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A semi-empirical approach to CO₂ laser kinetics

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Abstract. An effective relaxation constant for the CO₂ (00*v*) and CO(*v*) vibrational levels has been experimentally obtained from measurements in the discharge. Using this relaxation constant and known excitation cross sections, a comprehensive picture of the kinetics of the CO₂-He laser has been obtained. This approach does not require knowledge of the electron energy distribution function. Populations and temperatures of different vibrational levels have been calculated, as well as energy transfer rates to these levels. Quantitative results are presented and compared with otherwise known data on small-signal gain and energy transfer rates.

1. Introduction

The kinetics of electrically excited CO₂ lasers have been treated rather extensively in recent years (Moore *et al* 1968, Gordiets *et al* 1967, 1968). In order to present a comprehensive picture of the processes which turn a glow discharge into an effective lasing mechanism, various theoretical models have been suggested (Gordiets *et al* 1967, 1968). These suffer, however, from the lack of precise knowledge of the electron energy distribution function as well as from uncertainty of accurate values for vibrational excitation and relaxation of CO and CO₂ by electrons. The relaxation rates for vibration-vibration (*v-v*) and vibration-translation (*v-T*) energy transitions are relatively well known (Taylor and Bitterman 1969); a maxwellian electron distribution function is assumed with an electron density N_e and electron temperature T_e , and relaxation processes by electrons are usually neglected in these models.

In order to obviate the above mentioned difficulties and shortcomings, a different approach is presented here which does not require knowledge of the electron distribution function and also does not depend on the accurate knowledge of the electron density.

This approach is essentially based on known excitation and relaxation cross sections, and where they are not known, experimentally obtained rates are used in order to construct and solve the necessary rate equations.

The basic assumption here concerning the electron distribution is that the ratio of the powers expended for the excitation of two relevant levels is insensitive to the form of electron distribution function. The assumption is based on the following information.

The most important electron-vibrational excitation interactions of CO and CO₂ molecules in CO₂ lasers are due to the following processes, with their relevant cross sections:

- (i) CO(*v*=0) → CO(*v*=1, 2, . . .): σ_c ;
- (ii) CO₂(000) → CO₂(001): σ_2 ;
- (iii) CO₂(000) → CO₂(010): σ_1 .

The cross sections σ_1 , σ_2 and σ_c are quasi-resonant; the energy range in which σ_c and σ_2 are at all significant is 0.3–3.0 eV (Boness and Schulz 1968, Schulz 1964) and 0.1–1.5 eV for σ_1 (Stamatovic and Schulz 1969). Both energy ranges nearly coincide and are narrow in comparison with the energy range of the electrons in the discharge. Therefore the ratio

$$\rho_{c,2} = \frac{p_c}{p_2}$$

of the amount of energy p_c expended per unit time in exciting one CO molecule from the ground level to the levels $v=1, 2, \dots$ and the energy p_2 required for the excitation of one CO₂ molecule to (00 v) levels is approximately independent of the electron energy

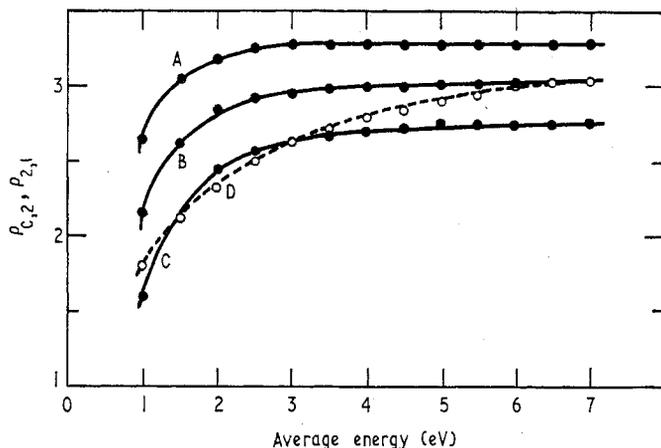


Figure 1. Variation of the ratios $\rho_{c,2} = p_c/p_2$ and $\rho_{2,1} = p_2/p_1$ with average electron energy: A, $\rho_{c,2}$, CO vibrational temperature $T_c = 1000$ K; B, $\rho_{c,2}$, $T_c = 1400$ K; C, $\rho_{c,2}$, $T_c = 1800$ K; D, $\rho_{2,1}$.

