

Dissociation of carbon dioxide in sealed-off CO₂ waveguide lasers with radio-frequency excitation

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Abstract. A mathematical model describing the dissociation of carbon dioxide in sealed-off CO₂ waveguide and slit lasers with radio-frequency excitation is presented. The theoretically calculated degrees of dissociation of CO₂ were tested experimentally. It was demonstrated theoretically and experimentally that the degree of dissociation increases by 5%–10% with increase in the specific pump power. It was established that the degree of dissociation of carbon dioxide in lasers with the slit design of the discharge channel was approximately 1.5 times higher than in the usual waveguide lasers.

1. Introduction

CO₂ lasers with radio-frequency (rf) excitation of the active medium are being used increasingly in a number of technological and medical devices. Compared with the excitation of the active medium by a dc discharge, the use of high-frequency pumping in CO₂ lasers with an output power of ~10–100 W makes it possible to obtain a greater power per unit length of the active element [1] and to ensure reliable operation of a sealed-off laser for 10⁴ h and longer [2]. It has been noted [3] that the long service life of CO₂ lasers with rf excitation is primarily due to a significant weakening of the electrode sputtering.

It is well known that one of the main mechanisms limiting the output power of such lasers is the inevitable dissociation of carbon dioxide by electron impact in a gas-discharge plasma. As a result of various chemical reactions occurring both in the active volume and on the surface of the discharge channel, the initial chemical composition of the active medium changes under these conditions owing to the appearance of carbon monoxide, and of molecular and atomic oxygen. According to the published data [4, 5], the concentration of nitrogen in the discharge hardly changes.

Furthermore, it has been pointed out [6] that the dynamic 2CO₂ ↔ 2CO + O₂ equilibrium is established in the discharge and that the rate of regeneration of CO₂ depends on the properties and temperatures of the discharge-channel walls and also on the amount of oxygen adsorbed on them. Thus, determination of the dependence of the degree of

dissociation of CO₂ molecules (in sealed-off CO₂ waveguide lasers with rf excitation) on the discharge parameters, on the characteristic features of the heterogeneous reactions, etc. constitutes a problem of practical importance.

This communication describes the study of a mathematical model involving simultaneous solution of the equation of continuity, the kinetic Boltzmann equation, and the heat conduction equation. This model describes the dissociation of carbon dioxide in sealed-off CO₂ waveguide lasers. The model makes it possible to calculate the steady-state concentrations of the CO₂, CO, O₂, and O molecules as a function of the initial chemical composition of the active medium, of the discharge parameters, of the electron concentration in the discharge, of the geometry and characteristic features of the design of the discharge channel, and also of the material of the walls.

Experimental measurements were made of the degree of dissociation of carbon dioxide in CO₂ lasers as a function of the deposited rf power and of the discharge channel configuration. The experimentally measured degrees of dissociation are in good qualitative and quantitative agreement with the values calculated theoretically.

2. Mathematical model describing the dissociation of CO₂ molecules

Within the framework of the adopted model, we shall begin by making the following simplifying assumptions: (1) nitrogen oxides are ignored in the dissociation kinetics, since the rate constants for their formation and hence their concentrations are small [5]; (2) the contribution of the ion–molecule reactions to the establishment of the chemical composition of the neutral species is negligible, because the concentration of the charged species is much lower than that of the neutral plasma components; (3) the near-electrode space-charge layers do not exert a significant influence on the kinetics of the heterogeneous reactions occurring on the walls of the discharge channel. We shall assume that an rf field is applied to planar electrodes of width b separated by a distance d from one another and that the electrode surfaces are equipotential (Fig. 1). Since the rf oscillation period is much shorter than the characteristic dissociation, recombination, and diffusion times of the neutral species, the continuity equation for the i th mixture component is of steady-state nature and it assumes the form

$$\frac{\partial}{\partial x} \left(D_i \frac{\partial N_i}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_i \frac{\partial N_i}{\partial y} \right) + Q_i = 0, \quad (1)$$

where N_i and D_i are, respectively, the concentration and the diffusion coefficient of the i th neutral component; Q_i is

