Features of nonlinear IR absorption of $(CF_3)_3CBr$ molecules at vibrational excitation levels exceeding the dissociation energy

V. P. Apatin and G. N. Makarov

Spectroscopy Institute, USSR Academy of Sciences

(Submitted 20 February 1986)
Zh. Eksp. Teor. Fiz. **91**, 1219–1232 (October 1986)

Nonlinear (multiphoton) IR absorption by the large polyatomic molecule $(CF_3)_3CBr$ in the field of a high-power CO_2-laser pulse is investigated in a cell at various gas pressures and in a molecular beam. A strong dependence of the absorbed energy and of the cross section σ for nonlinear absorption on the gas pressure is observed at high vibrational excitation levels ($\varepsilon \gtrsim D$, where ε is the internal energy of the molecule and D is the dissociation energy). A steep decrease of σ with increase of the pump energy density is observed (at $\Phi \gtrsim 0.5$–1.0 J/cm^2) under condition of collisionless molecule excitation (low pressures, molecular beam), but no steep decrease of $\sigma(\Phi)$ is observed in the presence of collisions. The influence of a buffer gas (Ar) on the character of the $\sigma(\Phi)$ dependence is investigated in the steep-decrease region. Addition of Ar at a pressure $\gtrsim 20$ Torr prevents a decrease of σ. Two-frequency excitation of $(CF_3)_3CBr$ in a molecular beam is affected. It is shown that the decrease of $\sigma(\Phi)$ at the indicated energy densities is not due to molecule dissociation during the exciting laser pulse. Possible causes of the steep decrease of the absorption cross section and of its dependence on the gas pressure at excitation levels higher than the dissociation energy are discussed.

1. INTRODUCTION

One of the causes of the interest in the study of the interaction between relatively large ($s \gtrsim 30$, where s is the number of vibrational degrees of freedom) polyatomic molecules and a strong IR field[1] is the possibility of vibrationally exciting them to energies ε greatly exceeding their dissociation energy D ($\varepsilon \gtrsim 2D$).[2] This possibility does not contradict the Rice-Ramsperger-Kassel-Marcus (RRKM) theory of monomolecular reactions,[3] is an important property of large polyatomic molecules, and distinguishes them from small or medium ($s \lesssim 12$) molecules. Strong excitation of small molecules above the dissociation limit increases greatly (with decrease of s) the energy-localization probability per bond, in view of the statistical character of the molecule's internal energy distribution among the vibrational degrees of freedom. The result is a rapid increase of the rate $k(\varepsilon)$ of the molecules' monomolecular decay. It follows from the RRKM theory, and also from experiments on a number of molecules ($C_6H_5CH_2NH_2$, Ref. 4, $C_6F_{13}I$, Ref. 5, $(CF_3)_3CBr$, Ref. 6, $(CF_3)_2CI$, Ref. 7) that molecules vibrationally overexcited in the electronic ground state can have quite long lifetimes ($\approx 10^{-6}$–10^{-3} s), i.e., low molecular-decay rate constants $k(\varepsilon)$. This makes it possible to obtain, by the method of IR multiphoton excitation,[1] high densities of vibrationally overexcited molecules and perform with them experiments that explain better the intramolecular dynamics. One such experiment can be direct measurement of $k(\varepsilon)$,[4–7] from which one can determine the width of the vibrational-distribution function of the excited molecules[8] (and which is also of considerable interest for chemical kinetics[2]). Other possibilities are study of the dynamics of excitation of levels above the dissociation limit,[6] and determining the IR spectra of transition of vibrational states above the dissociation limit.

Much information on the interaction between molecules and IR laser emission can be obtained from measurements of the energy absorbed by the molecules from an IR field and on the cross section for nonlinear absorption. We observed[6] in measurements of the lifetimes of vibrationally overexcited $(CF_3)_3CBr$ molecules in a molecular beam that the energy absorbed by the molecules from the IR field, at a pump energy density $\Phi = 0.8$–1 J/cm^2 tended to saturate (the nonlinear-absorption cross section σ decreased abruptly), even though the measured dissociation rate constant $k(\varepsilon)$ did not exceed 10^4 s^{-1} at the indicated energy densities, i.e., the molecules hardly dissociated during the exciting pulse. Earlier,[2] however, when the same molecule was excited in a cell at a pressure 0.6 Torr, an almost monotonic increase of the absorbed energy was observed, with Φ increasing up to ≈ 5 J/cm^2. A decrease in the slope of the plot of $\langle n \rangle (\Phi)$ was observed only at $\Phi \gtrsim 3$ J/cm^2 ($\langle n \rangle$ is the number of photons absorbed on the average per molecule). This was attributed to dissociation of the molecules during the exciting laser pulse, while the radicals $(CF_3)_3C^\bullet$ produced by dissociation of the molecules were further fragmented by the same pulse. It follows thus from the results of Refs. 2 and 6 that when the molecules are excited in a cell at relatively high gas pressures the cross section for IR multiphoton absorption by $(CF_3)_3CBr$ depends differently on the energy density than in a molecular beam. To ascertain the causes of this difference and to understand better the manner in which the molecule acquires energy from the laser-pulse IR field under different conditions, we have investigated in detail IR mulitphoton absorption by $(CF_3)_3CBr$ in a cell at various gas pressures in the range 0.05–1 Torr, and also in a molecu-

0038-5646/86/100721-08$04.00

lar beam. The absorbed energy and the cross section σ for nonlinear absorption were found to depend strongly on the gas pressures at high levels ($\varepsilon \gtrsim D$) of vibrational excitation. A steep decrease of σ with increase of the pump energy density (at $\Phi \gtrsim 0.5$–1 J/cm^2) was observed under conditions of collisionless excitation of the molelcules (low pressures, molecular beam), but no such decrease of σ occurs in the collision regime. The influence of a buffer gas (Ar) on the $\sigma(\Phi)$ dependence in the region of the abrupt drop is investigated. Addition of Ar ($\gtrsim 20$ Torr) prevents σ from decreasing. The use of the method of two-frequency excitation of $(CF_3)_3CBr$ in a molecular beam shows that the abrupt drop of $\sigma(\Phi)$ is not due to dissociation of the molecules during the time of the exciting pulse.