distribution. For instance (see figure 1), for a maxwellian distribution with average energies ranging from 1.5 to 7.5 eV and a vibrational temperature of the CO molecule of 1400 K

$$2.7 < \rho_{c,2} < 3.0. \quad (1)$$

For the same conditions

$$2 < \rho_{2,1} = \frac{p_2}{p_1} < 3 \quad (2)$$

where p_1 is the energy expended in unit time for the excitation of a CO₂ molecule from the ground level to the (010) level. This is also true when the distribution functions are nonmaxwellian, as has been shown by Nighan (1970). In our computations of p_c , p_1 and p_2 we used experimentally determined cross sections (Boness and Schulz 1968, Schulz 1964, Stamatovic and Schulz 1969); the relaxation rates v -E were obtained from the principle of detailed balancing, and the anharmonicity of the CO molecule was neglected.

We define in §2.1 an effective relaxation constant K , which involves all relaxation processes from CO₂(00 v) and CO(v) levels and is determined experimentally in a CO₂-He laser.

In §2.2 we give a detailed justification and experimental description for the determination of the effective relaxation constant K .

In §3 we construct the rate equations and discuss the assumptions made.

In §4 we present and discuss the solutions of the rate equations and compare them with results obtained by other authors.

2. Effective relaxation rate

2.1. Theoretical considerations

We assume the existence of three separate vibrational temperatures for each vibrational mode of the CO₂ molecule: T_1' [($\nu 00$) mode], T_1 [($0\nu 0$) mode] and T_2 [(00ν) mode], where $T_1' \approx T_1$ because of strong v-v coupling between the ($\nu 00$) and ($0\nu 0$) modes. Similarly, T_c is the vibrational temperature of the CO molecule, and $T_c \approx T_2$. These temperatures are approximately constant throughout the active volume V of the laser (which is taken to be the volume of the laser beam).

For stationary conditions without lasing (superscript 0) and while lasing (superscript L) with a total output power P_L , one can write the energy balance equations

$$P_2^0 + P_c^0 - BE_N^0 - B'E_M^0 = 0 \quad (3)$$

$$P_2^L + P_c^L - BE_N^L - B'E_M^L - \frac{P_L}{V} \frac{h\nu_2}{h\nu_L} = 0. \quad (4)$$

P_2 and P_c are the powers per unit volume expended in exciting the CO₂(00ν) and CO($\nu=1, 2, \dots$) levels respectively; $h\nu_2$ and $h\nu_L$ are energies of the CO₂(001) level and of a laser photon; E_N and E_M are the vibrational energies per unit volume stored in the states CO₂(00ν) and CO(ν) respectively; and B and B' are effective relaxation rates of the levels CO₂(00ν) and CO(ν).

B and B' include (i) v-v and v-T relaxations, (ii) spontaneous emission CO₂(00ν) \rightarrow CO₂($00\nu-1$), (iii) losses by diffusion to the wall, and (iv) relaxation by collisions with electrons from the mode CO₂(00ν) to CO₂($\nu 00$) and CO₂($\nu_i \nu_j 0$). Let

$$S = S_1(T_1) S_2(T_2)$$

where

$$S_1 = (1 - x_1')(1 - x_1)^2, \quad S_2 = 1 - x_2$$

$$x_1 = \exp\left(-\frac{h\nu_1}{kT_1}\right), \quad x_1' = \exp\left(-\frac{h\nu_1'}{kT_1}\right), \quad x_2 = \exp\left(-\frac{h\nu_2}{kT_2}\right).$$

Here $h\nu_1'$ and $h\nu_1$ are the energies of the CO₂(100) and (010) levels. Then (Gordiets *et al* 1968)

$$E_M = Mx_2h\nu_2/(1 - x_2), \quad E_N = NS_1h\nu_2x_2/(1 - x_2)$$

where N and M are the total numbers of CO₂ and CO molecules per unit volume.

