Excitation of vibrational levels in the $N^{14}H_3$ molecule by radiation from a CO_2 laser

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The excitation of vibrational levels of the NH_3 molecule in the field of a CO_2 laser is studied theoretically and experimentally. Continuous and pulsed excitation is employed. The population of the rotational net (aggregate of rotational sublevels) of the first vibrational level $\nu'' = 1$ was monitored on the basis of the electron-vibrational absorption spectrum. The population of the vibrational level $\nu'' = 1$ due to excitation of the ammonia molecule by radiation from a continuous CO_2 laser was shown to be due to thermal heating of the gas by laser radiation. About 40% of the rotational net of the first vibrational level is populated by pulsed excitation of the ammonia by infrared radiation from the laser. However, considerable thermal population of the level is also produced.

1. INTRODUCTION

The development of laser sources of monochromatic intense infrared (IR) radiation has uncovered a possibility, in principle, of selective action on molecules in a gas by tuning the emission frequency to definite vibrational-rotational transitions in the absorption spectrum of the molecule. In 1966, Borde and co-workers[1] heated ammonia gas in this manner by radiation from a high-power cw CO_2 laser. This heating was accompanied, at high emission intensity, by glow and by dissociation of the molecules$^{1)}$. This experiment was performed under conditions of strong relaxation of the vibrational excitations to translational degrees of freedom, and the dissociation mechanism, as noted in[1], was thermal. A similar conclusion was arrived at by Losev et al.[3].

Greatest interest attaches, of course, to selective non-equilibrium excitation of definite oscillations and levels of the molecule, since this uncovers an obvious possibility of realizing selective chemical reactions controlled by laser radiation, a possibility under discussion almost from the time that lasers were discovered. To this end it is necessary, in the simplest case, to obtain selective heating of a definite molecule vibration, i.e., to excite many vibrational levels of one vibrational band of the molecule. In other words, it is necessary that the vibrational temperature of one degree of freedom greatly exceed the translational temperature and the temperature in the remaining vibrations. Such a possibility was discussed theoretically in a number of papers[4-6]. In a recent experiment,[7] the emission of a continuous HF laser induced vibrational excitation of the CH_3OH molecule. It was observed in that study that the role of the CH_3OH molecules in the chemical reaction is much more important than that of CD_3OD, and this predominance was attributed to selective excitation of the molecules by the laser radiation. This explanation cannot be regarded as satisfactory, since the rapid vibrational relaxation of the excited molecules should lead to an equilibrium heating of a mixture of molecules.

The difficulties in the unambiguous explanation of processes that lead to dissociation and chemical reactions of molecules excited by IR laser radiation are caused to a considerable degree by the absence of effective methods of investigating the vibrational states of molecules. We have developed a direct method of studying the populations of the vibrational levels of the molecule by measuring the intensity of the absorption lines in the transitions of molecules from the investigated vibrational states to an excited electronic state. We studied experimentally the change in the population of the vibrational levels of the ν_2 band of the NH_3 molecule following excitation with radiation from a cw CO_2 laser. The change of the population was registered by measuring the intensity of the electron-vibrational absorption lines in the $\tilde{A} - \tilde{X}$ transition of the NH_3 molecule; these lines lie in the ultraviolet (UV) band[8]. The scheme of the employed transitions is shown in Fig. 1. The method makes it possible to investigate the change of the population of the high-lying vibrational levels with high temporal and spectral resolution. The sensitivity attained in the experiment was such that the changes of only 3–5% in the populations of the vibrational levels could be registered.

We shall show that the population of the vibrational levels of the NH_3 molecules in the pressure range from 1 atm to 20 Torr in the radiation field of a continuous CO_2 laser is determined by the thermal excitation rather than by the radiative excitation. We find that when the molecular gas pressure exceeds a certain critical value, the population of the vibrational levels in the field of cw laser radiation is always determined by thermal excitation, and at lower values it is determined by radiative excitation.

In the case of excitation of NH_3 molecules by a pulsed laser, one can distinctly separate the regions of the pure radiative excitation of the vibration levels from the pure thermal regions. In the case of pulsed excitation, an appreciable gap between the vibrational and translational temperatures is observed.

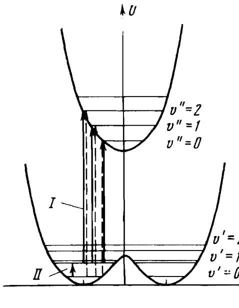

FIG. 1. Scheme of electron-vibrational transitions of the NH_3 molecule: I–probing UV radiation (2000–2250Å), II–exciting IR laser emission.

