Investigation of SF_6 molecule absorption in a wide range of infrared-laser intensity

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The transition from linear absorption in the ν_3 vibration of SF_6 to multiphoton absorption in the CO_2-laser radiation intensity range $1–10^6$ W/cm^2 is investigated experimentally. The absorption of the molecule in the transition intensity region up to $10^3–10^4$ W/cm^2 can be satisfactorily explained if account is taken the multiphoton and single-photon weakly forbidden transitions $\Delta R \neq 0$ and $\Delta n \neq 0$ are taken into account.

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1. INTRODUCTION

The importance of taking into account weakly forbidden transitions in the analysis of the excitation of molecules by laser radiation was pointed out in Ref. 1. Of great importance for the understanding of multiphoton molecule excitation is the study of the transition from linear absorption and simple saturation of vibration-rotational transition to absorption of molecules at higher intensities. The character of this transition should depend quite strongly on the types of transitions and on the concrete mechanism of the multiphoton absorption of the molecules.

The characteristic value of the saturation power of molecular transitions in the absence of collisions, as a function of the dipole moment of the transition, is $1–10^2$ W/cm^2 (0.1–10 μJ/cm^2),[1)] and the molecule dissociation thresholds lie in the range 0.01–1 GW/cm^2 (1.0–100 J/cm^2), corresponding to a range of variation of the laser-radiation intensity of approximately 9 orders of magnitude. The presently available data pertain to both low and relatively high intensities.

At low laser intensities, 0.1–100 W/cm^2 (0.01–10 μJ/cm^2), the absorption of certain molecules was investigated previously[2-5] in connection with a study of self-induced transparency and with research on Q-switching of IR lasers with the aid of cells with absorbing gases. The main shortcoming of these studies is that they were made at relatively large thicknesses of the optical layer. In this case, at a laser intensity of the order of the saturation intensity, $I \approx I_{sat}$, the absorbing layer becomes strongly bleached and the intensity of the laser radiation is unevenly distributed over the length of the layer. The latter circumstance makes it impossible to determine with sufficient accuracy the average number of the absorbed photons per molecule in the illuminated volume. Among the other shortcomings of these studies were the relatively high gas pressures used in the experiments or else that the investigations were made in a relatively narrow range of intensities.

Data obtained by a number of authors[6-11] at relatively high intensities $I \gtrsim 10^4$ W/cm^2 ($\gtrsim 1$ mJ/cm^2) point to a relatively monotonic increase of the energy absorbed by complex molecules, in the form of a power function with exponent that approaches unity for certain molecules. There are no data on the absorption by molecules in the intermediate intensity region.

In the present study we investigated the dependence of the energy absorbed in SF_6 on the radiation intensity of a CO_2 laser in the intensity range $1–10^6$ W/cm^2 (10^{-7}–0.1 J/cm^2). The study of molecule absorption in such a wide range of intensities is in itself a rather complicated problem. The experiments were therefore performed with a laser setup[12] without continuous frequency tuning, at fixed frequencies of the CO_2 laser and with the working mixture at atmospheric pressure. The interpretation of the results at intensities up to approximately 10^4 W/cm^2 takes into account the weakly forbidden transitions $\Delta R \neq 0$ and $\Delta n \neq 0$. Some preliminary results are given in Ref. 13.

2. MEASUREMENT PROCEDURE AND EXPERIMENTAL RESULTS

We measured in the experiments the absorption of the radiation of a CO_2 laser in uncooled gas cells filled with SF_6 (Fig. 1). To eliminate the influence of collisions, the measurements were performed at a gas pressure lower than 0.4 Torr.

We used for the measurements an electroionization CO_2 laser[12] with pulse energy up to 0.2 J and duration 150 nsec at a laser-mixture pressure 1 atm. The laser resonator was made up of a 100 lines/mm diffraction grating and a flat semitransparent mirror located 150 cm away. The spectral width of the laser radiation, measured with a scanning Fabry-Perot interferometer

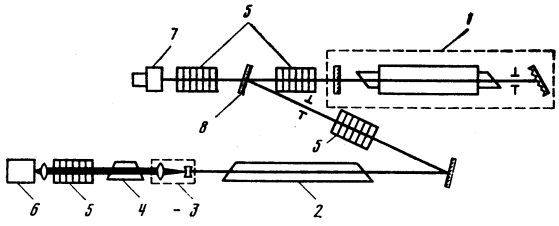

FIG. 1. Measurement setup: 1—CO_2 laser, 2, 4—cells with SF_6; 3—telescope, 5—set of attenuators, 6—"svod" photoreceiver, 7—thermcouple pile, 8—semitransparent mirror.

