SEALED CARBON DIOXIDE (CO_2) LASER

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Abstract

ABSTRACT

The sealed CO_2 laser is part of the family of high-efficiency lasers, mainly due to the small energy difference between the pump levels and the laser transition levels. Its output power is generally limited to a few watts, due to the cooling method of the gas mixture (which is done by diffusion to the tube walls). The scaling parameter used is power per unit length. The best sealed CO_2 lasers can achieve between 0.3 W/cm and 0.4 W/cm, which limits the power of these lasers to around 30-40 watts, even with effective cooling, due to size constraints.

The sealed version is limited by the dissociation of the CO_2 molecule. Indeed, the interaction of energetic electrons from the discharge with CO_2 molecules causes the gradual decomposition of the molecular gas, which dissociates into carbon monoxide (CO) and oxygen (O_2).

In this book, we highlight all the parameters that may explain the mechanism of CO_2 molecule dissociation. We will then describe the various methods for the recombination of the CO_2 molecule. Finally, several solutions have been proposed to carry out the "reverse catalysis", a process that regenerates CO_2.

I.
Introduction

I. Introduction

Sealed CO_2 lasers are valuable tools for various scientific and medical applications. However, this type of laser does not maintain a constant power output due to the dissociation of the CO_2 molecule and the formation of various other products such as nitrogen oxides, carbon monoxide, and others. The dissociation of the CO_2 molecule has been recognized as the primary cause of the limitation in the operational lifetime and output power of sealed CO_2 lasers.

The kinetics of the different dissociation products and their relative concentrations depend on various parameters, such as current density, the composition of the gas mixture, electrode materials, laser configuration, and the presence of certain contaminants, notably moisture and oxygen. These studies have attracted significant attention a long time. It is evident that, following this dissociation, other processes, such as energy transfer between CO and N_2 molecules, as well as the possible formation of complex molecules, take place, making the CO_2 laser a highly complex system to study.

Several methods to highlight this effect involve spectroscopic studies, either through direct analysis of the CO_2 molecule or by analyzing the dissociation products (CO

and O_2). These methods include spectroscopic techniques that examine the visible line of the CO molecule's Angstrom band (4835 Å), mass spectrometry, gas chromatography, laser diode spectroscopy, and others.

Dissociation reduction has been shown to be possible by increasing the pressure for all mixtures used. The addition of nitrogen and helium also reduces dissociation compared to CO_2 alone. Thus, some proposed methods to maintain the composition of the gas mixture involve the use of specific electrodes or the addition of certain additives, such as Xe, H_2, and water vapor. The use of homogeneous catalysts, such as platinum and palladium, which are deposited inside the discharge tube, or the use of heterogeneous catalysts such as Pt/SnO_2, Pd/SnO_2, Au/MnO_2, and Cu/MnO_x, has been widely accepted. It is important to note that these catalysts require appropriate temperatures to be active. Additionally, some discharge tube configurations, such as the use of three tubes, have also been adopted.

The objective of this work is to study the various recombination techniques for the CO_2 molecule in a sealed carbon dioxide laser, as well as the development of a sealed oscillator with a few watts of power. To achieve these goals, the work is structured as follows: In the first part, we will

highlight all the parameters that could help explain the dissociation mechanism of the CO_2 molecule. In the second part, we will focus on the different CO_2 recombination methods. The aim is to design a CO_2 laser with a longer lifespan and characteristics suitable for several applications.

II.
Overview of the CO_2 Molecular Laser

1. The CO_2 Laser

With its industrial, medical, and scientific applications, the carbon dioxide (CO_2) laser is undoubtedly one of the most important gas lasers. The transitions between rotational-vibrational levels of the CO_2 molecule **[1]** correspond to numerous infrared emissions at wavelengths ranging from 9 to 11 micrometers. The CO_2 laser can deliver continuous powers ranging from fractions of a watt for scientific applications to tens of kilowatts for material processing, with remarkable efficiencies (up to 30%). It can also produce very brief, intense pulses of a few millijoules for infrared telemetry, or several kilojoules for research applications in controlled nuclear fusion. This versatility arises because there are several distinct types of CO_2 lasers that share the same active medium but differ significantly in their internal structure and, more importantly, in their functional characteristics.

The active medium of a CO_2 laser generally consists of a mixture of carbon dioxide, nitrogen, and helium. Each of these three components plays a crucial role, although this

type of laser can function using only CO_2, albeit with lower efficiency.

The linear CO_2 molecule has three vibrational modes: the symmetric mode ν_1 (10^00), the bending mode ν_2 (02^00, 02^20), and the asymmetric mode ν_3 (00^01) **[1]**. Each of these modes is quantized, with their first excited levels located at 1337 cm^{-1}, 667 cm^{-1}, and 2349 cm^{-1}, respectively, relative to the ground state. These levels are further subdivided into sublevels corresponding to the quantization of the rotational energy of the molecule. The vibrational energy levels involved are briefly illustrated in the energy diagram of the CO_2-N_2 system in **Fig.1.**

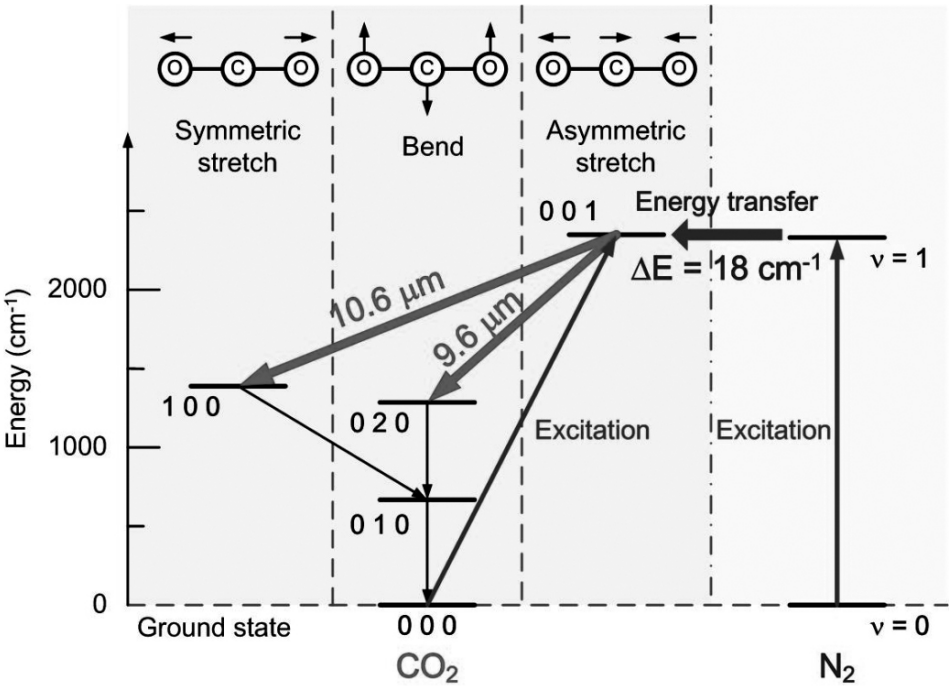

Fig.1. CO_2-N_2 Energy level diagram and vibrational modes.

Before reviewing some studies, it is important to recall the operating principle of the CO_2 laser and the main causes of dissociation.

When an electric discharge is established in the gas mixture, CO_2 molecules are preferentially excited to the 00°1 level of the asymmetric mode, while nitrogen molecules are excited (with a higher probability) to their first vibrational state, the metastable state v = 1. Due to the small energy difference

(18 cm^{-1}) between these levels, resonant exchange collisions between N_2 molecules (v=1) and CO_2 molecules in their ground state efficiently and continuously channel CO_2 molecules to the 00°1 level, as shown in the following equation:

$$N_2(v=1) + CO_2(00^00) \rightarrow N_2(v=1) + CO_2(00^01) + \Delta E = 18cm^{-1} \quad (1)$$

This process is very fast $k \approx 6\times10^{-13}\ cm^3/s$ **[2]**.

When population inversion is established, stimulated emission occurs through two channels: either towards the 10°0 level of the symmetric mode (10.6 μm), or towards the 02°0 level of the bending mode (9.6 μm). These metastable states have a lifetime of approximately 2.10^{-3} seconds at a pressure of a few torrs.

The rotational sublevel splitting gives rise to two prominent emission lines in each of the 10 μm and 9 μm bands, with the most intense line appearing at 10.6 μm **[3]**.

The de-excitation of the lower levels occurs through a cascade from the 02°0 level to the 01^10 level, and then to the ground state. The presence of N_2, due to its role as an energy reservoir, significantly improves the operation of the CO_2 laser.

The de-excitation process of the level follows the equation:

$$CO_2\left(01^10\right)+M\rightarrow CO_2\left(00^00\right)+M+\Delta E=667cm^{-1} \quad (2)$$

He is slow for $M=CO_2$ and N_2 ($k=5\times10^{-15}\ cm^3/s$) and relatively fast for $M=He$ ($k=1.2\times10^{-13}\ cm^3/s$). The presence of Helium thus improves the de-excitation of the lower levels, particularly the 01^10 level, and prevents the accumulation of CO_2 molecules at this level, which would ultimately destroy the population inversion. Due to their high thermal velocity, helium atoms efficiently thermalize the populations of these lower levels **[2]**. It should be noted that the role of helium is not limited to depopulating the lower level; it also facilitates the ignition and maintenance of the luminous discharge **[3]**. Furthermore, helium has high thermal conductivity, which aids in cooling the CO_2 in the discharge zone. It is important to prevent the overheating of CO_2 to avoid the thermal population of the 01^10 level, which is positioned at a low energy state. Additionally, the presence of large amounts of helium in the discharge prevents the dissociation of CO_2 by the discharge electrons, which remains the main drawback in sealed lasers.

The optimal composition of the mixture (CO_2, N_2, He) and the operating pressure vary significantly from one device to another. In a typical flow laser, the pressures can range from 10 to 50 Torr, and the concentrations are 15% for CO_2 and N_2, and 70% for He **[4]**. In the case of a sealed laser, the pressure of the gas mixture is much lower and depends on the length of the tube. Its active medium is typically made up of a CO_2/N_2/He mixture in the proportions of 1/1/4 ratio. This choice, suggested by Patel **[5]**, has been validated in most lasers built at the USTHB Quantum Electronics Laboratory (Laser Physics) in Algeria **[6-9]**.

In general, continuous operation occurs at low pressure, but pulsed lasers can also operate using atmospheric pressure discharges.

2. CO_2 Molecule Dissociation

The sealed version of the CO_2 laser is limited by the dissociation of the CO_2 molecule. Indeed, the initiation of the electric discharge through the gas mixture in a continuous CO_2 laser involves a multitude of energy exchange processes, including:

- Collisions of the first and second kinds between molecules and electrons.
- Emission and absorption of radiation by a molecule.
- Molecular dissociation.
- Electron attachment, etc.

Each of these processes is characterized by its cross-section or its reaction rate.

Due to the diversity of these physico-chemical processes, studying a gas under the influence of a severe electrical discharge is very difficult to carry out. This complexity is further increased by the presence of various elements in the mixture. It can give rise to several molecular species (CO, O_2, O_3, NO_2, N_2O). Some of these species depopulate the vibrational levels of the CO_2 and N_2 molecules or alter the

discharge operating conditions. Furthermore, the formation of negative ions can lead to discharge instabilities.

A model of the chemical phenomena occurring in a gas was developed by W.J. Wiegand and W.L. Nigahan **[10]** to study the temporal evolution of neutral and charged species in electrical discharges through a CO_2/N_2/He mixture. This model accounts for approximately 300 reactions, including: ionization, dissociative attachment, electron detachment, recombination, dissociation, and others (see **Table.1.**).

Table.1. Different types of reactions most commonly encountered in a laser mixture.

Type of reaction	Reaction	Rate (cm^3/s)
Ionization	$e + CO \rightarrow CO^+ + 2e$ $e + N_2\left(A\Sigma_u^{+3}\right) \rightarrow N_2^+ + 2e$	10^{-14} à 2.10^{-12} 10^{-11} à 10^{-9}
Dissociative attachment	$e + CO_2 \rightarrow CO + O^-$	3.10^{-13} à 2.10^{-12}
Recombination	$e + O_2^+ \rightarrow O + O$ $O^- + O_2^+ \rightarrow O + O$	2.10^{-8} 10^{-7}
Electronic detachement	$O^- + CO \rightarrow CO_2 + e$	5.10^{-10}
Dissociative	$e + CO_2 \rightarrow CO + O + e$	10^{-11} à 2.10^{-10}

These various processes are commonly encountered in typical laser mixtures, within a pressure range from 1 to 100 Torr and an electron temperature ranging from 0.5 to 2 eV.

