

# Effect of mid- and far-infrared emission from excited ammonia on the absorption of intense TEA CO<sub>2</sub> laser radiation

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When ammonium molecules are excited by the intense radiation of a TEA CO<sub>2</sub> laser, reemission is observed in the mid-infrared (MIR,  $\lambda \approx 12 \mu\text{m}$ ) and far-infrared (FIR,  $\lambda \geq 100 \mu\text{m}$ ) ranges even at comparatively low ammonia pressures  $p \leq 0.1$  torr. The effect of this process on the IR absorption of ammonia under collisional and collisionless excitation conditions at ammonia pressures from 0.5 to 0.03 torr has been investigated experimentally. The dependence of the energy of the MIR and FIR emission on the ammonia pressure and on the pump energy density has been studied. Special attention has been focused on the kinetics of the appearance of MIR and FIR emission at various ammonia pressures and on the measurement of the time delay of the reemission pulses relative to the exciting pulse of the CO<sub>2</sub> laser. It has been established that the reemission in the MIR range has a pronounced collisional character. As the ammonia pressure decreases, the intensity drops sharply (as  $p^3$ ), and the delay time relative to the exciting laser pulse increases. At the same time, reemission in the FIR range [in the case of the resonant excitation of ammonia in the 9R(30) line of the CO<sub>2</sub> laser] is observed during the pump pulse down to  $p \leq 0.03$  torr. Coupling the rotational sublevels of the molecules by transitions, FIR emission plays a role in rotational relaxation and thereby causes an increase in the IR absorption of ammonia even under collisionless excitation conditions. © 1995 American Institute of Physics.

## 1. INTRODUCTION

Despite the abundance of results from investigations of the multiphoton excitation and dissociation of molecules by intense IR laser radiation,<sup>1–3</sup> there is still no clear understanding of the mechanisms of the excitation of molecules in low vibrational states, anomalously strong absorption, and the involvement of a large fraction of molecules from many rotational states in the interaction with an IR field.<sup>4–8</sup> At the same time, knowledge of these mechanisms is extremely important both from the fundamental viewpoint, for understanding the physics of the interaction of a multilevel quantum system with an intense IR field, and from the practical viewpoint, for optimizing directed photophysical and photochemical processes.

Several models (dynamic field broadening of transitions,<sup>9,10</sup> anharmonic splitting of levels,<sup>11</sup> saturation of weak transitions,<sup>12</sup> rotational compensation of anharmonicity,<sup>13</sup> and multiphoton transitions<sup>14,15</sup>) have been proposed to explain the excitation of molecules in an intense IR laser field.

Some experimental data on multiphoton excitation are satisfactorily explained using these models. On the other hand, most of the observations, including the results on the excitation of molecules from individual vibration-rotation states,<sup>7,8,16</sup> are not explained by the existing theoretical models.<sup>17,18</sup> This refers primarily to the results on the excitation efficiency and on the anomalously strong absorption of molecules in an intense IR laser field. The experimentally observed absorption of molecules greatly exceeds the theoretically predicted value.

The statements encountered in the literature to the effect

that exact knowledge of the spectroscopy of the lower vibrational levels, particularly consideration of all the multistep and multiphoton transitions, will make it possible to account for all the observed excitation characteristics have not yet been confirmed.

To better understand the mechanism of the excitation of molecules in the lower vibration–rotation transitions, in Ref. 19 we selected a comparatively simple system, viz., the ammonia molecules, NH<sub>3</sub>. Multiphoton excitation is extremely ineffective in this case due to the large inversion splitting of the levels of the excited  $\nu_2$  mode.<sup>20</sup> Another useful special feature of ammonia is that it has a well resolved vibration-rotation spectrum in the  $\nu_2$  band.<sup>21</sup> This makes it possible to selectively vary the excitation conditions from exact resonance with a specific transition of the molecule to large detuning of the laser emission frequency from the nearest molecular vibration-rotation line even when a discretely tunable TEA CO<sub>2</sub> laser is used.

It was shown in Ref. 19 that ammonia can be efficiently excited by nonresonant pumping owing to dynamic field broadening and that the anomalously strong absorption observed is attributable to the generation of far-infrared (FIR) radiation, which eliminates the narrow rotational neck, during the IR excitation of ammonia. Emptying of the nonresonant rotational sublevels by resonant pumping of ammonia in single-photon vibration-rotation transitions was subsequently discovered at comparatively low ammonia pressures ( $p \leq 0.05$  torr) in Ref. 22. This finding is qualitatively consistent with the results in Ref. 19 on the generation of FIR

radiation during the excitation of  $\text{NH}_3$  by a pulsed  $\text{CO}_2$  laser.

At the same, it follows from Ref. 19 that the anomalously strong absorption of ammonia is only partially attributable to the generation of FIR radiation, since the absorption of energy from the IR field by the molecules significantly exceeds the calculated value even when reemission in the FIR range was taken into account. In  $\text{NH}_3$  excitation reemission may occur also in the mid-infrared (MIR) range.<sup>23</sup>

It is clear that molecular absorption is affected by reemission only if it occurs during the exciting pulse and is sufficiently efficient. At the same time, the efficiency of reemission can depend greatly on the excitation conditions (the  $\text{NH}_3$  pressure in the cell, the energy of the exciting pulse, the detuning of the laser frequency from the transitions in the molecule, etc.). For this reason, it would be interesting to investigate the influence of MIR and FIR emission on the absorption of ammonia under diverse excitation conditions. This was the purpose of the present research.