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was ~0.008 cm^{-1}. Since the spectral interval between the axial modes of the resonator is 3.3×10^{-3} cm^{-1}, this value corresponds to approximately three modes in the laser emission spectrum. We used in the laser a mixture CO_2:N_2 = 1:2. The impact width of the gain lines amounted in this case 0.18 cm^{-1}. The measurements were performed on the lasing lines $P(14)$, $P(18)$, $P(22)$, and $P(26)$ in the 10.6 μm band of the CO_2 laser emission. The absorption of the SF_6 was measured on the transition in the R branch [$P(14)$ line of the CO_2 laser] and P branch (remaining laser lines) of the ν_3 band. The measurements covered the intensity range from 1 to 4×10^6 W/cm^2 (3×10^{-7}–0.6 J/cm^2).

The laser radiation was directed into the absorbing cell and was then registered with a cooled Ge:Au photoreceiver. Part of the laser radiation at the input of the absorbing cell was diverted in order to measure the reference signal. The intensity of the radiation at the entrance to the cell and ahead of the photoreceiver was varied with sets of calibrated filters made up of layers of teflon film 30 μm thick. The total range of variation of the intensity at the entrance to the cell reached in this case 6–7 orders of magnitude. Since the transmission of the filter system depends quite strongly on the orientation and angle of setting of each filter, the accuracy of the filter setting was carefully monitored. The minimum photoreceiver sensitivity was 10 W (1 μJ). To measure the absorption in the SF_6 at a radiation power density <10 W/cm^2, a 4-power telescope was placed at the entrance of the gas cell to spread the laser beam.

The measurements were performed using cells of lengths 12, 65, and 145 cm, inasmuch as in a constant cell length the thickness of the optical layer changes during the course of the measurement by one or two orders of magnitude, and reliable measurements of the absorption at high and low intensities become impossible.

The measurement consists of recording the signal at the exit from first evacuated and then gas-filled cells, and of varying the intensity of the laser radiation in the cells and ahead of the receivers with the aid of calibrated filters, and comparing the measured and reference signals. From the known geometry of the cell illumination, we determined the total number of molecules in the absorbing gas volume

$$N=N_0V=N_0S_{\text{eff}}L,$$

The average number of absorbed photons

$$\langle n\rangle=\frac{\mathcal{E}_{\text{in}}}{h\nu}\frac{1}{N_0S_{\text{eff}}L}\ln\frac{\mathcal{E}_{\text{in}}}{\mathcal{E}_{\text{out}}} \qquad (1)$$

and the parameter

$$\delta=\frac{S_{\text{eff}}h\nu\langle n\rangle}{\mathcal{E}_{\text{in}}}=\frac{1}{N_0L}\ln\frac{\mathcal{E}_{\text{in}}}{\mathcal{E}_{\text{out}}}. \qquad (2)$$

The parameter δ has the dimension cm^2 and is close in its physical meaning to the product of the multiphoton absorption cross section σ by the fraction q of the molecules that take part in the absorption ($\mathcal{E}_{\text{in}}$ and $\mathcal{E}_{\text{out}}$ are the energies of the laser pulse at the entrance and exit

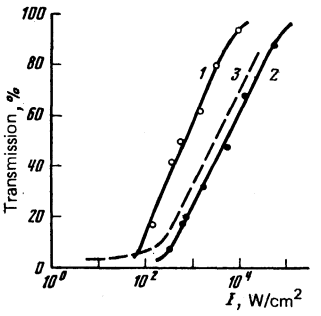

FIG. 2. Induced transparency of cells at large optical thickness of the absorbing layer: 1) cell length L = 65 cm, gas pressure p = 0.16 Torr, laser line $P(14)$; 2) L = 65 cm, p = 0.16 Torr, laser line $P(18)$; 3) data of Ref. 2 [p = 0.01 Torr, L = 9.5 m, and laser line $P(20)$].

from the cell; N_0 is the molecule concentration, and L is the length of the cell). To increase the accuracy of the determination of $\langle n\rangle$ and δ the experiments were performed at a moderate optical-layer thickness $\varkappa$. Since the duration of the laser pulse in the experiment remained unchanged (t_p = 150 nsec), the energy and power scales of the laser radiation are in a one-to-one correspondence in this case. Some measurements of the absorption at high intensities of the laser radiation, $\geq10^6$ W/cm^2 (0.1 J/cm^2) were performed previously using an optical-acoustic detector.[7]

The results of the investigations of the absorption of the CO_2 radiation in the ν_3 band of SF_6 are shown in Figs. 2–5. At a relatively large optical thickness of the absorbing layer, a characteristic rather strong induced transparency of the gas is observed (Fig. 2), recalling in general outline the transparency noted in earlier studies.[2-3]

