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Nonlinear Absorption and Far-Infrared Generation Under the Excitation of Ammonia Molecules by Strong IR Radiation

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We have investigated the excitation of $^{14}\text{NH}_3$ molecules (the pressure is $10^{-2} - 1$ Torr) under the effect of pulse radiation of the CO_2 -laser in a wide range of fluences ($\Phi = 10^{-3} - 10 \text{ J/cm}^2$) and detunings of the laser frequency from the absorption lines of the vibrational-rotational transition of the ammonia band ν_2 . It is shown that the efficient excitation of ammonia under the influence of nonresonance IR radiation is due to the power broadening. In this case the calculation, which employs no fitting parameters, describes the experimental results within experimental errors. It is shown that the abnormally high absorption of ammonia in the case of resonance pumping is associated with an intense FIR generation which leads to elimination of the rotational bottle neck under the excitation of molecules.

KEY WORDS: Far-infrared, NH_3 spectra, absorption, generation.

INTRODUCTION

Investigations of the interaction of high-power IR laser pulses with molecular gases have led in recent years to the intense development of a new physical field—IR photophysics and photochemistry. The reviews and monographs, which have already appeared, give insight into the wide possibilities of both fundamental investigations and applications—such as laser isotope separation and initiation of non-thermal chemical reactions (see, for example, Reference 1 and 2).

In many cases the primary photoprocess, which precedes the intra or intermolecular energy exchange or chemical reactions, is the multiple-photon IR excitation (MPE), i.e. the rapid selective heating of the vibrational degrees of freedom of the resonance absorbing gas components. In spite of the successful utilization of the MPE for studying a great variety of physico-chemical processes the microscopic description of light absorption by a polyatomic molecule is far from completion. This concerns even such an idealized (but realized in experiment!) situation when in the pre-determined IR field an isolated molecule is excited, which is the case of the collisionless MPE.

Proceeding from the generally accepted classification of the vibrational molecular levels,¹ it is possible to formulate one of the outstanding problems of theory as follows: Due to what mechanisms does the molecule absorb several IR quanta and does it find itself in the region of the vibrational quasi-continuum where according to the common viewpoints the MPE is associated with the intramolecular broadening of spectra? In the literature there are arguments that the exact knowledge of the spectroscopy of the lower vibrational levels, notably the inclusion of all multistep and multiple-photon transitions, will make it possible to explain all the MPE characteristics observed. However, these arguments have not been finally confirmed as yet. Moreover, in those cases where theoretical models provide good agreement with some experimental data (e.g. Reference 3) using the same assumptions leads to a dramatic discrepancy with the other, more complete data.⁴

In our work we have specially chosen an object (NH_3) for which the MPE is extremely inefficient due to a large value of the inversion splitting of levels of the IR active mode ν_2 .⁵ This enables one to investigate separately the excitation of the $0 \rightarrow 1$ transition in the case of those frequency detunings and fluences of laser radiation when for many other polyatomic molecules the MPE just leads to their dissociation as a result of absorption of 20 to 40 IR photons. The masking effect of the MPE on the characteristics of an elementary act of absorption is thereby ruled out. Another useful feature of ammonia is the fact that it has a well resolved vibrational-rotational spectrum of the band ν_2 . This makes it possible, even when using a line-to-line tunable TEA CO_2 -laser, to vary selectively the excitation conditions—from the exact resonance with a specific transition of a molecule to large detunings of the laser frequency from the nearest

vibrational-rotational molecular line. Figure 1 presents regions of the ammonia IR absorption spectra with the designation of NH₃ lines⁶ and the position of the experimentally used frequencies of the CO₂-laser with respect to these lines.

The nonlinear absorption of ammonia molecules has already been investigated in a number of papers.⁷⁻⁹ In particular, precisely for NH₃ the possibility of laser separation of isotopes under the IR-UV excitation was demonstrated.¹⁰ Below we give the results of a more comprehensive systematic study of the IR absorption of NH₃ with varying the three main parameters which determine the experimental conditions—the exciting field frequency, the laser fluence and the gas pressure. It will be seen that the major part of experiment was carried out under significantly collisional conditions, which is associated with the rapid collisional relaxation of ammonia ($(p\tau)_{\min} \sim 7 \text{ ns} \cdot \text{Torr}$).¹¹ Therefore both the experiment itself and its theoretical description are similar in ideology to References 12 and 13. In those papers the IR