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2. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 2. The setup consisted of the following principal parts: I—$CO_2 : N_2 : H$ laser with selection of the vibrational-rotational transitions; II—UV radiation block; III—cell with investigated gas, IV—recording system.

The ammonia was excited in the cell by radiation from either a cw CO_2 laser or from a pulsed CO_2 laser with selection of the rotational-vibrational transitions. The active medium of the cw CO_2 laser was contained in a water-cooled glass tube 2 of length 150 cm and inside diameter 8 mm, through which a $CO_2 : N_2 : He$ mixture was drawn at a rate of 3 m/sec at a pressure 5—10 Torr. The laser resonator length was 200 cm. One of the resonator mirrors was a flat steel polished mirror 1 with a hole of 1 mm diameter at the center. The dispersion element was a diffraction grating 3, with 100 lines per mm cut on AMTs-brand aluminum. The grating ensured an approximate radiation concentration of 80—85% in first order at $\lambda \sim 10\mu$, and operated in the anticollimation regime.

The laser has made it possible to tune the generation frequency to the frequency of the vibrational-rotational transition of the P and R branches of the 9.6-micron (00^01-02^00) band (approximately 35 lines) and of the 10.6-micron (00^01-10^00) band (approximately 40 lines). The bulk of the laser-emission power was drawn from the zeroth order of the grating. The radiation power in the experimentally-employed P(32) line of the (00^01-10^00) band was 20—25 W and could be varied stepwise by changing the number of discharge gaps. The diameter of the output beam was 5 mm.

The laser was tuned to the frequency of the P(32) line of the 00^01-10^00 band (932.96 cm^{-1}), which nearly coincides with the asQ(5, 3) transition of the NH_3 molecule. According to Shimizu[9], the detuning of the frequency of the P(32) line from the center of the absorption line is approximate 0.95 GHz. At 12—15 Torr, however, the coefficient for absorption of the weak signal by the ammonia at the given line is 8×10^{-3} cm^{-1} $Torr^{-1}$, reaches 10^{-3} cm^{-1} $Torr^{-1}$ at a pressure close to 20 Torr, and become independent of the pressure up to ~400 Torr. The laser emission frequency was monitored against the IR absorption by ammonia in a control cell 8 of length 12 cm, in which the ammonia pressure was ~10—15 Torr. To this end, a fraction of the laser radiation (~2—3 W) was extracted from the resonator through an opening in mirror 1. This beam was split into two parts. One passed directly to the IR receiver 9, and the other passed through a control cell 8 with ammonia and then to a GeAu photoresistor 9 cooled with liquid nitrogen. The signals from both receivers were fed to a two-beam oscilloscope. The frequency was tuned by setting to maximum absorption and maximum output power at the zeroth order of the grating.

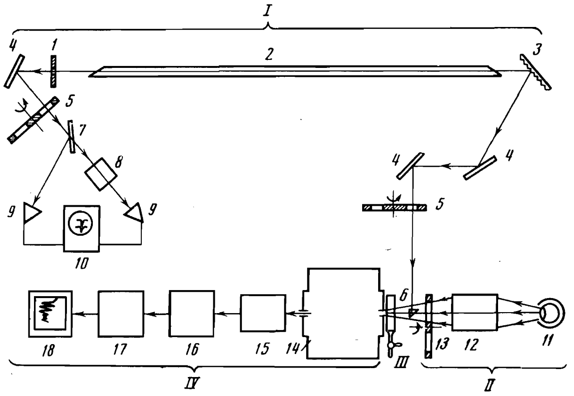

FIG. 2. Diagram of experimental setup: I—tunable CO_2 laser (1—output mirror of laser resonator, 2—laser tube, 3—diffraction grating, 4—mirrors, 5—modulators, 6—rotating prism, 7—plane-parallel plate, 8—control cell with NH_3, 9—IR receiver, 10—two-beam oscilloscope); II—UV radiation block (11—hydrogen lamp, 12—condenser, 13—modulator); III—cell with ammonia, IV—recording system (14—MDR-2 monochromator, 15—photomultiplier; 16—amplifier, 17—synchronous detector, 18—automatic recorder).

When working in the pulsed regime, a second discharge tube was placed in the CO_2 laser and made it possible to produce a transverse discharge in the gas. All the remaining elements remained unchanged. The pulsed laser also operated on one rotational-vibrational line and emitted an energy of 50—60 mJ. The beam excitation cross section was 0.1 cm^2. The UV radiation source II was a DVS-25 stabilized hydrogen lamp. The radiation from the lamp was focused with condenser 12 on the heater of the monochromator 14.