The most important features in the behavior of the curves shown in Figs. 3–5 are: 1) the absence of sharp breaks on going through the boundary of saturation of the linear absorption (marked by a vertical arrow on the left) and 2) formation of horizontal sections (plateaus) on the $\delta(I)$ curve at laser intensities up to 10–100 W/cm^2 (1–10 $\mu J/cm^2$)—Figs. 4 and 5. At low intensities, the average number absorbed photons increases in pro-

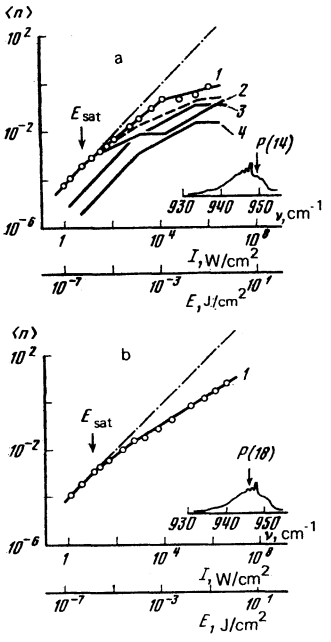

FIG. 3. Dependence of the average number of absorbed photons $\langle n\rangle$ per molecule on the CO_2 laser intensity: a—on the $P(14)$ line, b—on the $P(18)$ line. Curves: 1) results of the measurements, 2, 3, 4) approximations of the absorption on the respective transitions ^0R, $\Delta n\neq0$; ^0R, $\Delta n=0$, and ^1Q, $\Delta n\neq0$. Dashed curve—approximation of the total absorption, dash-dot lines—continuation of linear absorption, E_{sat}—saturation energy of the allowed transitions. In the lower right is shown the absorption-band contour.

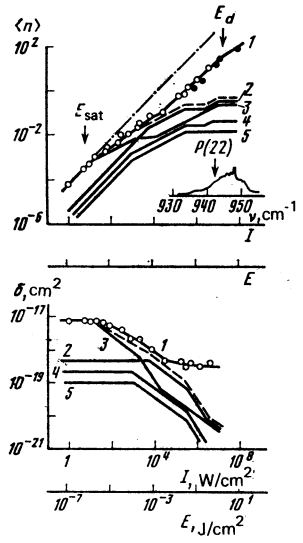

FIG. 4. Dependence of the values of $\langle n\rangle$ (number of photons per molecule) and δ on the intensity of the CO_2-laser radiation on the $P(22)$ line. Curves 1) experimental data, 2–5) approximation of the absorption and the respective transitions ${}^0P$, $\Delta n \neq 0$; ${}^0P$, $\Delta n = 0$; ${}^{-1}Q$, $\Delta n \neq 0$, and ${}^{-1}P$, $\Delta n \neq 0$. The dashed curves correspond to the approximations for the total absorption. E_d is the threshold dissociation energy.

portion to the intensity, while the quantity δ is approximately constant, as is typical of linear absorption. The absorption coefficients measured in this region agree satisfactorily with the data on linear absorption[14] (see Table I).

Deviations from linear absorption (dash-dot lines) start to appear at a power density 2–20 W/cm^2 (0.3–3 μJ/cm^2). The increase of the average number of absorbed photons proceeds in this case most rapidly for the long-wave wing of the absorption band [on the $P(22)$ and $P(26)$ lines], in qualitative agreement with the previously observed[7] shift of the maximum of the multiphoton absorption and dissociation towards lower frequencies. The rate of increase of the average number of absorbed photons can be characterized by the exponent in the approximation $\langle n\rangle \propto I^a$. At an intensity $I \gtrsim 10^4$ W/cm^2, this exponent is maximal for the long-wave wing of the absorption band, $a = 0.95$–1, and gradually decreases to $a = 0.3$ on going to the R branch of the absorption band [laser line $P(14)$]. The corresponding exponent for the quantity δ changes at the same time from 0 to -0.7. At lower intensities (including at the limit of saturation of the linear absorption), the exponent a amounts to 0.8–0.9. Thus, we have experimentally established the character of the transition from linear to multiphoton absorption in the intensity range of interest to us.

