

Observation of anomalous absorption by ammonia in intense IR laser light

V. N. Likhman, G. N. Makarov, and V. M. Sotnikov

*Institute of Spectroscopy, Academy of Sciences of the USSR, 142092, Troitsk, Moscow Oblast**

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Observations reveal that pumping ammonia molecules on an individual vibrational–rotational transition by intense light from a TEA CO₂ laser ($I \gtrsim 10^6$ W/cm²) results in an effective radiative excitation of these molecules from other rotational states of both symmetric and asymmetric vibrational levels of the ν_2 mode, which is excited. The transitions from these states are detuned 50–100 cm⁻¹ from the pump frequency. This result should be taken into consideration in analysis of the multiphoton IR excitation of molecules.

1. The most important question for reaching an understanding of the physics of multiphoton excitation and dissociation of molecules by intense IR light¹ is the mechanism by which a large fraction of the molecules are drawn from numerous rotational states into the interaction process.^{2–4}

Akulin *et al.*⁵ have explained the emptying of many rotational states during multiphoton IR excitation of molecules as resulting from a saturation of multiphoton resonances in the system of low-lying vibrational levels. In our opinion, the question is still open, since many experimental results^{3,4,6} on the excitation of molecules from individual rotational states cannot be explained satisfactorily by the existing theoretical models,^{7,8} even by those incorporating multiphoton transitions.

There are two questions of particular interest in this connection. (1) Does the efficiency of the excitation of molecules from many rotational states depend on whether the pump is at resonance with some particular transition in the molecule? (2) Is there an emptying of many rotational states during the excitation of simpler molecules, for which multiphoton processes in the system of low-lying levels are improbable at moderate IR intensities?

In an effort to learn about these questions, we have deliberately selected a simple system: the ammonia molecule. In NH₃, vibrational–rotational transitions can be spectrally resolved well,⁹ so it is possible to excite molecules either at a resonance with individual transitions or away from a resonance. The probability for multiphoton processes in the system of low-lying levels is low at moderate IR intensities ($I < 10^5$ – 10^7 W/cm²), because of the pronounced anharmonicity of the vibrations, itself a consequence of an inversion-related splitting of the levels of the ν_2 mode, which is excited ($\Delta\nu_{\text{anharm}} \simeq 300$ cm⁻¹ on the $1a$ – $2s$ transition).

2. In the experiments, we measured the energy absorbed by the molecules under collisionless excitation conditions ($p\pi_p \ll p\tau_{\text{rot}}$, where p is the ammonia pressure, τ_p is the length of the laser pulse, and τ_{rot} is the rotational relaxation time of ammonia; here

we have $p\tau_{\text{rot}} = 50 \text{ ns}\cdot\text{Torr}$ in the ground state and $20 \text{ ns}\cdot\text{Torr}$ in the first excited vibrational state¹⁰). We also used the method of a double IR–IR resonance. In this method, two identical CO_2 lasers were used to measure the bleaching of several transitions in ammonia during resonant excitation of the NH_3 on other transitions, under the condition $p\tau_d \ll p\tau_{\text{rot}}$ (where τ_d is the delay between the exciting laser pulse and the probing laser pulse). We carried out similar measurements during nonresonant excitation of the molecules. The extent of bleaching was found as $\eta = (\sigma_0 - \sigma_e)/\sigma_0$, where σ_0 and σ_e are the absorption cross sections of NH_3 for the probing light without preliminary excitation of the molecules and after such excitation, respectively.

In order to raise the sensitivity and the accuracy of the measurements in this study of the bleaching of ammonia, we also used an optoacoustic method to measure the absorbed energy, under conditions of a double IR–IR resonance. Under the conditions $p\tau_d \ll p\tau_{\text{rot}}$ and $\tau_d \ll \tau_{\text{OA}}$ ($\tau_{\text{OA}} \gtrsim 100 \mu\text{s}$ is the rise time of the signal in the optoacoustic cell), the height of the optoacoustic signal is, during the application to the ammonia of exciting and probing pulses on transitions which are not coupled by common rotational sublevels,

$$S(\nu_1 + \nu_2) = S_0(\nu_1) + S_e(\nu_2) \leq S_0(\nu_1) + S_0(\nu_2),$$

where $S_0(\nu_1)$ and $S_0(\nu_2)$ are the heights of the optoacoustic signals observed during separate application of the exciting and probing IR pulses, respectively, and $S_e(\nu_2)$ is the optoacoustic signal on the probed transition after the application of the pump pulse to the molecules. The extent of the bleaching for the probing pulse was found as $\eta = 1 - [S(\nu_1 + \nu_2)]/[S_0(\nu_1) + S_0(\nu_2)]$.