Cell III with ammonia gas was mounted directly in front of the monochromator slit. The cell had sodium-chloride windows, transparent both in the IR and the UV regions. The cell length was 1 cm and the diameter 3 cm.

The CO_2-laser radiation was guided with a system of mirrors and with a rotating NaCl prism through the cell with the ammonia coaxially with the lamp radiation. The rotating prism had faces measuring 5 × 5 mm. Owing to the small dimensions, the prism hardly interfered with the incidence of the bulk of the UV radiation on the cell. This geometry has made it possible to illuminate with the CO_2 laser beam practically the entire ammonia volume in the cell exposed to the UV radiation.

The recording system consisted of an MDR-2 monochromator (14), and FEU-39 photomultiplier (15), a V6-4 amplifier (16), a KZ-2 synchronous detector (17), and an ÉPP-09 automatic recorder (18). We registered the electron-vibrational transmission spectrum of ammonia, corresponding to the transition from the ground electronic state to the first excited electronic state without irradiating the ammonia with the CO_2 laser and with excitation. The apparatus made it possible to register the spectra in two regimes. In one regime, modulator 13 was used to modulate the UV beam while modulator 5 of the fundamental IR beam was turned off. In this case the synchronous detection was based on the UV-beam modulation signal, and the measured quantity was the transmission $\eta(\lambda_{UV}, P_{IR})$ of the ammonia in the UV region in the presence of exciting IR radiation with intensity P_{IR}. In the other regime the modulator 13 was turned off, but the modulator 5 was used to chop the exciting IR beam. The synchronous detection was effected in this case by the IR modulation signal, and the measured quantity was the difference between the transmission of the ammonia in the UV band in the presence of IR radiation (η) and without the IR (η^0), i.e., we measured the difference transmission spectrum $\Delta\eta(\lambda_{UV}) = \eta^0(\lambda_{UV}) - \eta(\lambda_{UV}, P_{IR})$. This registration method enabled us to observe a change $\Delta\eta$ not less than 3% in the transmission of the ammonia.

When the excitation was with emission of a pulsed CO_2 laser, the signals were registered directly with a photomultiplier and a long-persistence S1-29 oscilloscope.

3. RESULTS OF EXPERIMENT WITH CONTINUOUS CO_2 LASER AND DISCUSSION

The electron vibrational transmission spectrum of ammonia in the region 2000—2250 Å without laser irradiation and with it is shown in Fig. 3 (v″ is the vibrational sublevel of the ground electronic state, and v′ is the sublevel of the first excited electronic state). We see that when ammonia is excited with IR from a laser, the intensity of the lines connected with transitions to the zeroth and first vibrational levels of the excited electronic states increases, whereas the intensity of the lines for the transitions to higher vibrational levels decreases. For a more accurate measurement of this effect, we obtained the difference transmission spectrum, which is also shown in Fig. 3. This dependence becomes clearly manifest in the appearance of a negative signal at the location of the vibrational bands v′ − v″ = 2, 3, 4.

The observed changes in the electron-vibrational spectrum of ammonia are undoubtedly connected with the change in the distribution of the gas molecules over the vibrational levels of the ground electronic state. The question is, however, whether these changes in the electron-vibrational spectrum of the molecule enable us to assess the distribution of the molecules over the vibrational levels of the ground electronic state. To this end, however, it is necessary to know the electron-vibrational spectra of the NH_3 molecule from different vibrational levels of the ground electronic state, i.e., the Franck-Condon factor. The calculations of the Franck-Condon spectrum for this molecule were carried out in different approximations in a number of papers[10,11]. The most detailed analysis and comparison of the obtained values of the Franck-Condon factor with experiment were performed by Harshbarger[11].

Figure 4 shows the distribution of the intensity in the electron-vibrational spectrum of the NH_3 molecule in the case when 50% of the particles are at the zero vibrational levels and 50% are at the first vibrational level of the ground electronic state; this would correspond to complete saturation of the first vibrational transition. For comparison, we present also the spectrum in the case when all the molecules are at the lower vibrational level.

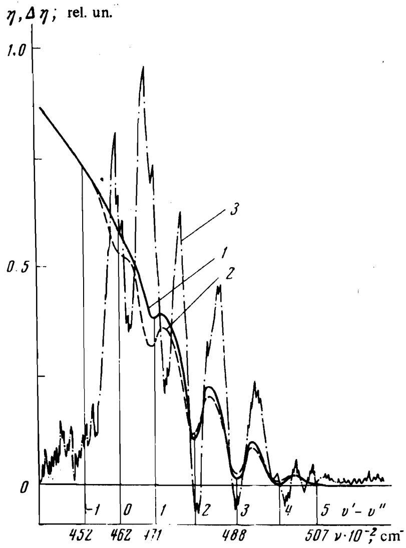

FIG. 3. Electron-vibrational transmission spectra of NH_3: 1—without excitation with laser radiation, 2—with excitation of CO_2 laser radiation, 3—difference transmission spectrum. Ammonia pressure 50 Torr, cell length 1 cm.

