LUMINESCENCE OF A MOLECULAR GAS UNDER THE ACTION OF CO_2 LASER PULSES

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A study was made of the ultraviolet and visible luminescence emitted from NH_3 and C_2F_3Cl gases as a result of absorption of CO_2 laser radiation pulses. The luminescence appeared only above a certain threshold value of the laser power. The dependence of this threshold on the gas pressure was determined and the luminescence power was measured as a function of the power of CO_2 laser pulses. No delay was observed between the luminescence and the laser radiation pulses. The importance of the vibrational heating of the molecules by the laser pulses, followed by dissociation and emission of light from the dissociation products, was considered alongside other possible luminescence mechanisms.

1. INTRODUCTION

THE development of high-power infrared lasers has made it possible to investigate the resonance interaction between strong fields and molecular systems. Bordé et al.[1] observed visible luminescence of ammonia under the action of continuous radiation emitted by a high-power CO_2 laser at a frequency equal to the rotational-vibrational absorption line of the ν_2 band of NH_3. This was attributed in[1,2] to the thermal heating of the NH_3 molecule by the laser radiation to a high temperature. Similar experiments were subsequently carried out in which CO_2 laser radiation was absorbed by BCl_3 crystals.[3] The development of high-power pulsed atmospheric-pressure CO_2 lasers[4] has made it possible to study the effects produced in a molecular gas by high-power infrared radiation pulses. In particular, optical breakdown and luminescence were observed in various molecular gases when CO_2 laser radiation was focused in them.[5,6] In contrast to earlier observations of optical breakdown in gases transparent to laser radiation (see the review given in[7]), the breakdown was now observed in resonantly absorbing gases.

The present paper reports the results of an investigation of the luminescence and optical breakdown in NH_3 and C_2F_3Cl under the action of CO_2 laser radiation pulses. It was found that visible luminescence appeared at a certain threshold laser power P_{th}^{lum} and the intensity of this luminescence increased with the laser power. It was also found that optical breakdown occurred at a higher threshold power $P_{th}^{br} > P_{th}^{lum}$. These two effects could be distinguished particularly clearly in the case of NH_3.

We studied the mechanism of the subthreshold luminescence in absorbing gases. It seemed that this could be due to the vibrational heating of the molecules followed by the dissociation and emission of radiation from the dissociation products. Studies of the time characteristics of the luminescence indicated that the vibrational heating mechansim was far too slow and could not explain the appearance of luminescence pulses of 200–300 nsec duration immediately after 200–500 nsec laser pulses. We also observed ultraviolet
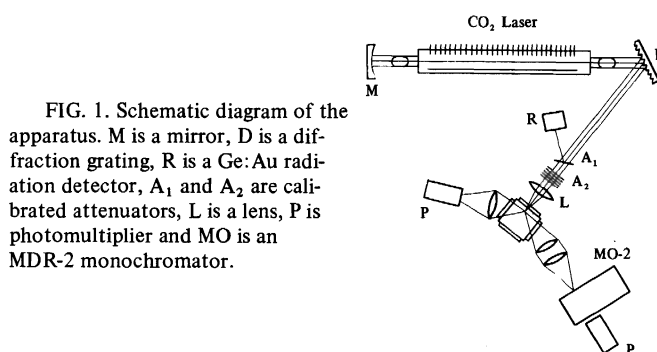

FIG. 1. Schematic diagram of the apparatus. M is a mirror, D is a diffraction grating, R is a Ge:Au radiation detector, A_1 and A_2 are calibrated attenuators, L is a lens, P is photomultiplier and MO is an MDR-2 monochromator.

luminescence, which was evidence of the excitation of higher electronic terms of the NH_3 molecule and which could not be due to the laser excitation of even the highest vibrational levels of the ground electron state of NH_3.

