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Diode Laser Spectroscopy of the Dynamics of Multiphoton Excitation of SF₆ Molecules by CO₂ Laser Pulses

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The dynamics of excitation by CO₂ laser pulses of SF₆ molecules from individual rotational sublevels J'' of the ground vibrational state have been investigated in a pulsed molecular jet under essentially collisionless conditions. At different energy fluences of exciting laser pulse $\Phi = 10^{-5} + 10^{-1} \text{ J/cm}^2$, the dependences of the fraction f_j of excited molecules on the rotational quantum number J'' have been obtained, when SF₆ molecules were excited on the 10P(16) CO₂ laser line, as well as on the 10P(18) and 10P(14) lines at $\Phi = 0.1 \text{ J/cm}^2$. Comparison of experimental results with theoretical predictions^{18–20} shows rather strong disagreement between theory and experiments both in the population of the $\nu_3 = 1$ state and in the role of multiphoton transitions. It is shown that the narrowing of the exciting laser pulse spectrum (the 10P(16) line, $\Phi \approx 10^{-2} \text{ J/cm}^2$) results in drastic decrease of the fraction of excited molecules from the ($\nu_3 = 0, J'' = 4$) state which is most resonant with laser radiation.

KEY WORDS: Diode laser spectroscopy, MP excitation, SF₆.

INTRODUCTION

Numerous experiments carried out from the early 1970s and to the present day (see Reference 1) indicate the presence of collisionless

infrared multiple photon excitation (MPE) and dissociation of a wide range of molecules (SF_6 , BCl_3 , OsO_4 , CF_3I *et al.*) at IR laser intensities of 10^6 to 10^9 W/cm^2 . SF_6 molecules are a classical object of study used in this field. In turn, MPE studies of SF_6 molecules stimulated numerous investigations of the spectroscopy of these molecules (see Reference 2 and the references therein).

According to current concepts, the IR MPE process of SF_6 molecules may be conventionally subdivided into two stages. At first stage the molecule "rises" along the lower discrete levels of the ν_3 resonant mode to the boundary of the so-called quasi-continuum (QC) of vibrational states. Attainment of this QC corresponds to the molecule absorbing six to seven quanta^{3,4} of $h\nu = 10^3$ cm^{-1} energy. At the second stage the molecule acquires further energy in the QC range, where the vibrational motion gradually loses its mode individuality.

The problem of quantitative description of the MPE process at the lower vibrational levels could be considered solved if a theoretical model (including a spectroscopic description of the molecule and its interaction with the laser field) was available and its inferences were in reasonable agreement with experimental data. Comparison of theoretic and experimental results should include: populations of vibrational states; molecule distribution along rotational levels within the vibrational states; the fraction of molecules that did not interact and the fraction of molecules attaining QC; the dependences of these characteristics on the exciting laser emission frequency and energy fluence.

The spectroscopy of SF_6 molecules at the ν_3 mode which is resonant with the emission of a CO_2 laser has been investigated experimentally up to $v = 3$ states, with the most accurate molecular constants obtained in studies of the fundamental $\nu_3 \leftarrow 0$ band by saturated absorption spectroscopy techniques,⁵ in measurements of the overtone $3\nu_3 \leftarrow 0$ transition with a difference-frequency laser,⁶⁻⁸ and in measurements of two-photon absorption during $2\nu_3 \leftarrow 0$ transitions.⁹ These constants provide a means of computing the positions of vibrational-rotational (V-R) levels of the ν_3 resonant mode up to $v = 3$ with an accuracy to within 1×10^{-3} cm^{-1} . Prediction of higher levels, however, requires further theoretic and experimental studies and is complicated by the fact that along with the ν_3 mode, its interactions with other vibrational modes (as well as spurious resonance effects between separate V-R levels) have to be taken into account.

The distribution of molecules along the lower V–R levels has as yet not been adequately studied. The distribution of SF₆ molecules along the vibrational levels of the ν_3 mode has been investigated by CARS probing of the ν_1 mode¹⁰ for the case of excitation by the 10P(16) and 10P(20) CO₂ laser lines under collisionless conditions provided by cooling the SF₆ gas to about 150 K. According to these findings, the molecules after excitation can be divided into three quantitative ensembles: a “cold” ensemble composed of molecules that failed to interact with the laser emission; a “warm” ensemble of molecules populating the lower discrete levels of the resonantly absorbing mode; and a “hot” ensemble of molecules excited into the range of the vibrational quasicontinuum. In particular, at exciting energy fluences of 0.1 J/cm² at the 10P(16) line of a CO₂ laser (50 ns pulse duration) about 70% of molecules remain at the ground state, 5% are excited into the quasicontinuum, and the rest are distributed among the lower discrete levels, with about 15–18% of all molecules in the $\nu_3 = 1$ state. Unfortunately, the CARS technique of probing the ν_1 mode does not provide resolution of even anharmonic splitting of states with $v = 2$ because of the high symmetry of SF₆ molecules and therefore, the distributions observed are integrated over both the vibrational and rotational sublevels of the state with a given v . In Reference 10 the molecules are assumed to be equally distributed along the anharmonically split sublevels, this leading to a Boltzmann distribution of molecules in the “warm” ensemble with an effective temperature $T_{\text{vib}}^{\text{eff}}$ of 1500 K to 2000 K. Such a distribution is, however, doubtful under radiational collisionless excitation conditions and is rather a result of the assumptions made.

