# Multiphoton dissociation of $C_3F_6O$

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Major characteristics of multiphoton absorption and multiphoton dissociation of hexafluoropropene oxide (HFPO) were studied. Spectral relationships of the average number of IR photons absorbed per molecule and the yield of multiphoton dissociation were determined in the range of 1040—985 $cm^{-1}$ at different laser fluences. At the laser line 1025.3 $cm^{-1}$, the effect of collisions with buffer gases on the HFPO multiphoton absorption and multiphoton dissociation was studied and the $q$-factor was determined ($q = 0.6$ at $\Phi = 0.55$ $J$ $cm^{-2}$). Characteristic features of HFPO decomposition under collisional conditions ($p_{HFPO} > 0.1$ Torr) were discussed. An anomalous difference in the values for quantum efficiency of multiphoton dissociation for long-wave and short-wave wings of HFPO absorption band was revealed. A procedure for correlating the experimental and theoretical data on the yield of multiphoton dissociation (when the $q$-factor is unknown) was suggested, and corresponding calculations were performed for the frequency 989.6 $cm^{-1}$.

**Key words:** multiphoton absorption, multiphoton dissociation, hexafluoropropene oxide, quasicontinuum, $V—T$ relaxation, vibrational energy distribution, vibrational excitation, monomolecular decomposition.

Previously,[1] when studying pulse laser pyrolysis of hexafluoropropene oxide (HFPO) in the presence of $SF_6$ as a sensitizer, we obtained the line spectrum of this compound, which exhibited a strong absorption band in the region of $\nu_{C-F} = 1016$ $cm^{-1}$, which overlapped several lines (9P and 10R) of the TEA $CO_2$ laser. Furthermore, in accordance with the known criterion,[2] because of a high density of vibrational levels, the HFPO molecule has a low quasicontinuum limit, which we estimated at ~2800 $cm^{-1}$. Due to these facts and a low destruction threshold ($E_a = 36.5$ kcal/mol),[1, 3] HFPO is a suitable object for studying the processes of multiphoton absorption and multiphoton dissociation in relatively low-energy IR fields (<1 J $cm^{-2}$).

In this work, we studied major characteristics of the HFPO multiphoton absorption and multiphoton dissociation as a function of the laser fluences ($\Phi$) and frequency ($\omega_L$) of the laser radiation and the effect of collisions with the buffer gas on the HFPO absorption and dissociation.

## Experimental

A TEA $CO_2$ laser ($\tau_{1/2} = 100$ ns) tunable in 9- and 10-μm regions was used as a source of IR radiation. Laser radiation passed through a cylindrical stainless steel cell 8.2 cm long and 1.5 cm in diameter with $BaF_2$ face windows, and was recorded with a calibrated IMO-2N power meter. After irradiation, the content of the cell was analyzed with a 3700 chromatograph and a Specord 75 IR spectrophotometer. The pulse-repetition frequency of IR radiation in all experiments was 0.15 Hz.

Absorption of IR radiation of the $CO_2$ laser and decomposition of HFPO was studied at the short-wave wing of the HFPO absorption band (1040—1023 $cm^{-1}$) and at its long-wave wing (990—985 $cm^{-1}$). Within the study of multiphoton absorption, the pressure of HFPO ($p_{HFPO}$) varied in the range of 0.8÷8 Torr (in this case, the absorbed energy was no more than 30 %), and in the study of multiphoton dissociation, $p_{HFPO}$ was 0.1 Torr. The effective multiphoton absorption cross-section (σ) and the average number of IR photons absorbed by HFPO molecules (<$n$>) was determined by direct calorimetry. The values σ and <$n$> were calculated using well known formulas:[4]

$$\sigma = \ln(E_0 / E_{pas}) / N_{HFPO} l, \quad (1)$$

$$\langle n \rangle = (E_0 - E_{pas}) / hc\omega_L N_{HFPO}, \quad (2)$$

where $E_0$ is the energy of the incident laser radiation, $E_{pas}$ is the energy passed through the cell, $N_{HFPO}$ is the number of HFPO molecules in the irradiated volume, and $l$ is the length of the cell. The yield of HFPO multiphoton dissociation (β) was calculated from the relationship

$$\Delta c/c_0 = 1 - (1-\beta X)^n, \quad (3)$$

where $n$ is the number of pulses, $X$ is the ratio of the cell volume irradiated with the laser to the total volume, and $\Delta c/c_0$ is the extent of HFPO decomposition in the cell, which was determined by chromatography. IR spectroscopy and chromatography analyses of the content of the cell after irradiation indicated that only tetrafluoroethylene and perfluoroacetaldehyde were present as the HFPO decomposition products.

