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A QUANTITATIVE THEORY OF AN ELECTRON-BEAM-EXCITED CARBON MONOXIDE GAS DYNAMIC LASER

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10. ABSTRACT

A new concept for a high power CO gas dynamic laser, coupling a supersonic expansion nozzle and an electron beam preionizer-sustainer discharge system, that promises both the high efficiency of an electrically pumped CO GDL and the high power of a thermally pumped CO GDL. CO GDLs are still in the laboratory stage, but a laser efficiency of 47% has been obtained in an electric CO laser--the highest so far attained with an electric CO2 laser is 33%. CO lasers' broadband spectral output makes it possible to choose the lines to match preferred transmission windows. The superiority of the proposed laser to existing CO lasers for atmospheric application is shown. General operational characteristics of a CO laser, and a state of the art review of the various types of continuous-wave CO lasers are given. The principle of anharmonic (V-V) pumping is presented, and the excitation and inversion mechanisms of these CO lasers are described. Finally, a quantitative theory is formulated to describe the new laser, and then a frozen flow approximation of the problem is proposed.

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A Quantitative Theory of an Electron-Beam-Excited Carbon Monoxide Gas Dynamic Laser: I. Formulation

C. C. Chen

A Report prepared for

UNITED STATES AIR FORCE PROJECT RAND

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PREFACE

As part of a continuing program of studies conducted for the U.S. Air Force, The Rand Corporation attempts to anticipate and assess the impact of potential new weapon systems, either as threats to U.S. forces or as useful tools for U.S. employment. The advent of laser technology is such a case. Among the numerous lasers of interest, two important candidates are the much studied carbon dioxide (CO_2) laser, which operates at a wavelength of 10.6 μm, and the carbon monoxide (CO) laser, which operates at about 5 μm.

There has been some suggestion that a CO laser may have some advantages over a CO_2 laser system. Thus, it is desirable to determine the optimum design for a high-power laser suitable for military applications. The present report proposes a new CO gas dynamic laser (GDL) that could have the high efficiency of an electrically pumped CO GDL and the high power of a thermally powered CO GDL (the preliminary Rand research that focused on this new laser concept was conducted in December 1971*). A review of the kinetic processes in CO lasers and a quantitative formulation of this proposed new CO laser are also presented here. Numerical results providing the laser performance will be obtained and reported later.

This report has four sections. The Introduction and Sec. II are directed at those Air Force personnel who have some knowledge of basic laser physics and classical gas dynamics and who are involved in laser research planning and in laser application studies. In these sections, particular emphasis is placed on establishing the current state of the art and reviewing the kinetic processes in CO lasers. The last two sections are directed at those Air Force personnel who are interested in a detailed, quantitative theory of CO lasers. This report, in general, should be useful to anyone with a working knowledge of laser physics and physical gas dynamics who is involved in laser technology research, but particularly to Air Force personnel in the Weapons Laboratory and DCS/Research and Development.

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*While the present report was in review, the author's attention was drawn to an independent publication using the same concept: J. W. Rich, J. A. Lordi, and S. W. Kang, *Semi-Annual Technical Report Supersonic Electrically Excited Laser Development: 7 June 1972 to 7 December 1972*, Report No. WG-5164-A-1, Calspan Corporation, Buffalo, New York, February 21, 1973.

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SUMMARY

A new concept for a carbon monoxide (CO) gas dynamic laser (GDL) is proposed. The concept proposes the coupling of a supersonic expansion nozzle and an electron-beam (E-beam), ionizer-sustainer discharge excitation system. It is thought that this system could have both the high efficiency of an electrically pumped CO GDL and the high power of a thermally pumped CO GDL.

In discussing the kinetic processes in CO lasers, the superiority of this new CO laser over the existing CO lasers for atmospheric application is demonstrated. A brief review of the general operational characteristics of a CO laser and a state-of-the-art review of the various types of CO lasers are given. Then the principle of anharmonic (V-V) pumping is presented together with the excitation and inversion mechanisms of these CO lasers.

A quantitative theory is formulated to describe this new CO laser. The rate equation describing the vibrational distribution of the CO molecule in a gas mixture is first given, and a discussion of each of the physical processes represented by the rate equation is presented. Next, the steady quasi-one-dimensional adiabatic flow equations are used to study the nozzle flow. Finally, a small-signal gain coefficient for the vibrational-translational transitions of the CO molecule is derived.

A frozen flow approximation of the problem is proposed. It is shown in the case of the E-beam-excited CO GDL that conditions exist such that the characteristic flow time is short in comparison with the vibration-translation relaxation time. Therefore, it can be assumed that the vibrational energy is frozen during transit through the nozzle and that the vibrational relaxation process is decoupled from the flow process. Flow properties can be calculated using the local thermodynamic state of the gas and the well-known isentropic gas equations with constant ratio of specific heats. Essentially, the entire problem is reduced to solving the time-dependent rate equations with all the transition rates as given quantities.

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I. INTRODUCTION

Recent developments in carbon monoxide (CO) lasers[1-9] have shown that a CO laser is potentially a powerful and efficient source of coherent radiation in the 5-μm wavelength region. Successful operations of both thermally pumped and electrically pumped CO gas dynamic lasers (GDLs) have been demonstrated.[10-13] For the time being, the CO GDL is still in the laboratory stage, but it may prove to be a more efficient laser system than the carbon dioxide (CO_2) GDL because the quantum efficiency of the CO laser is nearly 100 percent while that of the CO_2 laser is about 40 percent. In fact, a laser efficiency of 47 percent has been obtained in an electric CO laser,[7] in contrast to the maximum efficiency of 33 percent obtained so far in an electric CO_2 laser.[14]

Due to the broad-band spectral output of the CO lasers, it is possible to choose the lines to match atmospheric transmission windows that are equal to or better than the performance at 10.6 μm, and the feasibility of CO laser's line selection for atmospheric transmission at low gas pressure has been demonstrated.[15]

Theoretical calculations of atmospheric attenuation for CO laser lines[16,17] have shown that there exist many atmospheric transmission "windows" in CO laser spectra. So far, the only CO laser devices that have produced laser lines matching some of the atmospheric windows are GDLs.[10-13] Furthermore, it can be observed from calculated absorption coefficients that there exist many lines of a CO laser that have equal or better atmospheric transmittance than those of a CO_2 laser.

A typical CO laser operates between the vibrational-rotational bands of the CO molecules. Thus, the successful operation of a CO laser requires an efficient means of vibrationally exciting the CO molecules and establishing a population inversion among the energy states. It is believed that anharmonic (V-V) pumping plays an important role in the successful operation of all kinds of CO lasers with the exception of the chemical CO laser. It has been shown that, under the conditions of a low translational temperature coupled with a high

degree of vibrational excitation, some of the vibrational-state populations of a diatomic gas can be totally or partially inverted due to the anharmonicity of the molecule.[18] Thus, low translational temperature and initial vibrational excitation are essential to the operation of a CO laser.

There are two prevailing methods for producing low translational temperature in the laser medium; one is a cryogenic bath for the laser discharge tube, and the other is supersonic expansion. The typical cryogenic-bath cooling technique used so far is to put the laser discharge tube in a liquid nitrogen bath such that the tube wall is maintained at the liquid nitrogen temperature ($\sim 77°K$), and the gas inside the tube is cooled by conduction. However, this technique limits the gas temperature in the discharge tube to no colder than about 100°K, whereas in the supersonic expansion cooling techniques, the gas is cooled volumetrically, and a uniform gas temperature less than 100°K is easily obtainable.

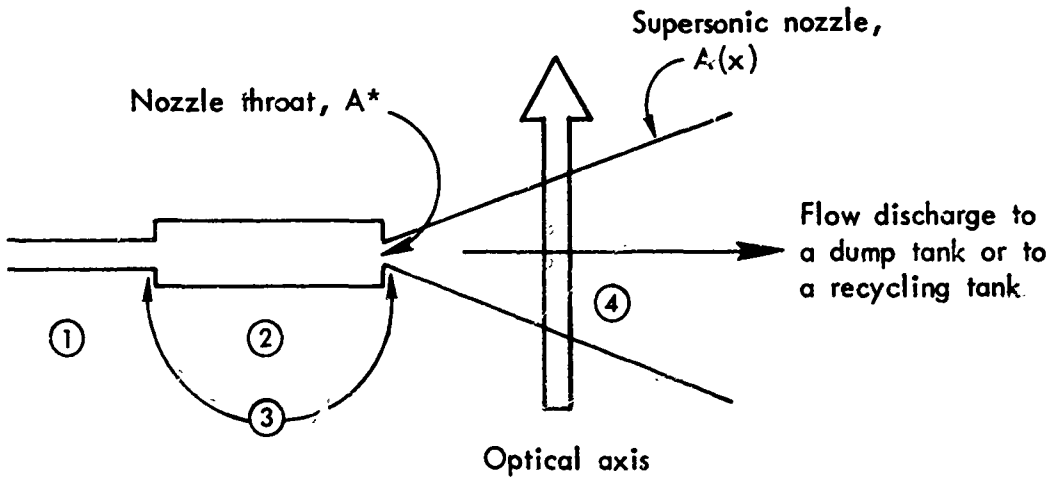
It is also observed in Ref. 7 that the CO laser efficiency increases with decreasing gas temperature and that there is a gradual shift of the threshold lasing band to lower and lower vibrational bands as the gas temperature is decreased. It can be further inferred from the findings of Ref. 13 that in order to match the maximum number of atmospheric "windows" available to a CO laser, it is necessary to operate the laser in a gas temperature less than 77°K. It appears that only supersonic expansion cooling can achieve this low temperature requirement with relative ease. Therefore, for lower atmosphere applications, where the use of atmospheric "windows" is important, supersonic expansion cooling for the CO laser system is far superior to any other currently available cooling technique. Thus, supersonic expansion provides the ideal cooling technique independent of the excitation source. A CO GDL utilizes supersonic expansion to achieve the low gas temperature required for efficient V-V pumping in contrast to the case of the CO_2 GDL in which supersonic expansion has been used mainly to obtain vibrational freezing conditions in the upper laser level.[19]

Having established the superiority of the supersonic cooling technique for the efficient operation of a CO laser, we want to search for

the optimum means of obtaining a high degree of vibrational excitation in the gas medium. Again, there are two prevailing methods of achieving this goal: (1) the thermal excitation technique and (2) the electrical excitation technique. In the thermal excitation technique, the energy source for the initial vibrational excitation of the CO molecules is supplied by thermal energy (high gas temperature). In the electrical excitation technique, the necessary source of vibrational excitation of CO molecules is supplied by the electrons in an electrical discharge.

A schematic diagram of a typical CO GDL is presented in Fig. 1. In a typical thermally pumped CO GDL,[10] the hot gas mixture (about 2000°K) in the reservoir is created by a shock tube attached to the reservoir in station 1. This high, reservoir gas temperature is necessary to provide the energy source (thermal energy) for the initial excitation of the CO molecules. In a typical electrically pumped CO GDL,[12] the gas mixture is injected into the reservoir through station 1. In this case, the reservoir also serves as a discharge tube through the use of a pair of ring electrodes concentric with the gas flow. The cathode is formed by the nozzle throat itself, and the anode is located at the entrance of the reservoir. The laser optical cavity can be placed in any desired position in the supersonic expansion region with its optical axis perpendicular to the flow direction.

In the present study, a new CO GDL, pumped by a preionizer-sustainer discharge system is proposed. The particular preionizer used in this study is an electron beam (E-beam). A schematic diagram of this E-beam-excited CO GDL is presented in Fig. 2. Electrons produced in the thermionic emitter, controlled by a grid, are accelerated, through thin foil, into the reservoir (which is also the laser excitation region) where a gas mixture of CO and some other gases (e.g., N_2, Ar, and He) is present. The sustainer field, applied across the reservoir, that supplies energy to the electrons, controls the electron temperature. Then, the vibrationally excited CO mixture is supersonically expanded into a nozzle to achieve the necessary cooling. The laser cavity can be placed in any desired position in the supersonic expansion region, and the optical axis is perpendicular to the flow axis.



