Investigation of collisionless excitation of SF_6 and NH_3 molecules in an intense IR laser field by means of a tunable diode laser

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The pulsed CO_2-laser excitation of SF_6 and NH_3 molecules from different rotational sublevels J'' of the ground vibrational state in a pulsed molecular beam was investigated in essentially collisionless conditions. Dependences of the fraction f_J of the excited molecules on the rotational quantum number J'' were derived for various energy densities of the excitation pulse in the range $\Phi = 10^{-5}$–10^{-1} J/cm^2 for excitation of SF_6 at the $10P(16)$ CO_2-laser line as well as the $10P(18)$ and $10P(14)$ laser lines for $\Phi \leqslant 10^{-1}$ J/cm^2. These dependences have a clearly expressed resonant structure. The factors determining molecular excitation efficiency were investigated. The $f_J(\Phi)$ dependences were obtained for SF_6, $^{14}NH_3$ and $^{15}NH_3$ in the $\Phi = 10^{-6}$–$4 \cdot 10^{-1}$ J/cm^2 range for different levels of frequency detuning $\Delta\nu$ (to 0.1 cm^{-1}) of the excitation radiation with respect to the molecular transitions. The dependences are similar for the SF_6 and NH_3 molecules that generally manifest different spectroscopic behavior. The molecular excitation efficiency drops precipitously with $\Delta\nu$ and as the number of modes in the excitation pulse spectrum decreases. A comparison of experimental results from SF_6 excitation with theoretical predictions[8,9] has revealed a significant discrepancy of theory and experiment both with regard to the population of the $v_3 = 1$ state and the role (efficiency) of multiphoton transitions. Possible causes of the discrepancy are discussed including the neglect of the actual temporal and modal structures of the excitation pulse.

1. INTRODUCTION

Many experiments performed since the early 1970s (see, for example, Ref. 1) have revealed that collisionless IR multiphoton excitation (MPE) and dissociation in 10^6–10^9 W/cm^2 fields exist for a wide range of polyatomic molecules (SF_6, BCl_3, OsO_4, CF_3I, etc.). According to existing concepts the vibrational excitation of a polyatomic molecule can be divided into two stages. In the first stage the excited molecule is "elevated" over the lower vibrational levels of the resonant mode to the edge of the so-called quasi-continuum (QC) of the vibrational states. Reaching the QC corresponds to absorption of 6–7 quanta of energy $h\nu = 10^3$ cm^{-1} (Refs. 2,3). In the second stage the molecule acquires energy in the QC, where there are no distinct individual vibrational modes.

In spite of the extensive experimental material devoted to molecular MPE, there has been no satisfactory explanation of the first stage of this process, the absorption of the first few IR quanta by the excited molecule. The issue is not the absence of an experimentally adequate theoretical model but rather insufficient experimental data to make a quantitative comparison to calculation results.

The problem of a quantitative description of the MPE process at the lower vibrational levels could be regarded solved if a theoretical model existed (including a spectroscopic description of the molecules and their interaction with the laser field) whose results agree reasonably with the experimental data. In the comparison of calculation and experimental results the following aspects of the excitation process are of interest: The populations of the vibrational states; the distribution of the molecules over the vibrational levels in a given vibrational state; the fraction of noninteracting molecules and the fraction of molecules attaining the QC as well as how these characteristics depend on the frequency and energy density of the exciting laser radiation.

The SF_6 molecule is the classical object of investigation for MPE studies. The spectroscopic parameters of the ν_3 mode of this molecule (resonant with CO_2-laser radiation) have been investigated in considerable detail.[4] A number of studies have appeared in recent years devoted to MPE dynamics at the lower vibrational levels of the SF_6 molecule where there are sufficient experimental results to permit a quantitative comparison to theory. Thus, studies[5,6] employed CARS probing of the ν_1 mode to investigate the distribution of SF_6 molecules over the different vibrational states of the ν_3 mode after CO_2-laser pulse excitation and the integral populations of the first few ($v_3 = 0$–3) vibrational states of the excited mode for both the rotational and anharmonically split vibrational sublevels are also derived.

At the same time in order to explain the mechanism behind the progression of the molecule over the lower discrete levels from MPE primary interest lies in the experimental determination of the molecular distribution over the rotational sublevels of each vibrational state. At present such a distribution can be obtained only by the double IR-IR resonance technique using a tunable diode laser (TDL) as the probe radiation source.

Important advantages of using a pulsed TDL as the probe source include high absorption sensitivity allowing measurements at gas pressures below 1 mtorr ($N \leqslant 3 \cdot 10^{13}$ cm^{-3}), high spectral resolution $\Delta\nu_{res} \approx 10^{-3}$ cm^{-1} and the ability to determine the absorption spectrum after a single pulse.

Previous studies[7] have applied the double IR-IR resonance technique to SF_6 molecules cooled in a supersonic jet to the rotational temperaure $T_{rot} \approx 18$ K to investigate the dependence of the depletion of the separate rotational sub-

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levels of the ground vibrational state on the frequency and energy density of the excitation radiation. The measurements were carried out for the case of molecular excitation and probing perpendicular to the molecular flow. Here the delay τ_d between the excitation and probe time is 120 μs and since the molecular concentration in the excitation region is $(1.5\text{–}6) \cdot 10^{13}$ cm^{-3} (this corresponds to an effective pressure $p^* = 0.5\text{–}2$ mtorr) the rotational relaxation over $\tau_d = 120\,\mu$s could somewhat distort the molecular distribution resulting from MPE.

The purpose of the present study is to investigate the dynamics of vibrational MPE in the lower vibrational levels of the SF_6 molecule in essentially collisionless conditions. Experimental investigations of the MPE-induced depletion of different rotational sublevels of the ground vibrational state of the SF_6 molecule begun in Ref. 7 are continued and the experimental results compared to theoretical calculations[8–10] appearing after the publication of Ref. 7.

The present study provides new results making it possible to determine the population of the $v_3 = 1$ state and the influence of the mode composition of the CO_2-laser radiation on the efficiency of collisionless excitation of molecules from different rotational sublevels. A comparison of experimental results to calculations[8–10] has revealed a serious discrepancy in the population data of the lower discrete molecular levels after excitation and in the role of the multiphoton transitions. We discuss possible causes of this discrepancy and the primary drawbacks of these theoretical approaches.

The fraction f_J of molecules excited from the J level as a function of the energy density Φ of the exciting radiation with different amounts of laser frequency detuning from the vibration-rotational molecular transitions are investigated to establish the fundamental physical factors influencing the progression of molecules from the separate ground state rotational levels. Analogous dependences are obtained for $^{14}NH_3$ and $^{15}NH_3$ molecules. These relations are compared for SF_6 and NH_3 whose excitation can be considered within the framework of the two-level model. The influence of the spectral width and mode composition of the CO_2-laser radiation on the molecular depletion efficiency from a separate rotational level is investigated.

2. EXPERIMENT

2.1. Setup

An experimental configuration analogous to that used in[7] was employed for the measurements. A block diagram of the set-up is shown in Fig. 1a. A pulsed supersonic jet was used for molecular cooling. Unlike Ref. 7 these experiments employed a slit-type nozzle with a 2×0.2 mm^2 slit size. By varying the nozzle gas pressure (undiluted by the medium) over a 0.1–0.5 atm range we controlled the molecular concentration in the excitation and probe zone over a range $N \approx (0.35\text{–}1.75) \cdot 10^{13}$ cm^{-3} (effective pressure $p^* = 0.1\text{–}0.5$ mtorr). TDL measurements revealed that the distribution among the rotational sublevels of the ground vibrational state differs slightly from a Boltzmann distribution, although it can be roughly characterized by the rotational temperature $T_{\text{rot}} \approx 25\text{–}30$ K for SF_6 and 90–100 K for NH_3.