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## Results and Discussion

The effective cross-section of multiphoton absorption $\sigma$ and the average number of absorbed photons $<n>$ as functions of the laser fluences $\Phi$ were determined in the range of $\Phi$ = 0.05—0.7 J cm$^{-2}$ for frequencies 1039.4—1025.3 cm$^{-1}$ and in the range of $\Phi$ = 0.05—0.25 J cm$^{-2}$ for frequencies 1023.2 and 989.6—985.5 cm$^{-1}$. The magnitude of $\sigma$ varied in the range from $2 \cdot 10^{-20}$ to $1.7 \cdot 10^{-18}$ cm$^2$. The spectrum of the number of absorbed photons $<n>(\omega_L)$ is presented in Fig. 1 and compared with the spectrum of linear HFPO absorption. Although the maximum of the linear absorption band falls into the region, where no generation of a $CO_2$ laser occurs, Fig. 1 indicates that, with increasing radiation density $\Phi$, broadening of the absorption band and its long-wave shift occur, which is typical for multiphoton absorption of polyatomic molecules.

It has been known[4] that the parameter $<n>$ may be represented by a power function of the laser fluences $<n> \sim \Phi^{\alpha}$. We found a similar power dependence of experimental values $<n>$ for all of the laser generation lines in the region 1025—1040 cm$^{-1}$ with the parameter $\alpha$ increasing monotonically from 0.76 to 1.0. Furthermore, in this region, the form of the function $\sigma(\Phi)$ also changes monotonically: at $\omega_L$ = 1025.3 cm$^{-1}$ $\sigma$ decreases by one half ($\sigma = 1.7 \cdot 10^{-18} \div 8 \cdot 10^{-19}$ cm$^2$), and at $\omega_L$ = 1039.4 cm$^{-1}$ $\sigma$ remains unchanged in the same $\Phi$ range ($\sigma = 1 \cdot 10^{-19}$ cm$^2$). This indicates that, with increasing shift of the exciting frequency $\omega_L$ from the center of the linear absorption band, multiphoton absorption gradually changes to virtually linear absorption ($\sigma$ is independent of $\Phi$ and $<n> \sim \Phi$). Note that the values $<n>$ are significantly higher at rather small radiation density than those for the molecules like $SF_6$, $CF_3I$, and $(CF_3)_2CO$.[4—6]

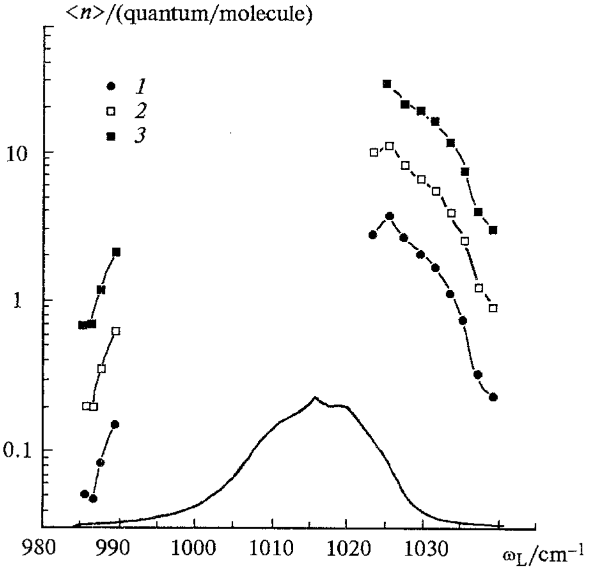

**Fig. 1.** The number of photons absorbed by HFPO molecules ($\Phi$/J cm$^{-2}$): 0.05 (*1*), 0.2 (*2*), and 0.7 (*3*). The solid line is the contour of the HFPO linear absorption band at $p_{HFPO}$ = 0.8 Torr.