Equations (3) and (4) can now be written as

$$P^0 - E^0K = 0 \quad (5a)$$

$$P^L - E^LK = \frac{P_L}{V} \frac{h\nu_2}{h\nu_L} \quad (5b)$$

where $E = E_N + E_M$ and $P = P_2 + P_c$ for both superscripts L and 0, and K is the effective relaxation constant

$$K = \frac{1}{1 + M/NS_1} \left(B + B' \frac{M}{NS_1} \right). \quad (6)$$

From (5) we get

$$K \left(\frac{E^0 P^L}{E^L P^0} - 1 \right) = \frac{P_L}{V} \frac{h\nu_2}{h\nu_L} \frac{1}{E^L}. \quad (7)$$

The energy E stored per unit volume in the vibrational levels CO_2 (00ν) and CO (ν) changes significantly when the discharge is switched from a non-lasing to a lasing state; at the same time $P^0/P^L \approx 1$, because the change of the population of the CO_2 and CO ground states (which most molecules occupy) is small. With this assumption (7) can be rewritten

$$K(E^0 - E^L) = K\Delta E = \frac{P_L}{V} \frac{h\nu_2}{h\nu_L}. \quad (8)$$

From the last equation, K can be calculated if the energy difference ΔE is known.

2.2. Experimental determination of K

Figure 2(a) shows the experimental arrangement in which ΔE has been measured.

A mechanical chopper situated within the laser cavity switches the discharge periodically from a lasing to a non-lasing condition. The same chopper can be also placed outside the laser cavity. Typical oscillograms with the chopper within and outside the cavity are shown in figure 2(b).

Let n be the switching frequency of the chopper, and ϵ_1 and ϵ_2 the average laser power when the chopper is within the laser cavity (Ch. 1 in figure 2a) or outside the cavity (Ch. 2). E is the energy per unit volume stored in the vibrational levels CO_2 (00ν) and

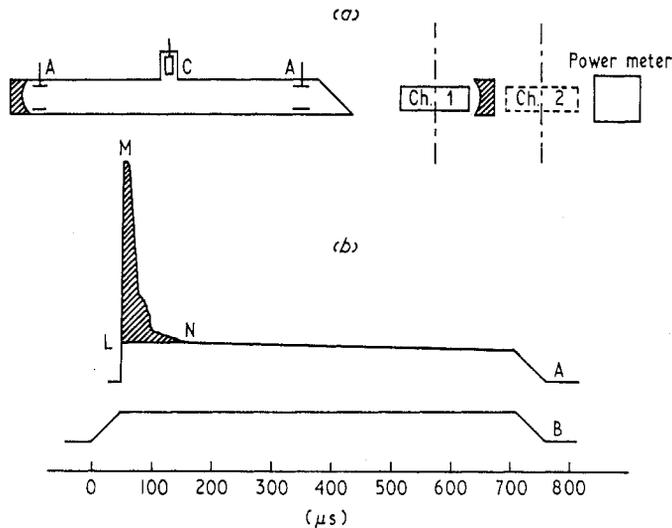


Figure 2. (a) Experimental arrangement. (b) Laser power (arbitrary units) as a function of time: A, chopper within the laser cavity; B, chopper outside the laser cavity.