The cooled molecules were excited by a clipped TEA CO_2-laser pulse. Pulse duration was ≈ 100 ns (at half-amplitude), radiation energy ≈ 1 J. Without auxiliary selective elements in the laser cavity the spectral lasing linewidth was 0.035 cm^{-1} at half-maximum. The exciting radiation intensity was varied by means of CaF_2 attenuators; excitation energy density was controlled over a broad range from 10^{-6} to 0.4 J/cm^2.

A $Pb_{1-x}Sn_xSe$ TDL fabricated by the Lebedev Physics Institute of the Academy of Sciences of the USSR was used as the probe radiation source. The TDL operated in the 900–1000 cm^{-1} range in a pulse-periodic condition. The spectral resolution, determined by the TDL tuning rate $d\nu/dt = (1\text{–}3) \cdot 10^{-3}$ cm$^{-1}/\mu$s and the speed of the recording system, was $1 \cdot 10^{-3}$ cm^{-1}. An HgCdTe photoconductive cell was used to record diode laser radiation. The time constant of the IR detector was $\tau_d \approx 500$ ns. The detector signal was amplified by a low-noise amplifier ($e_n = 2$ nV/Hz$^{1/2}$) and was injected to a storage oscilloscope or a high-speed analog-to-digital converter connected to a microcomputer. The jet molecular spectrum was recorded in a single pulse with a signal-to-noise ratio better than 100. In order to reduce error from jet instability and CO_2-laser power irregularities the measurement results were averaged over at least 10 pulses. A digital time delay system controlled the synchronization of the separate units to better than 10 ns. The delay τ_d between the excitation and probe times was less than 10–15 μs.

Figure 1b, shows a geometrical configuration of the molecular excitation and probe scheme. Molecular excitation was achieved by aa counterpropagating CO_2-laser beam. The TDL probe radiation ran perpendicular to the jet. The excitation and probe radiation had parallel polarization planes. A multiple-pass three-mirror system with a 185 mm base length configured in a 28-pass White scheme was employed to improve sensitivity. The probe region had transverse dimensions of less than 0.5×2 cm. Conical diaphragms were used to control the molecular jet width, varying between 3 and 12 cm in the probe region.

A set of diaphragms and screens was used to eliminate parasitic CO_2-laser radiation of the IR detector and the diode laser. The TDL radiation was also transmitted through a

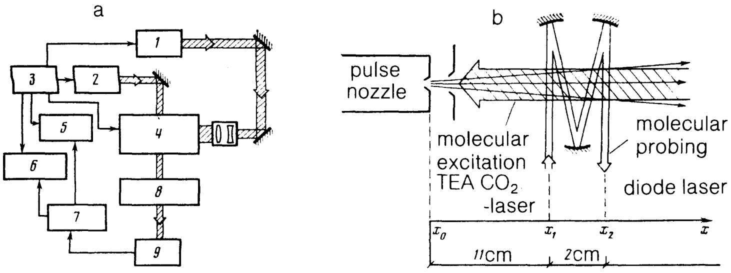

FIG. 1. Experimental setup. a—Block diagram: 1—TEA CO_2-laser; 2—diode laser; 3—synchronizer; 4—pulsed beam vacuum chamber; 5—high speed ADC recording system; 6—recording oscilloscope; 7—broadband amplifier; 8—MDR-2 monochromator; 9—HgCdTe photoconductive cell. b—Geometrical configuration. The multipass mirror system is configured in a 28-pass White scheme.

monochromator to isolate a $\sim 0.5\ \text{cm}^{-1}$ segment.

Note the essentially collisionless natuure of molecular excitation in the experimental conditions. The particle density in the excitation and probe zone corresponded to a pressure $p^* \leqslant 0.5$ mtorr which yields a value $p^*\tau_p \leqslant 0.05$ ns · torr at a CO_2-laser pulse duration of $\tau_p = 100$ ns. This is significantly below the corresponding values for rotational relaxation of NH_3 ($p^*\tau_{\text{rot}} \geqslant 7$ ns · torr[11]) and even further below that of SF_6 $p^*\tau_{\text{rot}} = 35$ ns · torr[12]). The delay τ_d between the excitation and probe times was less than 156 μs, yielding $p^*\tau_d \leqslant 7.5$ ns · torr. Therefore for the SF_6 molecule this experimental geometry made it possible to virtually eliminate the influence of relaxation on the populations of the probed levels over the selected delay τ_d. A correction to relaxation over the time τ_d (see Sec. 3.5) was introduced in investigating excitation in $^{14}NH_3$ and $^{15}NH_3$ molecules.

2.2. Methodology

The TDL experiments measured the absorption amplitude A at the center of the probed line and its change ΔA after the CO_2-laser pulse. The relative change in the absorption (brightening) coefficient $f^* = \Delta A / A$ was then determined. In all measurements the value of A was less than 20% of the diode laser signal amplitude. As we know[13] the interpretation of f^* largely depends on whether the measurements are carried out in two-level double resonance (DR) where the excited and probed transitions coincide or in three-level DR where the initial state is common to the excited and probed transitions, while the final states are different.

Simplified schemes of the SF_6 and NH_3 levels indicating the excited and probed transitions are given in Fig. 2. It was assumed that in the majority of experiments excitation and probing of the SF_6 molecules took place in conditions of three-level DR. This assumption is based on the following arguments. We will consider a situation where the $10P(16)$ CO_2-laser line is used for molecular excitation, while the brightening effect is measured at different lines in the R-branch of the ν_3 band. The excitation frequency $\nu_e = 947.74$ cm^{-1} shifts by $0.23\ \text{cm}^{-1}$ from the center of the Q-branch of the ν_3 band of the SF_6 molecule and falls between the frequencies of the $P(4)$ and $P(5)$ transitions. Frequency detuning levels $\Delta\nu = |\nu - \nu_{\text{rot}}|$ for the closest transitions are $0.066\ \text{cm}^{-1}$ for $P(3)$, $0.009\ \text{cm}^{-1}$ for $P(4)$, $0.048\ \text{cm}^{-1}$ for $P(5)$ and $0.106\ \text{cm}^{-1}$ for $P(6)$. The rotational levels of SF_6 in the $\nu_3 = 1$ state split from Coriolis interaction into three sublevels characterized by the rotational quantum number R ($R = J' - 1, J', J' + 1$). According to the selection rule $\Delta R = 0$ the transitions in the R-branch link sublevels with $R = J' - 1$, while in the P-branch they link sublevels with $R = J' + 1$. As usual J'' refers to the ground vibrational state, while J' refers to the vibrationally-excited state $\nu_3 = 1$. We will now consider the depletion of the rotational level $J'' = 4$ of the ground vibrational state as our example.

It is clear from Fig. 2 (left) that in the state $\nu_3 = 1$ the sublevel $J' = 3, R = 4$ can be populated due to the proximity of the frequencies of the $P(4)$ transition and the $10P(16)$ laser line ($\Delta\nu = 0.01\ \text{cm}^{-1}$) by excitation of the $10P(16)$ CO_2-laser line at $947.74\ \text{cm}^{-1}$. At the same time the sublevel $J' = 5, R = 4$ will not be populated due to the significant frequency detuning of the $R(4)$ transition from the $10P(16)$ line ($\Delta\nu \approx 0.5\ \text{cm}^{-1}$). It cannot be populated through the $P(6)$ transition either, since the sublevel $J' = 5, R = 6$ is populated in this case.

