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CO_2 LASERS

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CONTENTS

1. INTRODUCTION

THE present review is devoted to one of the most promising laser types, the CO_2 laser.

The first gas laser was realized by Javan, Bennett, and Herriott in 1961 [1]. This was a continuously operating laser using a Ne-He mixture. The construction and the operating principle of the first lasers are described in the popular articles of Schawlow [2]. By the time Bennett wrote the first review devoted to gas lasers (December 1962) [3], continuous generation was realized for forty different transitions in the range from 0.63 to 12 μ, and ten different gas systems and four excitation mechanisms were already used. The period from 1963 through 1965 was characterized by new significant advances. Ionic and molecular lasers were discovered. The spectral region in which spectral generation was obtained was broadened both in the short-wave direction (0.27 μ) and towards longer wavelengths (120 μ). A summary of the research on gas lasers during that period is contained in Bennett's second review [4].

Generation in a number of lines of two vibrational-rotational bands of the CO_2 molecule in the 10 μ region was discovered in 1964 [5]. The generation power was 1 mW. Almost simultaneously, similar results were obtained by the authors of [6]. In 1965, at the Puerto Rico Conference on Quantum Electronics, Patel reported attainment of a power on the order of 10 W, the entire power being concentrated in two vibrational-rotational lines. The power was increased by three orders of magnitude by adding to the CO_2 nitrogen, by carrying out the experiment in a stream of the working mixture [7,8], and replacing the high-frequency supply to the gas discharge by a dc supply. Following this conference, many investigators concentrated their efforts on the study of just this type of laser, in view of its high power and large efficiency. In fact, whereas the most widely employed type of continuous gas laser, the neon-helium type, can be characterized by efficiencies on the order of 10^{-5}—10^{-4} and a power 10—20 mW, and argon ion lasers by values 10^{-3}—10^{-2} and 2—5 W, respectively, the efficiencies of CO_2 lasers reach 10^{-1} at powers on the order of hundreds of watts.

Such considerable progress in the development of CO_2 lasers were attained by the following means: a) addition of considerable amounts of He to the CO_2-N_2 mixture [9,10] or to pure CO_2 [9]; b) addition of water vapor [11], and c) cooling the gas-discharge tube [10,12]. An important role was played also by research on the choice of optimal designs of tubes of Fabry-Perot resonators and optimal partial pressures and stream velocities of the mixture.

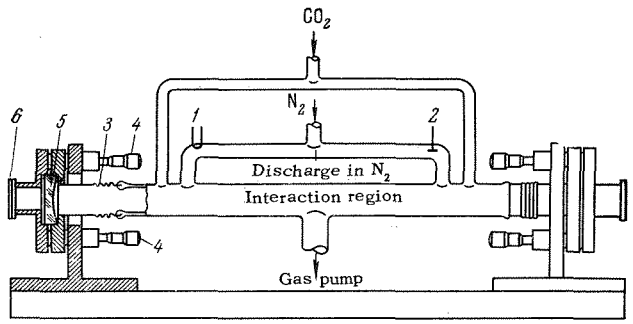

FIG. 1. Apparatus for producing $CO_2 - N_2$ lasing with separate N_2 excitation. Parts: 1–cathode, 2–anode, 3–bellows, 4–adjusting screws for internal mirror, 5–mirror, 6–NaCl window.

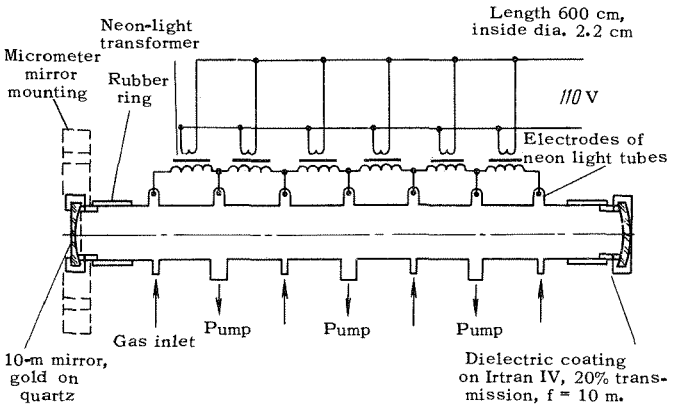

FIG. 3. Gas-discharge tube, the use of which yields more than 100 W power.

The present review covers papers published up to 1 November 1966, with inclusion of the results reported at the IV International Conference on Quantum Electronics (Phoenix, Arizona)[13-18].

2. CONSTRUCTIONS OF TUBES AND FABRY-PEROT RESONATORS

A generation power on the order of 10—20 W was first attained by Patel using the apparatus shown in Fig. 1[7]. An essential feature of the installation was excitation of a stream of nitrogen in a dc discharge; this stream was then mixed with a stream of CO_2 in a volume free of electric field. The CO_2-N_2 mixture was continuously pumped by a forevacuum pump at a rate of 6 m/sec. According to Patel's interpretation (see also [6]), in the N_2 and CO_2 interaction region, resonant transfer of energy to the CO_2 molecules from the vibrationally-excited N_2 molecules is realized and causes inversion of the laser-level population (see Sec. 7).

According to the papers delivered at the Phoenix Conference, researchers have given up separate excitation systems, using only systems in which the CO_2-N_2 mixtures are fed directly to the discharge tube. It must be borne in mind, however, that lasers

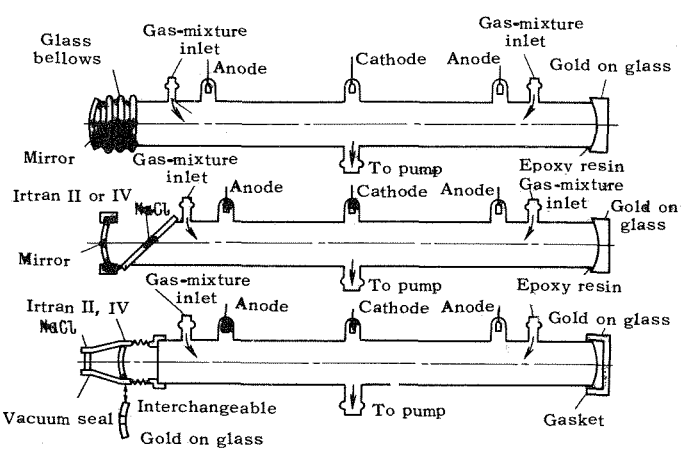

FIG. 2. Gas-discharge tubes used in medium-power lasers.

with separate excitation of the N_2 may be useful for many physical investigations, particularly to assess the role played by the degree of vacuum.

Modern CO_2 laser designs are shown in Figs. 2 and 3[13]. The laser discharge-tube lengths range from 1 to 6 m and the diameters from 22 to 75 mm. Further increase in the tube diameter is hindered by the pinching of the gas-discharge column, which occurs at diameters exceeding 40 mm for the N_2-CO_2 mixture and exceeding 70 mm for the N_2-CO_2-He mixtures. The discharge is fed with either direct current or ordinary high-frequency alternating current. When direct current from several dozen to hundreds of milliamperes is used, power supplies up to 15 kV are required. Both cold and heated cathodes are used.

Figure 2 shows the construction of tubes used to obtain relatively low generation powers, and Fig. 3 a tube for the production of coherent radiation with a power exceeding 100 W[13]. It is seen from Fig. 2 that both internal and external mirrors are used. In the latter case, the radiation emerges through an NaCl window installed at the Brewster angle. Windows transparent in the 9—11 μ region can be made not only of NaCl, but also of KCl, Ge, and Si; the latter should have only intrinsic conductivity.

The Fabry-Perot resonator mirrors can be metallic (Au, Al) or dielectric, sputtered on glass or quartz. The mirrors are secured with epoxy resin. In the case of substrates that are not transparent to infrared radiation, the power from the laser is decoupled through a round central opening in the mirror or through openings of different configurations. Mirrors of Irtran-II and Irtran-IV are widely used for power extraction. These materials are pressed polycrystalline ZnS and BaS.

The tube of the high-power CO_2 laser shown in Fig. 3 is 6 m long and 22 mm in diameter. AC supply is used. The tube is sectionalized, so that individual meter segments, each one meter long, can be employed. One mirror is made of gold on a quartz substrate ($f = 10$ m), and the second, outlet mirror is

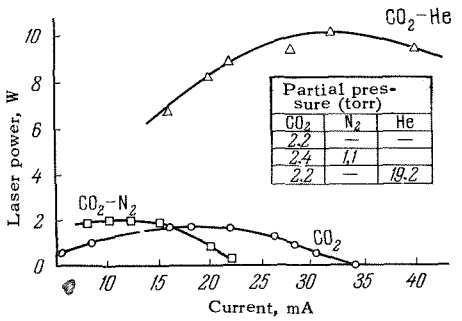

FIG. 4. Power vs. current in a laser with a static gas system at different mixture compositions.

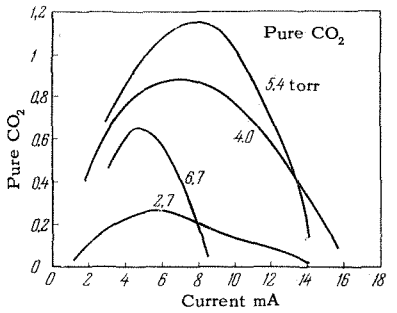

FIG. 5. Power vs. current in laser with pure CO_2, in the case of a static gas mixture at different CO_2 pressures (jacket temperature 20°C).

made with a dielectric coating of Irtran-IV and has a transmission of 20%.

A notable recent advance is the attainment of high generation power in the CO_2 bands not only in continuous-flow systems, but also in sealed ones; according to [19] the service life of such tubes can reach 100 hrs and more.

3. PRINCIPAL EXPERIMENTAL RESULTS

Typical results of investigations of CO_2-laser power using different mixtures are shown in Table I and in Fig. 4 [9,13]. The tube length was 96 cm, the diameter 21 cm, one mirror was opaque and of gold, and the other, with 12% transmission, was made of Irtran-II. The focal lengths of the mirrors were 6 m. The results obtained with a flow-through system are listed in Table I. It is seen from the table that the CO_2-He and CO_2-N_2 mixtures give comparable powers (5.25 and 4.5 W). The use of a three-component mixture increases the generation power by almost four times (to 18 W). In a sealed system, using the same tube and pure CO_2 or CO_2+N_2 (see Fig. 2), the optimal generation powers are comparable (~2W). With increasing current in the CO_2-N_2 mixture, the generation power drops off more rapidly than in pure CO_2. Addition of He to the CO_2-N_2 mixture in a sealed system increases the power to 19 W, i.e., by almost one order of magnitude. Similar results were obtained for a laser operating with pure CO_2 in a sealed tube 1 m long and of 10.5 mm diameter, at voltages 7—10 kV and currents 5—10 mA [12]. As seen from Fig. 5, a power up to 1.2 W was obtained at the optimal pressure 5.4 torr.