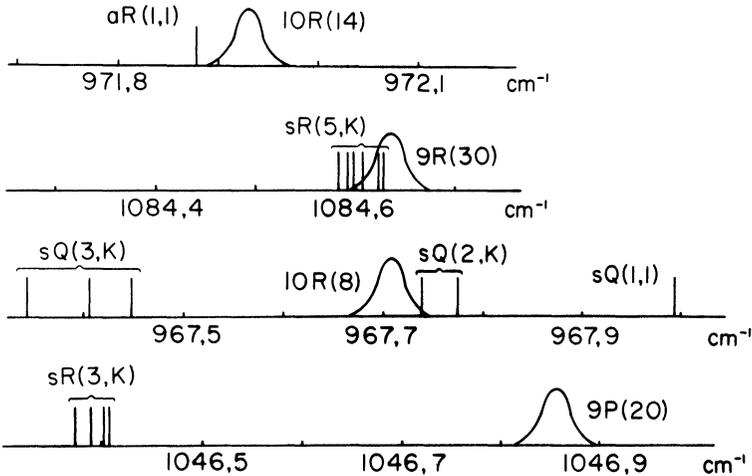


Figure 1 The frequency position of the lines (multiplets) of ammonia relative to the exciting lines of radiation of the CO₂-laser. The minimum detunings of the absorption lines from the centre of the laser line are:

$$\begin{aligned} aR(1,1) - 0.040 \text{ cm}^{-1}; & \quad sR(5,K) - 0.006 \text{ cm}^{-1}; \\ sQ(2,K) - 0.031 \text{ cm}^{-1}; & \quad sR(3,K) - 0.44 \text{ cm}^{-1}. \end{aligned}$$

The Doppler and collisional widths of the ammonia absorption lines under the experimental conditions are, respectively: $\Delta\nu_D \approx 4 \times 10^{-3} \text{ cm}^{-1}$ and $2\gamma_{\text{col}} \approx 1.1 \times 10^{-3} \text{ cm}^{-1}$ (at $p = 1 \text{ Torr}$). The width of the laser line is $\Delta\nu_{\text{las}} \sim 0.03 \text{ cm}^{-1}$.

excitation of ozone was investigated under the conditions of rotational relaxation and collisional broadening of the levels.

Preliminarily we make one more, quite trivial at first glance, remark. Dealing with an ensemble of molecules in any real experiment, it is necessary to make absolutely certain that the data obtained are correctly interpreted in terms of the quantities recalculated per particle. In the simple case, for example, it is necessary to take into account the optical thickness of an absorbing layer, but there may also be more significant changes in the parameters of the external field in passing through the medium, in particular, generation of new frequency components. This, in turn, may significantly affect the IR absorption—not only lead to reradiation of energy in other ranges but also change the cross sections for the primary process.

For ammonia the generation of both the far-infrared (FIR) (e.g. References 14 and 15) and the medium-infrared (MIR) (12–13 μm) radiation (e.g. Reference 15) with the pumping by a pulsed CO_2 -laser was demonstrated and studied in detail. However, to the best of our knowledge, these processes have not been discussed in connection with the possibility of their influence on the IR absorption, in particular, in the experiments on the MPE. At the same time, as will be shown below, under the standard conditions of such experiments (the pressure is $p \sim 0.1\text{--}1$ Torr, the duration of the pumping pulse is $\tau_p \sim 10^{-7}$ s, the laser fluence is $\Phi \approx 1$ J/cm², and a single-pass cell of length $l = 1$ m) only the inclusion of the process of FIR generation makes it possible to make both ends meet in an attempt to interpret the data obtained theoretically.

This also determines the structure of our paper. Section 2 is devoted to the description of experiment and to the results obtained on the IR absorption. Their interpretation and elucidation of the domain of applicability of the standard theory are given in Section 3. The experimental confirmation of the fact that the discrepancy between theory and experiment is due to FIR generation is outlined in Section 4. The concluding Section 5 covers the discussion and conclusions.

EXPERIMENT: IR ABSORPTION

For the excitation of ammonia molecules, use was made of a pulsed TEA CO_2 -laser tunable in frequency with the aid of a grating. The

lasing pulse represented a peak (the fwhm \approx 100 ns) with no "tail", which was obtained due to the use as an active medium of a mixture of gases with a small nitrogen content (CO₂:N₂:He = 4:1:16). The width of the spectrum of laser radiation is $\Delta\nu_{\text{las}} \sim 0.03 \text{ cm}^{-1}$. In order to attain a uniform distribution of the radiation intensity over the beam cross section, the most homogeneous central part of the laser spot was separated out with the aid of a diaphragm 1.5 cm in diameter. After the diaphragm the radiation was directed into an ammonia cell. In experiments, use was made of chemically pure ammonia at room temperature. The cell (1 m long and 2.7 cm in diameter) was made of stainless steel and provided with Brewster windows of NaCl.