Integral depletion of the ground vibrational state of SF₆ molecule was also observed by CARS probing techniques in Reference 11, but these findings, however, are inadequate to evaluate the effects of collisions in the excitation process. The signals from excited states were not observed.

The mechanism of excitation of molecules along the lower discrete levels during MPE can be examined experimentally by determining molecule distributions among the rotational sublevels of each vibrational state. Such distributions may be studied by the IR–IR double resonance method using a tunable diode laser as the source of probing emission.

Earlier, this method was used to investigate SF₆ molecule spectroscopy at room temperature^{12–14} and under cooling¹⁵ to about –100°C. Such cooling, even though it does eliminate hot absorption bands, yet encompasses a great number of rotational sublevels of the ground state in the initial distribution of molecules and the development of a theoretical model of MPE remains problematic due to the vast amount of computation required.

The initial distribution can be significantly simplified by using dynamic cooling in a supersonic jet, this method allowing studies of both ground state depletion¹⁶ and populations of excited states¹⁷ under certain conditions.

Previous publications¹⁶ were concerned with studies of depletion of individual rotational sublevels of the ground vibrational state as functions of exciting laser frequency and energy fluence, using the double IR–IR resonance method and SF₆ molecules cooled in a supersonic jet to a rotational temperature $T_{\text{rot}} = 18$ K. These measurements were carried out with molecule excitation and probing in a direction normal to the molecular jet, as shown in Figure 1a. The time delay τ_{δ} between the instants of excitation and probing was up to 120 μs and since the molecule concentration in the excitation zone was $(1.5 - 7) \times 10^{13} \text{ cm}^{-3}$ (this corresponding to an effective pressure p^* of about 0.5 to 2 mTorr), rotational relaxation during this time delay could distort the distribution of molecules resulting from MPE to a certain extent.

The purpose of the present study is to investigate the dynamics of IR MPE in the range of the low vibrational levels of ³²SF₆ molecules under essentially collisionless conditions. Experimental studies of depletion of various rotational levels of the ground vibrational state of SF₆ molecules as a result of MPE are continued beyond those of Reference 16 and experimental findings are compared with theoretic data from References 18–20. The paper presents new results which allow estimates of the $\nu_3 = 1$ state population to be made and provide data on the effects of the mode composition of a CO₂ laser emission on the efficiency of collisionless molecule excitation. Comparison of experimental data with theoretical results^{18–20} shows serious disagreement in the data on the population of the lower discrete levels of molecules after excitation. The possible causes of these discrepancies are discussed along with the major defects of the theoretic approaches used.

EXPERIMENTAL SET-UP AND METHOD

The geometry used for molecule excitation and probing is presented in Figure 1b. SF₆ molecules were cooled by a pulsed supersonic jet from a nozzle with a 0.2 mm × 2 mm slit. The pressure of the SF₆ gas (without a carrier) in the nozzle was 0.1 to 0.5 atm, this providing a molecule concentration in the probing zone of $(0.35 - 1.75) \times 10^{13} \text{ cm}^{-3}$ and corresponding to an effective pressure $p^* = 0.1$ to 0.5 mTorr.

SF₆ molecules were excited by the TEA CO₂ laser pulses of about 100 ns duration (FWHM) without a tail and with energy up to 1 J. The spectral width of the CO₂ laser emission was approximately 0.035 cm^{-1} (at half height), the laser resonator length constituted 150 cm.

The emission of a PbSnSe diode laser was used as the probing signal, with the laser operating in the pulse-periodic mode. The spectrum was registered during each individual pulse with a signal-to-noise ratio of at least 100 and spectral resolution of about $(1 \text{ to } 3) \times 10^{-3} \text{ cm}^{-1}$, this latter determined by the diode laser frequency tuning rate during the pulse, which constituted $(1 \text{ to } 3) \times 10^{-3} \text{ cm}^{-1}/\mu\text{s}$, and the time constant of the registering system ($\tau = 500 \text{ ns}$). A digital system of time delays was used to synchronize the experimental individual units with an accuracy to within 10 ns.