① = Shock tube driver section in the case of a thermally pumped CO GDL, gas mixture inlet in an electrically pumped CO GDL

② = Nozzle reservoir

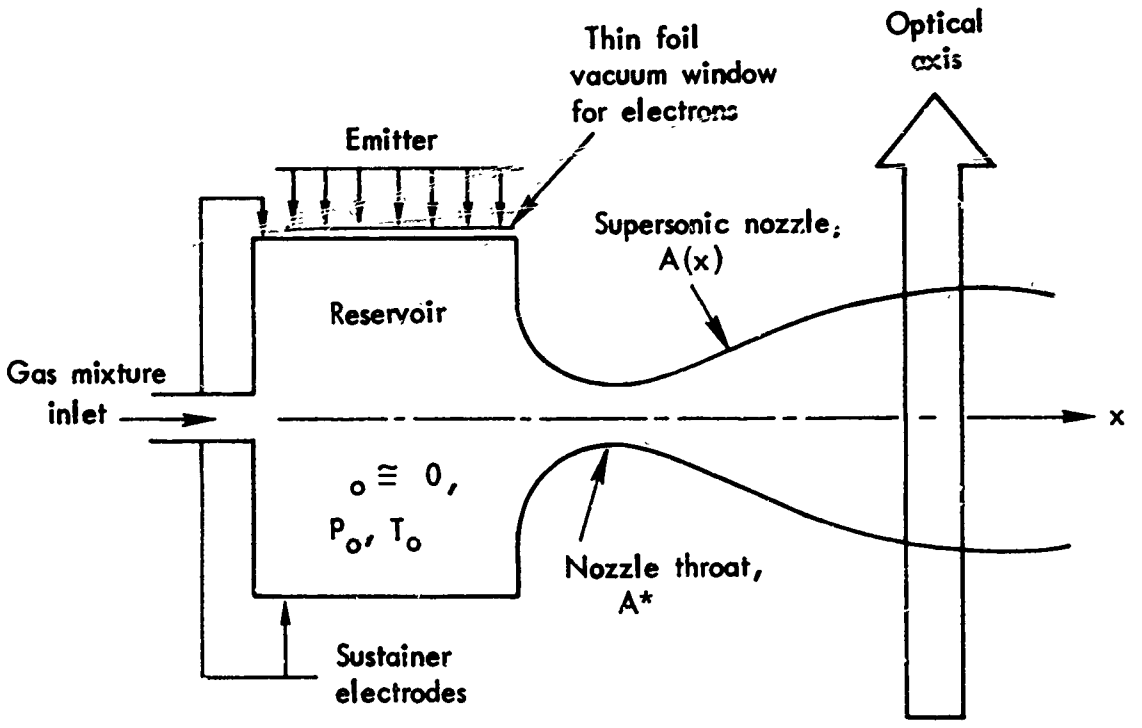
③ = Ring electrode concentric with flow in an electrically pumped CO GDL

④ = Supersonic nozzle

A* = Area of nozzle throat

A(x) = Area of the supersonic nozzle

Fig.1 — Schematic diagram of a carbon monoxide gas dynamic laser (CO GDL)



$u_o \cong 0$ = Reservoir velocity
P_o = Reservoir pressure
T_o = Reservoir temperature
$A(x)$ = Area of the supersonic nozzle
A^* = Area of the nozzle throat
x = Axial flow coordinate

Fig.2 — Schematic diagram of an E-beam-excited CO GDL

In considering different kinds of CO GDLs for potential applications, it is found that the thermally pumped CO GDL[10,11] is a poor choice because of the extremely high area ratio ($A(x)/A^*$) (typically, $A(x)/A^*$ is of the order of a thousand) needed to cool a gas from the reservoir gas temperature of 2000°K down to around 100°K. The extremely high $A(x)/A^*$ necessitates the use of a very small nozzle throat for a given laser cavity size. The smallness of the nozzle throat limits the rate of mass flow, which in turn limits the laser power output. A more reasonable alternative is an electrically pumped CO GDL[12,13] which requires a much smaller $A(x)/A^*$ (typically, $A(x)/A^*$ is of the order of ten) because of the much lower reservoir gas temperature, $\cong$ 500°K. The low reservoir gas temperature in this case is due to the fact that it is very difficult for the more energetic electrons to transfer their energy elastically to the slower (colder) atoms. The electrically pumped CO GDL also has a much higher laser efficiency than the thermally pumped CO GDL because of the highly efficient electron-impact vibrational excitation of the CO molecules.[20-22]

The conventional electrically pumped CO GDL is difficult to scale in pressure, volume, and power. The source of the difficulty is that, in the ordinary two-electrode discharge normally used for exciting electrically pumped gas lasers, the electrons that provide the excitation of the laser states must also reproduce themselves to maintain a discharge at a substantial rate of ionization. Such gas discharge instabilities as arcs are usually associated with substantial ionization rates. The mechanisms of such instabilities are very complex and not yet well understood. Furthermore, the optimum electron temperature for efficient excitation of molecular vibrational states suitable for laser action is usually much lower than the value needed for substantial electron-impact ionization. In this case, the electron temperature cannot be tuned to the desired value for efficient excitation of the molecular vibrational laser states. It was found by Persson[23] that stabilized plasmas could be produced if the electron-ion production mechanism in the plasma was made independent of the applied electric fields through the use of an external electron production source such as E-beam injection or photoionization. Therefore, the most ideal

arrangement in electrically excited gas lasers is to have separate mechanisms to produce electrons for the discharge and to control the electron temperature. Due to the intrinsic difficulties of the ordinary two-electrode discharge, it is felt that the proposed new CO GDL, pumped by a preionizer-sustainer discharge system, would have the advantages of both the high efficiency of a conventional electrically pumped CO GDL and the high power of a thermally pumped CO GDL.

In the preionizer-sustainer discharge system, the first high-voltage preionizer, using a small amount of energy, creates the electron density uniformly between its electrodes through a vacuum window. The main sustainer discharge applies a proper voltage to this volume of plasma to control the electrons to a temperature for efficient laser pumping but not to a temperature necessary for ionization. Thus, the dominant amount of energy is put into the gas by the sustainer exactly where it is desired for vibrational excitation of the CO molecules. A successful demonstration of such a system in pulse operation of a high-power, efficient CO_2-N_2 laser has been reported.[24]

In the case of CO lasers, the optimum electron temperature for excitation of the CO vibrational states ($v < 8$) is around 1 eV,[21] which is much lower than the value where significant ionization of the CO molecule takes place by electron impact.[25] Therefore, if electrons can be produced volumetrically in the gas, they can be adjusted to the optimum electron temperature for vibrational excitation of CO molecules by applying a voltage across the gas, which, itself, does not produce ionization. Thus, the discharge is inherently stable and can be scaled up both in pressure and in size. One sophisticated technique for doing this is the E-beam ionizer-sustainer discharge system[26,27] in which the E-beam produces the electron density in the laser discharge region while the sustainer field controls the electron temperature. The electron temperature and electron density are, therefore, independently adjustable for this device, leading to a wide range of discharge conditions not accessible with simple discharge techniques.

In the present study, an effort has been made to construct a quantitative formulation to describe the kinetic processes in the proposed concept of an E-beam-excited CO GDL.

Numerical results providing nonequilibrium vibrational population distribution along the nozzle, small-signal laser gain and laser performance will be obtained later. Parametric calculations will be made to determine optimum initial conditions in the excitation region of this CO laser system. There does not appear to be any theoretical study devoted to the present system. Previous theoretical studies have been mainly concerned with the thermally excited CO GDL,[28,29] the cooled direct-discharge-excited CO laser (electrical CO laser),[30-32] and the electrically excited CO-N_2 mixing laser.[33]

In Sec. II, a brief review of the general operational characteristics and spectroscopy for different kinds of CO lasers is given. The principle of V-V pumping is presented together with the excitation and inversion mechanisms of these CO lasers.

The detailed formulation of the E-beam-pumped CO GDL is developed in Sec. III, in which the steady quasi-one-dimensional adiabatic flow equations are used to study the nozzle flow.[34] The frozen flow approximation of the problem is discussed in detail in Sec. IV.

II. KINETIC PROCESSES IN CARBON MONOXIDE LASERS

A review of the kinetic processes in CO lasers is presented in this section to provide the necessary background material for showing that the new laser proposed in Sec. I is superior to the existing CO lasers for atmospheric applications. A brief review of the general operational characteristics of a CO laser and the principle of partial inversion is given. Then a state-of-the-art review of the various types of continuous-wave (CW) CO lasers is presented. These CW CO lasers include the following: the electric CO laser, the CO-N_2 flow laser, the CO GDL, and the chemical CO laser. Finally, the principle of V-V pumping is presented together with the excitation and inversion mechanisms of these CO lasers.

GENERAL OPERATIONAL CHARACTERISTICS OF A CO LASER

Carbon monoxide, being a diatomic molecule, has only a single vibrational mode (in contrast to the three different vibrational modes of a CO_2 molecule) corresponding to only one ladder of energy level. One unique feature of the diatomic molecule laser is that because of the anharmonicity of the vibrational levels, laser transition occurring between the upper vibrational levels, v and v - 1, causes an enhanced inversion between v - 1 and v - 2 levels; likewise, the relative population between v + 1 and v are also further inverted. Thus, the vibrational energy can be extracted as coherent radiation through several pairs of levels for which the populations are sufficiently inverted. Therefore, it is possible for CO lasers to have a nearly 100 percent quantum efficiency. The quantum efficiency used here is defined as the ratio of the laser quantum energy to the energy required to excite selectively the ground-state molecule to the upper vibrational laser level.

Furthermore, for CO, as a result of rapid redistribution of vibrational energy among the levels, a molecule reaching a terminal laser level can be reexcited, and thus, the absence of lasing on the lower levels need not limit the efficiency. This advantage is in contrast to the CO_2 system, in which the energy of the lower laser level is rapidly dissipated as heat through vibration-translation (VT) collisional

relaxation. In general, many diatomic molecules (e.g., HCℓ, HBr, HF) cannot utilize the V-V pumping principle in laser actions because of the very fast VT collisional relaxation processes that cause the molecules to lose vibrational energy as heat before they have time for the rapid redistribution of vibrational energy among the levels. The CO molecule is an ideal molecule to exploit the V-V pumping principle in its laser action since its VT relaxation time is relatively long. Typically, the VT collisional relaxation times for $v = 1 \rightarrow v = 0$ at room temperature are around 1 atm-sec for CO-CO,[34-38] 10^3 atm-sec for CO-Ar,[36] and 10^{-3} atm-sec for CO-He.[39]

Due to the cascading laser action, the CO laser has a very broadband laser spectrum. In a typical CW electric CO laser, the laser transitions run from $v = 5$ to $v = 18$[3] (up to $v = 37 \rightarrow 36$ when the laser is Q-switched,[2] and down to $v = 3 \rightarrow 2$ in the case of an electric-discharge GDL).[13] In contrast to the CO laser system, the CO_2 laser system operates mostly on the lowest excited levels of two vibrational modes (001 to 100) at a wavelength of 10.6μm.

Nearly all CW CO lasers operate according to the principle of partial inversion, whereas CO_2 lasers can achieve total or complete inversion between the lowest levels of coupled vibrational modes for small-signal gain operations. The requirement for laser action in a vibrational-rotational partial inversion is[40]

$$\frac{N_{v'J'}}{g_{J'}} > \frac{N_{vJ}}{g_J} , \qquad (1)$$

where $N_{v'J'}$ = The number density of the upper laser state in the specified vibrational state v' and rotational state J'.

N_{vJ} = The number density of the lower laser state in the specified vibrational state v and rotational state J.

$g_{J'} = 2J' + 1$, the degneracy of the rotational state J'.

$g_J = 2J + 1$, the degeneracy of the rotational state J.

and the degeneracy of the vibrational state is unity. Complete or total inversion is defined by the condition

$$N_{v'} > N_v , \qquad (2)$$

where $N_v = \sum_J N_{vJ}$. In other words, in total inversion, the population of the vibrational state of the upper laser level is always greater than that of the lower laser level, whereas in the partial inversion case, population inversion can be achieved even though $N_{v'} \leq N_v$.

Assuming that $T_{r'} = T_r$, i.e., the same rotational temperature in the upper and lower vibrational states, and that both the rotators and the vibrators have a Boltzmann distribution, it can be shown that Eq. (1) becomes[40]

$$\frac{T_r}{T_v} < \frac{E_o(J') - E_o(J)}{E_o(v) - E_o(v')} , \tag{3}$$

where T_v is the vibrational temperature. For a rigid rotator, $E_o(J') = BJ'(J' + 1)$ is the energy of the rotational state J' relative to the $J' = 0$ state of the same vibrational level, v, and B is the rotational constant; similarly, $E_o(J)$ is the energy of the rotational state J. For an harmonic oscillator, $E_o(v) = v\omega_e$ is the (rotationless) energy of the vibrational state v relative to $v = 0$ and ω_e, the vibrational frequency; and $E_o(v')$ is the energy of the vibrational state v'. Note that $E_o(v) - E_o(v')$ is always a negative quantity. The right-hand side of Eq. (3) is positive for P-branch transition ($J' = J - 1$), is zero for Q-branch transitions ($J' = J$), and is negative for R-branch ($J' = J + 1$). It follows that the laser requirement can only be met for Q and R branches if T_v is negative, i.e., if $N_{v'} > N_v$ (complete inversion); there can be no stimulated emission due to partial inversion in the Q or R branches.

In fact, one can predict which of the P-branch transitions can exhibit laser action under conditions of partial inversion for an harmonic oscillator and rigid rotator by substituting the energy expressions into Eq. (3) as follows:

$$\frac{T_r}{T_v} < \frac{2JB}{\omega_e} . \tag{4}$$

It seems that there exists a minimum value of J, J_{min}, for any ratio T_r/T_v such that the laser action will be fulfilled for all $J > J_{min}$, where

$$J_{min} \simeq \frac{\omega_e}{2B} \cdot \frac{T_r}{T_v} . \tag{5}$$

As T_r/T_v is decreased, J_{min} decreases. Thus, favorable lasing conditions are obtained by lowering the rotational temperature (kinetic temperature) of the medium and by increasing the vibrational temperature. Now for an anharmonic oscillator, Eq. (5) becomes

$$J_{min} \simeq \left(\frac{E_o(v') - E_o(v)}{2B}\right) \frac{T_r}{T_v} . \tag{6}$$

Then it can be observed for a particular T_r/T_v that J_{min} will be lowest for high vibrational bands, owing to the progressive decrease in $E_o(v') - E_o(v)$.

REVIEW OF VARIOUS KINDS OF CW CO LASERS

Continuous-wave lasing on CO vibrational-rotational bands has been obtained in four different laser systems. They are (1) the direct-discharge-excited CO laser (electric), (2) the CO-N_2 flow laser,[3] the CO GDL laser, and (4) the chemical CO laser. Reviews of these different CO laser systems are presented below.