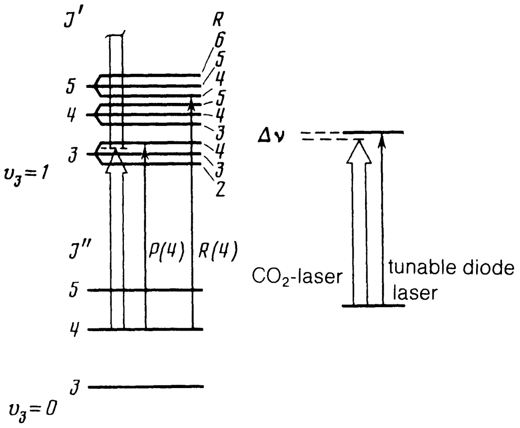

FIG. 2. Simplified schemes of the VR levels of SF_6 and NH_3 molecules. Left: Excitation of SF_6 molecule by a CO_2-laser at $947.74\ \text{cm}^{-1}$ at the $10P(16)$ laser line (broad arrow) and diode laser probing of the $P(4)$ and $R(4)$ transitions of the ν_3 band of SF_6 (thin arrows); right: Excitation of the VR transition in the NH_3 molecule by CO_2-laser radiation with frequency detuning $\Delta\nu$ and TDL probing of this same transition.

In order to more easily correlate the radiation power densities used for excitation with the frequency detuning levels we note that at the maximum excitation energy density used in the present study, $\Phi \approx 10^{-1}\ \text{J/cm}^2$ (intensity $I \approx 1$ mW/cm^2), the average Rabi angular frequency $\Omega_R = \mu_{01} E / \hbar\sqrt{3}$ calculated for the dipole moment of the transition $\mu_{01} = 0.437 D$[14] with linearly polarized excitation field ($E \approx 27$ kV/cm) reaches a value of $\approx 2.2 \cdot 10^{10}\ \text{s}^{-1}$ corresponding to $\Delta\nu_R = \Omega_R / 2\pi c = 0.1\ \text{cm}^{-1}$.

The assumption that the upper probed (in the R-branch) level is not populated during the excitation process implies equality of f_J (the fraction of molecules that have excited the emptied level of the ground state) to the observed brightening magnitude $f_J = f_J^*$. Here we have ignored the dependence of the dipole moment of the transition on the M-projection of J onto a fixed axis in space. We note that an exact relationship between the observed change in the absorption (brightening) coefficient f_J^* and the fraction of molecules f_J leaving the lower level depends on the specific theoretical model used to describe the excitation process.

The NH_3 molecules were excited and probed in two-level DR. The measurements were carried out at the vibration-rotational (VR) transitions of the $^{14}NH_3$ and $^{15}NH_3$ molecules in the ν_2 band[15,16] for which it was possible to select the CO_2-lasing line with $\Delta\nu$ detuning below $0.1\ \text{cm}^{-1}$. Here we assume that the probability of two or more photon transitions at the experimental energy densities $\Phi \leqslant 0.4\ \text{J/cm}^2$ is negligible due to the high effective anharmonity of the ν_2 mode. Therefore in the excitation of NH_3 we are essentially dealing with a two-level system. Bearing in mind the contribution to brightening f_J^* of the transitions from the upper level to the lower level we find that the fraction of molecules excited from the lower level is $f_J = f_J^*/2$.

3. RESULTS

3.1. Depletion of the rotational sublevels of the ground vibrational state of SF_6 under excitation at the $10P(16)$ CO_2-laser line

Figure 3a, shows how the fraction f_J of field-interacting molecules depends on the rotational quantum number

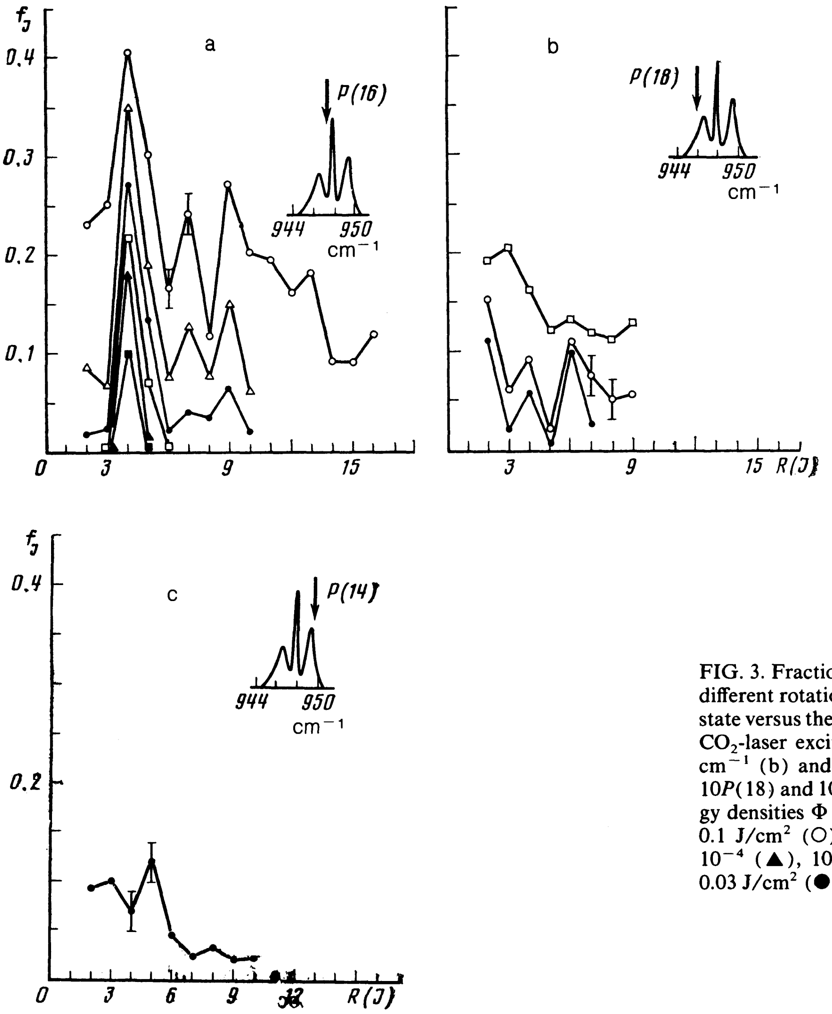

FIG. 3. Fraction f_J of SF_6 molecules excited from different rotational levels of the ground vibrational state versus the rotational quantum number J'' for CO_2-laser excitation at 947.74 cm^{-1} (a), 945.98 cm^{-1} (b) and 949.48 cm^{-1} (c) of the $10P(16)$, $10P(18)$ and $10P(14)$ lines, respectively. The energy densities Φ of the excitation radiation are: a—0.1 J/cm^2 (○), 0.03 (△), 0.01 (●), 10^{-3} (□), 10^{-4} (▲), 10^{-5} (■); b—0.136 (□), 0.05 (○), 0.03 J/cm^2 (●); c—0.136 J/cm^2 (●).