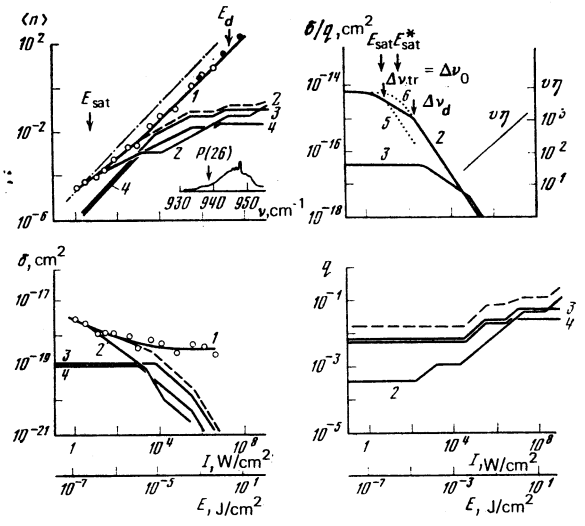

FIG. 5. Dependence of the values of $\langle n\rangle$ (photons/molecule) and δ on the intensity of the CO_2 laser radiation on the $P(26)$ line and the approximations of the parameters δ/q, $v\eta$, and q. Curves: 1) results of measurements, 2–4) approximations for the transitions ${}^0P$, $\Delta n = 0$ (2), ${}^0P$, $\Delta n \neq 0$ (3), and ${}^{-1}P$, $\Delta n = 0$ (4). The dotted curve 5 shows the variation of the parameter δ/q at $\Delta\nu_{tr} = \Delta\nu_{hom}$ (saturation energy E_{sat}), while curve 6 shows the same at $\Delta\nu_{tr} = \Delta\nu_{Dopp}$ (saturation energy E^*_{sat}). The transition from the saturation of the homogeneously broadened sections of the Doppler contour of the absorption line to the saturation of the contour as a whole is approximated by a straight line in the interval marked by the arrows. The dashed curves correspond to approximation with total allowance for all the transitions.

TABLE I. Some characteristics of the ν_3 oscillation modes of SF_6.

CO_2 laser line	mode of ν_3 band	K, cm^{-1}	J	$N_J\cdot10^{-8}$	ν_{tens}, cm^{-1}	v	$q\cdot10^4$
$P(26)$	$-{}^2P$		30	13	0.1	1	
	$-{}^1P$		50	17.5	0.6	1	52
	$\{-{}^1Q\}$		75	10	0.7	6	64
	${}^0P_w$		>100	<2.5	>1.2	1	52
	${}^0P$	0.06 (0.09)	>100	<2.5	>1.2	1	1.5 (3.7)
$P(22)$	$\{-{}^2P\}$		18	6.5	0.035	4	
	$-{}^1P$ *		32	13.5	0.24	1	27
	$-{}^1Q$ *		43	17	0.22	1	58
	$\{{}^0P_w\}$		75	10	0.7	5	125
	${}^0P$	0.33 (0.26)	75	10	0.7	3	10 (11)
$P(14)$	${}^0R_w$ *		30	13.0	0.1	1	150
	${}^0R$ *	0.31 (0.29)	30	13.0	0.1	1	15 (13)
	${}^1Q$		12	3	0.015	1	32
	${}^1R$		8	1.1	0.014	1	
	${}^2R$		5	0.5	0.0027	1	

Notes. 1. The curly brackets mark multiphoton resonances, the asterisks indicate the nearest absorption branches.
2. The values of K in the round brackets are those taken from Ref. 4 for linear absorption in SF_6, normalized to the value 0.44 cm^{-1} for the $P(18)$ line of the CO_2 laser. The latter quantity was obtained by averaging the data over the spectral band 0.008 cm^{-1} (Ref. 15) corresponding to the width of the laser-emission line.
3. The fraction q of the involved J, C, and n levels is given for low intensities of the laser radiation. The parentheses contain the values of q obtained from the experimental curves at $\sigma_{all} = 6.7\times10^{-15}$ cm^2.

3. DISCUSSION OF EXPERIMENTAL RESULTS

We shall discuss the results within the framework of the model of multiphoton excitation of molecules in weakly forbidden transitions.[1] According to this model, single-photon and multiphoton (multistep) transitions with a definite number of step contribute to the absorption of the laser emission by the molecules. The laser-emission absorption registered in the experiments is determined as the sum over all the possible transitions. Some data on multiphoton and single-photon transitions are given in Table I.

The expression for the average number of absorbed photons can be written in the form

$$\langle n\rangle=\sum_B\langle n\rangle_B=\sum_B n_B(\nu,\mathscr{E})\,q_B(\nu,\mathscr{E}),\qquad(3)$$

where n_B is the average number of photons absorbed by the molecule, q_B is the fraction of molecules belonging to the J,R,C, and n states excited at the given frequency from the ground level to the v-th vibrational level on transitions in a definite branch marked by the index B. The summation is over all the branches that contribute to the absorption, and (I) is the energy (power) of the pulse laser radiation.

The approximate expression for the fraction of the excited molecules is of the form

$$q_B(\nu,I)=\sum_{J_B}N_{J_B}\sum_C g_C\left[\frac{\Delta\nu_{\text{int}}(I)\,S(C,J)}{\Delta\nu_{\text{tens}}(J_B)}\tau_{\text{eff}}\right]^{n_B},\qquad(4)$$

where N_{J_B} is the relative population of the rotational levels of the ground state for excitation in the B branch; g_C is the relative population of the system of levels with symmetry C; S is the number of n-components in the tensor structure of the absorption spectrum with the same initial n-sublevel ($S=1$ for allowed transitions and $S=\alpha_C J_B$ for weakly forbidden transitions, where α_C is an additional parameter); $\Delta\nu_{\text{int}}$ is the spectral interval in which the laser radiation interacts with the molecules; $\Delta\nu_{\text{tens}}$ is the spectral width of the tensor structure of the branches, and τ_{eff} is a correction coefficient for the transitions between the vibrationally excited states.