In 1975, J.F. Prince and A. Garscadden **[11]** detected the presence of negative ions in a continuous laser discharge containing a CO_2/N_2/He gas mixture at a pressure of 1 Torr. Among these ions, they identified NO_2^- and NO_3^-. These ions result from electron production through electron-molecule collision processes and attachment reactions. Other studies also revealed the presence of CO_3^- and NO_4^- ions.

All the processes mentioned obviously depend on the electron concentration, the energy distribution of electrons, the operating pressure range, and the E/N ratio, which represents the ratio between the electric field and the density of neutral particles (reduced field).

3. Dissociation Mechanism

The study and control of the CO_2 molecule dissociation process in an electrical discharge are of significant interest because the vibrational levels of this molecule are used for laser action.

Indeed, electron-molecule and molecule-molecule collisions have been proposed as dominant processes. The most widely accepted mechanism involves the CO_2^- ion (see equation 3), as it requires only a threshold energy of 3.7 eV, whereas the bond energy (CO-O) is 5.5 eV.

$$e + CO_2 \rightarrow CO_2^- \rightarrow CO + O^- \qquad (3)$$

The lifetime of atomic oxygen produced by reaction (3) depends on the tube diameter, gas pressure, and wall material **[12]**, with a typical lifetime of 80 ms for a tube diameter of 2.2 cm.

For two specific temperatures, two peaks in the effective cross-section have been observed **[13]** for this reaction. The effective cross-sections for the formation of these two states are the most significant: $\sigma_1 = 10^{-16} cm^2$ et $\sigma_2 = 8.10^{-17} cm^2$

Through pressure variation measurements, for low current densities (< 1 mA/cm²), using CO_2 at pressures below 4 Torr, dissociation is significantly more pronounced compared to that caused by reaction (3) **[14]**. As a result, process (4) has been proposed, with a single peak for the effective cross-section of $3.5.10^{-17}$ cm^2, at 6.9 eV, and a threshold energy of 6.1 eV.

$$e + CO_2 \rightarrow CO_2^*\left(^3\Pi\right) + e = CO + O + e \qquad (4)$$

Studies on dissociation and ionization show that the dissociation coefficient is twice as large as the ionization coefficient. In fact, dissociation occurs through neutral molecules. This result is expected, considering that the dissociation energy of the CO_2 molecule is 5.5 eV, while its ionization energy is 14.4 eV. Therefore, dissociation is caused by low-energy electrons, which have less energy than those required for ionization. None of the other mechanisms, (such as dissociative recombination or molecule-molecule collisions) appear to have a significant effective cross-section.

4. Influence of certain Parameters on CO_2 Molecule Dissociation

Several parameters influence the dissociation of the CO_2 molecule, primarily depending on the gas mixture, discharge current and pressure of the mixture.

To highlight the influence of pressure and current on all plasma parameters, a study **[15]** examined the variation in

relaxation time and dissociation degree as a function of pressure and current.

a. Temporal Evolution of CO_2 Decomposition

The study of the decomposition of the CO_2 molecule is based on the simultaneous measurement of the visible CO line at 483.53 nm (transition $B^1\Sigma, v=0 \rightarrow A^1\Pi, v=1$) and the N_2 line at 380.49 nm (transition $C^3\Pi, v=0 \rightarrow B^3\Pi, v=2$). The change in the intensity of the band can be attributed to variations in the concentration of CO and the change in the electronic energy distribution function (EEDF). To eliminate the effect of the EEDF, the intensity of N_2 is recorded simultaneously. The following two equations illustrate the method:

$$I_{CO} = k_{CO}[CO]\eta_{CO}(EEDF) \qquad (5)$$

$$I_{N2} = k_{N2}[N2]\eta_{N2}(EEDF) \qquad (6)$$

Where I_x the intensity of species is$x$, $[X]$ is the density of species x in the ground state. η_x is the EEDF of the ground state, and $k_x$is a proportionality factor.

Since N_2 has threshold energy close to that of CO and excitation primarily occurs through electron impact, the ratio depends only on the concentrations:

$$I_{CO}/I_{N2} = K[CO]/[N_2] \quad (7)$$

Where K is a constant independent of the discharge parameters. Assuming that nitrogen does not dissociate, the concentration of N_2 is known, and the concentration of CO can therefore be calculated after calibration, along with the degree of conversion:

$$\delta_{CO2} = [CO]/[CO_2]_{initial} \quad (8)$$

The assumption that nitrogen dissociation is negligible is supported by Hokazono et al. **[16]**, who demonstrated that the decomposition rate of N_2 is 10^2–10^3 times lower than that of CO_2 under typical E/N conditions.

To determine the constant K, a calibration measurement was performed on an N_2/CO mixture where the CO concentration was 8%, varying the pressure and current. It was found that the ratio I_{CO}/I_{N2} varies linearly with the CO concentration, confirming the validity of the assumptions

used for determining the CO concentration. Details of the method can be found in **[17]**.

The study of the temporal evolution of CO_2 molecule dissociation has shown **[18]**, **[19]** that the dissociation of the CO_2 molecule quickly reaches an equilibrium state (from a few milliseconds to a few seconds). This equilibrium could be explained by the presence of a recombination reaction. However, dissociation could affect nearly 80% of the active molecules.

The temporal evolution of the spectral bands of N_2 and CO_2 is shown in **Fig.2 [15]**. The decrease in N_2 intensity is linked to changes in the electron energy distribution function (EEDF), induced by plasma chemistry **[20]**. The temporal variation in the CO line can be explained, on the one hand, by the increase in CO intensity due to electron impact dissociation of CO_2, and on the other hand, by the simultaneous change in the EEDF.

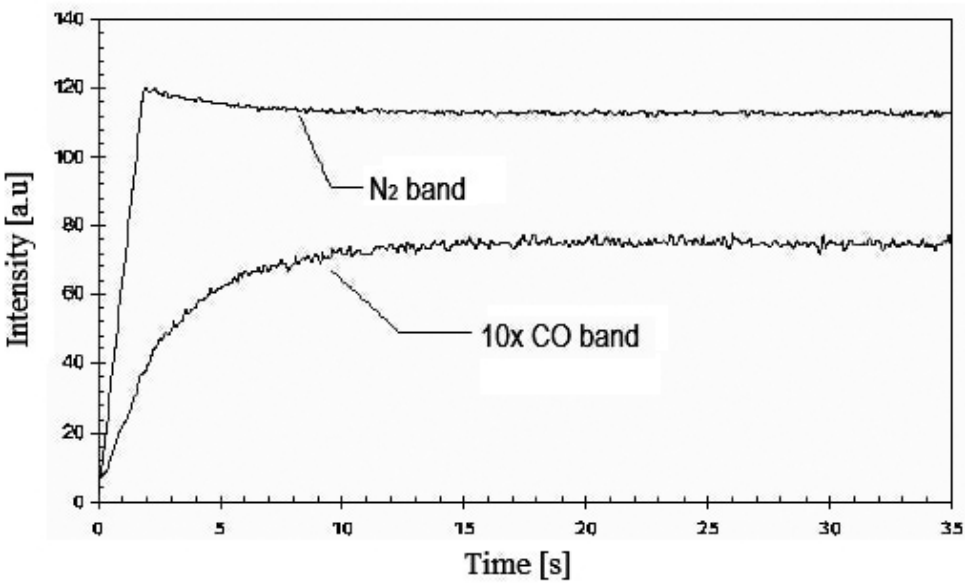

Fig.2. Temporal evolution of CO and N_2 intensity, pp = 3 Torr, I = 10 mA.

The time to reach quasi-equilibrium increases with increasing pressure (**Fig.3**) and decreasing discharge current. To understand this behavior, it should be noted that, at the onset of the discharge, the temporal evolution of CO_2 decomposition is entirely governed by the following equation:

$$e + CO_2 \rightarrow CO + O + e \qquad (9)$$

The two processes (10) and (11) begin to play a role as soon as the CO concentration reaches a sufficiently high level:

$$CO + O + M \rightarrow CO_2 + M \qquad (10)$$

$$CO + O + wall \rightarrow CO_2 + wall \qquad (11)$$

By neglecting these regeneration reactions, the primary temporal evolution of the discharge can be described as follows:

$$\delta_{CO2}(t) = [1 - \exp(-t/\tau)] \qquad (12)$$

Where τ is the relaxation time, equal to:

$$\tau = 1/n_e k_{dis} \qquad (13)$$

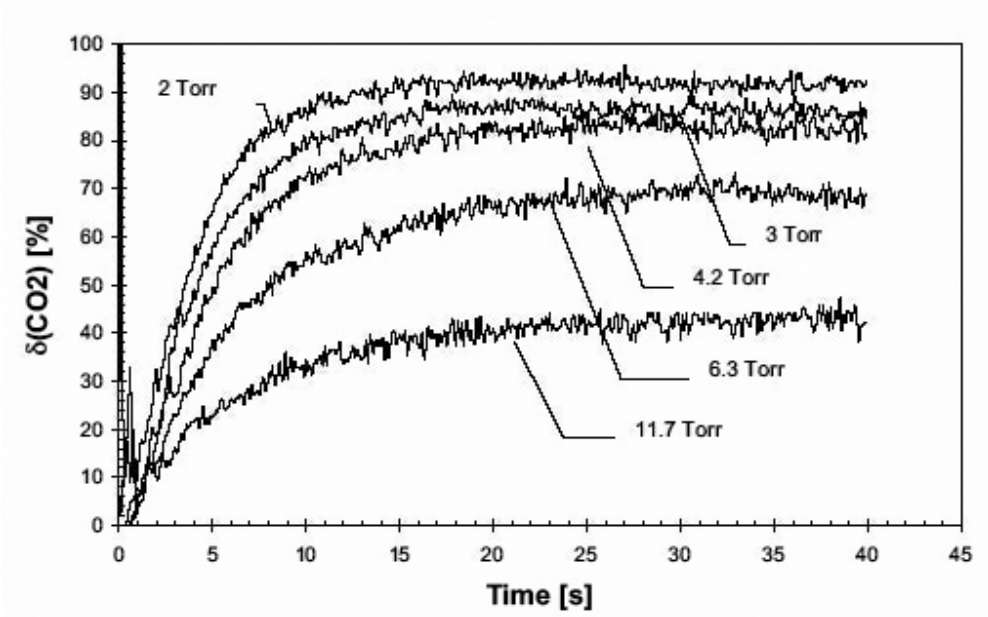

Fig.3. Temporal evolution of δ_{CO2} (I = 10 mA).

where n_e is the electron density and k_{dis} is the dissociation rate. The latter depends on the reduced electric field and, consequently, decreases with increasing pressure (**Fig.4**), which explains the pressure dependence of τ (**Fig.5**).

On the other hand, the variation of E/N as a function of current is small, and therefore the decrease in τ with current (**Fig.6**) can primarily be attributed to the increase in electron density.

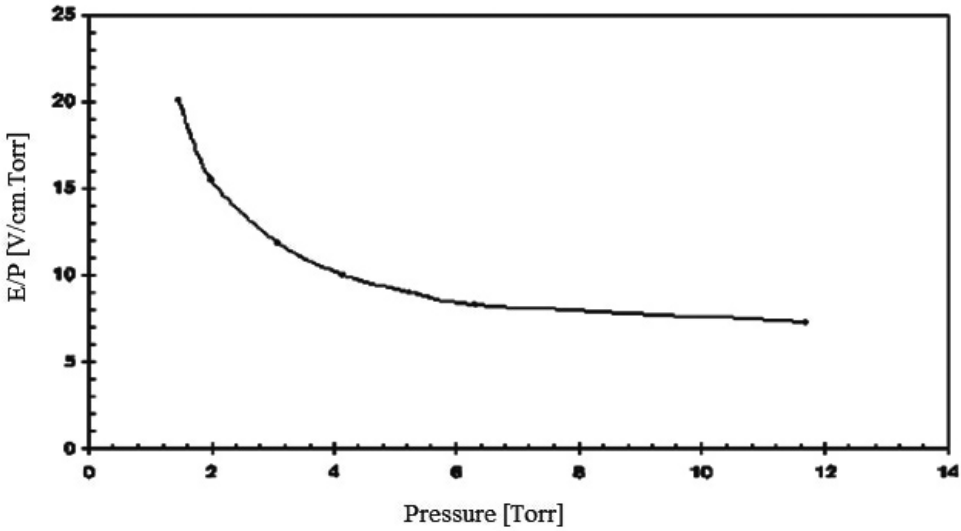

Fig.4. Reduced electric field E/P as a function of pressure (I = 10 mA).

