Multiphoton absorption of infrared laser radiation by SF_6 molecules cooled in a supersonic jet

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An investigation was made of multiphoton absorption of radiation emitted from a pulsed CO_2 laser by SF_6 molecules cooled in a supersonic pulsed jet. Transit-time measurements were used to determine the characteristics of the molecular beam (jet). Accumulation of the vibrational energy by the molecules was observed in a wide range of laser radiation energies from $\approx 10^{-2}$ to 5 J/cm^2, depending on the energy density and frequency of the exciting radiation. A study was made of the dependence of the absorption cross sections on the excitation energy density. Multiphoton absorption spectra were obtained for the ν_3 vibration. A study was made of the influence of the initial vibrational temperature of the molecules on the energy accumulation process. An estimate was obtained of the fraction of the molecules interacting with the laser radiation. The role of the intensity in the multiphoton absorption process was investigated.

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I. INTRODUCTION

The excitation of high vibrational states and the dissociation of polyatomic molecules by infrared laser radiation have been both investigated quite thoroughly,[1] particularly in the case of the SF_6 molecule. However, some of the problems of the greatest interest in the understanding of the process of the interaction between molecules and high-power infrared laser radiation have not yet been fully resolved. These problems include, for example, the following: a) the mechanism of the excitation of a molecule in the range of lower vibrational–rotational transitions (overcoming of the anharmonicity of the molecular vibrations); b) the mechanism of radiative capture by infrared laser radiation of molecules from many rotational states[2]; c) the role of the laser radiation intensity in the molecular excitation process; d) the increase in the fraction of molecules interacting with laser radiation at moderate excitation energy densities.[3,4] Detailed studies of these problems under conditions when the investigated gas is in a cell at room temperature is difficult because of the influence of collisions and of the distribution of molecules between many vibrational–rotational states. For example, in the case of SF_6 at room temperature about 70% of the molecules are distributed between high vibrational states, whereas there are only 30% of the molecules at the ground vibrational level.[5] Collisions affect the excitation of SF_6 by CO_2 laser pulses already at pressures of ≈ 10 mTorr (Ref. 6).

The spectroscopy of such molecules can be simplified by cooling the gas in a cell. Several experiments were carried out recently[7–10] on multiphoton absorption in SF_6 at temperatures 140–150 K. At 140 K already about 90% of the molecules are in the ground state.[5]

The influence of collisions can be eliminated by performing experiments at low gas pressures. However, at such gas pressure ($p \lesssim 0.1$ Torr) it is difficult to determine the energy absorbed in the multiphoton excitation of molecules by the method of direct calorimetry because of the relatively small proportion of the absorbed energy compared with the incident energy, and the optoacoustic detection method is insufficiently sensitie at low pressures.[11] Therefore, in Refs. 7–10, as in the majority of the work carried out on multiphoton absorption (see, for example, Refs. 1 and 12), the gas densities were fairly high ($\rho \approx 7 \times 10^{15}$–$2 \times 10^{16}$ cm^{-3}). The study of multiphoton absorption at low gas pressures ($\lesssim 10^{-3}$–10^2 Torr) became possible[6,11] only because of the use of recently developed pyroelectric detectors made of polycrystalline organic films[11] and used to determine the absorbed energy.

It was shown in Refs. 7–10 that the main characteristics of multiphoton absorption in SF_6 at low temperatures differ considerably from those at room temperature. Cooling has the following effects: 1) there is a considerable reduction in the absorption cross section in the long-wavelength part of the linear absorption spectrum[8,10]; 2) the multiphoton absorption spectrum becomes considerably narrower and its maximum shifts toward higher frequencies (up to the Q branch of the $v = 1 \leftarrow v = 0$ transition).[7] Both these processes occur because of a reduction in the population of high vibrational states (ν_6, $2\nu_6$, ν_5, ν_4, ...), which have a considerable population at room temperature.[5] However, since fairly high concentrations of SF_6 were used in Refs. 7–10, many characteristic features of multiphoton absorption were not manifested because of collisions. The advantages of cooling of the investigated gas can be fully utilized only if the influence of collisions on the excitation process is eliminated completely. Therefore, it would be of considerable interest to investigate multiphoton absorption in molecules cooled in a supersonic jet.[13] This should make it possible to achieve relatively low rotational and vibrational temperatures, which would simplify greatly the spectroscopy of molecules and eliminate completely the influence of collisions.

We investigated multiphoton absorption in SF_6 molecules cooled in the course of free pulsed flow from a nozzle. We determined the characteristics of the resultant molecular beam (jet). We studied the process of accumulation of the

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vibrational energy by the molecules in a wide range from $\approx 10^{-2}$ to 5 J/cm^2 as a function of the energy density and frequency of the exciting radiation. The dependence of the absorption cross sections on the excitation energy density was found. The multiphoton absorption spectra were recorded. A study was made of the influence of the distribution of the investigated molecules between the vibrational states on the energy accumulation process. An estimate was obtained of the fraction of the molecules interacting with laser radiation. The role of the intensity in the multiphoton absorption process was investigated.

II. APPARATUS AND MEASUREMENT METHOD

The apparatus is shown schematically in Fig. 1. A pulsed molecular beam source, similar to that described in Ref. 14, was used. The duration of a pulse (during which the nozzle was open) in the case of SF_6 was about 40 μsec at midamplitude. The diameter of the nozzle aperture was 0.75 mm. The pressure in the nozzle was $\leqslant 5$ atm. The total number of the SF_6 molecules escaping from the nozzle during one pulse at a pressure of 5 atm was $\approx 1 \times 10^{17}$. The vacuum chamber was evacuated to pressures of $(2-4) \times 10^{-6}$ Torr.

