

Diode laser spectroscopy of SF₆ molecules, cooled in a pulsed jet, with IR multiphoton excitation

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(Submitted 22 February 1983)

Pis'ma Zh. Eksp. Teor. Fiz. **37**, No. 8, 365–368 (20 April 1983)

The dynamics of the depletion of separate vibrational-rotational states with IR multiphoton excitation of molecules, cooled in a pulsed jet, are studied for the first time with the help of a frequency-tunable diode laser. The fraction of molecules excited by the laser pulse from separate rotational sublevels is measured and its dependence on the excitation conditions is studied.

PACS numbers: 33.80.Kn, 33.10.Jz, 33.20.Ea

1. An important problem from the point of view of understanding the physics of multiphoton excitation (MPE) of molecules in a strong IR laser field¹ is the problem of the mechanism by which molecules are drawn into the interaction process. The purpose of this paper is to describe the first experimental results on the investigation of this problem by the method of double IR-IR resonance using a frequency-tunable diode laser for the probing radiation.¹⁾ Aside from its high spectral resolution ($\cong 10^{-3}$ – 10^{-4} cm⁻¹), this method is also quite sensitive, which makes it possible to perform the experiments at gas pressures $\lesssim 10^{-3}$ mm Hg, i.e., in an essentially collisionless excitation regime. The experiments were performed with SF₆ molecules, cooled to $T_{\text{rot}} \lesssim 40$ K and $T_{\text{vib}} \cong 160$ K in a pulsed supersonic jet. This greatly simpli-

fied the spectroscopy of the molecules. The absorption spectra of the diode laser radiation were used to observe the depletion of the rotational sublevels of the ground vibrational state of molecules under the action of the pulsed CO₂ laser. The fraction f_J of molecules excited by the laser radiation from separate rotational sublevels was measured. The dependences of f_J on the energy density and frequency of the exciting pulse were studied.

2. The experimental setup (with the exception of the diode spectrometer) is described in detail in Ref. 4. SF₆ molecules in the pulse jet were excited at a distance 6 cm from the nozzle by a CO₂ laser pulse (80-nanosecond peak with 0.8-microsecond trailing edge, energy per pulse ≤ 2.0 J), and the excited molecules were probed with a diode laser 5.5 cm downstream from the excitation zone (11.5 cm from the nozzle). The exciting and probing laser beams were oriented through the jet perpendicular to its axis. The density of molecules in the jet in the excitation and probing zones for SF₆ pressures in the nozzle of 1–5 atm was $\leq (1.5\text{--}7) \times 10^{13}$ cm⁻³ and $\leq (0.3\text{--}1.5) \times 10^{13}$ cm⁻³, respectively. The time of flight of molecules out of the excitation zone up to the probing zone was $\simeq 100$ μ s. To measure the delay time between the exciting and probing pulses, a coaxial excitation geometry was used in a number of experiments (the CO₂ laser radiation was oriented up-stream). A diode laser based on PbSnSe, operating in the pulsed regime, was used in the experiments.⁵ The frequency tuning rate was $(2\text{--}3) \times 10^{-3}$ cm⁻¹/ μ s. The region 946.3–948.2 cm⁻¹ was chosen for probing. This region nearly completely overlapped the frequency ranges of the *P* and *Q* branches of the transition $v = 1 \leftarrow v = 0$ of the excited mode ν_3 . The spectral resolution was limited by the recording system and in our experiments constituted ≈ 0.003 cm⁻¹. This permitted resolving separate rotational components of multiplets of the *P* branch, corresponding to states with $J < 20$, which are primarily populated at $T_{\text{rot}} \leq 40$ K.

3. The oscillograms showing the change in absorption (bleaching) of SF₆ in the region of the multiplets *P*(10) and *P*(9) and the *Q* branch of the transition $\nu_3 = 1 \leftarrow \nu_3 = 0$ with pumping by a CO₂ laser pulse are shown in Figs. 1a and 1b. The frequency of the diode laser in the entire range of the *Q* branch in Fig. 1b was scanned over a time $\simeq 50$ μ s, while the time of flight of the spatial distribution of the excited molecules through the probing region was $\simeq 35$ μ s. For this reason, the real picture of bleaching of the *Q* branch, which we observed "in parts," differs slightly from that shown in Fig. 1b. It is evident from Figs. 1a and 1b that the action of a CO₂ laser pulse causes appreciable bleaching of SF₆, which is related to molecules leaving the ground vibrational state (depletion of rotational sublevels). The fraction f_J of molecules excited by the CO₂ laser and the fraction $f_J^0 - f_J$ remaining in the ground state can be determined from the bleaching of separate lines.