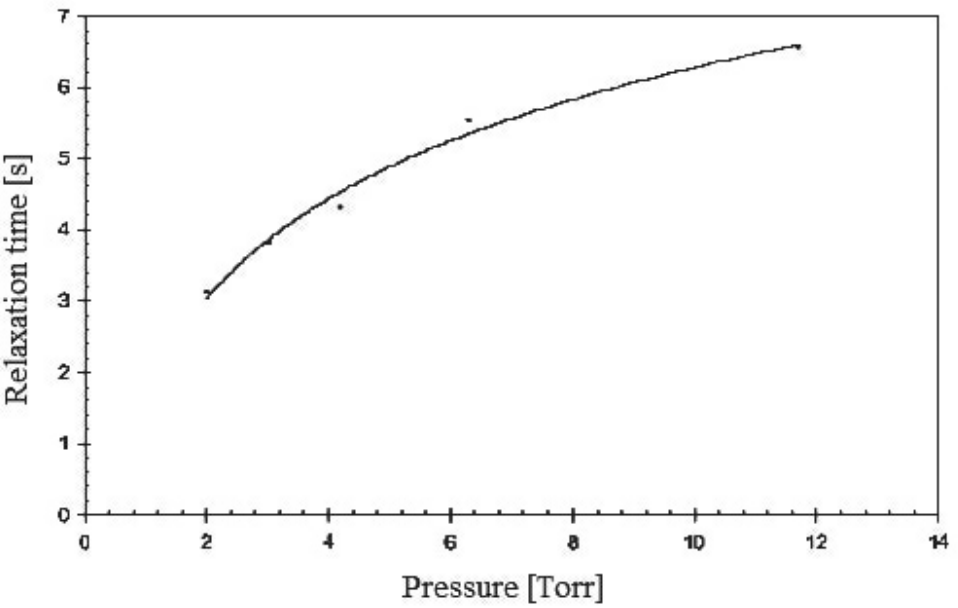

Fig.5. Relaxation time τ as a function of pressure (I = 10 mA).

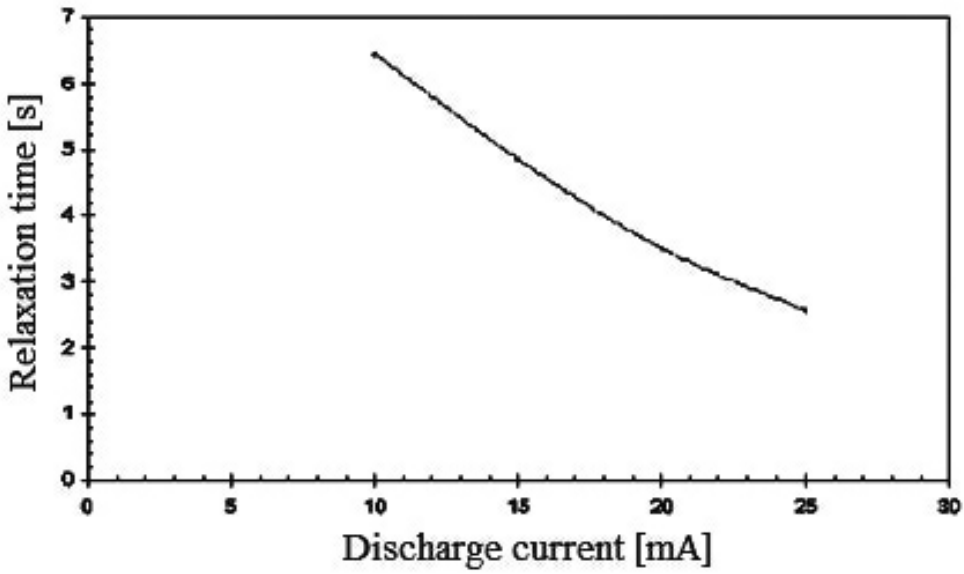

Fig.6. Relaxation time τ as a function of discharge current (p = 12 Torr).

b. Influence of Pressure

The influence of pressure and current is of great importance for optimizing laser operation, as these are two parameters directly linked to laser power.

Increasing the pressure results in an increase in electron density, which, at first glance, seems to favor dissociation. However, increasing the pressure shifts the energy distribution of electrons toward lower energies, making them less effective and consequently weakening the dissociation effect of the CO_2 molecule. This has been demonstrated **[21]** for all the mixtures considered (**Fig.7**). Additionally, increased pressure may favor the reverse recombination reaction.

In fact, the degree of CO_2 decomposition decreases from 90% at a pressure of 2 Torr to 30% at a pressure of 22 Torr (see **Fig.8**). Such a strong pressure dependence can be explained, according to numerical simulations by Cenian et al. **[22]**, **[23]**, by the significant dependence of the reduced electric field (E/N) and, consequently, the correlation between the CO_2 dissociation rate and pressure.

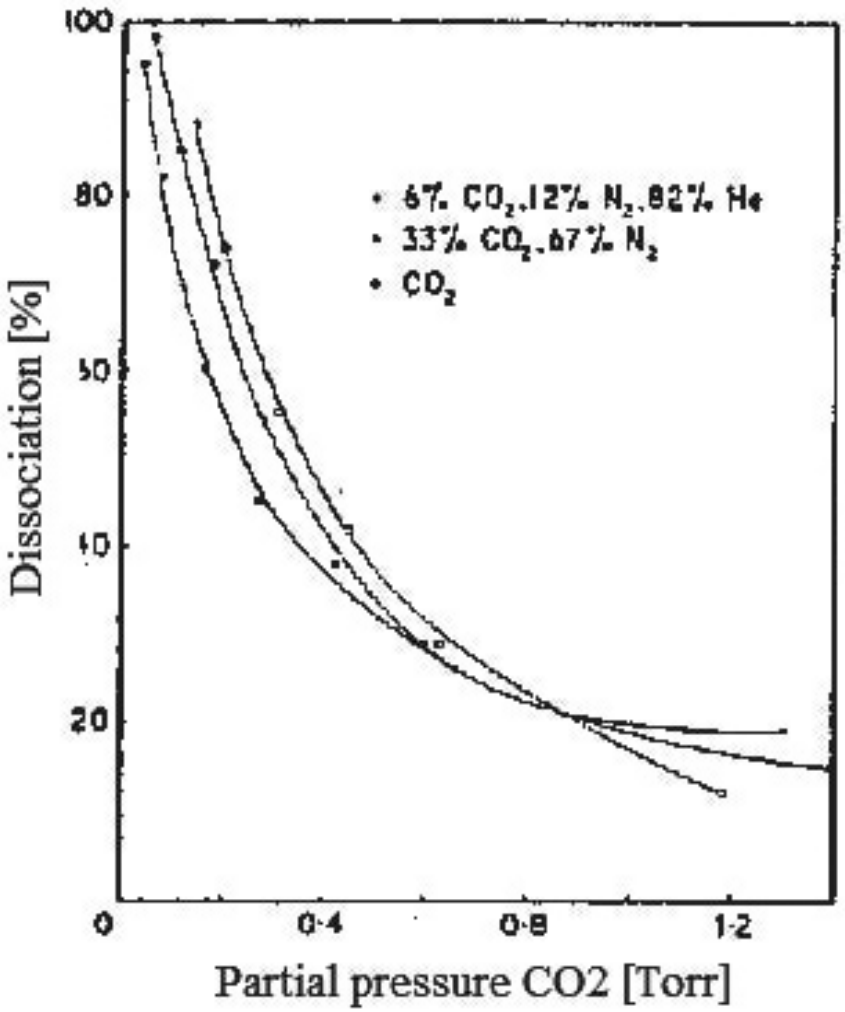

Fig.7. Influence of pressure and mixture **[12]**.

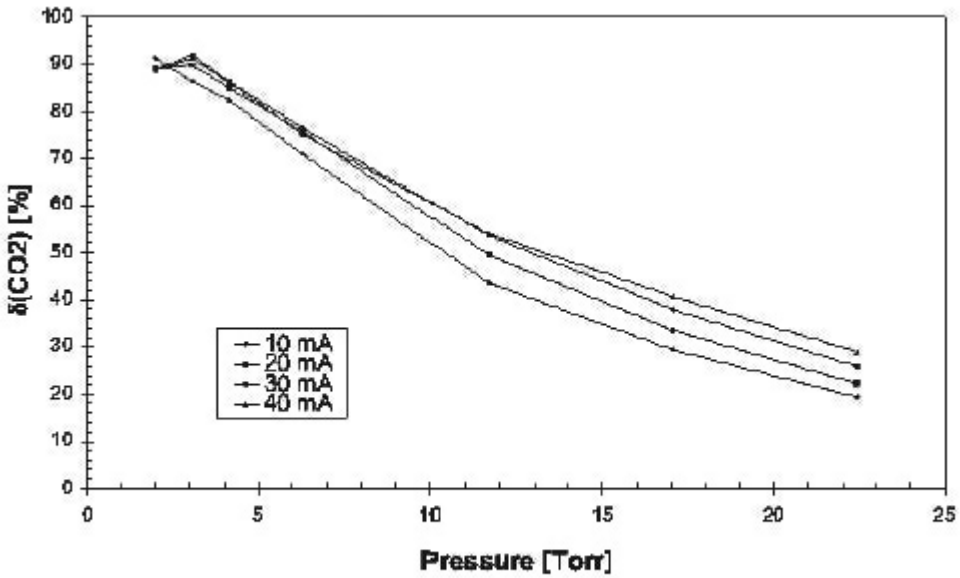

Fig.8. δCO_2 as a function of pressure.

c. Influence of the Mixture [24]

The curves in **Fig.7** show that dissociation is more significant in pure CO_2 than in the binary mixture with N_2, which in turn is more significant than in the ternary mixture with He. On the other hand, the dissociation process is more pronounced in the CO_2-N_2 mixture than in the CO_2-He mixture. This is primarily due to the fact that the ionization

potential of nitrogen (15.58 eV) is lower than that of helium (24.47 eV).

These results corroborate existing findings on laser power, which is higher for a ternary mixture with a high concentration of Helium.

d. Influence of Current and Flow Rate

A simple theoretical model was proposed to examine the influence of current on dissociation. This model assumes that dissociation is driven by electron-molecule collisions and does not consider the molecular recombination of carbon monoxide with oxygen **[24]**.

This influence is expressed by the equation:

$$\ln\left(\frac{P_0}{P_t}\right) = \frac{\beta_1 IL}{v_d eD} \qquad (14)$$

Where P_0 and P_t are the initial and partial pressures, respectively, after a time t, which represents the residence time of the CO_2 molecule in the positive column of the discharge. I is the discharge current, L the tube length, v_d

the electron drift velocity, D the gas flow rate, and β_1 the dissociation rate due to direct collisions with an electron. Second-kind collisions have been neglected, as they are significantly less frequent than first-kind collisions.

Fig.9 show the evolution $\ln\left(\frac{P_0}{P_1}\right)$ as a function of the current for a fixed flow rate and as a function of the flow rate for a fixed current and pressure.

The non-linearity of the curves can be explained by the dependence of β_1 on the current. An increase in current leads to an increase in dissociation, followed by the CO_2 reformation reaction occurring at a higher rate. On the other hand, the flow rate reduces dissociation by introducing a proportion of new active molecules, effectively increasing the effective partial pressure of CO_2 **[25]**.