The vibrational excitation of the SF_6 molecules was achieved by the use of pulses emitted from an atmospheric-pressure CO_2 laser whose output frequency was tuned discretely to individual vibrational–rotational transitions in the CO_2 molecule by a diffraction grating. A laser pulse consisted of a peak of ≈ 80 nsec duration at midamplitude and a tail of 0.8 μsec duration (at midamplitude). One transverse mode was selected by stops inside the laser resonator. The distribution of energy over the cross section of the illuminated stop was near-Gaussian. The energy carried by a laser pulse was up to 1.5 J. About 60% of the energy was contained in the tail part of the pulse. The laser energy was measured with a thermopile, which was first calibrated using a TPI-1 meter for the absolute determination of the energy. The SF_6 molecules were excited at a distance of 6 or 11.4 cm from the nozzle. In the former case the laser and molecular beams intersected at right-angles, whereas in the latter case they intersected at 45°. The laser radiation was focused slightly in the interaction zone by a long-focus lens ($f = 1$ m) made of NaCl.

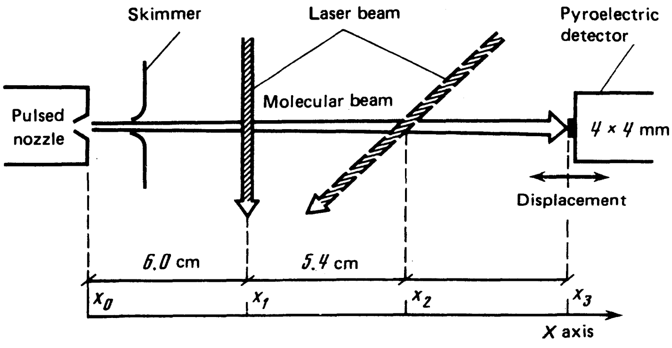

FIG. 1. Schematic diagram showing the apparatus, where x_0 and ξ_i ($i = 1,2,3$) denote the distances from the nozzle to the points of intersection of the molecular beam by the laser beam and to the pyroelectric detector, respectively. The distance x_0–x_3 is not greatly affected by the displacement of the detector along the X axis.

A pyroelectric detector made of a polycrystalline organic film was used to determine the energy absorbed by the SF_6 molecules. This pyroelectric detector was similar to that described in Ref. 11. A detector of this type was used by us earlier[6] to study multiphoton absorption in SF_6 contained in a cell. The pyroelectric detector used in the present study had a higher sensitivity and a better time resolution (≈ 5 μsec). The higher sensitivity, compared with the detector used in Ref. 6, was achieved by reducing the thickness of the upper electrode to $\lesssim 0.05\,\mu$, whereas the better time resolution was due to the evaporation of a thinner pyroelectric active film and the use of substrates with a high thermal conductivity (sapphire instead of glass). A signal induced by the beam of molecules in the pyroelectric detector was first amplified (by a factor of 100) and then applied to an oscilloscope. The experiments were carried out on molecules in a molecular beam formed by a skimmer and also without formation of a beam. In both cases the detector was used to find the energy of the molecules traveling inside a solid angle determined by the dimensions of the active component of the pyroelectric detector (4×4 mm) and by the distance between the nozzle and the detector. This distance could be varied by moving the detector along the beam axis, but in most cases the detector was located at a fixed distance of 16.8 cm from the nozzle.

The absorbed energy was deduced with the aid of the pyroelectric detector by measuring the internal (vibrational) energy of the molecules which reached the surface of the active component of the detector where this energy was transformed into heat and such heat induced the observed signal. In the absence of an exciting laser pulse the detector signal was proportional to

$$S_0 \sim nv(E_a + E + mv^2/2) \sim nvE_0, \tag{1}$$

where n is the number density of the molecules on the detector surface; v is the velocity of the molecules; m is the mass of the molecules; E is the energy of a molecule (representing the sum of the vibrational, rotational, and "local" translation energies); E_a is the heat of the adsorption per molecule; E_0 is the total energy, given by the expression enclosed in parentheses. In the case of vibrational excitation of molecules by a laser pulse the signal was proportional to

$$S_L \sim nv(E_0 + E_n), \tag{2}$$

where E_n is the energy absorbed by a molecule from a laser pulse.

Figure 2 shows oscillograms of the signals generated by the pyroelectric detector in the absence of excitation (lower trace) and when the SF_6 molecules were excited by a laser pulse. The signals shown in Fig. 2 represent the transit-time spectra of the "cold" and vibrationally excited SF_6 molecules in the beam. The additional (compared with the unexcited molecules) signal is a measure of the energy absorbed by the molecules from a laser pulse when the vibrations are excited.[15] It should be noted that since at distances of $x > 6$ cm from the nozzle, where the molecules were excited, the number of collisions of SF_6 in the jet was negligible, we could assume that there was no V–T relaxation in SF_6. Therefore, the transit-time spectra obtained by this method for vibra-

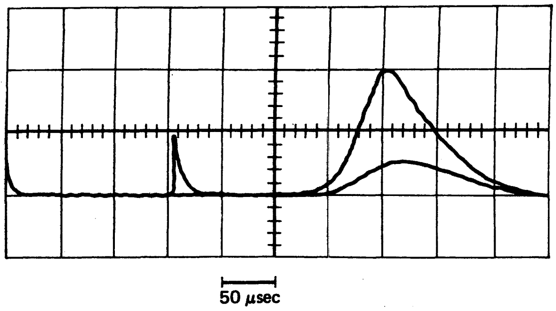

FIG. 2. Oscillograms showing the signals from a detector (transit-time spectra of SF_6) in the absence of excitation (lower trace) and in the case of vibrational excitation of the SF_6 molecules (upper trace) by a CO_2 laser pulse. The SF_6 molecules were excited at a distance of 6 cm from the nozzle. The SF_6 pressure in the nozzle was 5 atm. The distance from the nozzle to the detector was 16.8 cm. The horizontal scale is 50 μsec/div. The first (on the time scale) signal represents scattered laser radiation.

tionally excited molecules should be identical with the transit-time spectra of the cold molecules.

III. DETERMINATION OF THE MOLECULAR BEAM CHARACTERISTICS

In the investigation of multiphoton absorption the most important factor is the distribution of the internal energy of the molecules (vibrational and rotational temperatures), whereas in many other experiments (such as those involving a study of the elastic and inelastic collisions and chemical reactions), it is necessary to know also the distribution of the kinetic energy of the molecules in a beam. We determined these characteristics from transit-time measurements and the energy balance. The experimentally determined transit-time spectra were analyzed employing a standard (with two parameters) expression for the distribution of the number density of molecules between the velocities in a supersonic molecular beam[13]:

$$n(v) \sim (v/u)^2 \exp[-(v-u)^2/\alpha^2]. \quad (3)$$

The parameters in Eq. (3) are the jet (beam) velocity u and the most probable molecular velocity $\alpha = (2kT/m)^{1/2}$ in a coordinate system linked to the beam (jet). In the expression for α the quantity T represents the local translational temperature of the molecules in the beam.

