TECHNICAL REPORT

VIBRATIONAL POPULATION DISTRIBUTIONS IN NONEQUILIBRUIM NOZZLE EXPANSION FLOWS

By: William S. Watt and Joseph W. Rich

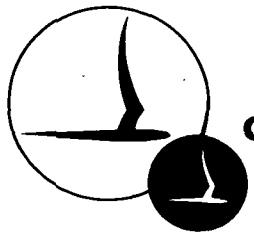## CAL No. RM-2731-A-1

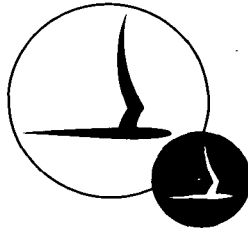## CORNELL AERONAUTICAL LABORATORY, INC.

OF CORNELL UNIVERSITY, BUFFALO, N.Y. 14221

CORNELL AERONAUTICAL LABORATORY, INC.
BUFFALO, NEW YORK 14221

VIBRATIONAL POPULATION DISTRIBUTIONS IN NONEQUILIBRIUM NOZZLE EXPANSION FLOWS

FINAL REPORT

CAL Report No. RM-2731-A-1
Contract No. NASW 1843
May 1971

Prepared for:

Headquarters
National Aeronautics and Space Administration
Fluid Dynamics Branch, Code RRF
Washington, D.C. 20546

PREPARED BY: _William S. Watt_
William S. Watt

APPROVED BY: _Charles E. Treanor_
Charles E. Treanor
Head, Aerodynamic
Research Department

Joseph W. Rich
Joseph W. Rich

FOREWORD

ABSTRACT

Experimental measurements and theoretical calculations of the vibrational-population distribution in nonequilibrium nozzle expansion flows of gas mixtures are reported. These studies were directed toward determining whether vibrational-energy exchange pumping could lead to laser action on the vibrational bands of a diatomic molecule. Three different types of experiments were conducted. These showed (a) that vibrational energy was preferentially transferred from N_2 to CO in supersonic nozzle flows containing these gases; (b) that under some conditions this vibrational-energy exchange pumping mechanism created population inversions in the vibrational levels of CO and (c) that at large expansion ratios the magnitude of these population inversions was sufficient to sustain lasing in the nozzle. A theoretical model was developed to calculate vibrational-state population distributions in gas dynamic expansions of a mixture of diatomic gases. Although only isothermal calculations have been completed, these data indicate that population inversions are predicted for conditions similar to those obtained in the nozzle expansion flows.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Cont.)

I. INTRODUCTION

Vibrational energy is exchanged between molecules at a rapid rate and, in general, this process maintains or tends to establish Boltzmann distributions throughout the vibrational energy states of molecules. These exchange processes make no appreciable contribution to the overall vibrational energy, but can affect the distribution of this energy during vibrational relaxation.[1] This report summarizes the results of experimental and theoretical studies which were directed toward examining the nature of the population distribution produced by vibrational energy exchange processes. These include the exchange of vibrational quanta among different species and also the exchange of vibrational quanta among the vibrational states of an individual species.

It was first shown theoretically[1] that vibrational energy exchange could result in non-Boltzmann vibrational distributions in anharmonic molecules. This effect was greatest for conditions where a high degree of vibrational excitation and a low translational-rotational temperature occurred. Such a situation is achieved in supersonic flows expanding from a high-temperature plenum. In the supersonic flow environment the energy in translation is insufficient to maintain the same vibrational temperature among molecular species; as a result vibrational energy exchange tends to distribute a larger fraction of the energy into the species with the smaller vibrational energy spacing. In particular, for a binary mixture where the molecules are viewed as harmonic oscillators the gases have been shown[2,3] to attain Boltzmann-like vibrational distributions at vibrational temperatures T_{v_1} and T_{v_2} related by

$$\theta_1 / T_{v_1} - \theta_2 / T_{v_2} = (\theta_1 - \theta_2)/T \qquad (1)$$

Here θ_1 and θ_2 are the characteristic vibrational temperatures of the molecules and T is the local translational temperature. By inspection, it can be seen that the difference between T_{v_1} and T_{v_2} can be large

when T_{v_1} and T_{v_2} are much greater than T and when $(\theta_1 - \theta_2)$ is comparable to T. Equation (1) predicts that in supersonic flows of a mixture of CO and N_2, the species with the lower characteristic vibrational temperature, CO, will gain energy at the expense of the species with the higher characteristic vibrational temperature, N_2.

In addition to mixtures of gases where nearly resonant interspecies vibrational energy transfer occurs, the theory predicts[1] that vibrational exchange among the vibrational states of an anharmonic oscillator can result in preferential population of the upper states at the expense of the lower states. Again, the conditions of high vibrational energy, comparable to the characteristic vibrational temperature if the distribution were Boltzmann, and low translational temperature are required. Indeed for certain conditions the theory predicts partial or total population inversions among some vibrational states.

These theoretical predictions have recently been verified by the production of high-power cw lasing on the vibrational bands of carbon monoxide in a supersonic-nozzle expansion flow.[4,5] These observations, which were first made by McKenzie[4] and independently at CAL[5] (and are reported in detail below), have been made for flows which do not contain nitrogen or other diatomic species[5] as well as those in which interspecies vibrational-energy exchange between nitrogen and the CO is allowed.[4,5] In addition the developers of the N_2^* - CO flow laser[6] and the direct-discharge-excited CO laser[7] recognize that the vibration-vibration exchange mechanism is most likely operative in these systems. Subsequent experimental[8,9] and analytical work[8,10] has tended to support these hypotheses.

The experimental work described below was initially concerned with the measurement of CO population distributions in nozzle-expansion flows of CO in nitrogen. The results of this investigation show that nitrogen transfers vibrational energy to CO as predicted[10] by Eq. (1). The data also indicated that the magnitude of the effect was sufficient to cause population inversions among the upper vibrational levels of the CO. Subsequent experiments demonstrated that population inversions could indeed be created and that these could sustain laser oscillation.[5]

The apparatus and experimental techniques used are described in Section II, and the results obtained are discussed in Section III. Supporting theoretical work and analytical calculations are presented in Section IV.

II. APPARATUS AND EXPERIMENTAL TECHNIQUES

The data were obtained by several experimental techniques which are described below. In each case however the observations were made of supersonic-nozzle flows expanding from a reflected-shock heated gas supply.