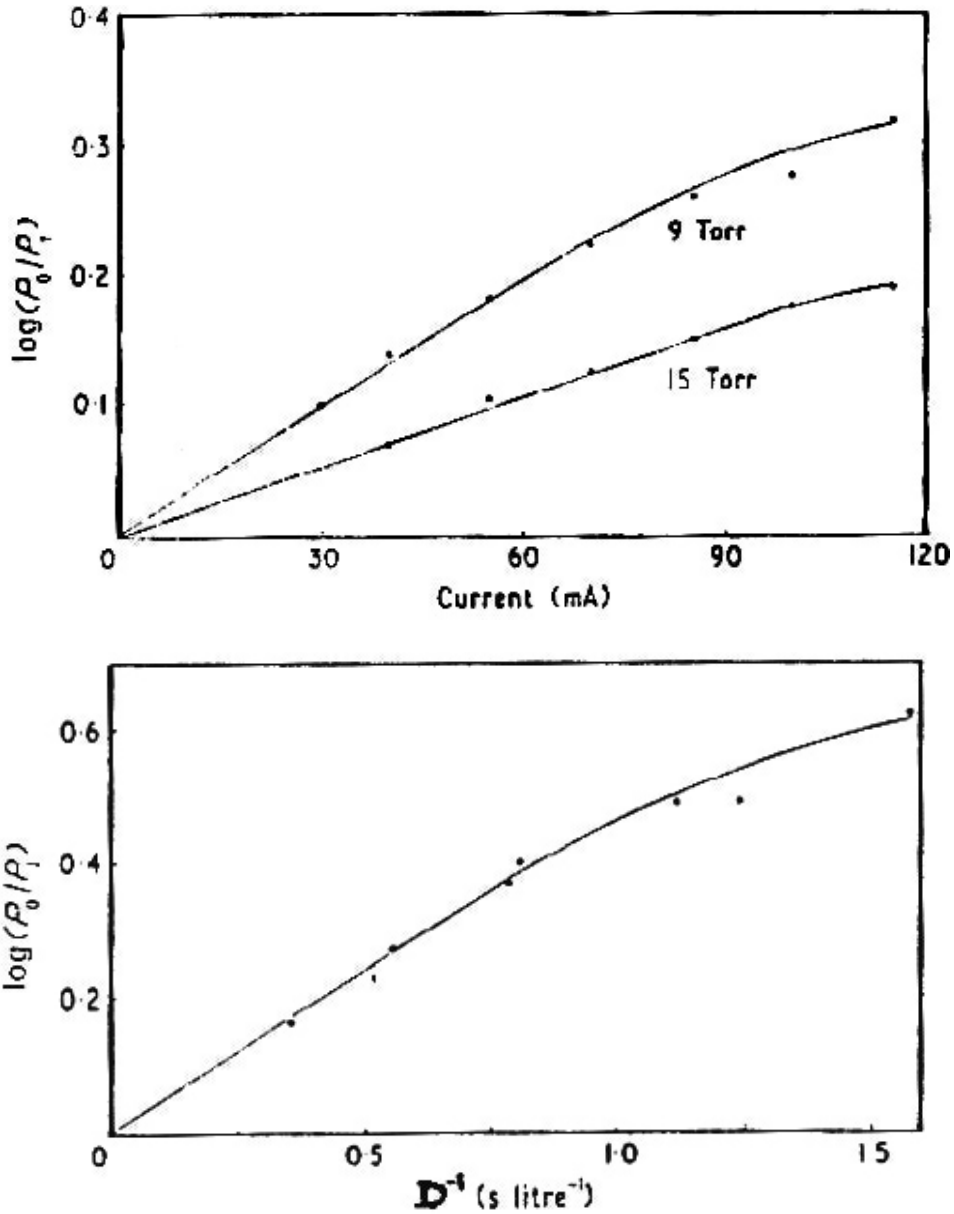

Fig.9. Influence of current and flow rate **[24]**.

In **Fig.10**, it can be observed that the increase in CO concentration with rising current is abrupt at high pressures (for low (E/N). Since the variation of the reduced electric field with current is minimal, the change in dissociation is attributed to changes in electron density and the regeneration rate (reactions 10 and 11).

On the one hand, the current density—and consequently the production of CO molecules through collisions with electrons—increases with the discharge current.

On the other hand, at low pressure, the CO concentration remains almost constant as the current varies. At high pressure, the CO concentration is low and increases almost linearly with current.

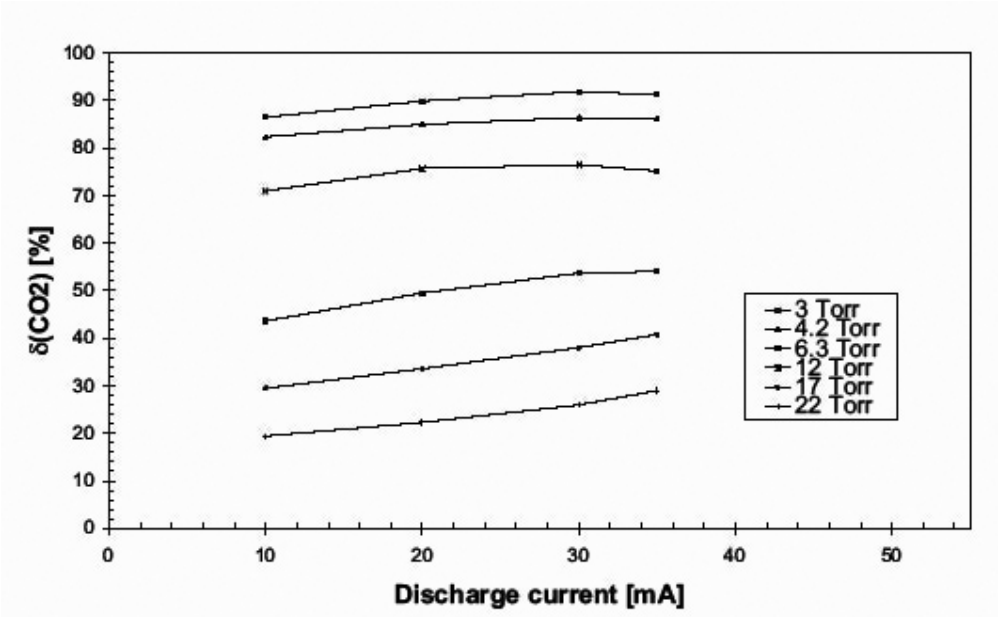

Fig.10. Relaxation time τ as a function of discharge current (p = 12 Torr).

e. Influence of the Discharge Volume

The influence of the discharge volume has also been studied **[15]**. A significant reduction in the active discharge volume affects the temporal evolution of the laser mixture. Reducing the discharge volume increases the relaxation time (see **Fig.11**). This increase requires more time to reach a stable CO concentration (equilibrium). Equilibrium must be established between the dissociation zone and the region where only CO_2 molecule regeneration processes occur,

which involve the three dissociation and regeneration processes, either on the tube walls or with another molecule.

No difference in the degree of CO_2 decomposition is observed between the two discharge configurations shown in **Fig.11**.

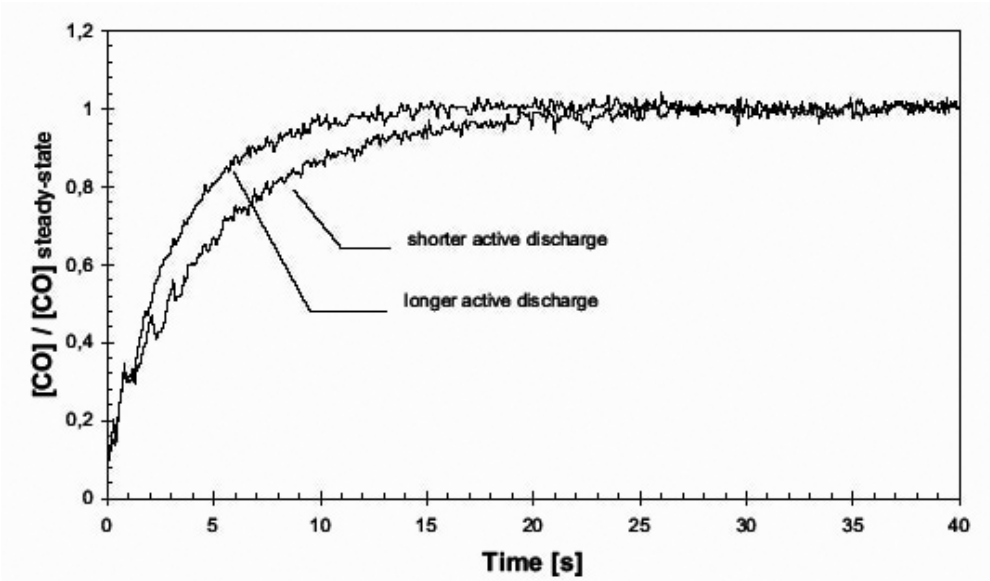

Fig.11. Comparison of δ_{CO2} for different discharge configurations.

III.
Solving the Problem of CO_2 Molecule Dissociation

1. Recombination Reaction

In the previous study, we highlighted the detrimental role that dissociation can play in a CO_2 laser. It reduces the number of active molecules (by approximately 80%) that contribute to generating the laser effect. On the other hand, CO molecules couple with N_2 molecules to de-excite them, absorbing a significant portion (about 20%) of the electrical energy, all within very short time intervals. To address this issue, numerous attempts have been made to counteract this phenomenon. Most studies agree that complete elimination is not possible.

The recombination reaction occurs via the pathway:

$$CO\left(^1X\Sigma^+\right)+O\left(^3P\right)\rightarrow CO_2^*\rightarrow CO_{2(001)}+h\nu \qquad (15)$$

It is important to note that the atomic recombination of oxygen impedes the recombination reaction of the CO molecule. This atomic recombination occurs through several reactions:

- On the tube wall:

$$O + O \xrightarrow{wall} O_2 \quad (16)$$

- By collision with a gas molecule:

$$O + O + M \rightarrow O_2 + M \quad (17)$$

- If the concentration of molecules from reactions (16) and (17) is sufficiently high, another reaction (18) can occur, leading to the formation of ozone:

$$O + O_2 + M \rightarrow O_3 + M \quad (18)$$

Followed by reaction (19)

$$O + O_3 \rightarrow 2O_2 \quad (19)$$

Alternative pathways for recombination have also been proposed by other authors **[21]**, including:

$$CO_{(v)} + CO_{(u)} \rightarrow CO_2 + C \quad (20)$$

$$CO\left(a^3\Pi\right) + CO \rightarrow CO_2 + C \quad (21)$$

$$CO + C \xrightarrow{wall} CO_2 + C \quad (22)$$

However, these reactions are unlikely to occur as no carbon deposition has been observed on the walls of the tube.

2. Some Proposed Solutions to Solve the Dissociation Problem

The study discussed in the previous section provided a clear understanding of the dissociation mechanism and allowed for testing the influence of certain factors. An increase in pressure and a decrease in discharge current reduce the dissociation rate. Additionally, other extrinsic solutions can contribute to the recombination of the molecule.

a. Gas Flow

The establishment of a slow flow was proposed early on as a way to reduce the dissociation effect of the molecule. Indeed, it alone helps eliminate a significant amount of dissociation products **[26]**, **[17]**. Another advantage is that it contributes to cooling the laser. However, our study focuses solely on addressing the problem of CO_2 molecule dissociation in a sealed laser.

b. Effect of Xenon [27]

The addition of a low-ionization-potential gas, such as Xenon, to the gas mixture can help reduce the number of high-energy electrons present, thereby delaying CO_2 dissociation. Furthermore, the effect of Xenon is not limited to improving the laser's lifetime; it also helps reduce the operating voltage without affecting the output power, thereby increasing the laser's efficiency (see **Fig.12** and **Fig.13**).