The work included an experimental investigation of how the MIR and FIR radiation generated when ammonia was pumped by intense radiation from a TEA  $\text{CO}_2$  laser affects the absorption of  $\text{NH}_3$  under collisional and collisionless excitation conditions at pressures from 0.5 to 0.03 torr. The energy of the emitted radiation was studied as a function of the  $\text{NH}_3$  pressure and the energy density of the exciting pulse. Special attention was focused on an investigation of the kinetics of appearance of MIR and FIR emission at various ammonia pressures and on measurement of the time delay of the reemitted pulses relative to the exciting pulse of the  $\text{CO}_2$  laser.

## 2. EXCITATION OF AMMONIA MOLECULES

Diagrams of the experiments devised to measure the energy absorbed by  $\text{NH}_3$  molecules and to observe reemission in the MIR and FIR ranges are presented in Fig. 1.

A pulsed TEA  $\text{CO}_2$  laser, which can be tuned by means of a diffraction grating, was used to excite the ammonia molecules. The output pulse, which had the form of a peak with a width of  $\approx 100$  ns at half-maximum and no "tail," was achieved by employing a mixture of gases with a small nitrogen content as the active medium ( $\text{CO}_2:\text{N}_2:\text{He}=4:1:16$ ). The width of the emission spectrum of the laser  $\Delta\nu_L \approx 0.013$   $\text{cm}^{-1}$  (Ref. 24). To achieve a uniform distribution of the emission intensity over the cross section of the beam, the most homogeneous central part of the spot was cut out by a diaphragm with a diameter equal to 1.5 cm. Beyond the diaphragm, the radiation was directed into a cell with ammonia. Chemically pure ammonia at room temperature was used in the experiments.

The cells for measuring the energy absorbed by the  $\text{NH}_3$  molecules were fabricated from stainless steel and had Brewster windows made from NaCl or KBr. The lengths of the cells were equal to 100 cm and 25 cm, and their diameter was equal to 2.7 cm. Cells with lengths equal to 100 cm, 200 cm, and 260 cm (and a diameter of 2 cm) made from a copper tube and replaceable windows (NaCl or KBr entrance windows and KBr, Teflon, or crystalline quartz exit windows) to permit the excitation of  $\text{NH}_3$  by the emission of a

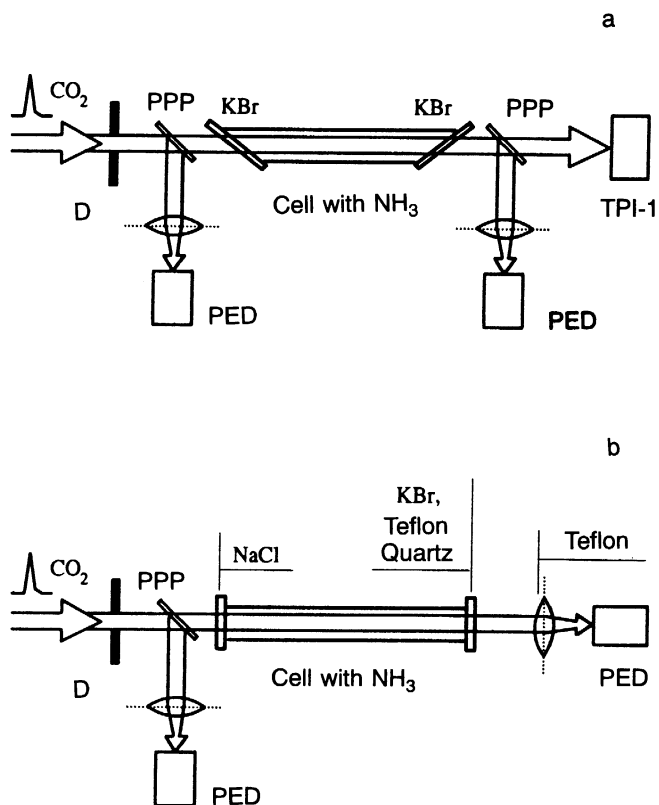


FIG. 1. Diagrams of the experimental apparatus for measuring the energy absorbed by  $\text{NH}_3$  molecules (a) and for measuring the energy of the MIR and FIR radiation generated when ammonia is excited by a TEA  $\text{CO}_2$  laser (b) TPI-1—absolute energy meter, PED—pyroelectric detector, PPP—plane-parallel plates, D—diaphragm.

$\text{CO}_2$  laser and detection of the IR output emerging from the cell were used in the experiments to observe the MIR and FIR emission. Before the gas was admitted, the cells were evacuated to  $p \approx 10^{-3}$  torr.

In these experiments the ammonia molecules were excited in most cases by the  $9R(30)$  line of the  $\text{CO}_2$  laser ( $1084.63$   $\text{cm}^{-1}$ ), which is in fairly close resonance with the  $sR(5,K)$  multiplet of  $^{14}\text{NH}_3$ . The detuning to the nearest  $sR(5,0)$  line is  $\Delta\nu \approx 0.006$   $\text{cm}^{-1}$ . The detuning to the  $sR(5,1)$  and  $sR(5,2)$  lines is  $\Delta\nu \approx 0.01$   $\text{cm}^{-1}$  and  $\Delta\nu \approx 0.025$   $\text{cm}^{-1}$ , respectively.<sup>21</sup>

For the purpose of ascertaining the conditions under which reemission in the MIR and FIR ranges is observed,  $\text{NH}_3$  was also excited in other lines:  $10P(32)$  at  $932.96$   $\text{cm}^{-1}$ ,  $10R(8)$  at  $967.71$   $\text{cm}^{-1}$ ,  $10R(14)$  at  $971.93$   $\text{cm}^{-1}$ , and  $9P(20)$  at  $1046.85$   $\text{cm}^{-1}$ . The emission of the TEA  $\text{CO}_2$  laser in these lines is also absorbed strongly by ammonia.<sup>19</sup> The frequency detuning to the nearest ammonia lines (multiplets) is:  $\Delta\nu \approx 0.03$   $\text{cm}^{-1}$  for  $10P(32)$  and  $aQ(5,3)$  of  $^{14}\text{NH}_3$ ,  $\Delta\nu \approx 0.03$   $\text{cm}^{-1}$  for  $10R(8)$  and  $sQ(2,K)$ ,  $\Delta\nu \approx 0.05$   $\text{cm}^{-1}$  for  $10R(14)$  and  $aR(1,1)$ , and  $\Delta\nu \approx 0.44$   $\text{cm}^{-1}$  for  $9P(20)$  and  $sR(3,K)$  of  $^{14}\text{NH}_3$ .