2. EXPERIMENTAL SETUP AND PROCEDURE

The experimental setup, comprising a pulsed molecular beam and a frequency-tunable atmospheric-pressure transverse-discharge CO_2 laser (of the TEA type), as well as the method used to measure the absorbed energy in the molecular beam, are described in detail in Refs. 6, 9, and 10. We describe here only briefly only the data pertaining to our experiment.

A molecular $(CF_3)_3CBr$ beam mixed with Ar and He, in a respective ratio 1 :1 :10 (total pressure in the nozzle 2.5 atm) was excited at a distance 6 cm from the nozzle by a CO_2-laser pulse (peak 100 ns at half-maximum, with a tail 0.6 μs long containing $\approx 50\%$ of the energy; total energy in pulse up to 3 J). In a number of cases the molecules were excited by a pulse that was shortened (by optical breakdown in air or by using a nitrogen-free mixture). The laser emission propagated perpendicular to the molecular-beam axis. The laser frequency was tuned to lines coinciding with the ν_{21} (963 cm^{-1}) or ν_6 (934 cm^{-1}) vibration[11] of the molecule (see Fig. 1). The laser beam was gently focused with an NaCl long-focus lens ($f = 1$ m) onto the region of the intersection with the molecular beam. The dimensions of the spot in the interaction region were 7×6 mm. The energy absorbed by the beam molecules from the laser-pulse field was measured. The detector was a high-speed (2–5 μs) pyroelectric receiver with a 4×4 mm active element, which could be displaced along the beam axis. The signal from the detector was fed through an amplifier to an S8–12 oscilloscope.

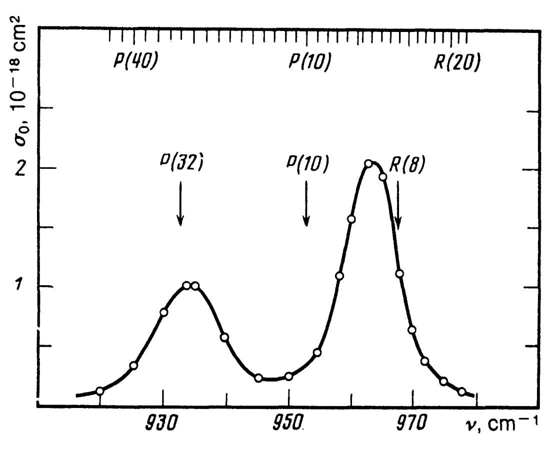

FIG. 1. Linear absorption by $(CF_3)_3CBr$ in the CO_2 lasing region. The arrows show the frequencies (laser lines) at which the molecules were excited.

Since the vibrationally excited molecules decay at a rate $k(\varepsilon)$ and consequently the beam-molecule energies depend on the travel time t_t (or on the distance x from the excitation region; to the receiver, $t_t = x/v$, where v is the molecule velocity),[6] it was necessary to measure the molecule energies at various distances from the excitation region (1.4 cm$\leqslant x \leqslant$11.7 cm), to be able to determine the $E_a(\Phi)$ dependence (E_a is the absorbed energy) in the excitation region from the character of the variation of the molecule energy with distance.[6] Note that in the experiments with a molecular beam the absorbed energy was measured in relative units.

Multiphoton absorption by $(CF_3)_3CBr$ in a cell was investigated by direct calorimetry of the absorbed energy. We measured the incident energy of the exciting laser pulse and that passed by a cell with $(CF_3)_3CBr$ (and also by an empty cell). The cells used in the experiments were 1 and 0.3 m long (with inside diameter 3.4 cm). The laser beam was passed through a diaphragm to obtain a spot with approximately equal density over the beam cross section, and was focused into the cell with a long-focus lens ($f = 1$ m). The laser-beam cross section averaged over the cell length was ≈ 0.35 cm^2. In most experiments, the absorbed energy did not exceed 10–12% of the incident, so that no correction was introduced for the energy-density variation (due to absorption) along the cell axis.

The absorbed energy was defined as $E_a = E_{inc} - E_t$, where E_{inc} and E_t are the laser-pulse energies incident and transmitted through the cell. The absorbed energy is expressed in photons absorbed on the average per molecule:

$$\langle n \rangle = E_a/\hbar\omega N V, \tag{1}$$

where $\langle n \rangle$ is the average number of absorbed photons per molecule, $\hbar\omega$ the laser-emission photon energy, N the molecule density in the cell, and V the gas volume illuminated by the laser emission.

The cross section for linear absorption was defined as

$$\sigma = -\ln(T)/Nl, \tag{2}$$

where $T = E_t/E_{inc}$ is the gas transmission and l is the length of the absorbing layer. When $(CF_3)_3CBr$ was excited in a molecular beam we could not determine σ from Eq. (2). Since, however, only an insignificant fraction of the incident energy was absorbed in this case, it could be assumed with good accuracy[10] that the cross section for multiphoton absorption is equal to E_a/Φ. We have therefore put $\sigma = E_a/\Phi$.

3. RESULTS

The $(CF_3)_3CBr$ molecule has in the emission region of the CO_2 laser two absorption bands, ν_6 at 934 cm^{-1} and ν_{21} at 963 cm^{-1} (Ref. 11). Their intensities differ by approximately a factor of two. Figure 1 shows the cross sections for linear absorption of these vibrations, determined from spectra obtained with an IR-75 interferometer. The arrows show the frequencies of the CO_2-laser lines [$R(8)$, $P(10)$ and $P(32)$] used in most cases to excite the molecules. The lines $P(10)$ and $R(8)$ coincide with the low- and high-frequency wings of the more intense ν_{21} band, and the $P(32)$ line with the maximum of the ν_6 band.

Figure 2 shows plots of the average number $\langle n \rangle$ of photons absorbed per molecule vs the energy density Φ of the exciting pulse, for the indicated lines at various $(CF_3)_3CBr$ pressures in the range from 0.05 to 0.6 Torr. It can be seen that at $\Phi < 0.7$–0.8 J/cm^2 the value of $\langle n \rangle$ for the $P(10)$ and $P(32)$ lines increases with energy density like $\Phi^{1.1}$ in the investigated range. For the $R(8)$ line, $\langle n \rangle$ is approximately proportional to $\Phi^{0.8}$ in the region $\Phi < 0.3$–0.4 J/cm^2. Thus, the $\langle n \rangle(\Phi)$ dependences do not deviate greatly from linearity in the indicated range. Below the energy densities indicated above, $\langle n \rangle$ is independent, at the measurement accuracy ($\approx 5\%$), of the gas pressure p in the range from 0.05 to 0.6 Torr.