1. Shock Tube and Nozzle

A conventional shock tube with 2-1/2" square cross section was used to process the gas. High-pressure helium or hydrogen was used to generate the shock waves and the conditions of temperature, density and pressure behind the reflected shock wave were calculated from the measured incident shock velocity. The shock tube was separated from the nozzle by a thin copper diaphragm which bursts upon experiencing the pressure pulse created by the reflected shock. The nozzle flow is thus initiated and remains quasi-steady for approximately 2 msec.

The conical nozzle has a 7.5° half angle and a 0.375" diameter contoured throat. Optical ports are provided at local-to-throat geometric area ratios $A/A^* = 8$, 32, 128, 256 and 512. These can be fitted with optical windows or laser mirrors which allow observations throughout the spectral region from 0.12 μm to 12 μm. The nozzle exit is connected to a large dump tank which prevents the pressure in the nozzle from rising during the test-flow period. A photograph of the end of the shock tube, the nozzle and dump tank is shown as Fig. 1. This illustration shows the experimental setup for the laser amplification experiments described below.

2. Gases

Research grade gases were used for the test-gas mixtures. No additional purification steps were taken. The gas mixtures were prepared in a stainless steel mixing tank and agitated by means of a magnetic stirrer for about one hour prior to loading the shock tube.

3. Experimental Techniques

a. Band Reversal Spectroscopy

For measuring the CO vibrational temperature in flows of CO in nitrogen, the technique of band-reversal spectroscopy was used. This technique had previously been developed at CAL for measuring the vibrational temperature of infrared-active molecules in shock-wave and nozzle-flow environments.[11-13] Details of the optical apparatus, background radiation source, spectroscopic technique and method of data reduction to obtain vibrational temperatures are given in Ref. 11. The method consists of measuring the relative emission and absorption intensities of the CO over a narrow spectral region ($\sim 0.1\mu$) centered at 4.6μ. This spectral region is isolated by using infrared filters.

In the present experiments it was found that the use of separate optical channels for the emission and absorption measurements proved difficult for low radiant intensities. Thus a modulated beam method was devised to provide relative emission and absorption intensities using a single optical channel.

The method essentially consists of viewing a background radiation source of known temperature through the test gas. The radiation from the background source is successively interrupted by means of a mechanical chopper prior to entering the test section. When the background source is shielded from the test section by the chopper, the observed radiant intensity corresponds to the emission by the test gas; when the background source is exposed, the observed radiant intensity corresponds to absorption of the test gas relative to the brightness temperature of the background source over the particular spectral region. In this way, the relative emission/absorption intensities can be alternately recorded photometrically in a single optical channel.

An example of the data obtained by modulated-beam band-reversal spectroscopy is shown in Fig. 2. The radiation is monitored by a liquid-nitrogen cooled In:Sb photovoltaic detector whose output is amplified and displayed on an oscilloscope. The detector response to the background

radiation source prior to flow arrival is labeled I_o. Arrival of the gas flow is signified by the observed emission of the gas I_{em} and the relative intensity of the gas w. r. t. the background radiation source I_{abs}. This latter signal may indicate a net absorption if the test gas is at a lower temperature than the background source or, as in the case shown, may indicate a net emission if the test gas is hotter than the source.

In order to reduce the experimental data to vibrational temperature, the effective brightness temperature of the background radiation source in the spectral region of interest is required. This is most conveniently obtained by measuring the relative emission and absorption intensities of a gas sample at a known temperature. By using a gas sample prepared in the equilibrium region behind an incident shock wave, the source brightness temperature can be determined in situ and optical losses due to reflection and absorption by window materials, etc. are accounted for. More detailed descriptions of these calibration experiments are given in Refs. 11 and 12.

The infrared filters isolate the radiation from a number of rotational transitions in the CO fundamental. Due to anharmonicity, this means that the technique is sensitive only to the population distribution in the lowest energy levels. However, since most of the molecules are in these levels, an accurate measurement of the total energy in vibration is obtained although no information is gained about the population distribution in the upper levels. This is exemplified by the observation of inversions in these upper levels which correspond to much higher vibrational temperatures than indicated by band-reversal measurements for similar gas conditions.

4.   Laser Amplification Experiments

To search for population inversions in expanding flows of CO , several techniques were available. The one chosen was to incorporate the nozzle into the optical cavity of a discharge-excited CO laser and to observe the effect of the nozzle flow on the overall laser output.

The experimental arrangement is shown in Fig. 1. The discharge tube and totally reflecting laser mirror are located on one side of the nozzle

6

with the output coupling mirror and detection scheme on the other. The optical axis of the laser is aligned to pass through the nozzle at a given observation station which is fitted with calcium fluoride windows.

Before firing the shock tube to generate the reservoir of gas which feeds the nozzle flow, the CO laser is ignited and aligned. At this point the nozzle is evacuated to $\sim 3 \times 10^{-5}$ torr. When the nozzle flow is initiated, the CO-containing mixture flows down the nozzle and, depending on the vibrational distribution of the CO, acts as a lossy element, gain element or transparent element within the laser cavity. Correspondingly the laser output is observed to decrease, increase or remain unchanged.

The advantage of this technique is that it provides a means of detecting small inversion levels which would not be large enough to provide sufficient gain to overcome practical cavity losses. These measurements are more useful than a lasing-no lasing decision and allow the optimization of the gas temperature and pressure before self-sustained laser oscillation is attempted.

This method, however, has the disadvantage that it allows monitoring only of population differences in the gas flow corresponding to transitions which are above or close to threshold in the discharge. As is now known, the nozzle flow is predominantly inverted on lower vibrational transitions than the discharge. Nevertheless these gas conditions which were found to be optimum for laser amplification, were also found to induce lasing and thus provided a valuable starting point for the self-sustained lasing study.

5.   Laser Oscillation

To provide an optical cavity within the nozzle, highly reflecting 0. 5" diameter laser resonators were installed perpendicular to the flow. These were mounted only in the $A/A^* = 512$ observation plane which provides a cavity approximately 20 cm long. The mirrors consist of a gold-coated 4 meter radius concave reflector and a gold-coated germanium flat. Output coupling of approximately 3% was provided by leaving a central hole in the gold coating of the germanium substrate.