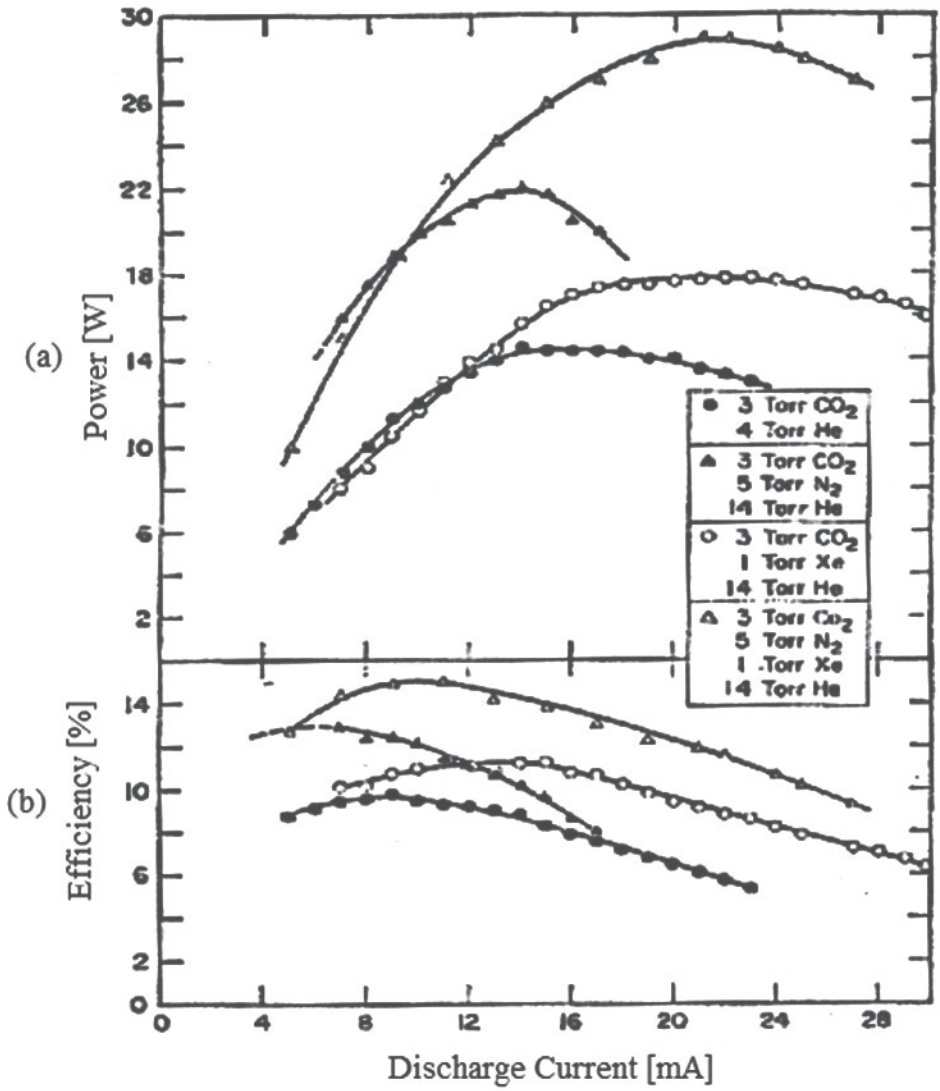

Fig.12. Effect of Xenon on the sealed CO_2 laser for CO_2-He and CO_2-N_2-He mixtures (a) Laser power as a function of discharge current, (b) Efficiency as a function of current.

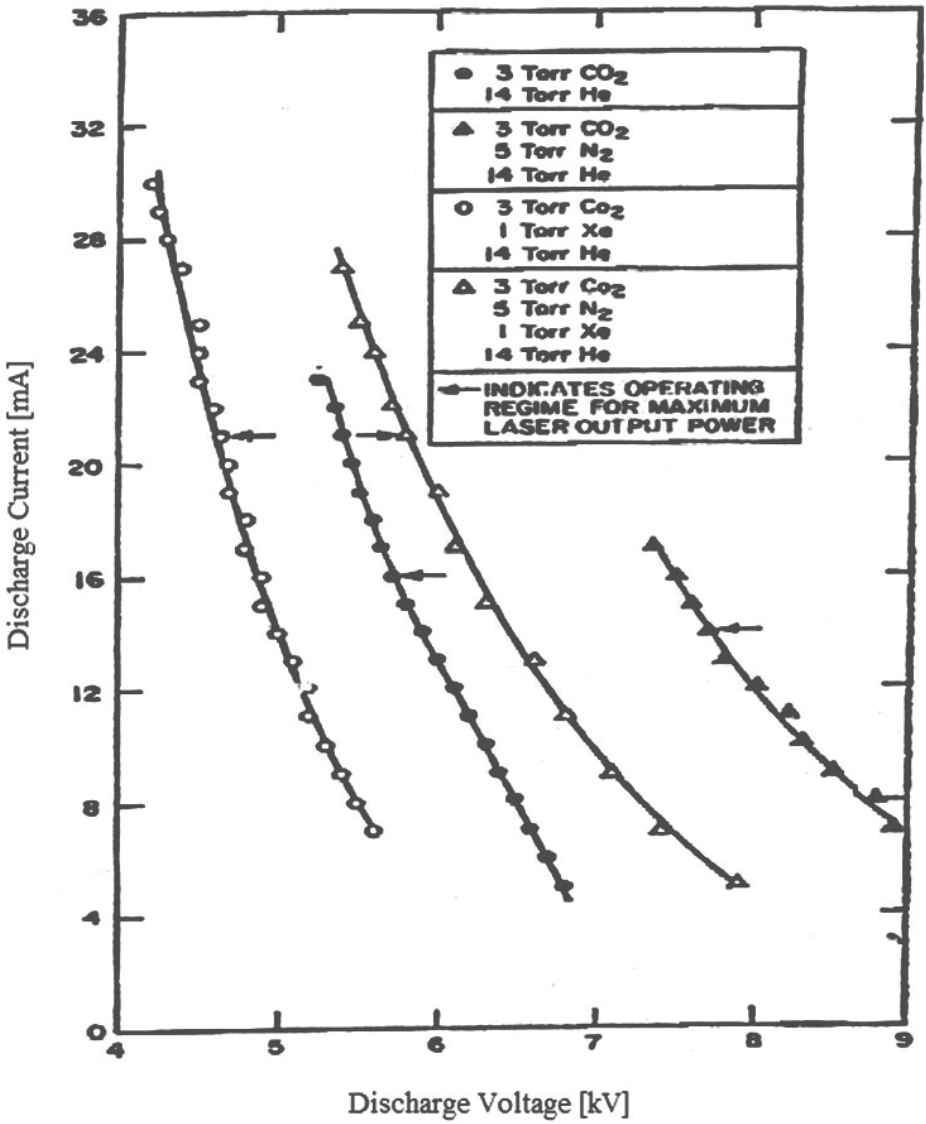

Fig.13. Effect of Xenon on the current-voltage characteristic of the sealed CO_2 laser. Platinum cathode, inter-electrode distance 52 cm.

c. Effect of Water Vapor

The addition of water vapor to the gas mixture significantly increases the laser's lifetime. W.J. Witteman and H.W. Werner **[28]** suggested that the effect of water vapor occurs via the hydroxyl radical (OH). This radical reacts with CO to form CO_2 and H_2:

$$OH + CO \rightarrow CO_2 + \frac{1}{2} H_2 \qquad (23)$$

Thus, water vapor helps enhance the relaxation of the lower laser level, resulting in a substantial increase in power. Indeed **[29]**, less than 10% of the CO_2 molecules are dissociated when 0.6 Torr of water vapor is added to a low-pressure mixture excited by a 70 mA current (i.e., under conditions of high dissociation). Furthermore, visual inspection of the discharge along the laser tube shows that the addition of water vapor changes the discharge color from light blue to purplish pink. It is important to note that increasing the water vapor pressure leads to a decrease in laser power because H_2O molecules can de-excite N_2 molecules before CO is formed. Moreover, the optimal concentration of water vapor in the gas depends on the diameter of the discharge tube **[30]**.

d. Effect of Hydrogen

Smith and Browne **[31]** demonstrated qualitatively that the addition of a small amount of hydrogen (0.1 to 0.5 Torr) enables the regeneration of the molecule with the same dissociation rate. The effective partial pressure of hydrogen is approximately 0.2 Torr; beyond this pressure, hydrogen alters the energy distribution of the electrons responsible for exciting the upper laser level (001) and instead accelerates the de-excitation of the populations at this level. If hydrogen is added to the gas mixture [CO_2 : N_2 : He], the following reactions occur:

$$H + O_2 \rightarrow OH + O \qquad (24)$$

$$O + H_2 \rightarrow OH + H \qquad (25)$$

The second reaction competes with the recombination of atomic oxygen on the walls of the tube. In fact, it represents an additional source of loss for atomic oxygen.

In addition to these two reactions, there is also the three-body reaction:

$$H + O_2 + M \rightarrow HO_2 + M \qquad (26)$$

Follow-up to the reaction:

$$O + HO_2 + M \rightarrow OH + O_2 \qquad (27)$$

These three reactions contribute solely to the formation of the OH radical, which in turn aids in the reformation of the molecule. **Fig.14** shows the effect of hydrogen on dissociation as well as on laser power.

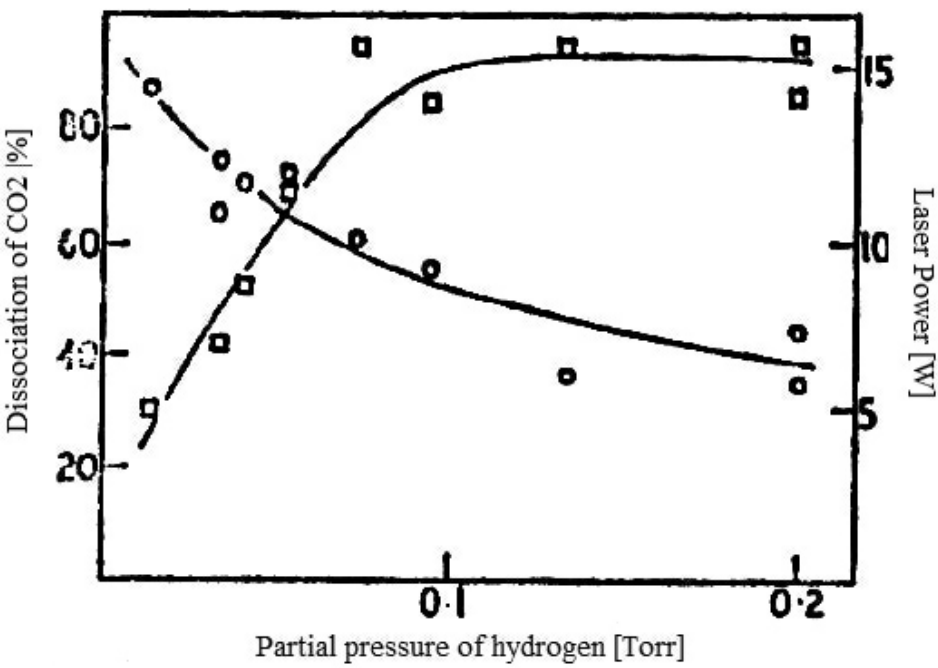

Fig.**14.** Effect of hydrogen on dissociation and laser power.

Note:

Carbon monoxide (CO) can also be added to the gas mixture to improve the efficiency of the CO_2 laser **[30]**, although it does not contribute to energy transfer in the same way as nitrogen, due to the large energy difference between the vibrational level V=1 of CO and the excited level of CO_2 (170 cm^{-1}). The addition of CO to the CO generated from CO_2 decomposition affects the concentration of CO_2. Even with these disadvantages, the vibrational excitation of CO_2 is much more efficient with CO than with electronic excitation.

e. Nature of the Cathode

In addition to the various molecular processes occurring within the discharge, gases can also react with the electrodes, particularly with the cathode. These reactions are slower than the dissociation reaction because they depend on the diffusion distances of the molecules **[31]**.

Furthermore, not only can the cathode react chemically with the gas mixture, but other phenomena can also occur, such as cathode sputtering, deposition on the cathode, the tube,

and the windows. These processes most often lead to poisoning of the medium, thereby reducing laser performance, especially if the laser is intended for sealed operation.

Several metals have been tested, including oxidizable materials, complex materials, and others.

f. Oxidizable Materials

Aluminum (Al), zirconium (Zr), tantalum (Ta), silver (Ag), copper (Cu), and other metals oxidize with oxygen to form Al_2O_3, ZrO_2, Ta_2O_5, AgO, CuO. As can be seen, these reactions represent an additional loss of oxygen and, consequently, hinder the reformation of CO_2.

g. Catalytic Materials

A catalyst increases the reaction rate by introducing new reaction pathways and lowering the activation energy or Gibbs free energy of activation. By doing so, it increases the reaction rate or lowers the reaction temperature. It is important to note that the catalyst does not alter the total Gibbs free energy of the reaction, which is a state function

of the system, and therefore has no effect on the equilibrium constant. The catalyst must be stable and compatible with the electrical and optical conditions of the laser. Common catalytic cathodes include nickel, tungsten, and molybdenum (see **Fig.15**). Dissociation remains high due to the formation of complexes such as $Ni(CO)_4$, $Mo(CO)_6$, and others, in the form of deposits on the walls surrounding the cathode or in the gas phase when the temperature is high.

The use of platinum or its alloy with rhodium in a 90%-10% ratio resulted in low dissociation rates (35%-40%) **[33]**. Good performance has also been observed with stainless steel.