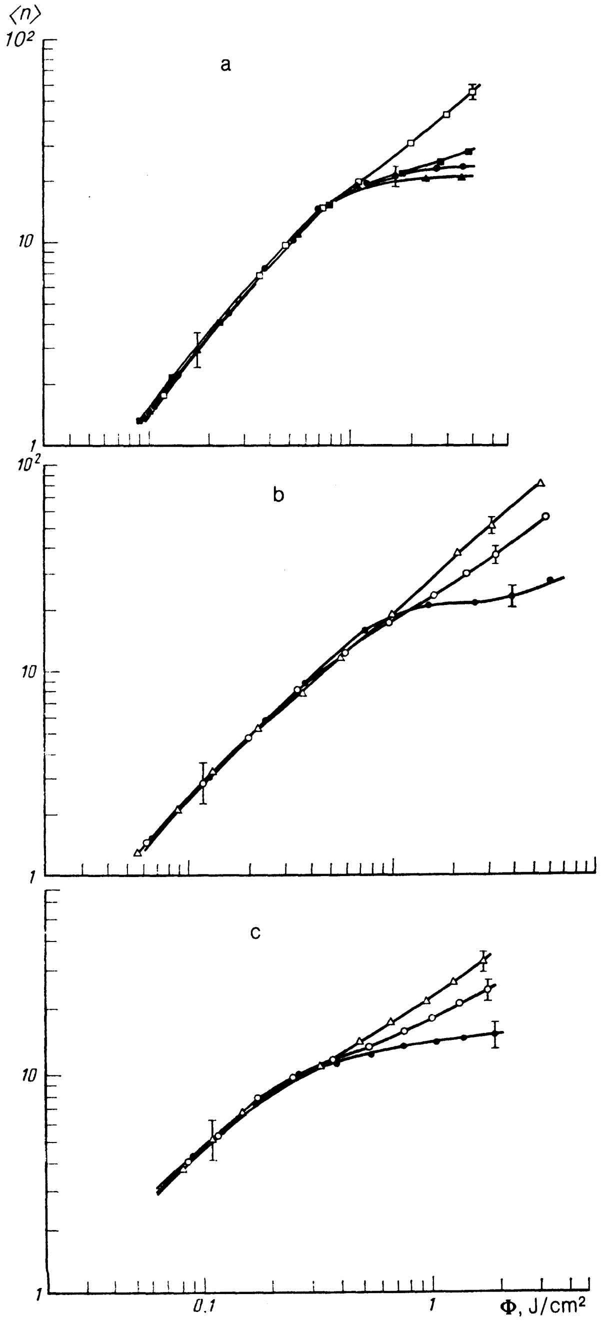

FIG. 2. Average number of photons absorbed per molecule vs the energy density of the exciting pulse at the frequencies of the lines $P(10)$—a, $P(32)$—b and $R(8)$—c at $(CF_3)_3CBr$ pressures in the cell 0.05 (▲); 0.1 (●); 0.15 (■); 0.2 (○); 0.4 (△) and 0.6 (□) Torr.

The main result of the data of Fig. 2 is that at energy densities $\Phi \gtrsim 0.5$–0.8, J/cm^2 the growth of $\langle n \rangle$ decreases steeply as a function of Φ($\langle n \rangle$ becomes practically saturated) at low gas pressures ($p \approx 0.05$–0.1 Torr), whereas at $p \gtrsim 0.4$–0.6 Torr the value of $\langle n \rangle$ continues to increase with energy density, just as at smaller Φ. At the latter energy densities $\langle n \rangle \gtrsim 20$ for the lines $P(10)$ and $P(32)$ and $\langle n \rangle \gtrsim 16$ for $R(8)$ The vibrational energy possessed by the molecules at room temperature

$$\varepsilon_{\rm osc} = \sum_{i=1}^{s} \frac{\hbar\omega_i}{\exp(\hbar\omega_i/kT) - 1}, \tag{3}$$

where $\hbar_{\omega_i}$ are the oscillation frequencies[11] and $s = 36$ is the number of vibrational degrees of freedom of the molecule, is approximately equal to five CO_2-laser emission photons. Consequently, at the considered values of Φ, even if all the molecules in the irradiated volume interact with the laser pulse, their internal energy exceeds the dissociation energy ($D \approx 24\,000$ cm^{-1}, Ref. 2) or is comparable with it.

We shall use the designation "saturation energy Φ_s" for the energy density at which saturation of $\langle n \rangle(\Phi)$ sets in. It follows thus from Fig. 2 that $\langle n \rangle$ is independent of the gas pressure at $\Phi < \Phi_s$ and a strong dependence of $\langle n \rangle$ on p is observed at $\Phi > \Phi_s$. For example, at $\Phi = 3$ J/cm^2 we have for the $P(10)$ line $\langle n \rangle \approx 21$ at $p = 0.05$ Torr and $\langle n \rangle \gtrsim 40$ at $p = 0.6$ Torr. Note that at 0.4 and 0.6 Torr $\langle n \rangle$ reaches values $\gtrsim 60$ when the energy is increased to 4–5 J/cm^2, i.e., the energy absorbed in this case exceeds substantially the dissociation energy. The character of the energy acquisition observed by us at pressures $p \gtrsim 0.4$ Torr agrees well with the $\langle n \rangle(\Phi)$ dependence obtained in Ref. 2 at a $(CF_3)_3CBr$ pressure $p = 0.6$ Torr. Some variation in the absolute value of $\langle n \rangle$ may be due to the fact that in Ref. 2 the molecules were excited at another frequency.