The energy absorbed was measured by the optothermal method using a pyroelectric detector fitted into the cell wall, as well as by the direct calorimetric method when pyroelectric detectors were used to measure the energy of an exciting laser pulse at the input and output of the cell. The optothermal method of measuring the energy absorbed with the aid of pyroelectric detectors was described in detail in Reference 16. The maximum absorption in the cell was no more than 10–12%. The calibration was made by the results of direct measurement of the input and output laser energy $\Phi \approx 0.3 \text{ J/cm}^2$ using a calorimeter. For the excitation of ammonia, use was made of the following lines of the 9 μm and 10 μm laser generation bands: 10R(14) – 971.93 cm^{-1} , 10R(8) – 967.71 cm^{-1} , 9R(30) – 1084.63 cm^{-1} and 9P(20) – 1046.85 cm^{-1} . Figure 1 shows the relative position of the laser lines and the ammonia vibrational-rotational lines or multiplets, which are nearest to them in frequency, (the selection rules: $\Delta J = 0, \pm 1$; $\Delta K = 0$; $a \leftrightarrow s$) and which belong to the band of the IR active mode ν_2 of the molecule.

Figure 2a gives the dependences of the absorbed energy obtained (expressed in terms of the number of quanta per molecule $\langle n \rangle$) on the energy fluence for all four CO₂-laser frequencies used. Here

$$\langle n \rangle = E_{\text{abs}} (\hbar\omega_{\text{las}}VN)^{-1},$$

E_{abs} is the energy absorbed, ω_{las} is the laser frequency, V is the irradiated volume of gas in the cell, and N is the molecular concentration. In all cases the curves $\langle n(\Phi) \rangle$ have a region of linear increase and the pronounced tendency towards saturation. For the most resonance case (the line 9R(30) of the CO₂-laser) the data have been obtained at

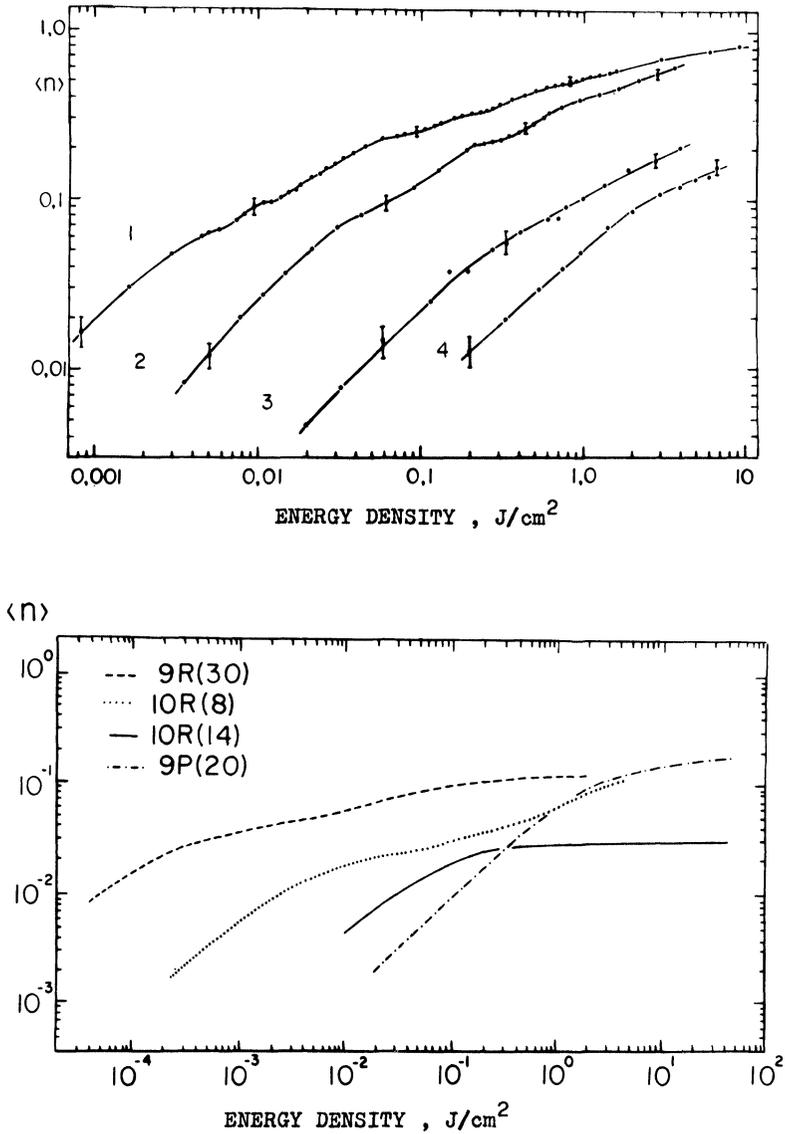


Figure 2 The dependence of the average number of absorbed photons per molecule on the laser fluence (a), experiment. The excitation on the lines 9R30(1), 10R8(2), 10R14(3) and 9P20(4) of the CO_2 -laser, (b), the calculation which neglects a possible FIR radiation; 9R30, (---); 10R8, (····); 10R14, (—) and 9P(20), (-·-·-).

an ammonia pressure of $P = 0.5$ Torr and in the other cases at $P = 1$ Torr.