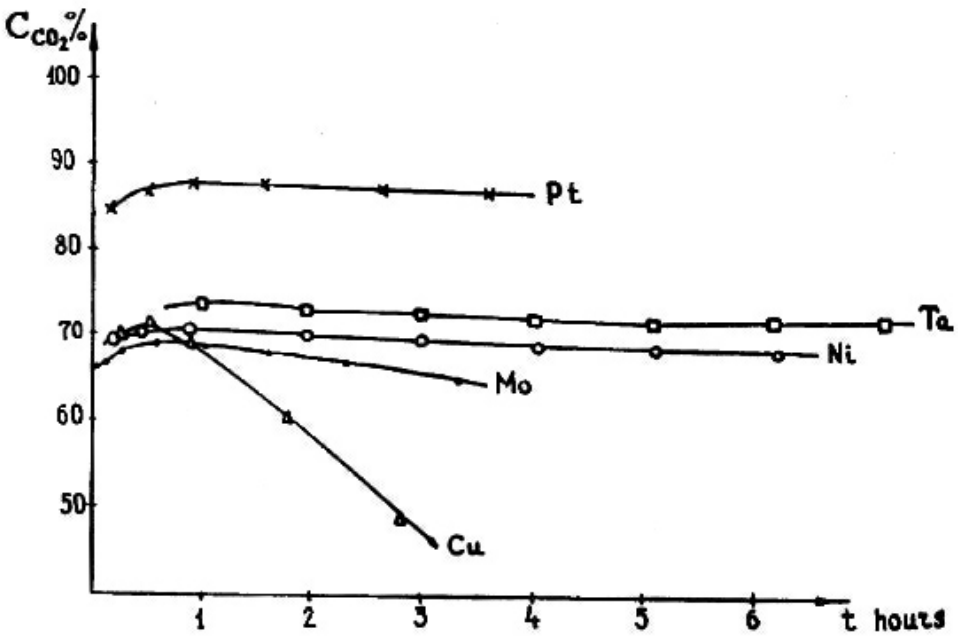

Fig.15. Time evolution of CO_2 concentration with different electrode metals **[32]**.

h. Heating the Cathode

Another technique was presented by Carbone, who employed an externally heated nickel cathode. A lifetime of 1,000 hours was achieved, and the CO_2 concentration was maintained through the desorption of CO_2 from the cathode **[34]**, **[35]**.

Hermann modified this technique **[36]** by using a self-heating nickel cathode in a tube pre-filled with hydrogen to achieve a long lifetime and high power (see **Fig.16**). He suggests that the heated nickel cathode acts as a hydrogen source for the tube to desorb CO_2 and that the power increases observed with the addition of water vapor or hydrogen may not result from greater relaxation of the laser's lower level but rather from a reduction in the dissociation rate, thus keeping the CO_2 pressure closer to its optimal value.

Studies show that it is not just the heated nickel cathode that contributes to the long lifetime in this case, and even in Carbone's method, but the presence of hydrogen is necessary to achieve this performance (see **Fig.17**). The optimal hydrogen pressure is about 0.2 Torr.

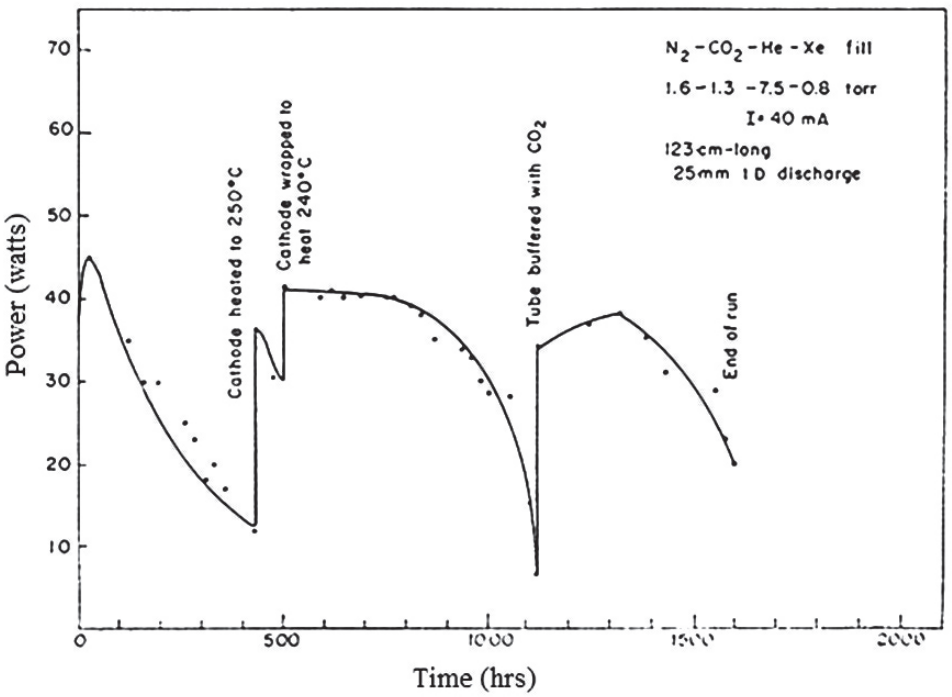

Fig.16. Temporal evolution of laser power with a hollow nickel cathode **[36].**

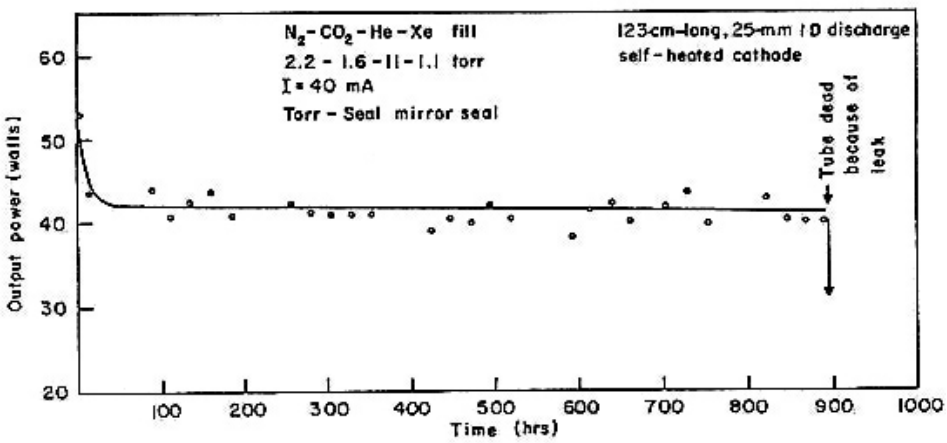

Fig.17. Temporal evolution of laser power with a hollow nickel cathode after hydrogen pretreatment **[36]**.

i. Cold Cathode [37]

The cold cathode of a CO_2 laser should have a very low sputtering rate, a minimal number of negative ions in the sputtering products, and no consumption of oxygen. These conditions can be satisfied by selecting the cathode material from the first group (IB) of the Mendeleev periodic table **[38]**, which forms semiconductor oxides (Cu, Ag, Au). Silver, which is intrinsically oxidized by silver-copper

alloys, and pure copper meet most of these requirements in a He-CO_2-CO-Xe gas mixture.

Tests on the gas mixture, the nature of the cathode, and its geometry ensure that the CO_2 laser's lifetime can reach 10,000 hours (almost a year) or more. Ag-CuO and pure copper are the most promising materials. (See **Fig.18, 19**)

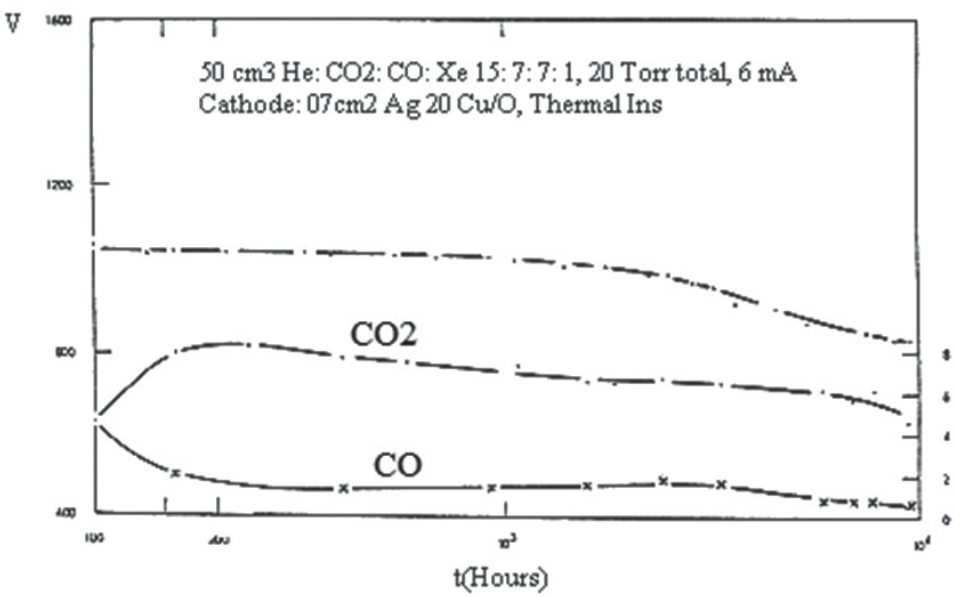

Fig.18. Ag-CuO cathode. Temporal evolution of voltage (upper curve); temporal evolution of partial pressures of CO_2 and CO (lower curves).

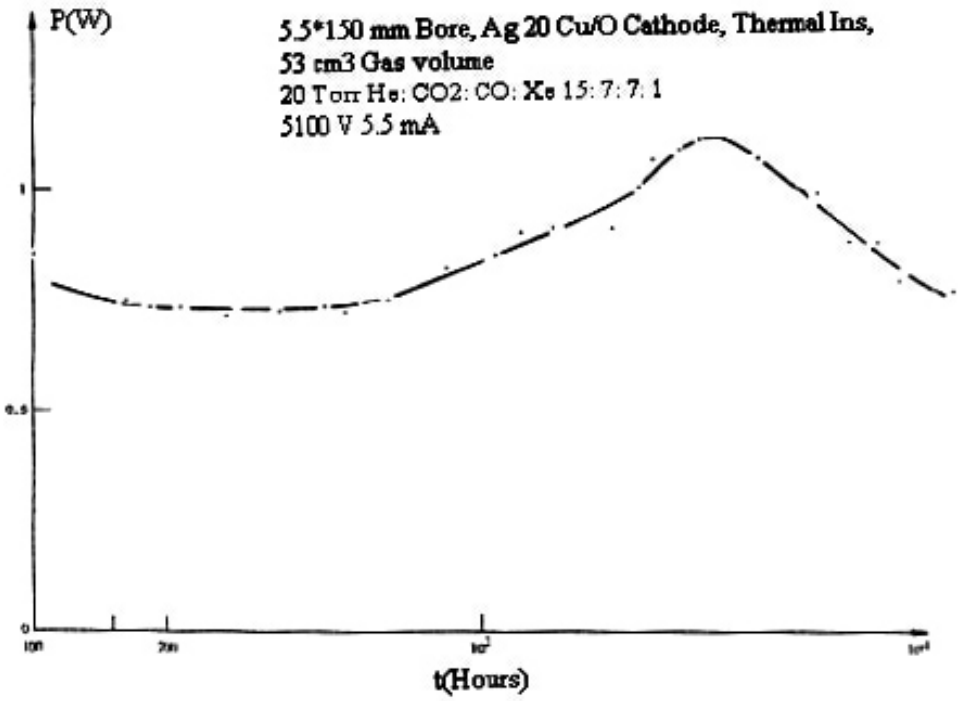

Fig.19. Temporal evolution of CO_2 laser power.

It should be noted that the equilibrium between CO_2 and CO molecules depends solely on local processes **[31]**. However, processes at the cathode level can contribute to the recombination of the CO_2 molecule, provided that the distance (d) between the cathode and the positive column is smaller than the diffusion distance of a reformed CO_2 molecule at the cathode.

$$d \le \left(\frac{2D\tau_A 760}{P} \right)^{1/2}$$

Where P is the gas pressure in Torr, and D is the diffusion coefficient in cm²/s

$\tau_A = \left(k'_A n\right)^{-1} = k_A^{-1}$. n and k'_A are respectively the electron density and the dissociation rate.

Dissociation decreases at the cathode, contributing to its catalytic effect, but increases as the distance from the cathode increases (see **Fig. 19**). As a result, the use of a catalytic cathode creates a density gradient of CO_2, CO, and O in the cathodic region, while the positive column remains in a state of high dissociation.