2. EXPERIMENTS ON NH_3

The apparatus employed is shown schematically in Fig. 1. We used a transversely excited pulsed CO_2 laser,[4] which produced up to 70–80 mJ in the form of 200–300 nsec pulses. A diffraction grating with 100 lines/mm was used as the resonator mirror and enabled us to tune the lines of the P and R branches within a wide range near 9.6 and 10.6 μ. The laser radiation was focused by a lens (made of KRS-5) into a gas-filled cuvette. The focus was located 5 mm beyond the entry window. The focal length of the lens was f = 3.5 cm and the diameter of the focal spot was ≈0.1 mm. The luminescence and the breakdown radiation escaped through a side window of the cuvette (all the windows were made of NaCl) and was collected by a lens either on the sensitive area of a photomultiplier or on the entry slit of an MDR-2 monochromator. The spectrum of the radiation emitted in the course of breakdown in NH_3 and C_2F_3Cl was also recorded with an STE-1 spectrograph.

The luminescence and breakdown in ammonia were studied using the asQ(5,3) line of the ν_2 band of NH_3, which coincided quite well with the P(32) λ = 10.72 μ
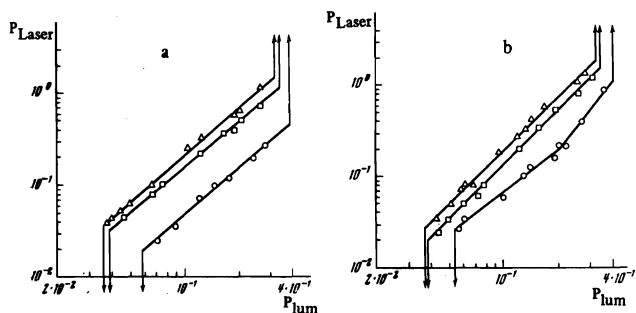
FIG. 2. Dependences of the luminescence power in the visible (5900Å $< \lambda_{lum} <$ 6500Å, Fig. 2a) and in the ultraviolet (3200Å $< \lambda_{lum} <$ 3500Å, Fig. 2b) spectral regions on the power of CO_2 laser radiation.

line of the CO_2 laser. The absorption coefficient at this wavelength was independent of the pressure (beginning from 50 torr) and was equal to 1 cm^{-1}.

The focused radiation of the P(32) line emitted by the CO_2 laser generated luminescence in ammonia. Figure 2 shows the dependences of the luminescence power in the visible (5900—6500 Å) and ultraviolet (3200—3500 Å) parts of the spectrum on the power of the CO_2 laser radiation, obtained at various NH_3 pressures. The necessary wavelengths were selected with colored-glass filters. The luminescence appeared above a certain threshold value of the CO_2 laser radiation power P_{th}^{lum}, which increased with decreasing pressure. The luminescence power increased practically proportionally to the power of the CO_2 laser radiation right up to a second threshold P_{th}^{br} at which a breakdown occurred and the luminescence intensity increased by a factor of 10^4—10^5.

We also studied the spectral and temporal characteristics of the luminescence and the breakdown radiation emitted from NH_3. The luminescence was passed through a monochromator and recorded with an FÉU-39 photomultiplier. A complex system of bands in the visible region, attributed by Isenor and Richardson[5] to the NH_2 radical, was accompanied by a strong band with maxima at 3360 and 3370 Å, which was most probably due to NH.[8] It was important to note that the duration of the luminescence pulses in the visible region, where it was independent of the wavelength, was different from the duration in the ultraviolet region.

Figure 3 shows the luminescence pulses obtained in different parts of the spectrum and the breakdown radiation pulse in the visible region. The duration of the luminescence pulses at λ = 3360 Å was 200—250 nsec and in the visible region it was 1.5—2 μsec (Fig. 3). There was no delay between the luminescence pulses and the CO_2 laser pulses (this was determined to within $\Delta\tau$ = 30 nsec). The luminescence spectrum emitted from the breakdown region in NH_3 consisted mainly of the lines of nitrogen atoms and ions.