Figures 4 and 5 show by way of illustration the calculated dependences of the quantities $\langle n\rangle$ and δ on the intensity of the laser radiation, and give by way of example for the laser line $P(26)$ the parameters δ/q and q for the resonances with index $m=1$. For multiphoton transitions the parameter δ/q has the meaning of a cross section.

A characteristic feature of the absorption spectrum in the ν_3 band of SF_6 at room temperature is the large contribution of the thermal bands. For many sections of the absorption spectrum, particularly in the region of the CO_2 laser lines, the thermal bands form a quasicontinuous absorption spectrum. We can therefore assume the model of a quasicontinuum of fully overlapping Doppler-broadened lines.

We assume also a simplified model of the spectral composition of the laser radiation in the form of three modes of fixed frequency.

At the gas pressure 0.35 Torr used in the experiments, the characteristic time that describes the damping of the high-frequency dipole moment of the molecules is 100 nsec,[16] which is less than the duration of the laser pulse (150 nsec). This circumstance, as well as the multimode composition of the laser radiation, justifies the use in our case of the model of incoherent excitation of the molecular states. The general picture of the absorption of the laser radiation by the molecules when the radiation intensity varies in a wide interval is quite complicated. We consider the absorption of laser radiation on the basis of simplified models.

It is convenient to break off the dependences of the indicated parameters into a number of sections in accordance with the magnitude of the broadening of the transitions in the laser field

$$\Delta\nu_{\text{tr}}=2\mu E/h\qquad(5)$$

(μ is the matrix element of the transition, E is the amplitude of the light field, and h is Planck's constant).

We consider first single-photon transition and the region of low intensities of the laser radiation at a transition field broadening smaller than or equal to the Doppler width of the line, $\Delta\nu_{\text{tr}}\leqslant\Delta\nu_{\text{Dopp}}$. Since the homogeneous (impact) width of the absorption lines $\Delta\nu_{\text{hom}}=2\times10^{-4}$ cm^{-1} under the conditions of the performed experiment and is one-fifth the Doppler width $\Delta\nu_{\text{Dopp}}=10^{-3}$ cm^{-1}, the character of the saturation of the absorption lines changes with increasing intensity. A transition takes place from saturation of the Doppler-broadened absorption-line contours within the limits of the homogeneous width to saturation of the Doppler contour as a whole. Since a quantitative description of this transition is complicated,[17] we consider a simplified approach. For one-photon transitions, at a broadening $\Delta\nu_{\text{tr}}$ smaller than the homogeneous line width $\Delta\nu_{\text{tr}}<\Delta\nu_{\text{hom}}$, the expression for the average number of photons $\langle n\rangle$ and for the parameter δ can be written in the form[18]

$$\langle n\rangle_B=q_B n_B=\sigma_0{}^B q_B\frac{\mathscr{E}_{\text{sat}}{}^B}{h\nu}\left[1-\exp\left(-\frac{\mathscr{E}}{\mathscr{E}_{\text{sat}}{}^B}\right)\right],\qquad(6)$$

and

$$\delta=\frac{\sigma_0 q}{(\mathscr{E}/\mathscr{E}_{\text{sat}}{}^B)}\left[1-\exp\left(-\frac{\mathscr{E}}{\mathscr{E}_{\text{sat}}{}^B}\right)\right],\quad \mathscr{E}_{\text{sat}}{}^B=\frac{h\nu}{2\sigma}\frac{\Delta\nu_{\text{hom}}}{\Delta\nu_{\text{Dopp}}}\theta,\qquad(7)$$

where the coefficient θ is of the order of unity. The general picture of the saturation of the absorption for single-quantum transitions is the following. When the energy $\mathscr{E}$ rises above $\mathscr{E}_{\text{tr}}$, a "Bennett hole" appears on the absorption-line contour, with a width and depth that increase gradually with increasing laser-pulse energy. The plot of the average photon number $\langle n\rangle$ saturates in this case, and the parameter δ, which is proportional to the coefficient of nonlinear absorption, begins to decrease in inverse proportion to $\mathscr{E}$.