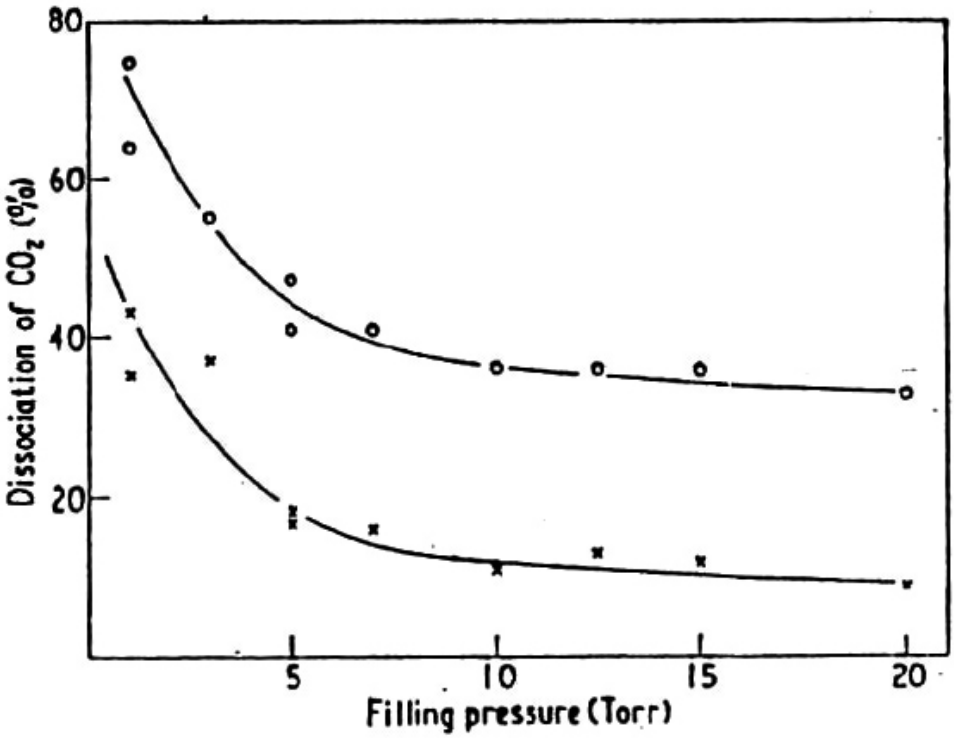

Fig.20. Evolution of dissociation at two positions of the tube **[31].**

j. Catalyst Distribution along the Positive Column of the Discharge

The idea of distributing the catalyst along the discharge tube is based on a detailed study using different catalysts **[39]-[42]** at appropriate temperatures. For a CO_2-N_2-He gas mixture, the degree of CO_2 dissociation can exceed 80% (without hydrogen). The dissociation rate can be reduced to 40% by distributing platinum along the discharge tube. For a CO_2-N_2-He-Xe mixture, the laser can operate for over 3,000 hours (almost 4 months). In this system, hydrogen and deuterium are undesirable additives because they reduce the excitation rate of the upper laser level **[39]**.

It is known that the combination of metals with oxides results in a more active catalytic component than metal films. Moreover, this component can compensate for oxygen deficiency in the discharge. Experiments by A.K. Tripathi **[42]** showed that these catalysts selectively adsorb CO_2 when coated inside the discharge tube or placed in an external reactor. This affects the composition of the gas mixture and consequently the laser's efficiency. The activity of these catalysts, such as Pt/SrK, Pd/SnO, and Pt/MnO,

depends on the pretreatment conditions and deteriorates with prolonged use.

Other studies have shown that gold catalysts have been introduced in the literature, and their use in CO_2 lasers has yielded more promising results. The distribution of gold as a catalyst along the discharge tube has been studied **[40]**, where two laser devices (laser A with the gold catalyst and laser B without) were investigated. **Fig.21** summarizes the significant role that the distributed catalyst along the discharge tube can play in both sealed and flow-type lasers.

Laser B can only deliver 63 W/m for the sealed laser and 83 W/m for the flow laser, which is comparable to other results **[43]**. On the other hand, laser A shows a significant improvement in efficiency with an increase in input power. The optimal power is 122 W/m and a lifetime of 800 hours can be achieved in the presence of the catalyst.

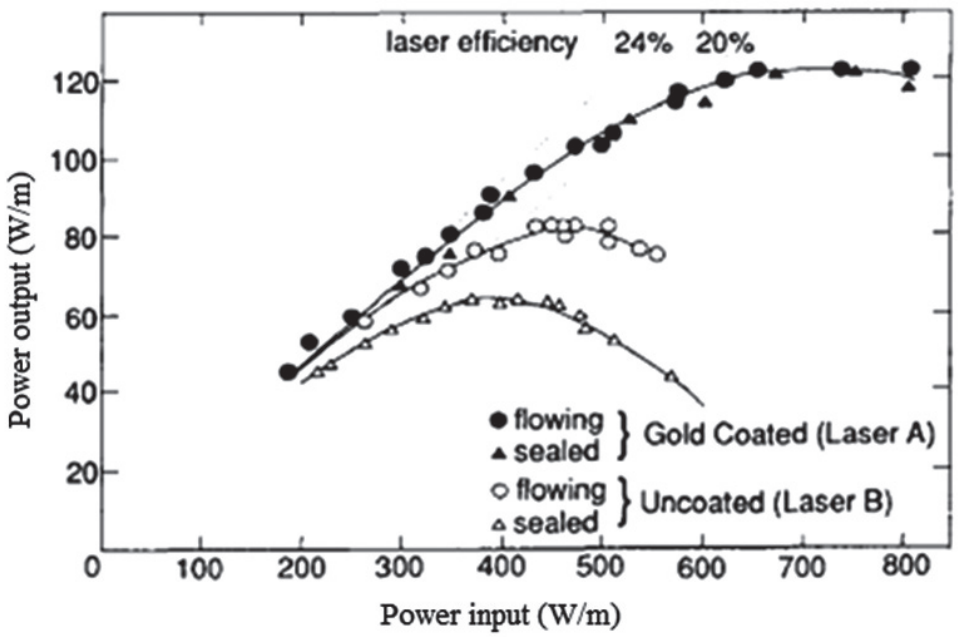

Fig.21. Output power as a function of input power for the sealed and flow configurations of lasers A and B at optimal pressure **[40]**.

3. New Configuration of the CO_2 Laser

To achieve a more stable laser, i.e., to reach equilibrium, and to prevent the catalyst from influencing the operating conditions of the laser (such as temperature), the usual configuration of the laser was modified. The laser system now consists of three tubes: one for the electrical discharge, one for the water jacket, and a third tube serving as a reservoir for the catalyst and appropriate gases.

The incorporation of such secondary chambers and structures allows for the acquisition of an approximate equilibrium state, ensuring that the catalyst does not affect the gas mixture. This results in a uniformly stable discharge, a long lifetime, and high laser efficiency.

For the reservoir to be active, materials such as ceramics, quartz, agglomerated materials, clay, porcelain, and alumina (Al_2O_3) are used **[44]**.

The temporal evolution of laser power was examined **[42]**, both with and without the catalyst, showing that the laser power tends to zero after 17 days of operation without the catalyst, whereas it can last for five months with the catalyst maintained at 400 K (see **Fig.22**).

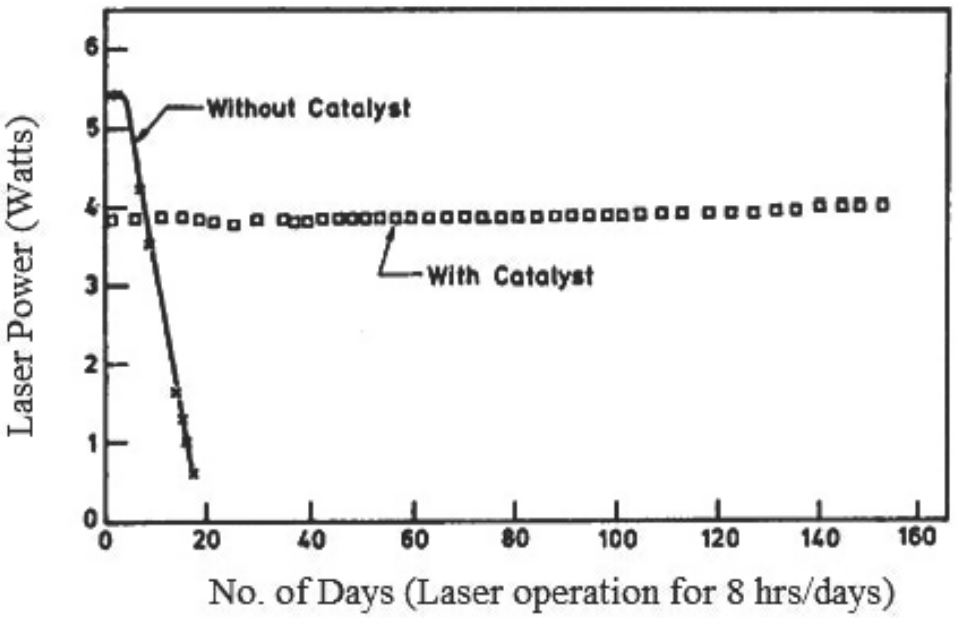

Fig.22. Temporal evolution of laser power with and without catalyst (at 400°C), CO_2: N_2: He = 1:2:10, at a pressure of 17 mbar and a current of 12 mA.

Fig.23 illustrates the laser power and the concentrations of CO_2 and CO as a function of the catalyst temperature. It shows that at 300 K, CO_2 is adsorbed by the catalyst, with 20% of CO_2 available for discharge and 42% of CO. Under these conditions, the laser power is zero. The increase in laser power, resulting from the rise in catalyst temperature,

is due to the higher CO_2 pressure and the lower CO pressure. At temperatures above 400 K, no CO_2 is adsorbed. Beyond this temperature, laser power decreases, although CO_2 concentration continues to rise, and CO concentration remains low (5%). Furthermore, the evaluation of the water temperature at all points along the laser indicates that power losses are not due to an increased gas temperature. The study also showed that the concentration of NO and NO_2 is in the range of 15-20 ppm, both with and without the catalyst. These oxides do not affect the laser's performance.

4. Gas Mixture Regeneration Method for CO_2 Lasers [45]

To reduce the amount of oxygen that could cause an arc discharge during the dissociation of the CO_2 molecule thereby reducing the output power, and to lower the operating costs associated with the use of the rare gas He, it is recommended to recombine the CO_2 molecule by recycling the gas mixture.

The method aims to regenerate the gas mixture and maintain the activation of the catalyst. To recombine the CO with O_2

formed in the discharge, the used gas is brought into contact with a catalyst (e.g., Pt-Al_2O_3) at an appropriate temperature (200°−300°C for this catalyst).

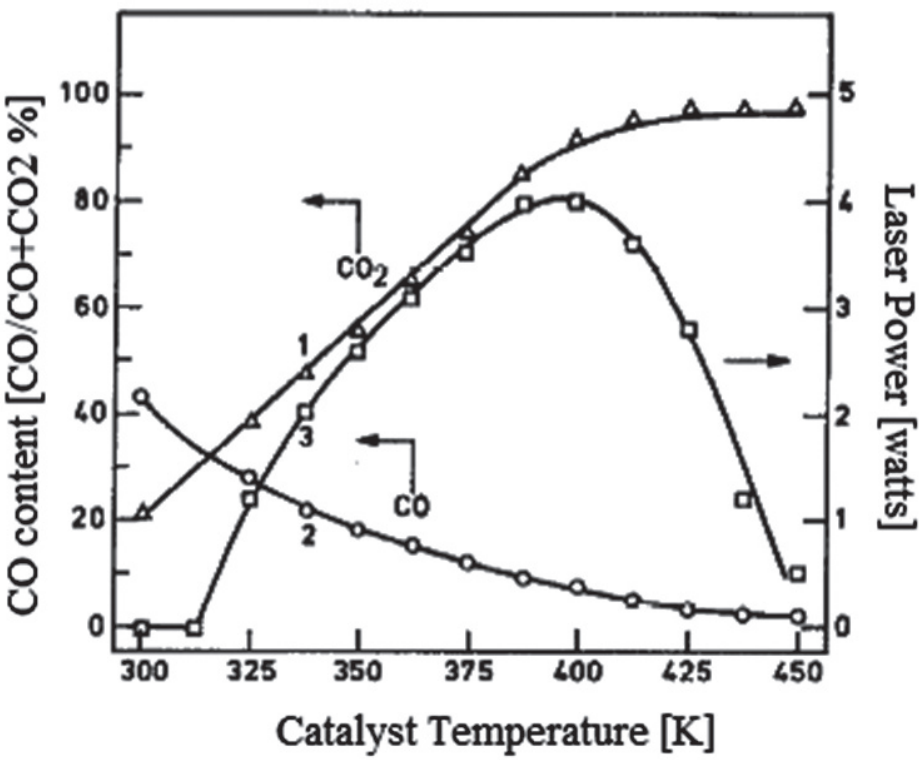

Fig.23. Effect of catalyst temperature on the output power of the sealed CO_2 laser and on the concentrations of CO and CO_2 in the CO_2: N_2: He mixture (1:2:10) at a pressure of 17 mbar and a current of 12 mA.