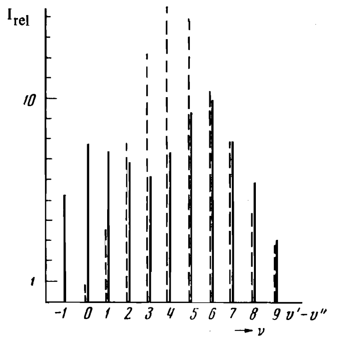

FIG. 4. Theoretical distribution of the intensity in the electron-vibrational absorption spectrum of the ammonia molecule (the calculations are based on [11]): solid lines—case of 50% population of the zeroth and first-excited vibrational levels of the ground electronic state; dashed—absorption spectrum of NH_2 molecule at room temperature.

It should be noted that Harshbarger[11] obtained the value of the Franck-Condon factor for transitions from different vibrational levels of the ground electronic state to vibrational sublevels of the first excited state with allowance for only one fully-symmetrical normal vibration (ν_2) of the NH_3 molecule. There appears in the spectrum also another fully-symmetrical vibration ν_1 with frequency ~3000 cm^{-1}. However, in the first three long-wave absorption bands of the NH_3 molecule (v′ − v″ = 0, 1, 2) this vibration makes no contribution whatever. Thus, it is seen from the spectrum shown in Fig. 4 that the electron vibrational spectrum of the NH_3 molecule makes it possible in principle to separate the cases of the thermal Boltzmann radiation population of the vibrational levels. To this end it is necessary either to analyze the new band in the electron-vibrational spectrum of the NH_3 molecule (for example, v′ − v″ = −1), or to carry out an exact quantitative analysis of the electron-vibrational progression. In our experiment, the recording apparatus was unable to detect new bands in the electron-vibrational spectrum of the NH_3 molecule.

The experimental data shown in Fig. 3 indicate that qualitatively the character of variation of the spectrum corresponds to the theoretical one, but in this case the changes in the spectra are small in comparison with those predicted by the theory, both in the case of thermal heating of ammonia to T = 1000° K, and for some significant population of the first vibrational level of the ground electronic state by induced transitions in the field of the laser radiation.

To ascertain whether the change in the electronic absorption spectrum is caused by slight heating or slight population of the first level by the radiation, one can measure the time lag of the changes in the spectrun. If the cause is the thermal effect, then a lag occurs, and if the cause is direct excitation of the level, then there is practically no lag. To this end, we measured the dependence of the change of the intensity of each electron-vibrational band as a function of the modulation frequency of the electron-beam intensity. The results of these measurements are shown in Fig. 5. The amplitude of the

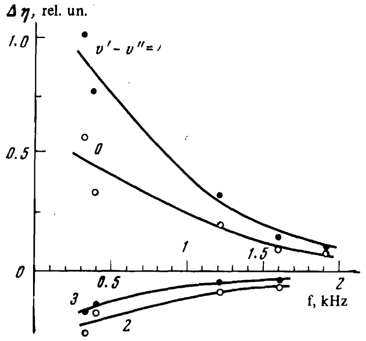

FIG. 5. Dependence of the amplitude of the difference signal on the laser-beam modulation frequency for the electron-vibrational lines v′–v″ = 1, 0, 3, 2 (the numbers on the curves). The ammonia pressure in the cell is 100 Torr.

difference signal $\Delta\eta = \eta^0(\lambda_{UV}) - \eta(\lambda_{UV}, P_{IR})$ decreases with increasing modulation frequency. This indicates that in the investigated pressure range the ammonia is thermally heated under the influence of the laser beam. The dependence of the amplitude of the difference signal on the modulation frequency of the laser radiation gives for the thermal-relaxation time a value ~0.8 msec at a gas pressure 100 Torr.

To estimate the temperature of the laser-irradiated ammonia from the changes in the absorption spectrum, the cell with the ammonia was heated with the aid of a heater. A comparison of the changes in the spectrum due to laser heating and ordinary heating has made it possible to estimate the laser-heating temperature of the ammonia, which reached 500°K under the described conditions.

