the MPD spectrum: by 1.5-2 orders of magnitude when the frequency  $\omega_{\rm L}$  shifted by 5–10 cm<sup>-1</sup>. Thus, a relatively small frequency range in which MPD of HFPO occurs and which corresponds to the absorption band of HFPO in the range of v = 1020 cm<sup>-1</sup> can be isolated. In the case of focusing radiation we obtained an almost continuous spectrum of MPD of HFPO (see Fig. 4) within the whole studied range of  $\omega_{\rm L}$ , which substantially differs from the spectral parameters of MPD of HFPO without focusing. It can be seen from Fig. 4 that the MPD spectrum of HFPO can be divided into two regions. In the frequency range  $\omega_{\rm L} < 1050 \,{\rm cm}^{-1}$  the  $f(\omega_{\rm L})$ dependence repeats in general the contour of the absorption band of the linear IR spectrum of HFPO. The f values decrease by more than an order of magnitude at the long-wave shoulder of the MPD spectrum ( $\omega_{\rm I}$  = 989.6–967.7 cm<sup>-1</sup>), while they decrease only fourfold at the short-wave shoulder ( $\omega_L = 1025.3 - 1050 \text{ cm}^{-1}$ ). The MPD yield of HFPO increases again in the range of  $\omega_L > 1050 \mbox{ cm}^{-1}.$  The frequency  $\omega_L = 967.7 \mbox{ cm}^{-1}$  is the boundary of the MPD spectrum, because no decomposition of HFPO was observed at lower radiation frequencies. Another boundary frequency  $\omega_{I} =$ 1090.0 cm<sup>-1</sup> is caused only by possibilities of the CO<sub>2</sub>-laser. It should be mentioned that in the linear spectrum of HFPO in the range between strong absorption bands at v = 1020 and 1122 cm<sup>-1</sup> there is a very weak absorption band at v = 1075 cm<sup>-1</sup> overlapped by strong bands. Due to this band, the frequency range from 1025.3 to 1090 cm<sup>-1</sup> always contains absorption of IR radiation with a cross section not smaller than  $1 \cdot 10^{-20}$  cm<sup>2</sup>. However, there is disagreement between the changes in the absorption cross section (more than two orders of magnitude) in the mentioned frequency range and the changes in the yield of MPD of HFPO, which amounts to only fourfold.

This difference in the spectra of MPD of HFPO with and without focused radiation<sup>7</sup> (see Fig. 4) cannot be caused only by the increase in the pressure of the reagent from 0.1 Torr (see Ref. 7) to 1.2 Torr in this experiment, although at moderate radiation densities this resulted in an increase in the decomposition of HFPO without a noticeable increase in the multiphoton absorption (MPA) of IR radiation.<sup>7,25</sup> The main reason is the fact that for HFPO the transition from the regime of unfocused radiation to focused radiation is accompanied only by a sharp increase in the radiation density, while the character of the processes that occur in the decomposition of HFPO remains unchanged, because the effect of geometric specific features of HFPO on MPD in the regime of focused radiation should be unimportant, as mentioned above. It is known<sup>24</sup> that an increase in the radiation density results in broadening and the long-wave shift of MPD and MPA spectra of various reagents. The same effect is seen in Fig. 4: the MPD spectrum of HFPO with focusing radiation is broader than that without focusing. The decomposition of HFPO at the large long-wave shift (up to 52  $\,\mathrm{cm}^{-1}$ ) of the  $\omega_L$  frequency relative to the maximum of the absorption band of HFPO at v = 1020 cm<sup>-1</sup> allows one to provide a similar explanation for the increase in the MPD yield of HFPO in the range of  $\omega_1 = 1050 -$ 1090  $\text{cm}^{-1}$ , which is shifted by approximately the same value to the long-wave region from the maximum of the absorption band at v = 1122 cm<sup>-1</sup>. This region can be considered as a long-wave shoulder of the MPD spectrum related to the absorption band of HFPO at v = 1122 cm<sup>-1</sup>. Thus, the continuous MPD spectrum of HFPO with focusing radiation can be explained by the fact that the MPD spectra of HFPO corresponding to the absorption bands at v = 1020 and 1122 cm<sup>-1</sup> are overlapped at their considerable broadening, which is caused by the high density of laser radiation. This broadening of the peaks and smoothening of the spectrum as the power density of laser radiation increases has been already observed for MPA of the reagent.<sup>27,28</sup>