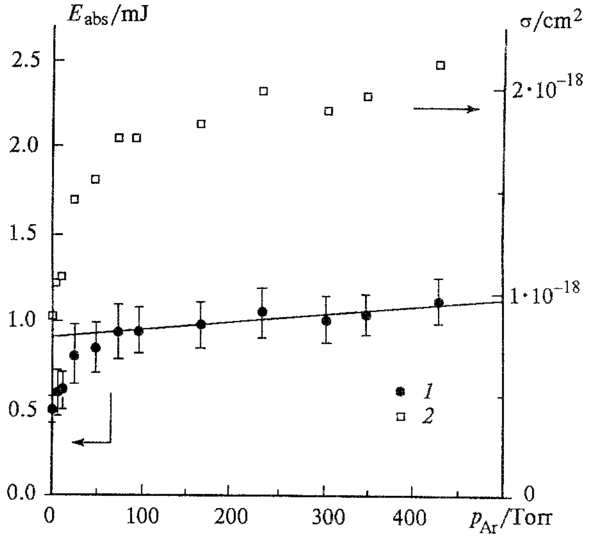

**Fig. 2.** Dependence of the absorbed energy (*1*) and the effective cross-section of multiphoton absorption (*2*) on the pressure of Ar ($p_{HFPO}$ = 0.5 Torr and $\omega_L$ = 1025.3 cm$^{-1}$).

The dependence of the absorbed energy $E_{abs}$ on the pressure of argon as a buffer gas ($p_{HFPO} = 0.2 \div 1.2$ Torr) was studied at the frequency $\omega_L$ = 1025.3 cm$^{-1}$, where the largest value of multiphoton absorption was observed (Fig. 2). At high pressure of the buffer gas, the effective cross-section of multiphoton absorption increases drastically, and at the Ar pressure above 70 Torr, a linear growth of absorption occurs due to the transmission of the vibrational energy from HFPO molecules to Ar atoms in the process of *V—T* relaxation during the laser pulse. These data were used for determining the fraction of molecules that fall in the quasicontinuum (*q*-factor) by the method proposed in Ref. 7. Inasmuch as the average energy of molecules in the quasicontinuum is independent of the presence of a buffer,[8]

$$q = E^0_{abs}/E_{sat}, \qquad (4)$$

where $E^0_{abs}$ is the absorbed energy in the absence of a buffer and $E_{sat}$ is the extrapolation of $E_{abs}(p_{Ar})$ to $p_{Ar}$ = 0 (which fits the condition $q$ = 1). The value of the *q*-factor was found to remain unchanged (Table 1) within the experimental error when increasing the HFPO pres-

**Table 1.** *q*-Factors of HFPO molecules at $\omega_L$ = 1025.3 cm$^{-1}$

| $p_{HFPO}$/Torr | $\Phi$/J cm$^{-2}$ | $<q>$ |
|---|---|---|
| 0.2 | 0.50 | 0.43±0.25 |
| 0.5 | 0.59 | 0.60±0.12 |
| 1.2 | 0.54 | 0.60±0.06 |

sure from 0.2 to 1.2 Torr. This is in agreement with the data that we obtained previously: at $\omega_L$ = 1025.3 cm$^{-1}$, the effective cross-section of the absorption of laser radiation remains unchanged when increasing the HFPO pressure to 1.5 Torr.[9] The value of the *q*-factor determined for HFPO at $\Phi$ = 0.55 J/ cm$^2$ $\langle q \rangle$ = 0.6 correlates well with the available data for polyatomic molecules.[4,7,8]

The second part of this work deals with the study of multiphoton dissociation of HFPO. As known,[3] the following reactions occur within the HFPO decomposition:

$$C_3F_6O \rightarrow CF_3CFO + :CF_2,$$
$$2\ :CF_2 \rightarrow C_2F_4.$$

The activation energy of the primary reaction of HFPO decomposition is 36.5 kcal/mol,[1,3,10–12] which makes it possible to determine the destruction threshold of HFPO, $D \approx 12800$ cm$^{-1}$. This value is significantly lower than the dissociation energy of the molecules $SF_5NF_2$, $S_2F_{10}$, and $CF_3I$ most readily decomposing within multiphoton dissociation, for which $D$ = 17500—20000 cm$^{-1}$. [2,4,13]