CO (ν). The change in E because of the transition from the non-lasing to the lasing state is equal to the vibrational energy stored in LMN (figure 2b):

$$\Delta E = \frac{\epsilon_1 - \epsilon_2}{Vn} \frac{hv_2}{hv_L} \quad (9)$$

where V is the active volume of the laser. By substituting this formula into (8) we obtain

$$K = \frac{nP_L}{\epsilon_1 - \epsilon_2} \quad (10)$$

From equation (10) it is possible to calculate K from measurements of the cw laser power P_L and of the average power obtained with the chopper within and outside the cavity (ϵ_1, ϵ_2). It is worthwhile to note that the determination of K from (10) is independent of the effective laser volume V .

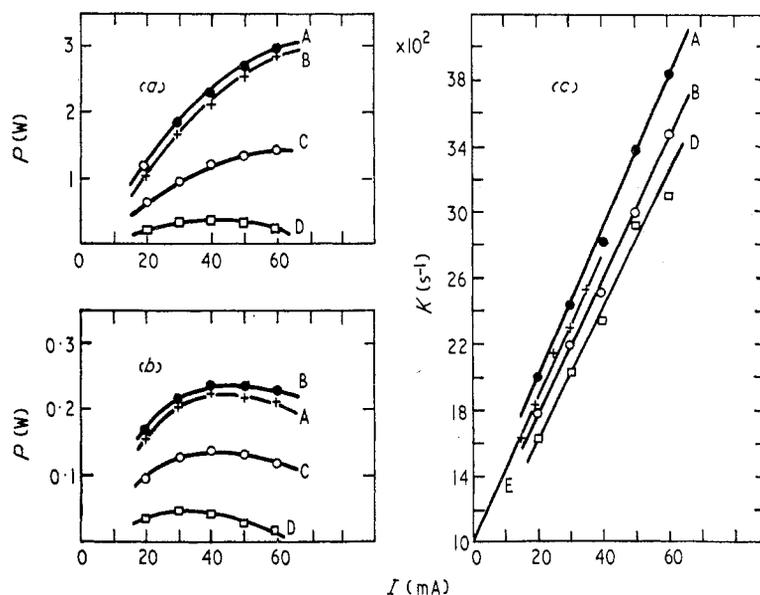


Figure 3. (a) The dependence of the laser power P_L on the discharge current. (b) The dependence of the average power difference with the chopper inside and outside the cavity on the discharge current. (c) The dependence of the effective relaxation rate on the discharge current. He 3.3 Torr. A, CO₂ 1.2 Torr; B, CO₂ 0.8 Torr; C, CO₂ 0.6 Torr; D, CO₂ 0.4 Torr; E, CO₂ 1 Torr.

Measurements for the determination of K were made in gas mixtures with partial pressures of He of 3.3 Torr and CO₂ varying in the range 0.4–1.2 Torr. The diameter of the laser tube was 2.7 cm and the laser beam diameter 0.7 cm. The cathode–anode distance was 47 cm and the gas flow 0.5 litre s⁻¹.

Figure 3 shows the measured values of $\epsilon_1 - \epsilon_2$ and of P_L , and the values of K , computed from (10), as a function of the discharge current I . The curves of $K(I)$ are straight lines; their slope does not depend strongly on the partial pressure of CO₂. From the intersection of the lines with the ordinate, the relaxation coefficient at zero current (ie without relaxation of CO₂ (001) by electrons and the presence of CO) can be measured.

For example, we find the effective relaxation constant at zero current for $P(\text{CO}_2)=1$ Torr as $K_0=1000 \text{ s}^{-1}$. With Moore *et al*'s (1968) values ($K_{\text{spont}}=430 \text{ s}^{-1}$, $K_{\text{He}}=85 \text{ s}^{-1} \text{ Torr}^{-1}$, $K_{\text{CO}_2}=350 \text{ s}^{-1} \text{ Torr}^{-1}$), the total relaxation constant at zero current is $K=1060 \text{ s}^{-1}$.

3. Assumptions and construction of rate equations

3.1. Assumptions and their justification

We shall now discuss assumptions which make, for a given case, the solution of the rate equations (5) possible. The assumptions are as follows.