The dimensions of the luminescence region, particularly the length, increased with increasing intensity of the CO_2 laser pulses although the brightness did not rise very fast. The dimensions of the luminous region and the photomultiplier signal were used to estimate the order of magnitude of the concentration of the NH radicals in the region of λ = 3360 Å. The data on the

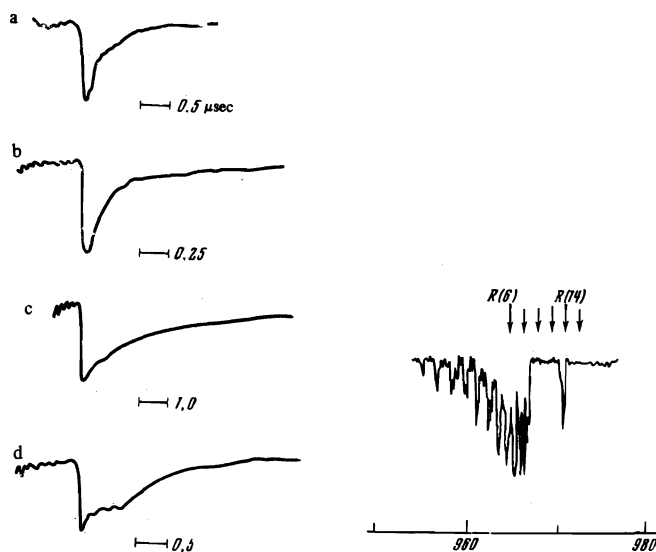FIG. 3   FIG. 4

FIG. 3. Oscillograms of pulses: a—intensity of the CO_2 laser radiation; b—intensity of the ultraviolet luminescence (3200Å $< \lambda <$ 3500Å); c—intensity of the visible luminescence (5900Å $< \lambda <$ 6500Å); d—intensity of the breakdown radiation.

FIG. 4. Absorption spectrum of the NH_3 .:cule. [10] The wavelengths from the left to right in cm^{-1} (asterisks are used to denote coincident lines):

NH_3 molecule		CO_2 laser	
R(1.1)	971.92*	R(16)	973.29
Q(1,K)	968.03	R(14)	971.93*
Q(2,K)	967.79	R(12)	970.55
Q(3,K)	964.40	R(10)	969.14
Q(4,K)	966.70	R(8)	967.71
Q(5,K)	966.21**	R(6)	966.25**

photomultiplier sensitivity and the light-collection geometry indicated that at a pressure of 100 torr about 10^5 photons were emitted at λ = 3360 Å (corresponding to the transition $^3\Pi \rightarrow$ $^3\Sigma$ in NH[9]) into the solid angle of 4π sr. Near the luminescence threshold the luminous volume was V $\approx d^2 l$ = 2.5 × 10^{-6} cm^3. Thus 10^{10}—10^{11} photons/cm^3 were emitted into the angle of 4π sr. If we assumed that the quantum efficiency of the luminescence was unity, we concluded that 10^{10}—10^{11} cm^{-3} of the NH radicals were generated in the excited electronic state when the concentration of NH_3 was 3 × 10^{18} cm^{-3}. Thus, the number of the NH radicals per unit volume was much smaller than the concentration of the NH_3 molecules. The concentration of the excited NH_2 radicals was of the same order of magnitude as the concentration of the NH radicals.

It was interesting to note a certain observation made in the present investigation and reported also by Isenor and Richardson.[5] When the power of the CO_2 laser pulses reached the required value, the luminescence appeared first in the focal region, where the emission stopped after ~50 nsec but the regions adjoining the focus continued to luminesce. This was attributed in[5] to the "burnout" of ammonia in the focal region. Our estimates indicated that relatively few excited dissociation products were generated. This was because the first excited electronic state of NH_3 was located below the dissociation energy[9] and the dissociation products arising from this state could only

be NH or NH_2 in the ground state, i.e., the products of the dissociation NH_3 were not excited. Such dissociation obviously affected the major fraction of the ammonia present. The small number of the NH and NH_2 radicals which were excited and luminesced appeared as a result of dissociation from higher electronic states.