The energy absorbed in the NH_3 was measured with a pyroelectric detector.¹¹ This detector was mounted in a cell 10 cm from the entrance window (the length of the cell was 100 cm, and its diameter was 3 cm). An absolute calibration was carried out by measuring the energy absorbed in the NH_3 by a direct calorimetric method, in which we used TPI-1 energy meters. During the calorimetric measurements of the ammonia bleaching, the energy of the probing laser pulse incident on the cell with the NH_3 and the energy of the pulse transmitted through the cell were also measured with pyroelectric detectors. The synchronization of the pulses was monitored within ± 50 ns with the help of a Ge: Au IR detector. The intensity of the probing IR pulse was lower by a factor of $10\text{--}10^3$ than that of the exciting pulse. In each laser we used a nitrogen-depleted mixture ($\text{CO}_2:\text{N}_2:\text{He} = 4:1:16$), in order to generate predominantly tail-free pulses ($\tau_p \simeq 100 \text{ ns}$ at half-maximum).

3. Figure 1 shows the optical scheme of the excitation and probing of NH_3 , along with the frequency positions of the ammonia lines (multiplets) with respect to the exciting lines of the light from the CO_2 laser. The ammonia was also excited and probed on other transitions. The $9R(30)$ line of the CO_2 laser coincides quite well with the $sR(5, K)$ multiplet of ammonia ($\Delta\nu \simeq 0.006 \text{ cm}^{-1}$ for the nearest line). For the case of the $sQ(2, K)$ transition we have $\Delta\nu \gtrsim 0.03 \text{ cm}^{-1}$.

Figure 2 shows the average number of absorbed photons per molecule, $\langle n \rangle$, versus the ammonia pressure for the case in which the NH_3 is excited on the $sR(5, K)$ transition, for various energy flux densities Φ of the exciting laser light

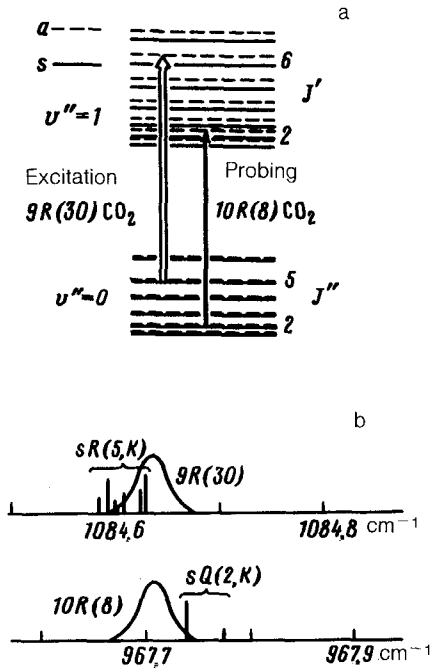


FIG. 1. a—Optical scheme of the excitation and probing of the ammonia; b—frequency positions of the ammonia lines (multiplets) with respect to the exciting lines of the CO₂ laser.

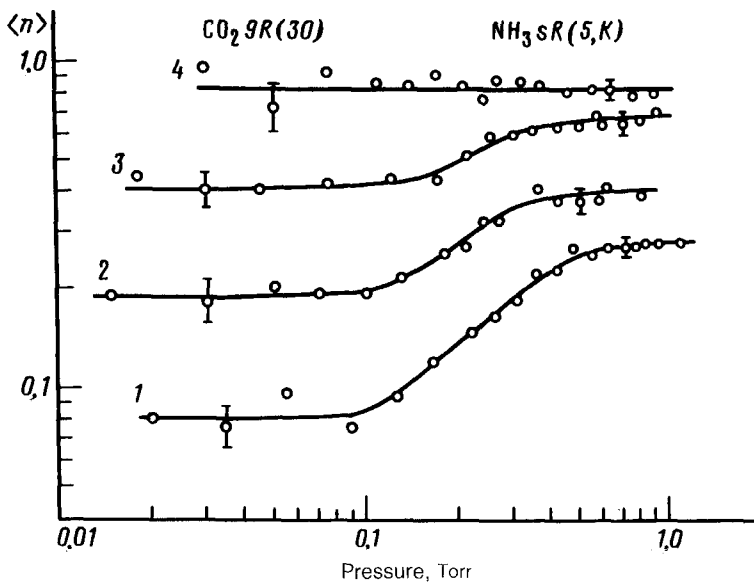


FIG. 2. Average number of absorbed photons per molecule versus the ammonia pressure during excitation of the NH₃ on the sR(5,K) transition by the 9R(30) laser line. 1—The energy flux density is 0.1 J/cm²; 2—0.25; 3—2.5; 4—10 J/cm².