(i) For our experimental conditions, the relative partial pressure of CO produced by dissociation in the discharge is given by the empirical formula (Gasilevich *et al* 1969)

$$C = \frac{[\text{CO}]}{[\text{CO}] + [\text{CO}_2]} = \frac{M}{M+N} = 0.6 \times 10^{-2} I. \quad (11)$$

Here I is the discharge current in mA ($I < 80$ mA), and $[\text{CO}]$ and $[\text{CO}_2]$ are the partial pressures of CO and CO_2 respectively.

(ii) As was shown in the introduction (see figure 1 and equations (1) and (2)), we assume

$$\frac{P_c}{P_2} = \frac{p_c}{p_2} \frac{M_0}{N_0} = \rho_{c,2}(T_2) \frac{M_0}{N_0} = \rho_{c,2}(T_2) \frac{M}{NS_1} \quad (12)$$

and

$$\frac{P_2}{P_1} = \frac{p_2}{p_1} = 2-3 \quad (12')$$

(p is the respective energy expended per molecule).

(iii) Let E_1 be the energy stored in all vibrational levels of the CO_2 molecule, excluding the $(00v)$ levels. We assume further that all those levels (levels '1') are in thermal equilibrium with a common temperature T_1 , and that the energy is relaxed from them mainly via the levels $\text{CO}_2(0v0)$. The relaxation rate is $q(T) = q_{\text{He}}(T) + q_{\text{CO}_2}(T) + q_{\text{CO}}(T)$, where T is the temperature of the gas. The numerical value used in our calculations was taken from Taylor and Bitterman (1969). Then for steady-state conditions,

$$\frac{dE_1}{dt} = -q \left[1 - \exp\left(-\frac{h\nu_1}{kT}\right) \right] (E_1'(T_1) - E_1'(T)) + P^* = 0. \quad (13)$$

Taking into account the degeneracy of the levels $(0v0)$, one can write

$$E_1' = \frac{2h\nu_1 x_1}{(1-x_1)^3} NS = \frac{2h\nu_1 x_1}{1-x_1} NS_3, \quad S_3 = (1-x_1)S_2.$$

P^* is the power which is transferred by various processes to levels '1':

$$P^* = P_1 + P_2 + P_c - \Delta$$

where P_1 is the power which is transferred directly to levels '1', and Δ is the part of powers P_c and P_2 which does not ultimately reach levels '1'.

(iv) We assume that the following processes contribute to Δ : (a) diffusion of CO₂ (00v) and CO (v) molecules from the active volume and relaxation at the wall; (b) spontaneous emission of radiation leading to the transition CO₂ (00v) \rightarrow CO₂ (00v-1); (c) in the case of lasing, loss of laser quanta.

Therefore

$$\Delta^0 = \frac{D_{\text{CO}_2}}{\Lambda^2} E_{N^0} + \frac{D_{\text{CO}}}{\Lambda^2} E_{M^0} + AE_{N^0}$$

$$\Delta^L = \frac{D_{\text{CO}_2}}{\Lambda^2} E_{N^L} + \frac{D_{\text{CO}}}{\Lambda^2} E_{M^L} + AE_{N^L} + \frac{P_L}{V} \frac{h\nu_2}{h\nu_L}$$

where D_{CO_2} and D_{CO} are the diffusion constants for CO₂ and CO molecules respectively, Λ is the diffusion length, and A is the spontaneous emission rate. Equation (13) can now be rewritten as

$$\frac{x_1(T_1)}{1-x_1(T_1)} = \frac{x_1(T)}{1-x_1(T)} + \frac{P_1+P_2+P_0-\Delta}{2q(1-x_1(T))NS_3h\nu_1} \quad (14)$$

(v) The translational temperature T on the discharge tube axis can be determined from considerations of heat transfer (Franzen and Collins 1972):

$$T(r) = \frac{P_{\text{in}}}{L} \frac{J_0(2.4r/R)}{\alpha 2\pi 2.4J_1(2.4)} + T_w, \quad r=0. \quad (15)$$

Here P_{in}/L is the part of the input electrical power per unit length of the discharge which is transferred to the translational degrees of freedom. α is the heat conductivity of the gas mixture (Hirschfelder *et al* 1964). T_w is the wall temperature. J_0 and J_1 are Bessel functions of zero and first order.