The distribution of the number density of molecules between the velocities was determined as follows. The beam molecules were excited at a point x_1 located $L = 10.8$ cm from the pyroelectric detector (Fig. 1). The delay time between a beam pulse and a laser pulse was selected to obtain the maximum signal so that the molecular beam density at the point of intersection was maximal at the moment of passage of a laser pulse. An analysis was made of the form of the experimentally determined transit-time spectra of the vibrationally excited molecules. Since the characteristic dimensions of the excitation region ($\Delta x \approx 2$–3 mm) were small compared with the transit distance L, the time evolution of the additional signal associated with E_n [see Eq. (2) and Fig. 2] could be described accurately[16] by the probability function for the density of the vibrationally excited molecules reaching the detector, i.e., by the expression

$$P(t) \sim t^{-4} \exp[-(Lt^{-1}-u)^2/\alpha^2]. \quad (4)$$

The parameters u and α were found by fitting the transit-time spectra deduced from Eq. (4) to those found experimentally.

The points in Fig. 3 represent the transit-time spectrum of the SF_6 molecules found experimentally by the method just described. The continuous curves are the calculated transit-time spectra with the following parameters: $u = 450$ m/sec (for all three curves) and $\alpha = 58.5$ m/sec or $T = 30$ K (curve 1), $\alpha = 67.6$ m/sec or $T = 40$ K (curve 2), $\alpha = 75.5$ m/sec or $T = 50$ K (curve 3). The maxima of the calculated transit-time spectra are normalized to the maximum of the spectrum found experimentally. The best agreement with the experimental results is obtained for $u = 450$ m/sec and $\alpha = 67.5 \pm 3.0$ m/sec or $T = 40 \pm 3$ K.

If it is assumed that the rotational temperature of the molecules in a beam does not differ greatly from the translational temperature (which is clearly justified in the case of SF_6 because the rotational relaxation process is complete in a time less than that required for one gas-kinetic collision[17]), we can estimate the vibrational temperature of the molecules employing the formula for the energy balance[13,18]:

$$4kT_0 - 2kT - {}^1/_2 m\langle v^2\rangle = {}^3/_2 kT_{\mathrm{rot}} - \int_{T_{\mathrm{vib}}}^{T_0} C_V^{\mathrm{vib}}\, dT, \quad (5)$$

where $4kT_0$ is the energy of a molecule before its escape from the nozzle and the other terms in Eq. (5) describe the energy of a molecule in a beam. In the case when $T_{\mathrm{rot}} \approx T$ we can use Eq. (5) to determine the vibrational temperature T_{vib} if we know C_V^{vib} in the temperature range $T_{\mathrm{vib}} \leqslant T \leqslant T_0$. In the range 150–300 K the numerical value of C_V^{vib} is[18]:

$$C_V^{\mathrm{vib}} = 0.03552kT - 2.639k \ \mathrm{J \cdot mole^{-1} \cdot deg^{-1}}. \quad (6)$$

Assuming that $T_{\mathrm{rot}} \approx T = 40 \pm 3$ K, we found from Eq. (5) that $T_{\mathrm{vib}} = 160 \pm 10$ K.

The rotational temperature of the SF_6 molecules in the beam (jet) was also estimated from the measurements of small-signal absorption (at energy densities $\lesssim 10\,\mu\mathrm{J/cm^2}$) at the frequencies of the $P(12)$–$P(20)$ CO_2 laser lines. The absorption was measured in the jet at a distance of 6 cm from the nozzle. The absorption was enhanced by passsing the laser radiation twice across the jet in the forward and reverse directions. The transmitted and incident energies were measured with the aid of pyroelectric detectors. In this way we were able to determine the absorption at a level of 2–3% of

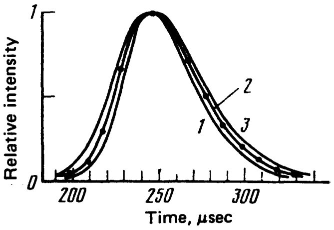

FIG. 3. Transit-time spectrum of a vibrationally excited SF_6 molecule (points) found experimentally. Curves 1–3 represent calculated transit-time spectra.

the incident radiation power. In these experiments the attenuation of the signal was observed only at the frequencies of the $P(14)$, $P(16)$, and $P(18)$ lines. The maximum attenuation ($\approx 14\%$) occurred at the frequency of the $P(14)$ line, for which the small-signal absorption coefficient of the SF_6 molecules at $T \approx 40$–50 K was greater than for the other lines (see Fig. 6 below). The results of these measurements confirmed, in our opinion, that the rotational temperature of the SF_6 in the jet was low and differed little from the translational value. Cooling of the SF_6 molecules in the supersonic jet to temperatures $T_{\text{vib}} \approx 170$ K and $T_{\text{rot}} \approx 60$ K was recently reported also in Ref. 19.

IV. MEASUREMENTS OF MULTIPHOTON ABSORPTION IN SF_6 AND DISCUSSION

1. Dependence of the absorbed energy on the excitation energy density

Figure 4 gives the dependences of the absorbed energy E_n on the energy density of the incident radiation Φ for the $P(14)$, $P(16)$, and $P(18)$ lines of the $10.6\,\mu$ CO_2 laser band (the frequencies of these lines were closest to the R, Q, and P branches, respectively, of the linear absorption spectrum of SF_6 at $T \approx 40$ K). The SF_6 molecules were excited at a distance of 11.4 cm from the nozzle. The SF_6 pressure in the nozzle was 5 atm. The absorbed energy was described well by the dependence $E_n \propto \Phi^n$, where n varied approximately from 0.5–0.6 for the $P(14)$ and $P(16)$ lines in the energy density range $\Phi \lesssim 0.1$–0.2 J/cm^2 to $n = 1.4$–1.7 for all three lines in the range $0.2 \leqslant \Phi \leqslant 2.0$ J/cm^2. Further increase in the energy density again reduced the slopes of the plots. Throughout the investigated range of the energy densities the absorption was maximal at the frequency of the $P(16)$ line.