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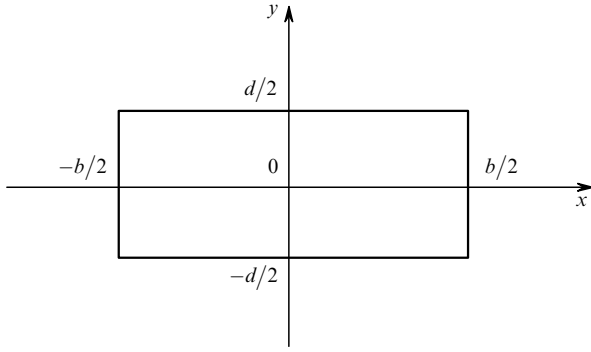


Figure 1. Schematic diagram of the discharge gap.

the density of the species of the i th kind formed and destroyed per unit volume as a result of chemical reactions. The system of equations (1) must be supplemented by boundary conditions reflecting the formation and destruction of species on the walls of the discharge channel having the dimension $b \times d$:

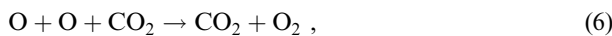
$$D_i \frac{\partial N_i}{\partial x} \Big|_{x=b/2} = -D_i \frac{\partial N_i}{\partial x} \Big|_{x=-b/2} = P_{bi},$$

$$D_i \frac{\partial N_i}{\partial y} \Big|_{y=d/2} = -D_i \frac{\partial N_i}{\partial y} \Big|_{y=-d/2} = P_{di}. \quad (2)$$

Then, averaging Eqn (1) over the discharge-channel cross section and taking into account the system of equations (2), we obtain

$$\frac{2}{b} P_{bi} + \frac{2}{d} P_{di} + \langle Q_i \rangle = 0. \quad (3)$$

In considering the CO_2 dissociation kinetics, we shall take into account the following reactions:



Reactions (7) and (8) take place on the discharge-channel walls.

Reactions (4)–(8) were selected from a large number of homogeneous and heterogeneous processes on the basis of the following considerations: (1) the reactions are similar to those which reflect the principal mechanisms of the generation and destruction of CO_2 and O molecules in the glow-discharge plasma in CO_2 , and which have been investigated in detail [7]; (2) for these reactions, it is possible to neglect the destruction of CO_2 and O_2 as a result of dissociative attachment, compared with their destruction as a result of dissociation by direct electron impact, since the rate constants for reactions (4) and (5) are much greater than those for the dissociative-attachment reactions; (3) three-species reactions of the type $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$, which occur in the active volume, are ignored because their corresponding constants are small [8] and reaction (6) is selected from all reactions of the type $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$ since it has the highest rate constant [7]. The need to take into

account reactions (7) and (8) is dictated in this instance also by the fact that the heterogeneous-recombination reactions on the discharge-channel walls actually play the main role in the establishment of the chemical composition of the active medium [6]. Evidently, the rate constants for reactions (7) and (8) depend on temperature and the sorption properties of the walls. The sorption properties are in their turn determined both by the material of the walls and by the state of their surface.

It is noteworthy that the rate-constant data for reactions (7) and (8) are extremely scanty and, in view of the lack of the necessary information, we shall employ in our model the results obtained from molybdenum glass [7]. In this case, the expressions for the recombination fluxes P , corresponding to reactions (7) and (8), assume the form

$$P_7 = k_7[\text{O}][\text{CO}], \quad (9)$$

$$P_8 = k_8[\text{O}]/[\text{CO}], \quad (10)$$

where k_7 and k_8 are given in Ref. [7]. Denoting the rate constants of reactions (4), (5), and (6) by k_4 , k_5 , and k_6 , respectively, and assuming that all four discharge-channel walls are made from the same material, we transform the system of equations (3) for CO_2 and O_2 as follows, taking into account expressions (4)–(10):