4. COMPARISON OF THERMAL AND RADIATED POPULATION OF THE VIBRATIONAL LEVELS BY CONTINUOUS RADIATION

In the experiment, the power of the laser beam in the cell with ammonia did not exceed 100 W/cm², which was utterly insufficient to saturate the absorption of the vibrational transition 0 → 1 of the ν_2 band even at pressures on the order of 20 Torr. The experimentally observed bleaching of the ammonia is due not to radiative excitation but to thermal heating of the gas, which is accompanied by a decrease in the population difference of the vibrational levels 0 and 1. Let us examine this question in greater detail. We shall show simultaneously that it is impossible to attain radiative population by increasing the radiation power without lowering at the same time the pressure of the absorbing gas to a definite value (which is quite low for ammonia). We confine ourselves to the case of excitation of the lowest vibrational level of the molecule, as is the case with NH_3 molecules and CO_2 laser radiation.

The increase of the population of the first excited vibrational level as a result of radiative excitation is

$$\Delta N_{\text{rad}} = \frac{N_0}{2}\,\frac{P/P_{\text{rad}}}{1+P/P_{\text{rad}}},\quad P_{\text{rad}} = \frac{\hbar\omega_0}{2\sigma T_1}, \tag{4.1}$$

where N_0 is the density of the molecules on the ground vibrational level in the absence of radiation, P_{rad} is the power of the radiative saturation of the absorption, $\hbar\omega_0$ is the quantum energy, σ is the cross section of the 0 → 1 transition, and T_1 is the lifetime of the molecule at the excited vibrational level. On the other hand, the gas is inevitably heated as a result of relaxation of the excited molecules. The heating gives rise to Boltzmann population of the excited level, by an amount

$$\Delta N_{\text{ther}} = N_0 \exp\left(-\frac{\hbar\omega_0}{k\Delta T(P)}\right), \tag{4.2}$$

where $\Delta T(P)$ is the increase of the gas temperature and depends on the radiation power P. In (4.2) we neglect for simplicity the population of the higher vibrational levels. Appreciable population of the level and bleaching are reached at a certain power $P = P_{\text{ther}}$ determined from the condition

$$\Delta T(P_{\text{ther}}) \approx \hbar\omega_0 / k. \tag{4.3}$$

To compare the two excitation mechanisms it is necessary to find the dependence of ΔT on P, i.e., to solve the stationary problem of thermal conductivity. The magnitude and distribution of the temperature depend significantly on the geometry of the problem. We confine ourselves to the cylindrical case, which is closest to experiment on the excitation of molecules by a laser beam.

Let the light beam propagate along the axis of a cylindrical tube, on the surface of which (r = d) a constant temperature T_0 is maintained. The power absorbed per unit volume is determined by the expression

$$q(r) = P(r)e^{-\varkappa_0 X}\varkappa_0, \tag{4.4}$$

where $\kappa_0 = \sigma N_0$ is the absorption coefficient per unit length and X is the distance from the entrance of the beam into the tube. If it is assumed that the heat released along the tube is constant ($\kappa_0 X \ll 1$) and the thermal conductivity does not depend on the temperature, then the distribution of the temperature is determined by the expression[12]

$$\Delta T(r) = \frac{1}{\Lambda}\left[\ln\frac{d}{r}\int_0^r q(r_0)r_0\,dr_0 + \int_r^d \ln\left(\frac{d}{r_0}\right) q(r_0)r_0\,dr_0\right]. \tag{4.5}$$

If the light beam has a radius a, then the heating on the axis is equal to

$$\Delta T_0 = \frac{q_0 a^2}{2\Lambda}\ln\left(\sqrt{e}\,\frac{d}{a}\right),\qquad q_0 = q(0). \tag{4.6}$$

The heating on the beam boundary is reduced to one-half at $d = \sqrt{e}a$, so that at $d \gg a$ the distribution of the temperature inside the beam is almost homogeneous.

Actually, the thermal conductivity of the gas depends on the temperature. In the simplest case

$$\Lambda = \Lambda_0(1 + b\Delta T). \tag{4.7}$$

For example, for the NH_3 molecule we have $b = 5.5 \times 10^{-3}$ deg⁻¹[13] and Λ doubles at ΔT = 180°. The effect of the change of the thermal conductivity can be approximately taken into account by substituting Λ in (4.5) in the form of a function of the temperature and by solving the resultant equation for ΔT. This yields

$$\Delta T = [(1 + 4b\Delta T_0)^{1/2} - 1] / 2b, \tag{4.8}$$

where ΔT_0 is the heating at constant thermal conductivity Λ_0, and is determined by expression (4.6). Ultimately, with the aid of relations (4.3), (4.6), and (4.8), we obtain an expression for the thermal bleaching power

$$P_{\text{ther}} = \frac{\Lambda_0}{2a^2 b\ln(e^{1/2}d/a)\sigma N_0}\left[\left(\frac{2b\hbar\omega_0}{k} + 1\right)^2 - 1\right]. \tag{4.9}$$