7

The mirrors were placed with the downstream edge essentially flush with the nozzle wall. This minimizes the possible "dead gas" volume between the mirror and the main gas flow. The proximity to the flow has not resulted in any detectable damage to the mirror surfaces.

Laser power was determined by monitoring a fraction of the output intensity with Ge:Au detectors. A calibration was provided by comparison of the output measured with this detector against that from a cw electric-discharge CO laser of known power.

III.   RESULTS AND DISCUSSION

1.   Band-Reversal Measurements

In nozzle expansion flows of a mixture of CO in N_2 , theory predicts[1-3, 14] that vibrational energy is preferentially transferred from the N_2 to CO . In addition, the magnitude of the vibrational temperature difference which results from this effect is predicted to increase as the translational temperature of the flow decreases.   Thus, since the nitrogen vibrational energy freezes during the expansion process, the CO vibrational temperature should increase as the flow proceeds down the nozzle.

Band-reversal spectroscopy at 4. 6μ was used to measure the vibrational temperature of CO in nozzle expansion flows of 5% CO in N_2 . These measurements were made at nozzle area ratios A/A^* of 8 and 32, for gas mixtures which were processed by the reflected shock to temperatures in the range 2400 - 3400°K.   Pressures behind the reflected shock were maintained in the range 130 - 145 atmospheres.

The CO vibrational temperatures obtained are shown in Fig. 3, where the gas temperatures are given as the ratio of their observed value divided by the reflected-shock reservoir temperature.   Although there is some scatter in the data, it is immediately evident that the CO temperatures measured at A/A^* = 32 (■) are higher than those obtained at A/A^* = 8 (□) and in some cases are higher than the original reservoir temperature.

Similar results have been obtained elsewhere[3] in the expansion of CO - N_2 gas mixtures in a two-dimensional nozzle.   There the CO vibrational temperature was determined by monitoring the infrared emission from the CO first overtone at 2. 3 μm.

In Fig. 4 are shown the N_2 vibrational temperatures inferred from the measured CO temperatures by means of Eq. (1).

$$\theta_1/T_{v_1} - \theta_2/T_{v_2} = (\theta_1 - \theta_2)/T \qquad (1)$$

Here θ_1 and θ_2 are the characteristic vibrational temperatures of N_2 and CO , T_{v_1} and T_{v_2} are the vibrational temperatures of N_2 and CO and T is the translational temperature.

The inferred N_2 temperatures at $A/A^* = 32$ are seen to be similar to those obtained at $A/A^* = 8$, thus indicating that the N_2 vibrational temperature is frozen upstream of $A/A^* = 8$. However, as shown by the increase in the CO temperatures, vibrational energy exchange occurs between $A/A^* = 8$ and $A/A^* = 32$.

Previous measurements of N_2 vibrational relaxation at CAL[12, 13, 15-17] have suggested that in nozzle-expansion flow the relaxation rate was considerably faster than that measured in shock-wave flows. The N_2 vibrational temperatures inferred from the present data are higher than expected from the previous results. This difference is not yet accounted for[*] but in any case, does not affect the conclusions drawn concerning the V-V pumping data.

From the measured CO vibrational temperatures at $A/A^* = 32$, the levels in CO having population inversions can be inferred from the theory which was concurrently developed. Table I shows the quantum number, $V_{inversion}$, of the lowest vibrational level for which inversion occurs. It is seen from the table that inversions are predicted above levels

TABLE I

T_O	T	$T_{V_{CO}}$	$V_{inversion}$
2425	367	2520	11
2640	396	2780	11
2815	424	2670	12
2950	443	3100	11
3175	475	2980	12

$V = 11 - 12$, the result being apparently independent of reservoir temperature T_0 over the range investigated.

It is interesting to compare this prediction with the observed lasing levels in the powerful $CO-N_2$ and CO discharge lasers recently developed.[6, 7]

---

[*]However it is noted that the infrared source was calibrated with dual-beam optics as described in Ref. 11 and not with the single modulated beam used in the present experiments.

The developers suggest[6,7] that the pumping mechanism is probably the same V-V exchange process being investigated in these studies. These lasers operate with liquid N_2 cooling of the discharge and typical translational temperatures (T) are of the order of 200°K. The degree of vibrational excitation of CO in the N_2^* - CO flow laser, whose conditions correspond most closely to those here, has been studied by measuring the detailed sidelight spectrum.[6,8,9] Although the distribution was found to be highly non-Boltzmann, the population of the lowest levels (V = 0, 1, 2) was characterized by a vibrational temperature of approximately 3000°K,[6,8,9] which is comparable to those measured here. Under such conditions, the theory would predict the inversion to occur to levels down to V = 6 . This is indeed the behavior observed, since lasing occurs on bands from V = 6 to V = 22 . It is also interesting to note that the density levels in the present device are considerably higher than those which are optimum for the discharge laser.

2.   Laser Amplification Experiments

These experiments were designed to allow population differences in CO-containing nozzle flows to be detected by their effect on the output of a discharge CO laser in which the nozzle was incorporated. Measurements were made at A/A^* = 32 , 128 and 512 to determine the optimum gas composition and reflected-shock reservoir conditions for producing population inversions. At the larger area ratios, the translation-rotation temperature of the gas is further reduced and, as the theory predicts[1-3,14] and the data obtained show, population inversions are produced for a larger range of conditions.

At A/A^* = 32 the best gas mixture found to increase the laser power when the gas flow was initiated was 5% CO - 15% N_2 - 80% Ar and then only for a narrow range of reservoir pressure and temperature. The data are shown in Fig. 5 where the ratio of the laser output during the nozzle flow (I) to that before the gas flow is initiated (I_o) is plotted as a function of reservoir temperature. Thus values of I/I_o > 1. 0 indicate a population inversion in the expanding gas flow. Examination of the data in Fig. 1

11

indicates that a population inversion is produced at this area ratio for gas mixtures whose reservoir temperature is in the range 3850°K - 4350°K and whose reservoir pressure is about 90 atmospheres. At pressures above and below this value the laser output was always reduced by the arrival of the gas flow.