The dependence of the fraction f_J on the rotational quantum number (on the magnitude of the frequency detuning) when SF₆ is pumped at 947.74 cm⁻¹ [*P*(16) line of the CO₂ laser] are shown in Fig. 2. The probing was performed in the *P* branch of SF₆. The pumping frequency fell between the multiplets *P*(4) and *P*(5) of the transition $\nu_3 = 1 \leftarrow \nu_3 = 0$ in SF₆. It is evident from Fig. 2 that even for $\Phi < 0.02$ J/cm², when field-induced broadening ($\Delta\nu_{\text{br}} = \mu E / \hbar c \leq 0.04$ cm⁻¹) and the width of the generation line of the CO₂ laser ($\Delta\nu_{\text{gen}} \approx 0.035$ cm⁻¹) did not exceed the difference in frequencies between neighboring multiplets in the *P* branch, nearly all rotational states populated

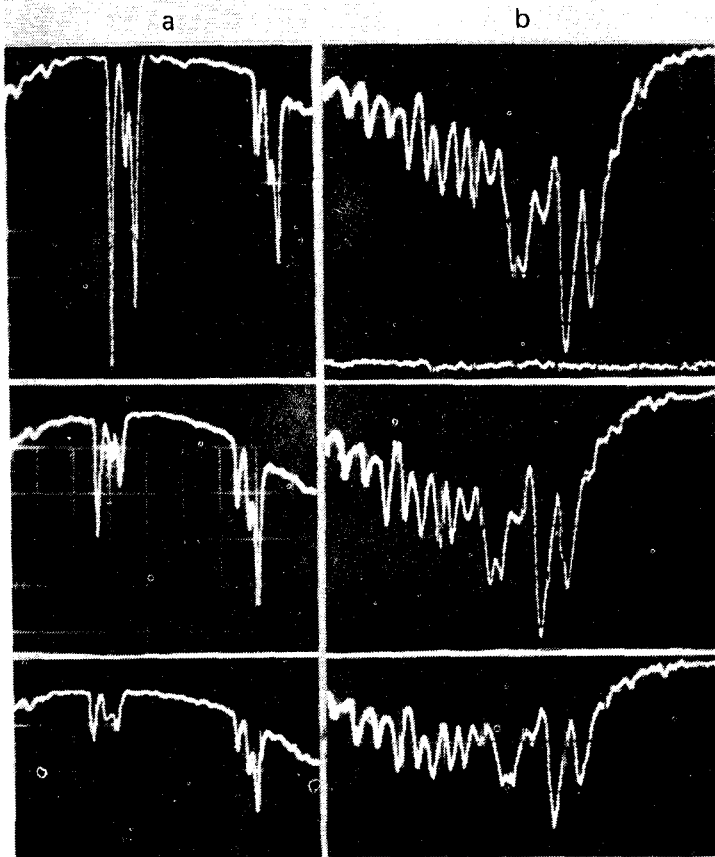


FIG. 1. Oscillograms showing the decrease in intensity (bleaching) of the multiplets $P(10)$ and $P(9)$ (a) and Q branch (b) of SF_6 under the action of CO_2 laser radiation. The oscillograms at the top show the absorption (downwards) of the diode laser radiation by SF_6 molecules in the jet without excitation. The zero level of the diode laser radiation in case (b) is shown beneath the Q branch. The oscillograms in the middle and at the bottom were obtained with excitation energy densities of 0.5 and 2.3 J/cm^2 . The excitation frequency was 947.74 cm^{-1} [$P(16)$ line of the CO_2 laser]. The SF_6 pressure in the nozzle was 5 atm. The scanning rate was $7.5\text{ }\mu s/division$ ($\cong 0.015\text{ cm}^{-1}/division$).

for $T_{rot} \lesssim 40\text{ K}$ interact with the laser radiation, independent of the extent of the frequency detuning. We also obtained similar results when the delay between the exciting and probing pulses was 5–10 μs (with coaxial excitation geometry). This indicates the absence of any influence of rotational relaxation. For $\Phi \lesssim 0.5\text{ J/cm}^2$, the rotational sublevels, transitions from which have the smaller frequency detuning from the exiting CO_2 laser pulse, are primarily depleted. For $\Phi \gtrsim 1.3\text{ J/cm}^2$, f_j is virtually independent of the rotational sublevel. The data obtained agree well with the results of Ref. 6, where depletion of many rotational states was observed with IR multiphoton excitation of molecules. For $\Phi = 0.5\text{--}1.3\text{ J/cm}^2$, the interaction of all rotational states was observed in the present experiments with SF_6 pumped at the frequencies of the

