

CHANNELS OF PRODUCT FORMATION AND EXCITED MOLECULES RELAXATION AT MULTIPHOTON DISSOCIATION OF CHLORODIFLUOROMETHANE

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C_2F_4 molecules have been for the first time directly proved to be generated in the reaction of vibrationally-excited molecules CF_2HCl . The contribution of this reaction to CF_2HCl multiphoton dissociation (MPD) products formation was shown to become predominant at the initial CF_2HCl pressures about ten Torr. Also fast relaxation of the highly excited molecules CF_2HCl on the product molecules C_2F_4 was discovered.

KEY WORDS: Multiphoton dissociation, chlorodifluoromethane, vibrational relaxation, vibrationally-excited molecules.

INTRODUCTION

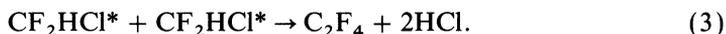
Chlorodifluoromethan (CF_2HCl) is known to be one of the most convenient gases for carbon isotope's laser separation.^{1–4} Under CO_2 -laser irradiation CF_2HCl molecules can absorb several quanta and then dissociate:



CF_2 -radicals recombination leads to the product formation:



It was found that CF_2HCl decomposition rate and selectivity remain quite high up to pressures of several tens of torr.^{5–8} On the basis of mass-spectrometer analysis of carbon isotope's distribution data in C_2F_4 authors of Ref. 9 supposed that in addition to (2) one more reaction takes part in C_2F_4 -production. Most probably this reaction is a direct interaction between two vibrationally excited molecules of CF_2HCl^* :



It was shown that selectivity of reaction (3) is high enough and its contribution into the product formation increases with CF_2HCl pressure.⁹ Nevertheless, all evidences

for involvement of reaction (3) were indirect and it was interesting to find direct confirmation of reaction (3) existence. Since the presence of CF_2 radicals in the (1)st channel and their absence in the (3)rd one is an important difference between channels (1) and (3), it is quite reasonable to measure CF_2 -radicals concentration after CO_2 -laser pulse and C_2F_4 concentration when all reactions have been completed. If the results would show that the amount of C_2F_4 is greater than half of CF_2 -radicals amount, then one can consider that the reaction (3) is responsible for this exceeding.

This paper is devoted to description of the results of such experiments. We managed to prove the reaction (3) existence and evaluate its contribution to the final products formation at different CF_2HCl pressures and also to study the influence of the reaction products— C_2F_4 and HCl —accumulation on the value of multiphoton dissociation yield of CF_2HCl molecules.

EXPERIMENT

CF_2 -radicals absorb ultraviolet radiation in the 235–258 nm band ($\tilde{\text{A}}(^1\text{B}_1) \leftarrow \tilde{\text{X}}(^1\text{A}_1)$ electron transition).¹⁰ Vibrational levels $v'_1 = 0$, $v'_2 = 2$ of the upper electron state and $v''_1 = 0$, $v''_2 = 0$ of the lower one take part in the absorption near 248.8 nm. Extinction coefficient in the maximum of absorption band ($\lambda = 249$ nm) at the temperature 298 K (to the base 10) is $\epsilon_{10}^{249} = 7620 \pm 400$ l/(mole·cm). (The absorption cross-section is $\sigma = 2.91 \cdot 10^{-17}$ cm²).¹¹ Absorption coefficient decreases with temperature growth: on $\lambda = 248.2$ nm extinction coefficient ϵ_{10}^{248} at $T = 1804$ K is 1300 l/(mole·cm) ($\sigma = 4.96 \cdot 10^{-18}$ cm²), at $T = 2085$ K $\epsilon_{10}^{248} = 1065$ l/(mole·cm) and at $T = 2875$ K $\epsilon_{10}^{248} = 813$ l/(mole·cm).¹² For vibrational temperature $T_v = 725$ K $\epsilon_{10}^{249} = 3875 \pm 300$ l/(mole·cm) ($\sigma = 1.48 \cdot 10^{-17}$ cm²).¹³ These data allow one to find approximate values of absorption cross-section for another temperatures.

In our experiments KrF-excimer laser radiation was used to probe the gas and determine CF_2 -radicals concentration ($\lambda_{\text{KrF}} = 248$ nm). Absorption cross-section value for CF_2HCl at this wavelength does not exceed $\sigma = 10^{-26}$ cm² (Ref. 14)—that is much more lower than this one for CF_2 . As laser pulse duration is 15–20 ns, only radicals on the definite vibrational-rotational level can interact with KrF-laser irradiation. Really, the time between two collisions of CF_2HCl molecule can be evaluated to be not less than 80 ns at CF_2HCl pressure of 1 Torr. Since 5–10 collisions must occur the rotational relaxation to be completed one can consider that under the probing laser pulse duration $\tau_1 = 20$ ns the molecule remains 'free' for the process of UV quanta absorption up to pressures of 20–40 Torr. That is why raise of radicals population on this level owing to vibrational-rotational exchange with the neighbouring levels can be neglected. This leads to a little less absorption of UV radiation than in the case when equilibrium population of lower level is maintained (at probing of the gas with continuous wave light, for example), but, on the other hand, this makes our method insensitive to gas pressure changes.

