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by

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OPTIMUM VIBRATIONAL EXCITATION OF CO MOLECULES IN CO-N₂ MIXTURES

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ABSTRACT

Vibrational excitation rates for CO and N₂ mixtures have been obtained from numerically computed electron energy distributions. It is found that the CO excitation rate may be enhanced by the addition of N₂. The optimum fraction of CO is found to be 30% at $E/N = 1.5 \times 10^{-16}$ V-cm² and increases to 60% at $E/N = 4.0 \times 10^{-16}$ V-cm².

Previous theoretical investigations of CO laser kinetics have failed to exhibit a significant increase in laser performance resulting from the addition of N₂ to the lasing mixture.¹⁻⁴ However, it is found experimentally that the inclusion of N₂ as one of the gas constituents is beneficial to CO laser performance.⁵⁻⁷ The present analysis of electron energy distribution functions in CO-N₂ mixtures demonstrates a peak in the CO vibrational excitation rate as a function of N₂ partial pressure. These results, when coupled with the sensitivity of CO laser efficiency to CO excitation,¹⁷ may be useful in resolving the discrepancy between theory and experiment.

A similar analysis of CO discharges has been performed in Ref. 20; however, the large partial pressure of He included in the analysis effectively compressed the E/N scale and masked the effects to be discussed in the present case. Using the numerical method described in Ref. 19, a series of calculations have been performed to obtain electron distribution functions as a function of the ratio of applied electric field to molecular number density, E/N, and N₂ partial pressure. The inelastic processes considered and data references used are given in Table I. The numerical solutions projected the distribution function onto 300 energy mesh points separated by intervals of .075 eV. With this resolution, energy

balance to better than one part in 10⁶ was obtained in all calculations. The accuracy of the cross sections was tested by comparing the presently computed transport coefficients in pure N₂ and CO to experimental values.¹⁴⁻¹⁶ Fifteen percent or better agreement was obtained at all points within the E/N range investigated. Figure 1 displays the computed drift velocity, v_d , as a function of the CO fractional concentration, f_{CO} .

Fig. 1. Electron drift velocity, v_d (cm/sec), in CO-N₂ mixtures for selected E/N (volt-cm²) as a function of CO fraction, f_{CO} .

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Notice that the drift velocity in most of the mixtures is larger than in either of the pure gases and reaches a maximum in the neighborhood of 20% CO, 80% N₂ depending weakly on E/N. Since the energy deposition rate in the gas is proportional to v_d (E/N), the maximum excitation per electron is achieved where v_d is maximum.

From the computed electron distribution, $n(\epsilon)$, the binary excitation rate to each vibrational level is determined by

$$R_v = \int_0^\infty n(\epsilon) \sigma_v(\epsilon) v(\epsilon) d\epsilon / \int_0^\infty n(\epsilon) d\epsilon \quad (\text{cm}^3/\text{sec}), \quad (1)$$

where $\sigma_v(\epsilon)$ is the cross section at energy ϵ for excitation of level v , and $v(\epsilon)$ is the velocity of electrons with energy ϵ .

Using the CO excitation rates computed from Eq. (1), the rate of production of CO vibrational energy per electron and per CO molecule is

$$\dot{Q}_{CO} = \sum_v E_v R_v \quad (\text{eV-cm}^3/\text{sec}), \quad (2)$$

where E_v is the energy of the v th vibrational level of CO. The energy deposition rate $\dot{Q}_{CO}$ is displayed in Fig. 2 as a function of f_{CO} for various E/N. Figure 3 displays the partition of the discharge power $v_d \times (E/N)$ among the various energy sinks of the gas. One observes that over the range of E/N investigated most of the energy goes into vibrational excitation, and furthermore for f_{CO} as low as 0.15, 80% of the discharge power is still being dissipated in CO vibrations at $E/N = 2. \times 10^{-16}$ V-cm².