This low value of the destruction energy for HFPO together with a sufficiently high cross-section of multiphoton absorbtion results in an efficient decomposition of HFPO molecules. Figure 3 shows the extent of HFPO decomposition in a reaction cell during one laser pulse $\Delta c/c_0$ as a function of the pressure of the reactant. From formula (3) it follows that $\Delta c/c_0$ cannot exceed the ratio of the irradiated volume of the cell to its total volume *X*, which was equal to 0.2—0.3 in our experiments. Hence, the observed excess of $\Delta c/c_0$ over *X* at $p_{HFPO} > 0.4$ Torr (Fig. 3) indicates that decomposition of HFPO also occurs outside the irradiated volume. Conceivably this result might be attributed to the fact that thermal dissociation of HFPO increases with pressure and becomes dominant over multiphoton dissociation at high pressures, because a high temperature (>1000 K) is developed as a result of post-pulse *V—T,R* relaxation of multiphoton-excited HFPO molecules (or vibrationally excited products of their decomposition) followed by a rapid expansion of the heated gas toward the walls of the reaction cell. Hence, $\Delta c/c_0$ is much larger than *X* and attains its limiting value 0.72 at the HFPO pressure 4 Torr. At higher HFPO pressure (5—6 Torr), more than 90 % of the energy of laser radiation is absorbed in the reaction volume, absorption becomes significantly nonlinear along the length of the cell, and a larger part of the molecules located near the outlet window of the cell ceases to absorb IR radiation efficiently, which results in a decrease in the extent of HFPO decomposition. Note that, for other molecules (*e.g.*, $SF_6$[14] and cyclo-$C_5F_8$[15]), the pressure dependence of the extent of decomposition is quite different in nature: the yield of multiphoton dissociation monotonically decreases with an increase in the pressure of the reactant. Evidently, this is due to the difference in destruction energies of HFPO and these compounds; in the case of $SF_6$ and cyclo-$C_5F_8$, this makes it impossible to attain by *V—T,R* relaxation the temperatures sufficient for their thermal decomposition in considerable quantities.

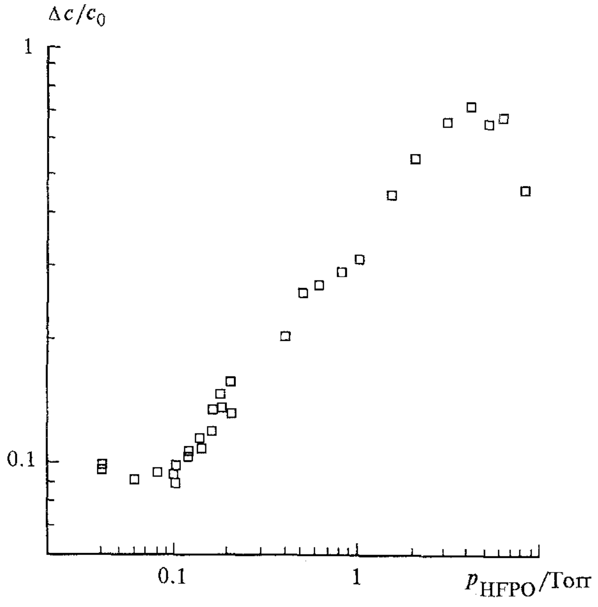

**Fig. 3.** Extent of HFPO decomposition in the reaction cell during one laser pulse $\Delta c/c_0$ ($\omega_L$ = 1025.3 cm$^{-1}$).

For separating multiphoton dissociation from competing processes of HFPO decomposition, operation at low pressure is necessary. Figure 3 indicates that the value $\Delta c/c_0$ remains unchanged at HFPO pressure $p_{HFPO} <$ 0.1 Torr, when the conditions for noncollisional multiphoton excitation of HFPO molecules occur ($\tau_{col} \approx$ 1.6 μs >> $\tau_{1/2}$). Thus, in the experimental determination of the yield of HFPO multiphoton dissociation, we chose the working pressure of HFPO 0.1 Torr.

The spectrum of HFPO multiphoton dissociation $\beta(\omega_L)$ (Fig. 4), like the spectrum $\langle n \rangle(\omega_L)$, exhibits a shift of IR absorption to the long-wave region relative to the maximum of linear absorption. Dependences b($\Phi$) in the form $\beta \sim \Phi^\alpha$ were determined for all exciting frequencies of laser radiation in the regions of 1036—1025 cm$^{-1}$ and 990—985 cm$^{-1}$.[4] It was found that the parameter a takes the values 3.3—5.8, and rather high yields of HFPO multiphoton dissociation b are observed at moderate values of $\Phi$ ($\beta \approx 0.1$ at $\Phi$ = 0.54 J cm$^{-2}$).