Excitation of the cooled SF₆ molecules was carried out directly in the probing zone. Such a geometry allows combination of a multipass mirror system (the White arrangement, 28 passes) with small time delays ($\tau_d = 10$ to $15 \mu\text{s}$) between excitation and probing, thus practically excluding the effects of collisions on the measurement results (at $p^* = 0.3 \text{ mTorr}$ the product $p^* \tau_d = 5 \text{ ns} \cdot \text{Torr}$, while the measured speed of rotational relaxation^{15,21} in terms of $p\tau$ constitutes $35 \text{ ns} \cdot \text{Torr}$). The width of the molecule jet in the probing zone was varied by diaphragms in the range from 3 to 12 cm. Parallel polarizations of the exciting and probing emissions were used.

The fraction of molecules excited from the ground vibrational state with the given rotational level characterized by the angular momentum J'' was measured by the diminution of absorption at individual spectral lines in the *R*-branch of the ν_3 fundamental band of ³²SF₆ molecules.

During measurements with the tunable diode laser the amplitude A at the centre of the absorption line and its variations ΔA after exposure to the CO₂ laser pulse were determined. In all cases the value of A did not exceed 20% of the probing emission power. When interpreting the

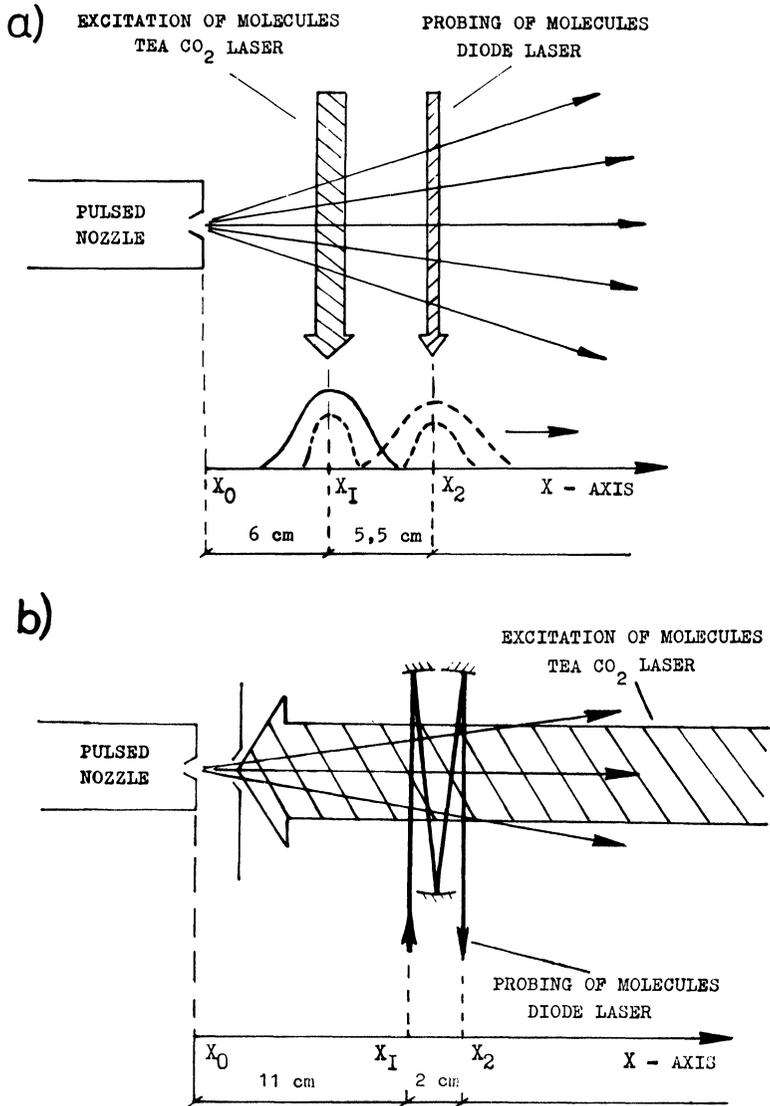


Figure 1 Geometry of molecule excitation and probing used (a) in Reference 16 and (b) in the present study.

value $f^*_J = \Delta A/A$ it was assumed that the upper level being probed is not populated if the probing is in the R -branch and excitation is from the “red” side of the Q -branch of the molecules absorption spectrum (at the 10P(16) and 10P(18) CO₂ laser lines); thus, the value of f^*_J is unequivocally related to the fraction of molecules f_J excited from the J'' level of the ground state: $f^*_J = f_J$.

A simplified diagram of SF₆ energy levels is shown in Figure 2, on which transitions corresponding to excitation by the 10(P16) line from a CO₂ laser and diode laser probing at the R(4) and P(4) lines of the SF₆ ν_3 band are shown. Rotational levels of SF₆ at the $\nu_3 = 1$ state are split as a result of Coriolis interactions into three sublevels, characterized by the rotational quantum number R ($R = J' - 1; J'; J' + 1$). According to the selection rule $\Delta R = 0$, transitions in the R -branch are between sublevels with $R = J' - 1$ and between sublevels with $R = J' + 1$ and 1 in the P -branch.