Since MPD of HFPO has been observed previously<sup>7</sup> at  $\Phi \approx 0.5 \text{ J cm}^{-2}$  at the  $\omega_1$  frequency displaced by 35 cm<sup>-1</sup> to the long-wave region from the maximum of the absorption band of HFPO at v = 1020 cm<sup>-1</sup>, we tried to observe MPD of HFPO without focusing at extreme frequencies of laser excitation near the frequency  $\omega_L = 1090$  cm<sup>-1</sup> shifted by 32 cm<sup>-1</sup> to the long-wave region from the maximum of the absorption band of HFPO at v = 1122 cm<sup>-1</sup>. It turned out that in the regime of multipulse unfocused radiation ( $\Phi = 0.23$ -0.35 J cm<sup>-2</sup>) at the frequencies  $\omega_L = 1084.6$ , 1086.9, and 1090.0 cm<sup>-1</sup> the decomposition of HFPO cannot be detected even by the more sensitive chromatographic method.

It should be mentioned that the ratio of the MPD yields of HFPO via reactions (5) and (1a)  $f_2/f_1$  remains unchanged within the experimental error as the  $\omega_L$  frequency increases within the 967.7 to 1090 cm<sup>-1</sup> range, although there is some tendency to increase in the range of  $\omega_L > 1040$  cm<sup>-1</sup>. This result agrees with the known fact that the multiphoton excitation of a molecule over various vibrational modes results in its statistical decomposition independent of the excitation frequency due to the fast randomization of the absorbed energy.<sup>29,30</sup> For example, it has been found<sup>26</sup> that the distribution of MPD products is independent of the frequency  $\omega_L$  for MPD of C<sub>3</sub>F<sub>7</sub>H at frequencies  $\omega_L$  corresponding to different absorption bands of the reagent.

Determining the  $f_2/f_1$  ratio by the distribution of perfluorinated acyl fluorides, we consider that the products of MPD of HFPO do not absorb laser radiation and do not undergo chemical transformations. This is correct only for  $C_2F_4$  and  $CF_2O_2$ , because the maximum of the absorption band closest to the region of generation of the CO<sub>2</sub>-laser in the linear spectrum of these compounds lies in the range of  $v = 1186 \text{ cm}^{-1}$  (the absorption band of  $C_2F_4$  (see Ref. 31)). However, CF<sub>3</sub>CFO has an absorption band in the region of generation of the CO<sub>2</sub>-laser with a maximum in the range of v = 1090 - 1095 cm<sup>-1</sup>.<sup>11</sup> It has been experimentally found that CF<sub>3</sub>CFO absorbs IR radiation at the frequency  $\omega_L = 1052.2 \text{ cm}^{-1}$ , but the energy absorbed at the radiation intensities realized in the experiments is insufficient for its monomolecular decomposition. It is likely that the vibrational excitation of  $CF_3CFO$  is sufficient for its decomposition, when HFPO and CF<sub>3</sub>CFO molecules simultaneously absorb radiation at frequencies  $\omega_L > 1040 \text{ cm}^{-1}$  (which are shifted to the long-wave region from the absorption band at v = 1090- $1095 \text{ cm}^{-1}$ ) and the absorbed energy is redistributed (this result has been experimentally observed when molecules of  $C_2H_4$  or  $C_2H_6$  and molecules of  $CF_2ClCH_2Cl$  simultaneously absorbed radiation<sup>19</sup>). It is known<sup>32</sup> that IR-induced MPD of a CF<sub>3</sub>CHO molecule, which is close in structure to trifluoroacetyl fluoride, results in the formation of :CF<sub>2</sub> in addition to other primary intermediate particles. If a similar process is supposed for CF<sub>3</sub>CFO, the multiphoton irradiation of HFPO at  $\omega_L > 1040 \text{ cm}^{-1}$  can result in partial decomposition of the CF<sub>3</sub>CFO molecule formed due to

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first pulses to give :CF<sub>2</sub> and CF<sub>2</sub>O. This assumption can explain the observed tendency to increase the  $f_2/f_1$  ratio in the given frequency range ( $\omega_L$ ).