J'' obtained for SF_6 excitation at the $10P(16)$ CO_2-laser line at 947.74 cm^{-1} for different energy densities Φ of the excitation radiation. As the figure clearly reveals in the $10^{-5} \leqslant \Phi \leqslant 10^{-2}$ J/cm^2 energy density range the molecules are markedly excited only from the $J'' = 4$ and $J'' = 5$ sublevels having a small detuning $\Delta\nu$ from the excitation radiation frequency: 0.009 and 0.048 cm^{-1}, respectively. The attraction of molecules from many rotational levels of the ground state becomes apparent at $\Phi \rangle 10^{-2}$ J/cm^2. At an energy density $\Phi = 0.1$ J/cm^2, the $f_J(J'')$ dependence is clearly resonant. According to[7] with further growth of Φ to 0.5–1.3 J/cm^2 the $f_J(J'')$ structure is smoothed out, while f_J reaches 0.5–0.7.

3.2. Population of the $\nu_3 = 1$ state of the ν_3 mode of SF_6 under excitation at the $10P(16)$ CO_2-laser line

We employed two different methods to obtain population data on the $\nu_3 = 1$ state. In both cases the experimental data indicate that even with excitation near the Q-branch of the ν_3 band at the $10P(16)$ CO_2-laser line only a small fraction of molecules exiting the ground state populates the vibrational level $\nu_3 = 1$.

In the first case we compared the experimentally-observed brightening of the absorption lines in the P- and R-branches for J'' in the $2 \leqslant J'' \leqslant 10$ range. Since it was assumed that the probability of populating the Coriolis sublevels with $R = J' - 1$ (see Fig. 2) of the excited vibrational state through the transitions in the R-branch is negligible, when populating the Coriolis sublevels with $R = J' + 1$ we could anticipate a significant difference in the brigthening levels of the lines in the P- and R-branches.

Measurements reveal that for all J'' values indicated above except $J'' = 4$ the anticipated difference in the brightening of the lines in the P- and R-branches is not observed. For $J'' = 4$ the $f^*(\Phi)$ dependences for the $P(4)$ and $R(4)$ lines are shown in Fig. 4a. A slightly larger value of f_J^* is observed for the $P(4)$ transition compared to $R(4)$. At an energy density $\Phi \approx 0.1$ J/cm^2 this difference means that less than 1/5 of the molecules excited by the CO_2-laser pulse from the $J'' = 4$ level of the ground vibrational state end up on the rotational level $J' = 3, R = 4$ of the $\nu_3 = 1$ state at the same time that the remaining molecules are excited to the upper-lying vibrational states.

In the second case in order to determine the population of the $\nu_3 = 1$ state we measured the induced absorption at ≈ 941.0 cm^{-1} corresponding to the Q-branch of the $2\nu_3(A_1) \leftarrow \nu_3$ transition. Since we did not identify the transitions in the spectrum, the observed absorption could also be caused by transitions between the upper-lying levels and would provide only the upper bound of the population of the $\nu_3 = 1$ state. The absorption level at 941.0 cm^{-1} revealed that less than 5% of the molecules leaving the ground state ended up in the $\nu_3 = 1$ state of the ν_3 mode.

3.3. Depletion of different rotational sublevels of the ground state of SF_6 under excitation at the 10*P*(14) and 10*P*(18) CO_2-laser lines

The present study also observed SF_6 molecules leaving many rotational levels of the ground state under CO_2-laser excitation at 945.98 and 949.48 cm^{-1} of the 10*P*(18) and 10*P*(14) lines, respectively (Fig. 3b,c). The detuning levels of these lines from the center of the *Q*-branch of the $0 \rightarrow 1\nu_3$ transition is 1.5 cm^{-1} for 10*P*(18) and 2.0 cm^{-1} for 10*P*(14).

The $f_J(J'')$ dependence in Fig. 3a–c have a variable structure most likely attributable to the existence of individual MPE channels under excitation at different CO_2-laser lines. We note that for excitation at the 10*P*(14) and 10*P*(18) CO_2-laser lines special attention is devoted to suppression of lasing at the neighboring 10*P*(16) line. This is to eliminate possible distortion (particularly for $J'' = 4$) in the f_J relations that could occur due to weak illumination at the 10*P*(16) line.

3.4. Depletion of the rotational sublevels of the SF_6 ground vibrational state as a function of CO_2-laser pulse energy density

The dependence of the depletion f_J of the lower rotational sublevel characterized by the quantum number J'' on the laser pulse energy density Φ was measured for the *P*(3)–*P*(6) transitions in the ν_3 band of the SF_6 molecule closest to the 10*P*(16) CO_2-laser line. The results are shown in Fig. 4b.

The most interesting fact is that the fraction of excited molecules $f_J(\Phi)$ is very heavily dependent on the detuning $\Delta\nu$ of the excitation radiation frequency from the vibration-rotational transition of the molecules; with small detuning, the $f_J(\Phi)$ dependence is nonlinear.

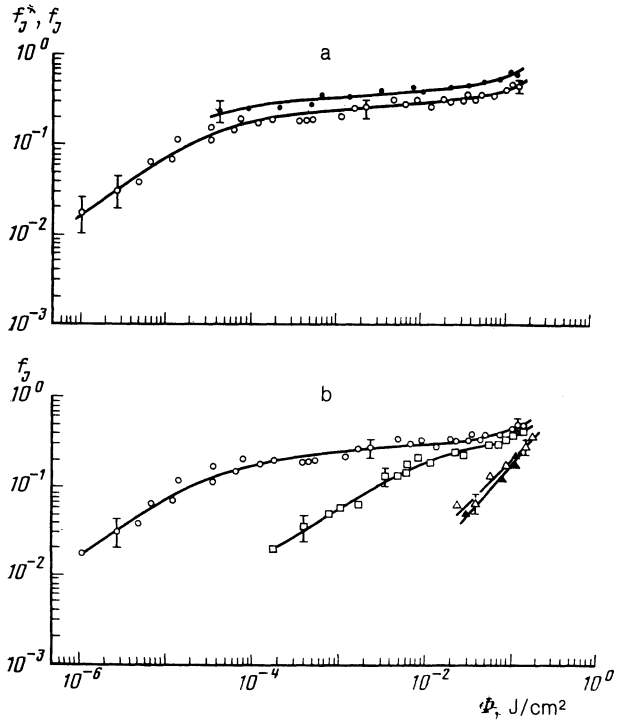

FIG. 4. SF_6 molecular excitation at 947.74 cm^{-1} of the 10*P*(16) CO_2-laser line. a—$f^*(\Phi)$, the observed brightening versus the energy density Φ of the CO_2-laser pulse at the *P*(4) (●) and *R*(4) (○) transitions of the ν_3 band; b—fraction $f_J(\Phi) \approx f^*_J(\Phi)$ of molecules excited from the rotational levels of the ground vibrational state with $J'' = 4$ (○) 5 (□), 3 (△), 6 (▲). The corresponding detunings for the $P(J'')$ transitions from the excitation frequencies is: 0.009, 0.048, 0.066 and 0.106 cm^{-1}.

3.5. Comparison of $f_J(\Phi)$ dependence for SF_6 and NH_3 molecules

In order to identify the mechanism responsible for the observed behavior of the $f_J(\Phi)$ dependences we carried out analogous measurements with $^{14}NH_3$ and $^{15}NH_3$ molecules. As noted above the high effective anharmonicity of the ν_2 mode resulting from inversion doubling interferes with multistage absorption in NH_3.

The anomalously-high rotational relaxation of ammonia creates some measurement difficulty.[11] Since the CO_2-laser-generated brightening f^*_J dropped over the delay between the excitation and probe times of $\tau_d = 10$–$15\,\mu s$, we measured the dependence of f_J on τ_d (Fig. 5) and extrapolated f_J to zero delay.