The energy absorbed by the  $\text{NH}_3$  molecules was measured by a direct calorimetric method. The energy of the  $\text{CO}_2$  laser pulse at the entrance to the cell and at the exit from it was measured in the experiments by pyroelectric detectors. The pyroelectric detectors were calibrated using a TPI-1 ab-

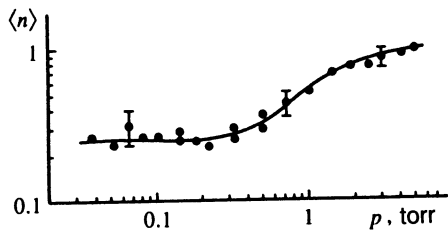


FIG. 2. Pressure dependence of the average number of photons absorbed by an ammonia molecule for the excitation of  $\text{NH}_3$  in the  $sR(5, K)$  transition at  $1084.6 \text{ cm}^{-1}$  by the  $9R(30)$  line of a  $\text{CO}_2$  laser. The energy density of the exciting pulse was  $\Phi=0.35 \text{ J/cm}^2$ .

solute laser output energy meter. Measurements were performed with and without gaseous  $\text{NH}_3$  in the cell. Plane-parallel  $\text{CaF}_2$  plates with a thickness of 1 mm served as attenuators of the laser output. Absolute adjustment was made using the results of direct measurement of the energy absorbed "in passing" by the TPI-1 meter at ammonia pressures equal to  $\approx 0.5$  torr.

Figure 2 presents the dependence of the average number  $\langle n \rangle$  of quanta absorbed by one  $\text{NH}_3$  molecule on the ammonia pressure for the excitation of  $\text{NH}_3$  by the  $9R(30)$  line of the  $\text{CO}_2$  laser when the energy density of the exciting radiation was  $\Phi=0.35 \text{ J/cm}^2$ . The parameter  $\langle n \rangle$  was defined as

$$\langle n \rangle = E_{\text{ab}} / \hbar \omega V N, \quad (1)$$

where  $E_{\text{ab}}$  is the laser output energy absorbed by the ammonia molecules,  $E_{\text{ab}} = E_{\text{in}} - E_{\text{tr}} - E_{\text{w}}$  ( $E_{\text{in}}$  and  $E_{\text{tr}}$  are the energies of the laser pulse incident to the cell and transmitted through it when  $\text{NH}_3$  is present in the cell,  $E_{\text{w}}$  is the energy loss in the windows of the cell,  $E_{\text{w}} = E_{\text{in}} - E_{\text{tr}}^0$  ( $E_{\text{tr}}^0$  is the energy of the laser pulse transmitted through the cell when no gas is present in it),  $\hbar \omega$  is the energy of a quantum of the laser output,  $V$  is the excited volume of gas in the cell ( $V = SL$ ,  $S$  is the cross-sectional area of the laser beam cut out by the diaphragm,  $L$  is the length of the cell), and  $N$  is the density of  $\text{NH}_3$  in the cell. The average value of the energy density was defined as  $\Phi = (E_{\text{in}} + E_{\text{tr}}) / 2S$ .

In order that the absorbed energy not exceed  $\approx 10\%$  of  $E_{\text{in}}$  ( $E_{\text{ab}} \approx 0.1 E_{\text{in}}$ ) over the entire range of  $\text{NH}_3$  pressures investigated, the dependence of  $\langle n \rangle$  on ( $p$ ) was measured with cells of different length:  $L = 2 \text{ m}$  (in the range  $p \leq 0.22$  torr),  $L = 1 \text{ m}$  ( $p = 0.1 - 0.6$  torr), and  $L = 20 \text{ cm}$  ( $p \geq 0.32$  torr).

It is seen from Fig. 2 that at ammonia pressures  $p \leq 0.2$  torr the energy absorbed per molecule is practically independent of the ammonia pressure. This is because the excitation of  $\text{NH}_3$  becomes collisionless at these pressures: the rotational relaxation time is greater than the laser pulse length [ $\tau_r > \tau_p$ ,  $p \tau_r \approx 50 \text{ ns} \cdot \text{torr}$  (Ref. 25),  $\tau_p \approx 100 \text{ ns}$  at half-maximum]. The increase in  $\langle n \rangle$  at  $p \approx 0.2 - 2.0$  torr is attributed to the involvement of a large fraction of the molecules in the interaction process due owing to rotational relaxation. The further increase in absorption at  $p \geq 2$  torr is probably also attributable to vibration-vibration ( $V-V$ ) exchange and vibration-translation ( $V-T$ ) relaxation processes [ $p \tau_{V-V} \approx 1.45 \mu\text{s} \cdot \text{torr}$  (Ref. 26),  $p \tau_{V-T} \approx 0.77 \mu\text{s} \cdot \text{torr}$  (Ref.