Direct-Discharge-Excited CO Laser (Electric)[1-3,7-9]

The conventional electric CO laser consists of a discharge tube of a few centimeters diameter and approximately one meter in length. The discharge tube that is used to excite the vibrational levels of the CO molecule is cooled by a static liquid-nitrogen bath. Typical gas components are 0.2 Torr of CO, 6 Torr He, and a slight amount of O_2 (< 0.1 Torr). The gas flow velocity through the laser is typically a few meters per second; thus, the gas is cooled by diffusion to the wall.

There are several interesting features of the electric CO laser: the extreme broad-band output in many high lying bands (up to $v = 37 \rightarrow 36$ when the laser is Q-switched;[2] see Table 1); the dramatic increase of output power when the laser is cryogenically cooled; the relatively long laser recovery times ($\simeq$ 350 μs, the time required to create the population inversion), and that the laser operates at slow flow velocities.

Table 1

SUMMARY OF TYPICAL CW ELECTRIC CO LASER OUTPUT SPECTRA

Vibrational Band	Transition	ν(vac. cm^{-1})
6→5	P(14)	1947.070
	P(15)	1952.888
	P(16)	1948.73
7→6	P(13)	1935.484
	P(14)	1931.38
	P(15)	1927.282
8→7	P(12)	1913.892
	P(13)	1909.907
	P(14)	1905.834
9→8	P(11)	1892.27
	P(12)	1888.32
	P(13)	1884.369
	P(14)	1880.330
10→9	P(11)	1866.748
	P(12)	1862.833
	P(13)	1858.918
	P(14)	1854.927
11→10	P(11)	1841.315
	P(12)	1837.427
	P(13)	1833.527
12→11	P(10)	1819.742
	P(11)	1815.939
	P(12)	1812.116
	P(13)	1808.233
13→12	P(12)	1786.854
	P(13)	1783.034
14→13	P(11)	1765.459

SOURCE: Ref. 3.

The long laser recovery time, ≃ 350 μs, is consistent with the observed time for equilibration of the CO vibrationally excited states via intra V-V pumping.[41,42] In the electric CO laser, the role of He appears to be that of lowering the gas translational and rotational temperature by increasing the rate of heat conduction to the cold walls of the discharge. This lowering of the gas temperature greatly enhances

the effect of V-V pumping and drastically reduces the rate of VT quenching. But the addition of He to CO would increase greatly the rate of VT collisional deexcitation of the vibrationally excited CO molecules;[36] thus, there is a tradeoff in adding He to CO gas in the operation of an electric CO laser.

Typically, the output power is in the tens of watts, and the electrical efficiency is around 20 to 40 percent. The highest efficiency so far is 46.9 percent, corresponding to a CW output power of 70 W, at a wall temperature of 77°K.[7] It is also found that the CO laser efficiency increases with decreasing gas temperature. In Ref. 7, the laser efficiency decreased from 46.9 percent at 77°K wall temperature to about 12 percent at 300°K wall temperature.

Recently, Kan and Whitney[9] applied a forced convective flow technique in an electric CO laser to maintain the low gas temperature required for efficient V-V pumping. The result was an order-of-magnitude enhancement of the output power density over what can be achieved from the same laser operated in the slow-flow diffusion-dominated mode. In Ref. 9, a maximum CW power of 400 W at an electrical efficiency of 20 percent has been obtained with this technique in a 2.5 cm-diam-bore, 1-m-long CO laser with a mean flow velocity of 120 m/sec through the tube. A gas mixture of He, CO, and N_2 was cryogenically precooled before it was introduced into the laser table, which was immersed in a liquid nitrogen bath. Table 2 shows a comparison of spectral distribution for the flow and diffusion lasers.

It is observed from Table 2, that for the same vibrational bands, the forced convective flow laser results in lower P-branch transition than the diffusion mode CO laser. According to the theory of partial inversion [e.g., Eq. (6)], it can be inferred that the gas temperature (e.g., rotational temperature, T_r) is lower in the convective flow CO laser assuming that both CO lasers have the same vibrational temperature, T_v (this assumption is quite reasonable considering the same discharge tube was used in Ref. 9 to operate both the flow lasers and the diffusion laser). Note also that the P-branch transitions decrease as the vibrational bands get higher in both of these lasers, which confirms the prediction of Eq. (6).

Table 2

COMPARISON OF SPECTRAL DISTRIBUTION FOR THE FLOW AND DIFFUSION LASERS

	Transition	
Vibrational Band	Forced Convective Flow	Diffusion Mode
5→4	P(12)	
6→5	P(12)→P(13)	
7→6	P(11)→P(13)	P(14)→P(16)
8→7	P(12)	P(15)→P(17)
9→8	P(11)→P(12)	P(13)→P(16)
10→9	P(10)→P(12)	P(13)→P(15)
11→10	P(10)→P(11)	P(14)
12→11	P(10)	P(14)→P(15)
13→12	P(9)→P(11)	
14→13	P(9)→P(10)	
15→14	P(9)	

SOURCE: Ref. 9.

CO-N_2 Flow Laser[4,5]

In the CO-N_2 flow laser, the typical laser components include a discharge tube to excite the N_2 gas and then a mixing region for CO and N_2 (similar to that of Patel's CO_2-N_2 laser). The N_2 gas is first vibrationally excited by an RF discharge; then the CO gas, which is mixed in small concentration in the N_2 stream, is vibrationally excited through V-V collisional exchange with the vibrationally excited N_2. The CO gas is injected into the N_2 stream to ensure a good mixing of the gases. Typical gas components are 0.3 Torr CO, 6 Torr N_2, and a very small amount of O_2 (< 0.05 Torr), and the linear flow rate of the gases varies from 13 m/sec to 45 m/sec. A laser power of 2 W was obtained with a flow rate of 45 m/sec in the laser tube for the following gas mixtures: 3 Torr of N_2, 0.25 Torr of CO, and 0.017 Torr of O_2; and a laser power of 0.5 W was obtained with 6 Torr of N_2, 0.3 Torr of CO, 0.005 Torr of O_2, and a linear flow rate of 13 m/sec. The fact that the faster flow laser gives a higher power output is presumably due to more efficient gas mixing and cooling. The spectral output of a typical CO-N_2 flow laser is shown in Table 3.[43]

Table 3

SPECTRAL DISTRIBUTION OF A CO-N_2 FLOW LASER OUTPUT

Vibrational Band	Transition
7→6	P(21)→P(23)
8→7	P(19)→P(24)
9→8	P(15),P(18)→P(24)
10→9	P(15)→P(17),P(19),P(21)→P(24)
11→10	P(16)→P(21)
12→11	P(14),P(15),P(17)→P(19)
13→12	P(15),P(17)→P(20)
14→13	P(15),P(17),P(18),P(21),P(22)
15→14	P(14)→P(16),P(18),P(19)
16→15	P(17)
17→16	P(19)

SOURCE: Ref. 43.

Due to the extremely slow rate of VT quenching of nitrogen gas, e.g., $p\tau_{N_2-N_2} \approx 10^3$ atm-sec at 300°K,[36] a large part of the energy of the vibrationally excited N_2 is stored as vibrational energy of molecules in their electronic ground state. The possibility of transferring this energy to molecules that have vibrational levels close to the first vibrational level of nitrogen by inelastic resonant collisions is recognized.[44] This result suggests that this type of energy transfer may play a dominant role in the mechanism of molecular lasers with active nitrogen. Studies on CO_2 and N_2O lasers support this interpretation,[45] but in the case of CO lasers, this interpretation does not explain all the unique features of the CO-N_2 lasers.

In the case of CO-N_2 lasers, the vibrational levels of N_2 communicate predomiantly with the first vibrational level of CO because of the quasi-resonant energy difference between the first vibrational levels of N_2 and CO (188 cm^{-1}).[33] This vibrational energy defect increases with vibrational level in CO due to its anharmonicity. Conversely, the higher levels of N_2 become more nearly resonant with the $v = 1 \rightarrow 0$ transition of CO, and the sixth and seventh levels of N_2 become resonant with the first and zero level of CO. Therefore, only

lower vibrational levels of the CO molecule are excited by the vibrationally excited N_2 molecule via intermode V-V collisional energy exchange. Thus, the fact that the CO-N_2 flow laser has high lying lasing bands up to $v = 17 \rightarrow v = 16$ cannot be explained by this phenomena of quasi-resonant vibrational energy transfer from active nitrogen to CO alone.

CO GDLs[10-13,46]

The term GDL is used here in a much broader sense than usual; it is used to denote any gas laser that employs a supersonic expansion technique independent of its excitation source. Successful operation of thermally pumped CO GDLs,[10,11] and electrically pumped CO GDLs[12,13] has been demonstrated. Recently, an electric-discharge CO-N_2 mixing GDL has been successfully demonstrated.[46]

It has been stated earlier that vibrational energy exchange can result in non-Boltzmann vibrational distributions in anharmonic molecules. This effect is greatest for conditions where a high degree of vibrational excitation and a low translational-rotational temperature occur. Such a situation can be achieved easily in supersonic flows expanding from a high temperature plenum chamber. Therefore, a CO GDL is the typical extension of the conventional CO laser. In addition to the fulfillment of the V-V pumping conditions, the CO GDL has the advantage of removing waste energy at a much faster rate than the conventional diffusion-mode lasers, the same advantage as a CO_2 GDL.

The thermally pumped CO GDL[10,11] typically is operated using mixtures of CO, N_2, and Ar. Rapid expansions of the gas are created either in a conical nozzle or a two-dimensional parabolic nozzle. The nozzle is generally driven by a shock tube with a cold helium driver. Equilibrium reservoir conditions are typically 2000°K and 100 atm. Optical cavities transverse to the flow at large expansion ratios ($A/A^* > 500$) create CW laser action for the duration of the steady flow. A maximum, so far, power output of 120 W has been obtained with a mixture of 5 percent CO, 15 percent N_2, and 80 percent Ar at $A/A^* = 577$.[10] The efficiency (based on the total enthalpy flow rate through the internal laser beam) thus obtained is 0.3 percent. There is no detailed

CO laser output spectra available in this device, but the typical laser output spectral characteristics, which include P-branch transitions from $v = 10 \rightarrow v = 9$ down to $v = 2 \rightarrow v = 1$, correspond to a wavelength span from 5.4 μm to 4.7 μm.

By serving as an energy reservoir from which N_2 vibrational energy is transferred directly to some of the laser vibrational states of CO, nitrogen plays a similar role in the CO laser to that which it plays in the CO_2-N_2 lasers. But the difference is that in the case of CO_2-N_2 lasers, N_2 plays a dominant role in the inversion mechanism, whereas in the case of CO-N_2 lasers. N_2 only serves as a source for pumping the lower vibrational levels of the CO molecules. The difference has been clearly demonstrated by laser action with only CO and Ar in a thermally pumped CO GDL.[11]

Due to the extremely sensitive dependence of V-V pumping on the gas translational temperature, the thermally pumped CO GDL turns out to be quite an impractical device. In order to create the conditions of a low translational temperature coupled with a high degree of vibrational excitation in the CO molecules, it is necessary to supersonically expand the flow of gas from a reservoir temperature of 2000°K to a gas temperature of around 100°K. Assuming that this is an ideal isentropic supersonic expansion, the A/A^* required to achieve such a condition is greater than 500 (in contrast to $A/A^* \simeq O(10)$ for CO_2-N_2 GDLs).[19] In fact, thermal pumping of the laser gases is, in principle, a relatively inefficient means of exciting the vibrational mode of the CO molecule because, at 2000°K, the reservoir conditions of the shock-tunnel-driven CO GDL, only about 25 percent of the equilibrium thermal energy is in the vibrational mode. Thus, this percentage represents an intrinsic upper limit on the maximum efficiency of a thermally pumped CO GDL.

Recently, two different groups have reported on the successful operation of electrically excited CO GDLs.[12,13] Typically, the electrically pumped CO GDL uses supersonic expansion to cool a direct discharge excited mixture of CO, N_2, and He (e.g., 15 percent CO, 5 percent N_2, and 80 percent He). The pressure in the plenum chamber is around 100 to 150 Torr. The gases then are expanded into a rectangular nozzle. Continuous laser output is obtained from optical cavities

transverse to the flow downstream from the throat. Maximum laser power obtained so far has been 16 W,† corresponding to an efficiency of 2 percent based on electrical power input.[13] Table 4 gives a typical spectral distribution of the electrically excited CO GDL output. In general, lasing occurs on the lower transitions and at lower rotational levels in a CO GDL than normally observed in conventional CW liquid-nitrogen-cooled CO lasers (compare the spectral distribution in Table 4 with that in Table 2). This downshift effect results from the lower translational temperature achieved in the supersonic expansion situation. Assuming that the translational temperature in the plenum is about 400 to 500°K (the gas is at ambient temperature before entering the plenum chamber[13]) then the gas temperature in the lasing region is estimated to be about 100°K.

In order to assess the effect of further gas dynamic cooling of the gas, Kan, Stregack, and Watt[13] also performed experiments with gas precooled to 196°K before entering the excitation region. As expected from the theoretical considerations, the spectral distribution shifted further downward to lower wavelengths and to lower rotational transitions in comparison with the uncooled case, as shown in Table 4. This result would appear to confirm the theoretical prediction and earlier experiments in Ref. 7: Cooling in a CO laser would shift the spectral distribution of the laser output to lower wavelengths. Thus, further gas dynamic cooling could, in principle, shift the spectral distribution to even lower wavelengths than obtained so far. Also, it was found that there was a 33 percent increase in the laser power output.