The slow rise of the absorption on increase in the energy density in the range $\Phi \lesssim 0.1$ J/cm^2 was clearly due to the fact that at these energy densities the role of multiphoton transitions in the absorption at the frequencies of the $P(14)$ and $P(16)$ lines was still slight. An increase in the energy density, when the frequency detuning for multiphoton transitions was compensated by the dynamic broadening of the vibrational–rotational lines due to the laser pulse field ($\Delta\nu_{\text{br}} = \mu E/\hbar c$ for $\mu \approx 0.43\,D$—see Ref. 20), resulted in predomination of the multiphoton transitions. The slope of the dependences $E_n(\Phi)$ then increased strongly. According to Ref. 21, where the energies of high vibrational levels of the ν_3 mode are given right up to $8\nu_3$, the frequency detuning in the case of two-photon transititons at the frequencies of the $P(18)$ and $P(16)$ lines and of three-photon transitions at the frequency of the $P(14)$ line were 0.18, 0.53, and 1.0 cm^{-1}, respectively. When the intensity of the field was determined using the envelope of a laser pulse, the intensities at the energy densities of 0.1–0.2 J/cm^2 were insufficient to compensate such detuning. For example, in the $\Phi = 0.1$ J/cm^2 case the field broadening of the lines, governed mainly by the leading (peak) part of the laser pulse, was $\Delta\nu_{\text{br}} \approx 0.1$ cm^{-1}. In fact, the laser pulse was not smooth so that the peak intensity and, consequently, the field broadening of the lines could be considerably greater than the values just quoted. The frequency detuning could also be compensated partly by the rotation of the molecules.[22] The observation that the slopes of the dependences $E_n(\Phi)$ obtained for the $P(18)$, $P(16)$, and $P(14)$ lines began to rise on increase in the energy density (in a sequence corresponding to the detuning given above) confirmed again, in our opinion, the multiphoton nature of the interaction at the frequencies of these lines in the range $\Phi \geqslant 0.1$–0.2 J/cm^2.

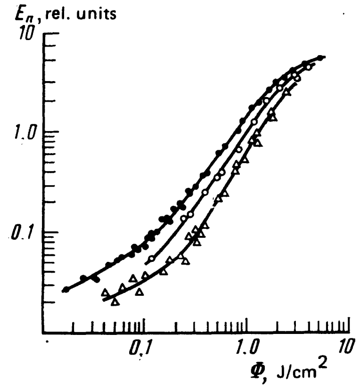

FIG. 4. Dependences of the energy absorbed per molecule on the energy density of the exciting radiation obtained for the following lines: △) $P(14)$; ●) $P(16)$; ○) $P(18)$; all these lines corersponded to the $10.6\,\mu$ band of CO_2 laser radiation. The SF_6 molecules in a jet were excited at a distance of 11.4 cm from the nozzle. The SF_6 pressure in the nozzle was 5 atm. The distance from the nozzle to the detector was 16.8 cm.

It is known (see, for example, Refs. 1 and 12) that in the majority of the experiments carried out on SF_6 at room temperature the dependences $E_n(\Phi)$ are not steeper than linear. In a wide range of the energy densities they can be described by the expression $E_n \propto \Phi^n$, where n ranges from 0.6 to 0.9.

This was clearly due to the fact that in these experiments the gas pressures were relatively high (~ 0.1–0.5 Torr), so that even at low excitation energy densities the proportion of the interacting molecules was high ($f \approx 0.4$–0.5 in Refs. 3 and 4), and also because the multiphoton nature of the absorption was not manifested in the $E_n(\Phi)$ dependences. However, in the case when the excitation of SF_6 occurred at a low gas pressure (13 mTorr) in an essentially collisionless regime, $E_n(\Phi)$ plots steeper than linear had been observed even at room temperature.[6] At 137 K the $E_n(\Phi)$ plots were steep for the $P(20)$ and $P(24)$ lines.[9] They were attributed to the absorption involving two- and three-photon transitions. In the subsequent investigations the same authors[23,24] used a high-pressure CO_2 laser with continuous frequency tuning and detected narrow two-photon resonance peaks in a system of low vibrational levels of SF_6.

The reduction in the slopes of the $E_n(\Phi)$ plots in the range $\Phi \gtrsim 2.5$ J/cm^2 was due to the fact that at these energy densities the proportion of the interacting molecules was of the order of unity[15] so that a further acquisition of the vibrational energy was proceeded mainly by an increase in the degree of excitation. The dissociation of the molecules then began and they started to "escape" from the beam. The maximum absorption at the frequency of the $P(16)$ line was due to the fact that this frequency agreed well with the Q branch of the $v = 1 \leftarrow v = 0$ transition of the excited ν_3 vibration, and also because of the relatively low rotational and vibrational temperatures of SF_6 (Ref. 25).

2. Dependences of the absorption cross sections on the excitation energy density

The results plotted in Fig. 4 could be used to find the dependences of the absorption cross section σ on the density of the incident radiation energy. As usual,

$$\sigma=-\ln (T)/Nl, \tag{7}$$

where $T = T_{tr}/E_{inc}$ is the transmission of the gas (E_{tr} and E_{inc} are the transmitted and incident energies, respectively), N is the gas density, and l is the length of the absorbing layer. Since, in our experiments only a small proportion of the incident energy was absorbed, the quantity $-\ln(T)$ could be quite accurately described by

$$-\ln(T)=\ln\left(1+\frac{E_n}{E_{inc}-E_n}\right)\sim\frac{E_n}{E_{inc}}\sim\frac{E_n}{\Phi}. \tag{8}$$