The dependences of the energy absorbed on the pressure of NH₃ at different fluences of exciting radiation Φ for the line 9R(30) are displayed in Figure 3. For the other lines the pressure dependences are analogous to those presented in Figure 3 at 0.1 J/cm^2 . In particular, for the most "nonresonance" line 9P(20) of the CO₂-laser (see Figure 1) the characteristic pressure at which there occurs saturation of the dependence $\langle n(p) \rangle$ is approximately one order of magnitude higher than that in the case of resonance excitation (9R(30), Figure 3).

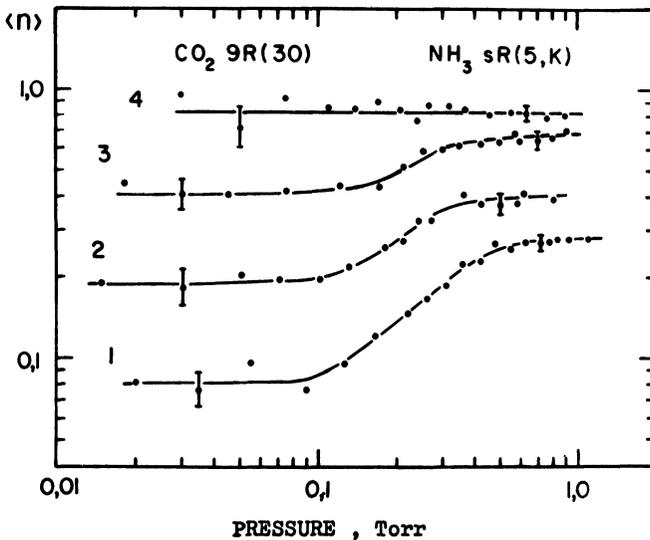


Figure 3 The dependences of the average number of absorbed photons per molecule on the ammonia pressure in the case of excitation on the line 9R30 at the fluences of 0.1 (1); 0.25 (2); 2.5 (3) and 10 (4) J/cm^2 .

SIMULATION OF THE IR ABSORPTION

The theoretical simulation of the excitation of NH₃ contains no fundamentally new points. For substantiating the approach used below we give the data, familiar in the literature, on the times of collisional relaxation. The minimum time $(p\tau)_{a-s} \sim 7 \text{ ns} \cdot \text{Torr}^{11}$ corresponds to the transition between the inversion (a,s) sublevels of the

vibrational ground state. At the same J and K the splitting between these sublevels is less than 1 cm^{-1} .⁵ Among the other transitions between the rotational states the maximum cross section corresponds to transitions with $(p\tau)_{\text{RR}} \approx 50 \text{ ns} \cdot \text{Torr}$ (the vibrational ground state $\nu_2 = 0$) and $(p\tau)_{\text{RR}} \approx 20 \text{ ns} \cdot \text{Torr}$ ($\nu_2 = 1$).¹¹

Since the duration of an exciting pulse was $\approx 100 \text{ ns}$ then at least at a pressure of $P > 0.1 \text{ Torr}$ the noncoherent rate equations for excitation hold.¹⁷ The most rapid dephasing process here is the a-s transition at $\nu_2 = 0$. Another factor, which leads to the noncoherent excitation of molecular levels is a relatively large width of the spectrum of the real laser pulse $\Delta\nu_{\text{las}} \approx 0.03 \text{ cm}^{-1}$ ($\Delta\nu_{\text{las}} \cdot \tau_p \gg 1$), which contains the nonsynchronized set of longitudinal and transverse modes.