The apparatus scheme for the measurements of CF_2 -radicals concentration is presented in Figure 1. TEA CO_2 -laser beam 13, transmitted through the telescope

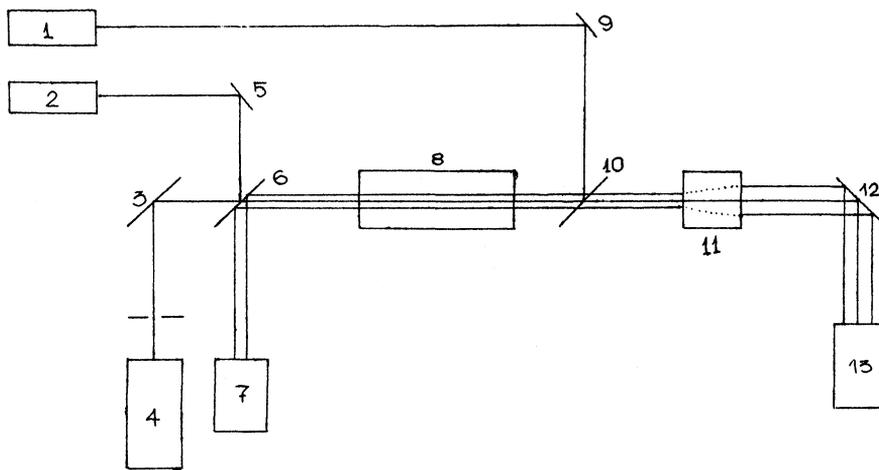


Figure 1 The apparatus for the measurements of CF_2 -radicals concentration.

11, passes along the axis of the cell 8. The stainless steel cell is used, its internal diameter is 3 cm and length is 10 cm; windows are made from BaF_2 . Diameter of CO_2 -laser beam at the entrance and at the exit of the cell is 1.2 cm. Part of the laser beam, passing through the cell, is declined by the beam splitter 6 to the entrance of calorimeter 7—it permits to measure irradiation energy which passes through the cell. To measure the CO_2 -laser energy at the entrance of the cell we use one more calorimeter to receive the beam declined by the beam splitter 10.

Probing UV-laser 4 beam is directed by mirror 3 along the cell axis towards CO_2 -laser beam. Diameter of UV-laser beam at the entrance and at the exit of the cell is ~ 0.3 cm. Part of the beam is directed to the photodetector 2 by plate 6 and mirror 5. After passing the cell part of the beam is reflected by plate 10 and mirror 9 to photodetector 1. The photodiodes PD21-KP were used as the detectors of UV-irradiation. These photodiodes are weakly sensitive to 248 nm wavelength irradiation, therefore the cells with rhodamine 6G solution in isopropanol were placed in the front of each of them. Thickness of these cells was 2 mm and diameter was 8 mm. Solution of the rhodamine was hermetically sealed by polypropylene films of $40 \mu\text{m}$ thickness. To avoid electromagnetic hindrances from electrical discharge of the lasers, we refused from wide band amplifier of the photodiode signal and used two-staged amplifier with amplification factor $\sim 10^3$ with internal time constant $\tau_{\text{PD}} \approx 2 \cdot 10^{-5}$ s. The shape of the signal at the exit of such amplifier is defined by time parameters of the amplifying path, and the amplitude of the signal with accuracy of $\tau_1/\tau_{\text{PD}} = 10^{-3}$ (τ_1 is duration of UV-laser pulse) is proportional to the integral of the probing beam intensity.¹⁵ This proportionality remains constant while the voltage of electric signal from photodiode is much less than characteristic voltage of its internal electric field; just for the photodiode that operates in photovoltage regime this voltage of p-n transition is about 0.6 V. In our case the maximum photodiode signal amplitude was 1 mV, therefore one can consider that our measurements were

performed in the linear regime. With the aid of pulse generator G5-60 and specially made synchronization of excimer and CO₂-lasers scheme delay between UV and IR-pulses could be varied from 0 to 30 μ s.

The measurements of the amplitudes of amplified signals were carried out with the help of oscilloscope C9-8, which was interfaced by the adapter for general use to IBM PC AT. The program was made so that after each pulse the measured data from both photoreceptors were delivered to PC AT, where they were treated and stored. The relative absorption of the probing beam was determined by the expression :

$$I/I_0 = k \cdot (U_1/U_2), \quad (4)$$

where I , I_0 are the intensities of the probing and calibrating beams, respectively, U_1 , U_2 are the amplitudes of the signals from the photoreceptors 1 and 2, k is the setting factor which was determined from the condition that $I/I_0 = 1$ when there are no particles in the cell which can absorb KrF-laser irradiation.