At the maximal energy fluence of 0.1 J/cm² (intensity $I = 1$ MW/cm²) used in the present study, the average Rabi frequency $\Omega_R =$

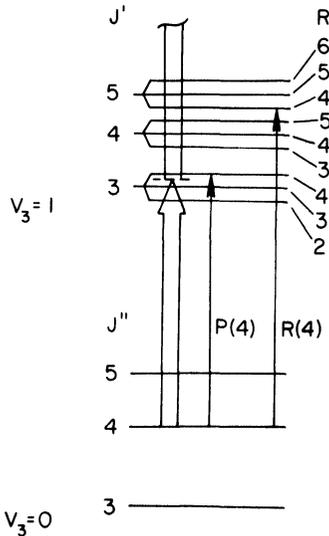


Figure 2 A simplified diagram of SF₆ molecule rotational levels at the $\nu_3 = 0$ and $\nu_3 = 1$ vibrational states. The thick arrow depicts excitation at the 947.74 cm⁻¹ frequency of the 10P(16) line of a CO₂ laser, thin lines show the transitions in the R - and P -branches of the ν_3 band being probed by a diode laser.

$\mu_{01}E/\sqrt{3}\hbar$, calculated for a transition dipole momentum²² $\mu_{01} = 0.437$ Deb and line polarization of the exciting field ($E = 27$ kV/cm), can attain values of about $2.15 \times 10^{10}\text{s}^{-1}$, this corresponding to $\delta\nu_R = \Omega_R/2\pi c \approx 0.12$ cm^{-1} .

The energy level diagram of Figure 2 indicates that excitation at the 10P(16) CO₂ laser line with a 947.74 cm^{-1} frequency can lead to populating the $J' = 3, R = 4$ sublevel in the $v_3 = 1$ state of SF₆ molecules due to small difference in the P(4) SF₆ transition and 10P(16) laser line frequencies ($\Delta\nu = 0.01$ cm^{-1}). At the same time, the $J' = 5, R = 4$ sublevel will not be populated because of the considerable frequency offset between the R(4) transition and the 10P(16) laser line ($\Delta\nu = 0.5$ cm^{-1}).

It should be emphasized once again that all measurement results reported here were obtained under essentially collisionless conditions of molecule interaction with the exciting IR laser field and probing. The effective molecule pressure p^* in the interaction zone was always below 0.5 mTorr, this corresponding to a product $p\tau_p \approx 0.05$ ns · Torr at a 100 ns pulse duration of the CO₂ laser. The time delay between excitation and probing never exceeded 15 μs , this resulting in $p^*\tau_d = 7.5$ ns · Torr.

RESULTS AND DISCUSSION

Figure 3 illustrates the fraction f_j of molecules interacting with the laser field as a function of the rotational quantum number J'' observed during SF₆ excitation by the 10P(16) line of a CO₂ laser at a 947.74 cm^{-1} frequency, with the energy fluence of the exciting emission as a parameter. As can be noted, noticeable molecule excitation is only from the $J'' = 4$ and $J'' = 5$ sublevels with small frequency offsets (0.009 and 0.048 cm^{-1} , respectively) from the exciting frequency; these experiments were carried out with the energy fluence ranging from 10^{-5} to 10^{-1} J/cm². The effect of involving molecules from many rotational levels of the ground vibrational state becomes pronounced at energy fluences above 10^{-2} J/cm² and at 0.1 J/cm² the $f_j(J'')$ function exhibits a distinct resonant structure. According to published results¹⁶ a further increase in energy fluence to 0.5 and 1.3 J/cm² this resonant structure becomes less pronounced and f_j attains values of 0.5 to 0.7 .

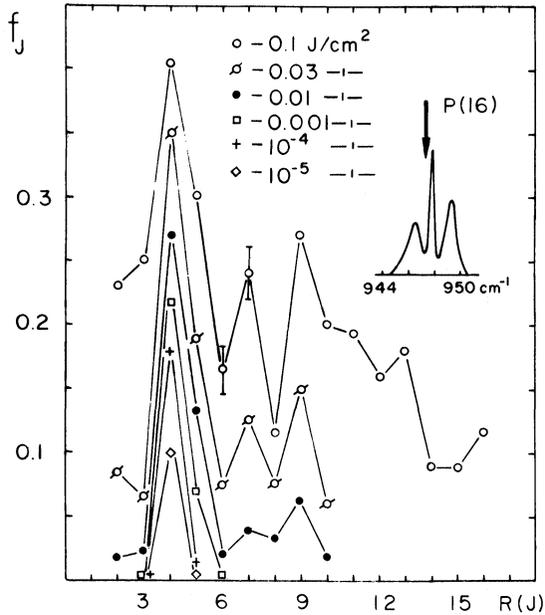


Figure 3 The fraction f_J of SF₆ molecules excited from individual rotational levels of the ground vibrational state by the 10P(16) CO₂ laser line as a function of the rotational quantum number J'' at various pulse energy fluences.

It is interesting to compare the results of Reference 16 and the present study with the results of model computations made in References 18–20.