It should be noted that $\langle n \rangle$ is also strongly deependent on the pressure of the buffer gas in the region $\Phi > \Phi_s$. Figure 3 shows plots of $\langle n \rangle(\Phi)$ obtained on excitation of $(CF_3)_3CBr$ (0.1 Torr) without a buffer gas as well as mixed with argon. The molecules were excited at the $P(10)$-line frequency. Addition of Ar at a pressure $\gtrsim 20$ Torr leaves the growth rate of $\langle n \rangle(\Phi)$ unchanged in the $\Phi > \Phi_s$ region.

Saturation of $\langle n \rangle(\Phi)$ is observed when $(CF_3)_3CBr$ is excited under collision-free conditions ($p\tau_p \lesssim 30$ ns·Torr, where τ_p is the duration of the exciting laser pulse). This is well confirmed by measurements of the energy E_a absorbed by the molecules in a molecular beam when the excitation process is essentially collision-free.[9,10] Figure 4 shows plots of $E_a(\Phi)$ for the lines $P(10)$ and $R(8)$, obtained by exciting

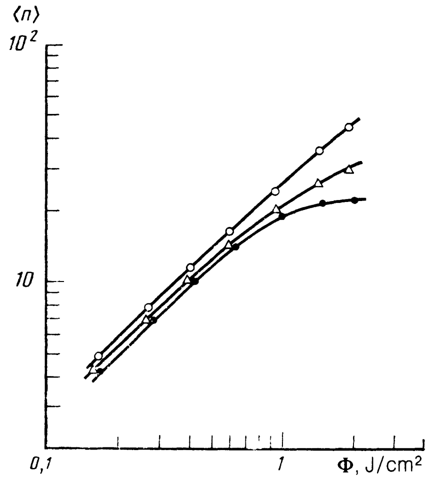

FIG. 3. Average number of photons absorbed per molecule vs the energy density of the incident radiation at the frequency of the $P(10)$ line in the case of excitation of $(CF_3)_3CBr$ (0.1 Torr) with a buffer gas (Ar). Buffer gas pressure: 0 (●); 6.6 (△) and 86 (○) Torr.

$(CF_3)_3CBr$ in a molecular beam. It can be seen that at $\Phi \gtrsim 1$ J/cm² the slope of the $E_a(\Phi)$ plot decreases sharply and E_a is practically saturated. A similar variation of the plots of $\langle n\rangle(\Phi)$ [or $E_a(\Phi)$] was observed by us for $(CF_3)_3CBr$ excited in a cell and in a molecular beam also at other frequencies equal to the absorption-band centers as well as to their wings.

This behavior of the $\langle n\rangle(\Phi)$ dependences means that if $(CF_3)_3CBr$ is excited under collision-free conditions the cross section σ for nonlinear absorption begins to decrease sharply when the energy density is increased in the region $\Phi > \Phi_s$, whereas in collisional excitation the value of σ does not change greatly in the region indicated. Figures 5 and 6 show plots of $\sigma(\Phi)$ obtained from the data of Figs. 2 and 4 for $(CF_3)_3CBr$ excited respectively in a cell and in a molecular beam. It can be seen from Figs. 5a, 5b, and 6 that at

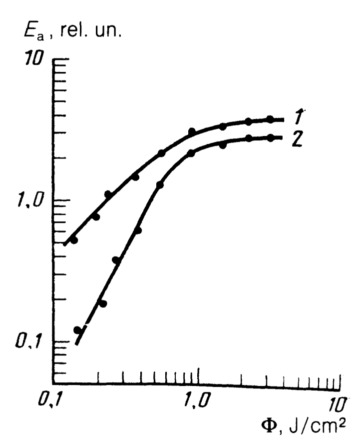

FIG. 4. Energy absorbed by $(CF_3)_3CBr$ molecules vs the energy density of the incident radiation at the frequencies of the lines $R(8)$ (1) and $P(10)$ (2) with the $(CF_3)_3CBr$ excited in a molecular beam.

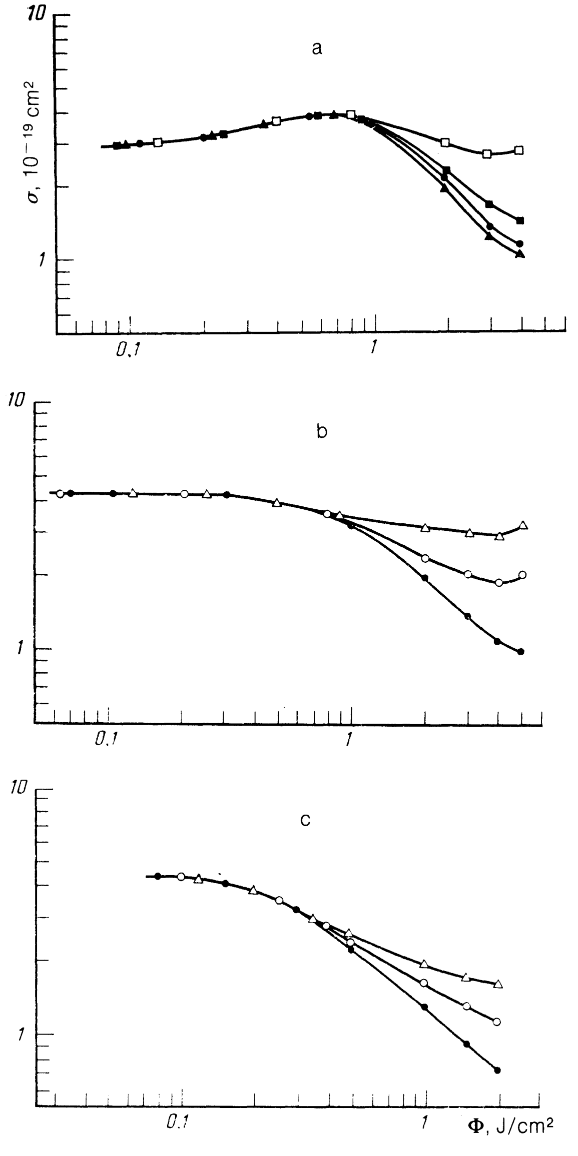

FIG. 5. Cross sections for nonlienear IR absorption by $(CF_3)_3CBr$ vs the energy density of the exciting pulse at the frequencies of the lines $P(10)$ (a), $P(32)$ (b), and $R(8)$ (c) at various $(CF_3)_3CBr$ pressures. The notation is the same as in Fig. 2.