To check laser spectrometer operation we filled optical gas cell with SO₂. It was found that up to 30 torr transmitted light intensity attenuation followed the Lambert-Beer law, and absorption cross-section of SO₂ at $\lambda = 248$ nm turned out to be $(7.5 \pm 0.3) \cdot 10^{-20}$ cm², that is near to data of Ref. 14. Under CO₂-laser influence (simultaneously at lines 9R (32)-9R (38)) on CF₂HCl absorption at $\lambda = 248$ nm was found. We attributed it to CF₂ radicals appearance in the irradiated gas volume. Weakening of UV signal increased with the increase of a delay between CO₂ and KrF-lasers pulses from 0 up to 10 μ s, then (up to 30 μ s) it remained constant. Radicals CF₂ concentration growth after CO₂-laser pulse finishing is due to after-pulse decomposition of CF₂HCl vibrationally-overexcited molecules. Within this time range one can disregard the influence of recombination (2) on CF₂ decreasing (characteristic time of this reaction at the initial CF₂ concentration of 10^{15} cm⁻³ is about 30 ms).¹⁶

The calibration of laser spectrometer was done by the following way. The cell was filled with the mixture CF₂HCl:Ar = 20:1 at the pressure of 2.1 Torr to be irradiated by 11 pulses of CO₂-laser with energy density of 1.26 J/cm². The attenuation of the probing UV pulse, delayed a time 9.6 μ s with respect to the beginning of CO₂-laser pulse, for the first pulse of a series makes up $I/I_0 = 0.97 \pm 0.02$. With the help of mass-spectrometer analysis of the content of the irradiated gas the yield of CF₂HCl-dissociation per pulse was found. The dissociation yield was determined with the expression:¹⁷

$$N_n/N_0 = (1 - \alpha \cdot \beta)^n, \quad (5)$$

where $N_n/N_0 = (H_{51}/H_{40})_{11}/(H_{51}/H_{40})_0$, $(H_{51})_0$ and $(H_{51})_{11}$ are respectively heights of the ion peaks $m/e = 51$ of CF₂HCl-molecule mass-spectrum before and after gas irradiation by 11 pulses of CO₂-laser, $(H_{40})_0$ and $(H_{40})_{11}$ are heights of the ion peaks $m/e = 40$ of argon (argon was used in our experiments as a bench-mark) before and after irradiation of the mixture, n is a number of pulses ($n = 11$), α is the fraction of the cell volume illuminated by the CO₂-laser ($\alpha = 0.18$). While substituting to the expression (5) the measured value $N_n/N_0 = 0.97 \pm 0.02$, one can find $\beta = 0.014 \pm 0.0003$, but it also means that CF₂-radicals concentration in the irradiated volume is equal $n_{CF_2} = \beta \cdot n_{CF_2HCl} = 10^{15}$ cm⁻³. The cross section for

absorption of UV laser radiation by CF_2 -radicals is $\sigma = (\ln(I_0/I))/(n_{\text{CF}_2} \cdot L) = 3 \cdot 10^{-18} \text{ cm}^2$ (here I_0/I is the deviation of UV laser intensities at the entrance and at the exit of the optical cell, which length is 10 cm). The obtained value of σ is approximately 3 times lower than the value found in Ref. 18 at the MPD of CF_2HCl investigation where the vibrational temperature of radicals was considered to be 1160 K. This discrepancy of the results more obviously is caused by the difference in experimental conditions: in Ref. 18 the data were obtained with probing the cell with the continuous wave light, when the molecules of a few vibrational-rotational levels, which are disposed not far from each other, can interact with the beam, while in our case, when the probing is produced by a short pulse of light, only the molecules of the single vibrational-rotational level may take part in absorption.

RESULTS AND DISCUSSION

In Figure 2 the experimental results on concentration of C_2F_4 produced in the irradiated volume (squares) and concentration of CF_2 -radicals in the same volume (crosses) dependences on CF_2HCl -pressure are shown. For more convenient comparing of the results the scale of ordinate for C_2F_4 molecules is made two times greater than the scale for CF_2 . CF_2 -radicals concentration was measured according to the technique described in the previous part. C_2F_4 concentration after n laser pulses was determined with the help of mass-spectrometer analysis by the diminishing of CF_2HCl concentration:

$$[\text{C}_2\text{F}_4]_{(n)} = \frac{1}{2} \cdot (N_0 - N_n). \quad (6)$$

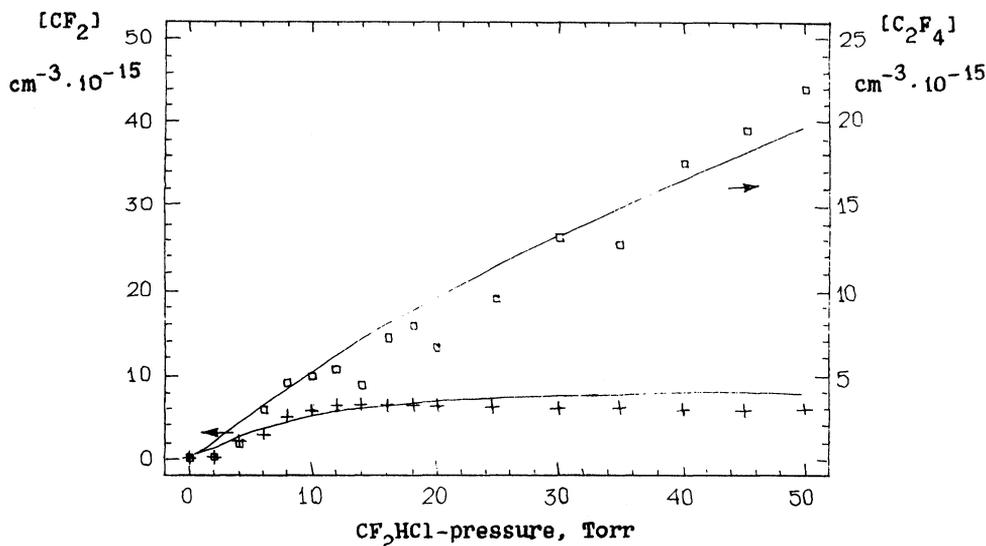


Figure 2 Experimental and calculated dependencies of C_2F_4 concentration (\square) and CF_2 concentration ($+$) on the initial pressure of CF_2HCl .

where $[C_2F_4]_{(n)} - C_2F_4$ concentration in the reaction cell after the n -th CO_2 -laser pulse, $N_0 - CF_2HCl$ concentration before irradiation, $N_n - CF_2HCl$ concentration after the n -th pulse. Using expression (5) one can easily determine C_2F_4 concentration in the reaction cell after the first CO_2 -laser pulse:

$$[C_2F_4]_{(1)} = \frac{1}{2} \cdot N_0 \cdot (1 - (N_n/N_0)^{1/n}). \quad (7)$$

It can be seen from Figure 2 that in the range of CF_2HCl pressures from 0 to 4 Torr C_2F_4 concentration is two times lower than CF_2 concentration in the limits of the experimental error. Since two radicals CF_2 can form only one molecule C_2F_4 and there is no other ways of CF_2 radicals elimination from the system, this result means that in this range of CF_2HCl -pressures CF_2 -radicals recombination is the single source of C_2F_4 formation. When pressure is higher than 4 Torr the quantity of C_2F_4 formed becomes more greater than the quantity which may be formed in the process of CF_2 recombination. It means that when increasing CF_2HCl pressure one more channel of C_2F_4 formation appears and this channel is more probably the reaction (3). The contribution of this second channel increases with CF_2HCl pressure increase; so at 20 Torr the contribution of the second reaction over-exceeds the contribution of the first one approximately in 1.5 times.

In the range of CF_2HCl pressures lower than 8 Torr the increase of CF_2 radicals concentration was observed, although at the following increasing of gas pressure in the cell radical concentration practically did not change. If one can suggest, that the value of dissociation yield does not depend upon initial gas pressure, the linear growth of radical concentration vs gas pressure should take place. The observed deviation from linear dependence can be explained if non-uniformity of CO_2 -laser power density along the cell is taken into account, higher is the gas pressure, more strongly does this non-uniformity reveal itself.

Let us consider that CO_2 -laser power density Φ changes along the cell according to the expression:

$$\Phi = \Phi_0 \cdot \exp(-\sigma_{CO_2} \cdot N_M \cdot l), \quad (8)$$

where Φ_0 is CO_2 -laser power density at the entrance of the cell, σ_{CO_2} is cross-section for absorption of CO_2 -laser beam by chlorodifluoromethane molecules, N_M is CF_2HCl concentration, l is distance from the entrance to the cell. It was found that within the experimental error this law is fulfilled quite perfectly. For dependence of dissociation yield on CO_2 -laser power density one can use the expression $\beta \sim \Phi^m$,¹⁷ where m is a constant. So one can consider that dissociation yield would change along the cell according to the expression:

$$\beta(l) = \beta_0 \cdot \exp(-m \cdot \sigma_{CO_2} \cdot N_M \cdot l), \quad (9)$$

where β_0 is dissociation yield value at the entrance of the cell at power density Φ_0 . Since CF_2 -radicals concentration is proportional to dissociation yield β , its change is described by the expression analogous to (9):

$$n(l) = n_0 \cdot \exp(-m \cdot \sigma_{CO_2} \cdot N_M \cdot l), \quad (10)$$

where $n(l)$ is CF_2 radicals concentration at the distance l from the entrance of the

cell, and $n_0 = n(0)$. While treating the experimental results this dependence was not taken into account, and CF_2 radicals concentration was considered to be constant along all the cell. So we determined the CF_2 concentration averaged along the axis of the cell n_{eff} , which is connected with n_0 by the following expression:

$$n_{\text{eff}} = n_0 \cdot \frac{(1 - (\Phi_L/\Phi_0)^m)}{m \cdot \ln(\Phi_0/\Phi_L)}, \quad (11)$$

where Φ_L is CO_2 -laser power density at the exit of the cell, or in a different way:

$$n_{\text{eff}} = n_0 \cdot \frac{(1 - \exp(-m \cdot \sigma_{\text{CO}_2} \cdot N_M \cdot L))}{m \cdot \sigma_{\text{CO}_2} \cdot N_M \cdot L}. \quad (12)$$