Computations in Reference 18 of the dynamics of SF₆ excitation from its ground vibrational state take into account the vibrational levels of the resonant ν_3 mode up to $\nu = 4$ (the “five-level” model). The positions of V–R levels were computed with anharmonic splitting taken into account along with centrifugal distortion and interaction between vibration and rotation. The rotational structure was computed up to $J = 30$; the exciting field was considered to be monochromatic and to be turned on and off instantaneously. The model took into account all possible transitions, up to four-photon transitions.

Computations in Reference 19 provide $f_J(J'')$ values for vibrational levels ν_3 from 0 to 3. Two models are treated: a simple anharmonic oscillator and rigid rotator; and a model taking into account spherical

anharmonic splitting, centrifugal distortion and Coriolis interaction, as in Reference 18. During the simple model computations the exciting emission is assumed to be monochromatic, in the second case the laser line was assumed to feature a Lorentz profile.

Finally, in Reference 20 $f_j(J'')$ relations are computed at various excitation intensities, taking into account only two vibrational states of the ν_3 resonant mode—the ground and first excited (the “two-level” model); these computations are aimed at discovering the causes of depletion of the ground vibrational state in the model used in Reference 18 and comparing the roles of single-photon and multiple-photon transitions.

Comparing the results of computations^{18,19} with the experimental data¹⁶ indicates fair agreement between theoretic and experimental findings at high (0.5 and 1.3 J/cm²) energy fluences of the 10P(16) line from a CO₂ laser. At energy fluences below 0.1 J/cm² the discrepancy becomes quite noticeable, especially in the $J'' = 4$ range; the authors of Reference 18 explain this disagreement by the effects of rotational relaxation on the population of the levels being probed during the 120 μ s time delay between excitation and probing. However, experimental data obtained at an equal energy fluence (e.g., at 0.1 J/cm²) indicate that reducing the p^*t_d p-product from about 100 ns · Torr in Reference 16 to not over 7.5 ns · Torr in the present study does not practically affect the value of $f_j(J'')$. It is thus evident that the effects of collisions during the long (120 μ s) time delay in Reference 16 were insignificant, only somewhat smoothing out the dependence patterns.

Let us now compare the experimental data of the present study with theoretical results. Figure 4 illustrates $f_j(J'')$ relations corresponding to excitation energy fluence 0.1 J/cm² ($I = 1$ MW/cm²). Here the results for the “five-level” model¹⁸ are presented by a thin solid line, a dashed line depicts $f_j(J'')$ computations within the framework of the highly simplified “two-level” model²⁰ and small circles represent experimental data. As can be noted, the “five-level” model¹⁸ gives a fairly accurate description of the $f_j(J'')$ pattern, following practically all the local maxima and minima observed at $J'' \geq 8$. An attempt¹⁹ to identify one of these maxima consisted in relating it to two-photon resonance from the $|vJJ\rangle = |0010\rangle$ level to the $|228\rangle$ level. However, a more distinct maximum can be noted at $J'' = 9$ (initial state $|009\rangle$). Therefore, referring the structure of the $f_j(J'')$ function to a type of transition requires recomputation using refined spectroscopic constants, in parti-

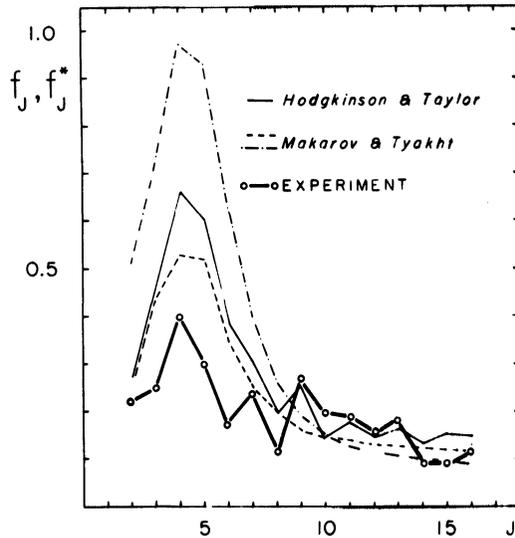


Figure 4 Theoretical depletion $f_J(J'')$ of rotational levels of the ground vibrational state of SF₆ molecules due to excitation by the 10P(16) line of a CO₂ laser within the framework of the “five-level” model¹⁸ (solid thin line), “two-level” model²⁰ (dashed line), and the experimental results of the present study (depicted by circles). The dot-and-dash line depicts theoretical value²⁰ of relative diminution $f_J^* = \Delta A/A$ of absorption A when SF₆ transitions are probed in the P -branch of the ν_3 band.

cular, for the $2\nu_3$ level.⁹ What concerns the f_J maximum at $J'' = 4$, it can be noted that at J'' ranging from 3 to 6 the theoretic value is higher than experimentally observed by a factor of more than 1.5.