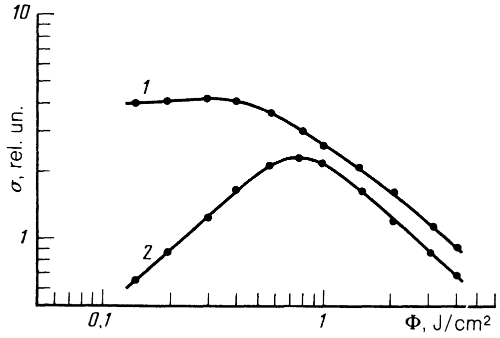

FIG. 6. Cross sections for nonlinear IR absorption vs the energy density at the frequencies of the lines $R(8)$ (1) and $P(10)$ (2), with the $(CF_3)_3CBr$ excited in a molecular beam.

$\Phi \gtrsim 0.8$–1 J/cm^2 the value of σ decreases rapidly (approximately as Φ^{-1}) with increasing energy density. In the case of Fig. 5c, the decrease of σ is somewhat slower. Note that when $(CF_3)_3CBr$ is excited in a molecular beam at the frequency of the $P(10)$ line the absorption cross section in the region $\Phi < 0.8$ J/cm^2 increases with increasing pump-energy density.

It follows from Fig. 5 that at $\Phi \approx 0.1$ J/cm^2 the cross section σ for multiphoton absorption is 1.5–2 times smaller than the cross section σ_0 for linear absorption (see Fig. 1).

4. DISCUSSION OF RESULTS

The fact that the absorbed energy is independent of pressure for $(CF_3)_3CBr$ gas at $\Phi < 0.7$–0.8 J/cm^2 means absence of the rotational "bottleneck" effect[12] that limits the fraction of molecules involved in interaction in the lower transitions. It is probable that the high density of the vibrational-rotational levels of the IR absorption band of $(CF_3)_3CBr$ are homogeneously broadened, so that the emission depletes effectively all the rotational sublevels. Absence of (or weak) dependence of the absorbed energy on the gas pressure was observed earlier in the excitation of other polyatomic molecules (CF_3COCF_3, Ref. 13, S_2F_{10}, Ref. 14, derived butyl-acetate[15]), while in Ref. 16 the energy absorbed by excited SF_5NF_2 (0.1 Torr) was independent also of the exciting-pulse intensity when the latter was changed by a factor of 100. The absence of a rotational "bottleneck" that limits the fraction of the excited molecules is an interesting feature of large polyatomic molecules.

Large molecules are also characterized by nearly linear $\langle n\rangle(\Phi)$ dependences.[17] The reason is that they have a high density of vibrational levels (a low vibrational-quasicontinuum limit), and absorption in a quasicontinuum is close to linear. Analysis of the dependence of the absorption cross section on the laser-pulse energy densities in the aforementioned molecules[13–16] shows that σ remains practically constant up to energies $\approx 10^{-2}$ J/cm^2, so that the absorption is close to linear. In the case of $(CF_3)_3CBr$ the cross section for multiphoton absorption also decreases slowly with increasing Φ, as indicated by the fact that σ at $\Phi = 0.1$ J/cm^2 is only 1.5–2 times smaller than the cross section for linear absorption. The increase of σ (steep $E_a(\Phi)$ plot for molecules excited in a $P(10)$ beam) in the 0.1–0.6 J/m^2 region is probably due to the red shift of their absorption band with increase of vibrational energy. It is also possible that direct multiphoton transitions appear at the given frequency in the case of cooled molecules.[10]

The decrease of σ with further increase of the energy density is due mainly to two effects[14,16]: 1) dissociation of the molecules and 2) red shift of the multiphoton-absorption spectrum of the vibrationally excited molecules as a result of anharmonicity. It was shown in Ref. 16, by measurement of the dissociation yield $\beta(\Phi)$, that the main cause of the decrease of σ is molecule decay. It must be noted, however, that in none of the foregoing references was the dissociation process investigated as a function of time. But since vibrationally excited large polyatomic molecules (in contrast to small or medium ones) have small monomolecular-decay rate constants $k(\varepsilon)$, it is impossible, in the general case, to state on the basis of measurements of the dissociation yield $\beta(\Phi)$, without time resolution, that the molecules dissociated within the duration of the exciting pulse.

At relatively high gas pressures, molecules probably do dissociate also during the pump pulse. Thus, for example, in Ref. 18, on excitation of $(CF_3)_3Cl$ (0.3 Torr) mixed with O_2 (1.8 Torr), as well as in (2) on excitation of $(CF_3)_3CBr$ (0.6 Torr), a subsequent dissociation (by the laser pulse) was observed of the fragments $(CF_3)_3C^\bullet$ produced in the decay of the molecules. The absorption of $\gtrsim 60$ CO_2-laser photons by $(CF_3)_3CBr$ molecules at $\Phi \gtrsim 4$–5 J/cm^2 in the present experiments is apparently also due to the fact that at high pressures molecules can decay rapidly and take part in the absorption of the dissociation fragments. In this case, however, the molecule excitation and dissociation is due not to radiation alone but more readily to combined radiation and collision.

The steep decrease of σ at $\Phi \gtrsim 0.5$–0.8 J/cm^2, observed by us under collision-free conditions, is not connected with molecule dissociation during the exciting pulse. As for the results of using a molecular beam, we have already shown in Ref. 6 that the lifetime of $(CF_3)_3CBr$ molecules vibrationally overexcited in a molecular beam at the frequency of the $10P(10)$ line and at $\Phi \lesssim 3$ J/cm^2 is $\gtrsim 10^{-4}$ s, i.e., there is practically no molecule dissociation during the pump-pulse time. For excitation at the frequency of the $10R(8)$ line at the same energy densities, the lifetimes of the vibrationally excited molecules is even longer.