The relatively high efficiency, ≃ 2 or 3 percent obtained in an electrically excited CO GDL (as compared to 0.3 percent in a thermally pumped CO GDL), is partly due to the highly efficient electron-impact vibrational excitation of CO molecules.[20,21] Besides high efficiency, a much smaller A/A^* [≃ 0(10)] is required to cool the gas temperature

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†A maximum power of around 100 W has been obtained in a CO GDL device at the Naval Research Laboratory, Washington, D.C., recently. (Private communication with Dr. T. Kan at the Naval Research Laboratory, Washington, D.C., October 1972.)

Table 4

SPECTRAL DISTRIBUTION OF AN ELECTRICALLY EXCITED CO GDL OUTPUT FOR GAS ENTERING THE PLENUM AT AMBIENT TEMPERATURE AND AT 196°K

Vibrational Band	Rotational Transitions		Wavelength Range (μm)
	At Ambient Temperature	At 196°K	
3→2		P(8)→P(10)	4.857→4.877
4→3	P(9)→P(11)	P(7)→P(10)	4.910→4.949
5→4	P(9)→P(12)	P(7)→P(11)	4.974→5.024
6→5	P(8)→P(11)	P(7)→P(10)	5.039→5.079
7→6	P(7)→P(10)	P(6)→P(10)	5.095→5.136
8→7	P(7)→P(10)	P(6)→P(9)	5.163→5.205
9→8	P(7)→P(9)	P(6)→P(9)	5.233→5.265
10→9	P(6)→P(8)		

SOURCE: Ref. 13.

to 100°K, or below, because of the much lower reservoir temperature, ≈ 400 to 500°K (for the uncooled case). This relatively low reservoir temperature is the result of the electric-discharge excitation technique that produces a high degree of vibrational excitation in CO molecules by electron impact without, at the same time, increasing the gas translational temperature substantially.

However, there is one drawback to the conventional electrically excited CO GDL: It is very difficult to scale, both in pressure and discharge diameter, in the ordinary two-electrode discharges normally used for exciting electrically pumped gas lasers. This limitation, both in discharge pressure and size, is due to the fact that in such a discharge arrangement the electrons that provide the excitation of the laser states must also reproduce themselves to maintain the discharge. Therefore, the electron temperature cannot be controlled to the desired optimum value for excitation of the laser states. This particular limitation would also limit the power output of a direct-discharge-excited gas laser because the ultimate power output of such a laser is proportional to the discharge pressure and size.

In order to develop a CO GDL that would have the relatively high efficiency of an electrically pumped CO GDL but with much higher power

output, it is first necessary to develop a novel discharge system that is inherently stable and can be scaled up both in pressure and in size. One of the CO laser systems that satisfies these requirements is the E-beam-pumped CO GDL proposed in this study. In this proposed CO GDL, the E-beam current density controls the electron density produced in the laser discharge region, while the sustainer field, which supplies energy to the gas, controls the electron temperature. Thus, the electron temperature and electron density in the plasma are independently adjustable, leading to a stable, uniform-tuned, high-power-density plasma that is not wall controlled, and hence a high-power, efficient CO GDL.

CO Chemical Laser[6,47-49]

In a typical CW CO chemical laser, a mixture of He and O_2 is passed through a discharge region that produces partial dissociation of O_2, while the resulting discharge products (e.g., O, O_2, He, etc.) are being swept into a mixing region where CS_2 is injected into the discharge product mixture stream to ensure a good mixing of the gases. The resultant laser emission consists of a number of vibration-rotation bands of the excited CO product. A sample of the laser transitions in a CW CO chemical laser is presented in Table 5.

Table 5

LASER TRANSITIONS IN A CW CO CHEMICAL LASER

Vibrational Band	Rotational Transitions
7→6	P(15)
8→7	P(12)→P(18)
9→8	P(13)→P(18)
10→9	P(13)→P(17)
11→10	P(13)→P(17)
12→11	P(13)→P(16)

SOURCE: Ref. 6.
NOTE: Conditions are as follows: $p(O_2)$ = 1.3 Torr; p(He) = 4.5 Torr; CS_2 flow rate = 400 μmole/sec; O flow rate = 400 μmole/sec; T = 435°K; Total power: 75 mW.

The chemistry can be very complex in an electric-discharge-initiated CW CO chemical laser owing to the large number of chemically active ingredients formed by the electric discharge. But the chemical reactions responsible for laser action in the CO chemical laser system seem to be the following:

$$O + CS_2 \rightarrow CS + SO + 30 \text{ kcal/mole} , \tag{7}$$

and

$$O + CS \rightarrow CO^* + S + 75 \text{ kcal/mole} , \tag{8}$$

where CO^* denotes the vibrationally excited CO molecule. The atomic oxygen is obtained through the partial dissociation of the oxygen molecule in the discharge. The reaction expressed by Eq. (8) is very fast and causes the CO product to be in a highly excited vibrational state. According to the infrared chemiluminescence from the reaction in Eq. (8), Hancock and Smith[50] showed that the CO was formed selectively in high vibrational levels and that a complete inversion existed between a number of adequate vibrational levels. In fact, the heat of reaction, $\Delta H = 75(\pm 5)$ kcal/mole for the reaction expressed in Eq. (8), is sufficient to populate levels up to, and including, $v = 13(\pm 1)$ for the CO molecule. Recently, Jeffers[48] observed R-branch emission from a CW CO chemical laser. This observation seems to confirm the finding reported in Ref. 50 that a complete inversion existed between a number of adjacent vibrational levels resulting from the reaction expressed in Eq. (8).

It was also found that helium was needed in the oxygen dissociator for efficient operation. Only weak, sporadic bursts of CO laser emission were obtained with only oxygen in the dissociator. The role of He here appears to be the following: (1) to lower the gas translational temperature, (2) to enhance the dissociation of molecular oxygen, and (3) to prevent the diffusion of excited or active species to the wall where relaxation processes may occur.

One variation of the chemical CW CO laser is the premixed chemical CW CO laser.[47] In this CO chemical laser, a premixed mixture of CS_2, O_2, and He is passed into the discharge region. Typical operating pressures are He = 100 Torr, O_2 = 2.5 Torr, and CS_2 = 0.1 Torr. The chemistry of this laser is quite similar to that of the mixing laser.

Another more interesting example of the CW CO chemical laser is the CO flame laser.[49] Laser action was observed from vibrationally excited CO produced in a free-burning, low-pressure CS_2-O_2 flame. The flame was ignited by a glow discharge above the burner. The burner was made of a horizontal planar array of parallel tubes; and alternate tubes were used for injection of CS_2 and O_2, respectively. Once the ignition started, the discharge was turned off and the flame remained totally self-sustaining as long as the supply of reagents was maintained. CW laser oscillation was observed on the following three CO vibration-rotation transitions: P(11) line of $v = 8 \rightarrow 7$ at 5.216 μm, P(12) line of $v = 9 \rightarrow 8$ at 5.297 μm, and P(10) line of $v = 11 \rightarrow 10$ at 5.421 μm; and the total laser output was about 1 mW. The difference between the flame laser and the conventional CW CO chemical laser described earlier is that the flame laser is a self-sustaining CO chemical laser, whereas the conventional one is a non-self-sustaining CO chemical laser. The flame laser is approaching the limit as a completely chemical $CS_2 + O_2$ laser in the sense that no outside energy source is needed as soon as the flame is ignited.

One of the most important differences between the self-sustaining and non-self-sustaining chemical lasers is that the self-sustaining system must have chain-branching reactions. A chain-branching reaction is defined as a reaction step that leads to the production of more chain carriers than are consumed. Thus, the chain-branching reactions usually maintain a steady-state concentration of chain carriers by replacing those lost by diffusion out of the flame or by chain-breaking reactions occurring within the flame itself. Due to the complexity of the flame chemistry, only the following possible set of chain-branching reactions for the low-pressure CS_2-O_2 flame system was considered in Ref. 49:

$$CS_2 + O \rightarrow CS + SO \; ; \tag{7}$$

$$SO + O_2 \rightarrow SO_2 + O \; . \tag{7a}$$

$$CS + O \rightarrow CO^* + S \; ; \tag{8}$$

$$S + O_2 \rightarrow SO + O \; . \tag{8a}$$

As indicated before, the electrical discharge CS_2-O_2 chemical laser requires only the reactions expressed in Eqs. (7) and (8), but the self-sustaining flame laser requires all four reactions. In fact, Eq. (7a) together with Eq. (8a) complete the chain-branching reaction such that only one chain carrier, S, is needed to produce two chain carriers, O.

PRINCIPLE OF V-V PUMPING, EXCITATION, AND INVERSION MECHANISMS IN CO LASERS

Principle of V-V Pumping

In anharmonic oscillators, the V-V collisions tend to transfer energy preferentially from levels of large energy spacing to ones of smaller spacing; that is, energy tends to flow up the vibrational ladder. The highest vibrational levels to be pumped in this manner are determined by the VT (i.e., the vibrational energy is exchanged with the translational or rotational energy modes of the colliding molecules) or radiative decay processes that become significant at higher vibrational levels.

In fact, it has been shown in Ref. 18 that under the conditions of a low translational temperature coupled with a high degree of vibrational excitation, some of the vibrational state populations of a diatomic gas can be totally or partially inverted due to the anharmonicity of the molecule. This phenomenon can be shown by the solution to the steady-state rate equation for species in the vibrational state, v, of a diatomic molecule considering only V-V energy exchange. The solution is:[18]

$$n_v = n_o \exp[-(vE_1/kT_v) + (vE_1 - E_v)/kT] \ , \tag{9}$$

where n_v is the number density of the molecules in the vibrational state v, and E_v is the energy of the vibrational state v. T is the translational temperature, and T_v is the equivalent vibrational temperature. When $T_v = T$, the distribution is exactly a Boltzmann distribution at temperature T. For lower vibrational levels where $vE_1 \simeq E_v$, Eq. (9) approximates a Boltzmann distribution at an equivalent vibrational temperature, T_v. For cases where $T >> T_v$, the second term in the exponential argument in Eq. (9) is relatively small; therefore, even at higher energy levels, the distribution is Boltzmann-like. But for cases where $T_v >> T$, there are significant departures from a Boltzmann distribution. In this case, it can be observed that, for a given T_v, the higher vibrational states are overpopulated in comparison with a Boltzmann distribution at "temperature" T_v, since the term $(vE_1 - E_v)/kT$ is not negligible in comparison with the term vE_1/kT_v,

$$\frac{(vE_1 - E_v)/kT}{vE_1/kT_v} = \frac{(vE_1 - E_v)}{vE_1} \cdot \frac{T_v}{T} \ . \tag{10}$$

In this case, even though $(vE_1 - E_v)/vE_1 << 1$, since $T_v/T >> 1$, then, Eq. (10) becomes

$$\frac{vE_1 - E_v}{vE_1} \cdot \frac{T_v}{T} \simeq 0(1) \ . \tag{11}$$

For the CO molecule, we have

$$\frac{vE_1 - E_v}{vE_1} \cdot \frac{T_v}{T} \simeq \frac{(v - 1)}{162} \frac{T_v}{T} \ ;$$

the value of the equivalent vibrational temperature, T_v, is different for each different vibrational quantum number v. From the experimental data

obtained with an electric CO laser in Ref. 51, a plot was made of the vibrational temperatures inferred from the data fit to states above $v = 2$ at a gas temperature of 230°K. Since, at $v = 4$, T_v was estimated to be about 3000°K, then

$$\frac{vE_1 - E_v}{vE_1} \cdot \frac{T_v}{T} \simeq 0.25 \ .$$

At $v = 8$, $T_v \simeq 7500$°K, then

$$\frac{vE_1 - E_v}{vE_1} \cdot \frac{T_v}{T} \simeq 1.4 \ .$$

This effect of overpopulation in comparison with a Boltzmann distribution at "temperature" T_v obviously increases with increasing vibrational quantum numbers, as shown, until such effects as VT losses and radiative decay processes beome dominant.