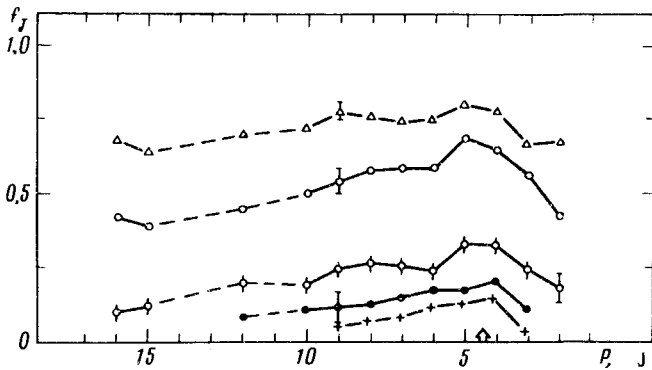


FIG. 2. Fraction of excited molecules as a function of the rotational quantum number J (magnitude of detuning) with excitation energy densities 0.01 (+); 0.02(●); 0.1 (◊); 0.5 (○) and 1.3 J/cm² (△). The probing was performed in the P branch of SF₆. The pumping frequency (indicated by the arrow) and SF₆ pressure in the nozzle are the same as in Fig. 1.

$P(12)$, $P(24)$, and $P(28)$ lines of the CO₂ laser, which are significantly (by 2–10 cm⁻¹) detuned from the linear absorption spectrum (LAS) for $T_{\text{rot}} \lesssim 40$ K.

The dependences of the fraction f_J of molecules excited from the rotational sub-levels $J = 5, 6, 10$, and 16 on the energy density with SF₆ pumped at frequency 947.74 cm⁻¹ are shown in Fig. 3. It is evident that in the entire range of energy densities studied, f_J is maximum for the level $J = 5$, which has the smallest frequency detuning from the pumping radiation, smaller for the levels $J = 6$, and 10, and minimum for the level $J = 16$. As Φ is increased, the fraction f_J increases more rapidly for levels, from which transitions $v_3 = 1 \leftarrow v_3 = 0$ have the highest detuning from the pumping fre-

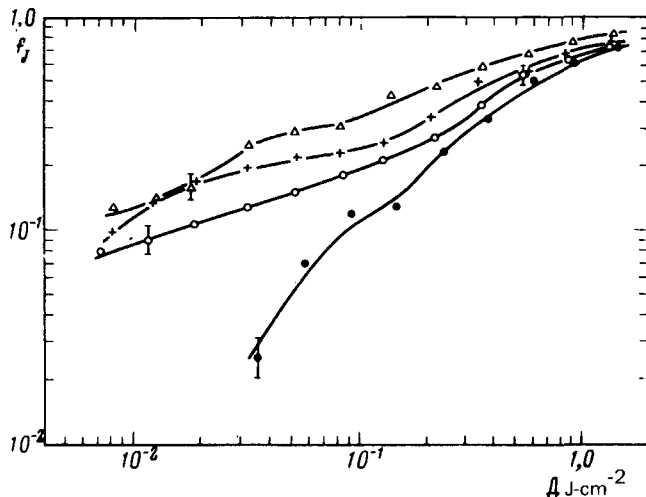


FIG. 3. Fraction of excited molecules with rotational sublevels $J = 5$ (△), $J = 6$ (+), $J = 10$ (○) and $J = 16$ (●) of SF₆ as a function of the excitation energy density. The pumping frequency and pressure of SF₆ in the nozzle are the same as in Fig. 1.

quency. For $\Phi \geq 1.3 \text{ J/cm}^2$, f_j for all rotational sublevels studied attains the value $\approx 0.7-0.8$.

In our opinion, the interaction of all rotational states is related to the dominating role of direct multiphoton transitions, including higher-order transitions, for the lower discrete levels. (Two photon resonances in the system of lower vibrational levels of SF_6 were observed in Ref. 7). When the detuning of the pumping frequency from LAS [$P(12)$, $P(24)$, and $P(28)$ lines] is large, the molecules are immediately excited to levels $v \geq 3-4$ and then acquire energy in the quasicontinuum. For pumping on the $P(16)$ line of the CO_2 laser, two- and three-photon transitions apparently occur at energy densities $\Phi \leq 0.02 \text{ J/cm}^2$. The multiphoton interaction is probably due to the complex structure of the high-lying vibrational-rotational states and due to compensation as the excitation energy density of frequency detunings by field-induced broadening increases. Apparently, this accounts for the stepped nature of the dependences $f_j(\Phi)$ in Fig. 3.

In conclusion, we note that the method described above also permits studying how the high-lying vibrational-rotational levels are populated by IR multiphoton excitation of molecules.

We thank V. G. Koloshnikov and V. S. Letokhov for support and interest in the work and A. A. Makarov for useful discussions of the results.

¹⁾Resonances in the transition $2\nu_3 \leftarrow \nu_3$ of SF_6 were observed in Refs. 2 and 3 using this method.

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Translated by M. E. Alferieff

Edited by S. J. Amoretty