Since, however, we were unable in Ref. 6 to measure decay times shorter than $2\cdot 10^{-5}$ s, we performed in the present study the following experiment. We measured the energy absorbed by the $(CF_3)_3CBr$ molecules in a molecular beam in the case of two-frequency excitation. The purpose of these experiments was to show that the decrease of σ [the saturation of $\langle n\rangle(\Phi)$] at $\Phi \gtrsim 1$ J/cm^2 is not connected with molecule dissociation during the exciting pulse. With $\langle n\rangle(\Phi)$ saturated, the molecules in the beam were excited by a pulse from another laser, delayed by 1 ± 0.05 μs, with an energy density Φ_2 and with a frequency detuned from the frequency of the first laser by 15–20 cm^{-1} towards the red. If the decrease of σ is due to dissociation of the molecules, by the instant of the second pulse their density decreases steeply, and the energy absorbed from the second pulse is therefore small. (Note, however, that at certain frequencies E_a can be increased by fragment absorption.) If, however, the molecules do not dissociate during the time of the pulse, they absorb energy from the second pulse, since the absorption spectrum of the excited molecules is shifted towards the red by the anharmonicity.

Figure 7 shows plots of $E_a(\Phi)$ obtained by exciting $(CF_3)_3CBr$ in a molecular beam a two frequencies [$\hbar\omega = 966.3$ cm^{-1}, line $R(6)$, and $\hbar\omega = 952.9$ cm^{-1}, line $P(10)$] under conditions when saturation of $\langle n\rangle(\Phi)$ was observed for the first field. It can be seen from Fig. 7 that action of the second pulse increases substantially the absorbed energy E_a. Simultaneously, an appreciable increase is observed in the monomolecular-decay rate constant $k(\varepsilon)$ measured by the method described in Ref. 6. A similar result

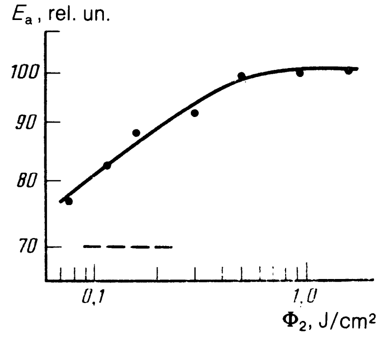

FIG. 7. Dependence of the absorbed energy on the energy density of the incident radiation at the frequency $\hbar\omega_2$ on excitation of $(CF_3)_3CBr$ in a molecular beam by two-frequency radiation [$\hbar\omega_1 = 966.3$ cm^{-1}, line $R(6)$ and $\hbar\omega_2 = 952.9$ cm^{-1}), line $P(10)$]. The energy density at the $\hbar\omega_1$ field frequency is $\Phi_1 = 2$ J/cm^2. The dashed line shows the level of the energy absorbed from the first field.

was observed by us on excitation of the molecules at other frequencies $\hbar\omega_1$ and $\hbar\omega_2$.

To cast light on the question of molecule decay during the pump pulse, $(CF_3)_3CBr$ was also excited in a molecular beam by pulses of varying intensity (duration), differing by a factor 3–4 at equal energy. If the molecules decay during the pump pulse, the molecule excitation rate is $W = \sigma I \lesssim k(\varepsilon)$, where I is the radiation intensity. By increasing the intensity it is possible to change this ratio and arrive at the condition $W \gtrsim k(\varepsilon)$. In this case more energy should be absorbed, since the molecule can be excited to higher levels. No differences in the absorbed energy was observed in these experiments, in the region up to $\Phi \approx 3$ J/cm^2, when pulses of different duration were used.

The foregoing results show that at the indicated energy densities the $(CF_3)_3CBr$ molecules do not decay in the molecular beam during the exciting pulse.

We proceed now to discuss the results with room temperature in the cell. Note that the weak dependence of the absorbed energy on the pressure of the buffer gas (He, Xe) at low energy densities, and the considerably stronger dependence at high densities, was observed for S_2F_{10} in Ref. 19. This was attributed by the authors to the fact that addition of a buffer at high energy densities leads to collisional deactivation of the excited molecules and to a decrease of the dissociation yield, and consequently enables the molecules to absorb more energy. (Note that these dependences were differently explained in Ref. 20 on the basis of allowance of the relaxation processes that occur during the succeeding stages of excitation.) An appreciable enhancement of $\langle n \rangle$, attributed to molecule deactivation, was observed in Ref. 2 when $(CF_3)_3CBr$ was excited at $\Phi \gtrsim 3$ J/cm^2 with I_2(≈ 12 Torr) added. Of course, collisional deactivation of molecules increases the absorption and must be taken into account.

Whether or not the abrupt decrease of σ on excitation of $(CF_3)_3CBr$ under noncollision conditions is due to molecule dissociation during the exciting pulse can probably be verified, as described above, with the aid of two-frequency experiments. However, the very fact that the absorbed energy depends strongly on the gas pressure at $\Phi > \Phi_s$ and that this dependence has a threshold (with respect to Φ) indicates, in our opinion, that the saturation of $\langle n \rangle (\Phi)$ (the decrease of σ) is unrelated to molecule dissociation. Were this not so, the increase of $\langle n \rangle$ with increase of gas pressure could be attributed, just as in Ref. 19, only to collisional deactivation of the molecules under conditions when they dissociate effectively. It is difficult, however, to explain our results by using this model. It can be seen from Fig. 2, for example, that at 0.05 and 0.1 Torr the values of $\langle n \rangle$ at 1 and 3 J/cm^2 differ insignificantly. This means that the number of excited molecules and also the average level of their vibrational excitation are approximately the same.[21] It follows hence that the monomolecular rate constant $k(\varepsilon)$ also increases slowly in the indicated range, and the lifetimes of the excited molecules at 1 and 3 J/cm^2 do not differ greatly. (This is precisely the result observed by us in Ref. 6.) The rates of collisional deactivation of the excited molecules should therefore also differ little at the indicated energy densities. It can be seen from the same figure, on the other hand, that whereas at $\Phi = 1$ J/cm^2 the value of $\langle n \rangle$ increases insignificantly when the $(CF_3)_3CBr$ pressure is increased from 0.1 to 0.6 Torr, at $\Phi = 3$ J/cm^2 $\langle n \rangle$ increases by 2–2.5 times. This result is difficult to understand in the framework of collisional deactivation. It must furthermore be noted that in these experiments we observed an increase of $\langle n \rangle$ with increase of the pressure of the $(CF_3)_3CBr$ gas itself, and not only when a buffer was added.