In Reference 20 the main drawbacks of the assumptions made in the theoretical computations have been studied and conclusions of Reference 18 have been shown to disagree seriously with experimental data. Figure 4 indicates the practical identity of $f_J(J'')$ relations obtained from complex computations¹⁸ with five vibrational states (ν_3 from 0 to 4) taken into account and from simple computations²⁰ of the “two-level” ($\nu_3 = 0; 1$) model, excluding only certain fine details of the structure. This is evidence that within the framework of the “five-level” model depletion of the ground vibrational state is mainly due to single-photon $1 \leftarrow 0$ transitions from the ground to the first excited vibrational state ν_3 , while the contribution of multiphoton transitions

is negligible. Molecules that leave the ground state populate mainly the $\nu_3 = 1$ state and this should lead to essentially different values of induced transparency when probing the *R*- and *P*-branches. In Figure 4 the f_J^* function according to the theoretical models¹⁸⁻²⁰ with probing in the *P*-branch is shown by a dashed line. At the same time, experimental data¹⁶ and measurements of the present study show f^* values observed on the *P*- and *R*-branches to coincide for all *J* values to within the accuracy of measurements, except $J'' = 4$ (Figure 5). The higher f_J^* value for the P(4) transition, as compared to that of transition R(4), at an energy fluence of about 0.1 J/cm² corresponds to about 20% of molecules leaving the $J'' =$ level of the ground vibrational state due to interaction with the CO₂ laser pulse occurring in the ν_3 state at the $J' = 3$, $R = 4$ rotational level. This estimation takes into account the dependence of the matrix element of the transition dipole momentum of SF₆ molecules from the *M*-projection of the angular momentum onto the direction of polarization of the CO₂ laser emission.

To investigate the population of the $\nu_3 = 1$ state the induced absorption was also measured at a 941.0 cm⁻¹ frequency, this corresponding to the *Q*-branch of the $2\nu_3(A_1) \leftarrow \nu_3$ transition. Since the spectrum transitions were not identified, the observed absorption

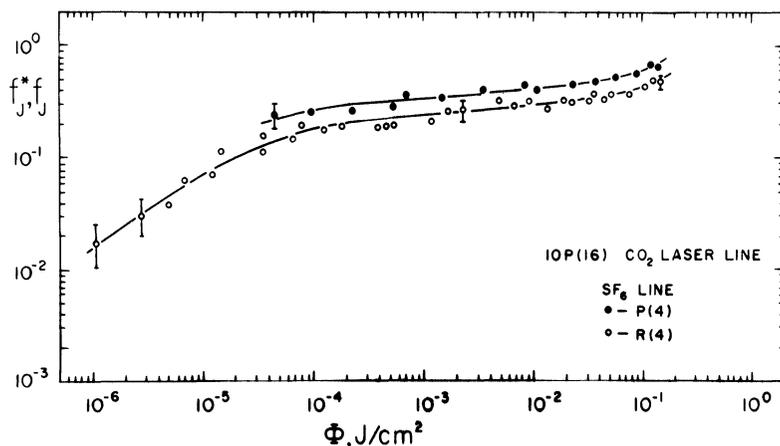


Figure 5 Observed relative diminution $f_J^* = \Delta A/A$ of absorption *A* as a function of energy fluence Φ of the CO₂ laser pulse: darkened circles-on P(4) transitions; light circles-R(4) transitions of the ν_3 band of SF₆. Molecules were excited at the 947.74 cm⁻¹ frequency of the 10P(16) CO₂ line.

could be caused by transitions between higher levels and thus establishes only the upper limit of state ν_3 population. The absorption observed at a 941.0 cm^{-1} frequency corresponds to not over 5% of the molecules leaving the ground vibrational state remaining at the ν_3 state.

Note, that only a small fraction of molecules (about 20% of molecules at the $|vJ\rangle = |04\rangle$ level) is excited via the P(4) transition to the $|13\rangle$ level; no wonder, therefore, that no molecules excited via other transitions in the *P* and *Q*-branches are observed in the $\nu_3 = 1$ state. At the P(4) SF₆ transition the frequency offset from the 10P(16) CO₂ line is about 0.009 cm^{-1} , i.e. twice less than the TEA CO₂ laser spectrum half-width (0.018 cm^{-1}). At all other transitions the frequency offset is considerably in excess of the laser radiation spectrum width.