It follows that the absorption cross section can be regarded as simply proportional to the slope of $E_n(\Phi)$. Figure 5 shows the $\sigma(\Phi)$ dependences obtained for the $P(14)$, $P(16)$, and $P(18)$ lines. In the range $\Phi \lesssim 0.1$–0.2 J/cm^2 the absorption cross sections decrease. A considerable rise of the absorption cross sections is observed at energy densities $0.2 \lesssim \Phi \lesssim 2.0$ J/cm^2, the steepest rise being that for the $P(14)$ line. At still higher energy densities $\Phi \lesssim 2.0$ J/cm^2 the absorption cross sections fall again. The rise of the absorption cross sections at $0.2 \lesssim \Phi \lesssim 2.0$ J/cm^2 is due to the multiphoton nature of the interaction. The $\sigma(\Phi)$ dependences given in Fig. 5 differ considerably from those obtained for SF_6 at room temperature[26,27] and at 140 K (Ref. 10). According to the data of Ref. 10, in the case of the $P(12)$–$P(20)$ lines there is no significant increase in the absorption cross sections right up to $\Phi = 1.0$ J/cm^2. This is clearly also related to the fact that the gas densities were relatively high ($\rho = 1.0\times10^{16}$ cm^{-3}) so that the multiphoton nature of the absorption was not manifested in the dependences $\sigma(\Phi)$. When SF_6 cooled in a pulsed jet was excited, the proportion of the interacting molecules was low and a rise of the absorption cross sections in the range $\approx$0.2–2.0 J/cm^2 was observed in Ref. 15 for a number of lines [$P(14)$–$P(24)$].

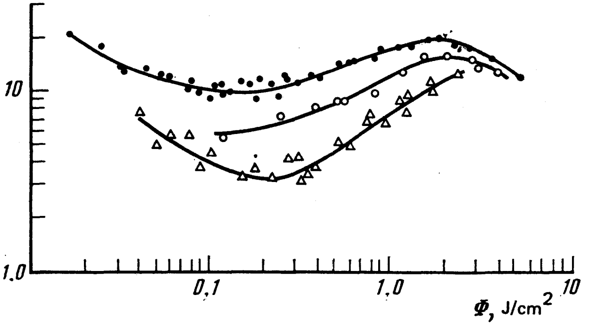

FIG. 5. Dependences of the absorption cross sections on the energy density of the incident radiation for the $P(14)$ (△), $P(16)$ (●), and $P(18)$ (○) lines of the 10.6 μ band at the carbon dioxide laser. Conditions for the excitation of SF_6 were the same as in the case of Fig. 4.

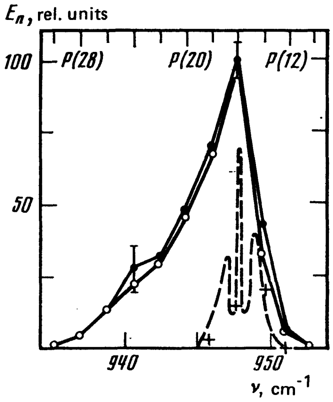

FIG. 6. Frequency dependences of the energy absorbed in the excitation of the ν_3 vibration of SF_6 at excitation energy densities of 0.5 (open circles) and 1.0 (black dots) J/cm^2. The excitation conditions were the same as in the case of Fig. 4. The spectra were normalized to the maximum for the $P(16)$ line. The dashed curve shows, for comparison, the spectrum of the linear absorption of the ν_2 vibration at $T \approx 55$ K taken from Ref. 28. The crosses represent our results obtained in the measurement of the small-signal absorption for the $P(12)$–$P(20)$ lines (see Sec. III).

3. Frequency dependence of the absorbed energy

Figure 6 shows the frequency dependences of the absorbed energy (which we shall call the multiphoton absorption spectra) at energy densities of the incident radiation amounting to 0.5 and 1.0 J/cm^2. These spectra are normalized to the maximum of the $P(16)$ line. For comparison, the lower part of the figure gives the linear absorption spectrum of SF_6 cooled in a supersonic stream to 55 K, as reported in Ref. 28. The width of the multiphoton absorption spectra is $\Delta\nu \lesssim 5$ cm^{-1} (at midamplitude). These spectra are considerably narrower than those obtained at the same energy density in Refs. 7 and 9 at temperatures of 140 and 137 K, respectively. This can be explained by the considerably lower rotational temperature of SF_6 in these experiments, and also by the collision-less excitation regime.[25] The absence of influence of collisions on the excitation process accounts also for the observation that an increase in the energy density from 0.5 to 1.0 J/cm^2 produces hardly any deformation of the multiphoton absorption spectra. It should be pointed out that the spectra shown in Fig. 6 represent only the contours of the frequency dependence of the multiphoton absorption. Multiphoton absorption spectra with sharp resonances can be obtained using lasers with continuous frequency tuning.[23,24]

It is clear from Fig. 6 that the absorption is relatively high even at the $P(24)$ and $P(26)$ lines with frequencies such that the $v = 1\leftarrow v = 0$ transition the interaction is with the rotational SF_6 states with quantum numbers in the range $J \gtrsim 120$ (Ref. 29), which are practically empty at $T_{rot} \approx 40$ K. Their populations are only $\sim 10^{-8}$ of the population of the more strongly filled rotational states with $J \approx 16$–18 or of the order of 10^{-6} of the populations of the rotational sublevels with $J \approx 32$–33, which are in resonance with the frequency of the $P(18)$ line.[30,31] At the energy density $\Phi = 1.0$ J/cm^2 the field-broadening of the lines is insufficient (the Rabi frequency is $\nu_R \approx 0.3$ cm^{-1}) to compensate the frequency detuning for the $V = 1\leftarrow v = 0$ transition in the case of the

$P(24)$–$P(26)$ lines and thus ensure interaction with the populated rotational sublevels. Therefore, the role of the $v = 1 \leftarrow v = 0$ transitions in the absorption is negligible in the low-frequency wing. Moreover, the large frequency detuning has the effect that the rotational sublevels (with $J \lesssim 30$) populated at $T_{\text{rot}} \approx 40$ K cannot participate in the process of absorption at the frequencies of the $P(24)$, $P(26)$,... lines even in the case of two- and three-photon transitions. Therefore, only multiphoton transitions of higher order or weak transitions[32] may be responsible for the absorption in the low-frequency wing. However, it should be pointed out that since the probability of weak transitions with $\Delta R > 0$ decreases proportionally to J^4 (Ref. 33), it follows that at low temperatures the relative contribution of weak transitions to the absorption should decrease considerably.