Partial pressure, Torr			Laser power, W	Efficiency
CO_2	He	N_2		
0.6	—	3.6	4.5	2.9
1.3	11.5	(0.004) *)	5.25	1.5
2.7	7.8	3.5	18.0	4
1	—	(0.003) *)	0.41	

*Uncontrolled nitrogen impurity

Table I. Power and efficiency of CO_2 laser at different partial gas pressures

The effect of adding nitrogen to the CO_2 is illustrated in Fig. 6 [12]. We see that the optimal ratio of the CO_2 and N_2 pressures is close to 1:2. Even greater powers (up to 20 W), were obtained by Frapard with pure CO_2, when working with sealed tubes in which previously 50 W power was attained with the CO_2-N_2 mixture [15].

Cooling the sealed gas-discharge tube to −60°C doubled the efficiency and the generation power in both CO_2 and CO_2-N_2 lasers (Fig. 7) [12].

Witteman [11,16] investigated the influence of water vapor on the generation power of the CO_2-N_2 mixture. The diagram of his experimental setup is shown in Fig. 8 [11]. An interesting methodological improvement was the use of a germanium plate to decouple the generation power. By varying the inclination of the plate it was possible to pick off different amounts of power from the laser. Figure 9 illustrates the influence of the water-vapor concentration on the output power of a CO_2-N_2 laser [11]. When working with a 2-m tube filled with CO_2-N_2 to which H_2O at a partial pressure 0.2 torr was added, Witteman obtained a generation power of 20 W [11]. In his subsequent investigation, using a four-component mixture CO_2-N_2-He-H_2O in a sealed laser, he reached 70 W [16].

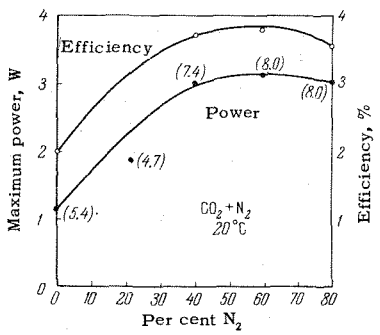

FIG. 6. Power and efficiency of CO_2-N_2 laser vs. percentage composition (the numbers in the parentheses give the optimal total pressure in torrs).

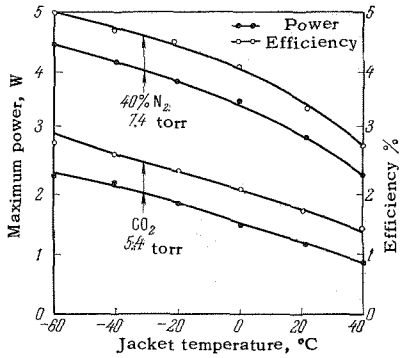

FIG. 7. Laser power and efficiency vs. jacket temperature.

A still greater increase in power (by a factor of 8) can be obtained, according to Rosenberger[19], by adding hydrogen (~0.5 torr) to a flow-through CO_2+N_2 laser (1 and 4 torr, respectively).*

We note that although large powers were obtained in sealed CO_2 lasers, even higher powers are obtained in flow-through lasers. Thus, Patel and his co-workers[10] obtained a maximum power of 106 W using a CO_2-N_2-He mixture at a stream velocity 6 m/sec and with dc supply; when rectified but unfiltered current was used, the peak generation output power was 183 W. Frapard[15] mentioned in a paper at the Fourth International Conference on Quantum Electronics that he attained a generation power of 280 W with a continuously operating laser. According to the published data, the maximum continuous power of a CO_2 laser was obtained by Statz and amounts to 500 W[20].

4. SPECTRAL COMPOSITION OF CONTINUOUS LASER RADIATION

In the first investigations[5,6], generation was observed at the rotational-vibrational lines of the P branches of the 00^01-10^00 and 00^01-02^00 bands of the CO_2 molecule, with rotational quantum numbers ranging from J = 11 to J = 37 for the 00^01-10^00 band and from J = 21 to J = 33 for the 00^01-02^00 band. The highest generation power was obtained at J = 23 (00^01-10^00) and J = 27 (00^01-02^00).

By adding air to CO_2, Howe[21] observed generation with power on the order of 0.1 mW at rotational lines from J = 14 to J = 26 of the R branch of the 00^01-10^00 band of the CO_2 molecule. The most intense was the R(20) line. It was established in later investigations that when the generation power increases the number of simultaneously generating lines

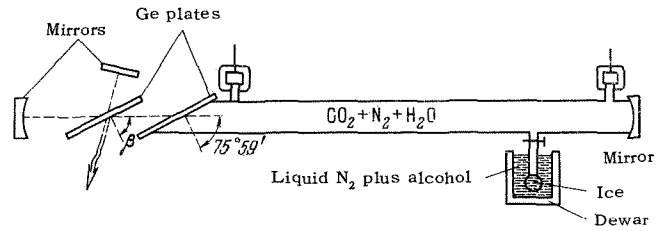

FIG. 8. Setup for investigating the influence of H_2O impurities on the power and efficiency of a laser.

decreases, and at the largest power the generation is observed at 1–2 lines[8,10]. This shows clearly, first, that the largest gain is obtained at J ≈ 20–30 and, second, that competition exists between the different transitions. To eliminate the competition between different transitions, Moeller and Rigden[13] placed a diffraction grating, which served as a discriminating device, in the resonator cavity. Moeller and Rigden's setup is illustrated in Fig. 10. The discharge tube was 6 m long and 22 mm in diameter, and was fed with 60 Hz ac. The tube had an internal mirror with 2% transmission, made of Irtran-IV with dielectric coating. At the other end of the tube was a window of NaCl, mounted at the Brewster angle. A diffraction grating 2 cm wide and with 70 lines/mm was placed 5 m from the mirror. The theoretical resolution of the grating was 1400. The cavity was tuned to different wavelengths by rotating the grating, and this enabled Moeller and Rigden to observe not only generation in a much larger number of P-branch lines of the CO_2 bands than before, but also generation in R-branch lines.

Figure 11 shows the generation spectrum of the CO_2 molecule in the 00^01-10^00 band. It is similar to the absorption spectrum of the CO_2 molecule[22]. The large number of lines of both the P and the R branch have comparable intensities.

Using a mirror with 2% transmission, the output power was 0.27 W/m for the strongest lines. For a very small number of the most intense lines, generation could be obtained also with a mirror having a 30% transmission and an output power 4 W/m. For comparison we indicate that when working with ordinary mirrors of 20-m radius, the total output power with the same tube was 130 W.

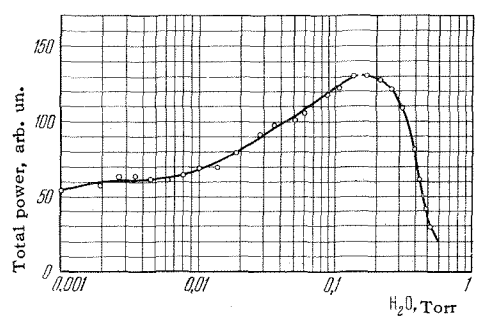

FIG. 9. Influence of water vapor on laser power.

*It must be noted that Rosenberger's comparison of the influence of water vapor and hydrogen was not made correctly. The water-vapor and hydrogen contents were calculated with the aid of equilibrium constants that are suitable under equilibrium conditions but not under gas-discharge conditions, when the composition is determined by electronic processes.

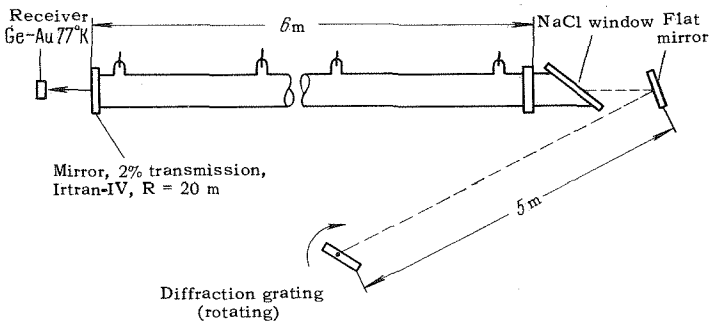

FIG. 10. Laser tube with diffraction grating, the use of which make possible generation at a record number of lines.

Frapard[15,23] carried out similar work, but used in the resonant cavity not a diffraction grating but an NaCl prism.

The results of his investigations are listed in Tables II, III, and IV.

As seen from Table II, he observed generation at 27 lines of the P-branch (from P_4 to P_{56}) and 26 lines of the R-branch (from R_4 to R_{54}) of the 00^01-02^00 transition.

In the 00^01-10^00 transition (Table III), he observed generation of 29 lines of the P-branch (from P_4 to P_{60}) and 25 lines of the R-branch (from R_4 to R_{52}).

Frapard discovered also generation at the P-branch lines of still another band of the CO_2 molecule, namely the transition 01^11-03^10 (Table IV); 25 lines from P_{19} to P_{40} were registered. However, no generation was observed at P_{20} and P_{22}.

Recently, in addition, generation was obtained by Howe and McFarlane at the P-branch lines of the 01^10-11^00 transition in the 11 μ region[24] and by Hartmann and Kleman in a large number of transitions (14^00-05^10, 14^00-13^10, 21^10-12^20, 03^11-02^21, 24^00-23^10) in the region from 11 to 18 μ[25]. We note, however, that the generation power in all these transitions was much lower than at the 00^01-10^00 transition.

Thus, the foregoing investigations established the possibility of obtained generation at the transitions of the CO_2 molecule in the region from 9 to 18 μ, and (no less important a factor) demonstrated the possibility of varying the wave number of the laser in intervals of 1–2 cm^{-1}, which is very important for a number of both physical and practical problems.