This V-V pumping effect is basically a consequence of the principle of detailed balancing relating the reverse rate to the forward rate for V-V transitions. A simple explanation can be given in terms of the following two-molecule, four-level system, shown in Fig. 3:[30] molecule A with two vibrational states, 0 and 1, colliding with molecule B that also has two internal states, 4 and 5. Assuming that molecule A is initially in state 1 and molecule B is initially in state 4, they exchange vibrational energy on collision, molecule A making the transition $1 \rightarrow 0$ and molecule B making the transition $4 \rightarrow 5$ (indicated by the solid arrows in Fig. 3). Actually, this collisional process can be described by the following chemical reaction,

$$A(1) + B(4) \underset{P^{5,4}_{0,1}}{\overset{P^{4,5}_{1,0}}{\rightleftharpoons}} A(0) + B(5) + \Delta E \ , \qquad (12)$$

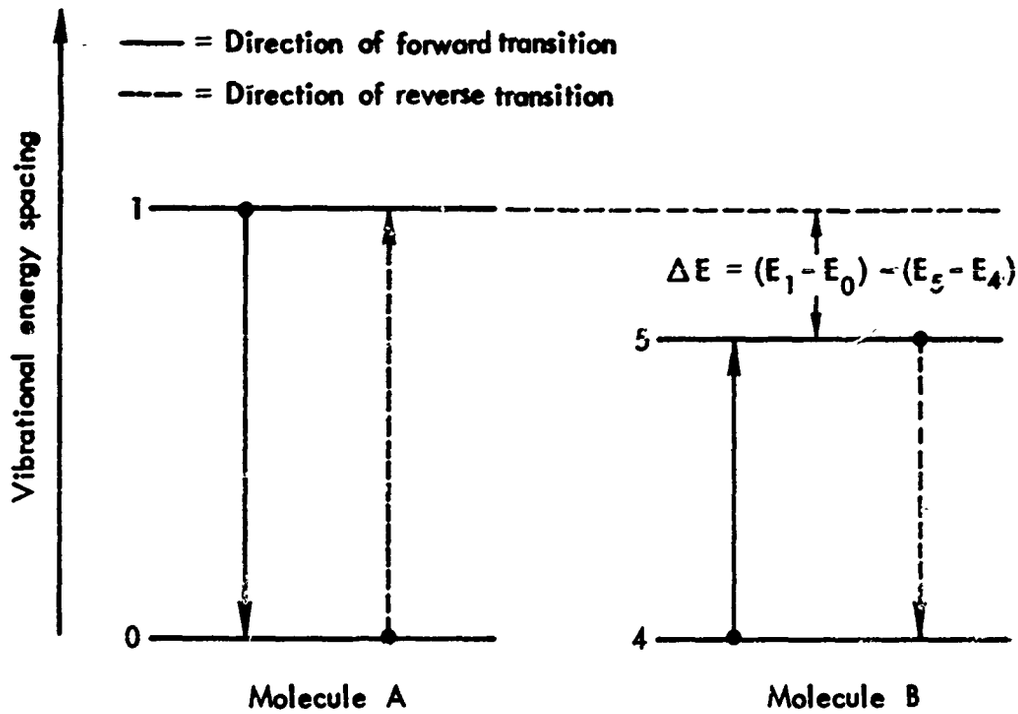

Fig.3 — V-V pumping in a two-molecule, four-level system (Ref. 30)

where ΔE is the resonance energy defect--i.e., the energy difference $\Delta E = (E_1 - E_0) - (E_5 - E_4)$--and $P_{1,0}^{4,5}$ and $P_{0,1}^{5,4}$ are the forward and reverse transition rates for this process, respectively. In the forward process, the excess energy, ΔE, must be carried away by the external modes (translation or rotation) during the collision. If the external modes are in equilibrium at a translational temperature, T, then the transition rate of the reverse process, $P_{0,1}^{5,4}$, indicated by the dotted arrows in Fig. 3, can be related to the transition rate of the forward process, $P_{1,0}^{4,5}$ through the use of the principle of detailed balancing in the following way:

$$P_{0,1}^{5,4} = \exp(-\Delta E/kT)\, P_{1,0}^{4,5} \,. \tag{13}$$

It can be observed from Eq. (13) that the inequality, $P_{1,0}^{4,5} \gg P_{0,1}^{5,4}$, is valid for $\Delta E/kT \gg 1$, i.e., the solid arrow process can occur much more

rapidly than the reverse process. Under such conditions, molecule B with the smaller energy spacing is "pumped" at the expense of molecule A. Thus, a population inversion between levels 5 and 4 of molecule B tends to be created.

This same reasoning can be applied to the intra V-V pumping of anharmonic diatomic molecules, such as CO, simply by considering the molecules in the upper vibrational levels as one species and those in the lower levels as another. Since this pumping is a result of the anharmonicity of the molecule, the pumping is, therefore, enhanced by decreasing the translational temperature. Take the CO molecule as an example:

$$\Delta E_{1,0}^{4,5} \simeq 106\text{cm}^{-1} ,$$

and

$$\Delta E_{1,0}^{4,5}/k \simeq 153°\text{K} ,$$

resulting in

$$P_{0,1}^{5,4} \simeq \exp(-\ 153/T)\ P_{1,0}^{4,5} .$$

The intra V-V pumping is effective in this case only if the translational temperature, T, is much less than 153°K. Similarly,

$$P_{0,1}^{8,7} \simeq \exp(-\ 268/T)\ P_{1,0}^{7,8} ,$$

i.e., according to this theory, the higher vibrational levels can be pumped more easily.

Another observation can be made about Eq. (13) in the following relaxation process:[7]

$$CO(5) + CO(0) \rightarrow CO(4) + CO(1) + \Delta E . \qquad (14)$$

When the resonance energy defect ΔE in Eq. (14) becomes comparable to or greater than kT, the molecules CO(5) will be inhibited from relaxing

by collision with CO(v = 0). Therefore, by setting ΔE equal to kT, one can predict the threshold vibrational level from the gas temperature, T, or better yet, one can estimate what the gas temperature, T, would be if a certain threshold vibrational level is required of the CO laser. The energy defect can be related to the fundamental constants of the molecule such that $\Delta E = 2\omega_e x_e (v - 1)$,[52] where $\omega_e x_e$ is one of the vibrational constants. For example, if a $3 \rightarrow 2$ vibration-band transition is desired (v = 3), then the temperature of the gas, T, should be less than 76.5°K; if v = 2, $T \lesssim 38$°K (however, for T much less than 70°K, condensation of CO may occur). This gradual shift of the threshold band to higher and higher vibrational bands as the gas temperature is increased has been found in very good agreement with experimental observation.[7] This observation has a very far-reaching implication: If lower vibrational transitions are desired in a CO laser (e.g., say, down to $3 \rightarrow 2$ band or $2 \rightarrow 1$ band) for better atmospheric transmission in lower atmosphere, the gas temperature must be less than 77°K or lower. This very low gas temperature requirement limits the gas cooling technique to a very selected few; in fact, even a liquid nitrogen cryogenic cooling technique does not satisfy the requirement for cooling the gas to less than 77°K since the temperature of the liquid nitrogen itself is typically about 77°K. Again, a supersonic expansion cooling technique seems to be the obvious one to use in this case.

Excitation and Inversion Mechanisms in CO Lasers

It is generally believed that V-V pumping plays a dominant role in establishing the population distribution in the electric CO laser, in the CO-N_2 flow laser, and also in the CO GDL, although the method of supplying energy to the vibrational mode initially differs in all three systems. In contrast to the preceding three systems, the role of V-V pumping in the CW chemical CO laser is still not settled.

In view of the many vibrational bands that lase in the electric CO laser system, the kinetic mechanism responsible for creating the observed population inversion cannot be explained by simple one-step resonance transfer between an excited metastable and the CO molecule,

as is done in the CO_2 laser. Also, it is unlikely that the population inversion is being created by electronically excited CO states decaying to vibrationally excited, ground-electronic-state CO because of the observed long laser recovery time. Electronic decay would occur in a much shorter time scale than the observed recovery time. Again, in view of the slow flow velocity required in the electric CO lasers and the continued lasing action when flow through the laser is stopped entirely, the production of vibrationally excited CO by chemical reaction pumping is not very plausible.

It is believed that the primary pumping mechanism in the directly excited electric CO laser is by direct electron impact excitation of the lower CO vibrational states followed by V-V pumping of the CO molecules to the lasing levels. According to the principle of V-V pumping, some of the vibrational-state populations of a diatomic gas can be totally or partially inverted when the conditions of a low translational temperature coupled with a high degree of vibrational excitation are satisfied. In the electric laser, the high-energy electrons of the glow discharge supply the necessary source of vibrational excitation via resonance electron excitation[20] of the CO molecules. The cooling of the laser provides the required low translational temperature.

The large increase in the power of the electric CO laser as it is cooled is probably due to two mechanisms. Primarily, the V-V pumping effect increases with decreasing translational temperature as pointed out previously. Secondly, due to the extreme temperature dependence of the VT relaxation rates,† a decrease in translational temperature also decreases the losses due to VT relaxation. With increasing translational temperature, the VT quenching rates increase rapidly, finally becoming large enough in themselves to prevent the V-V pumping of the higher vibrational levels.

The long laser recovery time, $\simeq$ 350 μs at 0.2 Torr of CO, observed by Osgood, et al.,[2,3] during Q-switching of their electric CO laser, differs from that observed by Yardley[41] by a factor of 3 with the observed time for equilibration for the CO vibrationally

†See Fig. 1 of Ref. 18.

excited states via intra V-V pumping, $p\tau \simeq 200$ μs Torr. But, Yardley reasoned that the CO pressure inside the laser reported in Ref. 2 is at least a factor of 2 higher than 0.2 Torr, since the pressure measurements were made downstream from the laser tube. Furthermore, Osgood, Eppens, and Nichols[3] observed a steady decrease in the laser recovery time caused by a step-wise increase in CO pressure. On the basis of these experiments, it may be concluded that this laser recovery time is determined by the V-V exchange processes among the CO molecules.

In the case of the CO-N_2 flow laser, the primary pumping mechanism seems to be the following: the excitation of the lower vibrational levels of the molecules via intermode V-V energy exchange with the vibrationally excited N_2, followed by rapid redistribution of vibrational energy via intra-mode V-V pumping between CO molecules. Again, in this laser system, the vibrationally excited N_2 molecules supply the necessary source of vibrational excitation of the CO molecules via near-resonant intermode V-V collisional energy transfer. The fast flow of the gases inside the laser tube provides some kind of cooling effect to maintain a low translational temperature.

Now, as far as the CO GDLs are concerned, the low translational temperature, of course, is provided by the supersonic expansion technique in all the GDL systems. However, the source for the high degree of vibrational excitation is different in the two GDL systems discussed before, e.g., the thermally pumped CO GDL and the electrically pumped CO GDL. In the thermally pumped CO GDL, the energy source for the initial vibrational excitation of the CO molecules is supplied by the thermal energy in the high temperature ($\simeq 2000°K$) plenum chamber. Whereas in the case of the electrically pumped CO GDL, the necessary source of vibrational excitation of the CO molecules is supplied by the high energy electrons of the glow discharge in the plenum chamber via resonance electron impact excitation. Furthermore, there is a very important difference in the reservoir conditions between these two types of CO GDLs. In the thermally pumped CO GDL, the reservoir conditions are at equilibrium with the reservoir temperature, e.g., the CO molecules are distributed according to Boltzmann distribution at the reservoir temperature. In contrast to the thermally pumped CO GDL,

the reservoir conditions in the electrically pumped CO GDL are non-equilibrium.

In the case of the CW chemical CO laser, Wittig, Hassler, and Coleman[6] postulated that the chemical reaction is the dominant excitation process and intramode V-V collisional energy exchange is the dominant relaxation process. Judging from the CW chemical CO laser spectra output (Table 5) and the gas temperature in the laser ($\approx$ 450°K), the excitation and inversion mechanism suggested by Wittig, Hassler, and Coleman for this laser system is very plausible simply because the conditions in this laser do not satisfy completely the requirements of the principle of V-V pumping. At a translational temperature of 450°K, the intra V-V pumping is effective only for $v \geq 13$ laser transitions (i.e., $v = 13 \rightarrow 12$ and upwards). Also, the estimated threshold level is about $v = 13$. The absence of lasing levels above $v = 12 \rightarrow v = 11$ in the CW chemical CO laser work reported in Ref. 6 seems to suggest that V-V pumping is definitely not a dominant inversion mechanism in this laser system.

III. QUANTITATIVE FORMULATION OF THE PROBLEM

In the present study, an effort has been made to formulate quantitatively the concept of a new CO GDL laser, pumped by a preionizer-sustainer discharge system proposed earlier in Sec. I. Numerical results providing nonequilibrium vibrational population distribution along the nozzle and small-signal laser gain will be provided in a subsequent study.

Previous theoretical investigations of electric CO lasers[30-33] were concerned mainly with the solutions to a system of steady-state, vibrational-rate equations. In the case of CO GDLs, only the thermally pumped GDL was analyzed in detail.[28,29] In this case, the problem can be described by nonsteady flows with vibrational relaxation; the system of rate equations is coupled with the conservation equations for mass, momentum, and energy. The initial conditions for the rate equations are given by the Boltzmann distribution at the reservoir temperature since the reservoir condition is at thermodynamic equilibrium. The problem described in the present study is similar to the analysis of a thermally pumped CO GDL except that the initial conditions are given by the solutions of the rate equations describing the nonequilibrium vibrational distribution in the reservoir because the condition there is not at thermodynamic equilibrium.

The time-dependent rate equation describing the vibrational distribution of the CO molecule in a gas mixture is given, together with a discussion of each of the physical processes represented by the rate equations. These physical processes are the following: vibrational excitation of the CO molecule by electron impact; spontaneous radiative decay of the vibrationally-excited CO molecule; intramode near resonant V-V collisional energy exchange among CO molecules; intermode near resonant V-V collisional energy exchange between CO and N_2 molecules; VT collisional energy exchange between CO and CO molecules, between CO and N_2 molecules, and between CO molecules and atoms. Then, the nonlinear conservation equations describing the steady quasi-one-dimensional flow are presented. Finally, the small-signal gain coefficient for the vibrational-translational transitions of the CO molecule in the laser cavity is derived.