3.2. The semi-empirical rate equations

In the following we shall show how one can use the rate equations, the quantities measured by means of the chopper experiment (effective relaxation constant, laser power in cw and switched conditions) and other easily accessible quantities (gas temperature, input power) to obtain information about the vibrational temperatures T_2 (of the CO (v) and CO₂ (00v) levels) and T_1 (of other CO₂ vibrational levels), and P_2 (power input into the CO₂ (00v) levels) and P_1 (power input into other vibrational levels). All four quantities T_2 , T_1 , P_2 and P_1 will be derived for non-lasing as well as for lasing conditions.

According to (14), for lasing conditions

$$\frac{x_1(T_1^L)}{1-x_1(T_1^L)} = \frac{x_1(T)}{1-x_1(T)} + \frac{P_1^L+P_2^L+P_0^L-\Delta^L}{2q(1-x_1(T))NS_3^Lh\nu_1} \quad (16)$$

Additionally, for the lasing steady state and emission of the P(20) line (Gordiets *et al* 1967)

$$N_2^L = N_1^L + \frac{tc}{2L} \frac{1}{B(20)} \quad (17)$$

where N_2^L and N_1^L are the populations per unit volume of the upper and lower laser levels, t is the transmittivity of the output mirror, and L is length of the laser. $B(20)$ is given by

$$B(j) = (2j+1)chB_j, \quad j-1 \left(\frac{m}{2\pi kT} \right)^{1/2} \frac{hcR}{kT} \exp \left(-\frac{hcR}{kT} j(j+1) \right),$$

where $j=20$, B_j , $j-1$ is the Einstein coefficient for stimulated transitions from an upper level ($v, j-1$) to a lower ($v-1, j$), and R is the rotational constant of the CO_2 molecule.

The effective relaxation constant K of the levels $\text{CO}_2(00v)$ and $\text{CO}(v)$ is already known. Equation (5b) becomes

$$P_2^L + P_c^L = KE^L + \frac{P_L}{V} \frac{hv_2}{hv_L} \quad (18)$$

Substituting here P_c^L from (12), one obtains

$$P_2^L = \frac{KE^L + (P_L/V)(hv_2/hv_L)}{1 + \rho_{c,2} M/NS_1} \quad (19)$$

and according to (12')

$$\frac{P_2^L}{P_1^L} = 2-3. \quad (20)$$

From the equations (16), (17), (19) and (20) one can calculate T_1^L , T_2^L , P_1^L and P_2^L . Equation (20) determines the limits of error of these calculations.

Let us assume that $T_1^0 \approx T_1^L$. Then the common vibrational temperature T_2^0 of the $\text{CO}_2(00v)$ and $\text{CO}(v)$ levels in the non-lasing condition can be found from the following equation:

$$\Delta E = E^0 - E^L = hv_2(M + NS_1^L) \left(\frac{x_2^0}{1-x_2^0} - \frac{x_2^L}{1-x_2^L} \right). \quad (21)$$