For comparing the spectra of HFPO absorption and multiphoton dissociation, we employ the concept of the quantum efficiency of multiphoton dissociation φ:[16]

$$\varphi = D \cdot \beta / \langle E \rangle, \qquad (5)$$

where $\langle E \rangle$ is the average energy of laser radiation absorbed by HFPO molecules. The value φ makes it possible to compare experimental data on multiphoton dissociation for different values of $\Phi$ and radiation frequencies $\omega_L$, because it is independent of the *q*-factor.

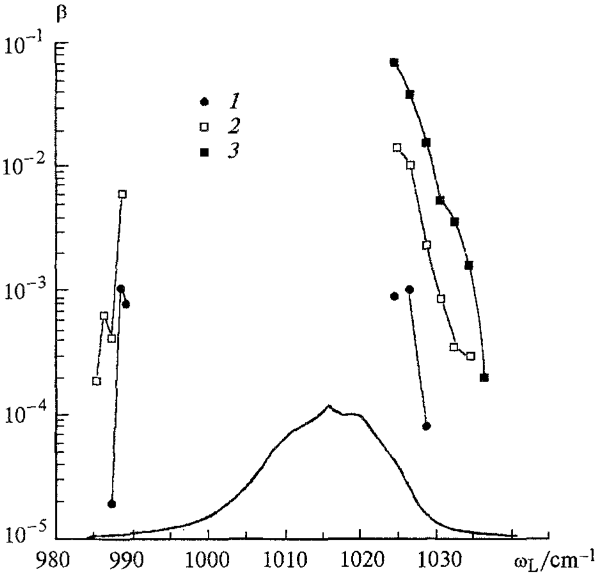

**Fig. 4.** Spectrum of the yield of HFPO multiphoton dissociation β at the laser fluence ($\Phi$/J cm$^{-2}$): 0.15 (*1*), 0.3 (*2*), and 0.45 (*3*). The solid line is the HFPO linear absorption.

The values $\langle E\rangle$, β and φ for some frequencies of laser radiation at $\Phi$ = 0.25 J cm$^{-2}$ are given in Table 2, which indicates that the values φ for the frequencies closest to the maximum of linear absorption from the long-wave side are more than an order of magnitude larger than those for the frequencies closest to the maximum of linear absorption from the short-wave side. Note that the absolute values of quantum efficiencies are extremely low; in the short-wave region of the spectrum of multiphoton dissociation, they are no more than 0.04 even at $\Phi$ = 0.43 J cm$^{-2}$, which is significantly smaller than the values obtained, for example, for $CF_3I$.[16] Apparently, a more complex HFPO molecule has a rather long lifetime of the excited state because of the redistribution of energy through a large number of vibrational degrees of freedom. On the other hand, as Table 2 indicates, the average absorbed energies at the frequencies $\omega_L$ = 1025.3 and 989.6 cm$^{-1}$ differ nearly by a factor of 20, although the yields of multiphoton dissociation are approximately the same. Qualitative explanation of this fact can be similar to that proposed in Ref. 17. At the long-wave wing of the spectrum of multiphoton dissociation, the frequency of the exciting radiation 989.6 cm$^{-1}$ (compared to $\omega_L$ = 1025.3 cm$^{-1}$ at the short-wave wing) is significantly less efficient in the excitation of the lowest vibrational levels of HFPO because of a large shift from the center of the linear absorption band (which results in a lower value of the *q*-factor), but, because of the long-wave frequency shift, it has a large absorption cross-section in the quasicontinuum.[4] Thus, for $\omega_L$ = 989.6 cm$^{-1}$, a higher level of molecular excitation must occur in the quasicontinuum, and the yield of multiphoton dissociation is determined primarily by the value of the *q*-factor. According to our estimation, 3 % of HFPO molecules are already in the quasicontinuum at 298 K. Hence, by varying the unknown value $q$ ($q \geq 0.03$) and assuming the definite form of the distribution of molecules by energy, one can explain the yields of multiphoton dissociation observed in the experiment. Thus, at $\Phi$ = 0.25 J cm$^{-2}$ for the Boltzmann distribution of molecules by energy, we calculated the $q$ values providing the best agreement between the experimental and theoretical yields of multiphoton dissociation. In this calculation, we used two variants of the theoretical estimation for β: the fraction of molecules with energies higher than the destruction energy of HFPO ($D$ = 12800 cm$^{-1}$) and the fraction of molecules with the rate constant of monomolecular decomposition[18] $k(E) \geq 1/\tau_{col} = 6.1 \cdot 10^5$ c$^{-1}$ ($k(E)$ was calculated by the Forst's method[19,20]). The theoretical and experimental yields of multiphoton dissociation agree at $q$ = 0.105 for the first variant and at $q$ = 0.07 for the second variant (Fig. 5).