One should also point out that in the case of the laser-pulse dissociation of clusters present in a jet,[34] for example when dimers are dissociated, one may expect formation of rotationally and vibrationally hot SF_6 molecules that absorb laser radiation at lower frequencies. However, only the hypothesis of the appearance of hot molecules in very high densities (amounting to tens of percent) can account for such a strong absorption at frequencies $\nu \lesssim 941$ cm^{-1}. In our experiments (bearing in mind the nozzle geometry and the SF_6 pressures in the range $p_0 \leqslant 5$ atm) it is unlikely that clusters can form in high densities in a jet because SF_6 is a gas that is difficult to condense.[35] Moreover, the strong absorption in the low-frequency wing is observed also at SF_6 nozzle pressures of $p_0 \lesssim 1.0$ atm when the formation of clusters in a jet, proportional to p_0^2 (Ref. 34), is considerably less likely. The absorption in the low-frequency wing is, in our opinion, primarily due to multiphoton transitions to $v \geqslant 4$ levels and due to subsequent acquistion of energy in the quasicontinuum.

4. Dependence of the absorbed energy on the intensity

The role of the intensity was determined by measuring the energy absorbed when SF_6 was excited by pulses of different shape. The pulses employed in this study were of the kind shown in Fig. 7. The first (long) pulse used in all the experiments described in the present study had a peak which was of ≈ 80 nsec duration at midamplitude and a tail of ≈ 0.8 μsec duration (also at midamplitude). The distribution of the energy between the peak and the tail was $\approx 40\%$ and $\approx 60\%$, respectively. The second (short) pulse had a peak of ≈ 100 nsec duration at midamplitude but no tail. Such a CO_2 laser pulse was obtained using a nitrogen-free mixture. Judging by the shape of the pulses, we estimated that the average intensities of the pulses for the same energy differed by a factor of 6–7 and the peak intensities differed approximately by a factor of 2.

Figure 8 shows the dependences $E_n(\Phi)$ for the $P(14)$, $P(16)$, and $P(18)$ lines obtained on excitation of SF_6 with long and short pulses. Similar dependences were obtained by us also for the $P(12)$ and $P(20)$–$P(28)$ lines. For all the lines it was found that the absorption of the short pulse was approximately twice as strong for the same energy densities in the range ≈ 0.2–1.5 J/cm^2. In the case of the $P(16)$ and $P(18)$ lines the slope of the dependences $E_n(\Phi)$ was considerably less for the short pulse: $n \approx 1.4$ and $n \approx 0.9$ for the long and short pulses, respectively. This was clearly due to the fact that in the case of the $P(16)$ and $P(18)$ lines an increase in the pulse intensity because of the field broadening resulted in the interaction of a relatively greater (than at other frequencies) proportion of the molecules, because these lines agreed best with the linear absorption spectrum of SF_6 at $T_{\text{rot}} \approx 40$ K and at the same time the frequency detuning in the case of two-photon transitions was small for these lines.[21] When the energy density was in the range $\Phi \gtrsim 3.0$ J/cm^2 the absorption of the short pulse in the case of the $P(16)$ line was only slightly greater ($\lesssim 10\%$) than for the long pulse. Since at these energy densities the proportion of the interacting molecules was of the order of unity for the $P(16)$ line (see below), the same absorption in the case of pulses of different intensity indicated that the average degree of excitation (or absorption in the quasicontinuum) depended little—in the investigated range—on the intensity. In the case of the other lines the proportion of the interacting molecules was small even when the pulse intensity was higher. Therefore, in the case of excitation by long or short pulses the slopes of the dependences $E_n(\Phi)$ were basically similar.

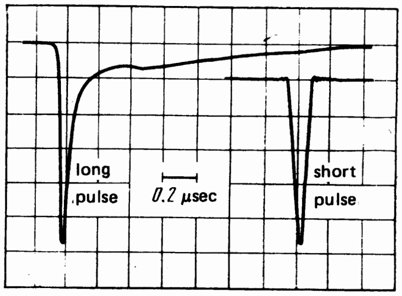

FIG. 7. "Long" and "short" CO_2 laser pulses used to excite SF_6 in a study of the role of the intensity in the absorption. The shape of these pulses gives an idea only of the time dependences of the envelopes of the pulses. In both cases the pulses were of the multimode type.

The dependence of the multiphoton absorption in SF_6

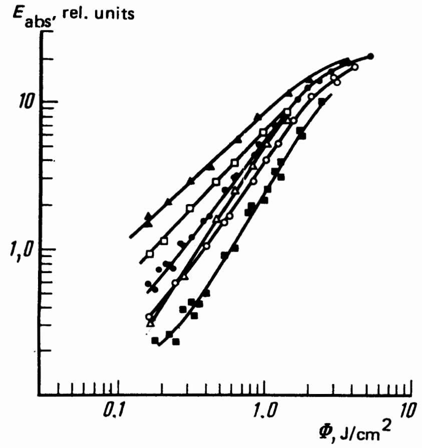

FIG. 8. Dependences of the absorbed energy on the energy density of the exciting radiation in the case of the $P(14)$, $P(16)$, and $P(18)$ lines of the 10.6 μ band of the carbon dioxide laser used to excite SF_6 in a jet by long (■, ●, ○) and short (△, ▲, □) pulses. The SF_6 molecules were excited at a distance of 6 cm from the nozzle. The excitation conditions were the same as in the case of Fig. 4.

on the intensity had been investigated before.[26,27,36,37] The experiments were carried out at room temperature of SF_6. Variation of the intensity, keeping the energy constant, was achieved either by altering the pulse duration[26,27,37] or by using single-mode or multimode pulses.[27,36] The results obtained in these experiments were quite contradictory. For example, it was found in Ref. 36 that at energy densities $\Phi \lesssim 10^{-2}$ J/cm^2 the absorption cross section in the case of excitation of SF_6 by multimode pulses was approximately 2.3 times greater than in the case of excitation by single-mode pulses, whereas at high energy densities there was no difference between the absorption. In Refs. 26 and 27 it was reported that at energy densities $\Phi \lesssim 0.5$ J/cm^2 the absorption in the case of a 500-psec pulse was approximately twice as strong as in the case of a 100-nsec multimode pulse, and the difference between the absorptions was observed right up to energies ~3.0 J/cm^2. Elsewhere[37] it was reported that there was no increase in the absorption on reduction in the pulse duration from 1.5 μsec to 15 nsec.