$$\frac{2(b+d)}{bd} k_7[\text{O}]_w[\text{CO}]_w - \langle k_4 n_e[\text{CO}_2] \rangle = 0, \quad (11)$$

$$\frac{2(b+d)}{bd} k_8 \frac{[\text{O}]_w}{[\text{CO}]_w} + \langle k_6[\text{O}]^2[\text{CO}_2] \rangle - \langle k_5 n_e[\text{O}_2] \rangle = 0, \quad (12)$$

where n_e is the electron concentration; $[\text{O}]_w$ and $[\text{CO}]_w$ are the O and CO concentrations at the walls. Considering n_e in Eqns (11) and (12) as a parameter and replacing the averaging over the cross section by concentrations averaged over the cross section, we obtain

$$\frac{2(b+d)}{bd} k_7[\text{O}]_w[\text{CO}]_w - k_4 n_e[\text{CO}_2] = 0, \quad (13)$$

$$\frac{2(b+d)}{bd} k_8 \frac{[\text{O}]_w}{[\text{CO}]_w} + k_6[\text{O}]^2[\text{CO}_2] - k_5 n_e[\text{O}_2] = 0. \quad (14)$$

In the presence of just two dielectric walls in the discharge channel, the coefficient $2(b+d)/bd$ in Eqns (13) and (14) is replaced by the coefficient $2/b$ or $2/d$.

The system of equations (13) and (14) must be supplemented by the balance equations for carbon and oxygen [9]:

$$[\text{CO}_2] + [\text{CO}] = [\text{CO}_2]^*, \quad (15)$$

$$\frac{[\text{CO}_2] + [\text{CO}]}{2[\text{CO}_2] + [\text{CO}] + 2[\text{O}_2] + [\text{O}]} = \frac{1}{2}, \quad (16)$$

where $[\text{CO}_2]^*$ is the initial CO_2 concentration. By solving the system of equations (13)–(16), it is possible to find the CO_2 , CO, O_2 , and O concentrations in the active medium as well as the degree of dissociation α of carbon dioxide defined by the relationship

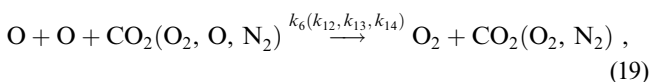
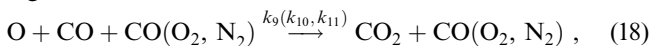
$$\alpha = \frac{[\text{CO}_2]^* - [\text{CO}_2]}{[\text{CO}_2]^*}. \quad (17)$$

Strictly speaking, two different definitions of the degree of dissociation can be encountered in the literature. According to one of them, the degree of dissociation is the relative loss of CO₂ molecules, which corresponds to formula (17). According to the other, $\alpha = [\text{CO}]/([\text{CO}] + [\text{CO}_2])$. However, if the carbon balance defined by Eqn (15) is maintained, which we established experimentally, these two definitions are identical. Formula (17) is also convenient because, in the experimental determination of the degree of dissociation on the basis of the results of the mass-spectrometric analysis of the composition of the active medium, a mass spectrometer with a high (greater than 5000) resolving power is not needed. Such a high resolving power is necessary for the identification of the mass peaks corresponding to N₂ and CO in the determination of the degree of dissociation when the other formula is used.

Evidently, the calculation of the degree of dissociation from the solution of the system of equations (13)–(16) is a self-consistent problem. This is due to the fact that the constants k_4 and k_5 , calculated from the electron energy distribution function (EEDF), depend on the chemical composition of the active gas mixture. This problem was solved by the method of successive approximations. In the first stage, the constants k_4 and k_5 were calculated from the EEDF in the initial gas mixture. They were then substituted in the system of equations (13)–(16) and the solution of this system was used to determine, to a first approximation, the chemical composition of the active medium.