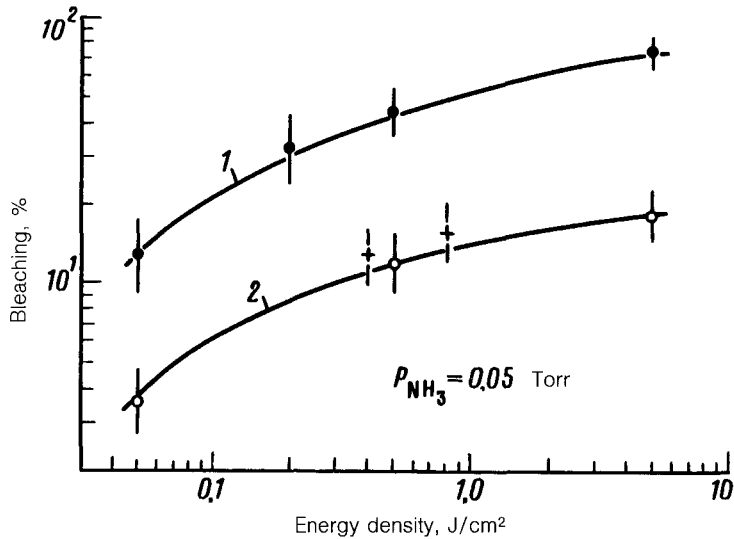


FIG. 3. 1—Bleaching of the $sQ(2,K)$ transition during pumping of ammonia on the $sR(5,K)$ transition; 2— inversely, bleaching of the $sR(5,K)$ transition during pumping of the NH_3 on the $sQ(2,K)$ transition. The independent variable is the energy density of the exciting pulse.

($\langle n \rangle = E_{AB} / \hbar\omega NV$, where E_{ab} is the absorbed energy, $\hbar\omega$ is the energy of the laser photon, and N and V are the density and laser-illuminated volume of the gas, respectively, in the cell). At ammonia pressures $p \lesssim 0.1$ Torr, there is essentially no rotational relaxation during the laser pulse ($\langle n \rangle$ does not depend on p). At $p \gtrsim 0.1$ Torr we observe an increase in $\langle n \rangle$, because a large fraction of the molecules are drawn into the interaction by virtue of the rotational relaxation. It can be seen from Fig. 2 that at high values of Φ the role played by the rotational relaxation in increasing the absorption becomes negligible. At $\Phi = 2.5$ and 10 J/cm² we find $\langle n \rangle \simeq 0.4$ and 0.8 , respectively, even under collisionless excitation conditions (at $p = 30$ mTorr, for example, we have $\tau_{rot} \simeq 15\tau_p$). It would not be possible to explain such a strong absorption by the NH_3 under the assumption that only the small fraction of the molecules ($\simeq 3\%$) which are in the ($v'' = 0s, j'' = 5$) state at $T \simeq 300$ K interact with the IR field. As was shown in Ref. 6, the strong absorption of the ammonia is due in part to a reradiation in the microwave range. Even if we take this microwave emission into account, however, we would find it difficult to explain such a strong absorption of the ammonia at low pressures. It is thus natural to suggest that molecules from other rotational states are also interacting with the IR light.

Figure 3 shows the bleaching of the $sQ(2,K)$ transition during the pumping of the NH_3 on the $sR(5,K)$ transition (line 1) and, inversely, the bleaching of the $sR(5,K)$ transition during pumping of the ammonia on the $sQ(2,K)$ transition (line 2), versus the energy density of the exciting pulse. These results were obtained by the optoacoustic method at a pressure of 0.05 Torr and at $\tau_d = 100 \pm 50$ ns. The plus signs on line 2

show results found on the bleaching of NH_3 through measurements of absorption across sections for the probing IR light. During excitation of the NH_3 on the $sR(5,K)$ transition, a strong bleaching of the ammonia was also observed on other transitions [$aR(1,1)$, at 971.88 cm^{-1} , and $aQ(5,3)$, at 932.99 cm^{-1}]. During pumping of the NH_3 on other transitions, in contrast, we observed a bleaching of the $sR(5,K)$ transition at a level of 3–15%. This bleaching was stronger, the better the resonance of the pump light with the NH_3 transition being pumped. In contrast, during excitation of the ammonia at frequencies distant from the resonance with transitions in the molecule [on the lines $9R(28)$ and $9R(26)$, for example, which are only 1.1 and 2.3 cm^{-1} from the $sR(5,K)$ transition], the bleaching of the $sR(5,K)$ transition and of other transitions did not exceed (at $I \lesssim 10^7 \text{ W/cm}^2$) $\approx 2\%$, which was the lowest value measurable under these experimental conditions.

4. In summary, these experiments on the particular case of NH_3 have revealed the following: (1) A radiative excitation of molecules from many rotational states occurs during pumping of one-photon transitions (at $I \gtrsim 10^6 \text{ W/cm}^2$). (2) The efficiency at which other rotational states are emptied depends strongly on whether the exciting field is at resonance with some transition in the molecule.

The sharp decrease in the efficiency of the excitation of molecules from many rotational states when the pump frequency is moved away from resonance with one-photon transitions cannot be explained satisfactorily on the basis of a mechanism which has a large fraction of the molecules being drawn out of many rotational states through multiphoton transitions.

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