We also studied the effect of the initial pressure of HFPO on its decomposition with focused radiation. The dependence of the yield of MPD of HFPO on its pressure for the frequencies  $\omega_L = 1025.3$  and 1029.4 cm<sup>-1</sup> and the incident energy  $E_0 = 150$  mJ is presented in Fig. 5. It turned out that the yield of MPD of HFPO monotonically increases as the pressure increases within the range of  $p_0(C_3F_6O) = 0.6-20$  Torr. This contradicts the known literature data,<sup>19</sup> where the yield of MPD of CF<sub>2</sub>ClCH<sub>2</sub>Cl passed through a maximum in the range of p = 4-5 Torr when focused radiation was used. The authors of Ref. 19 explained the observed decrease in the MPD yield of the reagent at p > 5 Torr by an increase in the optical density of the system and deactivation of excited molecules due to the V-T-relaxation. In our experiment when  $p_0(C_3F_6O) =$ 20 Torr, not less than 75 % of the incident energy is absorbed in the system; however, the yield of MPD continues to increase. This can be explained by the fact that the thermal decomposition of HFPO both inside and outside of the irradiated volume of the reaction cell makes a considerable contribution into the total degree of decomposition of HFPO. As mentioned above, MPD of HFPO should occur in the whole irradiated volume at any energy  $E_0$ . The V-T,R-relaxation of the vibrational energy of undecomposed HFPO molecules and products of MPD of HFPO results in the thermalization of the system and expansion of the heated gas to the zone outside the irradiated volume, where HFPO can thermally decompose via reaction (1a). The considerable contribution of the thermal decomposition of HFPO, which even predominates at high pressures, into the total degree of decomposition is confirmed by the fact that the maximum observed values of the yield of MPD of HFPO (f) at  $p_0(C_3F_6O) = 20$  Torr are  $\approx 1 \cdot 10^{-2}$ , while the fraction of the irradiated volume is not higher than  $4.2 \cdot 10^{-3}$ . Thus, the increase in the f values at high pressures of HFPO is likely caused by the enlargement of the effective zone, in which HFPO thermally decomposes, around the irradiated zone of the reaction cell. As found earlier, the increase in the pressure of HFPO higher than 1.5 Torr results in an increase in the effective cross section of MPA of HFPO<sup>25</sup> and the simultaneous deactivation of vibrationally excited HFPO molecules due to the V-T-relaxation, which should result in a decrease in the fraction of HFPO decomposition due to MPD itself and, hence, in a decrease in the fraction of reaction (5) in the overall decomposition. The data presented in Fig. 6 agree completely with this assertion: the observed ratio of the yields of MPD of HFPO  $(f_2/f_1)$  passes through a maximum and then decreases as the pressure increases. It is noteworthy that the similar explanation for the dependences of absolute and relative yields of MPD of reagents on their pressures was suggested in Refs. 19, 21, and 22 with the only

10  $P(C_3F_6O)/Torr$ 



**Fig. 5.** Pressure dependence of the MPD yield of HFPO (f) at  $E_0 = 150$  mJ for the frequencies  $\omega_L = 1025.3$  (I) and 1029.4 cm<sup>-1</sup> (2).

0

1



**Fig. 6.** Ratio of the MPD yields of HFPO  $f_2/f_1$  at various initial pressures of the reagent.  $E_0 = 150 \text{ mJ}$ ,  $\omega_{\rm L} = 1025.3 \text{ cm}^{-1}$  (1) and 1029.4 cm<sup>-1</sup> (2).

distinction that the collision-induced or thermal decomposition of reagent molecules was considered only in the irradiated zone of the reactor, where the radiation density was lower than the threshold density for the lowest-energy channel of decomposition.

Since the method of IR spectrophotometry is not sufficiently sensitive, the multipulse regime of irradiation was always used for reliable identification of formed acyl fluorides (especially CF<sub>2</sub>O) at pressures of HFPO  $p_0(C_3F_6O) < 5$  Torr. Therefore, in order to check the dependence of the distribution of products of MPD of

HFPO on the number of pulses, the experiments with pressure  $p_0(C_3F_6O) = 20$  Torr were performed in the one-pulse regime of irradiation. It is found that  $CF_2O$  is formed in the system after the first laser pulse and, hence, it is the product of the primary stage of HFPO transformation. This fact proves the existence of the high-energy channel (5) of HFPO decomposition upon its MPD in strong IR fields.

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