Using the above mentioned suggestion about the independence of dissociation yield on gas pressure, i.e. $n_0 = \beta_0 \cdot N_M$, one can see that while enhancing pressure

$$\lim_{N_M \rightarrow \infty} n_{\text{eff}} = \frac{\beta_0}{m \cdot \sigma_{\text{CO}_2} \cdot L}, \quad (13)$$

the value of the measured CF_2 concentration should approach a constant, and that was experimentally observed. The experimental dependence may be approximated by the function $y \equiv A \cdot (1 - \exp(-B \cdot X))$ and one can find with the help of the least square method the values of the coefficients A and B. Using the expressions (12) and (13) it is easy to get the values $m = 1.03$ and $\beta_0 = 0.024$. The curve with these parameters is shown in Figure 2. The main feature of the dependence of the relation of C_2F_4 concentration to CF_2 concentration upon CF_2HCl pressure is the growth of this relation in all investigated range of pressures. The growth of this relation at low pressures may be explained, if one takes into account that the reaction of the excited molecules is the bimolecular reaction. Product yield of this reaction is proportional to the second power of excited molecules concentration:

$$P_r(1) \sim n^*(1)^2 = n\delta^2 \cdot \exp(-2 \cdot m \cdot \sigma_{\text{CO}_2} \cdot N_M \cdot L), \quad (14)$$

and if one would make a supposition about proportionality of excited molecules concentration to the initial concentration of chlorodifluoromethane N_M , the expression for $\text{Pr}(1)$ would be:

$$P_r(1) = \gamma \cdot N_M^2 \cdot \exp(-2 \cdot m \cdot \sigma_{\text{CO}_2} \cdot N_M \cdot L), \quad (15)$$

where γ is a coefficient.

Full change of chlorodifluoromethane concentration (as the result of dissociation and reaction) measured with mass-spectrometer should be described by the expression:

$$\begin{aligned} |\Delta N_M|_{\text{ms}} = & \chi \cdot N_M \cdot (1 - \exp(-2 \cdot m \cdot \sigma_{\text{CO}_2} \cdot N_M \cdot L)) \\ & + \frac{\beta_0}{m \cdot \sigma_{\text{CO}_2} \cdot L} \cdot (1 - \exp(-m \cdot \sigma_{\text{CO}_2} \cdot N_M \cdot L)), \end{aligned} \quad (16)$$

where χ is a constant not depending on N_M .

We approximated our experimental dependence by the function $y = A \cdot (1 - \exp(-B \cdot x)) + C \cdot x \cdot (1 - \exp(-2B \cdot x))$. The obtained curve is shown on

Figure 2; one can see that the function describes the experimental results quite well. It is also seen by the character of the dependence that at sufficiently high pressures the relation $|\Delta N_{M}|_{ms}/n_{eff(UV)}$ should be described by the function $y = 1 + \vartheta \cdot N_M$. Such type of dependence was really observed in our experiments.

At high pressures of CF_2HCl one can see the slight decrease of the experimental value of CF_2 concentration as compared to the calculated curve. This decrease more probably can be caused by the violation of an assumption about constancy of dissociation yield β_0 while CF_2HCl pressure changes.

The plot of the relation of the probing beam energy absorbed in the cell to the energy of the incident beam vs number of CO_2 -laser pulse at the initial CF_2HCl pressure of 20 Torr is presented in Figure 3. One can see that the initial exponential fall in $(I_0 - I)/I_0(n)$ is replaced after $n \approx 140$ by the plateau, and when $n > 200$ the UV beam passes the cell without losses in its intensity. The assumption that all the molecules CF_2HCl had already been dissociated up to this moment is incorrect: the mass-spectrometer analysis of the irradiated mixture revealed that after the 200th laser pulse CF_2HCl content in the gas is equal to 37% of its initial value. The same character has the dependence of the relation of the CO_2 -laser energy absorbed in the cell to the energy at the entrance of the cell (curve 2): when $n > 120$ the absorption of IR emission does not change. Those dependencies may be caused by the