We consider now the possible causes of the abrupt decrease of $\sigma(\Phi)$ when the molecules are excited under collisionless conditions and the absence of such a decrease when collisions are present. Naturally, the decrease of $\sigma(\Phi)$ is due to the anharmonicity of the molecule vibrations. It must be noted here, too, that anharmonicity of the vibrations manifests itself differently in the manner in which energy is accumulated in the presence and absence of collisions. We consider therefore the molecule excitation in these two cases (see also Ref. 22).

In the presence of collisions it is possible, for example, to offset by rotational relaxation a rather large frequency detuning (or anharmonicity of the vibrations), comparable with the width $\Delta\nu_{\text{vib}}$ of the vibrational absorption band.[12] In the absence of collisions, however, the frequency detuning that can be offset is much smaller, comparable with the width $\Delta\Gamma$ of the homogeneously broadened absorption line (or with the field broadening $\Delta\nu_R = \mu E/\hbar c$, where μ is the dipole moment of the transition and E is the laser pulse intensity, if $\Delta\nu_R > \Delta\Gamma$). Therefore if $\Delta\Gamma < \Delta\nu_{\text{vib}}$ and $\Delta\nu_R < \Delta\nu_{\text{vib}}$, the molecules excited in the absence of collisions become nonresonant with the field at lower excitation energy densities and undergo a smaller number of successive transitions than in the presence of collisions.

However, as already mentioned, in the case of the $(CF_3)_3CBr$ molecules the vibrational relaxation, at least at $\Phi < \Phi_s$, does not influence the energy-accumulation process. It is possible that rotational relaxation assumes a role at high levels of vibrational excitation. This can occur, for example, if the molecules are excited to the higher transitions predominantly via states that are not highly populated, and longer times are needed for the rotational relaxation.[12]

We regard as more probable in this case the role of vibrational-vibrational *V-V* relaxation. Collisional *V-V* exchange leads to excitation and deexcitation of the molecules, to a change of their quantum states, and to transfer of the excitation to other modes. Whereas in the absence of collisions the vibrational distribution function $f(\varepsilon_{\text{vib}})$ of the excited molecules is narrow compared with the Boltzmann distribution function, collisional *V-V* exchange leads to a broadening of the distribution $f(\varepsilon_{\text{vib}})$. The molecules that land in the low-energy wing of the Boltzmann distribution are then "additionally" excited by the laser radiation, so that the energy absorbed is increased. It must be noted, however, that if the laser pulse produces an ensemble of only "hot" molecules and there are no "cold" molecules present[23] (and this probably is indeed the case when $\langle n\rangle(\Phi)$ is saturated, see also Refs. 6 and 7), a change to a Boltzmann distribution will not increase substantially the absorbed energy as compared with the case of collisionless excitation. In fact, as soon as the low-energy molecules become excited to a higher level, they cease to be resonant with the field and saturation of $\langle n\rangle(\Phi)$ sets in. The maximum increment of the absorbed energy does not exceed in this case the energy corresponding to the half-width $\delta_{1/2}$ of Boltzmann distribution function $f(\varepsilon_{\text{vib}})$. Let us estimate this value, using the known vibrational distribution functions.[24,25] In the case of molecules with a large number s of vibrational degrees of freedom we have $\delta = \bar{\varepsilon}_{\text{vib}}/s^{1/2}$, where $\bar{\varepsilon}_{\text{vib}}$ is the average vibrational energy of the molecule. At $\varepsilon_{\text{vib}} \approx 25\,000$ cm^{-1} we have $\delta \approx 4200$ cm^{-1}. The increase of $\langle n\rangle$ can thus amount to only 2–3 photons.

It appears that not all the vibrational states interact equally effectively with the laser-emission field when the $(CF_3)_3CBr$ molecules are excited. Vibrational-vibrational relaxation between nearby states plays then a role similar to that of rotational relaxation. Collisional exchange causes the molecules that went off-resonance in the upper transition to change state and again enter into resonance with the radiation, becoming excited to higher levels. The increased absorption of $(CF_3)_3CBr$ following addition of Ar can be attributed to acceleration of the *V-V* exchange processes in the presence of the buffer gas.

It follows from the present results and the data of Ref. 6 that when $(CF_3)_3CBr$ molecules are excited under collisionless conditions, when $\langle n\rangle(\Phi)$ is saturated, the vibrational distribution function $f(\varepsilon_{\text{vib}})$ is narrow (the molecules are almost monoenergetically excited). This is probably why we have observed in Ref. 6 a nearly exponential decay of the overexcited molecules with time.

5. CONCLUSION

Let us summarize our main results and some of the ensuing conclusions.

1) Nonlinear IR absorption of the large polyatomic molecule $(CF_3)_3CBr$ was investigated in the field of a high-power CO_2 laser pulse, in the presence and absence of collisions, at vibrational-excitation levels exceeding the dissociation energy.

2) An abrupt decrease of the cross section $\sigma(\Phi)$ for nonlinear absorption was observed under conditions of collisionless excitation of the molecules (low pressures, $p\tau_{\text{pul}} \lesssim 30$ ns·Torr, molecular beam) in the region $\Phi \gtrsim 0.5$–1 J/cm^2. It was shown, using two-frequency excitation of the $(CF_3)_3CBr$ in a molecular beam, that the rapid decrease of $\sigma(\Phi)$ in the indicated range is not due to dissociation of the molecules during exciting pulse.

The absorbed energy (and the cross section σ for nonlinear absorption) was found strongly at $\Phi \gtrsim 0.5$–0.8 J/cm^2 on the pressures of $(CF_3)_3CBr$ and of the buffer gas (Ar). When $(CF_3)_3CBr$ is excited in the presence of collisions ($p\tau_{\text{pul}} \gtrsim 300$ ns·Torr) at $\Phi \gtrsim 3$ J/cm^2, the number of photons absorbed per molecule reaches $\langle n\rangle \gtrsim 45$, i.e., the energy absorbed is approximately double the molecule-dissociation energy.