As a matter of fact, for each initially populated level ($\nu_2 = 0; J, K$) it is sufficient to take into account only one transition to the vibrationally excited state, that is, the problem is represented as a set of excited two-level systems. In the model of strong collisions we write equations for the populations of the rotational sublevels, taking into account only the rotational relaxation and radiation transitions

$$\begin{aligned} \dot{n}_{JK} &= -W_{JK}n_{JK} + W'_{JK}n'_{JK} - kp(q_{JK}N - n_{JK}) \\ \dot{n}'_{JK} &= W_{JK}n_{JK} - W'_{JK}n'_{JK} - k'p(q'_{JK}N' - n'_{JK}) \\ \dot{N} &= \sum_{JK} (-W_{JK}n_{JK} + W'_{JK}n'_{JK}) = -\dot{N}' \end{aligned} \quad (1)$$

Here N and N' are the total populations of the ground and excited vibrational states, respectively; n_{JK} and n'_{JK} are the populations of the rotational sublevels, namely, the one initially populated and radiatively coupled to it, and W_{JK} and W'_{JK} are the rates of induced absorption and emission, which are inter-related by the detailed balance condition

$$W_{JK}/W'_{JK} = g'_{JK}/g_{JK} \quad (2)$$

where g_{JK} and g'_{JK} are the degeneracies of the corresponding rotational sublevels.

The expression for the rate of radiation-induced excitation in some incoherent case is of the form¹⁶

$$W_{JK} = 2\pi \overline{\Omega_{JK}^2} g'_{JK} G(\delta) \quad (3)$$

where $\overline{\Omega_{JK}^2} = \overline{\mu_{JK}^2} (\epsilon/2\hbar)^2$ is the mean square of interaction with the field (Ω_{JK} is the Rabi frequency), μ_{JK}^2 is the mean square of the dipole

moment of transition, ϵ is the field amplitude, and $G(\delta)$ is the form factor of the line shape, normalized in frequency to unity (δ is the detuning from the line centre). In our case, $G(\delta)$ is determined by the convolution of three contours—the Lorentz one, due to the uniform collisional broadening, the Doppler one with the fwhm $\Delta\nu_D \approx 4 \times 10^{-3} \text{ cm}^{-1}$ and the laser frequency contour which was approximated by the Gaussian line with the full width at the 1/e level of 0.03 cm^{-1} . At pressures of greater than 0.1 Torr the initial J, K state can be considered as additionally two-fold degenerate with an equilibrium population which is steady-state between the (a,s) sublevels.

The specific values of the matrix elements of the dipole moment μ_{JK} for a spherical top molecule can easily be expressed in terms of the vibrational dipole moment $\mu_{01} = 0.24 \text{ Deb}^{18}$ and the Hönl-London factors. It remains to determine only the used value of the collisional broadening of the line. For the hwhm γ_{col} we have

$$\gamma_{\text{col}} = \frac{1}{2}(kp + kp + k_{\text{asp}}) \quad (4)$$

Thus all the model parameters have been determined since the quantities q_{JK} and q'_{JK} are easily calculated at a predetermined temperature. Note that the equations of the type (1) were repeatedly used in describing the first stage of the MPE (excitation of the levels below the quasi-continuum). In our case, which we just tried to achieve, the model has no phenomenological parameters, that is, it admits an independent comparison with experiment.

The character of the solution obtained can readily be described qualitatively. Under the conditions of collisional relaxation the excitation of all molecules is determined by the efficient rate $\tilde{W}^{12,19}$

$$\tilde{W} \sim q \frac{W \cdot kp}{W + kp} \quad (5)$$

In particular, in the case of deep saturation ($W \gg kp$) we have $\tilde{W} \sim qkp$ (“the rotational bottle neck”). It is natural that the saturation energy (obtained from the condition $W \sim kp$) is significantly dependent on the detuning from the nearest resonance and increases with increasing δ . In those cases where the adjacent ammonia lines are sufficiently spaced apart, they are saturated at significantly different Φ and this may lead to a step-wise form of the dependence $\langle n(\Phi) \rangle$, which was also noted, in particular, in Reference 13.

The result of calculation for $\langle n(\Phi) \rangle$ is presented in Figure 2b.

Comparison with experiment (Figure 2a) is immediately indicative of two main points. Firstly, at small $\langle n \rangle$ (the region of linear increase with Φ) in all cases a satisfactory quantitative agreement has been obtained. In particular, all the curves are displaced relative to each other along the axis Φ in full accord with the increase in the detuning (see Figure 1), i.e. with the decrease in the linear absorption cross section. A somewhat greater, compared with all the other lines, distinction in the case of resonance excitation (9 R(30) of the CO_2 -laser) seems to be associated with the possibility, neglected in the calculation, of "burning" of some of the pulse modes, i.e. with the optical density of the medium. And secondly, a significant distinction between theory and experiment takes place for large Φ where the calculation predicts the saturation of the dependence $\langle n(\Phi) \rangle$ at smaller levels of the absorbed energy.