To define the optimum CO-N₂ mixture, the excitation rate $\dot{Q}_{CO}$ must be weighted by the fraction of CO present in the gas. The resulting product, $f_{CO} \dot{Q}_{CO}$ as a function of f_{N_2} , is displayed in Fig. 4 and represents the rate of CO vibrational energy generation per electron and per molecule of gas. It is found that the maximum rate of CO excitation occurs for $f_{CO} = 0.3$ at $E/N = 1.5 \times 10^{-16}$ volt-cm² and increases to $f_{CO} = 0.6$ as E/N is increased to

Fig. 2. CO vibrational energy production rate $\dot{Q}$ (eV/cm³/sec) per molecule and per electron for selected E/N (volt-cm²) as a function of CO fraction, f_{CO} .

4×10^{-16} volt-cm². In each case the peak excitation rate is approximately 30% greater than the rate of excitation in pure CO. Since the optimum fraction of CO increases with increasing E/N, pin-type lasers and others which run at relatively high E/N may operate best with little or no N₂ present.

The increase in CO excitation and electron drift velocity is a result of an increase in the number of electrons in $n(\epsilon)$ which penetrate the barrier presented by the CO vibrational levels. From Eq. (1) note that R_v depends on the overlap of $n(\epsilon)$ and $\sigma_v(\epsilon)$. In the CO, σ_v is larger in magnitude and has a lower threshold than in N₂.⁸ Hence, starting with pure CO and adding N₂, the vibrational barrier is initially diluted enough to allow greater overlap between the electron distribution and CO vibrational cross sections. This trend continues until the optimum CO/N₂ ratio is reached. Beyond this point, further addition of N₂ results in a net decrease of the vibrational barrier owing to the

Fig. 3. Partition of discharge power for CO/N₂ mixtures as a function of E/N. Two limiting mixtures are shown. The solid lines are for 80% CO, 20% N₂, while the broken lines depict 15% CO, 85% N₂.

Fig. 4. CO vibrational energy production rate per molecule of gas, $f_{CO} Q$, for selected E/N (volt-cm²) as a function of the N₂ fractional concentration, $f_{N_2} = (1 - f_{CO})$.

smaller σ_v 's in N₂ leading in turn to a net decrease in energy deposition within the gas. It should be noted that the addition of N₂ to CO will not degrade electron beam ionization efficiency since both molecules have the same mass and comparable ionization potentials.

Figure 5 shows the calculated sensitivity of the CO laser to the energy input per CO molecule. This curve was derived numerically using the techniques of Ref. 1 and has been presented in Ref. 17. The threshold for efficient operation is seen to decrease with temperature from a value of ~700 J/liter atm or about 0.2 eV/CO molecule at 300°K to ~300 J/liter atm at 200° K. The existence of this threshold can be understood as a requirement to produce a certain population of low-lying vibrational states before anharmonic pumping can establish an energy flow to the higher levels from which lasing occurs. With this predicted sensitivity to energy input per CO molecule, the modest dependence of CO pumping on N₂ concentration shown in Fig. 4 may be reflected by a much greater variation in laser output.

In conclusion it has been shown that the rate of energy deposition in the plasma is markedly increased by the addition of N₂ while the fractional power transfer to CO vibrations is large and remains essentially constant for the parameter range studied. Due to the expected sensitivity of CO laser operation on the excitation per molecule this

Fig. 5. Calculated efficiency of a CO laser as a function of the energy input per CO molecule.

increase in energy deposition may be magnified in laser output. It is thus suggested that with N_2 -CO vibrational energy transfer rates as slow as those given in Ref. 18 and employed in Refs. 1-2, the principal role played by N_2 in the CO laser is to adjust the characteristics of the electrical discharge for optimum vibrational excitation of CO.

TABLE I
MOLECULAR PROCESSES AND REFERENCES

Species	Momentum Transfer	Vibrational Excitation	Electronic Excitation	Dissociative Attachment	Impact Ionization
N_2	9	8,9	9	-	10
CO	11	8,11	12	13	10

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