Relations (6) and (7) hold true so long as the transition broadening in the field is not larger than the homogeneous width $\Delta\nu_{\text{tr}}\geqslant\Delta\nu_{\text{hom}}$. At higher intensities the parameter δ and the corresponding nonlinear-absorption coefficient decrease approximately in inverse proportion to $\mathscr{E}^{1/2}$ (Ref. 17), while $\langle n\rangle$ increases like $\mathscr{E}^{1/2}$. The character of the relation changes again at $\Delta\nu_{\text{tr}}\geqslant\Delta\nu_{\text{Dopp}}$. It is again described by expressions (6) and (7), but with $\mathscr{E}_{\text{sat}}^{*}=h\nu/2\sigma$.

In the interval $\Delta\nu_{\text{tr}}\leqslant\Delta\nu_{\text{Dopp}}$ the distribution of the molecules over the J,R,C and n states that become involved in the excitation remains unchanged and is determined from (4) with

$$\Delta\nu_{\text{int}}=3\Delta\nu_{\text{Dopp}}.\qquad(8)$$

With further increase of the line broadening in the laser field, $\Delta\nu_{\text{int}}$ increases approximately in proportion to $\mathscr{E}^{1/2}$ in accord with the increase of $\Delta\nu_{\text{tr}}$. This continues approximately until the broadening in the field becomes equal to the spectral interval between the laser modes, $\Delta\nu_{\text{tr}}=\Delta\nu_{\text{mod}}$. The increase of $\Delta\nu_{\text{int}}$ in this type of

broadening stops because of a super-position of the "holes" burnt in the absorption spectrum by the different oscillation modes.

Further increase of $\Delta\nu_{int}$ and of the fraction of the involved molecules sets in at $\Delta\nu_{tr} \geq 3\Delta\nu_{mod}$ and continues until the probability of capture from n sublevels becomes equal to unity. A subsequent growth of q is possible only by involving new J sublevels when the transitions are broadened in a field stronger than the tensor splitting of the levels, $\Delta\nu_{tr} \gtrsim \Delta\nu_{tens}$.

For multiphoton transitions with v steps and with identical cross section of the radiative transition on each step, the expression such as (6) for the number of absorbed photons will contain, generally speaking, not one exponential but a set of several exponentials with different arguments. For approximate estimates we can use expression (6) and (7), where

$$\mathcal{E}_{sat=v}\frac{h\nu}{2\sigma}\frac{\Delta\nu_{hom}}{\Delta\nu_{Dopp}}\theta \quad \text{if} \quad \Delta\nu_{tr}<\Delta\nu_{hom},$$

$$\mathcal{E}_{sat*=v}\frac{h\nu}{2\sigma} \quad \text{if} \quad \Delta\nu_{tr}>\Delta\nu_{Dopp}.$$

Table I gives certain data necessary for the analysis of multiphoton excitation of molecules: the measured coefficient K of linear absorption, the quantum number J for the absorbing transitions, the relative population N_J of the levels, the tensor splitting ν_{tens} of the branches, the vibrational level v to which the excitation takes place at $|\Delta R| \leq 2$, and the fraction q of the J, C, and n states involved in the excitation (to make the table general, it includes the branches ${}^{-2}P$, and ${}^{+2}R$ with change $|\Delta R| = 2$).

The cross section σ_{all} of the allowed transitions is not known with sufficient accuracy, and data on the cross section σ_w for weakly forbidden transitions are nonexistent. For the sake of argument, σ_{all} was assumed equal to 6.7×10^{-15} cm^2, while σ_w was chosen to obtain satisfactory agreement with experimental data. In the analysis we took into account only the transitions with $|\Delta R| \leq 1$.

The influence of the thermal bands was taken into account indirectly by correcting the fraction q of the involved molecules in the region of linear absorption in such a way as to obtain the measured coefficients of linear absorption.

Table II lists the set of data necessary to construct the dependences of the principal parameters on the intensity of the laser radiation. Besides the type of transition, the value of the cross section, the transition matrix element, and the saturation intensity, Table II gives also data on the intensities at which the transition broadening in the laser field becomes equal to the homogeneous and Doppler widths, to the intermode spectral interval, etc. For the $P(18)$ line of the CO_2 laser no estimates were made because of the rather complicated composition of the multiphoton resonances.

As seen from Figs. 3–5, the same set of parameters can be used to obtain, on a semi-quantitative level, satisfactory agreement with the results of experiments on different lines up to intensities 10^3–10^4 W/cm^2 (0.1 mJ/cm^2). It is important to emphasize that to explain the results it suffices to involve weakly forbidden transitions with a cross section amounting to only 0.005 of the cross section for the allowed transitions. As seen from the figures, when only allowed transitions are taken into account, the experimental results find no explanation already at a radiation intensity above several dozen W/cm^2 (several μJ/cm^2) (see Fig. 5).

TABLE II.