The $f_J(\Phi)$ dependences obtained for the $^{14}NH_3$ and $^{15}NH_3$ molecules are given in Fig. 6a,b. The smallest frequency detuning $\Delta\nu$ was $7 \cdot 10^{-4}$ cm^{-1} for the *aR*(2.0) transition in $^{15}NH_3$ from the 10*R*(42) CO_2-laser line, while the largest detuning ws $5 \cdot 10^{-4}$ cm^{-1} for the *aR*(0,0) transition in the same molecule from the 10*P*(16) line. A comparison of the $f_J(\Phi)$ relations shown in Figs. 4 and 6 reveals a qualitative correlation between the curves in NH_3 and SF_6. As with SF_6, the fraction of laser-excited NH_3 molecules drops precipitously as the detuning $\Delta\nu$ grows, and in the case of resonance ($\Delta\nu \leqslant 0.02$ cm^{-1}) the $f_J(\Phi)$ dependence is nonlinear over a broad range of energy densities $10^{-6} \leqslant \Phi \leqslant 10^{-1}$ J/cm². We can therefore assume that such behavior of the $f_J(\Phi)$ dependences for both SF_6 and NH_3 is determined more by the properties of the exciting laser field than by the specific nature of the molecular system.

3.6. The influence of the mode composition of CO_2-laser radiation

In order to determine the role of the mode composition of CO_2-laser radiation we measured $f_J(\Phi)$ in SF_6 for the $J'' = 4$ level for which resonant excitation conditions are achieved at the *P*(4) transition ($\Delta\nu = 9 \cdot 10^{-3}$ cm^{-1}) by excitation at the 10*P*(16) CO_2-laser line. Depletion was measured at the *R*(4) transition. The CO_2-laser radiation spectrum varied during the measurements in the following manner. First a "regular" pulse with several longitudinal

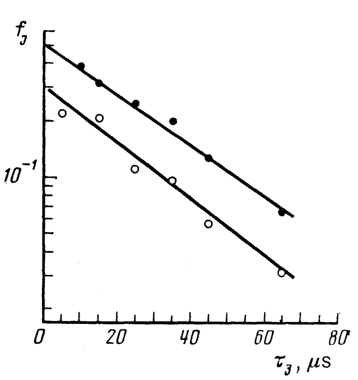

FIG. 5. The dependence of the fraction $f_J = f^*_J/2$ of excited NH_3 molecules on the delay τ_d between the excitation and probe times. The *aR* (2.2) (●) transition in the $^{15}NH_3$ molecule was excited at the 10*R*(40) line, while the *sQ*(2.2) (○) transition in the $^{14}NH_3$ molecule was excited at the 10*R*(8) CO_2-laser line.

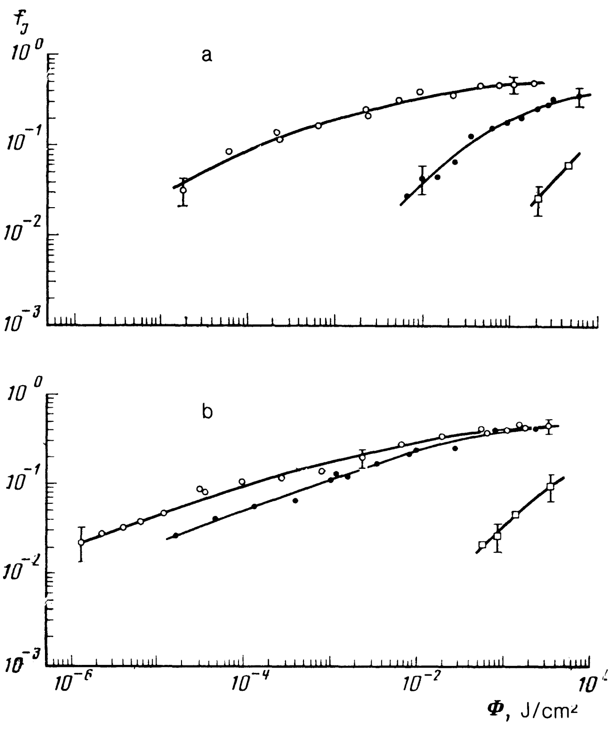

FIG. 6. The dependence $f_J(\Phi) = f_J^*(\Phi)/2$ of the fraction of NH_3 molecules excited from the rotational levels of the ground vibrational state on the CO_2-laser pulse energy density Φ. a—Excitation of the $sQ(5.4)$ (○), $sQ(2.2)$ (●) and $aR(1.1)$ (□) transitions of the $^{14}NH_3$ molecules at the $10R(6)$, $10R(8)$ and $10R(14)$ CO_2-laser lines, respectively. The corresponding detuning between the frequencies of the transitions and the excitation lines was 0.019, 0.031, 0.049 cm^{-1}; b—excitation of the $aR(2.0)$ (○), $aR(2.2)$ (●) and $aR(0.0)$ (□) transitions of $^{15}NH_3$ molecules at the $10R(42)$, $10R(40)$ and $10P(16)$ CO_2-laser lines, respectively. Corresponding frequency detunings: 0.0007, 0.013 and 0.050 cm^{-1}.

and transverse modes was used. Then the laser cavity diaphragm was used to isolate a single transverse mode. The longitudinal mode spectrum then narrowed due to the reduction in working medium pressure in the CO_2-laser to 0.5 atm. Finally a single longitudinal mode was extracted in the CO_2-laser spectrum by means of the cavity germanium Fabry-Perot etalon with a free dispersion range 0.05 cm^{-1}. The nature of successive changes in $f_J(\Phi)$ is shown in Fig. 7; this confirms the role of the mode structure of the radiation during the molecular excitation process. For example, in order to excite 5% of the molecules ($f = 0.05$) the pulse density Φ with a maximally-narrowed spectrum (with the Fabry-Perot etalon) must be more than two orders of magnitude (approximately a factor of 200) greater than in a broad spectrum pulse (the lower and upper curves in Fig. 7).

4. DISCUSSION

It is interesting to compare the experimental data obtained in Ref. 7 and in the present study with results from model calculations[8–10] based on the known molecular constants of SF_6. The positions of the VR levels of the CO_2-laser resonant ν_3 mode of the SF_6 molecule have been investigated experimentally up to states with $\nu_3 = 3$. The most accurate molecular constants have been obtained by investigating the $1\nu_3 \leftarrow 0$ fundamental band by saturated absorption spectroscopy,[18] by measuring the spectrum of the $3\nu_3 \leftarrow 0$ overtone

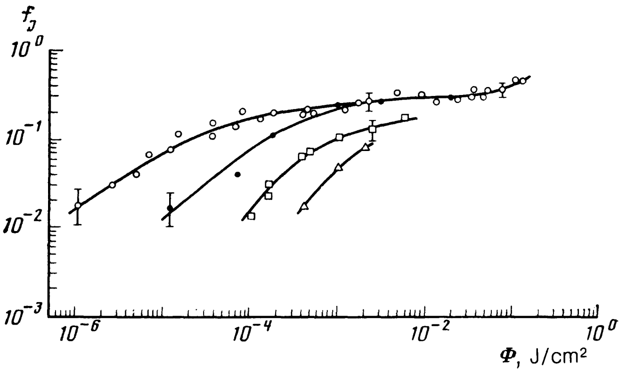

FIG. 7. Dependence $f_J(\Phi)$ of the depletion of the $J'' = 4$ level of SF_6 on the CO_2-laser pulse energy density Φ for exciting the $10P(16)$ line. These dependences were obtained with pulses of different modal composition: (○) a pulse with several transverse modes and more than ten longitudinal modes; (●) pulse with a single transverse mode, (□) narrowing of the spectrum of longitudinal modes, (△) one to two longitudinal modes in the spectrum.

transition on a different spectrometer[19–21] and by two-photon absorption at the $2\nu_3 \leftarrow 0$ transition.[22] These constants allow calculation of the VR levels of the ν_3 resonant mode to $\nu_3 = 3$ accurate to better than $1 \cdot 10^{-3}$ cm^{-1}. However, further experimental and theoretical studies are required to adequately predict the upper-lying levels, and these are complicated by the fact that it is necessary to consider not only the ν_3 mode but also its interaction with the other vibrational modes (including the random resonances between different VR levels).