An explanation for the observed temperature dependence is that at higher reservoir temperatures the translational-rotational temperature at $A/A^* = 32$ is too high for inversions to be created, whereas at lower initial temperatures there is insufficient energy stored in vibration. The pressure dependence presumably indicates that at pressures above 90 atmospheres V-T relaxation processes reduce the vibrational energy below the threshold value, while at pressures below 90 atmospheres there are insufficient collisions to allow the vibrational energy pumping mechanism to produce a population inversion.

Other gas mixtures which were used were 20% CO - 80% Ar, 5% CO - 95% N_2 and 5% CO - 45% N_2 - 50% Ar. In all cases, nozzle flows containing these gas mixtures were found to decrease the laser output.

At $A/A^* = 128$, similar results were found for the 5% CO - 15% N_2 - 80% Ar mixture. The data are shown in Fig. 6. While the same qualitative interpretation of the temperature and pressure dependencies can be given as in the above discussion, two features of the data should be noted. The first is that the maximum output is observed for a lower reservoir temperature and secondly that the population inversion in the gas flow is not increased by the reduction in translational-rotational temperature between $A/A^* = 32$ and $A/A^* = 128$. These observations may indicate that for the conditions of these experiments, the population inversion is limited by vibration-translation energy exchange among the upper levels. The rate of these processes increases with increasing vibrational quantum number and hence their freezing point in the nozzle occurs considerably farther down-stream than the freezing point corresponding to vibration-translation exchange of the lowest levels. Thus the magnitude of the population inversions is restricted until V-T freezing occurs among the relevant levels.

12

The data for 5% CO - 15% N_2 - 80% Ar at $A/A^* = 512$ are shown in Fig. 7. Here an increase in lasing was observed at all temperatures and pressures investigated with the maximum increase again at reservoir conditions of $\sim$ 4000°K and $\sim$ 89 atmospheres. The magnitude of the increase is twice that of the original laser output which is to be compared with the $\sim$ 25% increase at smaller expansion ratios.

This dramatic increase in the magnitude of the inversion, and the range of conditions for which inversion can be obtained, is due to the lower translational temperature at $A/A^* = 512$. The decrease in translational temperature allows not only more efficient vibrational-exchange pumping, and thus larger inversions, but also allows inversions to be created among a greater number of vibrational states. As will be seen later, this latter feature also enhances the sensitivity of the present technique by matching the inverted levels in the nozzle more closely to those inverted in the cooled discharge.

Increased laser output is also observed at $A/A^* = 512$ for 5% CO in nitrogen. The data are shown in Fig. 8. For this mixture the optimum reservoir conditions for increased lasing are 1900°K and $\sim$ 90 atmospheres, for which an increase in laser output of 67% was observed. At lower pressures the magnitude of the inversion is expected to be reduced and the data confirm this prediction. Indeed an increase in laser output at 45 atmospheres is found only for a reservoir temperature of 1750°K. At higher pressures an initial burst of increased output was followed by a strong decrease during the remainder of the test flow. The sensitivity of these data to reservoir temperature and pressure, indicates the interdependence of V-T and V-V processes and the translational temperature on the inversion producing mechanism.

Comparing the optimum conditions at $A/A^* = 512$ for these two gas mixtures, it is noted that the reservoir pressures are essentially equal. Although the reservoir temperatures are $\sim$ 4000°K and 1900°K, respectively, the translation-rotation temperature at $A/A^* = 512$ is $\sim$ 100°K in each case. In addition both gas mixtures have approximately the same

total energy in vibration at the equilibrium reservoir condition. Hence the better performance of the mixture containing argon would appear to be due to the lower vibration-translation energy loss probability in this gas.

As has already been pointed out, the technique allows monitoring only of the inverted transitions in the nozzle flow which correspond to transitions at or near threshold in the discharge. To identify the lasing transitions from the discharge, its output was scanned by a 0.5-meter Czerny-Turner spectrometer which has a grating blazed at 5 microns. Transitions between the rotational sublevels of adjacent vibrational states were observed from $V = 7$ to $V = 6$ up to $V = 13$ to $V = 12$, corresponding to lasing wavelengths of 5.08 - 5.55 microns. In addition, the strongest transitions were from levels $V \geq 10$ and the intensities were a strong function of the discharge current. At 8 mA the $7 \longrightarrow 6$ transition was not observed, but at 6.5 mA this transition reached threshold and at 5 mA lased strongly at the expense of the $13 \longrightarrow 12$ transition. Thus varying the discharge current provides a small measure of selectivity of the vibration-rotation transitions which can be detected.

The effect of varying the discharge current is shown in Fig. 3. It is clear that while the data for discharge currents of 8 mA and 6.5 mA fall within experimental uncertainty, a much larger increase in the laser output is found when the discharge current is lowered to 5 mA. This result suggests that transitions on low vibrational bands are preferentially pumped in the nozzle flow. This agrees well with the data of McKenzie,[4] who has examined the laser output from nozzle flows of similar gas mixtures.

For the optimum gas conditions at $A/A^* = 32$, theory predicts that inversions are created on levels $V \geq 11$. Thus amplification of the discharge output by the nozzle flow would be restricted to transitions originating in these levels, while absorption of the discharge output would presumably occur on levels $6 \leq V < 11$. The observed net increase in output would therefore appear to indicate a considerable inversion among levels $V \geq 11$, to overcome the reduction in power due to absorption among the lower levels. At $A/A^* = 512$, the lower translational temperature allows inversions to be created on levels $v \geq 3$, which corresponds

14

more closely to the levels above threshold in the discharge (ν = 7 to ν = 13). The largest observed output increase is of the order 1 watt, which is to be compared with the laser output of approximately 3 watts for similar reservoir conditions and self-sustained lasing in the nozzle (see Fig. 9). This indicates that at A/A^* = 512 the largest inversions are on transitions $\nu \leq 6$, which is in good agreement with spectroscopic studies of the gasdynamic CO laser.[4]

3.   Laser Oscillation in Nozzle

After installation and optical alignment of the laser mirrors at A/A^* = 512 , experiments were initiated with the 5% CO - 15% N_2 - 80% argon gas mixture. Lasing was immediately observed for the optimum conditions of temperature and pressure (3900°K and 90 atmospheres) which were found for the amplification experiments reported above. To verify that the radiation was indeed laser output, the spontaneous emission was measured by replacing one of the laser mirrors by a CaF_2 window. The result was to reduce the intensity of the output by at least four orders of magnitude.