An important point in the understanding of the luminescence mechanism was the question whether the luminescence produced by laser pulses was due to the tuning of the frequency of these pulses to the absorption line of the ammonia gas. We studied the appearance of the luminescence of NH_3 (the pressure of NH_3 in the cuvette was 90 torr) in the region of $\sim$970 cm^{-1}, where the ammonia had absorption lines coinciding with the laser emission lines. The absorption spectrum of NH_3 in the region of 950—980 cm^{-1}[10] is reproduced in Fig. 4. We tuned the laser frequency from the R(16) line to the R(4) line of the 10.6 μ band and found that strong luminescence was produced by the R(14) and R(6) lines, which coincided with the absorption lines of NH_3 (Fig. 4). No luminescence was observed on excitation with the R(16) and R(12) lines. A weak luminescence was observed also when ammonia was excited with the R(8) and R(10) lines because of partial overlap of the NH_3 lines at the particular pressure employed.

We could thus definitely say that the luminescence of NH_3 under the action of CO_2 pulses was due to the absorption of the laser radiation, i.e., it occurred only when the laser frequency was tuned to one of the absorption lines of ammonia.

3. EXPERIMENTS OF C_2F_3Cl

The luminescence and breakdown produced by CO_2 laser pulses were also investigated in gaseous C_2F_3Cl, which absorbed strongly the CO_2 radiation in the region of 9.6 μ. We found that, as in the case of ammonia, the visible luminescence was of threshold nature, i.e., the luminescence disappeared when the incident laser energy or power was reduced by more than 10% below the threshold. The luminescence threshold increased with decreasing pressure. The experimental dependence of the threshold energy E_{th} on the pressure of C_2F_3Cl is plotted in Fig. 5 for the P(12) line of the 9.6 μ band of the CO_2 laser radiation. This dependence could be approximated quite accurately by the expression $E_{th}p = 6.5 \times 10^2$ J·cm^{-2}·torr or by $P_{th}p = 2.51 \times 10^9$ W cm^{-2}·torr.

The described dependence of E_{th} on p occurred only when the lens focus was located 1—2 mm from the entry window of the cuvette so that the absorption of the laser radiation in front of the focus could be ignored. When the lens focus was shifted to a distance of 15—20 mm from the entry window the value of E_{th} was found to be practically independent of the C_2F_3Cl pressure in the 30—150 torr range.

The intensity of the luminescence and the dimensions of the luminous region increased with increasing laser radiation power. The luminous region was about 15 mm long and about 4 mm in diameter when the laser radiation power at the focus was $\sim 10^9$ W/cm^2 and the C_2F_3Cl pressure was 0.4 atm. In this case,
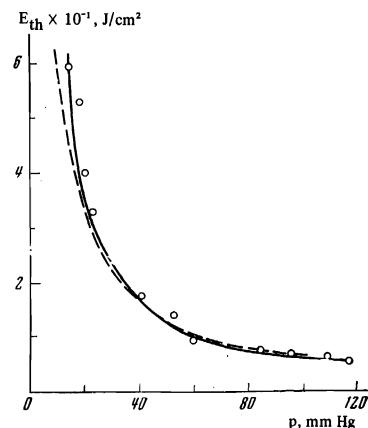

FIG. 5. Dependence of the luminescence threshold on the pressure of C_2F_3Cl.

the intensity of the emitted luminescence was 10^3 times higher than that near the threshold. This relatively large luminous region was observed for illumination with the P(12) laser line, which coincided with a strong absorption line of C_2F_3Cl. Illumination with radiation of wavelength λ = 10.2 μ, at which the absorption of C_2F_3Cl was very low, produced a typical optical breakdown spark similar to that observed in NH_3. However, in the case of C_2F_3Cl a strong green luminescence was observed around the spark in a region of about 10 mm in diameter, which was absent when C_2F_3Cl was illuminated with the strongly absorbed line of λ = 9.6 μ wavelength. Moreover, the duration of the luminescence resulting from illumination with λ = 9.6 μ and 10.2 μ wavelengths was different and equal to 1—1.5 and 0.3 μsec, respectively (the duration was measured at mid-amplitude).