In the second stage, the constants k_4 and k_5 were calculated from the EEDF in the gas mixture, the composition of which had been determined to a first approximation and were again substituted in the system of equations (13)–(16). The chemical composition of the active medium was then found to a second approximation and the iterative process was continued until the difference between the degrees of dissociation obtained in two successive iterations did not exceed 0.001. In the calculation of the EEDF from the solution of the kinetic Boltzmann equation, the cross sections for the interaction of electrons with the CO₂, N₂, O₂, CO, O, Xe, and He molecules were taken from Refs [10], [11], [12], [13], [14], [15], and [11], respectively. The cross sections for the dissociation of CO₂ and O₂ molecules by electron impact were taken from Ref. [7]. The temperature distribution in the discharge channel was calculated as in Ref. [16]. The parameter E/p , where E is the root-mean-square electric field strength in the plasma and p is the pressure of the gas mixture, was determined as a function of the rf pump power by the method described in Ref. [17].

Eqns (13) and (14) assume a different form in calculation of the degree of dissociation α in sealed-off CO₂ lasers with the slit design of the discharge channel. This is associated with the fact that, in the absence of dielectric walls, reactions (7) and (8) are ineffective on large-area metal electrodes. The volume processes then begin to play the main role in the establishment of the chemical composition of the neutral plasma components. In this case, we shall consider the following reactions:



where the reaction rate constants k_9 , k_{10} , and k_{11} are taken from Ref. [18], k_6 is from Ref. [7], and k_{12} , k_{13} , and k_{14}

are from Ref. [8]. For the above reactions, Eqns (13) and (14) then transform, respectively, as follows:

$$k_9[\text{O}][\text{CO}]^2 + k_{10}[\text{O}][\text{CO}][\text{O}_2] + k_{11}[\text{O}][\text{CO}][\text{N}_2] - k_4 n_e [\text{CO}] = 0, \quad (20)$$

$$k_6[\text{O}]^2[\text{CO}_2] + k_{12}[\text{O}]^2[\text{O}_2] + k_{13}[\text{O}]^3 + k_{14}[\text{O}]^2[\text{N}_2] - k_5 n_e [\text{O}_2] = 0. \quad (21)$$

Like the system of equations (13)–(16), the system (15), (16), (20), and (21) describes a self-consistent problem and the procedure used for its solution was described above.

3. Characteristic features of the laser design

We investigated waveguide lasers of different design (lasers 1–4). Metallo-ceramic waveguides with a 2.2 mm × 2.2 mm square section were used in waveguides 1 and 2. The laser cavities had a U-shaped configuration consisting of three highly reflecting and one beam-splitting planar mirrors. Among these, two nontransmitting mirrors were rotatable and ensured rotation by 180° and parallel transfer of the beam within the cavity.

The discharge chamber had one central electrode to which an rf voltage was applied, two diametrically opposite earthed electrodes, and two ceramic side plates. The active surfaces of the central and earthed electrodes and of the ceramic plate were polished to reduce the waveguide losses. The total length of the discharge channels was 580 mm. An aluminium alloy was used as the electrode material. Thin (~2 μm) Al₂O₃ films were deposited on the active electrode surfaces of laser 2.

Lasers 3 and 4 had the slit configuration of the discharge channel, formed by two water-cooled Kovar electrodes, in which the dimensions of the active region were 2.2 mm × 30 mm × 230 mm and 2.5 mm × 40 mm × 280 mm, respectively. The optical cavity was stable in the sections perpendicular to the electrode plane and unstable in the direction of the slit width. It consisted of two highly reflecting mirrors (convex and concave) disposed confocally. The radiation was coupled out of the laser cavity by diffraction on the edge of the convex mirror. The laser design features have been described in greater detail in Ref. [17].