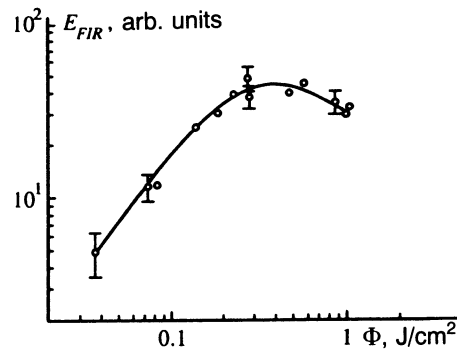


FIG. 3. Dependence of the energy of the FIR emission on the pump energy density for the excitation of  $\text{NH}_3$  in the  $sR(5, K)$  transition by the  $9R(30)$  line of a  $\text{CO}_2$  laser ( $p=0.16$  torr,  $L=260 \text{ cm}$ ).

27)]. As we shall see below, when the pressure increases, the efficiency of reemission in the MIR and FIR ranges also increases.

As is seen from Fig. 2, for example, at  $p \approx 1$  torr the average number of quanta absorbed by one molecule  $\langle n \rangle \approx 0.5$ , and at a pressure of 0.1 torr  $\langle n \rangle \approx 0.25$ . Such strong absorption by ammonia, especially under collisionless excitation conditions, is not explained using a two-level model.<sup>19</sup>

Even if it is assumed that all the molecules with a rotational quantum number  $J=5$ ,  $\approx 12\%$  in both the symmetric and asymmetric vibrational levels of the ground vibrational state at room temperature participate in absorption and that there are no other energy dissipation channels, the energy absorbed under collisionless excitation conditions must be considerably smaller than the experimentally measured value.

### 3. REEMISSION IN THE FIR AND MIR RANGES

#### 3.1. Energetic characteristics of reemission

As was shown in Ref. 19, one channel for the dissipation of energy when  $\text{NH}_3$  is excited by the intense emission from a TEA  $\text{CO}_2$  laser is reemission in the FIR range ( $\lambda \geq 100 \mu\text{m}$ ). The energy of the FIR emission was measured in Ref. 19 under  $\text{NH}_3$  excitation conditions similar to those in the present work, and the dependence of the energy of this emission on the ammonia pressure was obtained (it was found to be quadratic). However, the kinetics of the appearance of the FIR emission was not investigated in Ref. 19. It was established for only one fixed pressure  $p=0.5$  torr that reemission in the FIR range takes place during the exciting laser pulse.

In the present work we studied the kinetics of the appearance of FIR emission and obtained the dependence of its energy on the energy density of the exciting pulse. In addition, we also detected reemission in the MIR range ( $\lambda \approx 12 \mu\text{m}$ ), studied the kinetics of its appearance, and obtained plots of the dependence of its energy on the  $\text{NH}_3$  pressure and the pump energy density.

Figure 3 presents the dependence of the energy  $E_{\text{FIR}}$  of the FIR emission on the pump energy density in the case of the excitation of  $\text{NH}_3$  in the  $9R(30)$  line of a  $\text{CO}_2$  laser.

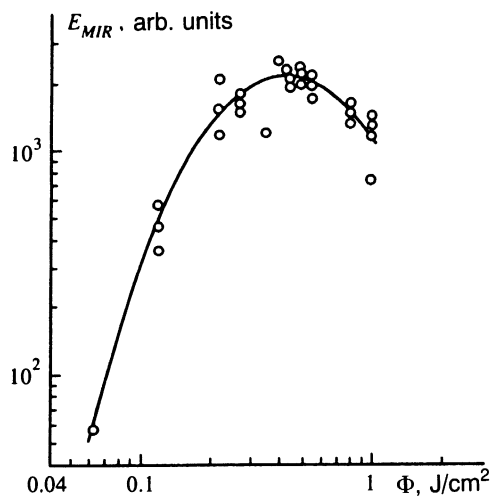


FIG. 4. Dependence of the energy of the MIR emission on the pump energy density for the excitation of  $\text{NH}_3$  in the  $sR(5,K)$  transition by the  $9R(30)$  line of a  $\text{CO}_2$  laser ( $p=0.2$  torr,  $L=260$  cm).

Ammonia was excited in a cell with a length of 260 cm at a pressure equal to 0.16 torr. In the range of energy densities investigated the dependence is linear from 0.03 to 0.2  $\text{J}/\text{cm}^2$ . When the pump energy density increases further, the energy of the submillimeter emission decreases. The maximum re-emission energy is observed at an energy density of the exciting pulse  $\Phi=0.4 \text{ J}/\text{cm}^2$ .

Figure 4 presents the dependence of the energy of the MIR emission on the energy density of the exciting pulse when the  $\text{NH}_3$  pressure in the cell is 0.2 torr. The remaining conditions for the excitation of ammonia were the same as in the case of Fig. 3 [the  $9R(30)$  line,  $L=260$  cm]. We note that the plot in Fig. 4 is steeper than the plot in Fig. 3. In the range of  $\Phi$  investigated it is nearly quadratic from  $\approx 0.06$  to 0.2  $\text{J}/\text{cm}^2$ . At  $\Phi=0.5\text{--}0.6 \text{ J}/\text{cm}^2$  the value of  $E_{\text{MIR}}$  reaches a maximum, and when the pump energy density increases further, its value decreases, as in the case of the submillimeter emission.