Quantity	Allowed transitions	Weak (single-proton) transitions
σ, cm^2	$6.7\cdot10^{-15}$	$3.8\cdot10^{-17}$
μ, dB	0.14	0.01
I_{sat}	$6(9\cdot10^{-7})$	$10^3(1.5\cdot10^{-4})$
I_{sat}*	$30(4.5\cdot10^{-6})$	$5\cdot10^3(7.5\cdot10^{-4})$
$I(E)$ at $\Delta\nu_{tr}$ equal to		
$\Delta\nu_{hom}=2\cdot10^{-4}$	$7(1.05\cdot10^{-6})$	$1.2\cdot10^3(1.8\cdot10^{-4})$
$\Delta\nu_{Dopp}=10^{-3}$	$1.8\cdot10^2(2.7\cdot10^{-5})$	$3\cdot10^4(4.5\cdot10^{-3})$
$\Delta\nu_{mod}=3\cdot10^{-3}$	$1.8\cdot10^3(2.7\cdot10^{-4})$	$3\cdot10^5(4.5\cdot10^{-2})$
$\Delta\nu_{las}=8\cdot10^{-3}$	$1.8\cdot10^4(2.7\cdot10^{-3})$	$3\cdot10^6(4.5\cdot10^{-1})$
$\Delta\nu_{therm}=0.3$	$6\cdot10^6(0.9)$	$1.1\cdot10^9$ (16.5)

Note. The values of the intensities I and of the energies E are given in W/cm^2 and in J/cm^2 (in parentheses); the values of $\Delta\nu$ are in cm^{-1}.

The absence of sharp breaks on the $n(\mathcal{E})$ and $\delta(\mathcal{E})$ curves on going through the boundary of linear-absorption saturation is due to the complicated character of the saturation of inhomogeneously broadened absorption lines by pulsed laser radiation. When the intensity exceeds the saturation limit, the plot of the average number of absorbed photons increases gradually (somewhat more slowly than $I^{0.5}$), even for single-photon transitions, as a result of the increase of the fraction of the involved molecules. The increase of the slope of the plot of $\langle n\rangle$ against $\mathcal{E}$ for the long-wave wing of the absorption band and the formation of the observed "plateau" on the initial section of the $\delta(\mathcal{E})$ curve (on the low-intensity side) can be attributed to multiphoton transitions. In the long-wave wing, the absorption bands of the chain of multiphoton transitions have a maximum "length," whereas in the short-wave wing and, in particular, at the $P(14)$ laser-line frequency, there are no multiphoton transitions.[1]

To explain the results of the experiments at intensities above 10^3–10^4 W/cm^2, allowance for only the "primary" chains of transitions is insufficient and it is necessary to take into consideration the possibility of formation of "secondary" chains of multiphoton transitions.

The "length" of the chain of the multiphoton transitions, within the limits of one and the same oscillation mode without a change in the sign of the Coriolis constant, is limited in principle because of the limitation on the quantum numbers and on the indices of the levels.[1] Thus, for example, the limits for the "longest" chain ${}^{-1}P_1$ is reached at $\Delta R = 4$ and is equal to 13.

The "length" of the chains can, however, increase because of formation of additional (secondary) chains and other types of oscillations. The possibility of formation of such chains is connected with the fact that, owing to different types of interactions, the highly excited vibrational states turn out to be "intermixed" and radiative transitions with sufficiently large cross sections

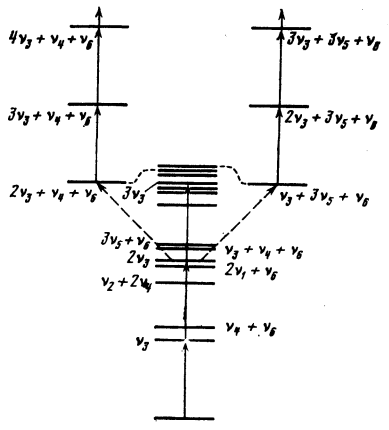

FIG. 6. Scheme showing the "elongation" and "branching" of chains of multistep transitions (using as an example the oscillation ν_3 of the SF_6 molecule). Vibrational levels with energy differing from the energy of the $n\nu_3$ states ($n=1, 2, 3$) by not more than 30 cm^{-1} are shown (the scale is arbitrary). The bent dashed lines mark the compensation of the detunings due to weakly forbidden transitions (see Fig. 7).

become possible to levels of other modes, and the latter can serve as starting levels for additional chains.

Figure 6 shows the scheme of some vibrational levels of the SF_6 molecule near the levels of the ν_3 oscillation. As seen from the figure, with increasing quantum number v of the ν_3 oscillation levels, the number of the closely lying levels of other oscillations increases rapidly. Figure 7 shows the Forter diagram, which illustrates schematically the possibility of continuing the chain. To continue the chain it is necessary that the position of the resonance in the ν_3 oscillation intersect in the (v, J) plane with one of the branches of the transition to the level of the composite oscillation. The result can be a restoration of the agreement between the quantum numbers, and it is this which ensures the formation of a longer chain.