The lasers were pumped by an rf oscillator with an output power up to 600 W, operating at a frequency of 81.36 MHz. The oscillator was connected to the laser head by a coaxial cable with a wave impedance of 50 Ω. Effective rf energy transfer to the plasma was ensured by a matching device based either on an autotransformer system (lasers 1 and 2) or on quarter-wave transformers [17] (lasers 3 and 4).

4. Experimental conditions

The lasers were connected by means of valves to a high-vacuum system, illustrated schematically in Fig. 2. The chemical composition of the active medium was analysed by a mass-spectrometric gas analyser of the MI-1201 type. In each experiment the lasers were subjected to a vacuum heat treatment which involved the evacuation of their vacuum volumes for 12 h at an outgassing temperature of 120 °C. A mass-spectrometric analysis of the gases released by the walls showed that the residual gas consisted mostly of water vapour.

The outgassing temperature was limited by the thermal stability of the dielectric coatings on the optical components

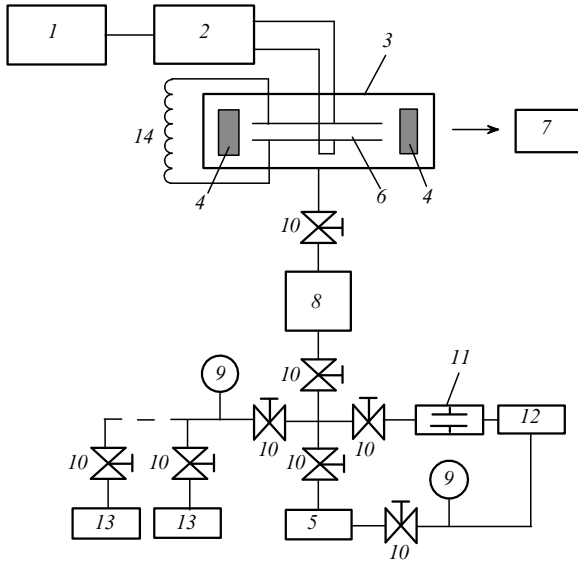


Figure 2. Schematic diagram of the experimental setup: (1) rf oscillator; (2) matching device; (3) investigated laser; (4) cavity mirrors; (5) evacuation system; (6) discharge structure; (7) power meter; (8) sampler; (9) vacuum gauges; (10) vacuum valves; (11) flow regulator; (12) mass-spectrometric analyser; (13) gas cylinders; (14) correcting inductor.

of the lasers. At the end of the treatment the residual-gas pressure did not exceed 1×10^{-8} Torr. The residual-gas pressure in the ion-source chamber of the analyser was less than 6×10^{-9} Torr. The lasers were filled with a gas mixture at a pressure monitored by a vacuum gauge to within $\pm 0.5\%$. Before the start of the measurements, the analyser was calibrated for all the gases expected in the lasers during their operation.

5. Results of measurements and discussion

Table 1 lists the degrees of dissociation α calculated theoretically and measured experimentally as a function of the specific (per unit area of the electrodes) rf pump power W_p in lasers 1 and 2 when the total pressure was $p = 100$ Torr and the gas mixture composition was $\text{CO}_2:\text{N}_2:\text{He}:\text{Xe} = 6:3.75:25:2$, and in lasers 3 and 4 operating at $p = 60$ Torr and with $\text{CO}_2:\text{N}_2:\text{He}:\text{Xe} = 1:1:3:0.3$. In these experiments account was taken of the fact that, according to Ref. [16], maintenance of the optimal thermal regime in the active medium requires that the specific pump power in the slit lasers be smaller by a factor exceeding 2 than in the waveguide lasers with a square discharge-channel cross section.

It can be seen from Table 1 that the theoretically calculated and experimentally measured degrees of dissociation

Table 1.