Let us compare now the radiation power and the thermal bleaching power of the molecular gas. The powers P_{rad} and P_{ther} depend in equal fashion on the radiative-transition cross section σ_0, but in entirely different manners on the molecule density N_0. The power needed for thermal excitation decreases with increasing pressure, and the power for the radiative bleaching, to the contrary, increases with increasing pressure, since the relaxation time of the vibrational excitation T_1 decreases with increasing pressure:

$$T_1 = \tau / N_0. \tag{4.10}$$

As a result, at a definite molecule density, which we shall call critical (N_{cr}), we have $P_{ther} = P_{rad}$, and the contribution of the two mechanisms to the population of the vibrational level becomes of the same order. From (4.1), (4.3), and (4.9) we have

$$N_{\rm cr} \approx \frac{1}{a}\left(2b\frac{\hbar\omega_0}{k}+1\right)\left[\frac{\Lambda_0\tau}{b\hbar\omega_0 \ln(e^{1/2}d/a)}\right]^{1/2}. \tag{4.11}$$

At $N \gg N_{cr}$, the population of the vibrational levels is determined exclusively by the thermal effect, and at $N \ll N_{cr}$ it is determined by radiative excitation. Naturally, this is strictly valid only for excitation of the lower vibrational level of the molecule. When high-lying levels are excited, it is necessary to take into account the difference between the relaxation rates of the different vibrations and the cascade population of the vibrational levels.

In the described experiments with ammonia, we have $b = 5.5 \times 10^{-3}$ deg^{-1}, $\Lambda_0 = 2.1 \times 10^{-4}$ W/cm-deg[13], $\tau \lesssim 30.6 \times 10^{11}$ sec/cm^3 ($T_1 < 10$ μsec at 1 Torr)[14], and $\hbar\omega = 2 \times 10^{-20}$ J ($\lambda \approx 10$ μ). The cell and beam radii are d = 1 and a = 0.3 cm, respectively. According to (4.11), the critical density is $N_{cr} \approx 5 \times 10^{16}$ cm^{-3} (1.4 Torr).

Thus, under the conditions of our experiment, the population of the vibrational levels is determined by the thermal and not by the radiative excitation. The power at which thermal bleaching is reached is, according to (4.9), $P_{ther} = 46$ W/cm^2 at an ammonia pressure 0.1 atm ($\kappa_0 = 10^{-2}$ cm^{-1} Torr^{-1}). This agreed with the experimentally observed bleaching of ammonia at $P \sim 100$ W/cm^2.

5. PULSED REGIME. MEASUREMENT RESULTS AND DISCUSSION

The experiment consisting of observing and investigating the time dependence of the intensity of the new lines in the electron-vibrational absorption spectrum of ammonia under the action of a CO_2-laser radiation pulse. The laser radiation pulse waveform is shown in Fig. 6.

Figure 7 shows oscillograms of the variation of the UV transmission spectrum of the NH_3 molecule under the influence of a laser emission pulse at different time sweeps. The registration was made with the new absorption line, corresponding to a transition from the level v″ = 1 of the ground electronic state to the level v′ = 0 of the first excited electronic state of the molecule. We register the quantity $I = I_0(1 - e^{-k})$, where I_0 is the density of the lamp light passing through the empty cell at the given wavelength, and k is the coefficient of UV absorption by the ammonia under the influence of the laser pulse (the abscissas represent the time). We investigated the changes induced in the electron-vibrational spectrum of the NH_3 molecule by a laser-emission pulse, as functions of the ammonia pressure and of the laser-pulse power.

As seen from Fig. 7a, the pulse of the variation of the transmission in the UV region of the spectrum has a characteristic peak that occurs during the time of the laser pulse, and a long exponential tail. It turns out that the duration of the peak of the pulse changes in a range 2–3 μsec when the pressure changes accordingly in the interval 400–100 Torr. The duration of the tail of the pulse varies relatively little with changing ammonia pressure (500–800 μsec) in measurements at a single fixed position of the cell. It should be noted, however, that the duration of the tail of the pulse depends significantly (500–1500 μsec) on the position of the cell with ammonia relative to the laser beam.

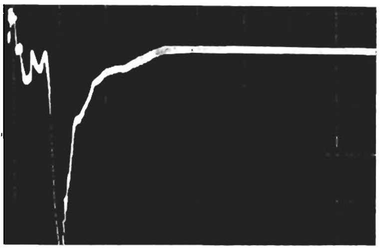

FIG. 6. Laser emission pulse. Sweep 1 μsec per division.