One should point out that in all these experiments the pressures of SF_6 were fairly high ($p \gtrsim 0.12$ Torr). At these pressures a change in the pulse altered the excitation conditions from collisionless (in the case of short pulses) to mainly of the collision type (for long pulses). The role of the intensity could be determined only in the case of essentially collisionless excitation. It was shown in Ref. 6 that in the collisonless regime (when the SF_6 pressure was 13 mTorr) at energy densities $\Phi \lesssim 0.2$ J/cm^2 the absorption of a pulse of 50 nsec duration was 3.5–1.5 times greater than in the case of a pulse with a tail part of ~0.6 μsec duration.

The role of the intensity in the excitation of SF_6 at low temperatures had not been investigated so far. The results reported in Fig. 8 demonstrate that in the investigated range of energy densities ($\approx$0.15–2.0 J/cm^2) the process of multiphoton absorption in SF_6 cooled in a supersonic jet was strongly dependent on the pulse intensity when the excitation regime was of the collisionless type. The role of the intensity depended strongly on the excitation frequency.

5. Influence of the vibrational temperature on the energy acquisition process

In the case of the SF_6 molecule at $T_{\text{vib}} \approx 160$ K, for which the results reported above were obtained, about 85% of the molecules were in the ground state.[5] Therefore, the absorption was mainly due to transitions from the ground state. It would be interesting to consider also the case when the rotational distribution of the molecules was fairly narrow, whereas the distribution of the molecules between the vibrational states was quite close to that at room temperature. Under these conditions one would expect absorption by high vibrational levels in the case of several of the CO_2 laser lines [beginning from the $P(16)$ line and going on to higher frequencies].

Since in the process of free expansion of a gas from a nozzle into vacuum the "freezing" of the vibrational temperature occurred much earlier than in the case of the rotational temperature,[13] the relationship between T_{rot} and T_{vib} should depend strongly on the distance from the nozzle to the observation zone. Therefore, depending on the position of a skimmer one could separate from a free jet a beam of molecules with different ratios of T_{rot} to T_{vib}. For example, when the skimmer was located at a distance of 2.5 mm from the nozzle, we separated a molecular beam for which the rotational and vibrational molecular temperatures at a distance of 6 cm from the nozzle where $T_{\text{rot}} = 50 \pm 10$ K and $T_{\text{vib}} = 230 \pm 15$ K (Ref. 25). At this vibrational temperature about 55% of the molecules were in the ground state and about 20% in the ν_6 state, with about 25% of the molecules distributed between higher states.[5]

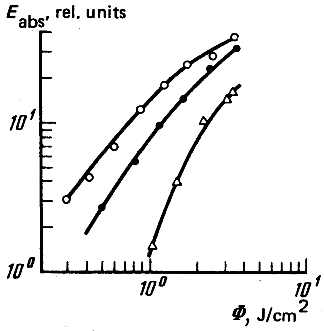

FIG. 9. Dependences of the energy absorbed per molecule on the density of the exciting radiation energy obtained for the $P(14)$, (△), $P(16)$ (●), and $P(18)$ (○) lines of the 10.6 μ carbon dioxide laser band in the case of a molecular SF_6 beam with the parameters $T_{\text{vib}} = 230 \pm 15$ K and $T_{\text{rot}} = 50 \pm 10$ K. The excitation conditions were the same as in the case of Fig. 4.

Figure 9 shows the dependences of the absorbed energy on the density of the incident radiation energy in the range $\Phi \approx 0.2$–4.0 J/cm^2 obtained for the $P(14)$, $P(16)$, and $P(18)$ lines at the temperatures $T_{\text{rot}} \approx 50$ K and $T_{\text{vib}} \approx 230$ K. A comparison of these dependences with the results plotted in Fig. 4 (for $T_{\text{rot}} \approx 40$ K and $T_{\text{vib}} \approx 160$ K) enabled us to understand better the role of the vibrational temperature. At $T_{\text{vib}} \approx 230$ K the absorption was maximal for the $P(18)$ line. The dependence $E_n(\Phi)$ for this line was less steep ($n \lesssim 1.1$) than at $T_{\text{vib}} \approx 160$ K ($n \approx 1.4$). On the other hand, in the case of the $P(14)$ line the slope of the dependence $E_n(\Phi)$ was even steeper ($n \lesssim 3$) than in the case shown in Fig. 4 ($n \approx 1.8$). The absorption at the frequency of this line was considerably less than for the $P(16)$ and $P(18)$ lines. For example, even when the energy density was 1.0 J/cm^2 the absorption in the case of the $P(14)$ line was 5–6 times less than for the $P(16)$ line, and approximately 10 times less than for the $P(18)$ line, wherease for $T_{\text{vib}} \approx 160$ K it was only 2 and 1.5 times less. Reduction in the slope of the dependences $E_n(\Phi)$ obtained for the $P(16)$ and $P(18)$ lines began at lower energy densities than those in Fig. 4. This behavior could be explained as follows. At the frequency of the $P(18)$ line at $T_{\text{vib}} \approx 230$ K the incident radiation interacted effectively with the molecules in the ground and higher vibrational states. The proportion of the interacting molecules was considerably greater than at $T_{\text{vib}} \approx 160$ K. In the case of the $P(14)$ line the converse was true: the proportion of the interacting molecules was even less than at $T_{\text{vib}} \approx 160$ K, because at the frequency of this line only the molecules at the ground state interacted with the laser radiation and the population of this state at $T_{\text{vib}} \approx 230$ K was approximately 1.5 times less than at $T_{\text{vib}} \approx 160$ K (Ref. 5). The dependence $E_n(\Phi)$ for the $P(14)$ line was nearly cubic. Clearly, it was three-photon transitions for which the frequency detuning was less than in the case of two-photon transitions[21] that were responsible for the absorption at the frequency of the $P(14)$ line at these energy densities. One should also point out that since the intermode anharmonicity shifted the frequencies of the transitions from high vibrational states toward lower frequencies, the $P(16)$ and $P(18)$ lines could excite the R branches of these transitions for which the dependences $E_n(\Phi)$ shown in Fig. 4 were steeper than for the P and Q branches. Nevertheless, the $E_n(\Phi)$ dependence for the $P(18)$ line in the case when $T_{\text{vib}} \approx 230$ K was less steep than for $T_{\text{vib}} \approx 160$ K. This was due to the fact that because of a large number of resonance transitions the proportion of the molecules interacting at the frequency of this line was considerably greater for $T_{\text{vib}} \approx 230$ K than for $T_{\text{vib}} \approx 160$ K.