It should be emphasized once again that we have not used the fitting parameters in the model. In order to confirm their physical significance as well as the applicability of the model at least for some cases, we separately compared the results of calculation and experiment for the most detuned laser line 9P(20) (Figure 4). In this case the character of

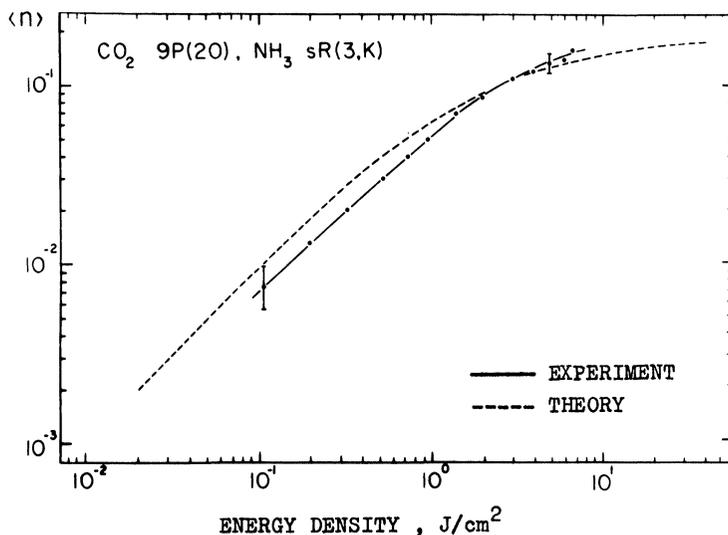


Figure 4 The experimental (— · —) and theoretical dependences of the average number of absorbed photons per molecule on the fluence of an exciting pulse for the line 9P(20) of the CO_2 -laser.

the saturation curve $\langle n(\Phi) \rangle$ is determined by the power broadening of transition. In fact, for $\delta \gg \Delta\nu_{\text{las}}, \Delta\nu_{\text{D}}, \gamma_{\text{col}}$ we have $W \sim \Omega_{\text{R}}^2 g_{\text{col}} \delta^{-2}$ and since $\gamma_{\text{col}} \sim kp$ then the saturation condition ($W \sim kp$) in this case signifies that the power broadening is approximately equal to the detuning value ($\Omega_{\text{R}}^2 \sim \delta^2$). A similar effect in the case of a dense relatively uniform spectrum of the vibrational-rotational transitions leads to the dependence $\langle n \rangle \sim \Phi^{1/2}$, which was observed, for example, in Reference 13 and was also interpreted in terms of the increase in the power broadening ($\Omega \sim \Phi^{1/2}$).

Excellent agreement of calculation with experiment, that was obtained in the case of nonresonance excitation on the 9P(20) line (Figure 4), shows that it is hardly reasonable to refine the model parameters, and the inadequacy of calculation for the other lines is explained by some way of energy dissipation from the IR field, that has been neglected so far.

EXPERIMENT: FIR GENERATION

We have already pointed out in the Introduction that under the IR excitation of ammonia there occurs a FIR generation associated with the transitions between the rotational sublevels of both the excited and the ground vibrational states.^{15,20} In order to verify how significant is this effect in our conditions (low pressures, a single-pass cell, the absence of mirrors), a special testing experiment was carried out. For detecting the changes in the frequency composition of the pumping IR radiation, the output window of the cell was made of crystalline quartz ≈ 1 mm thick, or of Teflon ≈ 5 mm thick. Thereby the radiation of the CO₂-laser was completely absorbed and the FIR emission in the region $\lambda \geq 80 \mu\text{m}$ could leave the cell. Such emission was reliably detected by a pyroelectric detector, as well as by a calorimeter at the output of the cell. The energy in the far infra-red region was measured with no frequency resolution. As an example, Figure 5 presents the dependence of the total energy E_{FIR} , radiated along the axis of the cell, on the gas pressure. The pumping beam cross section was $S \approx 2 \text{ cm}^2$. The FIR emission in both directions was assumed to be the same. It is evident from the figure that E_{FIR} is quadratically dependent on pressure when $p \leq 1$ Torr. (The decrease in the radiation energy at high pressures is due to the fact that the gas cell becomes optically thick for the IR pumping).