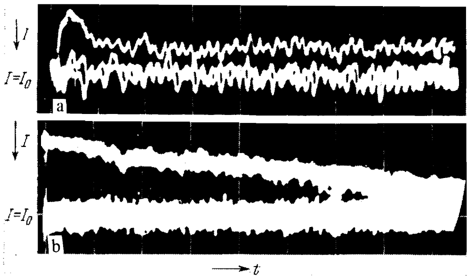

FIG. 7. Onset of absorption on the new line v′ = 0 ← v″ = 1: a—sweep 5 μsec per division, b—sweep 100 μsec per division.

We consider first the total duration of the pulse of variation of the electron vibrational spectrum of the NH_3 on the line corresponding to the transition (v′ = 0 ← v″ = 1) produced under the influence of laser radiation. The fact that the duration of this pulse changes little with changing ammonia pressure, and also the change of the total duration of the pulse as a function of the position of the cell, both indicate uniquely that the tail of the pulse is connected with the cooling of the gas heated by the laser beam. (The weak pressure dependence of the total pulse duration is due to the fact that the thermal conductivity of the gas does not depend on the pressure at high pressures.) At different positions of the cell with the ammonia relative to the laser beam, entirely different boundary conditions arise for the process of the cooling of the ammonia heated by the laser pulse, so that the total duration of the investigated pulse becomes dependent on the cell position. A simple estimate shows that the temperature of the ammonia in the laser-beam field, immediately after the passage of the laser pulse, before noticeable cooling of the gas can take place, is ~950°K at an ammonia pressure ~240 Torr in the cell. This corresponds to a ~17% population of the first vibrational sublevel (v″ = 1) as a result of thermal heating of the gas by the laser pulse. This yields the number of particles on the first vibrational sublevel (v″ = 1), namely ~40%, corresponding to almost complete saturation of the rotational branch of the first vibrational level.

Thus, when ammonia is excited by a laser pulse, ~40% of the aggregate of the rotational sublevels of the first vibrational level (v″ = 1) becomes populated, together with a weak (~5%) population of the second vibrational level (v″ = 2), which is probably connected only with the thermal heating of the gas. The weak dependence of the duration of the pulse peak of the resultant absorption on the gas pressure indicates that the radiative population of the first vibrational sublevel is preserved only during the laser pulse. Pulsed excitation has made it possible to observe the onset of new absorption lines, something impossible in the continuous regime under our conditions.

6. COMPARISON WITH THEORY IN THE CASE OF EXCITATION WITH PULSED RADIATION

Our results concerning the change of the population of the level v″ = 1 under the influence of a powerful laser pulse can be described within the framework of a simple model. Let the molecules be in a lower vibrational state v″ = 0 and let the laser radiation transfer them to the first vibrational level. We assume that the system of oscillators becomes heated by the laser radiation, since the vibrational energy goes over into heat with a probability $1/T_{V\to T}$, where $T_{V\to T}$ is the time of the vibrational translational relaxation. This process is described by the following equations:

$$\frac{dn_0}{dt}=-\sigma I(n_0-n_1)-\frac{n_0^{\text{equil}}-n_1}{T_{V\to T}}; \tag{6.1}$$

$$\frac{dn_1}{dt}=\sigma I(n_0-n_1)+\frac{n_1^{\text{equil}}-n_1}{T_{V\to T}} \tag{6.2}$$

$$\frac{\partial T}{\partial t}=\frac{\hbar\omega}{cN_0}\frac{(n_1-n_1^{\text{equil}})}{T_{V\to T}}, \tag{6.3}$$

where n_0 and n_1 are the total populations of the zeroth and first vibrational levels, N_0 is the molecule density, σ is the cross section for the radiative transition, I is the radiation intensity (photons/cm^{2}sec), and c is the specific heat per molecule.

The equilibrium concentrations of the molecules at the considered levels are

$$n_1^{\text{equil}}=N_0e^{-\hbar\omega/T}(1-e^{-\hbar\omega/T}), \tag{6.4}$$

$$n_0^{\text{equil}}=N_0(1-e^{-\hbar\omega/T}), \tag{6.5}$$

where T is the temperature and $\hbar\omega$ is the vibrational quantum energy. The system (6.1)—(6.3) is valid under the assumption that the time necessary to establish the Boltzmann distribution over the vibrational sublevels as a result of vibrational-vibrational exchange is $T_{V\to V} \ll T_{V\to T}$, and that the rotational relaxation time T_{rot} is much shorter than the reciprocal probability of the induced transitions σI, so that equilibrium over the rotational sublevels can be regarded as established.