**Table 2.** Average absorbed energy $\langle E\rangle$, yield of multiphoton dissociation (β), and quantum efficiency of multiphoton dissociation (φ) for HFPO molecules at $\Phi$ = 0.25 J cm$^2$

| $\omega_L$/cm$^{-1}$ | $\langle E\rangle$/ cм$^{-1}$ | β | φ |
|---|---|---|---|
| 987.6 | 415 | 0.00018 | 0.00569 |
| 988.6 | 571 | 0.00379 | 0.08478 |
| 989.6 | 751 | 0.01092 | 0.18568 |
| 1025.3 | 13078 | 0.00681 | 0.00667 |
| 1027.4 | 9717 | 0.00563 | 0.00737 |
| 1029.4 | 8213 | 0.00094 | 0.00145 |
| 1031.5 | 6827 | 0.00037 | 0.00070 |
| 1033.5 | 4878 | 0.00012 | 0.00031 |

However, at $\omega_L$= 1025.3 cm$^{-1}$, where the *q*-factor was determined experimentally, an obvious discrepancy occurs between the low yield of multiphoton dissociation and the high absorbed energy (Table 2). Assuming $q$ = 0.6 and considering the distribution of excited molecules by energy the Boltzmann distribution (because, in this case, $\langle E\rangle \approx$ 14500 cm$^{-1}$ > $D$),[21] we used both variants of estimating the yield of HFPO multiphoton dissociation at $\Phi$ = 0.25 J cm$^{-2}$. We obtained the values β = 0.59 for the first variant and β = 0.55 for the second variant (Fig. 5). Inasmuch as in both cases the major part of HFPO molecules in quasicontinuum must decompose, the choice of another type of distribution of vibrational energy of excited molecules (for example, close to the Poisson distribution[16]) probably will not change these estimates, because these energy distributions differ primarily at the edges. However, as indicated by Table 2, calculated values of β are almost two orders of magnitude larger than the experimental yield of multiphoton dissociation. This fact thus far remains unclarified.

Figure 6 presents the dependence of the yield of multiphoton dissociation β (at the pressure of the reactant $p_{HFPO}$ = 0.1 Torr) on the pressure of buffer gases

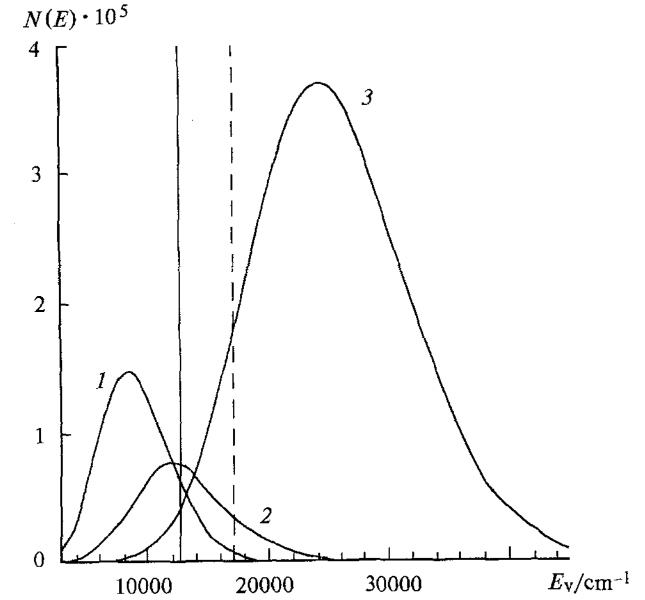

**Fig. 5.** Boltzmann energy distribution of HFPO molecules in the quasicontinuum at $\Phi$ = 0.25 J cm$^2$:
(*1*) $\omega_L$ = 989.6 cm$^{-1}$, $q$ = 0.105, $<E_q>$ = 7600 cm$^{-1}$, and $T_v$ = 912 K;
(*2*) $\omega_L$ = 989.6 cm$^{-1}$, $q$ = 0.07, $<E_q>$ = 11500 cm$^{-1}$, and $T_v$ = 1166 K;
(*3*) $\omega_L$ = 1025.3 cm$^{-1}$, $q$ = 0.60, $<E_q>$ = 24300 cm$^{-1}$, and $T_v$= 1970 K. $T_v$ is the temperature of HFPO molecules in the quasicontinuum corresponding to the absorbed energy $<E_q>$. The solid vertical line corresponds to the HFPO destruction energy $D$ = 12800 cm$^{-1}$, and the dashed line corresponds to the energy, at which $k(E)$ = $1/\tau_{col}$.