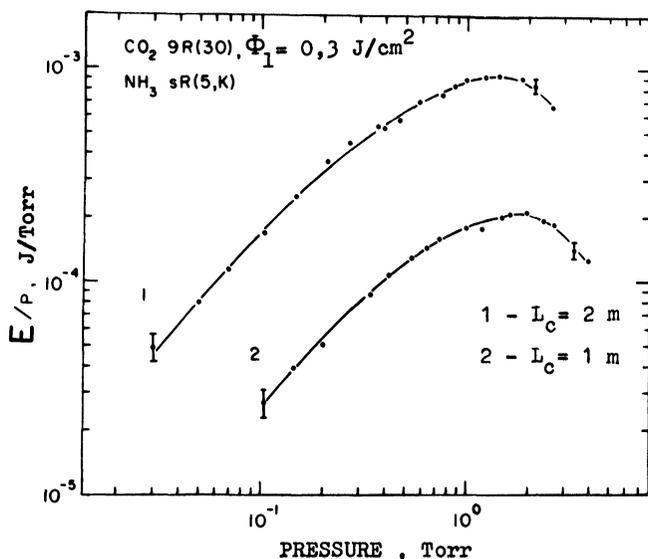


Figure 5 The dependence of the energy (normalized to pressure) of FIR radiation generated along the cell axis on the ammonia pressure under the excitation of $^{14}\text{NH}_3$ on the line 9R(30) of the CO_2 -laser in cells 2 m (1) and 1 m (2) long. The fluence of the laser pulse is $\approx 0.3 \text{ J/cm}^2$.

The next step consisted in the detection of emission directed aside from the cell axis. For this purpose the FIR emission was observed through the side window also made of crystalline quartz. The FIR energy, integrated over the whole side surface, is at least one order of magnitude greater than the energy of emission directed along the axis.

We give some of the specific values. In the case of resonance IR pumping with the energy $\Phi = 0.35 \text{ J/cm}^2$ (the line 9R(30) of the CO_2 -laser at a pressure of $P = 1$ Torr and at a cell length of $l = 1$ m) the total energy $E_{\text{FIR}} \approx 0.2$ mJ was radiated along the axis and approximately 10 mJ, aside from the cell. It will be noted that under the same conditions (Figure 2a) the IR absorption was approximately 28 mJ and the absorption value calculated (Section 3) was about 10 mJ, which corresponds to the excitation level $\langle n \rangle = 0.15$ photon/molecule.

In the case of IR pumping at the resonance frequency 9R(30) the functional dependence $E_{\text{FIR}}(\Phi)$ is slower than the linear one. At the same time, in the case of large detunings of the pumping frequency

from the ammonia absorption line the dependences $E_{\text{FIR}}(\Phi)$ at $\Phi \approx 0.5 \text{ J/cm}^2$ are much steeper. In particular, in using the line 9R(20) of the CO₂-laser (maximum detuning) the FIR energy, under the same conditions as those under which the dependence $\langle n(\Phi) \rangle$ was measured (Figure 4), was negligibly small ($\approx 10^{-5} - 10^{-6} \text{ J}$).

For the further interpretation of results it is necessary to elucidate whether the emission of FIR radiation occurs during or after the IR pumping pulse. Although the literature data^{14,15,20} confirm the simultaneity of the two processes, in our experimental conditions we could not directly record both pulses with the required time resolution. However, there is a simple method which enables one to answer this question. We used two identical cells with NH₃. A beam of the CO₂-laser was divided into two beams which were directed into different cells. After the passage of one of them the IR absorption was measured and the second cell (with the output window of crystalline quartz) was used for the FIR generation which was directed into the first cell. In the testing experiment the values of IR absorption in the presence of FIR radiation and without it were compared. Obviously, the IR absorption values in these two cases may be different only on condition that both pulses affect molecules simultaneously.

And this was indeed observed. In particular, for the pumping line 9R(30) at $\Phi \approx 0.3 \text{ J/cm}^2$ and $P = 0.5 \text{ Torr}$ the IR absorption in the presence of FIR radiation was approximately 20 to 25% in excess of the measurement result without it.

We note on the spot that the absolute values of the energy measured in far infrared directly prove the existence of cascade transitions between the rotational sublevels. In fact, for the absolute values given above in this Section the radiation energy with $\lambda > 100 \mu\text{m}$ is only two or three times smaller than that absorbed from the IR field ($\lambda \approx 9 \mu\text{m}$). Thereby the quantum yield of reradiation is several times greater than unity, which is possibly only due to cascades. Such cascade reradiation was already observed for ammonia,²⁰ in which case it was shown that radiation in the MIR range may also appear.¹⁵

DISCUSSION AND CONCLUSIONS

In the paper we have tried to achieve a rather modest objective—to investigate an elementary act of absorption of the first IR photon in a

polyatomic molecule using as an example a molecule with the well-known spectral and relaxation parameters. Attempts to simulate this process within the framework of standard theory have led to a significant discrepancy with experiment (Figure 2a, b). Certainly, the calculation itself employs some simplifying assumptions, e.g. the model of strong collisions. In this case, in particular, it is not considered that the collisional transitions between different rotational sublevels have also a significantly different probability.¹¹ However, the discrepancies between the more exact calculation, which takes it into account, and our simplified model become significant only in those cases where the saturation level $\langle n(\Phi) \rangle$ constitutes several tenths (the more exact theory gives a lower saturation level than our model does). But at the same values $\langle n(\Phi) \rangle$, as we have shown, a new qualitative effect becomes significant—FIR generation which leads to a new channel of the IR field energy dissipation. A sufficiently convincing, in our opinion, confirmation of the validity of the model is agreement between calculation and experiment in that case where no new frequency components of the field appear (Figure 4) and the saturation condition of $\langle n(\Phi) \rangle$ is determined by the power broadening ($\mu\epsilon/2\hbar \sim \delta$).