A suitable amount of moisture in the gas can trigger the reaction between H_2O and CO, followed by the reaction of H_2 with O_2. This process remains viable over a long period. Catalyst poisoning by NO_x is suppressed at this temperature. When the catalyst activity decreases, it can be recovered by reactivating it with a gas mixture of carbon monoxide, oxygen, and helium passed through the catalyst at a temperature of 400°C to 500°C.

Fig.24 and **Fig.25** illustrate the method of preheating the gas mixture and contacting it with a catalyst contained in a reactor to recombine CO with O_2. The heat from the reaction is used to preheat the gas mixture to be treated, and then the reacted gas is cooled to the appropriate temperature for reused. After the gas is cleaned, it is recycled back into the laser generator. The preferred reaction conditions for this regeneration are a temperature range of 80° to 200°C.

It is recommended to operate at low pressure to reduce the reaction temperature and minimize the size of the equipment. This method works well in some cases; however, under high laser power conditions, the catalyst activity decreases, and gas regeneration becomes insufficient.

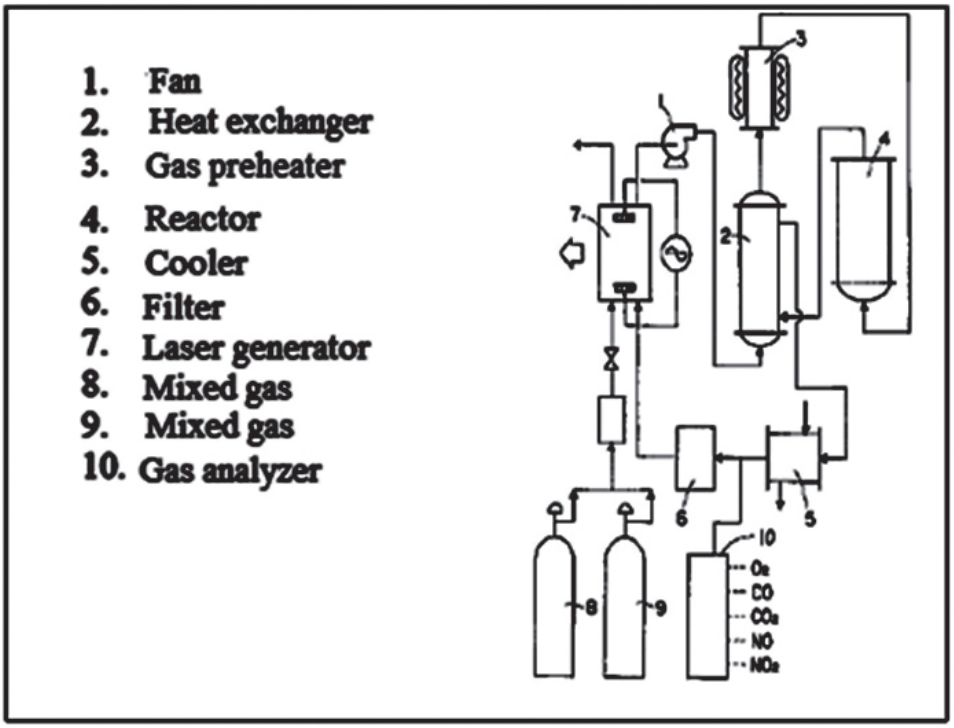

Fig.24. The components are as follows: 1: Fan - used to recycle the regenerated gas, 2: Heat exchanger, 3: Gas preheater, 4: Reactor filled with catalyst where CO, O_2, NOx, and H_2O interact to regenerate the laser gas, 5: Cooler - used to cool the regenerated gas, 6: Filter - used to remove impurities from the gas, 7: Laser generator, 8, 9: A means to supply He-CO-O_2 to the reactor, 10: Gas analyzer.

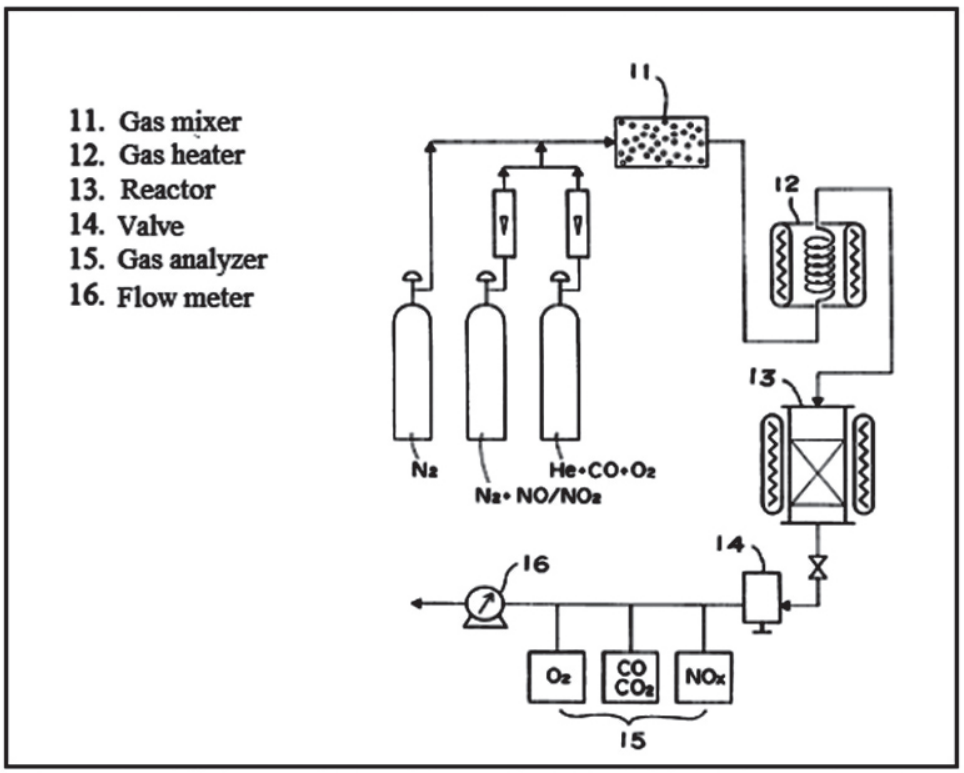

Fig.25. The components are: 11: Gas mixer, 12: Gas heater 13: Reactor, 14: Valve to maintain pressure, 15: Gas analyzer, 16: Flow meter.

The catalyst used is of the type: $Pt\text{-}Al_2O_3$ (supported Pt: 4.3 g/liter).

IV.
Conclusions

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The study focused on the dissociation of the CO_2 molecule in a sealed CO_2 laser. To clarify the issue of molecular dissociation, we identified the various processes occurring within the discharge that contribute to laser instability. We also examined the influence of specific parameters on CO_2 dissociation to determine the optimal gas mixture and operating conditions for extending the laser's lifespan. Adding appropriate additives to the gas mixture, using homogeneous and heterogeneous catalysts, and employing alternative laser structures are the primary solutions for not only increasing lifespan but also stabilizing the operation of the CO_2 laser.

For this work, we reached the following conclusions:

- The probability of producing nitric oxide (NO) in the discharge is much lower compared to carbon monoxide (CO), as the decomposition rate of N_2 is lower than that of CO_2 under typical E/N conditions.
- The presence of humidity in the discharge, in appropriate amounts, can enhance laser performance rather than degrade it.

- Carbon monoxide (CO) alone is not responsible for the loss of laser power; on the contrary, its presence can contribute to power enhancement. Therefore, adding small amounts of CO to the gas mixture is beneficial.
- Having an excess of oxygen atoms is advantageous for recombining CO_2 molecules, but their atomic recombination can hinder the recombination of CO molecules. Therefore, selecting the tube material, its diameter, and the gas pressure is crucial for the lifespan of atomic oxygen.
- The study of CO_2 dissociation is based on identifying its infrared spectral line and examining the visible spectral line of CO, as the presence of CO indicates CO_2 dissociation.
- Increasing the mixture pressure and reducing the discharge current weaken CO_2 dissociation.
- A reduced flow rate limits dissociation by introducing a proportion of new active molecules.
- Decreasing the discharge volume increases the relaxation time, thereby reducing dissociation.
- Adding xenon to the gas mixture can reduce the number of high-energy electrons, thereby delaying CO_2 dissociation. It also reduces the operating voltage

without affecting output power, thus improving laser efficiency.

- 0.6 Torr of water vapor and 0.2 Torr of hydrogen are appropriate amounts to reduce dissociation.
- The cathode material, cathode heating, and cold cathode significantly influence the lifespan of the CO_2 laser, but their influence remains local.
- The distribution of the catalyst along the positive column of the discharge tube addresses this issue.
- A three-tube CO_2 laser structure, where the third tube serves as a gas or catalyst reservoir maintained at an appropriate temperature, allows for a longer lifespan without affecting the gas mixture.
- A cost-effective method for extending the laser's lifespan involves circulating and reusing the gas mixture while preserving catalyst activity.

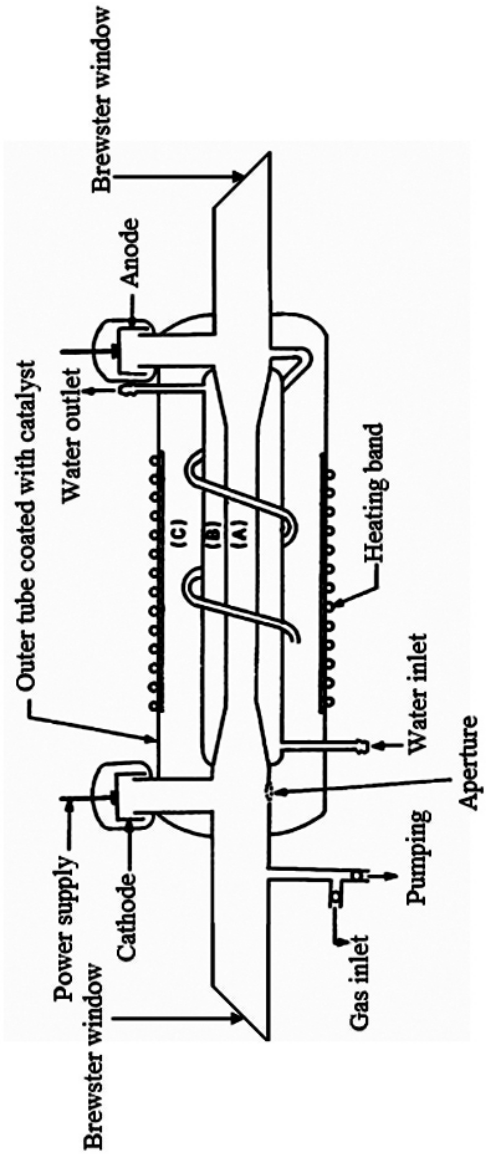
To achieve a more practical laser while maintaining high performance in terms of power and beam quality, consider the setup described below:

First, the laser we propose is sealed at its ends with Brewster windows. The choice of the laser cavity is based on both beam quality and laser power. However, these two

factors are often incompatible and depend on the specific application.

A concave-concave cavity can produce a stable transverse mode TEM01* (donut-shaped), which allows for very high power. Another geometry that enables operation in the fundamental mode is the plano-concave cavity, which is even easier to align. From the perspective of modal stability or achieving a monochromatic and single-mode laser, using a diffraction grating in place of one of the mirrors is also highly effective.

The choice of electrode material is crucial. For this configuration, silver is recommended as the electrode material. The selection of the catalyst should take into account its lifespan during operation, its oxidation rate, sputtering properties, and other factors, as well as the gas mixture used.


Brewster window
Anode
Water outlet
Outer tube coated with catalyst
(C)
(B)
(A)
Heating band
Water inlet
Aperture
Pumping
Gas inlet
Power supply
Cathode
Brewster window

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