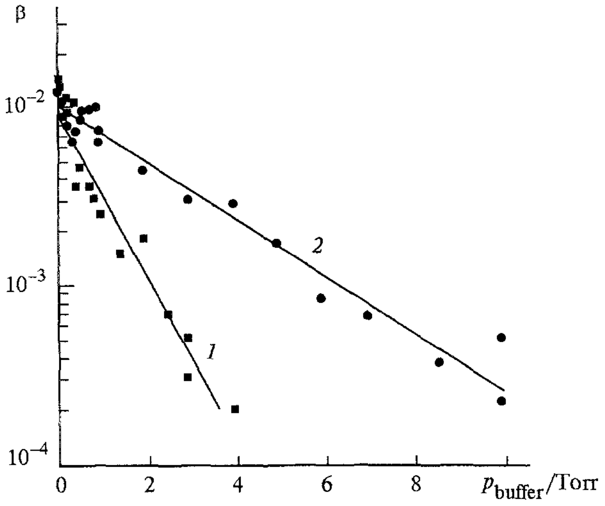

**Fig. 6.** The yield of HFPO multiphoton dissociation as a function of the pressure of buffer gases $SF_6$ (*1*) and Xe (*2*) at $\Phi$ = 0.25 J cm$^{-2}$ and $p_{HFPO}$ = 0.1 Torr; $\omega_L$ = 1025.3 cm$^{-1}$.

Xe and $SF_6$. An exponential decrease in the yield of HFPO multiphoton dissociation occurs with an increase in the pressure of buffer gases, and the constant that characterizes the efficiency of decreasing β is 2.9 times larger in the case of $SF_6$ as a buffer gas, than in the case of Xe. The qualitative character of this dependence is determined by the competition of monomolecular HFPO decomposition and the process of *V—T* relaxation of vibrational energy at the molecules of the buffer gas, especially after the completion of the laser pulse. The efficiency of *V—T* relaxation is characterized by the value $<\Delta\varepsilon>$, which is the average energy transmitted from the vibrationally excited molecule of the reactant to the molecule of the buffer gas during the collision; $<\Delta\varepsilon>$ is much larger for polyatomic buffers than for monoatomic buffers.[22] In addition to a decrease in the yield of multiphoton dissociation due to deactivation, collisions with the buffer gas during the laser pulse cause an increase in β as a result of an increase in the $q$-factor. The latter process plays a determining role when $q << 1$ (for rather simple molecules: $CDF_3$ [23] and $CH_2FCl$ [24]). In this case, with an increase in the pressure of the buffer gas, β first increases to some extent and then decreases. The observed yield of multiphoton dissociation can also grow with an increase in the pressure of the buffer gas, if the latter suppresses the reverse reaction of the radicals formed at multiphoton dissociation, as it occurs for $CF_3I$ and the buffer gas $O_2$;[25] in this case, the true yield of multiphoton dissociation decreases. For the molecules with $q \sim 1$, β gradually decreases with increasing pressure of the buffer gas. For HFPO, $q < 1$, but, as indicated by Figs. 2 and 6, when the pressure of the buffer gas increases, the increase in the yield of multiphoton dissociation due to the increase in the $q$-factor is significantly slower than the decrease in the yield of multiphoton dissociation due to deactivation. Thus, the monotonic decrease in β does not necessarily indicate that under the given conditions $q \simeq 1$, as was assumed previously.[15]

An exponential decrease in the yield of multiphoton dissociation is already known, for example, for $SF_6$[14] and perfluorocyclopentene[15]. Moreover, it was found that $SF_6$ decreases the yield of multiphoton dissociation 10 times more efficiently than Ar does.[15] This result is in agreement with our data, because the value $<\Delta\varepsilon>$ for Xe as a buffer gas is significantly larger than that for Ar.[22]

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