How may the generation of radiation in a new frequency region lead to the initiation of IR absorption? Under the collisional conditions during the saturation of the resonance vibrational-rotational transition the rate of absorption is limited by the finiteness of the rotational relaxation time. The lasing between the rotational sublevels of both the ground and excited vibrational states eliminates the rotational bottle neck, i.e. increases the efficient total absorption cross section (5). This effect is the more significant in the collisionless case when without its inclusion only a small resonance fraction of molecules ($\sim q_{JK}$ can be excited to a state with $\nu_2 = 1$. The intensity of FIR radiation increases with increasing energy of the IR pumping, therefore at large Φ the total absorption is also greater (see Figure 3).

Without carrying out the comprehensive spectral and temporal investigation of the FIR radiation generated, we did not discuss in detail the theoretical interpretation of this effect.²¹ We only give the estimate of the gain for the lasing transition ($\nu_2 = 1, J = 6, K = 0, a \rightarrow \nu_2 = 1, J = 5, K = 0, s$), $\Delta n = 67 \text{ cm}^{-1}$ (this transition was identified in Reference 15 and seems to take place, also, in our case).

The case considered corresponds to the IR pumping on the line

9R(30) of the CO₂-laser. At a pressure of $P \sim 1$ Torr the homogeneous width of the line of the rotational transition is greater than the Doppler one. Therefore the emission cross section at the centre of the line is $\sigma_0 = 4\pi m^2 \omega / \hbar c \gamma_{\text{col}} (\gamma_{\text{col}} = k'p)$. At $\mu \sim 1$ Deb we have $\sigma_0 \sim 10^{-13}$ cm². For the steady-state inversion population $N = qp$ ($q \geq 1\%$) the gain is $\alpha = \sigma_0 N \sim 30$ cm⁻¹. Then for the amplification under the saturation conditions for the homogeneously broadened line we have¹⁷

$$\frac{dI}{dz} = \frac{\alpha_0 I}{(1 + I/I_{\text{sat}})} \quad (6)$$

where I_{sat} is determined from the condition $\sigma_0 I_{\text{sat}} \sim kp$. For $I > I_{\text{sat}}$ (which takes place in our experiment) the intensity of the output radiation is $I_{\text{out}} \sim \sigma_0 N I_{\text{sat}} l$, i.e. the total energy E_{FIR} is

$$E_{\text{FIR}} \sim qk'lp^2 S \tau_p, \quad (7)$$

where S is the transverse cross section for the pumping beam. At $l = 1$ m and $P = 0.5$ Torr the substitution of the numerical parameters leads to excellent agreement between the estimate (7) and experiment (Figure 5). The quadratic dependence of E_{FIR} on pressure is also correctly described.

It is natural that this is only estimation. We have already pointed out that the value of the measured energy of FIR radiation (directed both along the axis and aside from the cell) reliably proves the existence of cascade transitions.

It should be stressed that in experiments which are similar in conditions the FIR generation was observed for quite a number of polyatomic molecules such as CH₃F, CH₂F₂, CF₂Cl₂ and others.²² Thus, this effect cannot be neglected either when describing the multiple-photon excitation, in particular, during the selective multiple-photon dissociation.^{1,2} Possibly, a similar effect also took place in References 12 and 13, where the IR absorption of ozone in the laser pulse field was investigated, and good agreement with the calculation at small $\langle n \rangle$ was not observed with increasing Φ .

We briefly formulate the main conclusions of our work:

(i) We have experimentally measured the energy, absorbed in ammonia, when varying the values of detuning of the frequency of the laser pulse IR field from the nearest vibrational-rotational transition in a wide range of IR laser fluence and of gas pressure.

(ii) It is shown that the efficient excitation of ammonia in the case of nonresonance pumping is possible due to the power broadening. This conclusion is confirmed by the quantitative description of experiment without using the fitting parameters in theory (Figure 4).

(iii) The abnormally high absorption observed is due to the FIR generation in the process of IR excitation, which serves as a source of elimination of the bottle neck. In this case the absorption of energy from the IR pumping field may be significantly higher than in the case of saturated absorption by ammonia molecules in the given laser field.

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