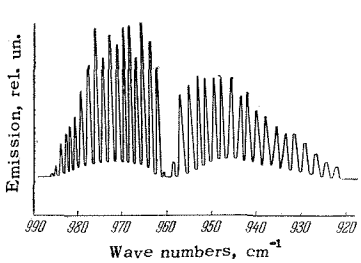

FIG. 11. CO_2 laser generation spectrum obtained with the aid of a rotating diffraction grating.

5. PULSED HIGH-POWER LASER

So far we have discussed only lasers operating in the continuous mode. The operation of a CO_2 laser in the pulsed mode was investigated in [5,26]. However, large generation power with CO_2 in the pulsed mode was first obtained by Frapard[15,27]. He produced current pulses of 10 μsec duration with the aid of capacitor banks. The peak voltage could reach 10 kV at a current of 1.1 A. The radiation was registered with an oscilloscope through a gold-doped germanium receiver cooled to 77° K. Pure CO_2 and CO_2+N_2, and CO_2 + He mixtures were investigated in a sealed discharge tube. Coherent emission was observed at 10.59 μ. When working with CO_2, the generation pulse width measured at $\frac{1}{3}$ the height was 500 μsec, and the peak power was 220 W, whereas the power obtained with the CO_2+N_2 mixture was 450 W. In both cases, generation occurred not only the time of the discharge but also in the decaying plasma. The largest emission peak power was obtained with the CO_2-He mixture and was equal to 825 W. Unlike the first two cases, no lag whatever was observed between the current and the stimulated emission, and this indicates in Frapard's opinion that the upper level of the CO_2 laser is electron-excited.

6. LASER IN COMBINATION WITH Q-SWITCHING TECHNIQUE[17,28]

To obtain repeated short CO_2 laser pulses of high output power, Javan and his co-workers used a Q-switching technique. A diagram of the setup is shown in Fig. 12[13]. The discharge tube of 2.54 cm diameter and 1.50 m length had windows of NaCl mounted at the Brewster angle. The resonator consisted of a mirror of 3 m radius of curvature and with an opening for the emission, and a flat mirror on a motor shaft. The total interferometer length was 2.1 m. The continuous laser power did not exceed several watts. The experiments were made with CO_2+N_2 and CO_2+N_2 + He mixtures. The He pressure was varied between 1 and 50 torr, the CO_2 pressure was less than 1 torr, and the N_2 pressure approximately 3 torr. The maximum Q-switching pulse-repetition frequency was

Table II. Wave numbers of CO_2 00^01-02^00 band lines observed in laser emission

Transition symbol	Measured wave number, cm^{-1}	Transition symbol	Measured wave number, cm^{-1}	Transition symbol	Measured wave number, cm^{-1}	Transition symbol	Measured wave number, cm^{-1}
P_4	957.76	P_{32} *)	932.92	R_4	964.74	R_{30} *)	982.08
P_6 *)	956.16	P_{34} *)	930.97	R_6 *)	966.18	R_{32} *)	983.19
P_8 *)	954.52	P_{36} *)	928.94	R_8 *)	967.73	R_{34} *)	984.35
P_{10} *)	952.88	P_{38} *)	926.96	R_{10} *)	969.09	R_{36} *)	985.42
P_{12} *)	951.16	P_{40} *)	924.90	R_{12} *)	970.50	R_{38} *)	986.49
P_{14} *)	949.44	P_{42} *)	922.85	R_{14} *)	971.91	R_{40} *)	987.56
P_{16} *)	947.73	P_{44} *)	920.77	R_{16} *)	972.24	R_{42} *)	988.63
P_{18} *) a)	945.94	P_{46} *)	918.65	R_{18} *) a)	974.61	R_{44} *)	989.61
P_{20} *) a)	944.15	P_{48} *)	916.51	R_{20} *) a)	975.90	R_{46} *)	990.54
P_{22} *) a)	942.37	P_{50} *)	914.41	R_{22} *) a)	977.18	R_{48} *)	991.47
P_{24} *) a)	940.51	P_{52} *)	912.16	R_{24} *) a)	978.47	R_{50} *)	992.46
P_{26} *) a)	938.66	P_{54}	909.92	R_{26} *)	979.67	R_{52}	993.34
P_{28} *)	936.77	P_{56} *) b)	907.73	R_{28} *)	980.87	R_{54}	994.18
P_{30} *)	934.88						

a) Strongest transition in group.
b) Transition coincides with P_{23} transition of the $00^01 - 03^00$ band.
*Observed in pure CO_2.

Table III. Wave numbers of CO_2 00^01-10^00 band lines observed in laser emission

Transition symbol	Measured wave number, cm^{-1}	Transition symbol	Measured wave number, cm^{-1}	Transition symbol	Measured wave number, cm^{-1}	Transition symbol	Measured wave number, cm^{-1}
P_4	1060.61	P_{32} *)	1035.46	P_{60}	1005.38	R_{28} *)	1083.48
P_6 *)	1059.04	P_{34} *)	1033.48	R_4	1067.50	R_{30} *)	1084.63
P_8 *)	1057.30	P_{36} *)	1031.56	R_6 *)	1068.89	R_{32} *)	1085.74
P_{10} *)	1055.58	P_{38} *)	1029.44	R_8 *)	1070.43	R_{34} *)	1086.84
P_{12} *)	1053.91	P_{40} *)	1027.38	R_{10} *)	1071.87	R_{36} *)	1087.90
P_{14} *)	1052.13	P_{42} *)	1025.27	R_{12} *)	1073.28	R_{38} *)	1088.97
P_{16} *)	1050.47	P_{44} *)	1023.17	R_{14} *)	1074.63	R_{40} *)	1090.04
P_{18} *) a)	1048.66	P_{46} *)	1021.03	R_{16} *)	1076.00	R_{42} *)	1090.99
P_{20} *) a)	1046.85	P_{48} *)	1018.85	R_{18} *) a)	1077.30	R_{44} *)	1092.00
P_{22} *) a)	1045.04	P_{50} *)	1016.67	R_{20} *) a)	1078.57	R_{46} *)	1093.01
P_{24} *) a)	1043.19	P_{52} *)	1014.46	R_{22} *) a)	1079.85	R_{48}	1093.85
P_{26} *)	1041.29	P_{54} *)	1012.25	R_{24} *) a)	1081.08	R_{50}	1094.81
P_{28} *)	1039.34	P_{56} *)	1010.00	R_{26} *)	1082.29	R_{52}	1095.71
P_{30} *)	1037.40	P_{58}	1007.76				

a) Strongest transition in group.
*Observed in pure CO_2.

limited by the speed of mirror rotation, which could not exceed 500 rps.

Under the best operating conditions, the energy in each pulse was 1.1 mJ. Subsequent investigations have shown that the Q-switching pulse-repetition frequency, determined by the relaxation time (~ 0.3 msec) of the aggregate of the levels participating in the generation, could be increased by almost one order of magnitude without loss of intensity in the Q-switching pulses. The upper limit of the pulse width was estimated, with the aid of a gold-doped germanium receiver, at 100 nsec. Subsequent investigations (see below) have shown, however, that the pulse duration is 20 nsec. Consequently, the peak power of the CO_2 laser was 50 kW.

Bridges [29] obtained Q-switching of the resonator of a CO_2 laser at a high repetition frequency. The gas-discharge tube was 50 cm long and 1 cm in diameter, and was filled with a mixture of CO_2 (4 torr) and N_2 (4 torr). The operation was carried out without gas flow, at a current 5 mA and a voltage 8 kV. A gold mirror with radius of curvature of 2 m and a flat dielectric-coating mirror with 8% transmission were used. The distance between mirrors was 8 m. In the continuous mode, the output power was 1 W at 10.6 μ. Tuning the resonator by longitudinally displacing the

Table IV. Wave numbers of CO_2 01^11-03^10 band lines observed in laser emission

Transition symbol	Measured wavelength, μ (vacuum)	Measured wave number, cm^{-1}	Calculated wave number, cm^{-1}	Transition symbol	Measured wavelength, μ (vacuum)	Measured wave number, cm^{-1}	Calculated wave number, cm^{-1}
P_{19}	10,9735	911,29	911,43	P_{34} *)	11,1485	896,98	897,11
P_{21} *)	10,9950	909,50	909,65	P_{35} *)	11,1555	896,42	896,57
P_{23} *) b)	11,0165	907,73	907,85	P_{36} *)	11,1735	894,97	895,11
P_{24} *)	11,0300	906,62	906,71	P_{37} *)	11,1790	894,53	894,61
P_{25} *)	11,0385	905,92	906,02	P_{38}	11,1980	893,02	893,09
P_{26} *)	11,0535	904,69	904,84	P_{39}	11,2035	892,58	892,64
P_{27} *)	11,0610	904,08	904,18	P_{40}	11,2235	890,99	891,05
P_{28} *)	11,0760	902,85	902,94	P_{41}	11,2295	890,51	890,64
P_{29} *)	11,0850	902,12	902,31	P_{42}	11,2295	890,51	888,98
P_{30} *) a)	11,1000	900,90	901,02	P_{43}	11,2545	888,53	888,61
P_{31} *)	11,1070	900,33	900,42	P_{44}	11,2770	886,76	886,89
P_{32} *)	11,1235	899,00	899,08	P_{45}	11,2805	886,49	886,57
P_{33} *)	11,1315	898,35	898,51				

a) Strongest transition in group.
b) Transition coincides with P_{56} transition of $00^01 - 02^00$ band.
*Observed in pure CO_2.

mirror made it possible to obtain generation at the rotational lines from P(16) to P(28).

When the mirror was moved at a speed of 16 m/sec through a distance on the order of one half the wavelength, generation was observed only at the P(20) rotational line. At higher speeds (>30 m/sec), the generation peak power decreased. At speeds lower than 16 m/sec, generation at the other lines observed in the continuous mode was also observed in succession during the time of mirror motion. Under optimal generation conditions (v = 16 m/sec) the duration of the generation pulse was of the order of 1 μsec at a peak power of 30 W. The time-averaged generation power was the same as in the continuous mode, i.e., 1 W. Bridges connects the time between two pulses in the optimal mode, on the order of 3×10^{-5} sec, with the relaxation time of the lower level; this, however, is not the only possible interpretation.