Further experiments indicated that lasing was also obtained for reservoir temperatures and pressures in the range 2100°K to 3900°K and 50 - 100 atmospheres. These few qualitative experiments indicated that the lasing output was greatest for temperatures near 2100°K and pressures of 100 atmospheres. These results agree well with the findings of McKenzie[4] who has also studied this gasdynamic lasing system.

Steady laser output was observed for the 2 msec duration of the main test flow. In addition, for the temperatures below 3000°K where helium was used as the shock-tube driver gas, lasing continued for up to 10 msec. This is attributed to further cooling of the test gas by mixing with helium at the test gas-driver gas interface. Although the laser output was lower during this mixing process, the major fraction of the total energy was radiated during this time.

The major emphasis of this phase of the experimental program was then directed toward determining whether lasing could be obtained for

mixtures of CO alone in argon. Theoretically it has been predicted[1] that as a result of anharmonicity in the CO molecule, vibrational energy could be preferentially transferred from lower to upper vibrational levels under the prevailing conditions of high vibrational energy and low translational and rotational temperature.

Experiments with 20% CO in argon immediately verified the theoretical predictions and lasing was obtained for a wide range of reservoir temperatures and pressures. The data obtained are illustrated in Figs. 9 and 10. In Fig. 9 the effect of reservoir pressure on laser output is shown, and it is seen that the optimum pressure is about 80 atmospheres. The filled data points (●) indicate experiments in which continuous lasing was not observed throughout the duration of the flow, but was observed as a transitory pulse during flow initiation.

The laser output depends on the condition that a large amount of energy is frozen in vibration and the collision frequency at $A/A^* = 512$ is sufficient to maintain vibrational energy exchange among the CO molecules. For a given reservoir temperature, the amount of energy frozen in vibration decreases with increasing pressure, while the collision frequency is directly proportional to the pressure. Thus the falloff in performance at pressures above 80 atmospheres is probably due to increased vibration-translation losses which reduce the energy content of the vibrational mode. However the magnitude of the falloff is greater than would be expected from the overall CO-argon V-T rate. A possible explanation for this would be that the population inversion is limited by V-T losses among the upper levels which processes are faster than the overall V-T rate.

The falloff in output at pressures below 80 atmospheres is due to fewer vibration-vibration exchange collisions which eventually produce an insufficient inversion to overcome the cavity losses. Using Bray's freezing criterion,[18] an estimate of the probability (p) of vibration-vibration exchange in a collision between CO molecules can be made from the falloff in power at low pressure. The value obtained, $p \approx 5 \times 10^{-3}$, is in good agreement with Mahan's long-range multipole interaction theory,[19] which

16

has been shown to be important[20] for the low translational temperatures of the present experiments.

The effect of reservoir temperature, at reservoir pressures near 80 atmospheres, is shown in Fig. 10. There it is seen that the output power increases by a factor of six as the reservoir temperature is decreased from 4000°K to 2000°K. This indicates the strong dependence of lasing on the translational temperature, which drops from about 100°K to about 50°K at $A/A^* = 512$ as the reservoir temperature falls from 4000°K to 2000°K. The lower translational temperature more than compensates for the concurrent loss of vibrational energy stored in the gas. This large effect on the output, as a result of lowering the translational temperature, is due to inversion being possible on not only a large number of vibrational states but also among more rotational levels in these states.

Steady lasing throughout the test-flow duration was observed below 4000°K; above this temperature lasing was confined to the initial portion of the flow. Again, when helium was the driver gas, lasing continued for as much as 14 msec due to further cooling by mixing with the driver gas at the test gas-driver gas interface.

The maximum laser power was 20 watts from a gas mixture which had been processed to 85 atmospheres and approximately 2000°K. The efficiency of the present system, based on the power output compared to the total enthalpy flow rate is between 0.01% depending on the initial gas conditions. The principal reason for this low efficiency is that most of the input energy is used in heating the translational and rotational modes of the gas and cannot be recovered as laser output. Of the energy which is frozen in vibration as a result of the nozzle expansion, 1% to 10% appears as laser output if allowance is made for the portion of the flow that does not pass between the mirrors.

In the present system, the mirror losses, including the coupling, are at least 7%. Thus for the 20 cm cavity length, the gain is estimated to be 0.002 cm^{-1}. This is comparable to that which has been measured for the electrically-excited liquid nitrogen-cooled CO laser.

17

While gasdynamic cooling gives the advantage of lower translational temperature than liquid nitrogen cooling, this is outweighed by the equilibrium energy distribution of the reflected-shock heating process and subsequent vibration-translation energy degradation. For example, for the conditions of maximum output, only 3% of the energy placed in the test gas is in the vibrational mode and more than two-thirds of this vibrational energy is lost before the onset of vibration-translation freezing. For electrical excitation, on the other hand, nonequilibrium conditions are immediately established with about half of the absorbed energy being placed in vibration under favorable conditions.[21]

In the electrically excited CO laser, several mechanisms are possible for producing population inversions. These include chemical recombination, electron excitation of the CO vibrational levels, and formation of electronically excited states of CO which decay to vibrationally excited ground state CO . For the equilibrium reflected-shock gas conditions produced in the experiments described here, chemical dissociation, ionization and the formation of electronically excited states in CO are negligible. Furthermore, even if the expanding gas maintained a Boltzmann vibrational distribution at the reservoir temperature with the rotational levels populated at the translational temperature, partial inversions are not produced for the conditions of the present experiments.

Thus the only plausible mechanism for the observed lasing is the vibrational energy exchange pumping scheme first proposed by Treanor et al.[1] Indeed the present results confirm that vibrational exchange among the vibrational states of a single diatomic species leads to preferential population of the upper states and produces inversions among these states.

IV. THEORETICAL

The theoretical phase of the project centered upon calculation of the vibrational-state population distribution at various points in the one-dimensional gas dynamic expansion of a mixture of diatomic gases. The model chosen utilized a one-dimensional, steady, inviscid flow assumption. Attention was confined to a binary gas mixture, and radiative energy loss was neglected. It was assumed that the gas flow was not significantly affected by the nonequilibrium vibrational processes, and hence temperature and density variations in the flow could be calculated from the standard isentropic relations.