THE VIBRATIONAL-RATE EQUATION

The phenomenological rate equation describing the distribution for the vibrational level, v, of the CO molecule in a gas mixture of N_2 molecules and some atoms (e.g., either helium or argon) can be written as follows:

$$\frac{dn_v}{dt} = \sum_{u'=0}^{v_e^*-1} \left(\nu_{u'v} n_{u'} - \nu_{vu'} n_v\right) \qquad \text{(electronic impact excitation)}$$

$$+ A_{v+1,v}\, n_{v+1} - A_{v,v-1}\, n_v \qquad \text{(spontaneous radiative emission)}$$

$$\left.\begin{aligned} &+ \sum_{u=1}^{v^*} \left(P^{u-1,u}_{v+1,v}\, n_{v+1}\, n_{u-1} - P^{u,u-1}_{v,v+1}\, n_v n_u\right) \\ &- \sum_{u=0}^{v^*-1} \left(P^{u,u+1}_{v,v-1}\, n_v n_u - P^{u+1,u}_{v-1,v}\, n_{v-1}\, n_{u+1}\right) \end{aligned}\right\} \text{(intramode V-V process)}$$

$$\left.\begin{aligned} &+ \sum_{s=1}^{s^*} \left(Q^{s-1,s}_{v+1,v}\, n_{v+1}\, N_{s-1} - Q^{s,s-1}_{v,v+1}\, n_v N_s\right) \\ &- \sum_{s=0}^{s^*-1} \left(Q^{s,s+1}_{v,v-1}\, n_v N_s - Q^{s+1,s}_{v-1,v}\, n_{v-1}\, N_{s+1}\right) \end{aligned}\right\} \text{(intermode V-V process)}$$

$$\left.\begin{aligned} &+ P_{v+1,v}\, nn_{v+1} - P_{v,v+1}\, nn_v + Q_{v+1,v}\, Nn_{v+1} - Q_{v,v+1}\, Nn_v \\ &+ R_{v+1,v}\, n' n_{v+1} - R_{v,v+1}\, n' n_v \\ &- \left(P_{v,v-1}\, nn_v - P_{v-1,v}\, nn_{v-1} + Q_{v,v-1}\, Nn_v - Q_{v-1,v}\, Nn_{v-1}\right. \\ &\quad \left. + R_{v,v-1}\, n' n_v - R_{v-1,v}\, n' n_{v-1}\right), \end{aligned}\right\} \text{(VT process)} \qquad (15)$$

and a similar equation for dN_s/dt,

where $u' < v$,

$v = 0, 1, 2, 3, \ldots, v^*$,

n_v = the number density of CO molecules in the vth vibrational state, molecules/cm^3,

v_e^* = highest vibrational level excited by electron impact,

v^* = highest bound energy level of the Morse anharmonic oscillation model for CO,

n = total number density of CO molecules, molecules/cm^3,

$\nu_{uv} = n_e \langle v_e \sigma_{uv} \rangle_{T_e}$, the vibrational transition rate of CO molecules from the vibrational state u to vibrational state v induced by electron impact, sec^{-1},

n_e = number density of electrons, electrons/cm^3,

$\langle u_e \sigma_{uv} \rangle_{T_e}$ = Maxwellian-velocity averaged electron excitation rate, cm^3/sec,

σ_{uv} = electron impact cross section for vibrational excitation, cm^2,

$A_{v,v-1}$ = Einstein coefficient for spontaneous transition from CO vibrational state v to state v - 1,

$P^{u-1,u}_{v+1,v}$ = intramode V-V transition rate of CO vibrational transitions from vibrational state v + 1 to state v, induced by collision with another CO molecule making a transition from the vibrational state u - 1 to state u, cm^3/sec,

$P_{v+1,v}$ = VT transition rate of CO vibrational transition from vibrational state v + 1 to state v, induced by collisions with CO molecules, cm^3/sec,

N_s = the number density of N_2 molecules in the sth vibrational state, molecules/cm^3,

N = total number density of N_2 molecules, molecules/cm^3,

s^* = highest bound energy level of the Morse anharmonic oscillator model for N_2,

n' = total number density of atoms, atoms/cm^3,

$Q^{s-1,s}_{v+1,v}$ = intermode V-V transition rate of CO vibrational transitions from the vibration state v + 1 to state v, induced by collision with N_2 molecules making a transition from the vibrational state s - 1 to state s, cm^3/sec,

$Q_{v+1,v}$ = VT transition rate of CO vibrational transition from vibrational state v + 1 to state v, induced by collisions with N_2 molecules, cm^3/sec,

$R_{v+1,v}$ = VT transition rate of CO vibrational transition from vibrational state v + 1 to state v, induced by collisions with the atoms, cm^3/sec.

Equation (15) is derived under the following assumptions:

1. The translational modes of all the molecular and atomic species are in equilibrium at a constant temperature, T. The rotational modes of CO and N_2 are assumed to be in good thermal contact with the translational mode through rapid collisions, so that these rotational modes can be assumed to be equilibrated to this temperature.
2. The only radiative process considered here is spontaneous radiative emission.
3. The vibrational states of both CO and N_2 molecules are approximated by a Morse anharmonic oscillator.
4. A Maxwell-Boltzmann distribution is assumed for the electrons in the reservoir at a constant electron temperature, T_e.
5. Only single quantum jump processes, $\Delta V = \pm 1$, are allowed for the vibrational transitions induced either by electron impact or through the V-V process.

In the order of their appearance, the terms on the right-hand side of the rate equation, Eq. (15), represent excitation and relaxation rates for the following processes: electron impact excitation; spontaneous radiative decay; intramode near resonant V-V collisional energy exchange among CO molecules; intermode near resonant V-V collisional energy exchange between CO and N_2 molecules; VT collisional energy exchange between CO and CO molecules, between CO and N_2 molecules, and between CO molecules and atoms. A brief discussion of each of these processes follows.

Electron Impact Excitation

The vibrational excitation of the CO molecule or N_2 molecule by

low energy (~1 to 3 eV) electron impact is very efficient due to resonant electron scattering.[53] According to the resonant electron scattering model presented in Ref. 53, the observed prominent peaks in the electron scattering cross sections of CO and N_2[20] may be interpreted as resonances of the incident electron wave in the potential well of the molecule. The trapping of the incident electron with a favorable resonance energy in the molecular potential well results in a temporary negative ion state of the molecule. After a short time, the life time of the negative ion state of the molecule, the electron escapes from the molecular potential well and the molecule may retain some of its energy resulting in a vibrationally excited state (e.g., CO, N_2). The location of the resonance determines the energy of the incident electron required to excite the molecule by this process. In the case of CO, the resonance is in the vicinity of 1.7 eV for the first vibrational level, whereas in the case of N_2, it is approximately 2 eV.[20] The excitation process may be represented by the following reactions:

$$e^-(E) + CO \rightarrow CO^- \ . \tag{16}$$

$$CO^- \rightarrow CO(v) + e^-(E') \ . \tag{17}$$

The vibrational excitation rate can be expressed as

$$\nu_{uv}\, n_u \ ,$$

where

$$\nu_{uv} = n_e \int_0^\infty \left[\sigma_{uv}(\varepsilon)\right] \left(\frac{2}{\pi^{1/2}}\right) \left[\frac{\varepsilon^{1/2}}{(kT)^{3/2}}\right] e^{-(\varepsilon/kT_e)} \left(\frac{2\varepsilon}{m}\right)^{1/2} d\varepsilon$$

$$= n_e \cdot \left(\frac{8}{\pi m_e}\right)^{1/2} \cdot (kT_e)^{-3/2} \int_0^\infty \sigma_{uv}(\varepsilon) e^{-(\varepsilon/kT_e)}\, \varepsilon\, d\varepsilon \ . \tag{18}$$

The excitation rate per CO molecule, ν_{uv}, can easily be obtained numerically by using the electron impaction excitation cross section data measured by Schulz.[20] The data for σ_{uv}, however, included only those cross sections for the excitation of CO molecules in the ground vibrational state, i.e., only for processes $0 \rightarrow v$, where $v = 1, 2, \ldots, 8$. Thus, in the present consideration, the electron impact excitation processes for $v > 0$ to the level $v'(v' > v)$ are neglected.

Spontaneous Radiative Emission

From the quantum theory of radiation, the Einstein A coefficient for a molecule in an initial vibrational state, v, to a final state, v - 1, can be expressed as

$$A_{v'v} = \frac{64\pi^4 \omega_{v'v}^3}{3h} |R_{v'v}|^2 , \tag{19}$$

where $\omega_{v'v}$ is the wave number between vibrational levels v' and v, and $|R_{v'v}|^2$ is the square of the vibrational dipole matrix element. Usually, $A_{v'v}$ is expressed in terms of A_{10} as

$$\frac{A_{v'v}}{A_{10}} = \left(\frac{\omega_{v'v}}{\omega_{10}}\right)^3 \left|\frac{R_{v'v}}{R_{10}}\right| , \tag{20}$$

where A_{10} is the transition rate for the $1 \rightarrow 0$ transition.

For the CO molecule, Penner[54] showed that a Morse potential is more appropriate than a quadratic potential in describing the matrix elements $|R_{v',v}|^2$, and the result for $\Delta v = 1$ is

$$\left|\frac{R_{v,v-1}}{R_{10}}\right|^2 = v\left(\frac{\frac{1}{x_e} - 2}{\frac{1}{x_e} - 2v}\right)^2 \left[\frac{\left(\frac{1}{x_e} - 2v - 1\right)\left(\frac{1}{x_e} - 2v + 1\right)}{\left(\frac{1}{x_e} - 3\right)\left(\frac{1}{x_e} - v\right)}\right] , \tag{21}$$

where $\omega_e x_e$ is one of the vibrational constants. For $\Delta v = 1$, Eq. (20) becomes

$$\frac{A_{v,v-1}}{A_{10}} = \left(\frac{\omega_{v,v-1}}{\omega_{10}}\right)^3 \left|\frac{R_{v,v-1}}{R_{10}}\right|^2 . \tag{22}$$

Thus, once the value of A_{10} for CO is known, the A coefficient can be calculated from the vibrational constants and quantum number. A value of 3.3×10^{-2} sec for A_{10} is obtained from the integrated-band intensity data for the $1 \rightarrow 0$ transition of the CO molecule in Ref. 54.

V-V Collisional Energy Exchange

Collisions between vibrationally excited molecules can result in excitation or decay of vibrational quanta by means of the V-V collisional energy exchange. If the vibrational energy exchange is within the same molecule (e.g., CO-CO), then it is called intramode V-V transition; if the vibrational energy transfer is between different molecules (e.g., $CO-N_2$), then it is called intermode V-V transition. For example, an intramode V-V process can be represented as

$$CO(v + 1) + CO(u) \rightleftarrows CO(v) + CO(u + 1) + \Delta E , \tag{23}$$

where $\Delta E = E_{v+1} - E_v + E_u - E_{u+1}$.

In the process shown in Eq. (23), vibrational quanta of energy are exchanged between molecules, with the excess of energy transferred to or from the kinetic energy. The collisional rates are predominantly determined from dipole transitions for which $\Delta v = 1$. Thus, transitions in which more than one quantum of vibrational energy is exchanged between the colliding molecules can be neglected.

If the molecules were harmonic oscillators, then $\Delta E = 0$, and the V-V process is called exact resonant energy-exchange process. Due to the anharmonicity of the CO molecule, the energy defect, ΔE, must be supplied by exchange with the translational (or rotational) modes of the colliding molecules, but usually, ΔE is very small for the intramode V-V process.

Experimental rates for V-V processes are usually measured at high temperatures ($\gtrsim 1000°K$)[55] and are somewhat scarce. There have been

some experimental measurements of CO-CO V-V collisional energy exchange rates at room temperature in Refs. 44 and 56. More recently, Wittig and Smith[57] have obtained some low-temperature (e.g., at ~254°K and ~100°K) data for CO-CO vibrational exchange rates. The most surprising element about these low-temperature data is the fact that the rates are almost temperature independent. The experimentally determined V-V exchange probabilities are for the following processes:

$$CO(v-1) + CO(v=1) \xrightarrow{P^{1,0}_{v-1,v}} CO(v) + CO(v=0) \ , \qquad (24)$$

where $4 \leq v \leq 11$.

In contrast to the experimentally determined V-V rates, there are many theories of V-V collisional rates.[58-74] Due to the complexity of the problems, there are many assumptions made in all the theories to make the problem tractable. Therefore, the theoretical expressions should be used with extreme care and, for the time being, only as a means to obtain the dependence of the rates on the vibrational quantum state and on the translational temperature.

The standard Schwartz, Slawsky, and Herzfeld (SSH) theory[58-60] for the calculation of the V-V transition probabilities assumes that the short-range repulsive interactions (e.g., the Lennard-Jones potential) are the dominant mechanism for V-V energy exchange. But in 1957, Mahan[65] suggested that long-range dipole-dipole interaction rather than the short-range repulsive force may be responsible for the resonant vibrational energy exchange between polar molecules at lower temperatures (e.g., molecules with large transition dipole matrix elements). Following Mahan's work, Sharma[68-72] has made a series of long-range interaction calculations of the transition rates for dipole and multipole coupling, and the results have shown that the temperature dependence of the transitions may differ markedly from those predicted by SSH theory.

Recently, Jeffers and Kelley[73] have made detailed calculations of V-V transfer probabilities for CO-CO collisions including both long-range and short-range interactions. Their results showed that the

relative contributions of the long- and short-range interactions to the V-V transfer probability depend on energy defect and temperature. Relatively good agreement between calculated and experimental transition probabilities was obtained in Ref. 73, permitting its authors to come to the following two important conclusions: (1) Long-range dipole-dipole interaction calculation describes quite adequately the near resonant V-V transfer probabilities in CO-CO collisions; but (2) as the vibrational energy defect increases, the long-range forces become ineffective and the short-range forces become dominant in determining the transition probability. But the calculated transition probabilities for V-V transfer in CO-CO collisions at 100°K do not agree with the experimental data by the Cambridge group.[57] In fact, the calculated and experimental values disagree not only in magnitude but also in their translational temperature dependence for gas temperatures less than 300°K. The low temperature experimental data[57] showed that the V-V transfer probabilities in CO-CO collisions are almost temperature independent; whereas the calculated values in Ref. 73 showed that the probabilities are strongly temperature dependent at all gas temperatures. Thus, the universal validity of the calculations made in Ref. 73 is somewhat in doubt especially at low temperatures. Since there is not enough reliable experimental data to favor any single theory so far, it appears, for the time being, that the best way to calculate the V-V transition rates would be to use any reasonable theory (e.g., SSH theory) with an adjustable parameter determined by matching to available experimental data.