The vibrational levels of the ν_3 resonant mode up to $\nu_3 = 4$, inclusively (five-level model) have been included[8] in calculating the excitation dynamics of the SF_6 molecule from the ground state. The position of the VR levels was calculated taking into account the anharmonic splitting, centrifugal distortion and vibrational interaction with rotation. The rotational structure was calculated up to $J = 30$. The excitation field was assumed to be monochromatic and its switch-on and switch-off instantaneous. The model accounted for all possible transitions up through four-photon transitions.

The $f_J(J'')$ dependence incorporating the rotational levels $\nu_3 = 0$–3 has also been studied.[9] Two models were considered: a model of a simple anharmonic oscillator and a hard top and a model that similarly accounts for[8] spherical anharmonic splitting, centrifugal distortion and Coriolis interaction. The excitation radiation was assumed to be monochromatic in the simple model and in the second case the laser line was assumed to have a Lorentz profile.

Finally $f_J(J'')$ was calculated[10] for various excitation intensities, taking into account only the two vibrational states of the ν_3 resonant mode, the ground state and the first excited state (two-level model), in order to clarify the causes of the depletion of the ground state in model of Ref. 8 and to compare the role of one- and multi-photon transitions.

A comparison of calculation results[8,9] and experimental results[7] shows satisfactory agreement between the theoretical $f_J(J'')$ dependences from Ref. 8 and the experimental data of Ref. 7 for values of Φ equal to 0.5 J/cm² and 1.3 J/cm² for SF_6 excitation at the $10P(16)$ CO_2-laser line. For $\Phi \leqslant 0.1$ J/cm² a noticeable difference appears, particularly in the $J'' = 4$ range. The authors of Ref. 8 attribute this difference to the influence on the population of the probed levels of rotational molecular relaxation occurring over the delay $\tau_d = 120\,\mu$s between the excitation time and the probe time. However a comparison of experimental results obtained with an identical energy density Φ (for example, $\Phi = 0.1$ J/cm^2) reveals that with a reduction of $p^*\tau_d$ from ≈ 100 ns · torr in Ref. 7 to $\leqslant 7$ ns · torr in the present study, the $f_J(J'')$ values remain virtually constant. This fact suggests that the influence of collisions over time $\tau_d = 120\,\mu$s in Ref. 7 was insignificant and only served to smooth out the structure of the dependences.

We will now compare the experimental data obtained in the present study to calculation results. Figure 8 shows the $f_J(J'')$ dependences corresponding to an excitation energy density $\Phi \approx 0.1$ J/cm^2 ($I \approx 1$ MW/cm^2). The thin solid curve represents results from the five-level model[8] while the dashed curve represents calculation of $f_J(J'')$ within the scope of the highly simplified two-level scheme[10] with the circles representing experimental results. It is clear that the five-level model[8] adequately describes the structure of the $f_J(J'')$ relation. The theoretical curve virtually follows all local maxima and minima observed for $J'' \geqslant 8$. Reference 9 attempted to identify one such maximum by assigning it to two-photon resonance from the $|vlJ\rangle = |0010\rangle$ level to the $|228\rangle$ level. It is, however, clear that a more strongly expressed maximum is observed for $J'' = 9$ (initial state $|009\rangle$). Therefore in order to assign the structure of the $f_J(J'')$ relation based on the transition types it is necessary to repeat the calculation using refined spectroscopic constants, particularly for the $2\nu_3$ level.[22] Regarding the f_J maximum at $J'' = 4$ we see that when $J'' = 3$–6 the theoretical values exceed experimental values by more than a factor of 1.5.

The primary shortcomings of the assumptions made in theoretical calculation have been identified[10] and it has been demonstrated that serious discrepancies exist between theoretical results[8] and experiment. Figure 8 clearly reveals that the $f_J(J'')$ dependences obtained from a complex calculation taking into account the five vibrational states $\nu_3 = 0$–4 and in a simple calculation within the framework of the two-level ($\nu_3 = 0,1$) model virtually coincide (with the exception of the fine structural details). This fact indicates that within the framework of the five-level model the primary contribution to the completion of the ground state comes from the $0 \rightarrow \nu_3$ single-photon transitions from the ground state to the first excited vibrational state $\nu_3 = 1$, while the contribution of multiphoton transitions to depletion is minor. Here the molecules abandoning the ground state preferentially populate the $\nu_3 = 1$ state within the framework of the model calculation. This will cause a significant difference in brightening f_J^* when probing the R- and P-branches. In Fig. 8 the $f_J^*(J'')$ dependence that occurs within the framework of models for probing the P-branch[8-10] is represented by the dot and dash curve. At the same time experimental data[7] and measurements carried out in the present study indicate that the values f_J^* observed in the P- and R-branches agree to within experimental error for all J'' in the $2 \leqslant J'' \leqslant 10$ range, except $J'' = 4$ (see Sec. 3.2).

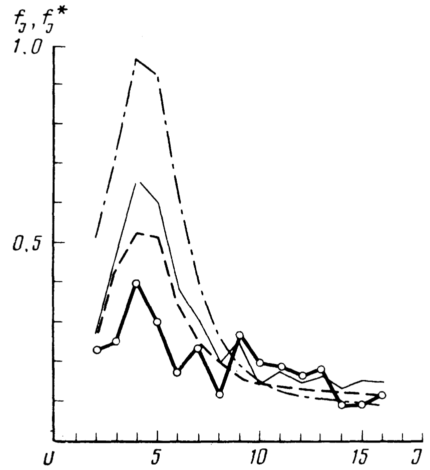

FIG. 8. Results from a theoretical calculation of $f_J(J'')$ of the depletion of the rotational levels of the ground state of the SF$_6$ molecule under excitation at the 10P(16) CO$_2$-laser line within the framework of the five-level model $v_3 = 0$–4[8] (thin solid curve); the two-level model $v_3 = 0$–1[10] (dashed curve) and experimental results obtained in the present study (open circles). The dot and dash curve represents the $f_{J^*}(J'')$ theoretical relation for transition brightening for SF$_6$ probing at the P-branch of the ν_3 band.

We note that since only a small fraction of the molecules on the $|vJ\rangle = |04\rangle$ level are excited via the $P(4)$ transition to the $|13\rangle$ level ($\leqslant 1/5$ of the total number of excited molecules), it is not surprising that molecules excited via other transitions in the P- and R-branches are not found in the $v_3 = 1$ state. For the $P(4)$ transition detuning of $\Delta\nu \approx 0.009$ cm^{-1} from the 10P(16) line is one-half the spectral linewidth of a TEA CO$_2$-laser (≈ 0.018 cm^{-1}). Frequency detuning significantly exceeds the lasing spectral width for all remaining transitions.