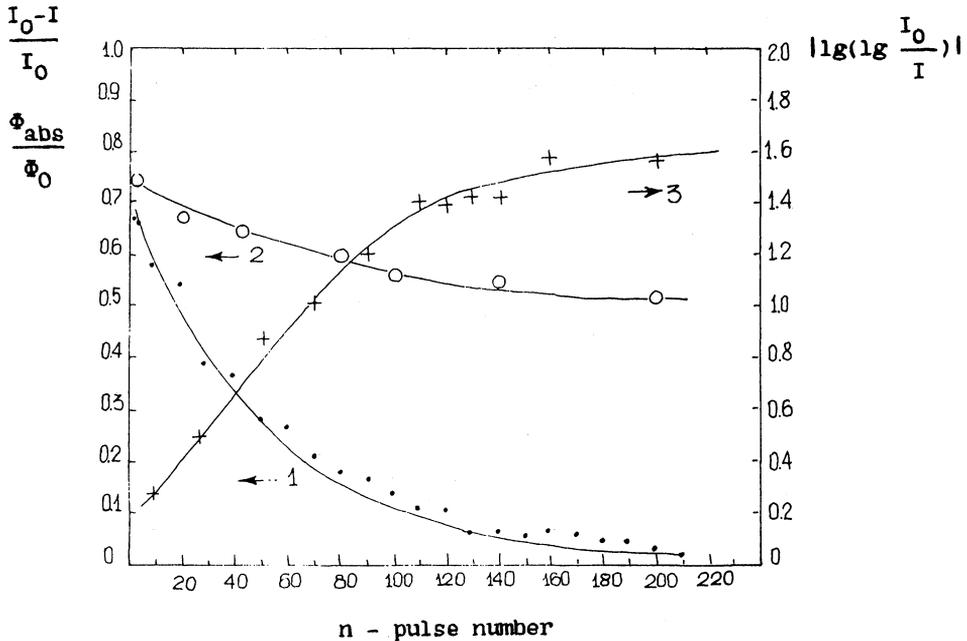


Figure 3 Plot of $(I_0 - I)/I_0$ -fraction of UV-beam energy ($\lambda = 248$ nm) absorbed in the cell (curve 1) and of relation of CO_2 -laser energy absorbed in the cell to the energy at the entrance of the cell (curve 2) vs CO_2 -laser pulse number. Initial CF_2HCl pressure 20 torr. Curve 3, the dependence of $|\lg(\lg(I_0/I))|$ upon the number of the pulse. I_0 and I , the energy of UV probing beam respectively at the entrance and at the exit of the cell.

accumulation of some substance in the cell as a number of pulses rises, which gives rise to fast relaxation of the excited molecules CF_2HCl . As the concentration of this substance increases, the moment is reached when both dissociation of CF_2HCl molecules and reaction of C_2F_4 formation at the collisions of vibrationally excited molecules CF_2HCl are ceased. As a result, firstly, CF_2 -radicals could not be detected in the gas after CO_2 -laser pulse, and, secondly, as CF_2HCl remains unchanged so does the part of IR irradiation, absorbed by the mixture. Besides this, there is one practical conclusion following the experimental results: in order to obtain reliable data gas should be irradiated by the limited number of CO_2 -laser pulses. The permissible number of pulses one can find from the condition of conservation of the linearity of the dependence $|\lg|(\lg(I/I_0))|_{(n)}$. Figure 3 demonstrates that this linearity has been kept up to the 60th pulse.

Only two substances are accumulated in the cell; C_2F_4 and HCl . To answer the question how does each of them influence the relaxation of the excited molecules CF_2HCl we carried out the experiments with model mixtures. The model mixtures were prepared on the basis of the ratio of gaseous components generated in the cell after its irradiation by 200 pulses of CO_2 -laser. The values of CF_2HCl , C_2F_4 and HCl pressures after the 200th pulse at various initial values of CF_2HCl pressure, determined using mass-spectrometer analysis, are presented in Table 1. When CF_2HCl relaxation on C_2F_4 was investigated the model mixture was prepared from these two gases, their partial pressures being chosen equal to those which were observed in the cell irradiated by 200 CO_2 -laser pulses. Figure 4 shows how does the portion of the absorbed in the cell IR beam energy $\Phi_{\text{abs.}}/\Phi_0$ (where $\Phi_{\text{abs.}} = \Phi_0 - \Phi_L$) change when irradiating the real mixture of gases CF_2HCl , C_2F_4 and HCl , obtained by the exposing of the neat CF_2HCl to 200 CO_2 -laser pulses, the same dependence for the model mixture (consisting only from CF_2HCl and C_2F_4) also being represented. One can consider that in the first approximation the curves coincide. It means that C_2F_4 is the main relaxant of excited molecules CF_2HCl . A little more higher absorption of IR beam by the real mixture as compared to the model mixture can be explained by the additional presence of HCl . It is interesting that the energy absorption in gas does not lead to CF_2HCl dissociation: in the whole range of investigated pressures both for real and model mixtures the absorption at $\lambda = 248 \text{ nm}$ was not observed. C_2F_4 formation owing to direct interaction of excited molecules CF_2HCl was not also observed: mass-spectrometer analyses showed that starting with the 200th pulse CF_2HCl concentration remained unchanged.