Figure 5 shows how  $E_{\text{MIR}}/p$  depends on the ammonia

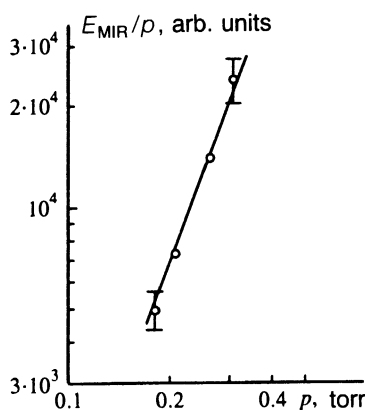


FIG. 5. Dependence of the energy of the MIR emission on the ammonia pressure for the excitation of  $\text{NH}_3$  in the  $sR(5,K)$  transition by the  $9R(30)$  line of a  $\text{CO}_2$  laser ( $\Phi=0.5 \text{ J}/\text{cm}^2$ ,  $L=260$  cm).

pressure. This dependence is also nearly quadratic, and without normalization to the pressure it is nearly cubic. The analogous dependence normalized to the ammonia pressure for submillimeter emission is linear.<sup>19</sup> Thus, both the dependence on the excitation energy density and the dependence on the ammonia pressure for MIR emission are steeper than those for FIR emission.

It follows from the results presented in Figs. 4 and 5 that the reemission of  $\text{NH}_3$  in the MIR range is inefficient at low ammonia pressures and low pump energy densities. For example, at the energy densities  $\Phi \approx 0.5 \text{ J}/\text{cm}^2$  which are optimal in the case of the excitation of  $\text{NH}_3$  in the  $9R(30)$  line of a  $\text{CO}_2$  laser, we observed emission in the MIR range only at  $p \geq 0.08$  torr ( $L=260$  cm). It was not observed at lower ammonia pressures. We note that we likewise did not detect it in the case of the excitation of  $\text{NH}_3$  at  $p \leq 4$  torr in other lines of the  $\text{CO}_2$  laser:  $10P(32)$ ,  $10R(8)$ ,  $10R(14)$ , and  $9P(20)$ . At the same time, emission in the FIR range was detected when ammonia was excited in these lines, but only at comparatively high pressures:  $p \geq 4$  torr in the  $10R(14)$  line, and  $p \geq 10$  torr in the  $9P(20)$  line. Here the energy density of the exciting pulse was  $\approx 0.5 \text{ J}/\text{cm}^2$ .

Thus, it should be concluded on the basis of the results obtained that in the case of the nonresonant excitation of ammonia in lines of the  $\text{CO}_2$  laser which are detuned from transitions of this molecule by  $0.03\text{--}0.45 \text{ cm}^{-1}$ , i.e., by an amount exceeding the output linewidth of the  $\text{CO}_2$  laser [ $\Delta\nu = 0.013 \text{ cm}^{-1}$  (Ref. 24)], the generation of MIR and FIR radiation is not observed in a cell without a resonator when  $p \leq 4$  torr,  $\Phi \leq 0.5 \text{ J}/\text{cm}^2$ , and  $L \leq 260$  cm. Therefore, the absorption of ammonia under these conditions is not subject to the influence of reemission.

### 3.2. Kinetics of the appearance of MIR and FIR emission

The next stage of the research involved studying the kinetics of the appearance of submillimeter and MIR emission the resonant excitation of ammonia in the  $sR(5,K)$  transition by the  $9R(30)$  line of the  $\text{CO}_2$  laser. For this purpose we used a pyroelectric detector with a response rise time equal to  $\approx 200$  ns. This enabled us to observe the form of the leading edges of the pulses of submillimeter and MIR radiation with the temporal resolution indicated, as well as the delay times of these pulses relative to the exciting pulse of the  $\text{CO}_2$  laser.

The signal from the pyroelectric detector was fed through an amplifier ( $\times 100$ ) into an S8-13 oscillograph. We measured the characteristic rise times of the leading edges of the FIR pulses at various ammonia pressures in the range from 0.025 to 0.6 torr and of the MIR pulses in the pressure range from 0.1 to 0.7 torr. The results are presented in Fig. 6. It was found that the emission in the MIR range has a collisional character. It is delayed relative to the exciting pulse of the  $\text{CO}_2$  laser, the delay being greater, the lower is the  $\text{NH}_3$  pressure. For  $p \leq 0.1$  torr the delay time is  $\geq 1.5 \mu\text{s}$ , which significantly exceeds the duration of the exciting pulse of the  $\text{CO}_2$  laser. Therefore, at  $p \leq 0.1$  torr reemission in the MIR range does not influence the absorption of ammonia also in the case of the resonant excitation of  $\text{NH}_3$  in the  $sR(5, K)$  transition by the  $9R(30)$  line of the  $\text{CO}_2$  laser. At the same

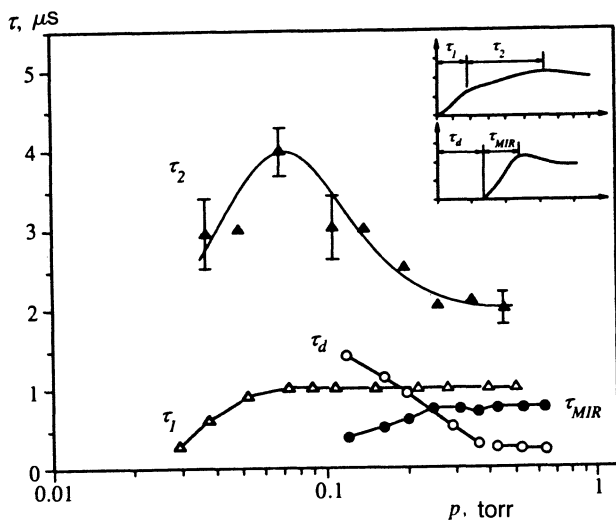


FIG. 6. Dependence of the characteristic rise times of the leading edge of the pulse of FIR radiation ( $\tau_1$  and  $\tau_2$ ), the delay time ( $\tau_d$ ) and the characteristic rise time of the leading edge of the pulse of MIR radiation ( $\tau_{MIR}$ ), on the ammonia pressure for the excitation of  $\text{NH}_3$  in the  $sR(5, K)$  transition by the  $9R(30)$  line of a  $\text{CO}_2$  laser ( $\Phi=0.35 \text{ J/cm}^2$ ,  $L=260 \text{ cm}^{-1}$ ).

time, FIR emission is observed over the course of the exciting pulse down to pressures  $p \approx 0.025$  torr. The leading edge of the pulse of FIR radiation is characterized by two times  $\tau_1$  and  $\tau_2$ , as is shown in Fig. 6, which depend in totally different manners on the ammonia pressure. We note the presence of a maximum on the plot of the dependence of  $\tau_2$  on the  $\text{NH}_3$  pressure.