Experimental data (see Sec. 3.2) on the small population of the $v_3 = 1$ state given in the present study are not in agreement with experimental results.[5,6] According to the results[5,6] obtained in collisionless conditions by cooling SF$_6$ gas to $T = 150$ K, it is possible to quantitatively decompose the molecules after excitation into three ensembles: A "cold" ensemble including molecules that have not interacted with the laser radiation; "warm" molecules that have populated the lower discrete levels of the resonantly-absorbing mode and the "hot" molecules excited near the vibrational quasi-continuum, while the remaining molecules are distributed between the lower discrete levels of the ν_3 mode; $\approx 15\%$ of all the molecules are in the $v_3 = 1$ state, i.e., one-half of the number of molecules that have left the ground state.

Total depletion of the ground state of SF$_6$ has also been observed by CARS-probing.[23] No signal attributable to population of the lower vibrational levels of the ν_3 mode by the excited molecules was recorded. Unfortunately the data given in Ref. 23 are not sufficient to establish whether collisionless excitation conditions were realized in this study.

The discrepancy between the experimental data given in the present study (see Sec. 3.2) and in Ref. 23 and the data from Refs. 5,6 make necessary further investigations of the molecular distribution among the vibrational levels of the resonant mode in MPE. We also note a Boltzmann molecular distribution was obtained[5,6] for the "warm" molecular ensemble with an effective temperature $T_{\rm VIB}^{\rm eff} \approx (1.5$–$2) \cdot 10^3$ K assuming a uniform molecular distribution among the anharmonically-split sublevels. However, such a distribution has a low probability with radial collisionless excitation and is more likely due to the assumptions made in this case.

The experimental results outlined above indicate that in our experimental conditions the $0 \rightarrow 1\nu_3$ single-photon transitions (populating the $v_3 = 1$ state) do not play a significant role in the depletion of the rotational levels of the ground state. This conclusion is in disagreement with the results from theoretical calculations in Ref. 8. First, according to calculation, the $v_3 = 1$ state will be heavily populated. Second, within the theoretical framework the two-, three- and four-photon transitions do not play a significant role in the depletion of the ground state.[10]

The primary reason for the discrepancy in the first case, as discussed in Ref. 10 is the experimentally inadequate assumption that the field is switched on instantaneously, which serves to increase the role of single-photon transitions with minor detuning of the $10P(16)$ line from the center of the Q-branch of the ν_3 band of SF_6. In order to demonstrate the importance of taking into account the actual temporal profile of the excitation pulse (i.e., the fact that the field is not switched on and off instantaneously), we will compare results for two model situations. In the first case a "monochromatic" field pulse with a square-wave temporal waveform acts on the two-level quantum system (the field is switched on and off instantaneously), while in the second case the pulse envelope is a hyperbolic cosine (the field is switched on and off smoothly). If we assume instantaneous field switching and $E(t) = E_0$ during the pulse, we can use the corresponding expression for the interaction of the amplitude-stationary field with the two-level system[24]:

$$W(t)=\frac{(\varkappa E_0)^2}{(\varkappa E_0)^2+(\Delta\omega)^2}\sin^2[(\varkappa E_0)^2+(\Delta\omega)^2]^{1/2}t/2, \tag{1}$$

where $\varkappa = \mu_{01}/\hbar\sqrt{3}$, $\Delta\omega = 2\pi c\Delta\nu$ ($\Delta\nu$ is the level of frequency detuning (in cm^{-1}), c is the speed of light). Expression (1) reveals that at a sufficient field intensity when $\varkappa E_0 \gg \Delta\omega$, the system will remain excited with a probability $\overline{W} = 0.5$.

There is also an exact expression for the excitation probability W of the two-level system when the pulse has a waveform $E(t) = E_0/\mathrm{ch}(t/\tau_p)$[25]:

$$W(\infty)=\sin^2(\pi\varkappa E_0\tau_p/2)/\mathrm{ch}^2(\pi\Delta\omega\tau_p/2)\leqslant\exp(-\pi\Delta\omega\tau_p). \tag{2}$$

Expression (2) shows that for $\Delta\omega\tau_p \gg 1$ the two-level system remains unexcited regardless of the field strength E_0. For $\tau_p \approx 50$ ns the inequality given above corresponds to $\Delta\nu \gg (2\pi c\tau_p)^{-1} \approx 10^{-4}$ cm^{-1}. Therefore for a "monochromatic" field the assumption of instantaneous switching of the field will cause a significant overestimate (exaggeration) of the fraction of excited molecules associated with detuning of the field frequency from the molecular transition frequency.

With regard to the discrepancy between theoretical results[8] and experiment on the second point (the insignificant role of multiphoton transitions) at least one of the reasons is the neglect of the actual (nonzero) CO_2-laser spectral width and its modal structure. The results given in sections 3.4 and 3.5 show that in collisionless conditions the vibrational excitation process in SF_6 and NH_3 molecules is qualitatively complex. The depletion efficiency of the lower rotational level drops precipitously with the amount of frequency detuning of the excitation radiation from the corresponding transition frequency, and with resonant conditions ($\Delta\nu \leqslant 0.02$ cm^{-1}) the $f_J(\Phi)$ dependence is nonlinear over a broad energy density range ($10^{-6} \leqslant \Phi \leqslant 10^{-1}$ J/cm^2). With successive "simplification" of the CO_2-lasing spectrum (conversion to a single transverse mode and narrowing of the longitudinal modes) a significant reduction in excitation efficiency is observed.

In the theoretical models[8,9] used today to describe the MPE process in SF_6 at the lower vibrational levels the laser field is taken as monochromatic, while the temporal pulse waveform is assumed to be square-wave. This is primarily due to the significant complication in the calculation by incorporating the actual (more or less smooth) temporal pulse waveform, to say nothing of employing a multimode field. The problem of describing the interaction of pulsed IR multimode radiation with a molecule has not, to the best of our knowledge, been discussed to date in the literature even for the simplest case of a two-level system and a two-frequency field. At present the experimental results indicate that the assumption of monochromaticity, i.e., neglecting the actual field structure and its temporal form is not physically justifiable.

We will consider the excitation conditions in greater detail in the present study. Since the CO_2-laser pulse duration was $\tau_p \simeq 100$ ns we can take the on and off times of the field with smooth switching to be $\tau_{\mathrm{ton}} \approx \tau_{\mathrm{off}} \approx 50$ ns. The longitudinal modes in the CO_2-laser spectrum for a cavity length $L = 150$ cm are separated by $\Delta\nu_L = (2L)^{-1} \approx 3 \cdot 10^{-3}$ cm^{-1}.

The profile of the absorption lines was inhomogeneously broadened due to the Doppler effect and at half-maximum had a width for, for example, $NH_3 \approx 3 \cdot 10^{-3}$ cm^{-1}. The homogeneously broadened lines within the inhomogeneously broadened profile can be ignored since less than 0.5% of the NH_3 molecules (and even fewer SF_6 molecules) experience collisions over the 100 ns laser pulse duration ($p^* \leqslant 0.5$ mtorr), while the radiation width of the transition is negligible.