The vibrational processes are described by kinetic equations governing the populations of the various participating vibrational states, i.e., a master equation description of the vibrational state populations. The notation adopted is similar to that of Ref. 1, i.e., if n_r is the number density of molecules of species 1 in the r th vibrational state, the governing equation is

$$\frac{dn_r}{dt} = P_{r+1,r}\left[n_{r+1}\,n - exp\left(-\frac{E_{r+1}-E_r}{kT}\right)n_r\,n\right] - P_{r,r-1}\left[n_r\,n - exp\left(-\frac{E_r-E_{r-1}}{kT}\right)n_{r-1}\,n\right]$$

$$+ \sum_s P_{r+1,r;s-1,s}\left[n_{r+1}n_{s-1} - exp\left(-\frac{E_{r+1}+E_{s-1}-E_r-E_s}{kT}\right)n_r\,n_s\right]$$

$$- \sum_s P_{r,r-1;s,s+1}\left[n_r\,n_s - exp\left(-\frac{E_r+E_s-E_{s+1}-E_{r-1}}{kT}\right)n_{r-1}\,n_{s+1}\right] \qquad (2)$$

$$+ Q_{r+1}\left[n_{r+1}N - exp\left(-\frac{E_{r+1}-E_r}{kT}\right)n_r\,N\right] - Q_{r,r-1}\left[n_r\,N - exp\left(-\frac{E_r-E_{r-1}}{kT}\right)n_{r-1}\,N\right]$$

$$+ \sum_R Q_{r+1,r;R-1,R}\left[n_{r+1}N_{R-1} - exp\left(-\frac{E_{r+1}+F_{R-1}-E_r-F_R}{kT}\right)n_r\,N_R\right]$$

$$- \sum_R Q_{r,r-1;R,R+1}\left[n_r\,N_R - exp\left(-\frac{E_r+F_R-E_{r-1}-F_{R+1}}{kT}\right)n_{r-1}\,N_{R+1}\right]$$

Here, N_R is the number density of molecules of species 2 in the R th vibrational state. n and N are the total number densities of species 1 and 2, respectively. $P_{r+1,r} \, n_{r+1,r}$ is the rate of production of r-state molecules from $(r + 1)$-state molecules, where energy is conserved by a change in translational energy (V-T process). $P_{s-1,r+1;s,r} \, n_{r+1} \, n_{s-1}$ is the rate of production of r-state molecules from $(r + 1)$-state molecules, where part of the energy is supplied by the exchange of vibrational energy with the vibrational transitions s-1 $\longrightarrow$ s (V-V process). Because of the anharmonicity, the remainder of the energy in this exchange must be supplied by the translational mode. E_R is the energy of the r th state of species 1, F_R is the energy of the R th state of species 2. The terms in Q are the corresponding transition probabilities for collisions between species 1 and 2. There are similar equations for the time history of N_R.

The energy levels E_r, F_R are calculated using the Morse anharmonic oscillator formula. The quantum state dependence of the specific rates, $P_{r+1,r}$, $Q_{r+1,r}$, etc. is calculated from the expression of Keck and Carrier.[22] The absolute magnitude of these rates is obtained from the Millikan and White[23] correlation for V-T processes, and the Rapp[24] correlation for the V-V processes.

The specific rates are strong functions of translational temperature, T . It is through this dependence, and also through the number densities n and N , that these kinetics equations are coupled to the gas dynamic environment. The mathematical description is therefore in the form of a large set of ordinary, first order differential equations. The system is also "stiff, " in that time scales of greatly varying length are involved in the approach to thermal equilibrium.

The preceding master equations have been programmed for machine solution. The time variation of T , n and N are supplied by a gas dynamic subroutine. The equations are not integrated individually, but an iterative moment method, recently developed by Bray,[14] is used. Bray's calculations were for the nozzle flow expansion of a single diatomic gas; in the present case, the calculation has been extended to a binary mixture.

At a given point in the flow (corresponding to a time t), the distribution functions n_r and N_R are first assumed to be the three-parameter function obtained by Treanor[1,2] to describe the quasi-steady state obtained by rapid V-V exchange among anharmonic oscillators, viz:

$$n_r = n_o e^{-r\gamma - E_r/kT}, \qquad r = 0, 1, 2, \cdots, n \qquad (3)$$

$$N_R = N_o e^{-R\gamma - F_R/kT}, \qquad R = 0, 1, 2, \cdots, m \qquad (4)$$

Among the upper states, where the specific rates are such that V-T processes dominate, the zeroth order iteration is taken to be a Boltzmann distribution at the translational temperature.

The time variation of the parameters n_o , N_o , r , and T is obtained by integration of moments of Eq. (1) and the one-dimensional flow equations. Bray's method,[14] however, provides a means of obtaining the deviation of the distribution from the assumed functional form. Having obtained an approximate time variation of the distribution function from the moment solution, the original master equations are reduced to a set of simultaneous algebraic equations governing the distribution function. These can be readily solved numerically. The corrected distribution function so obtained is then used in an iterative cycle to obtain better approximations both to the time variation of the moments and to the distribution function itself.

Initial runs have been made using the molecular parameters of N_2 (species 1) and CO (species 2). While the program is set up to make calculations in a supersonic nozzle flow, the present runs have been confined to an isothermal case, $T = 700°K = $ const. A value of $r = -3.48$ was chosen; if the molecules were modeled by harmonic oscillators, with the V-T processes neglected, this value of r would correspond to molecular vibrational temperature "$T_{V_{N_2}}$" $= 2500°K$, and "$T_{V_{C_o}}$" $= 3230°K$.

The distribution functions in N_2 and CO , for the above conditions, and after four iterations are shown in Figs. 11 and 12. The zeroth order iteration in this calculation was Eq. (2) for N_2 with n = 20 , and Eq. (3) for CO , with m = 25 ; these distributions are shown by the dotted curves in the figures. (Above the cutoffs at n = 20 and m = 25 , a Boltzmann distribution at 700°K was used.)

The iterative solution shows that this zeroth order choice is a severe underestimate of the populations above n = 20 and m = 25 . Complete convergence has not been obtained for the upper states, although they are tending to a 700° Boltzmann distribution at the highest quantum numbers. This behavior is, of course, consistent with the physics of the problem since V-T processes are extremely rapid among these upper levels. Despite the slow convergence, the general character of the distributions, and the inversion around states $r \approx 20$, is already displayed. The slight "flattening" of the curves in the vicinity of the maximum inversion is, however, almost certainly an artifact of the iterative procedure.