7. BASIC DATA ON THE CO_2 MOLECULE. SELECTIVE EXCITATION OF THE UPPER CO_2 LASER LEVEL BY VIBRATIONALLY-EXCITED NITROGEN

We have described above the main structural features of CO_2 lasers and the experimental facts obtained during their development and investigation. In the sections that follow we consider the present status of the generation mechanisms of lasers with CO_2 and its mixtures with different gases. However, before we start considering this question, we recall briefly the basic data on the CO_2 molecule, which will be needed in what follows. CO_2 is a linear symmetrical molecule. It has three fundamental oscillation modes: ν_1 —longitudinal symmetrical, ν_2 —deformational, and ν_3 —longitudinal asymmetrical (Fig. 13). The energy scheme of its lower vibrational levels is shown in Fig. 14[5,7,30]. The symmetrical oscillation ν_1 corresponds to the transition between the 10^00-00^00 levels. This transition is forbidden in the infrared region of the spectrum and can be observed only in the Raman spectrum. The deformational oscillation ν_2 corresponds to the strong transition 01^10-00^00. It appears in the infrared region of the spectrum at 15.6 μ. We emphasize that a Fermi resonance takes place between the states 10^00 and 02^00 (second quantum state of the deformational oscillation)[31,32], and consequently the distance between the 01^10 and 02^00 levels is not $\nu_2 = 667$ cm^{-1}, but only 618 cm^{-1}. The 00^01-00^00 transition (4.3 μ) corresponding to the antisymmetrical oscillation ν_3, is the strongest in the infrared region of the spectrum. Table V lists data on the integral absorption indices $\int k_\nu d\nu$ at 300° K of the CO_2 bands that are involved in the operation of CO_2 lasers[33,35]. The results given in this table were obtained with infrared devices of medium dispersion and pressure-broadening of the rotational lines, in order to exclude apparatus errors.

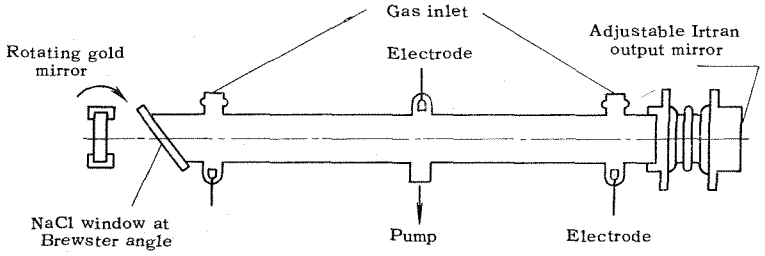

FIG. 12. Diagram of setup for Q-switching experiments with a CO_2 laser.

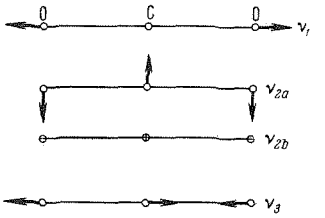

FIG. 13. Normal vibrations of the CO_2 molecule.

Under typical conditions, which occur in CO_2 laser operation, emission at the transitions 01^10-00^00 and 00^01-00^00, terminating at the ground vibrational state, is of the locked type.[18]. Estimates based on the data of Table V show that the radiative lifetime of the 00^01 level is shorter than 10^{-2} sec, and that of the 01^10 shorter than 1 sec. Typical lifetimes of the remaining levels participating in the CO_2 laser operation are of the order of seconds. For example, according to the latest measurements, the time constant of the 00^01-10^01 transition is 2.9 sec[36].

As already indicated above, explanations of the operation of the CO_2-N_2 laser, of its large power, and of its high efficiency were given in Patel's paper[7]. It is known that an electric discharge in nitrogen leads to a very effective formation of vibrationally-excited N_2 molecules (10–30% of the total number of the N_2 molecules)[37,38]. Since the N_2 molecule has identical nuclei, its dipole radiation is forbidden and decay of its excited vibrational levels is possible only via collisions. However, the cross section for collisions between N_2 molecules, leading to the transformation of vibrational quanta into translational energy, is very small (smaller than 10^{-23} cm^2[39]). Therefore, for ordinary laboratory sizes of the vessels and at N_2 pressures of 1 torr, the vibrational relaxation of N_2 is due essentially to collisions with the walls. The situation changes radically when CO_2 molecules are added to the N_2. Owing to the almost complete equality of the energies of the first vibrational level of N_2 and the 00^01 level of CO_2 (see Fig. 14) (ΔE = 18 cm^{-1}), the CO_2 molecules can draw energy from the N_2, and

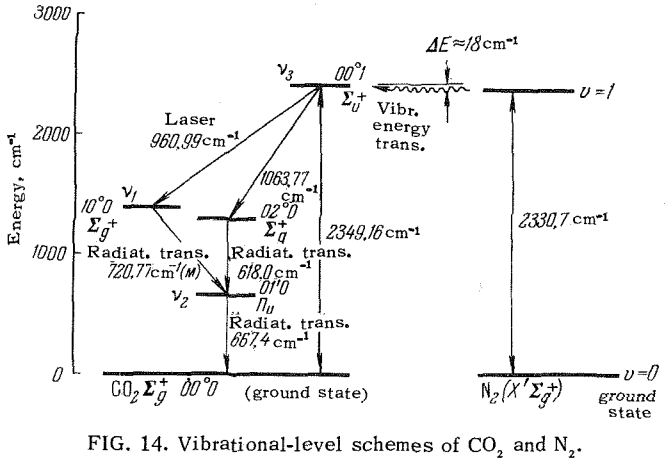

FIG. 14. Vibrational-level schemes of CO_2 and N_2.

Table V. Integral intensities for CO_2 vibrational-rotational bands (temperature 300° K)

Transition	Null line of band, cm^{-1}	$\int k_\alpha d\nu$ cm^{-2} atm^{-1}
00^00-00^01	2349	2706[33], 2500[34]
02^00-00^01	1064	0,0532[33], 0,045[34]
10^00-00^01	961	0,0219[33], 0,023[34], 0,0283[35]
01^10-10^00	721	7,5[33]
00^00-01^10	667	330[33]

this should lead to selective population of the CO_2 00^01 level. In view of the fact that the radiative strengths of the 00^01-10^00 and 00^01-02^00 laser transitions are much smaller than the strengths of the transitions from lower laser levels (10^00-01^10 and 02^00-01^10) (see Table V and Fig. 14), inversion sets in and becomes manifest in powerful generation. Such an interpretation of the mechanism ensuring population inversion in CO_2+N_2 lasers was developed by Patel.

This interpretation is in good agreement with the work of Morgan and Shiff[39], since according to their data the efficiency of quenching of vibrationally-excited nitrogen by CO_2 molecules is larger by three orders of magnitude than that of collisions with N_2 molecules.

8. DIRECT ELECTRONIC EXCITATION OF VIBRATIONAL LEVELS. POPULATION OF THE UPPER LASER LEVEL OF CO_2, CO_2+N_2, CO_2+N_2+He, AND CO_2+He LASERS

Patel's hypothesis regarding the selective excitation of the upper laser level of CO_2 lasers by resonant transfer of vibrational energy from N_2 molecules is sufficiently well founded and is presently accepted by all investigators. However, his explanation[8] of the large population of the vibrational levels of the ground electron state of N_2 as being due to electron-ion and atom-atom recombination, and also to cascades from excited electronic states, is not only unfounded, but also has low probability.

We have proposed in our paper[40] a much better founded and more likely hypothesis, that of direct electronic excitation of the vibrational levels of the N_2 and CO molecules, an excitation which is indeed the basic process ensuring a high degree of population of the upper level of CO_2 lasers. By assuming this hypothesis one can understand not only the high power level of CO_2-N_2 lasers, but also explain other very important experimental facts, which have likewise not been reliably interpreted. Namely, we can understand, first of all, why the power attained with

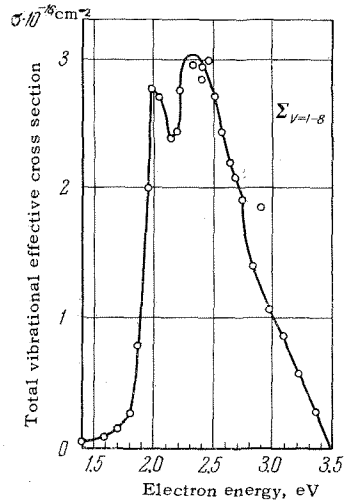

FIG. 15. Cross section for inelastic scattering of electrons by N_2 molecules vs. electron energy.

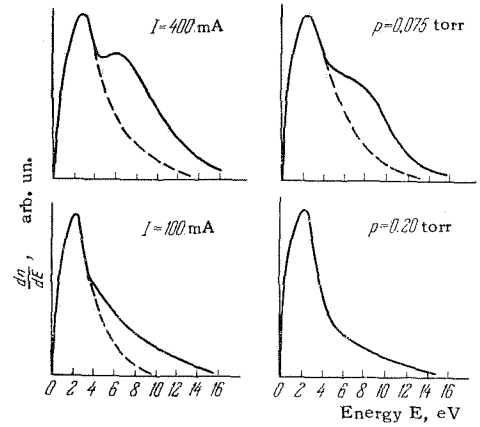

FIG. 17. Electron energy distribution function in positive column of a discharge in N_2.

lasers using pure CO_2 is comparable with the power obtained with $CO_2 + N_2$ lasers, and, second, explain the appreciable increase in the power when helium is added to both pure CO_2 and $CO_2 + N_2$. Our hypothesis is based on the experimental work of Schulz [41-43] and Swift [44].

Schulz investigated experimentally inelastic collisions between electrons and N_2 and CO_2 molecules, and established that the corresponding effective cross sections σ have a resonant character, are unusually large, and reach a maximum at electron energies 2.3 eV [$\sigma(e, N_2) = 3 \times 10^{-16}$ cm^2] and 1.7 eV [$\sigma(e, CO = 8 \times 10^{-16}$ cm^2]. His results are shown in Figs. 15 and 16. It is seen from the figures that the absolute values of the total cross sections, which take into account the excitation of the vibrational levels up to the eight, are very large at electron energies from 1.7 to 3.5 eV in the case of N_2 and at electron energies from 1.0 to 3.0 eV in the case of CO.