### 3.3. Discussion of results on the generation of MIR and FIR radiation

As was shown in Ref. 19 in the case of the excitation of ammonia in the  $sR(5, K)$  transition by the  $9R(30)$  line of a  $\text{CO}_2$  laser for  $\Phi=0.35 \text{ J/cm}^2$  and  $p=0.5$  torr ( $L=1 \text{ m}$ ), the energy of the FIR emission was  $E_{\text{FIR}} \approx 10 \text{ mJ}$  under conditions such that the total energy absorbed by the ammonia molecules was  $\approx 30 \text{ mJ}$ . Since a quantum of FIR output ( $\lambda \geq 100 \mu\text{m}$ ) is at least an order of magnitude smaller than a quantum from the  $\text{CO}_2$  laser, such a large energy can be reemitted only through cascade transitions. Such cascade reemission of ammonia was observed in Ref. 28. Figure 7 presents a diagram of the excitation of ammonia by the  $9R(30)$  line of a  $\text{CO}_2$  laser and several possible channels for reemission in the FIR and MIR ranges with consideration of the selection rules  $\Delta J=0, \pm 1$ ;  $s \leftrightarrow a$ . The  $K$  sublevels, which are associated with the projection of the angular momentum  $J$  onto the rotation axis, are not shown. The process of collisional rotational relaxation of the molecules is likewise not shown in Fig. 7. The fact that ammonia reemits in the MIR and FIR ranges when excited by a pulse from a  $\text{CO}_2$  laser is well known.<sup>23,28,29</sup> Ammonia molecular lasers with pumping by the output of a  $\text{CO}_2$  laser, which emit in both the MIR<sup>30,31</sup> and FIR<sup>32,33</sup> ranges, have also been thoroughly studied. However, fairly high ammonia pressures (several torr) are usually used with these lasers. The fundamental

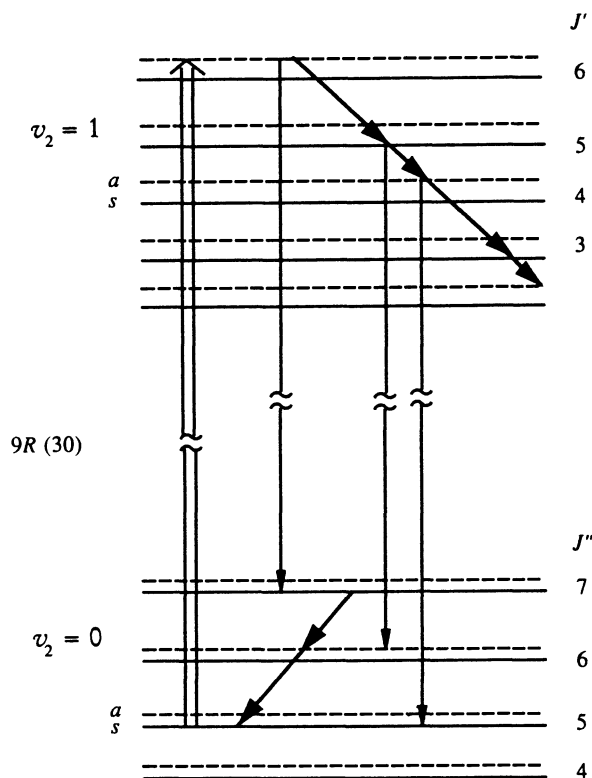


FIG. 7. Diagram of the excitation of  $\text{NH}_3$  in the  $sR(5, K)$  transition by the  $9R(30)$  line of a  $\text{CO}_2$  laser and some possible channels for the reemission of ammonia in the MIR (thin arrows) and FIR (thick arrows) ranges.

distinguishing feature of our experiments is that we observed the reemission of  $\text{NH}_3$  in a cell without a resonator and at low pressures in the range  $p \leq 0.1$  torr.

The wavelengths of the FIR emission were not identified in our experiments. Two cascades of transitions are possible in this range when ammonia is excited in the  $sR(5, K)$  transition: a cascade between the low-lying rotational sublevels of the excited vibrational state  $v_2=1$ , which begin from a state populated by the  $\text{CO}_2$  emission ( $J'=6, a$ ) and a cascade between the high-lying rotational sublevels of the ground vibrational state  $v_2=0$ , which ends at the level emptied by the  $\text{CO}_2$  emission ( $J''=5, s$ ). Lasing in the FIR range in a transition ( $v_2=1, J=6, K=0, a$ )  $\rightarrow$  ( $v_2=1, J=5, K=0, s$ ) with  $\Delta\nu=67.6 \text{ cm}^{-1}$  was identified in Ref. 23 and probably also occurred in our experiments. In the MIR range, as we established using an IR monochromator, the most intense emission is observed at  $828 \text{ cm}^{-1}$  and  $815 \text{ cm}^{-1}$  and is unquestionably associated with the  $sP(7, K)$  and  $aP(6, K)$  transitions, respectively.