The data in Figs. 11 and 12 also indicate two other features of the preferential partition of vibrational energy into the CO . These are that a larger number of levels are inverted in CO than in nitrogen and that these levels have larger populations than the inverted levels in N_2 . However, spontaneous radiative losses, which have been ignored, would tend to reduce the population in the inverted levels of CO .

The important effect of translational temperature has already been observed in the experimental data. The effect of this parameter on the theoretical calculations is shown in Fig. 13 where the calculated quasi-equilibrium populations of the CO vibrational levels are plotted as a function of translational temperature. There it can be seen that inversions are predicted only at translational temperatures below 1000°K. More dramatic, however, is the effect on the number of levels inverted and the population density in these levels as the temperature is reduced from 900°K to 700°K.

While the conditions chosen for these calculations do not correspond to the experimental data, the effect of lowering the translational temperature

is equivalent to expanding the test gas further in the nozzle. For given reservoir conditions of temperature and pressure, the laser amplification experiments have clearly shown that larger inversions are produced as the translational temperature is lowered.

V.   REFERENCES

1.   C. E. Treanor, J. W. Rich and R. G. Rehm, J. Chem. Phys. $\underline{48}$, 1798 (1968).

2.   C. E. Treanor, Cornell Aeronautical Laboratory, Report AF-2184-A-1 (Oct. 1966).

3.   J. D. Teare, R. L. Taylor and C. W. VonRosenberg Jr., Nature $\underline{225}$, 240 (1970).

4.   R. L. McKenzie, NASA TM X-62,006 (Oct. 1970); Appl. Phys. Letters $\underline{17}$, 462 (1970).

5.   W. S. Watt, Appl. Phys. Letters (to be published June 1971); also data presented herein.

6.   F. Legay, N. Legay-Sommaire and G. Taieb, Can. J. Phys. $\underline{48}$, 1949 (1970) and earlier references cited therein.

7.   R. M. Osgood Jr. and W. C. Eppers Jr., Appl. Phys. Letters $\underline{13}$, 409 (1968); R. M. Osgood Jr., W. C. Eppers Jr. and E. R. Nichols, I. E. E. E. J. Quant. Elec. Q. E. $\underline{6}$, 145 (1970).