VT Collisional Energy Exchange

In a VT collisional energy exchange process, the vibrationally excited molecule, after colliding with another molecule, ends up in another vibrational state such as

$$CO(v) + M \rightleftarrows CO(v - 1) + M + \Delta E \ , \qquad (25)$$

where M is a colliding molecule (or atom), and the excess energy, $\Delta E = E_v - E_{v-1}$, is supplied by or transferred to the translational

energy of the colliding molecules. The transition rates for VT processes decrease rapidly as ΔE increases. Furthermore, the VT collisional rates are dominated by the dipole transitions in which only a single vibrational quantum of energy is involved (i.e., $\Delta v = \pm 1$), thus, it is assumed that all multi-quanta VT processes are negligible.

There exist many experimental measurements of transition rates for VT processes. Some of the earlier experimental results have been summarized in Ref. 36. Several investigators have measured the VT relaxation rates at different temperature ranges for CO with various foreign gases.[35,37-39] Most of the data, however, were measured at room temperature or higher, and low temperature (lower than room temperature) VT relaxation rates for CO are still not available except for CO-He and CO-H_2, measured by Miller and Millikan.[39]

In contrast to the case of V-V transition rates, the VT relaxation rate theory is quite well established. In 1936, Landau and Teller[75] had already obtained the correct temperature dependence of the VT relaxation time ($\tau \propto T^{-1/6} \exp T^{-1/3}$) by using the correspondence principle. They first assumed that the intermolecular potential is of exponential form and also assumed that only short-range repulsive forces between the colliding partners are the dominant mechanism for VT energy exchange. Furthermore, they did not consider the physical model of the collision of two molecules, but rather the simplest case of a molecule, BC, being hit by an incident atom, A, along the direction of the molecular axis as shown in Fig. 4. By using the exponential interaction potential, Landau and Teller tacitly assumed that the collision is "adiabatic" since that particular interaction potential represents a weak interaction, i.e., the colliding molecules are turned around at a large separation and, therefore, any perturbation will be weak.

Quantum mechanical calculations of VT relaxation rates were also made.[58-60,76,77] Schwartz, Slawsky, and Herzfeld[59] used the same collision geometry as Landau and Teller but a different interaction potential. Considering that a Lennard-Jones, 6-12 interaction potential would describe the interaction better and offer the mathematical convenience of using an exponential potential, they fitted an exponential

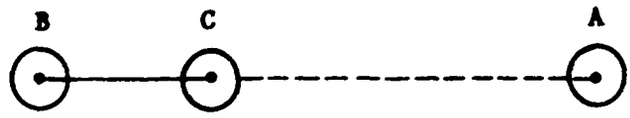

Fig.4 — Collision geometry for a head-on collision between incident atom A and molecule BC

function to the Lennard-Jones potential curve.[59] For a one-dimensional encounter, they found almost the same result as Landau and Teller, but their calculations represented an advance on the earlier analysis of Landau and Teller because a better interaction potential was used and a precise estimate could be made of the effective interaction distance, which was one of the uncertainties in the Landau-Teller analysis.

The theoretical considerations of Landau and Teller[75] and Schwartz, Slawsky, and Herzfeld,[58-60] (SSH theory) show that the dependence of the vibrational relaxation time on temperature is the following:

$$\tau = \tau_{col}\, A\, e^{bT^{-1/3}} , \tag{26}$$

where b is a constant, A is a slowly varying function of temperature, and τ_{col} is the average time between gas kinetic collisions as defined by the following:

$$\tau_{col} \cong \frac{\ell}{\bar{u}} = \frac{1}{n\bar{u}\sigma_{gas}} . \tag{27}$$

Here ℓ is the gas kinetic mean free path, $\bar{u}$ is the average particle velocity, n is the particle number density, and σ_{gas} is the gas kinetic cross section. Thus, a plot of $\ell n\tau$ as a function of $T^{-1/3}$ should yield an almost straight line. Experimental values measured for many different gases more or less follow the straight-line dependence of $\ell n\tau$ on

$T^{-1/3}$. This is evident from Fig. 5, which is taken from Ref. 36. The relaxation phenomena in gases are reviewed in Refs. 78 and 79, and the theory of vibrational relaxation is presented in detail in Ref. 80.

Even though SSH theory is an improvement over the Landau-Teller expression for calculating vibrational relaxation time for gases, there is still an adjustable parameter in the SSH formula. The standard method, then, of calculating vibrational relaxation times in gases is to use SSH theory with an adjustable parameter to be determined by matching to available experimental data.

By using the principle of detailed balancing, all the transition rates for the forward processes can be related to the corresponding reverse processes. For example, $P^{u,u-1}_{v,v+1}$, the intramode V-V rate for transitions from the vibrational state, v, to state v + 1 induced by collision with another CO molecule making a transition from the vibrational state, u, to state u - 1, can be related to the rate for the reverse process, $P^{u-1,u}_{v+1,v}$, in the following way:

$$P^{u,u-1}_{v,v+1} = P^{u-1,u}_{v+1,v} \exp\left[-(E_{v+1} - E_v + E_{u-1} - E_u)/kT\right], \tag{28}$$

where the energy defect, $\Delta E = (E_{v+1} - E_v) - (E_u - E_{u-1})$, is not zero for an anharmonic oscillator, and T is the translational temperature of the gas. Similarly, $P_{v,v+1}$, the VT rate for transitions from state v to state v + 1, can be related to $P_{v+1,v}$ by the following expression:

$$P_{v,v+1} = P_{v+1,v} \exp\left[-(E_{v+1} - E_v)/kT\right]. \tag{29}$$

A similar expression is used in the electron-impact terms where the electron temperature, T_e, is used.

After substituting these expressions into Eq. (15), the rate equation becomes:

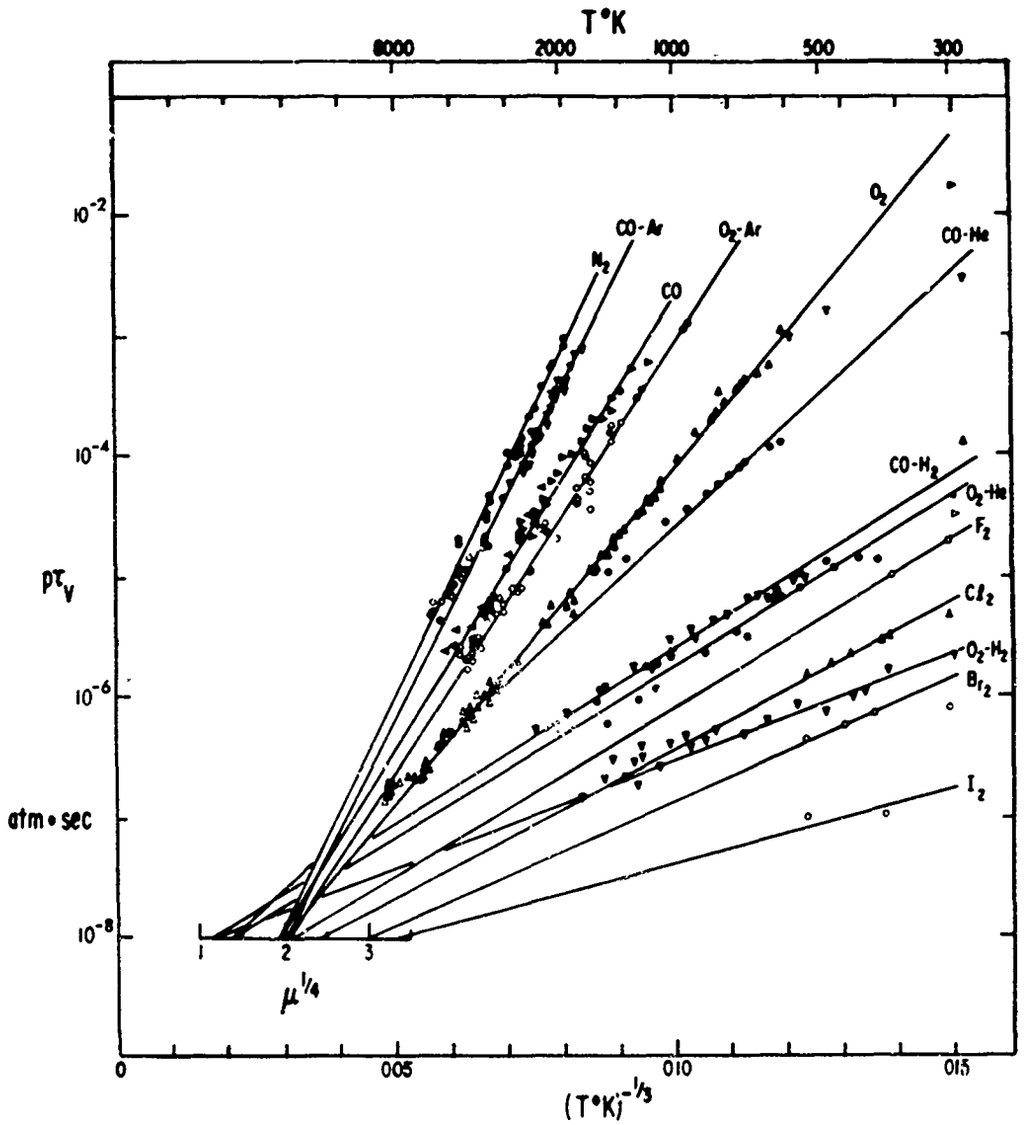

Fig. 5 — V-T relaxation rates, (by permission from R.C. Millikan and D.R. White, "Systematics of Vibrational Relaxation," Journal of Chemical Physics, Vol. 39, December 15, 1963)

$$\frac{dn_v}{dt} = n_e \sum_{u'=0}^{v_e^*-1} \nu_{u'v} \left\{ n_{u'} - n_v \exp\left[-\left(E_{u'} - E_v\right)/kT\right] \right\}$$

$$+ A_{v+1,v}\, n_{v+1} - A_{v,v-1}\, n_u$$

$$+ \sum_{u=1}^{v^*} P_{v+1,v}^{u-1,u} \left\{ n_{v+1} n_{u-1} - n_v n_u \exp\left[-\left(E_{v+1} - E_v + E_{u-1} - E_u\right)/kT\right] \right\}$$

$$- \sum_{u=0}^{v^*-1} P_{v,v-1}^{u,u+1} \left\{ n_v n_u - n_{v-1} n_{u+1} \exp\left[-\left(E_v - E_{v-1} + E_u - E_{u+1}\right)/kT\right] \right\}$$

$$+ \sum_{A=1}^{s^*} Q_{v+1,v}^{s-1,s} \left\{ n_{v+1} N_{s-1} - n_v N_s \exp\left[-\left(E_{v+1} - E_v + E_{s-1} - E_s\right)/kT\right] \right\}$$

$$- \sum_{s=0}^{s^*-1} Q_{v,v-1}^{s,s+1} \left\{ n_v N_s - n_{v-1} N_{s+1} \exp\left[-\left(E_v - E_{v-1} + E_s - E_{s+1}\right)/kT\right] \right\}$$

$$+ P_{v+1,v}\, n \left\{ n_{v+1} - n_v \exp\left[-\left(E_{v+1} - E_v\right)/kT\right] \right\}$$

$$- P_{v,v-1}\, n \left\{ n_v - n_{v-1} \exp\left[-\left(E_v - E_{v-1}\right)/kT\right] \right\}$$

$$+ Q_{v+1,v}\, N \left\{ n_{v+1} - n_v \exp\left[-\left(E_{v+1} - E_v\right)/kT\right] \right\}$$

$$- Q_{v,v-1}\, N \left\{ n_v - n_{v-1} \exp\left[-\left(E_v - E_{v-1}\right)/kT\right] \right\}$$

$$+ R_{v+1,v}\, n' \left\{ n_{v+1} - n_v \exp\left[-\left(E_{v+1} - E_v\right)/kT\right] \right\}$$

$$- R_{v,v-1}\, n' \left\{ n_v - n_{v-1} \exp\left[-\left(E_v - E_{v-1}\right)/kT\right] \right\} \qquad (30)$$

Note that in a V-V process, a quantum of vibrational energy is exchanged between the colliding CO molecules. The differences in energy of the various transitions, i.e., the energy defect,

$$\Delta E = (E_v - E_{v-1}) - (E_{u+1} - E_u) ,$$

is zero in the case of an harmonic oscillator (exact resonance transfer) but finite and small in the case of an anharmonic oscillator. The energy defect, ΔE, must be either carried away or supplied by exchange with the translational (or rotational) modes of the colliding molecules. Since most of the vibrational energy is merely exchanged within the vibrational modes of the CO molecule, the energy defect is usually very small.

NOZZLE FLOW EQUATIONS

Here, we are considering the steady adiabatic flow out of a reservoir and through a converging-diverging nozzle of a given area distribution, A(x), as shown in Fig. 2. In studying nozzle flow, it is usually assumed that the flow is one-dimensional,[34] i.e., conditions across each section are uniform. The nonlinear conservation equations describing the steady quasi-one-dimensional flow may be written down as follows:[34]

Conservation of mass:

$$\frac{d\rho}{\rho} + \frac{du}{u} + \frac{dA}{A} = 0 ; \tag{31}$$

Conservation of momentum:

$$\rho u du + dp = 0 ; \tag{32}$$

Conservation of energy:

$$u du + dh = 0 ; \tag{33}$$

where ρ is the density of the fluid, u is the axial flow velocity, p is the pressure, and h is the enthalpy. When the flow is in thermodynamic equilibrium, a set of four equations for the four unknowns, u, ρ, p, and h, can be obtained by adding the equation of state,

$$h = h(p,\rho) \ . \tag{34}$$

Furthermore, these conservation equations can be integrated into a system of purely algebraic equations. If the fluid medium can be represented by perfect gas, $dh = c_p dT$, where c_p is the specific heat at constant pressure, then all the flow variables can be obtained as functions of the local flow Mach number ($M \equiv u/a$, where a is the local sound speed), the reservoir conditions, and γ, the ratio of the specific heats of the gas. Also, the area ratio, $A(x)/A^*$, depends on M and γ only, thus, all the flow variables can be made functions of $A(x)/A^*$, which, in turn, is a known function of position along the nozzle axis, x. In other words, after specifying the reservoir conditions and the specific heat, the flow variables depend on x only.