In [43] Schulz measured not only the total cross sections but also the partial cross sections for the excitation of individual vibrational levels. It turned out that the excitation cross sections of the levels from

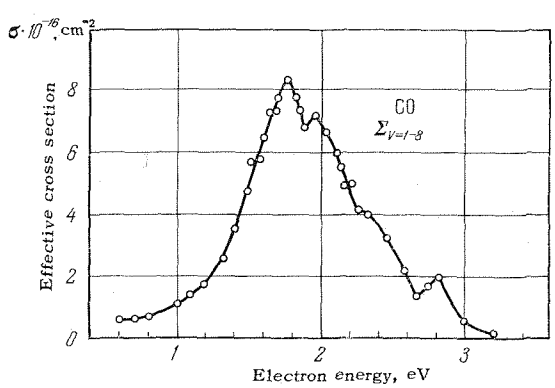

FIG. 16. Cross section for inelastic scattering of electrons by CO molecules vs. electron energy.

the first to the fourth are comparable with one another, and the excitation cross sections of the seventh and eighth are smaller by one order of magnitude. The interpretation of the large values of the electron-excitation cross sections of the vibrational levels and their resonant dependence on the electron energy is connected with the formation of short-lived negative ions N_2^- and CO^-. Theoretical calculations of the cross sections [45,46] have led to perfectly satisfactory agreement with Schulz's experimental data.

Figure 17 shows Swift's results, obtained in a study of the electron-energy distribution in a positive column of a glow discharge in N_2 [44]. It is seen that the electron distribution is patently not Maxwellian, with a maximum at 2.0—3.0 eV, and that with increasing pressure the maximum shifts towards lower energies and the number of fast electrons decreases appreciably. This result agrees with Schulz's data. The decrease in the number of electrons having energies close to 1.5 eV is due to the resonant interaction between the electrons and N_2. The decrease in the number of the fast electrons with increasing number of N_2 molecules (with increasing pressure) is due to the increase in the number of acts in which energy is transferred from the electrons to the N_2. Also in agreement with Schulz's data is the earlier work of Haas [47], according to which when a beam of monoenergetic electrons with arbitrary energies from 2 to 5 eV passes through nitrogen, only electrons with an average energy 1.5 eV remain.

In the case of $CO_2 + N_2$ lasers, which usually operate at pressures larger than in Swift's experiments, one can assume with sufficient assurance that an increase of the pressure up to 1 torr and the addition of CO_2 (a gas with lower ionization potential) can only lead to a decrease in the average electron energy. In addition, owing to the transition of the vibrational energy to the upper laser level of CO_2, an additional decrease will take place in the number of fast electrons. Thus, the average electron energy in the discharge, under conditions close to those obtaining in $CO_2 + N_2$ lasers, will be

not larger than 1.5—2 eV. This means in turn, when account is taken of the large value of $\sigma(e, N_2)$, that the main cause ensuring considerable concentrations of N_2 in excited vibrational states, is direct electron excitation. We emphasize that effective utilization of vibrationally-excited N_2 to populate the upper CO_2 laser level is possible not only at vibrational quantum number values $v(N_2) = 1$, but also up to values $v(N_2) = 4$, since at these values of v the anharmonicity of the N_2 molecule still does not lead to vibrational-quantum values differing from those of the 00^01 level of CO_2 by more than kT_0. The possibility of effectively using the group of vibrational N_2 levels for the excitation of the upper laser level of CO_2 favors the attainment of large efficiencies and powers in $CO_2 + N_2$ lasers.

It is easy to verify that direct electron excitation of the group of vibrational levels of N_2 ($v = 1—8$) and subsequent resonant transfer of energy to the CO_2 (00^0v) vibrational levels can ensure fully sufficient rates of population of the upper CO_2 (00^01) laser level to attain the observed large values of output generation powers.

By way of estimates let us assume that the electron density n_e in the glow discharge of a $CO_2 + N_2$ laser is at most 10^{10} cm^{-3}. (The order of magnitude of the electron density can be obtained from plots showing the dependence of the electron drift velocity in He, CO_2, N_2, and CO, shown in Figs. 3.6, 3.12, and 3.19 of Brown's book[48].)

By averaging the effective cross sections of the electron collisions leading to vibrational excitation of the N_2 molecules (see Fig. 15), we find that at an electron temperature 1 eV and at a nitrogen pressure of 1 torr, the rate of excitation of the nitrogen vibrational levels is 1.1×10^{18} sec^{-1}, and that at 2 eV it amounts to 1.3×10^{18} sec^{-1}.

A characteristic value of the generation power of a CO_2 laser is 10^6 erg-cm^{-3}sec^{-1}[11], corresponding to $\sim 10^{18}$ quanta per second. It can therefore be assumed that the main process ensuring the population of the upper laser level is direct vibrational excitation of the N_2 molecules by the electrons, with subsequent resonant transfer of the vibrational quanta to the CO_2 molecules.

Of course, one cannot exclude the possibility of pumping to the upper 00^01 laser level of CO_2 by other processes, particularly by collisions between the electrons and the CO_2 molecules. That this process can have a large efficiency is suspected on the basis of the plot of the electron-CO_2 collision probability given in Fig. 1.12 of Brown's book[48], and the latest work on the scattering of electrons by CO_2[80]. However, we cannot draw as unambiguous a conclusion as we do for the case of the N_2 and CO molecules, since the elastic and inelastic cross sections have not been separated in the case of CO_2 molecule. In one way or another, any additional pumping process will only improve the generation conditions and increase the output power of CO_2 lasers.

In all the foregoing arguments we have assumed a strong collisional coupling between the vibrational levels. This fact is, generally speaking, well known; in the case of the CO_2 molecules it is confirmed also by the work of Hocker et al.[49] It has turned out that after the vibrational 00^01 level of the CO_2 molecule is rapidly depleted, it becomes again populated, within a time of the order of 10^{-5} sec, as a result of the heavily populated higher levels. The aggregate of these levels serves indeed as the reservoir which can maintain high population of the upper laser level 00^01. We emphasize that in view of the low electron density ($\sim 10^{10}$ cm^{-3}), one N_2 molecule experiences only about 100 collisions with electrons per second, meaning that the establishment of stationary population of the vibrational levels of N_2 and CO_2 as a result of collisions with electrons is quite slow, and its characteristic time is of the order of 10^{-2} sec. In explaining the mechanism of generation in a pure-CO_2 laser, it must be borne in mind that an appreciable number of CO molecules is produced in the electric discharge[50], owing to the low dissociation energy of CO_2 (2.8 eV). Taking into account the large cross section for excitation of the vibrational levels of CO by electron impact, and also the fact that the difference between the energies of the vibrational level of CO and the upper laser level of CO_2 lies within the limits of kT_0 ($\Delta E_{CO_2CO} = 170$ cm^{-1}), we can propose that the role played by N_2 in the $CO_2 + N_2$ mixture is played by CO in the $CO_2 + CO$ mixture produced in a gas discharge in pure CO_2. The lower generation efficiency in pure CO_2 (in fact, in the $CO_2 + CO$ mixture) is also understandable, since $\Delta E_{CO_2CO} > \Delta E_{CO_2N_2}$, and, furthermore, the CO molecule, unlike N_2, does not have a zero dipole moment, leading to a decrease in the population of the vibrational levels of CO. The latter fact may be insignificant if dragging of the radiation takes place.

The increase with the generation power when He is added to the $CO_2 + N_2$ mixture and to pure CO_2 also have a natural explanation. In fact, helium gas has the highest ionization potential and the largest electron temperature in the gas discharge. Thus, according to the Schottky diffusion theory (see, for example, [51]), at a helium pressure $p_{He} = 10$ torr, the electron temperature in a tube of 2.5 cm diameter is 22,000°K, and at $p_{He} = 5$ torr it is 35,000°K, which is in good agreement with recent measurements made by Yu. B. Golubovskiĭ and Yu. M. Kagan (private communication). It can therefore be assumed that the addition of He to CO_2 or to the $CO_2 + N_2$ mixture will lead to an "equalization" of the distribution function, i.e., to compensation for the electrons knocked out of the discharge by resonant interaction with N_2 and CO. We note also that addition of He to CO_2 and to the $CO_2 + N_2$ mixture not only leads to an increase in the population of the upper laser level, but also to a decrease in the population of the lower laser level (see Sec. 9). This fact

is experimentally confirmed by the observed decrease in the intensity of the spontaneous emission from the lower laser level upon addition of He to the $CO_2 + N_2$ mixture[14].

Thus, the experimentally based hypothesis that the vibrational levels of CO and N_2 are directly electron-excited makes it possible to explain from a unified point of view a large aggregate of results obtained in the operation of CO_2 lasers, and primarily the high efficiency and the high power levels. On the other hand, the hypothesis of cascade population of the vibrational levels cannot lead to the observed efficiencies and powers of CO_2 lasers, under reasonable assumptions concerning the cross sections of the processes that lead to the cascade population and concerning the distribution of the electrons in the gas discharge, especially when the losses accompanying these processes are taken into account. Therefore the hypothesis of direct electron-excitation is the more reliable one. Of course, the last word belongs to experiment, and therefore it is necessary to study first of all the electron velocity distribution in electric-discharge plasmas in different gas mixtures used in CO_2 lasers.

9. VIBRATIONAL RELAXATION OF CO_2. LASER LEVEL POPULATIONS

a) Relaxation of Lower Laser Level

So far we have dealt only with the mechanism of populating the upper laser level of the CO_2 laser.

In this section we discuss the mechanism of formation of the inverse population as a result of effective decay of the lower level following collisions with heavy particles. As was first shown by V. A. Fabrikant[52-53], selective decay of the lower level can lead to population inversion by itself. The importance of this process in the case of CO_2 is beyond any doubt.

For concreteness we shall henceforth discuss the operation of the $CO_2 + N_2$ laser used by Witteman[11]. He used in his experiments a mixture consisting of CO_2 at a pressure of 1 torr (3.6×10^{16} molecules/cm^3) and N_2 at a pressure of 2.5 torr. The attained output power was 1.3×10^6 erg/cm^3 sec, corresponding to 7×10^{18} quanta of generated radiation. It is possible that the per-unit power has been somewhat exaggerated by Witteman, since he assumed that only $\frac{1}{8}$ of the volume of the gas-discharge tube participated in the radiation generation.

We note first that even the radiative transitions alone can lead to inversion, since the radiative time constant of the laser transition (2.8 sec) exceeds the radiative lifetime of the lower laser level (0.5 sec). At the same time, the strong radiation at 4.27 μ is locked. Thus, the lower laser level will become depleted more rapidly than the upper one. However, the rate of radiative decay cannot be reconciled with the large per unit power indicated above. In fact, the population of the lower 10^00 laser level should be not larger than 10^{14}—10^{15} cm^{-3}. Then, if the number of generated quanta in the continuously operating laser amounts to 10^{18} cm^{-3} sec^{-1}, it is necessary that the relaxation time of the lower level not exceed 10^{-4}—10^{-3} sec. Such short times can be ensured only via collision processes, and it is hardly necessary to take into consideration collisions with electrons, whose frequency will not exceed 100 per second even at a cross section $\sim 10^{-16}$ cm^2.