The experiments in which the influence of HCl on CF_2HCl MPD yield was investigated were carried out for the model mixture $\text{CF}_2\text{HCl}:\text{HCl} =$

Table 1 The pressures of the mixture gas-phase components (torr) after CF_2HCl irradiation with 200 CO_2 -laser pulses

Initial pressure CF_2HCl	2	4	6	8	10	12	14	16	18	20
Final Pressure CF_2HCl	1.98	2.5	3.3	4.18	4.8	5.43	6.14	6.84	7.2	7.5
C_2F_4	0.01	0.75	1.35	1.9	2.6	3.28	3.93	4.58	5.4	6.25
HCl	0.02	1.5	2.7	3.8	5.2	6.56	7.86	9.16	10.8	12.5

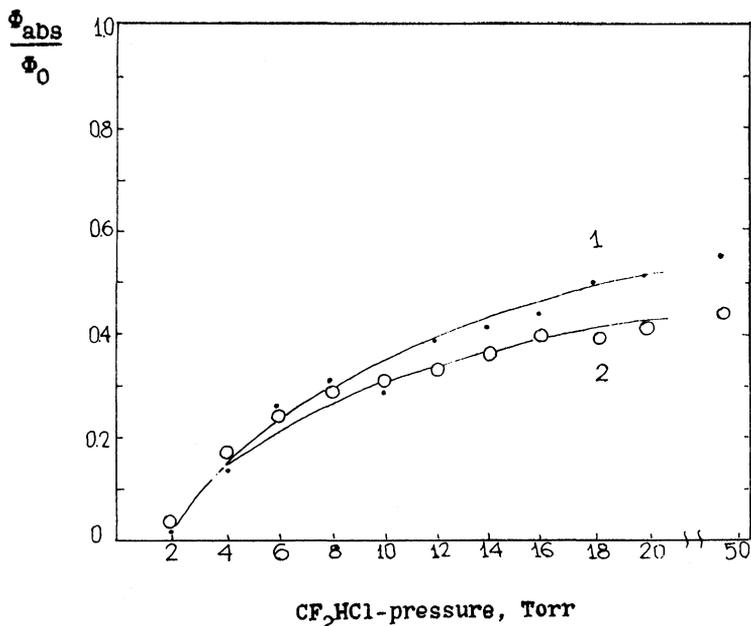


Figure 4 Plot of fraction of CO₂-laser energy absorbed in the cell vs initial gas pressure: (1) for the 200th pulse to the cell with neat CF₂HCl. (2) For the first pulse to the cell with model mixture CF₂HCl + C₂F₄, prepared according to Table 1.

7.5 Torr:12.5 Torr. The comparison of data of the dependence of UV-beam attenuation on the number of CO₂-laser pulses for this mixture and for the neat CF₂HCl points out their full identity (see Figure 5). This means that in our circumstances HCl practically does not affect the process of CF₂HCl multiphoton dissociation. But at the same time the adding of hydrogen chloride to CF₂HCl increases the amount of IR radiation energy absorbed by the gas (curves 2 and 3 on Figure 5). This increase of the portion of the absorbed energy does not lead, however, to the enhancement of the yield of C₂F₄ formation reaction at CF₂HCl collisions. Really, the results of the comparison of mass-spectral peaks heights $m/e = 51$ (molecule CF₂HCl) N_{200} and N_0 , respectively after the irradiation of the gas with 200 pulses and before the irradiation, for the model mixture CF₂HCl + HCl and for the neat CF₂HCl show that $(N_{200}/N_0)_{CF_2HCl}/(N_{200}/N_0)_{CF_2HCl+HCl} = 0.95 \pm 0.01$, i.e. the dissociation yield in the model mixture is even lower than in the neat CF₂HCl. But it means that the additional IR radiation energy absorbed by the gas due to increase of HCl content is consumed mainly to gas heating, without essential influence on the processes of dissociation and interaction between vibrationally excited molecules CF₂HCl.

Figure 6 shows how the total CF₂HCl MPD-yield and CF₂-radicals yield after the first CO₂-laser pulse change with increasing of C₂F₄ content in mixture. One can see that the yield of CF₂-radicals diminishes in two times at C₂F₄ pressure near 1.5 Torr. Those data permitted us to evaluate the rate constant of the reaction

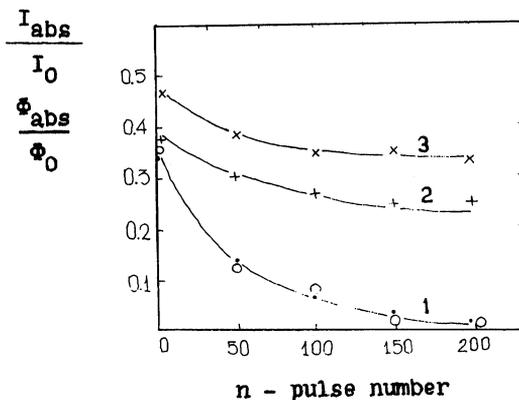


Figure 5 Development with a pulse number of the attenuation degree of UV beam for the mixture $\text{CF}_2\text{HCl}:\text{HCl} = 7.5 \text{ torr}:12.5 \text{ torr}$ (\cdot) and for CF_2HCl with initial pressure 7.5 torr (\circ) (curve 1). Curve 2, the dependence on the pulse number of the relative absorption of CO_2 -laser pulse energy for CF_2HCl at initial pressure 7.5 torr. Curve 3, the same for the mixture $\text{CF}_2\text{HCl}:\text{HCl} = 7.5 \text{ torr}:12.5 \text{ torr}$.