What concerns population of $J' \neq 4$ levels under the effect of dynamic power broadening, it should be noted that with more or less smooth pulse waveforms the conditions of its propagation will be adiabatic. As is known,²³ the two-level system remains undisturbed by a propagating pulse provided the frequency offset is great enough. A qualitative estimate can be made by assuming the field to be monochromatic. The excitation probability W for a two-level system excited by a pulse whose waveform is described as $E(t) = E_0/ch(t/\tau_p)$ is exactly described by:²⁴

$$W = \sin^2(\pi\kappa E_0\tau_p/2)/ch^2(\pi\Delta\omega\tau_p/2) \leq \exp(-\pi\Delta\omega\tau_p), \quad (1)$$

where $\kappa = \mu_{01}/\sqrt{3}\hbar$; $\Delta\omega = 2\pi c\Delta\nu$ ($\Delta\nu$ is the frequency offset in cm^{-1}); Eq. (1) indicates that at $\Delta\omega\tau_p \gg 1$ a two-level system remains unexcited, no matter how high the E_0 field intensity is. At a pulse duration $\tau_p = 50 \text{ ns}$ this inequality corresponds to a frequency offset $\Delta\nu \gg (2\pi c\tau_p)^{-1} = 10^{-4} \text{ cm}^{-1}$.

The result will be qualitatively different if the field is assumed to be turned off instantaneously. In this case $E(t)$ may be considered equal to E_0 during the pulse and the equation describing interaction between a two-level system and a field of constant amplitude becomes applicable.²⁵

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

Equation (2) indicates that the system will remain excited if the field intensity is high enough, i.e. $\kappa E_0 \gg \Delta\omega$. Thus, the assumption of an

instantaneously turned off field reevaluates the fraction of excited molecules.

The experimental data presented above indicate that the role of single-photon transitions $1 \leftarrow 0$ (which cause the $\nu_3 = 1$ state to be populated) in depletion of the ground state rotational levels is, apparently, insignificant.

This conclusion disagrees with theoretical results of Reference 18. First of all, the $\nu_3 = 1$ state should be greatly populated, according to these computations. In the second place, the role of two-, three- and four-photon transitions in depletion is insignificant, according to the theory.²⁰ The main cause of disagreement on the first item was discussed above and consists in the inadequacy of the assumption of an instantaneously turned off field: this leading to overestimation of the role of single-photon transitions at small frequency offsets between the 10P(16) line and the centre of the Q -branch of the $SF_6 \nu_3$ band. What concerns disagreement on the second item, at least one of the causes can be neglecting to take into account the actual (non-zero) width of the CO_2 laser emission spectrum and its mode structure.

The effects of the mode structure and spectral width of the CO_2 laser pulse were investigated by studying the efficiency of excitation, $f_J(\Phi)$, from the $J'' = 4$ level as a function of the energy fluence, at pulses of various mode compositions. The results are presented in Figure 6. The

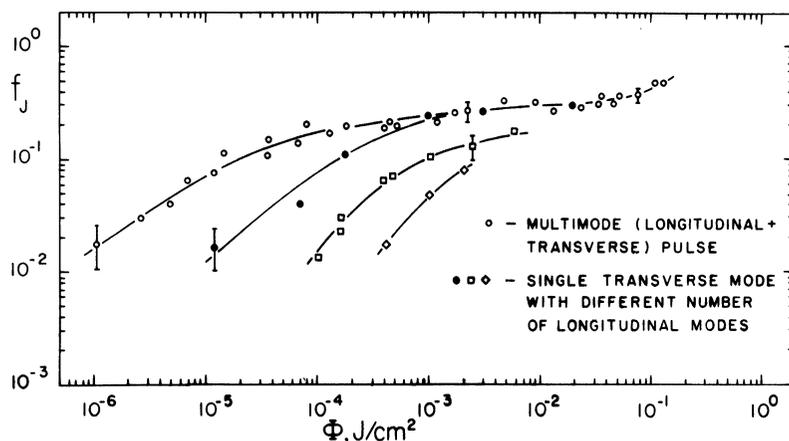


Figure 6 Depletion f_J of the $J'' = 4$ level as a function of energy fluence Φ in a CO_2 laser pulse, during excitation by the 10P(16) CO_2 line. Measurements were taken with pulses of various mode composition (see text).