Table VI. Relaxation times τ of the CO_2 01^10 level in the presence of impurity[57-61] (pressure 1 torr, temperature 300° K)

Impurity	Number of effective collisions Z_{10}	τ, sec	Impurity	Number of effective collisions Z_{10}	τ, sec
CO_2	51 330	$4.4 \cdot 10^{-3}$	H_2O	60	$5.2 \cdot 10^{-6}$
N_2	1 200	$1.04 \cdot 10^{-4}$	H_2	300	$2.6 \cdot 10^{-5}$
CO	230	$2.0 \cdot 10^{-5}$	He	2 600	$2.26 \cdot 10^{-4}$
NO	260	$2.26 \cdot 10^{-5}$			

At the same time, at a CO_2 pressure of 1 torr and at room temperature the total number of gas-kinetic collisions ($\sigma = 1.6 \times 10^{-15}$ cm^2) experienced by one CO_2 molecule with all other CO_2 molecules is 1.15×10^7 sec^{-1}. Therefore the collisions of the molecules with each other should be the main process causing the relaxation of the lower laser level. Indeed, according to Herzfeld's calculations[54], at least one out of 5×10^2 collisions of the excited 10^00 CO_2 molecule with the other molecules changes it to the state 01^10, i.e., the relaxation time of this level is 4.3×10^{-5} sec, which is in good agreement with the requirement that follows from the large values of the observed per unit generation powers.

It is clear, however, that if the lower deformation level 01^10 will not become sufficiently effectively depleted, then this will lead not only to an increase in its population but also to an increase in the number of the inverse processes of population of the lower laser level. Therefore, for population inversion it is necessary that the relaxation time of the 01^10 level be at least not larger than the relaxation time of the lower laser level. The relaxation times of the first level of the deformation vibration of the CO_2 molecules were investigated thoroughly both in pure CO_2 and in mixtures with different gases[54-69].

In Table VI these times are given for 300° K and 1 torr. In the case of a mixture of other gases ($CO_2 + M$) the relaxation time τ of the 01^10 level of the CO_2 molecule, at a total mixture pressure p, can be determined from the relation[57,58]:

$$\frac{1}{\tau} = \frac{p_{CO_2}}{\tau_{CO_2, CO_2}} + \frac{p - p_{CO_2}}{\tau_{CO_2, M}},$$

where τ_{CO_2,CO_2} and $\tau_{CO_2,M}$ are the relaxation times of the CO_2 molecule as a result of collisions with CO_2

and M molecules respectively at a pressure of 1 torr; $p = p_{CO_2} + p_M$ is the total pressure of the mixture. It is seen from the table that at a CO_2 pressure of 1 torr the decay of the 01^10 level will proceed much more slowly than the decay of the 01^00 level, and consequently, CO_2 molecules can become accumulated at the 01^10 level. On the other hand, addition of nitrogen at a pressure 2.5 torr leads to 01^10 level relaxation time of $\sim 4 \times 10^{-5}$ sec. It must also be borne in mind that a $CO_2 + N_2$ laser always contains CO and NO, the presence of which, even in small amounts, also greatly reduces the relaxation time of the 01^10 level.

A similar situation obtains also in a laser with CO_2. The CO produced in the gas discharge leads not only to a pumping of the upper laser level, but also to a very effective decay of the 01^10 level, and consequently of the lower laser level 10^00. The presence of CO even at a pressure of 0.5 torr leads to a relaxation time -4×10^{-6} sec, which is several times smaller than the relaxation time of the 10^00 level as a result of collisions with the CO_2 molecules.

It is also seen from the table that to reduce the relaxation time of the lower level it is necessary to have the same amounts of H_2 and even smaller amounts of H_2O. The presence of these relaxation-accelerating impurities is just the cause of the increased power of the CO_2 lasers in the experiments of Rosenberger[19] and Witteman[11].

In the foregoing qualitative consideration we disregarded the influence of the impurities in the CO_2 on the rate of direct decay of the lower laser level, i.e., on the rate of transition of the CO_2 molecule from the 10^00 state directly to the ground state. It is known that in pure CO_2 this is a very slow process[54]. Experimental data on the efficiency of this process in the presence of impurities are lacking, with the exception of the case of collisions with H_2O molecules, investigated by Witteman[11,16].

b) Influence of H_2O on the Rate of Relaxation of the Lower Laser Level

As already indicated above (see Sec. 3), Witteman succeeded in doubling the power of a sealed $CO_2 + N_2$ laser by adding water vapor. In analyzing the operation of the $CO_2 + N_2$ laser he, like Patel, assumed that the population of the upper laser level 00^01 of CO_2 was the result of resonant energy transfer from the vibrationally-excited nitrogen. However, he considered also the process of decay of the lower laser level 10^00 of CO_2, assuming that the principal process is thermal relaxation. He assumed that the population of the 10^00 level of CO_2 decreased as a result of a two-step process[63]. First, during the time of the molecular collisions, the energy of the symmetrical vibration ν_1 was transferred to the deformation type of vibrations with fundamental frequency $\nu_2 = 667$ cm^{-1}. The probability of this process is relatively large, since the quantum of deformational vibration ν_2 is approximately equal to half the quantum of ν_1. Therefore, either two molecules in the state 01^10 or one in the state 02^00 are produced upon collision of two CO_2 molecules of which one is in the state 10^00. This is followed by thermal relaxation of the deformation type of vibrations, and the energy of deformational vibration is transformed into energy of translational motion.

The next process is relatively slow and determines the rate of deactivation of the 10^00 level. According to data on the relaxation time, obtained with the aid of the shock-tube method, about 5×10^4 collisions are necessary for the transition of the CO_2 molecule from the 10^00 state to the ground state[64]. This means that the effective cross section of the indicated process is of the order of 10^{-20} cm^2. According to Witteman, the relaxation time of the 10^00 level indeed limits the power which can be obtained from a $CO_2 + N_2$ laser.

It turns out that the rate of the decay of the 10^00 level can be greatly increased by adding a small amount of water vapor[11]. The lowest oscillation frequency of the H_2O molecule, corresponding to the vibration of the angle between two OH bonds, is 1596 cm^{-1}. Within the limits of kT_0, the energy of this vibration is close to the energy of the symmetrical vibration of CO_2. It turns out that only a few collisions are needed for the molecule CO_2 in the 10^00 state to transfer its energy to the H_2O molecule. On the other hand, the relaxation of the vibrational energy of H_2O is very rapid. Its vibrational energy is transformed into translational energy by collision with other water molecules, owing to the large attraction forces due to the dipole-dipole interaction of the H_2O molecules. It was established[70,71] that only about ten collisions with other molecules are necessary for deactivation of a vibrationally-excited water molecule. It is the increase in the rate of relaxation of the lower laser level 10^00 that Witteman credits with the doubling of the $CO_2 + N_2$ laser power. This is the qualitative explanation of the effect observed by him. He confirmed his arguments also with theoretical calculations.

The thermalization of the vibrational CO_2 levels is much more rapid than the transition of the vibrational energy to the translational degrees of freedom, because the former process occurs during the time of resonance processes without exchange of energy with the translational motion. This means that we can describe the distribution of the molecules over the vibrational levels by means of the vibrational temperature T. If there is no water vapor, then the rate of relaxation of the energy E of the lower laser level of all the CO_2 molecules is given by the equation[65]

$$\frac{dE}{dt} = -\frac{p_0}{\tau_{11}}\{E(T) - E(T_0)\}, \qquad (1)$$

where τ_{11} is the CO_2 relaxation time, equal to 3×10^{-3} sec at 330° K and 1 torr, p_0 is the CO_2 pressure in torrs, and $E(T)$ and $E(T_0)$ are the true vibrational

energy of the CO_2 molecules per unit volume, and accordingly the vibrational energy when equilibrium obtains with the translational degrees of freedom.

It can be shown[11] that upon addition of water vapor at a partial pressure p_1 and with a relaxation time τ_{22}, the equation for the energy relaxation of the lower laser level of CO_2 will take the form

$$\frac{dE}{dt} = -p_0 \left\{ \frac{1}{\tau_{11}} + \frac{1}{\tau_{22}} \left(\frac{p_1}{p_0} \right)^2 \right\} \{E(T) - E(T_0)\}. \quad (2)$$

It follows from (2) that the energy relaxation time of the lower laser level in the $CO_2 + H_2O$ mixture is given by

$$\frac{1}{\tau} = \frac{1}{\tau_{11}} + \frac{1}{\tau_{22}} \left(\frac{p_1}{p_0} \right)^2. \quad (3)$$

Analyzing the results of his study of the dependence of a $CO_2 + N_2$ laser power on the partial pressure of the H_2O (see Fig. 9), Witteman noted that the power begins to increase at H_2O pressures exceeding 0.01 torr. This means that the rates of the relaxation of the lower laser level of CO_2, due to collisions with CO_2 and H_2O, are comparable. Consequently, according to (3), $\tau_{22} = 10^{-4}\tau_{11}$, and at a CO_2 pressure of 1 torr, $\tau_{22} = 3 \times 10^{-7}$ sec. This result agrees with the data obtained by the ultrasound-absorption method[70] and by the shock-tube method[71]. At H_2O pressures exceeding 0.01 torr, the relaxation time τ can be obtained with the aid of the simple relation

$$\tau = 10^{-4}\tau_{11} p_1^{-2}. \quad (4)$$

Witteman has thus demonstrated that when H_2O vapor is added the rate of relaxation of the lower laser level is indeed markedly increased, and this explains the observed increase in power.

c) Determination of the Population Difference of the Laser Levels of $CO_2 + N_2 + H_2O$ Lasers

The population difference of the laser levels of $CO_2 + N_2 + H_2O$ lasers was determined by Witteman in two modes: without generation and with generation at maximum power of 20 W. To determine the population difference of the laser levels, the angle of incidence β (see Fig. 8) on the germanium plate decoupling the power was reduced to the threshold generation conditions. For the rotational transition P_{22} of the 00^01-10^00 band this angle was found to be 25°. Practically all the losses in the resonant cavity were determined by the decoupling plate.