We also recorded the spectrum of the breakdown radiation emitted from C_2F_3Cl under the influence of laser radiation of the λ = 10.2 μ wavelength as well as the spectrum of the strongest luminescence excited by the λ = 9.6 μ laser radiation. These spectra were identical. They contained only the lines of the F atoms and of the C^{2+} and Cl^{2+} ions. Thus, the conditions for the dissociation of the molecules and for the excitation and ionization of atoms were the same in both cases. This was different from the observations of the luminescence of NH_3 which included the lines of the NH and NH_2 radicals. Obviously, partial dissociation of the molecules occurred near the luminescence threshold when the emission was weak. In contrast to NH_3, the regions of strong luminescence and optical breakdown in C_2F_3Cl were not separated by a threshold.

4. DISCUSSION

Our experiments on NH_3 and C_2F_3Cl show that the visible luminescence appears only on resonance between the absorption line of the gas and the emission line of the carbon dioxide laser. Therefore, it is natural to assume that the luminescence results from the vibrational heating of the molecules by the resonant infrared radiation followed by the dissociation in the laser field and the luminescence of the dissociation products. This mechanism of the action of infrared
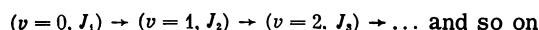
radiation on molecules is discussed, in particular, in[3,11,12]. However, a more detailed analysis of the kinetics of the excitation of the molecular vibrations by infrared laser radiation, given in[13], indicates that this mechanism is not responsible for the luminescence of a molecular gas under the action of laser radiation pulses.

According to Letokhov and Makarov,[13] the rate of injection of the vibrational energy E_{vib} into a molecular system as a result of interaction with monochromatic radiation satisfies the condition

$$dE_{vib}/dt < \hbar\omega_0 q/2\tau_{rot} \qquad (1)$$

where $\hbar\omega_0$ is the energy of the incident quanta; q is the relative proportion of the molecules at the lower rotational-vibrational level of a molecule which is in resonance with the field; τ_{rot} is the rotational relaxation time. The inequality (1) gives the upper limit and does not depend on the mechanism by which the molecules rise along the vibrational levels. An analysis of a specific excitation mechanism of the higher vibrational-levels (cascade excitation due to the vibrational-vibrational exchange) shows that this upper limit is even lower.

The only way of going outside the range specified in Eq. (1) is to consider the direct radiative excitation in all the successive rotational-vibrational transitions without rotational relaxation at intermediate vibrational levels, i.e., the excitation in accordance with the scheme

$(v = 0, J_1) \to (v = 1, J_2) \to (v = 2. J_3) \to \ldots$ and so on

In this case, the vibrational energy of a molecule rises in accordance with the law

$$E_{vib} = \hbar\omega_0(W_{exc}t)^{1/2}, \qquad (2)$$

where W_{exc} is the probability of an induced transition. However, in practice, this mechanism is inapplicable to the excitation of high levels in a real molecule because of anharmonicity.

Polyatomic molecules are usually characterized by $q \approx 10^{-2}-10^{-3}$ and the rotational relaxation time is $\tau_{rot} \approx 10^{-9}$ sec·atm. If we assume that these values hold for C_2F_3Cl and NH_3, we find that $dE_{vib}/dt < 0.63$ eV/μsec at a pressure of 1 atm. The visible luminescence appears immediately (to within $\Delta\tau \approx 30$ nsec) after the laser pulse. Before the emission of the luminescence the average energy of the molecules is $E_{av} \le \Delta\tau dE_{vib}/dt = 0.02$ eV, which is quite insufficient for the dissociation of the molecules. Thus, the vibrational heating of a molecule followed by dissociation does not contribute to the observed luminescence. This mechanism is excluded also by another important observation. The experimentally observed strong luminescence band of the NH radicals at $\lambda = 3360$ Å may be due to the excitation of higher unstable electronic states of NH_3 and not to dissociation from the ground electronic state which would occur in the case of strong vibrational heating of the molecules.