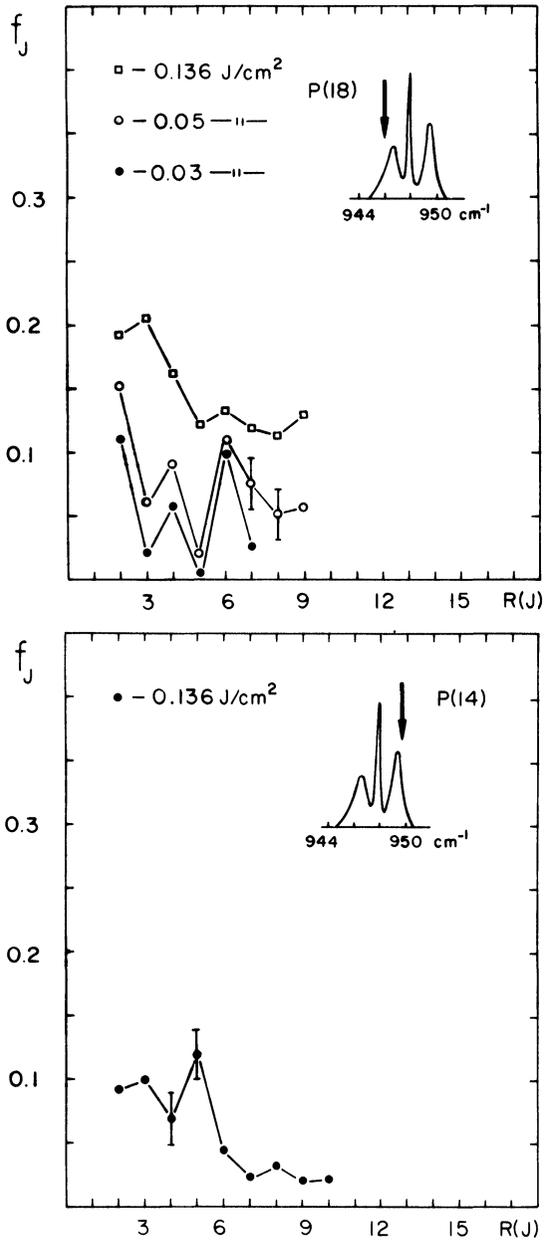


Figure 7 The fraction f_J of SF₆ molecules excited from individual rotational levels of the ground vibrational state as a function of the rotational quantum number J'' ; excitation at the 945.98 cm⁻¹ (a) and 949.48 cm⁻¹ (b) frequencies by the 10P(18) and 10P(14) lines, respectively, of a CO₂ laser.

$f_J(\Phi)$ dependence at $J'' = 4$ was measured with the usual spectral composition of the CO₂ laser pulse, when oscillations are on several transverse and more than a dozen longitudinal modes; these data are depicted by light circles. Then one transverse mode was separated with the aid of an iris-diaphragm in the CO₂ laser resonator; these measurements are shown by dark circles. The next step, depicted by small square, was narrowing the spectrum of longitudinal modes by reducing the working mixture pressure in the CO₂ laser to 0.5 atm. And, finally, one or two longitudinal modes were separated by means of a germanium Fabry-Perot etalon set at an angle in the CO₂ laser resonator (depicted by rhombs).

The curves in Figure 6 show that both the purification and narrowing of the emission spectrum essentially reduce the fraction of molecules interacting with the field. Thus, f_J attains a value of 5% at an energy fluence of 6×10^{-6} J/cm² with pulses of the usual (multimode) structure, while the same value with single or two-mode pulses requires an energy fluence more than two orders of magnitude higher—about 10^{-3} J/cm². The nonlinear character of the $f_J(\Phi)$ relation at $J'' = 4$ should also be noted.

Thus, it becomes evident that the presence of multimode oscillations in the CO₂ laser emission leads to a higher probability of multiphoton processes. This should be explicitly taken into account when comparing theoretic and experimental results.

In the present study we also observed departure of ³²SF₆ molecules from many rotational levels of the ground vibrational state under excitation by a standard CO₂ laser pulse at the 945.98 cm⁻¹ and 949.48 cm⁻¹ frequencies of the 10P(18) and 10P(14) lines, respectively (Figure 7). The frequency offset from the center of the Q-branch of the 1 ← 0 transition is 1.5 cm⁻¹ for the 10P(18) line and 2.0 cm⁻¹ for the 10P(14) line.

The $f_J(J'')$ relations shown in Figures 3 and 7 feature different structures, this being due, apparently, to the presence of individual MPE channels when excited by various lines of a CO₂ laser emission.

CONCLUSIONS

The main results of the present study can be formulated as follows:

- 1) $f_J(J'')$ functions of depletion of rotational levels of the ground

vibrational state of SF₆ molecules have been obtained under collisionless conditions with excitation by the 10P(16), 10P(18) and 10P(14) CO₂ laser lines. The energy fluence was varied from 10⁻⁵ to 10⁻¹ J/cm² when measuring $f_J(J'')$ under excitation by the 10P(16) line.

2) Comparison of the induced transparency observed on the *P*- and *R*-branches of the ν_3 band leads to the conclusion that with excitation by the 10P(16) CO₂ laser line only an insignificant part of molecules that leave the ground state populate the $\nu_3 = 1$ state. This conclusion is also confirmed by the absence of significant absorption in the 941.0 cm⁻¹ range, which corresponds to the *Q*-branch of the $2 \nu_3(A_1) \leftarrow \nu_3$ transition.

3) Comparison of experimental data with computation results obtained in References 18 and 19 shows serious disagreement between theory and experiments, both in the population of the $\nu_3 = 1$ state and in the role of multiphoton transitions. Possibly, one of the causes of underestimation of multiphoton transition probability in the computations is not taking into account the spectral width and mode composition of the exciting emission.

4) It is experimentally demonstrated that narrowing the emission spectrum of a CO₂ laser to one or two longitudinal modes drastically reduces the efficiency of molecule excitation from the $J'' = 4$ rotational level when SF₆ molecules are excited at the 947.74 cm⁻¹ frequency of the 10P(16) line of a CO₂ laser.

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