of CF_2HCl deactivation on C_2F_4 . Really in order to weaken the process of dissociation in two times the probability of the molecule's transition to the lower level, from which the dissociation is no longer possible, should become equal to the probability of CO_2 -laser quantum absorption by CF_2HCl molecule. Or, in other words, relaxation time should become equal to excitation time: $\tau_{\text{rel}} = \tau_{\text{exc}}$. The relaxation time $\tau_{\text{rel}} = 1/(k_{\text{rel}} \cdot [\text{C}_2\text{F}_4])$. Since during CO_2 -laser pulse the molecule absorbs 18 CO_2 -laser quanta one can consider the characteristic time of the excitation of CF_2HCl molecules, occupying the energy levels situated not far from the dissociation threshold,

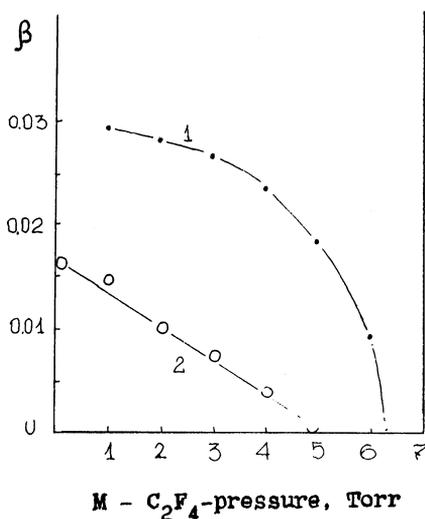


Figure 6 Plot of total CF_2HCl dissociation yield in one pulse (1) and of CF_2 -radicals yield (2) in the first pulse for the mixture $\text{CF}_2\text{HCl}:\text{C}_2\text{F}_4 = 7.5 \text{ torr}:M$ vs initial C_2F_4 pressure.

to be equal to $(10^{-6}/18)$ s. While comparing those values one can get an estimation of the rate constant of CF_2HCl relaxation on C_2F_4 : $k_{\text{rel}} \sim 5 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Thus, the relaxation of vibrationally excited CF_2HCl molecule occurs almost at every collision with C_2F_4 molecule. This estimate is made under the supposition that CF_2HCl molecule is excited over the dissociation threshold only by 1–2 quanta of CO_2 -laser, where the time of the dissociation is less than 10^{-7} s.¹⁷

In our experiments the dissociation yield does not exceed a few percent, that is why one can consider that at C_2F_4 pressures higher than 4 Torr each excited CF_2HCl molecule is surrounded by approximately a hundred of “cold” C_2F_4 molecules. The first stage of CF_2HCl vibrational energy relaxation is the resonance transfer of energy to C_2F_4 molecules promoted by the nearness of the frequencies of the bands ν_8 (1127 cm^{-1}), $\nu_4 + \nu_6$ (1214 cm^{-1}) and others of CF_2HCl and of the bands ν_{12} (1186 cm^{-1}) C_2F_4 ; and also of the bands ν_2 (1313 cm^{-1}) and ν_7 (1351 cm^{-1}) CF_2HCl and the band ν_{10} (1337 cm^{-1}) C_2F_4 .^{19,20} Then the vibrationally excited molecules lose their energy due to V-T relaxation. The same relaxation processes, where the presence of the frequency resonances between the excited and quenching molecules plays an important role, were observed for SF_6 multiphoton dissociation in the presence of NH_3 and C_2H_4 ,¹⁷ or for CF_2HCl MPD in the presence of CF_3Cl .²¹

Within the frames of the described mechanism one can also explain a weak action of HCl on relaxation of excited molecules CF_2HCl : the energy of the bands ν_1 (3023 cm^{-1}) and $\nu_1 + \nu_6$ (3435 cm^{-1}) appears to be the most close to the energy of the level $v = 1$ HCl ($\sim 2900 \text{ cm}^{-1}$); but because of the significant energy defect vibrational-vibrational exchange in the system $\text{CF}_2\text{HCl} + \text{HCl}$ would not be fast.

CONCLUSION

For the first time the existence of C_2F_4 formation at the binary collisions of vibrationally excited molecules CF_2HCl was directly confirmed. The input of this reaction to the products formation at CF_2HCl pressures of tens Torr was shown to become predominant. Discovering the fast relaxation of vibrationally excited CF_2HCl molecules on the product's molecules C_2F_4 due to the resonance energy exchange between those molecules seems to be the second significant result of this work; the rate constant of this process was estimated to be $5 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The presence of the process of “self-relaxation” restricts the degree of the initial matter conversion to the products at the irradiation of gas in the limited volume.

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