4) Analysis of the results shows that the steep decrease of $\sigma(\Phi)$ when the molecules are excited in the absence of collisions is due to anharmoncity of the molecule vibrations. Anharmonicity causes the molecules on the higher transitions to depart from resonance with the exciting radiation. The frequency detuning $\Delta\nu$, which can be offset when molecules are excited in the absence of collisions, is comparable with the width $\Delta\Gamma$ of the homogeneously broadened absorption line or with the dynamic field broadening if the latter is larger ($\Delta\nu \approx \Delta\Gamma$, $\Delta\nu_R$).

When the pressures of the $(CF_3)_3CBr$ and of the buffer gas are increased, collisions alter the vibrational-rotational states (distribution) of the molecules, so that the molecules that went off-resonance again become resonant with the radiation and are excited to higher levels. It is possible in this case to compensate for an appreciably larger frequency detuning, comparable with the width of the vibrational band. As a result, the molecules can undergo a larger number of vibrational transitions than in the absence of collisions.

5) To obtain $(CF_3)_3CBr$ molecules that are strongly overexcited above the dissociation limit in the absence of collisions, it is more effective to use two-frequency (multifrequency) IR excitation, with the frequency of the second field $\hbar\omega_2$ shifted towards the red side of the linear-absorption band.

6) Under conditions when $\langle n\rangle(\Phi)$ is saturated, high concentrations of long-lived molecules $(CF_3)_3CBr^*$ vibrationally overexcited above the dissociation limit can be obtained for experimental purposes. Interest attaches, in particular, to obtaining the IR absorption spectra of the overexcited molecules.

7) When $(CF_3)_3CBr$ molecules are produced in the absence of collisions and with $\langle n\rangle(\Phi)$ saturated, the resultant vibrational distribution is narrow (the molecule excitation is almost monoenergetic). By suitable choice of the pump frequency (see Figs. 2a, 2b and 2c), or by using two-frequency excitation, it is possible to vary the vibrational energy of such molecules. This is of great interest for chemical kinetics, and in particular for the measurement of the rate constants of the decay of monoenergetically excited molecules. It seems pos-

sible to observe also quite narrow IR absorption spectra of vibrationally overexcited molecules.

The authors thank V. S. Letokhov for support and for interest in the work, V. N. Bagratashvili, A. A. Makarov, and E. A. Ryabov for a helpful discussion of the results, and V. N. Lokhman for help with the experiments.

[1] V. N. Bagratashvili, V. S. Letokhov, A. A. Makarov, and E. A. Ryabov, Multiphoton Processes in Molecules in an IR Laser Field [in Russian], VINITI, 1980; V. N. Bagratshvili, V. S. Letokhov, A. A. Makarov and E. A. Ryabov, *Multiple Photon Infrared Laser Photophysics and Photochemistry*, Harwood, N. Y. 1985.

[2] V. N. Bagratashvili, V. N. Burimov, V. S. Letokhov, and A. P. Sviridov, Laser Chem. **1**, 133 (1983).

[3] P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions*, Wiley, 1972.

[4] H. Raisler, F. B. T. Pessine, and C. Wittig, Chem. Phys. Lett. **99**, 388 (1983).

[5] D. M. Rayner and P. A. Hackett, *ibid.* **110**, 482 (1984).

[6] V. M. Apatin and G. N. Makarov, Pis'ma Zh. Eksp. Teor. Fiz. **38**, 120 (1983) [JETP Lett. **38**, 141 (1983)].

[7] V. M. Apatin, V. N. Bagratashvili, S. I. Ionov, *et al.*, Chem. Phys. Lett. **127**, 438 (1986).

[8] V. N. Bagratashvili, S. I. Ionov, V. M. Kuz'min, and V. S. Letokhov, Zh. Eksp. Teor. Fiz. **91**, 766 (1986) [Sov. Phys. JETP 64 No. 3, (1986).

[9] V. M. Apatin, L. M. Dorozhkov, G. N. Makarov, and G. M. Pleshkov, Appl. Phys. B**29**, 273 (1982).

[10] V. M. Apatin and G. N. Makarov, Zh. Eksp. Teor. Fiz. **84**, 15 (1983) [Sov. Phys. JETP **57**, 8 (1983)].

[11] H. Burger and G. Pawelke, Spectrochim. Acta **35**A, 553 (1979).

[12] V. S. Letokhov and A. A. Makarov, Zh. Eksp. Teor. Fiz. **63**, 2064 (1972) [Sov. Phys. JETP **36**, 1091 (1973)].

[13] P. A. Hackett, C. Willis, and M. Gauthier, J. Chem. Phys. **71**, 2682 (1979).

[14] J. L. Lyman and K. M. Leary, *ibid.* **69**, 1958 (1978).

[15] G. P. Quigley and J. L. Lyman, *Laser-Induced Processes in Molecules*, Springer, 1979, p. 134.

[16] J. L. Lyman, W. C. Danen, A. C. Nilson, and A. V. Novak, J. Chem. Phys. **71**, 1206 (1979).

[17] O. P. Judd, *ibid.* **71**, 4515 (1979).

[18] A. I. Boriev, E. B. Gordon, A. A. Nadeikin, *et al.*, Chem. Phys. Lett. **105**, 555 (1984).

[19] J. L. Lyman, G. P. Quigley, and O. P. Judd, in: Multiple-Photon Excitation and Dissociation of Polyatomic Molecules, C. Cantrell, ed., Springer, Berlin, Report LA-UR 79-2605, 1981.

[20] W. Fuss and K. Kompa, Progr. Quant. Electr. **7**, 117 (1981).

[21] R. V. Ambartsumyan, G. N. Makarov, and A. A. Puretskii, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 246 (1978) [JETP Lett. **28**, 228 (1978)].

[22] V. M. Apatin and G. N. Makarov, Kvant. Elektron. (Moscow) **9**, 1668 (1982) [Sov. J. Quant. Electron. **12**, 1067 (1982)].

[23] R. V. Ambartzumian, V. S. Letokhov, G. N. Makarov, and A. A. Puretzky, Opt. Comm. **25**, 69 (1978).

[24] J. Troe, J. Chem. Phys. **66**, 4745 (1977).

[25] H. Hippler, J. Troe, and H. J. Wendelken, *ibid.* **78**, 5351 (1983).

Translated by J. G. Adashko