It can be shown that the assumption of a monochromatic laser field (i.e., neglecting the mode structure) yields an experimentally inadequate result. We assume that the single-mode laser radiation is tuned exactly to the center of the inhomogeneously-broadened absorption line of NH_3. In order to estimate what fraction of the molecules from the inhomogeneously broadened profile can be excited by a single-mode laser pulse we use expression (2). Expression (2) shows that the molecular excitation probability decreases as $\exp(-\pi\Delta\omega\tau_{\mathrm{on}})$ as a function of detuning. The width of the resulting dip in the inhomogeneously-broadened contour will be at $\tau_{\mathrm{on}} = 50$ ns$\leqslant 10^{-4}$ cm^{-1}, resulting in the excitation of several percent of the total number of molecules, and this result is independent of the field strength E. At the same time as is clear from Fig. 6 at sufficiently high values of Φ in the experiment it is possible to excite approximately 50% of the molecules, i.e., the maximum possible molecular fraction.

Such arguments in addition to the experimental results provided here indicate the significant role of multimode laser radiation for effective molecular excitation in collisionless conditions.

We note that if the excited molecules experience one or several collisions over the laser pulse duration (≈ 100 ns) (for NH_3 when $p^* \geqslant 50$ mtorr and for SF_6 when $p^* \geqslant 300$ mtorr) the role of the mode structure drops off significantly, since the nonresonant molecules are excited by field broadening and rotational relaxation.

4. CONCLUSION

We will formulate the primary results of this study.

1. The depletion of separate rotational levels of the ground vibrational state of SF_6 under excitation at the $10P(16)$, $10P(18)$, and $10P(14)$ CO_2-laser lines is investigated in collisionless conditions. The $f_J(J'')$ dependences of the fraction of excited molecules on the rotational quantum number are derived. With SF_6 excitation at the $10P(16)$ line the $f_J(J'')$ dependences are obtained over a broad energy density range $10^{-5} \leqslant \Phi \leqslant 10^{-1}$ J/cm^2. The $f_J(J'')$ dependences have a clearly expressed resonant structure.

2. We conclude from a comparison of the brightening effect of SF_6 observed in the P- and R-branches of the ν_3 band under IR pulse action that only an insignificant portion of molecules abandoning the ground state populate the $v_3 = 1$ state under excitation at the $10P(16)$ CO_2-laser line. This conclusion is also confirmed by the absence of significant absorption in the range near 941.0 cm^{-1} corresponding to the Q-branch of the $2\nu_3(A_1) \leftarrow 1\nu_3$.

3. A comparison of experimental results to calculation[8,9] reveals a serious discrepancy between experiment and theory both with respect to the population of the $v_3 = 1$ state and with respect to the role of multiphoton transitions. It is likely that one of the causes for the reduction in the probability of multiphoton transitions in the calculations[8,9] is the neglect of the spectral width and modal composition of CO_2-laser radiation.

4. The assumption of the importance of taking into account the spectral width and modal composition of the CO_2-laser radiation was qualitatively confirmed in an investigation of the vibrational excitation efficiency of the SF_6 and NH_3 molecules with different frequency detuning of the CO_2-laser radiation from the frequencies of the corresponding VR molecular transitions. It is demonstrated that the fraction f_J of excited molecules as a function of the energy density of the excitation radiation over a range $10^{-6} \leqslant \Phi \leqslant 10^{-1}$ J/cm^2 and of the frequency detuning are identical for such spectroscopically different molecules as SF_6 and NH_3 and are determined by the mode structure of the CO_2-laser radiation. It is demonstrated that the efficiency of molecular participation in the interaction with the laser field at a given frequency detuning drops precipitously as the CO_2-lasing spectrum becomes narrower.

Thus the present results indicate that the mode structure of the laser radiation plays a critical role both in one-photon molecular excitation and in multiphoton absorption processes.

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[1] V. N. Bagratashvili, V. S. Letokhov, A. A. Makarov and E. A. Ryabov, *Multiple photon infrared laser photophysics and photochemistry.* Gordon and Breach/Harwood Acad. Publ., 1985; Laser Chem. 1984, Vol. 4, p. 171.

[2] V. N. Bagratashvili, Yu. G. Vayner, V. S. Dolzhikov *et al.*, ZhETF **80**, 1008 (1981) [JETP **53**, 512 (1981)].

[3] Yu. S. Dolzhikov, V. S. Letokhov, A. A. Makarov *et al.*, ZhETF. **90**, 1982 (1986) [JETP **63**, 116/(1986)].

[4] R. S. McDowell, B. J. Krohn, H. Flicker and M. C. Vasquez, Spectrochim. Acata A. **42**, 351 (1986).

[5] S. S. Alimpiev, A. A. Mozhnatyuk, S. M. Nikiforov *et al.*, Tr. IOFAN. **2**, 136 (1986) [Trudy IOFAN (Proceedings of the Institute of General Physics, Vol. II: Laser Raman Spectroscopy in Crystals and Gases: New York, NOVA Science Publishers, 1987)].

[6] S. S. Alimpiev, B. O. Zikrin, L. Khol'ts *et al.*, Pis'ma v ZhETF. **38**, 349 (1983) [JETP Lett. **38**, 421 (1983)].

[7] V. M. Apatin, V. M. Krivtsun, Yu. A. Kuritsyn *et al.*, Pis'ma v ZhETF. **37**, 365 (1983) [JETP Lett. **37**, 431 (1983)]; Opt. Comm. **47**, 251 (1983).

[8] D. P. Hodgkinson and A. J. Taylor, Opt. Comm. **50**, 214 (1984).

[9] V. Tosa, I. Deac, P. Mercea *et al.*, Appl. Phys. B. **36**, 55 (1985).

[10] A. A. Makarov and V. V. Tyakht, Opt. Comm. **54**, 270 (1985).

[11] K. Veeken and J. Reuss, Appl. Phys. B. **34**, 149 (1984).

[12] M. Dubs, D. Harradine, E. Schweitzer *et al.*, J. Chem. Phys. **77**, 3824 (1982).

[13] J. I. Steinfeld and P. L. Houston, *Laser and coherence spectroscopy.* Edited by J. I. Steinfeld. Plenum Press, New York (1978).

[14] K. Kim, R. S. McDowell and W. T. King, J. Chem. Phys. **73**, 36 (1980).

[15] R. L. Pointer and J. S. Margolis, Mol. Phys. **51**, 393 (1984).

[16] R. D'Cunha, S. Urban, Rao Narahari *et al.*, J. Mol. Spectrosc. **11**, 352 (1985).

[17] L. C. Bradley, K. L. Soohoo and C. Freed, IEEE J. Quant. Electron. **QE-22**, 234 (1986).

[18] B. Bobin, C. J. Borde, J. Borde and C. Breant, J. Mol. Spectrosc. **121**, 91 (1987).

[19] A. S. Pine and A. G. Robiette, J. Mol. Spectrosc. **80**, 388 (1980).

[20] C. W. Patterson, B. J. Krohn and A. S. Pine, J. Mol. Spectrosc. **88**, 133 (1981).

[21] C. W. Patterson, B. J. Krohn and A. S. Pine, Opt. Lett. **6**, 39 (1981).

[22] C. W. Patterson, F. Herlemont, M. Azizi and J. Lemaire, J. Mol. Spectrosc. **108**, 31 (1984).

[23] E. L. Schweitzer and J. I. Steinfeld, Chem. Phys. **108**, 343 (1986).

[24] A. Allen and T. Eberli, *Optical Resonance and Two-level Atoms*, Wiley, New York (1975).

[25] N. B. Delone and V. P. Krajnov, *Atom v sil'nom svetovom pole* [*The Atom in an Intense Light Field*], Moscow, Energoatomizdat, 1984, p. 224.

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