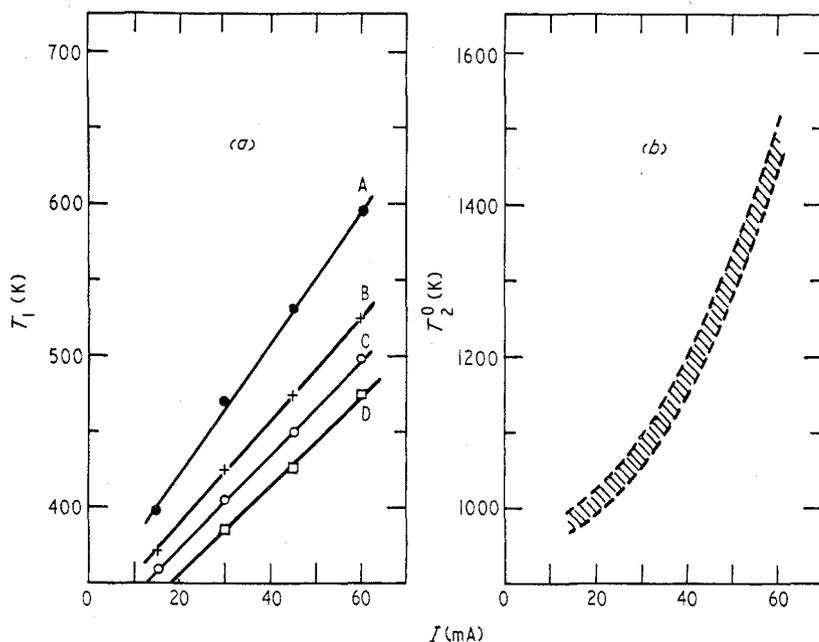


Figure 4. (a) Variation of the vibrational temperature T_1 of the CO_2 bending mode with discharge current: A, CO_2 1.2 Torr; B, CO_2 0.8 Torr; C, CO_2 0.6 Torr; D, CO_2 0.4 Torr. (b) Variation of the vibrational temperature T_2^0 of asymmetric stretch in non-lasing condition with discharge current. He 3.3 Torr.

Here the quantity ΔE is measured (compare (9)) and $x_2^L = \exp\{-hv_2/kT_2^L\}$ is already known from (16)–(20).

4. Results and conclusions

Equations (16)–(21) have been solved numerically for various experimental parameters such as discharge current and partial pressure of CO₂. The results are presented graphi-

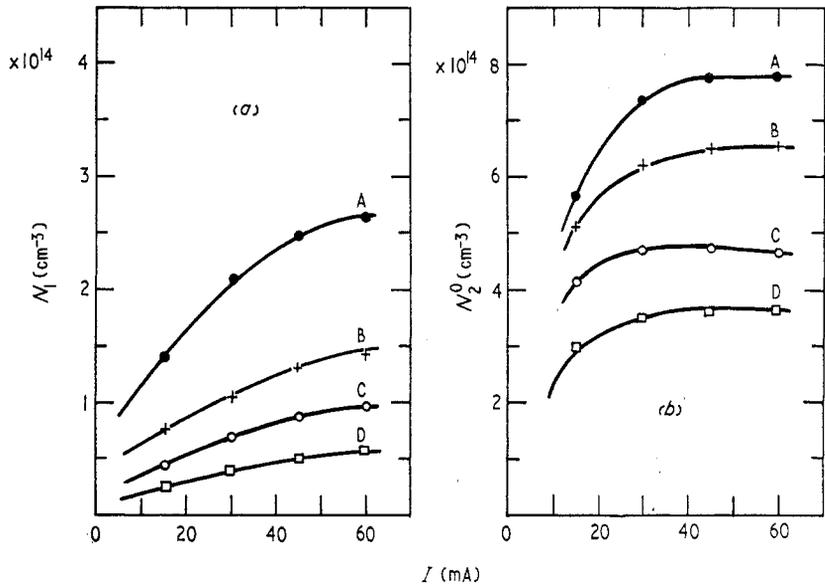


Figure 5. (a) Variation of the population of lower laser level with discharge current. (b) Variation of the population of upper laser level in a non-lasing condition with discharge current. He 3.3 Torr. A, CO₂ 1.2 Torr; B, CO₂ 0.8 Torr; C, CO₂ 0.6 Torr; D, CO₂ 0.4 Torr.