Without dwelling on the theoretical interpretation of reemission,<sup>34,35</sup> we present an estimate of the gain for the above transition in the submillimeter range at a pressure  $p=0.1$  torr, at which the collisionless excitation of ammonia is realized. For the ammonia  $v_2=1$  level we have  $p\tau_r \approx 20 \text{ ns}\cdot\text{torr}$  (Refs. 25 and 36), and the rotational relaxation rate constant  $k' = 1/p\tau_r = 5 \times 10^7 \text{ s}^{-1}\cdot\text{torr}^{-1}$ . Therefore, the homogeneous linewidth  $\gamma_{\text{col}} \approx k'p \approx 5 \text{ MHz}$  of the rotational transition is comparable to the Doppler linewidth at a fre-

quency  $\nu \approx 68 \text{ cm}^{-1}$  ( $\Delta\nu_D \approx 6 \text{ MHz}$ ). Hence the amplification cross section at the center of the line is  $\sigma_0 \approx 4\pi\mu^2\omega/\hbar c \gamma_{\text{col}}$ . For  $\mu \approx 1 \text{ D} = 10^{-18} \text{ esu}$  we find  $\sigma_0 \approx 10^{-12} \text{ cm}^2$ . For a stationary inverse population  $N = qp$  ( $q \approx 1\%$ , i.e., the percentage of excited molecules), the gain is  $\alpha = \sigma_0 N \approx 35 \text{ cm}^{-1}$ . Then for the gain under the conditions of a homogeneously broadened line we have<sup>37</sup>

$$dI/dz = \alpha I(I + I_{\text{sat}}), \quad (2)$$

where the saturation intensity is determined from the condition  $\sigma_0 I_{\text{sat}} \sim k'p$ . In the limit  $I \gg I_{\text{sat}}$  (as in our experiments), the intensity of the output radiation is  $I_{\text{out}} \sim \sigma_0 N I_{\text{sat}} L$ , and the total energy

$$E_{\text{FIR}} \sim qk' L p^2 S \tau_p, \quad (3)$$

where  $S$  is the cross section of the pump beam and  $\tau_p$  is the length of the pulse of submillimeter radiation. For  $L = 1 \text{ m}$  and  $p = 0.1 \text{ torr}$ , the substitution of specific parameters leads to agreement between estimate (3) and the experimental results in Ref. 19. The quadratic dependence of  $E_{\text{FIR}}$  on the pressure is also correctly described.

We note that FIR lasing has been observed under similar experimental conditions for several polyatomic molecules, such as  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CF}_2\text{Cl}_2$ , etc. (see Ref. 38 and the references cited therein). Therefore, this effect cannot be neglected when the multiphoton excitation of molecules is described. A similar effect may have occurred in Refs. 39 and 40, where the IR absorption of ozone under pulsed excitation was studied, and the good agreement with the calculations at small  $\langle n \rangle$  broke down as the pump energy density increased.

Let us now discuss the energetic and temporal characteristics of the MIR and FIR emission. One interesting special feature is the presence of a maximum on the plots of the dependence of  $E_{\text{FIR}}$  and  $E_{\text{MIR}}$  versus the energy density of the exciting pulse of the  $\text{CO}_2$  laser. Note that similar behavior, i.e., the achievement of a maximum value followed by a decrease in the output energy as the intensity of the exciting pulse increases, has been theoretically predicted<sup>41,42</sup> and experimentally observed<sup>43</sup> in optically pumped molecular lasers. This phenomenon is attributed to the nonlinear processes occurring in such lasers: two-photon transitions and the dynamic Stark effect.<sup>42,43</sup>

If a pump field and a stimulated-emission field are simultaneously present in a molecular medium and are coupled by a common level (for example, in Fig. 7 the  $J' = 6$ ,  $a$  level may be regarded as such a level), such a system is equivalent to a three-level molecular system interacting with two resonant fields (a pump field and a stimulated-emission field). As the strength of the pump field in such a system increases, the probability of two-photon transitions increases strongly, with a resultant rapid increase in the output energy of the molecular laser. Furthermore, saturation of the two-photon transitions occurs when  $I > I_{\text{sat}}$ . At the same time, as the intensity increases at  $I > I_{\text{sat}}$ , the dynamic Stark effect results in broadening of the lines and a decrease in gain. As a result, the output energy of the molecular laser drops.<sup>42,43</sup>

In our opinion, in the case of the excitation of  $\text{NH}_3$  and several other polyatomic molecules, there is another mecha-

nism for reducing the reemission energy as the pump energy increases, viz., the excitation of molecules to higher-lying vibration-rotation states and the resultant "depletion" of the population of the first vibrational level. In our opinion, this is confirmed by the monotonic increase in the energy absorbed by  $\text{NH}_3$  molecules as the energy density of the exciting pulse increases.<sup>19</sup>

Speaking about the energetic and temporal characteristics of reemission, we should dwell briefly on the possibility of observing the phenomenon of collective spontaneous emission or superradiance.<sup>44,45</sup> An important condition for observing superradiance is satisfaction of the inequality  $r < \lambda$ , where  $r$  is the distance between emitting particles and  $\lambda$  is the wavelength of the emission. In our case, this condition is satisfied, i.e.,  $r \ll \lambda$ , even at the low pressures investigated ( $p \approx 0.03 \text{ torr}$ ), since we have  $r \approx 10^{-5} \text{ cm} = 0.1 \text{ }\mu\text{m}$  and  $\lambda \approx 100 \text{ }\mu\text{m}$ .