We have to assume that there is some other faster luminescence mechanism. The visible luminescence appears in the range of laser radiation powers about an order of magnitude lower than the optical breakdown threshold which corresponds to electron avalanching. We may assume that initially electrons are generated and heated by the incident infrared radiation at power levels below the breakdown threshold. The luminescence threshold then represents the appearance of electrons of energies amounting to several electron-volts, which is sufficient for the excitation of the higher electronic states of the NH_3 molecule. These electrons lose their energy by interacting with the molecules and a continuous electron avalanche does not appear below the breakdown threshold. However, a certain number of electrons with energies of several electron-volts is still present and they excite the ammonia molecules. According to this model, a molecular gas luminescences under the action of short-lived electron avalanches which appear at power levels several times lower than the optical breakdown threshold, i.e., the power at which electron avalanches become continuous. This happens because of the relatively low excitation potential of the levels and the presence of the visible luminescence.

The electron mechanism of the excitation of the observed luminescence does not explain clearly why the luminescence threshold should depend on the resonance with the absorption line of a molecular gas. It is possible that a gas contains molecules which have captured electrons. When these molecules collide with vibrationally excited molecules they may lose the electrons. However, this mechanism of initiation of the subthreshold luminescence would require confirmation by special experiments.

5. CONCLUSIONS

The subthreshold luminescence of a molecular gas under the action of resonant infrared laser radiation pulses can be used in studies of the electronic states in molecules and of the radicals formed by the dissociation of the molecules. The luminescence threshold is ~ 1 GW/cm^2 and modern CO_2 lasers emitting energies of hundreds of joules can excite the luminescence and dissociate molecular gases in large volumes. The same method might be used to attain a nonequilibrium population of levels in the molecules and radicals and thus produce laser transitions.

[1]C. Bordé, A. Henry, and L. Henry, C. R. Acad. Sci. B262, 1389 (1966).

[2]V. V. Losev, V. F. Papulovskiĭ, V. P. Tychinskiĭ, G. A. Fedina, Khim. Vys. Energ. 3, 331 (1969).

[3]N. V. Karlov, Yu. N. Petrov, A. M. Prokhorov, and O. M. Stel'makh, ZhETF Pis. Red. 11, 220 (1970) [JETP Lett. 11, 135 (1970)].

[4]A. J. Beaulieu, Appl. Phys. Lett. 16, 504 (1970).

[5]N. R. Isenor and M. C. Richardson, Appl. Phys. Lett. 18, 224 (1971).

[6]V. S. Letokhov, E. A. Ryabov, and O. A. Tumanov, Opt. Commun. 5, 168 (1972).

[7]Yu. P. Raĭzer, Usp. Fiz. Nauk 87, 29 (1965) [Sov. Phys.-Usp. 8, 650 (1966)].

[8]A. G. Gaydon, The Spectroscopy of Flames, Chapman and Hall, London, 1957 (Russ. Transl., IIL, M., 1959).

[9] G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 3, Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York, 1966 (Russ. Transl., Mir, M., 1969), Chap. IV, Sec. 3.

[10] H. M. Mould, W. C. Price, and G. R. Wilkinson, Spectrochim. Acta 15, 313 (1959).

[11] N. D. Artamonova, V. T. Platonenko, and R. V. Khokhlov, Zh. Eksp. Teor. Fiz. 58, 2195 (1970) [Sov. Phys.-JETP 31, 1185 (1970)].

[12] Yu. V. Afanas'ev, É. M. Belenov, E. P. Markin, and I. A. Poluéktov, ZhETF Pis. Red. 13, 462 (1971) [JETP Lett. 13, 331 (1971)].

[13] V. S. Letokhov and A. A. Makarov, Zh. Eksp. Teor. Fiz. present issue, p. 2064 [Sov. Phys.-JETP, present issue, p. 1091].

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