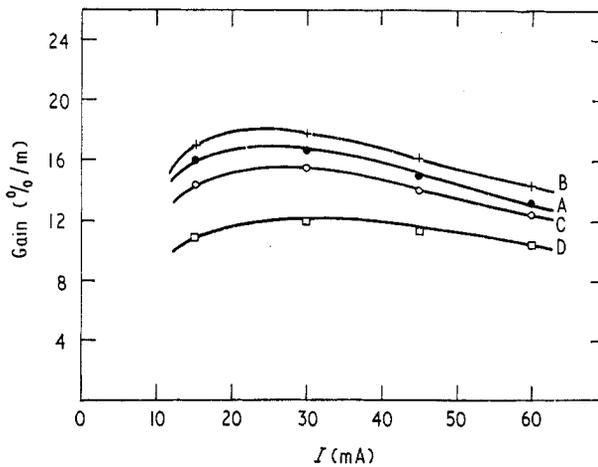


Figure 6. The dependence of the small-signal gain on the discharge current. He 3.3 Torr. A, CO₂ 1.2 Torr; B, CO₂ 0.8 Torr; C, CO₂ 0.6 Torr; D, CO₂ 0.4 Torr.

cally in figure 4. In parallel, the population N_1 of $\text{CO}_2(100)$ and the population N_2^0 of $\text{CO}_2(001)$ as a function of discharge current are presented in figure 5. The different dependence on current of N_1 and N_2^0 should be noticed. This result has been experimentally confirmed (Deutsch 1967). In the same paper (Deutsch 1967), small-signal gain measurements are given which are in agreement with our results shown in figure 6.

Figure 7 shows the calculated fractional power transfer into vibrational and electronic levels. The fractional power transfer is defined as the power transferred by electrons to certain levels divided by the total power input. It is seen that only about 25% of all electrical energy is converted into vibrational modes, whereas the major part is utilized

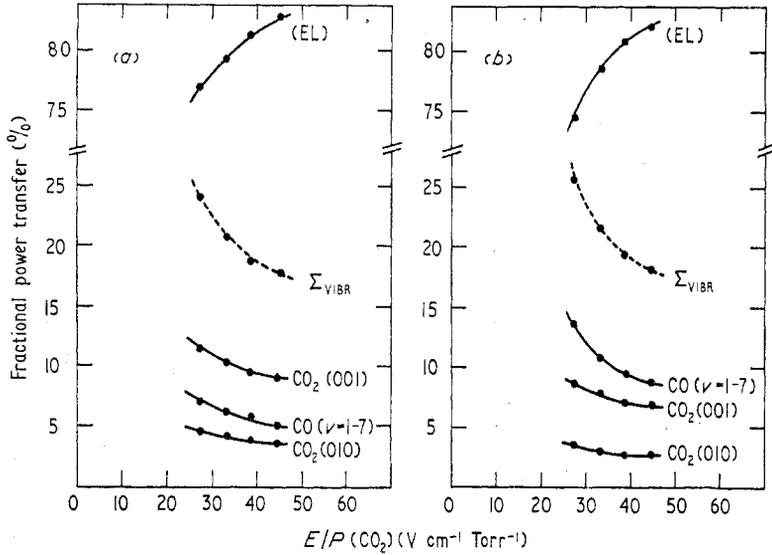


Figure 7. Fractional power transfer from the electrons to the vibrational and electronic levels of CO_2 and CO as a function of $E/P(\text{CO}_2)$: (a) discharge current $I=20$ mA; (b) $I=40$ mA.

for excitation of electronic levels, ionization and dissociation. These results agree with those obtained by Nighan (1970), who calculated these quantities using experimentally obtained cross sections and theoretically calculated electron energy distribution functions.

All these results justify the assumptions made in our calculations, and in particular the assumption that the fractional powers transferred to the relevant vibrational modes are insensitive to the shape of the electron energy distribution function. With this assumption and with the experimentally derived effective relaxation constant, a comprehensive picture of the kinetics of the CO_2 laser has been drawn.

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