The laser pulse can be approximated by the function

$$I(t)=\mathscr{E}_0b^2te^{-bt},$$

where $1/b = \tau_p$ is the pulse duration and ε_0 is the pulse energy. For comparison with experiment, we have integrated the system of equations numerically. Figure 8 shows the results of the calculation for the case when $\tau_p \sim 3T_{V\to T}$ and the saturation parameter is $R_0 = \sigma\varepsilon_0/\tau_p = 5$.

We next varied the ratio $\tau_p/T_{V\to T}$ keeping $R_0 = 5$ constant; this corresponded to a ~40% population of the first vibrational level v″ = 1. The ratio $\tau_p/T_{V\to T}$ was chosen such that the temperature of the tail of the pulse corresponded to the observed value (~1000° K). It turned out that the experimentally observed level populations at the peak and tail of the pulse agree with calculation at $\tau_p/T_{V\to T} \sim 10$. Since the population in our experiment amounted to 250—300 nsec, it is easy to obtain for the time of the vibrational-translational relaxation the values $T_{V\to T} \sim 25$—30 nsec at 240 Torr or $T_{V\to T} \sim 6$—10 nsec/atm. Bass and Winter[14] measured the time of vibrational relaxation for the molecule NH_3, and also discussed the vibrational-relaxation times cited by others. They quote a value 2.5 nsec/atm for $T_{V\to T}$. In our case, this value yields an anomalously high temperature, $T/\hbar\omega \sim 2.1$.

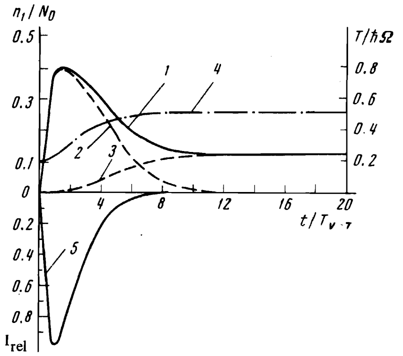

FIG. 8. Population of the first vibrational level (v″ = 1) as a function of the time in the case of interaction of a laser pulse. Curve 1—with allowance for heating of the gas by laser radiation, 2—radiative population of the level, 3—thermal population, 4—dependence of the temperature of the gas on the time following the action of a laser pulse, 5—laser pulse.

On the basis of our analysis we can draw the following conclusions. Continuous IR radiation of sufficient power, with a frequency that coincides with the absorption line on the vibrational-rotational transition of the molecule, leads to excitation of vibrational levels of the molecules, but the excitation mechanism differs essentially at lower and higher pressures of the molecular gas.

At pressures below a certain critical value (for typical cases it lies in the interval 1—10 Torr) one can attain a radiative excitation of the vibration level without accompanying heating of the gas. In this case one can count on realization of selective chemical reactions, whose activation energy E_a does not greatly exceed the quantum energy.

As to reactions with $E_a \gg \hbar\omega_0$ and dissociation of molecules by resonant IR laser radiation, this calls for excitation of high vibrational levels. This question is not discussed in the present article. We refer the reader to a paper[6] in which it is shown that the realization of radiative excitation of high vibrational levels with a separation of the vibrational temperature from the translational one is a rather complicated matter under the most optimistic assumptions, owing to the "bottleneck" effect that arises when molecules are excited in one vibrational-rotational transition of the band.

At pressures much higher than critical, excitation of vibrational levels of the molecule, including also high levels, proceeds exclusively by the thermal mechanism. Naturally, the chemical reactions observed in this case in mixtures, and the dissociation of the molecules, have a thermal character. We note that it is precisely under these conditions that all the hitherto known experiments on the observation of chemical reactions and dissociation of molecules under the influence of powerful IR laser radiation have been performed. This mechanism explains naturally the chemical reactions with $E_a \gg \hbar\omega_0$ and the dissociation of molecules with dissociation energy $E_d \gg \hbar\omega_0$.

In pulsed excitation, it is possible to obtain in practically all cases an appreciable deviation of the vibrational temperature. But even in this case the chemical reactions are selective only for a short time, during which the indicated temperature deviation obtains. Since the state of thermal heating after the relaxation is usually much longer than the time of the existence of the deviation of the vibrational temperature from the translational one, the only selective reactions will be those whose time is shorter than the lifetime of such a deviation.

The method used in the present paper to investigate the populations of the vibrational levels in electron-vibrational absorption spectra can be used for a detailed investigation of the excitation of molecules in the intermediate region, where both mechanisms are in effect.

[1)] Analogous experiments were subsequently performed with the BCl_3 molecule [2].

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