The results plotted in Figs. 4, 8, and 9 led us to the conclusion that the absolute value of the absorbed energy as well as the nature (slope) of the $E_n(\Phi)$ curves depended strongly on the initial proportion of the interacting molecules which was governed by the pulse intensity and by the gas temperature, i.e., by the distribution of the molecules between the vibrational–rotational states. In the case of the experiments carried out under static conditions, this proportion was also governed by the pressure of the gas in the cell.[6] It was the strong dependence of the absorbed energy and of the $E_n(\Phi)$ slope on the proportion of the interacting molecules that was responsible for the strong quantitative and qualitative differences between the dependences $E_n(\Phi)$ deduced from the multiphoton absorption results reported by different authors (see, for example, Refs. 1 and 12). The discrepancy between the results could be explained by the different shapes of the pulses used, their mode structure, and different SF_6 pressures at which the experiments were carried out in the various studies.

6. Estimate of the proportion of the interacting molecules

The results given in Fig. 4 can be used to estimate the fraction of the molecules interacting with laser radiation. It is clear from Fig. 4 that when the energy density was $\Phi \gtrsim 2.5$ J/cm^2, the slope of the dependence $E_n(\Phi)$ obtained for the $P(16)$ line was considerably less. In the range $\Phi \gtrsim 2.5$ J/cm^2 the Rabi frequency ($\nu_R = \mu E/\hbar c \gtrsim 0.7$ cm^{-1}) was known to be considerably greater than the width of the Q branch of the $v = 1 \leftarrow v = 0$, transition at $T_{\text{rot}} \approx 40$ K ($\Delta\nu_Q \lesssim 0.2$ cm^{-1}—see Ref. 28). Therefore, at these energy densities at least all the molecules from the ground state interacted with the laser pulses, i.e., the proportion of the interacting molecules was $f_1 \gtrsim 0.9$. At energy densities $\Phi = 4$–5 J/cm^2 we found that $f_1 \approx 1.0$. The average degree of excitation l_1 for the $P(16)$ line at energy densities 2–5 J/cm^2 observed in our experiments did not differ greatly from the average degree of excitation obtained in experiments when SF_6 was kept at room temperature. We could quite accurately assume that, for example, $l_1 \approx 25$ for $\Phi = 4.0$ J/cm^2 (Ref. 27). The ratio of the absorbed energies, equal to the ratio of the products $f_i l_i$ for $\Phi = 4.0$ J/cm^2 and for $\Phi = 0.1$ J/cm^2, was ~ 70, as demonstrated in Fig. 4. Consequently, if for $\Phi = 0.1$ J/cm^2 the average degree of excitation l_2 for the $P(16)$ line was equal only to just two quanta, the proportion of the interacting molecules was $f_2 \approx 0.16$. However, for $l_2 \gtrsim 3$, which was more likely than Ref. 4, it was found that $f_2 \lesssim 0.11$. The results in Fig. 4 indicated also that the fraction f for the excitation of SF_6 by the $P(14)$ and $P(18)$ lines was considerably less. Therefore, our estimates indicated that at moderate energy densities ≈ 0.1–0.2 J/cm^2 the proportion of the interacting molecules in our experiments was considerably (3–5 times) less than in the case of the excitation of SF_6 in a cell at room temperature.[3,4,6] This was associated with a strong reduction in the number of resonance transitions because of the cooling of the gas, and also due to the absence of collisions which might increase this proportion because of rotational relaxation.

V. CONCLUSIONS

Our study demonstrated that pyroelectric detectors based on polycrystalline organic films[11] with a time resolution of ≈ 5 μsec could be used to investigate infrared multiphoton absorption by polyatomic molecules in pulsed molecular beams (free jets), and also in diagnostics of the molecular beams themselves.

An investigation was made of the collisionless exctation of the SF_6 molecules (cooled first in a supersonic jet) by high-power CO_2 laser pulses. The results obtained led to the following principal conclusions.

1) The absorbed energy and, in particular, the nature of energy acquisition by the molecules depended strongly on the radiation intensity and on the temperature (internal energy) of SF_6, because the intensity of the pulses and the initial distribution of the molecules between the vibrational–rotational states determined the proportion of the interacting molecules.

2) Our results, like those reported in Refs. 9, 23, and 24, demonstrated that the main mechanism of the molecular excitation in the region of discrete levels was by multiphoton (two- and three-photon) transitions for which the frequency detuning was compensated by the dynamic broadening of the vibrational–rotational lines by the pulsed laser field.

3) The excitation of SF_6 at frequencies detuned greatly from the linear absorption spectrum in the direction of low frequencies clearly occurred as a result of multiphoton transitions of higher order. The molecules were excited directly to the $v \geqslant 4$ levels and then acquired energy in the quasicontinuum.

4) The characteristic features of multiphoton transitions were manifested clearly in the absorption only when the proportion of the excited molecules was small. It was then that steep dependences $E_n(\Phi)$ were observed and the absorption cross sections increased on increase in the excitation energy density.

5) At moderate energy densities of ≈ 0.1–0.2 J/cm^2 the proportion of the interacting molecules was considerably (by a factor of 3–5) less than in the case of excitation of SF_6 in a cell kept at room temperature.

This last result clearly indicated also that the number of interacting rotational sublevels was small when the energy density was moderate. Only at the frequencies at which there were simultaneous one-photon and/or multiphoton transitions of different order was the number of rotational states interacting with laser radiation quite large.

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