The time characterizing the emergence of the radiation from the resonator in the absence of a medium is given by the relation

$$\frac{dI}{dt} = \frac{I}{\tau_F},$$

where the time constant $\tau_F = L/cR$; L is the resonator length, R the reflection coefficient of the mirror system, including the decoupling plate. At threshold conditions the value obtained was $\tau_F = 1.4 \times 10^{-8}$. Further, the results of the measurement of the integral absorption coefficient of the 00^01-10^00 band at minimum pressure 100 torr[34] were used to calculate the lifetime, determined by the spontaneous radiative transition. It turned out to be 4.8 sec. This value has made it possible to calculate the probability of the rotational transition of the P branch of the 00^01-10^00 band:

$$A(00^01,\ J \to 10^00,\ J+1) = 10^{-1}\ \text{sec}^{-1}.$$

The density of the inversion of the rotational levels under threshold conditions is[72]:

$$n_2^J - n_1^{J+1}\frac{g_2}{g_1} = \frac{8\pi\nu^2}{Ac^2 g(\nu_0)\tau_F}. \quad (5)$$

Assuming that the form of the contour is determined by the Doppler effect, a value $g(\nu_0) = 2.5 \times 10^{-8}$ sec* was obtained at the center of the line. Substituting the obtained values in (5), the inversion of the rotational levels J = 21(00^01) and J = 22(10^00) was found to be

$$n_2^J - n_1^{J+1} = 2{,}1 \cdot 10^{13}\ \text{cm}^{-3}.$$

It was assumed in the calculation that the ratio of the statistical weights of the levels is 1.

In view of the fact that the relaxation of the rotational levels is much faster than that of the vibrational ones, it could be assumed that the population of the rotational levels is determined by Boltzmann's law with the gas temperature. This has made it possible to calculate $(N_2 - N_1)$, the inverse population of the vibrational levels 00^01 and 01^10, with the aid of the approximate relation

$$n_2^J - n_1^{J+1} = 2(N_2 - N_1)\frac{hcB}{kT}(2J+1)\exp\left\{-\frac{hcB}{kT}J(J+1)\right\}. \quad (6)$$

Substituting the value of $n_2^J - n_1^{J+1}$ in (6), we get $N_2 - N_1 = 6 \times 10^{14}$ cm^{-3}.

Similarly, at a reflection coefficient R = 0.1, corresponding to the maximum power (20 W) of the $CO_2 + N_2 + H_2O$ laser, the rotational inversion was determined with the aid of the formula[11,72]

$$(n_2^J - n_1^{J+1})_{\text{gener}} = \frac{8\pi\nu^2 R}{2c^2 g(\nu_0) LA}, \quad (7)$$

and found to be 2.2×10^{12} cm^{-3}, while the vibrational inversion was $(N_2 - N_1)_{\text{gener}} = 6 \times 10^{13}$ cm^{-3}.

Thus, Witteman succeeded for the first time in determining the inversion densities, both vibrational and rotational, for a laser operating with CO_2. We see that it exceeds by several orders of magnitude the inversion densities of all other gas lasers.

d) Processes Limiting the Radiation Power

The rate (per second) of populating the lower laser level can be calculated from data on the output power,

*The function $g(\nu)$, which describes the shape of the line, is so normalized that $\int_0^\infty g(\nu)\,d\nu = 1$. If the line has a Droppler contour, then $g(\nu_0) = 2(\pi \ln 2)^{1/2}/\pi\Delta\nu$, where $\Delta\nu$ is the line width.

if one knows the beam cross section, which in Witteman's experiment was 0.35 cm^2. At the largest powers, the rate I′ of population production per unit volume was 1.3×10^6 erg-cm^{-3} sec^{-1} without water vapor and 3×10^6 erg-cm^{-3} sec^{-1} when H_2O (0.2 torr) was added.

To calculate the rate of relaxation of the energy of the lower laser level, we note that the rate of the increase of its population is

$$\frac{dN_1}{dt} = \frac{I'}{h(\nu_3 - \nu_1)}.$$

Under stationary conditions, the rate of relaxation of the lower level should be equal to this quantity (we neglect decay due to the thermal relaxation of the upper level). Then the rate of energy relaxation dE/dt will be 2.1×10^6 erg-cm^{-3} sec^{-1} and 5×10^6 erg-cm^{-3} sec^{-1} in the absence and presence of water vapor respectively.

Using Eq. (1) and substituting in it the value of τ_{11} and $E(T_0) = E(330°K) = 13$ erg-cm^{-3}, we get $E(T) = 6000$ erg-cm^{-3}. The vibrational temperature corresponding to this value of E(T) is $T = 2300°K$.

Thus, the vibrational temperature of the lower laser level is much higher than the gas temperature, and therefore, in the absence of water vapor, the rate of deactivation of the lower laser level limits the power of the laser emission.

When water vapor is added (0.2 torr), the effective relaxation time, according to (4), will be 7×10^{-6} sec. Then calculation in accord with formula (2) shows that E(T) is approximately equal to $E(T_0)$. In other words, the vibrational temperature T is equal to the gas temperature T_0. This means that the relaxation of the lower laser level is sufficiently rapid, and that, in accord with the experimental observations (see Fig. 9), further addition of water vapor should no longer lead to a new acceleration of this rate.

After determining the vibrational temperatures of the lower laser level, it is easy to calculate the population density of this level. When water vapor is added, it is equal to $N_1 = 9 \times 10^{13}$ cm^{-3}. Using the inversions obtained above, we find that the population densities of the upper laser level in the absence and presence of generation are $N_2 = 7 \times 10^{14}$ and $N_2 = 1.5 \times 10^{14}$ cm^{-3} respectively.

We see thus that in the presence of water vapor 2% of all the molecules are at the upper laser level when the laser is not in operation, and 0.5% when it is in operation.

Similarly, in the absence of water vapor one can find that 25% of all the molecules are excited at the upper laser level if the laser is at threshold conditions.

We emphasize that Witteman has assumed in all his arguments that the rate of population of the upper laser level does not depend on the added water or on the laser power at which the measurements are made. In fact, however, one cannot exclude the possibility that the rate of population of the upper laser level is altered by the change in the operating conditions of the electric discharge.

In spite of the fact that some points of Witteman's reasoning can be subjected to criticism, his work is unique from the point of view of both results and interpretation. It is therefore worthy of close attention. All further research on CO_2 lasers should unconditionally be based on his results and interpretation.

e) Relaxation of Laser System

In considering the relaxation processes that occur in CO_2 lasers, it is necessary to take into account, besides the vibrational relaxation, also the rotational relaxation.* It is known that the characteristic time of the rotational relaxation, at ordinary temperatures, is much shorter than the time of vibrational relaxation. We can therefore assume a Boltzmann distribution of the rotational levels, at threshold conditions in the laser.

Analysis of the gain at a definite vibrational-rotational line shows that, unlike the R-branch, transitions in the P-branch can give amplification even when there is no population inversion of the vibrational levels [5]. Thus, the condition for generation to occur at the P-branch are more favorable than at the R-branch, and this is expressed in the greater ease of observing the P-branch experimentally.

The following circumstance should be borne in mind. As indicated above, in a high-power laser the entire radiation is as a rule concentrated in a small number of lines. This is the consequence of the fact that a considerable number of transitions, while having the gain required for the generation, nevertheless cannot generate because of the strong competition effects which result from the very long lifetime ($\sim 10^{-3}$ sec) of the 00^01 level and the very short thermalization time ($\sim 10^{-6}$—10^{-7} sec) necessary to attain a Boltzmann equilibrium for the rotational levels [73].

The experimental data on the relaxation times of the laser systems are quite significant both for the understanding of the generation mechanism and for practical purposes, since they permit an estimate of the advisability of using various gas mixtures. Javan and his co-workers [17,28] used a Q-switching technique to determine the times of vibrational relaxation of the gas mixtures used in CO_2 lasers. The data obtained by them give the relaxation time of the entire laser system and are of interest, in particular, because when they are compared with the relaxation times of individual vibrational levels, known from other investigations [54,58], it is possible to see which of them limit the inverse population of the laser levels.

*A more detailed analysis of rotational relaxation and its significance for the operation of CO_2 lasers can be found in the review by V. P. Tychinskiĭ in this issue p. 131).

The Q-switching pulse leads to such a rapid decrease of the inverse population of the laser levels, that no thermalization of the rotational levels takes place within the time of its action. This was established by an analysis of the spectral distribution over the different rotational levels. It has turned out that, unlike in the continuous mode, different rotational transitions generate independently, i.e., there is no time for thermalization to set in.

However, at high pressures, thermalization takes place even during the time of the Q-switching pulse, leading to a situation identical with the case of continuous generation, namely to a decrease in the number of the generated lines.

Immediately following the Q-switching pulse, the population difference is restored to the stationary value that obtains in the absence of generation. The time of establishment of this stationary value is determined principally by the lifetime of the vibrational levels. If the mirror rotation frequency is not too high, so that the time intervals between Q-switching pulses are longer than the level lifetimes, then the energy in each pulse does not depend on the mirror-rotation frequency. But when the repetition rates of the Q-switching pulses are comparable with or smaller than the lifetimes of the laser levels, then the energy in each pulse will decrease. In the experiments of Javan et al., the maximum mirror-rotation frequency was 500 rps, i.e., the minimum interval between pulses was 2 msec. Under these conditions, the intensity of the Q-switching pulses did not depend on the rotation frequency. But when additional generation pulses were obtained with the aid of a second fixed mirror located at an angle of approximately 18° to the laser axis, then it turned out that if the time interval between the main and supplementary pulses did not exceed 1 msec, then the generation intensity in the additional pulse was smaller than in the main pulse.

The relaxation time of the vibrational levels involved in the laser action was found to be 0.3 msec. It is surprising that the relaxation time, within certain limits of variation of the partial pressure, does not depend on these pressures, so that the composition of the mixture is not even indicated in [28]. The foregoing value must apparently be regarded as a certain typical time for customarily employed mixtures. The hypothesis advanced, that this time is determined by inelastic electron collisions, does not seem very likely to us.