For nonequilibrium flow, a third variable is needed in the equation of state to specify the state of the gas. Denoting this nonequilibrium variable by q, the equation of state then becomes

$$h = h(p,\rho,q) \ . \tag{35}$$

The introduction of the additional variable, q, requires an additional equation for the nonequilibrium process. In the case of vibrational nonequilibrium flow, q is represented by the vibrational energy e_v, and the additional equation is a relaxation equation for e_v. Thus, the three conservation equations together with the equation of state and the vibrational energy relaxation equation form a closed set of five equations for the following five unknowns: p, ρ, u, h, and e_v.

The vibrational relaxation equation is closely coupled to the flow properties through the dependence of the transition rates on the translational temperature and the number density of the gas.

On the other hand, the enthalpy equation involves the local vibrational energy term that, in turn, is determined through the vibrational relaxation equation. Simplified treatments of the problem of vibrational relaxation in nozzle flows using the linear rate equation suggested by Bethe and Teller[81] have been studied both numerically[82-85] and analytically[86-89] using expansion techniques.

SMALL-SIGNAL GAIN COEFFICIENT

When a small signal, I, propagates through a spatially homogeneous amplifying medium with an unsaturated gain coefficient, α_o, it is generally found that at depth x, the rate of amplification is

$$\frac{dI}{dx} = \alpha_o I \ . \tag{36}$$

But at the same time, the increase in intensity per unit length due to induced emission is

$$\frac{dI}{dx} = h\nu W_{u\ell}\left(n_u - \frac{g_u}{g_\ell} n_\ell\right) , \tag{37}$$

where n_u and n_ℓ are the population densities of the upper and lower levels, g_u and g_ℓ are the level degeneracies, and $W_{u\ell}$ is the stimulated (or induced) emission rate that is related to the Einstein A coefficient, A, in the following way:[90]

$$W_{u\ell} = \frac{\lambda^2 I}{8\pi\ h\nu} A g(\nu - \nu_o) \ , \tag{38}$$

where $g(\nu - \nu_o)$ is the intensity distribution function describing the lineshape. From Eqs. (36), (37), and (38) the gain coefficient can be obtained, as follows:

$$\alpha_o = \frac{\lambda^2 A}{8\pi} g(\nu - \nu_o)\left(n_u - \frac{g_u}{g_\ell} n_\ell\right) . \tag{39}$$

Now for the vibrational-rotational transitions of the CO molecule, the gain for a single P-branch rotational line (v', $J \rightarrow V$, $J + 1$) becomes

$$\alpha_{v',J\rightarrow v,J+1} = \frac{8\pi^3 \left|R_{v'v}\right|^2}{3h\lambda} g(\nu - \nu_o)(J + 1)\left(\frac{n_{v',J}}{g_J} - \frac{\eta_{v,J+1}}{g_{J+1}}\right), \quad (40)$$

where the following expression for $A_{v'J,vJ+1}$ has been used:

$$A_{v',J\rightarrow v,J+1} = \frac{64\pi^4}{3h\lambda^3} \frac{J + 1}{g_J} \left|R_{v'v}\right|^2 . \quad (41)$$

Assuming rotational equilibrium, ($T_r = T$), and that the rotational level population can be described by a Boltzmann distribution at a temperature T, we have,

$$\alpha_{v',J\rightarrow v,J+1} = \frac{8\pi^3 g(\nu - \nu_o) \left|R_{v'v}\right|^2}{3h\lambda kT} (J + 1)$$

$$\left\{B_{v'}n_{v'}e^{-[F_{v'}(J)/KT]} - B_v n_v e^{-[F_v(J+1)/KT]}\right\}, \quad (42)$$

where $F_v(j) = B_v J(J + 1) - D_v J^2(J + 1)$,

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2 ,$$

$$D_v = D_e + \beta_e(v + \tfrac{1}{2}) ,$$

and the values for the vibrational and rotational constants B_e, D_e, α_e, β_e, and γ_e are listed in Table 6.

The intensity distribution function $g(\nu - \nu_o)$ is a function of the line shape. For a Doppler-broadening line, the expression for $g(\nu - \nu_o)$ is[91]

Table 6

VALUES OF VIBRATIONAL AND ROTATIONAL CONSTANTS OF THE CO MOLECULE IN WAVE NUMBER, cm^{-1}

Constants	Values
ω_e	2169.83
$\omega_e x_e$	13.297
$\omega_e y_e$	0.0115
B_e	1.93141
D_e	6.18×10^{-6}
α_e	0.017520
β_e	-1.76×10^{-9}
γ_e	2.96×10^{-6}

SOURCE: Ref. 92.

$$g(\nu - \nu_o) = \frac{2(\ln 2)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}\Delta\nu_D} \exp\left\{-\left[\frac{2(\nu - \nu_o)}{\Delta\nu_D} \ln 2\right]^2\right\}, \tag{43}$$

where the Doppler linewidth, $\Delta\nu_D = \frac{2}{\lambda_o}\sqrt{\frac{2KT}{m} \ln 2}$, is the full width at half intensity. At line center, where $\nu = \nu_o$, $g(\nu_o)$ becomes

$$g(\nu_o) = \frac{\lambda_o}{\sqrt{2\pi KT/m}}, \tag{44}$$

where m is the mass of the molecule.

For a homogeneous broadening line (pressure or collision broadening line)[93]

$$g(\nu - \nu_o) = \frac{\Delta\nu_c}{2\pi} \frac{1}{\left[(\nu - \nu_o)^2 + \frac{1}{4}(\Delta\nu_c)^2\right]}, \tag{45}$$

where the line width, $\Delta\nu_c = \frac{\nu_c}{\pi}$, is the full width of the line at half intensity, and ν_c is the optical broadening collision frequency. At $\nu = \nu_o$, we have

$$g(\nu_o) = \frac{2}{\nu_c} . \tag{46}$$

Therefore, the small-signal gain coefficient for either a Doppler-broadening or a homogeneous-broadening line can be obtained by substituting Eq. (44) or Eq. (46) into Eq. (42).

IV. FROZEN FLOW APPROXIMATION

In general, the problem of vibrational nonequilibrium flow through a nozzle requires the solutions to a set of five coupled equations as outlined in Sec. III. But in the case of an electrically pumped CO GDL, there are cases such that the characteristic flow time, τ_f, is short in comparison with the VT relaxation time, τ_{vT}. In such cases, changes in the average vibrational energy of all oscillators remain small compared with the flow energy during transit, thus, a vibrationally-frozen flow approximation can be made. It simply means that whatever value the vibrational energy has, it plays no part in the energy exchange process; thus, the gas behaves as if the vibrational modes of the diatomic species were unexcited. Therefore, the overall flow properties may be decoupled from the vibrational relaxation process, and the local temperature, pressure, and flow velocity of the gas can be calculated using the well-known isentropic gas equations with a constant value of γ.

Essentially, in the case of a vibrationally frozen flow approximation, the entire problem is reduced to solving a set of time-dependent rate equations with all the transition rates as given quantities. But in the quasi-one-dimensional nozzle flow, it is much more convenient to use the axial flow coordinate, x, as the independent variable instead of the time, t. Using a simple transformation $d/dt = u\, d/dx$, the initial value problem is transformed into a boundary value problem with the boundary conditions given by the solutions to a set of steady-state rate equations describing the kinetic processes in the plenum chamber.

Actually, the vibrationally frozen flow approximation is quite a reasonable one for describing the electrically pumped CO GDL with the following gas mixtures: pure CO, CO-Ar, and CO-N_2 because of their long VT relaxation times. At 300°K, the VT relaxation time, $p\tau_{vT}$, for pure CO is about 1 atm-sec,[35-38] $p\tau_{vT}$ for CO-Ar is about 10^3 atm-sec.[36] It is expected that the value of $p\tau_{vT}$ for CO-N_2 is about 1 atm-sec, the same as that for pure CO since the $p\tau_{vT} \approx 0(100$ atm-sec$)$[36] for pure N_2, thus, the VT relaxation process for N_2-CO is probably via the near-resonant, intra-V-V process between CO and N_2 and then via the VT

relaxation of CO-CO. The typical gas mixture used in the conventional electrically pumped CO GDL is CO-N_2-He. For such a gas mixture, the VT relaxation time is essentially that of CO-He, $p\tau_{VT} \approx 10^{-3}$ atm-sec.[39] In this case, the vibrationally frozen flow approximation may not be very appropriate because of the fast VT relaxation time. In order to analyze the conventional electrically pumped CO GDL using a gas mixture of CO-N_2-He, the fully coupled equations described in Sec. III should be used.

But in the case of an electron-beam-pumped CO GDL, the optimum gas mixture is not necessarily the same as that in a conventional electrically pumped CO GDL. In fact, it is found that the optimum gas mixture in the operation of a high-pressure, electron-beam-stabilized, long-pulse transverse-discharge CO device appears to be that of CO-Ar.† Thus, it is not unreasonable to assume that this gas mixture of CO-Ar is also suitable for the operation of the proposed electron-beam-pumped CO GDL. Thus, we can apply the vibrationally frozen flow approximation to describe this problem.

Theoretically, the simplest systems to analyze are those devices using pure CO gas and a gas mixture of CO-Ar because there is only one set of rate equations to be solved with the frozen flow approximation. Specializing in these systems, we have the following rate equation:

$$u \frac{dn_v}{dx} = A_{v+1,v}\, n_{v+1} - A_{v,v-1}\, n_v$$

$$+ \sum_{u=1}^{v^*} P^{u-1,u}_{v+1,v} \left\{ n_{v+1}\, n_{u-1} - n_v n_u \exp\left[- \left(E_{v+1} - E_v + E_{u-1} - E_u \right)/kT \right] \right\}$$

$$- \sum_{u=0}^{v^*-1} P^{u,u+1}_{v,v-1} \left\{ n_v n_u - n_{v-1}\, n_{u+1} \exp\left[- \left(E_v - E_{v-1} + E_u - E_{u+1} \right)/kT \right] \right\}$$

†Private communication with Dr. M. L. Bhaumik, Laser Systems Department, of the Northrop Corporation, Hawthorne, Calif., November 1972.

$$+ \left(P_{v+1,v} n + R_{v+1,v} n'\right) \left\{n_{v+1} - n_v \exp\left[-\left(E_{v+1} - E_v\right)/kT\right]\right\}$$

$$- \left(P_{v,v-1} n + R_{v,v-1} n'\right) \left\{n_v - n_{v-1} \exp\left[-\left(E_v - E_{v-1}\right)/kT\right]\right\} , \tag{47}$$

where n' is zero for the pure CO case. Notice that there is no electron-impact excitation term in this equation since this particular process takes place only in the plenum chamber where the electron beam ionizer-sustainer discharge system is located. The boundary conditions for this set of equations are the CO vibrational state number densities in the plenum chamber that are given by the solutions to the set of the following time-independent rate equations:

$$\frac{dn_v}{dt} = 0$$

$$= n_e \sum_{u'=0}^{v_e^*-1} \nu_{uv} \left\{n'_u - n_v \exp\left[-\left(E'_u - E_v\right)/kT\right]\right\}$$

$$+ A_{v+1,v}\, n_{v+1} - A_{v,v+1}\, n_v$$

$$+ \sum_{u=1}^{v^*} P^{u-1,u}_{v+1,v} \left\{n_{v+1}\, n_{u-1} - n_v n_u \exp\left[-\left(E_{v+1} - E_v + E_{u-1} - E_u\right)/kT\right]\right\}$$

$$- \sum_{u=0}^{u^*-1} P^{u,u+1}_{v,v-1} \left\{n_v n_u - n_{v-1}\, n_{u+1} \exp\left[-\left(E_v - E_{v-1} + E_u - E_{u+1}\right)/kT\right]\right\}$$

$$+ \left(P_{v+1,v}\, n + R_{v+1,v}\, n'\right) \left\{n_{v+1} - n_v \exp\left[-\left(E_{v+1} - E_v\right)/kT\right]\right\}$$

$$- \left(P_{v,v-1} n + P_{v,v-1}\, n'\right) \left\{n_v - n_{v-1} \exp\left[-\left(E_v - E_{v-1}\right)/kT\right]\right\} . \tag{48}$$

In the case of pure CO molecules, γ is 1.4 for the vibrationally-frozen flow approximation. For $\gamma = 1.4$, all the flow properties have been calculated and tabulated as functions of local Mach number M (and area ratio $A(x)/A^*$). Therefore, only two sets of rate equations need to be solved. One is a steady-state rate equation describing the non-equilibrium vibrational distribution in the plenum chamber, the other one is a time-dependent rate equation describing the local nonequilibrium vibrational distribution along the nozzle. The first one is essentially a set of nonlinear simultaneous algebraic equations, the second one is a set of simultaneous differential equations with the boundary conditions given by the solutions to the first set. In the case of the CO-Ar gas mixture, however, $\bar{\gamma}$, the molar average value of γ, must be used. Then, the local flow properties can be computed using the well-known perfect gas equations for a constant isentropic exponent, $\bar{\gamma}$.

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