It is known that under the conditions of superradiance all  $N$  excited molecules in the interaction volume emit photons cooperatively, and the macroscopic dipole moment of the molecules is  $N$  times greater than the dipole moment of an individual molecule. Consequently, the emission is strongly directed, and it forms in a pulse, whose peak intensity is proportional to  $N^2$  and whose length equals<sup>45,46</sup>

$$\tau_p = 8\pi\tau_s/3\rho\lambda^2 l, \quad (4)$$

where  $\tau_s$  is the spontaneous lifetime of an individual dipole,  $\rho$  is the number density of the molecules, and  $l$  is the length of the medium. The pulse emitted is delayed relative to the exciting pulse by a time<sup>46</sup>

$$\tau_d = \frac{\tau_p}{4} (\ln \sqrt{2\pi N})^2, \quad (5)$$

which is necessary for phasing the dipoles and is usually 10–100 times greater than  $\tau_p$ .

In the case of amplified spontaneous emission, the individual dipoles are dephased, there is no time delay, and the peak intensity of the emission ceases to be proportional to  $N^2$ .

Let us estimate these times. The spontaneous decay probability  $\gamma_s$  equals<sup>47</sup>

$$\gamma_s = 1/\tau_s = \frac{4\omega^3}{3\hbar c^3} |d|^2 = \frac{32\pi^3}{3\hbar\lambda^3} |d|^2, \quad (6)$$

where  $\omega = 2\pi\nu$  is cyclic frequency,  $c$  is the velocity of light, and  $d$  is the transition dipole moment. If we take  $d = 1 \text{ debye} = 10^{-18} \text{ esu}$  and  $\lambda = 100 \text{ }\mu\text{m} = 10^{-2} \text{ cm}$  in order to evaluate  $\gamma_s$ , we obtain  $\gamma_s \approx 0.3 \text{ s}^{-1}$ , and  $\tau_s \approx 3 \text{ s}$ . To evaluate  $\tau_p$  and  $\tau_d$ , in (4) and (5) we set  $l = 100 \text{ cm}$ ,  $\rho = 3.5 \times 10^{13} \text{ cm}^{-3}$  ( $p = 0.1 \text{ torr}$ , and the percentage of excited molecules is assumed to be equal to 1%), and  $N = 3.5 \times 10^{13}$ , which is the total number of excited molecules. Plugging the value of  $\tau_s$  into (4) and (5) and performing the appropriate calculations, we obtain  $\tau_p \approx 7.5 \times 10^{-11} \text{ s}$  and  $\tau_d \approx 5 \times 10^{-9} \text{ s}$ .

It should be stated that the time resolution of our recording system did not enable us to observe such short times. The exciting pulse of the  $\text{CO}_2$  laser was also too long ( $\approx 100 \text{ ns}$ ) to measure such short durations. The maximum that we observed on the plot of  $\tau_2(p)$  (see Fig. 6) is possibly a mani-

festation of the aforementioned process of phasing and dephasing of the dipoles.<sup>46</sup> However, separate investigations are needed to establish this.

#### 4. CONCLUSIONS

In conclusion, we summarize the main results and their implications.

It has been shown in this paper that the excitation of ammonia molecules by the intense emission of a TEA CO<sub>2</sub> laser at the comparatively low ammonia pressures  $p \leq 0.1$  torr produces reemission in the MIR and FIR ranges.

The influence of this reemission on the absorption of ammonia under collisional and collisionless NH<sub>3</sub> excitation conditions has been investigated (at pressures from 0.5 to 0.03 torr in the case of the resonant excitation of ammonia and at  $\leq 10$  torr in the case of nonresonant excitation).

The energetic characteristics and the kinetics of the appearance of MIR and FIR emission, as well as the delay times of the pulses of MIR and FIR radiation relative to the exciting pulse of the CO<sub>2</sub> laser, have been studied.

It has been shown that in the case of the excitation of NH<sub>3</sub> in a cell without a resonator ( $L \leq 100$  cm) by lines of the CO<sub>2</sub> laser that are detuned from transitions of the molecule by  $\Delta\nu \geq 0.03$  cm<sup>-1</sup>, which exceeds the output linewidth of the CO<sub>2</sub> laser [ $\Delta\nu_L = 0.013$  cm<sup>-1</sup> (Ref. 24)], at pressures  $p_{\text{NH}_3} \leq 4$  torr and pump energy densities  $\Phi \leq 0.3$  J/cm<sup>2</sup>, MIR and FIR radiation is not emitted. Therefore, under these conditions the absorption of ammonia is not subject to the influence of reemission.

In the case of the resonant excitation of NH<sub>3</sub> in the  $sR(5,K)$  transition by the  $9R(30)$  line of the CO<sub>2</sub> laser at pressures  $p \geq 0.5$  torr and  $\Phi \geq 0.2$  J/cm<sup>2</sup>, MIR and FIR radiation is generated during the exciting laser pulse. Reemission deactivates excited molecules and increases the energy absorbed.

At low ammonia pressures ( $p \leq 0.1$  torr), at which a collisionless excitation regime is realized, only FIR radiation is generated during the exciting pulse of the CO<sub>2</sub> laser. Playing the role of rotational relaxation, submillimeter emission causes an increase in the absorption of ammonia even under collisionless excitation conditions.

The results obtained in Ref. 19 and in the present research show that the anomalously strong absorption of ammonia in the case of resonant excitation by a pulse from a TEA CO<sub>2</sub> laser is partially attributable to reemission in other ranges. At the same time, the combined set of results from Ref. 19 and the present research points out the existence of an unknown mechanism for the excitation of NH<sub>3</sub> molecules, since even with consideration of the reemission, the energy absorbed by the molecules significantly exceeds the value calculated using the two-level model.

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