Synchronization of the Q-switching with the pulsed supply of the discharge tube (so that the Q-switching occurs at arbitrary time during the pulse and after the pulse) has made it possible to establish that generation occurs also for an appreciable time following the current pulse, i.e., the population inversion is maintained even after the termination of the current pulse, in the after flow of the discharge, and this time is furthermore much longer than the duration of the generation in the afterglow when the mirrors are stationary and the tube is fed with similar current pulses. This shows that the free decay of the excited levels of CO_2 is much slower in the absence of generation than during continuous generation. By measuring the heights of the Q-switching pulses as a function of the time reckoned from the start of the current pulse, it was possible to study the relaxation time of the laser as a function of the partial pressures of CO_2, N_2, and He. It was found that at pressures on the order of 1 torr of N_2 and $\sim 10^{-3}$ torr of CO_2, this time is equal to several milliseconds.

As seen from the foregoing, a number of very important results were obtained in [28]. Worthy of particular attention is the fact that the relaxation time of the laser system as a whole, determined in this paper, coincided in order of magnitude with the relaxation time of the lower laser level [65]. Thus, in accord with Witteman's deductions (see above), the rate of deactivation of the lower laser level limits the power in this case.

The Q-switching method, albeit in a different version than in Javan's experiments, was used to study the relaxation time of the $CO_2 + N_2$ system by Bridges [29]. According to Bridges' interpretation, he obtained in his experiment a lower laser level lifetime of 3×10^{-5} sec (see above). Of the same order of magnitude is the relaxation of the level 10^00 for the transition to the 02^00 and 11^10 levels in the case of a 4 torr pressure of CO_2 [54]. This was precisely the partial pressure of the CO_2 in Bridges' experiments. The pressure of the nitrogen in the gas-discharge tube was also 4 torr. Collisions with N_2 molecules can only accelerate the relaxation of the 10^00 level. On the other hand, the relaxation times of the 01^10 level of CO_2 in the indicated mixture can be calculated accurately. It turns out also to be $\sim 10^{-5}$ sec. Thus, Bridges' experiments yield a certain relaxation time which is characteristic of a laser system and is determined by the relaxation times of the 10^00 and 10^10 levels. In the case of the mixture composition used by Bridges, the relaxation times of these levels turned out to be the same. For other mixture compositions, when the relaxation time of the 01^10 level is large, the relaxation time of the laser system will be determined by precisely this time. This apparently explains the differences between the experimental data concerning the relaxation times of laser systems (cf. [17,28], where a time 3×10^{-4} sec was obtained, coinciding with Witteman's deductions, as indicated somewhat earlier).

So far we have not touched upon the question of the vibrational relaxation of the upper laser level 00^01 of CO_2. The experiments of Javan and his co-workers [49] with Q-switching technique have made it possible to determine the effective collision cross section of a CO_2 molecule in the 00^01 state with a CO_2 molecule in the ground state 00^00, which leads to the relaxation of the 00^01 level. It was found to be $(3.3 \pm 0.3) \times 10^{-19}$

cm^2. At a CO_2 pressure of 1 torr and a temperature 300° K, this corresponds to an upper-level relaxation time 2.6×10^{-3} sec.

This value of the relaxation time differs by only a factor of 2 from the value 5.5×10^{-3} sec which can be obtained on the basis of the experimental data of Slobodskaya[81] (see, for example [54]). On the other hand, comparison of the results of Javan et al. with the theoretical data of Herzfeld[54] leads to a less satisfactory agreement. In fact, the most effective processes leading to the relaxation of the 00^01 level are the transition to the (11^10) state or to the (030) state, with the excess vibrational energy going over into kinetic energy, the collision cross section of these processes being respectively 1.93×10^5 and 3.92×10^5 times smaller than the gas-kinetic cross section. Allowance for these processes leads to a relaxation time 1.1×10^{-2} sec, i.e., a value four times larger than that obtained by Javan.

In concluding this section we note that the use of Javan's brilliant and highly promising procedure for determining the relaxation time of CO_2 laser systems has barely begun. In the papers cited above, valuable results were obtained, but the interpretations of the results, especially attempts to relate them with relaxation of definite levels involved in the laser action, are not unique and call for additional experiments. In addition, it is necessary to emphasize that for a unique interpretation it is necessary to know not only the initial composition of the mixture, but also the composition during the gas-discharge time. Yet in most cases the experiments are being carried out with insufficiently pure gases of unknown composition. On the other hand, as already mentioned, different impurities and newly produced gases (CO, NO, H_2O) can radically alter the relaxation time. These circumstances must be borne in mind when planning further experiments.

10. CERTAIN APPLICATIONS OF CO_2 LASERS

The first realized application of CO_2 lasers was for the investigation of nonlinear optical phenomena in the 10.6 μ region, in which investigation of nonlinear phenomena was heretofore impossible for lack of a suitable pumping source and also for the lack of information on the efficiency and phase matching of optical nonlinear materials that are transparent in this region[73,74]. The foregoing investigation is of special interest, since it is precisely in the infrared that the resonant vibrational frequencies of molecules lie, thus pointing to the possibility of obtaining very strong action on matter by using powerful infrared lasers[75].

Using a CO_2 laser operating in the continuous and Q-switching modes, Patel[73,74] obtained second-harmonic generation (SHG) in a large number of crystals (Te, Se, InAs, GaAs, ZnS, CdTe, CdS, CdSe). He established that the most suitable material for SHG is tellurium, which has the largest nonlinearity coefficient (compared with all other materials hitherto reported). Single-crystal Te has a large refractive index. It also has large positive birefringence (Fig. 18), which permits relatively easy phase matching between 10.5915 μ and the second harmonic of the wave at 5.2928 μ. Phase matching in Te takes place in a very wide region of wavelengths. At a continuous pump power of 0.17 W, he obtained SHG power of 10 μW. Figure 19 shows the dependence of the SHG power on the deviation from the phase-matching angle $\theta_m = 14° 31'$.

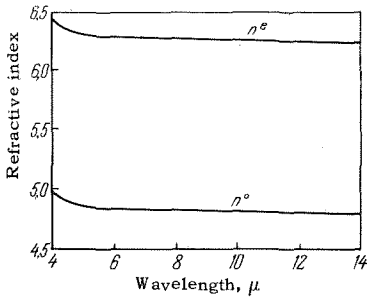

FIG. 18. Refractive index of Te vs. wavelength for the ordinary and extraordinary rays.

Repeated Q-switching of the CO_2 laser yielded SHG power of several watts in the pulse. Patel[73] advanced the hypothesis that a continuously operating generator, tunable in the range from 15 to 25 μ can be constructed by using a CO_2 laser as the pumping source and a Te crystal as the nonlinear material. In such a generator, owing to the very large nonlinear coefficient and to phase matching, the parametric-generation threshold can be reached at very moderate powers on the order of 20—100 mW.

A second field of CO_2 laser application will, of course, be communication. Since the laser wavelength is 10.6 μ, its emission falls in the transparency window of the atmosphere. Preliminary estimates show that the attenuation of CO_2 laser radiation passing through the earth's atmosphere in the vertical direction is less than 3 dB[13]. However, the use of CO_2 lasers for communication in the immediate future is made difficult by the insufficient development of detection and modulation techniques in the 10.6 μ region.

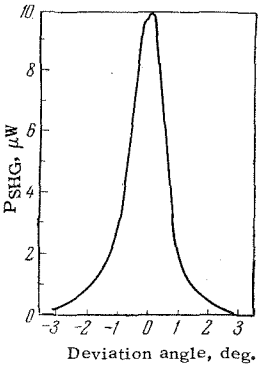

FIG. 19. Second harmonic generation power vs. deviation from the angle θ_m.

The next field of CO_2 laser application will be cutting and welding of materials. The use of lasers in medicine is highly promising. Finally, different military applications are possible. In particular, targets can be damaged with the aid of a laser beam if powers on the order of several kilowatts in the continuous mode are reached.

11. CONCLUSION

The investigation of the physical processes in CO_2 lasers and the study of their potential for different applications are only in the initial stage. Among the least investigated, although important, processes are those of the chemical-reaction type, including dissociation and recombination of different radicals produced in the gas discharge. It is known, for example, that there are a large number of chemical reactions which can raise diatomic molecules to vibrationally-excited states [76]. Much information concerning this question is contained in [77].

Another insufficiently investigated fact is the influence of the temperature on the laser power. At the same time, it has been proposed to produce population inversion in CO_2 by rapidly cooling the gas [78] and by adiabatically expanding a $CO_2 + N_2$ gas mixture [79].

Although CO_2 lasers are not yet used extensively, it can already be stated that this type of laser has greater prospects than any other laser constructed to date. The large power and efficiency attainable in sealed continuously operating CO_2 lasers, together with the experimentally observed tendency in the number of generated lines with increasing power, shows that in principle it is possible to construct a small laser that produces powerful continuous radiation at a single frequency and with appreciable efficiency.

Notes added in proof. 1. In a recent paper, (J. Appl. Phys. 37, 4278 (1966)), an abstract of which appeared earlier [18], H. Statz, C. L. Tang, and G. F. Coster measured and calculated the probabilities of the radiative transitions and the lifetimes of levels that are involved in the operation of CO_2 lasers. Along with Herzfeld's data [54] concerning the relaxation times, the results of Statz et al. are indispensable for solving the system of kinetic equations for the populations of the vibrational levels of the CO_2 molecule.

2. Whereas the relaxation of the lower level of the deformational vibration of the CO_2 molecule has been thoroughly investigated, information on the relaxation times of the laser levels are scanty and frequently contradictory. In this connection we note a new paper by T. L. Cottrell, I. M. Macfarlane, A. W. Read, and A. H. Young (Trans. Faraday Soc. 62, 2655 (1966)), according to which the relaxation time of the $00^0 1$ level of CO_2 at a pressure of 1 torr is 5.3×10^{-3} sec, in good agreement with the measurement of Javan et al. [49]

3. We have stated in Sec. 10 that the CO_2 laser emission is in the transparency window of the atmosphere. Indeed, using the effective cross sections for broadening collisions, obtained in [36], and recognizing that the earth's atmosphere contains 0.03% CO_2, we can readily verify that the line shape will be Lorentzian ($a = \Delta\lambda_L/\Delta\lambda_D \approx 10$), and that the absorption coefficient at the center of the line is $\alpha \approx 10^{-6}$ cm^{-1} at 300°K. This value of α agrees with the deductions of [13] (beam attenuation less than 3 dB). Nonetheless, one must not exclude other possible causes of absorption or scattering of laser radiation. The final answer to the question of the influence of the attenuation of the laser beam in the earth's atmosphere can only be obtained by direct experiment.

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