With increasing intensity of the laser radiation, the total length of the composite chain can gradually increase all the way to the dissociation limit. Formation

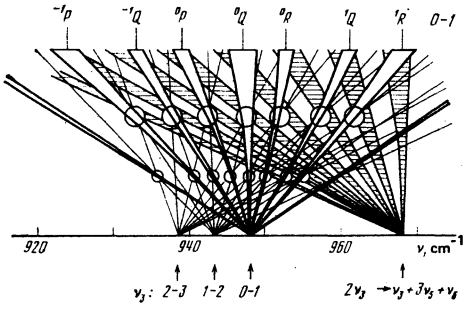

FIG. 7. Forter diagram for the transitions in the ν_3 oscillation and for the transition $2\nu_3 \rightarrow \nu_3 + 3\nu_5 + \nu_6$ (schematic). The arrows mark the centers of the ν_3 oscillations bands. Systems of branches that form multistep resonances start out from the centers (some of the resonances are marked by circles). On the top are given the identifications of the branches of the 0–1 transitions. The shaded bands correspond to individual branches of the band $2\nu_3 \rightarrow \nu_3 + 3\nu_5 + \nu_6$.

of "parallel" chain systems (branching of the chains) is also possible. Such a model is in essence a concretization of the "quasicontinuum" concepts.

In the general case laser radiation is absorbed upon saturation of a system of multiphoton transitions consisting of many "generations" of secondary chains with a certain branching factor $\varkappa$ and with a limited "length" of each composite chain. An analysis for a simplified chain scheme shows that allowance for the statistical weights of the levels and for the branching factor $\varkappa$ (at $\varkappa \lesssim 3-5$) leads to a change in the average number of the absorbed photons by a factor 1.5–2 compared with the "simple" unbranched chain. In the latter case, the average number of absorbed photons is

$$\langle n \rangle = {}^1/_2 q v \eta, \tag{9}$$

where v is the summary "length" of the chain, and q is the fraction of the excited molecules. To generalize the analysis, we have introduced in (9) a parameter that takes into account the intromolecular exchange of excitation energy[19-21] ($\eta = 1$ in the absence of exchange). This process can lead to a transfer of energy of excitation into oscillation modes that do not interact with the laser radiation. To compensate for the energy loss in the initial level chain, the molecule can again absorb a definite number of photons. Expression (9) can be used for a rough estimate of the average number of absorbed photons.

We do not know the dependences of v and η on the laser-radiation intensity. The products of these two quantities can be regarded as a variable parameter with the aid of which we can approximate the experimental data. The corresponding dependence of the product v is shown in Fig. 5. Since the dissociation energy of the SF_6 molecule is known and equals 3.27×10^4 cm^{-1} ($v = 35$), we can estimate η in the region of the dissociation threshold. Its value turns out to be ~60.

The parameter η can be smaller if suitable allowance is made for the statistical weights of the vibrationally excited states, for the branching of the chains, and also for the possible increase of the fraction q of the excited molecules on account of the turning on, at a certain laser intensity, multiphoton resonances with index $m \geq 2$ and nonresonant multiphoton transitions, and formation of an additional network of multiphoton resonances. At high intensities it is also necessary to take into account the possibility of transitions connected with the lifting of the forbiddenness of absorption in strong fields.[22]

CONCLUSION

We have experimentally investigated the transitions from linear absorption in the ν_3 oscillations of the SF_6 molecule to multiphoton absorption in the CO_2-laser intensity interval $1-10^6$ W/cm^2. We have shown that when account is taken of the allowed transitions $\Delta R = 0$ the calculated data begin to differ from the experimental ones at a power density above several dozen W/cm^2. The behavior of the absorption in the transition region of intensities up to 10^3-10^4 W/cm^2 finds a satisfactory quantitative explanation where an account is taken of

multiphoton and single-photon weakly forbidden transitions $\Delta R \neq 0$, $\Delta n \neq 0$. To explain the results of the experiments it suffices to take into account transitions with radiative-transition cross section amounting to only 0.005 of the corresponding value for allowed transitions. At higher laser intensity, the absorption can be attributed to the formation of successive "secondary" chains of multiphoton transitions and intramolecular exchange of excitation energy among the oscillation modes.

Of great interest from the point of view of explaining the mechanism of multiphoton absorption is the measurement of the fraction of excited molecules and of the character of the vibrational excitation of molecules in the intensity range 10^3–10^7 W/cm^2. Of primary significance are questions of the spectroscopy of vibrationally excited states of molecules. From the experimental point of view, definite interest attaches to analogous experiments with cooled gas to eliminate the influence of thermal bands.

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[1)]Here and below all the data on the power density I are given for a laser pulse of 1.5×10^{-7} sec duration. The laser-pulse energies are given in the parentheses.

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