$W_p/W \text{ cm}^{-2}$	Laser 1		Laser 2		Laser 3		Laser 4	
	α_{theor}	α_{exp}	α_{theor}	α_{exp}	α_{theor}	α_{exp}	α_{theor}	α_{exp}
5.07	–	–	–	–	0.597	0.73	–	–
5.36	–	–	–	–	–	–	0.601	0.82
7.84	0.451	0.61	0.333	0.49	–	–	–	–
11.75	0.464	0.65	0.342	0.54	–	–	–	–
15.67	0.472	0.66	0.353	0.56	–	–	–	–

are in good qualitative and quantitative agreement. The calculated results confirm the experimental finding that, on increase in the pump power by a factor of 2, the degree of dissociation increases only slightly (by 5%–10%). This can be explained by the fact that, as W_p increases, the gas temperature T in the discharge channel rises and the electric field strength E in the central part of the rf discharge decreases [17]. Since the pressure in the gas filling of the laser is equalised, the density N of the heated gas is less than that of the cold gas N_0 in the additional laser volume where the gas temperature is equal to the temperature of the cooled electrodes ($T_0 = 293$ K). Under these conditions, we have $p \sim N_0 T_0 = NT = \text{const}$ and the dissociation rate constants, calculated on the basis of the EEDF, depend on the parameter ET . Therefore, an increase in these constants as a result of an increase in T is partly compensated by a reduction as a result of weakening of E in the plasma.

It follows from the experiments that when a waveguide channel with four dielectric walls is employed the degree of dissociation is 20%–25% lower than for a waveguide with two ceramic side plates. It was established theoretically and experimentally that the highest degrees of dissociation correspond to a discharge channel without dielectric walls (a slit structure comprising two metal electrodes). The last two factors are physically associated with the fact that, in contrast to ceramic (dielectric) surfaces, metal surfaces adsorb practically no oxygen and this hinders the occurrence of reactions (7) and (8).

Despite the reduction in the specific power deposited in the CO_2 slit lasers by a factor exceeding two, compared with the reduction in the waveguide lasers [16], the degree of dissociation in the CO_2 slit lasers is extremely high ($\alpha = 0.73$ – 0.82). This precludes the extraction from such lasers of a greater amount of energy [16] than from the waveguide lasers. For this reason, bulk catalysts (for example gold catalysts) promoting the regeneration of CO_2 can be usefully employed to reduce the degree of dissociation in such lasers.

However, one must note that the theoretically calculated degrees of dissociation are somewhat lower than the experimental values. This can be explained by, first, the absence of precise data on the electron concentration (throughout the calculations it was assumed that $n_e = 10^{11} \text{ cm}^{-3}$). Second, owing to the absence of the necessary data on the rates of the heterogeneous reactions on ceramic surfaces, the corresponding data for molybdenum glass were employed.

Third, in the mathematical model describing the dissociation of CO_2 , we ignored the processes which limit the lifetime of a sealed-off CO_2 laser. There are two main processes of this kind: the irreparable loss of oxygen from the active medium associated with the oxidation of the metal electrodes and of the components of the vacuum jacket of the laser, and the irreparable loss of carbon monoxide from the active volume associated with the fact that the majority of the materials in the discharge chamber form complex compounds (carbonyls) [10]. Both processes shift the $2\text{CO}_2 \leftrightarrow 2\text{CO} + \text{O}_2$ reaction equilibrium to the right, which increases the degree of dissociation.

6. Conclusions

This communication presents a mathematical model describing the dissociation of CO_2 molecules in CO_2 waveguide lasers with rf excitation. This model is based on simultaneous solution of the equation of continuity, the heat conduction

equation, and the kinetic Boltzmann equation. It was demonstrated theoretically and experimentally that: (1) an increase in the pump power by a factor of two increases the degree of dissociation by 5%–10% since the resultant change in the plasma parameter ET , which determines the dissociation rate constant, is small; (2) when a waveguide channel with four dielectric walls is used, the degree of dissociation is 20%–25% less than in the case of a waveguide having only two ceramic side walls, whereas the degree of dissociation in the lasers with the slit design of the discharge channel consisting of two metal electrodes, is approximately 1.5 times greater than in the waveguide lasers.

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