8.   J. W. Rich, W. S. Watt and H. M. Thompson, Cornell Aeronautical Laboratory, Report RG-2921-A-1 (May 1971).

9.   J. W. Rich, J. Appl. Phys. (to be published May 1971).

10.   W. S. Watt, results shown in Ann. Rev. Fluid Mech. $\underline{2}$, 386 (1970); also data presented herein.

11.   A. L. Russo, J. Chem. Phys. $\underline{47}$, 5201 (1967).

12.   A. L. Russo and W. S. Watt, Cornell Aeronautical Laboratory, Report AF-2567-A-1 (Nov. 1968).

13.   A. L. Russo, Cornell Aeronautical Laboratory, Report AF-2567-A-2 (Dec. 1969).

14.   K. N. C. Bray, J. Phys. B. $\underline{1}$, 705 (1968); ibid $\underline{3}$, 1515 (1970).

15.   I. R. Hurle, A. L. Russo and J. G. Hall, J. Chem. Phys. <u>40</u>, 2076 (1964).

16.   I. R. Hurle and A. L. Russo, J. Chem. Phys. <u>43</u>, 4434 (1965).

17.   A. L. Russo, J. Chem. Phys. <u>44</u>, 1305 (1966).

18.   K. N. C. Bray, J. Fluid Mech. <u>6</u>, 1 (1959).

19.   B. H. Mahan, J. Chem. Phys. <u>46</u>, 98 (1967).

20.   J. W. Rich and C. E. Treanor, Ann. Rev. Fluid Mech. <u>2</u>, 355 (1970).

21.   W. L. Nighan, Phys. Rev. A <u>2</u>, 1989 (1970).

22.   J. Keck and G. Carrier, J. Chem. Phys. <u>43</u>, 2284 (1965).

23.   R. C. Millikan and D. R. White, J. Chem. Phys. <u>39</u>, 98 (1963).

24.   D. Rapp, J. Chem. Phys. <u>43</u>, 316 (1965).
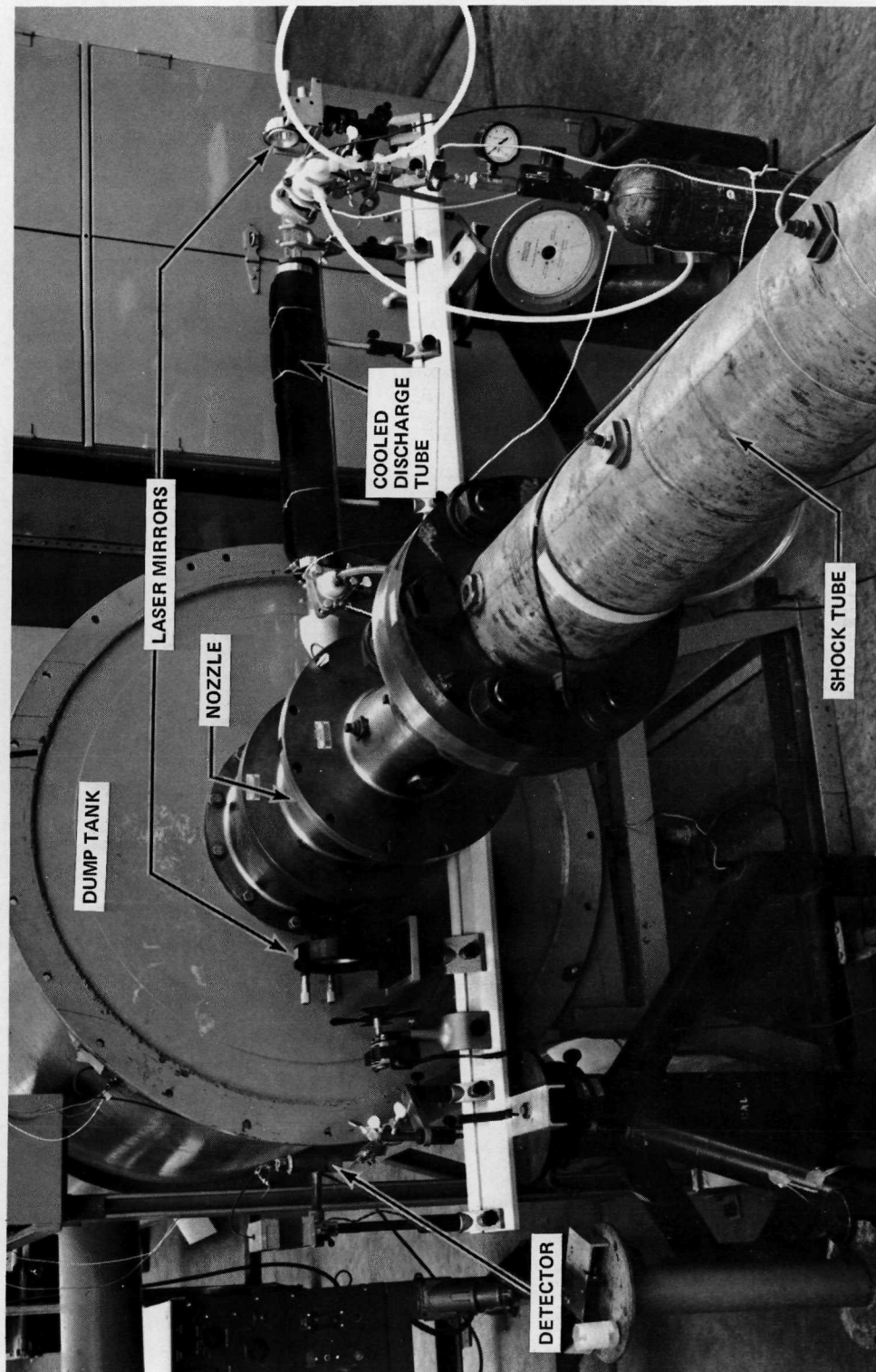
Figure 1   SHOCK TUBE AND NOZZLE INSTRUMENTED FOR LASER AMPLIFICATION EXPERIMENTS
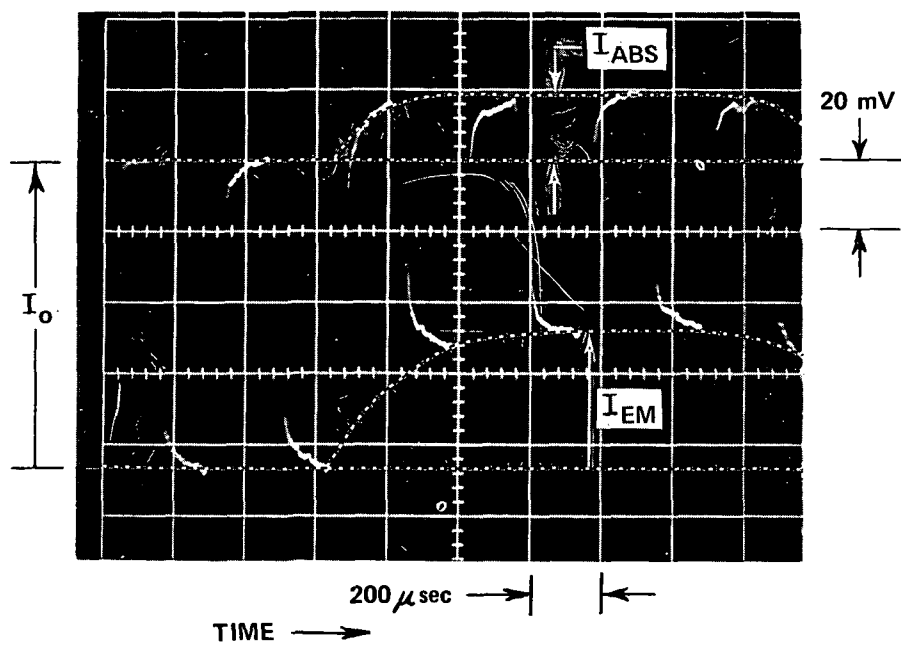
Figure 2 DATA OBTAINED BY MODULATED BEAM
BAND REVERSAL SPECTROSCOPY
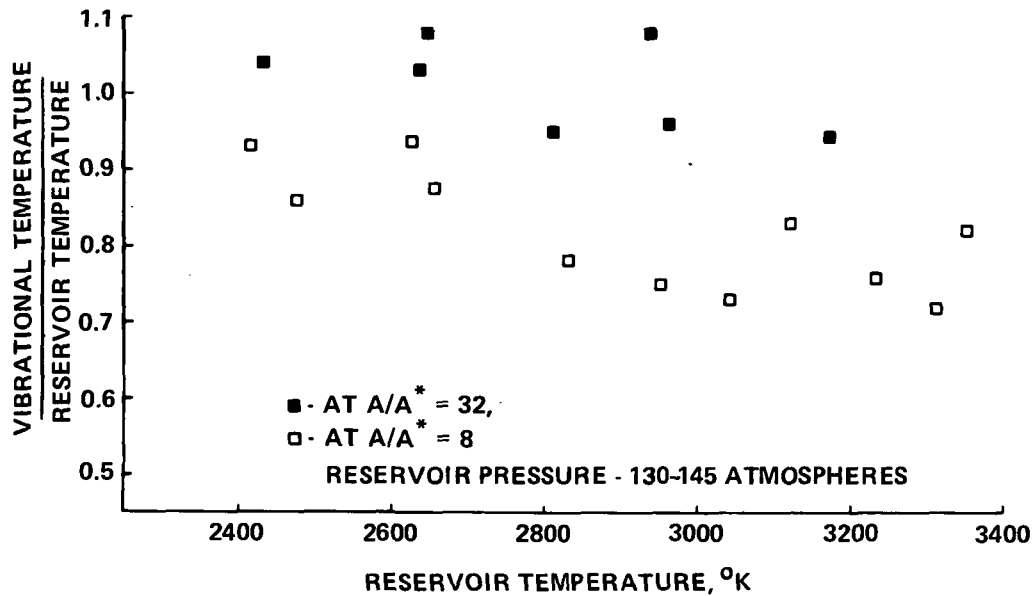
Figure 3 MEASURED CO VIBRATIONAL TEMPERATURES IN NOZZLE FLOWS
OF 5% CO - 95% N_2.
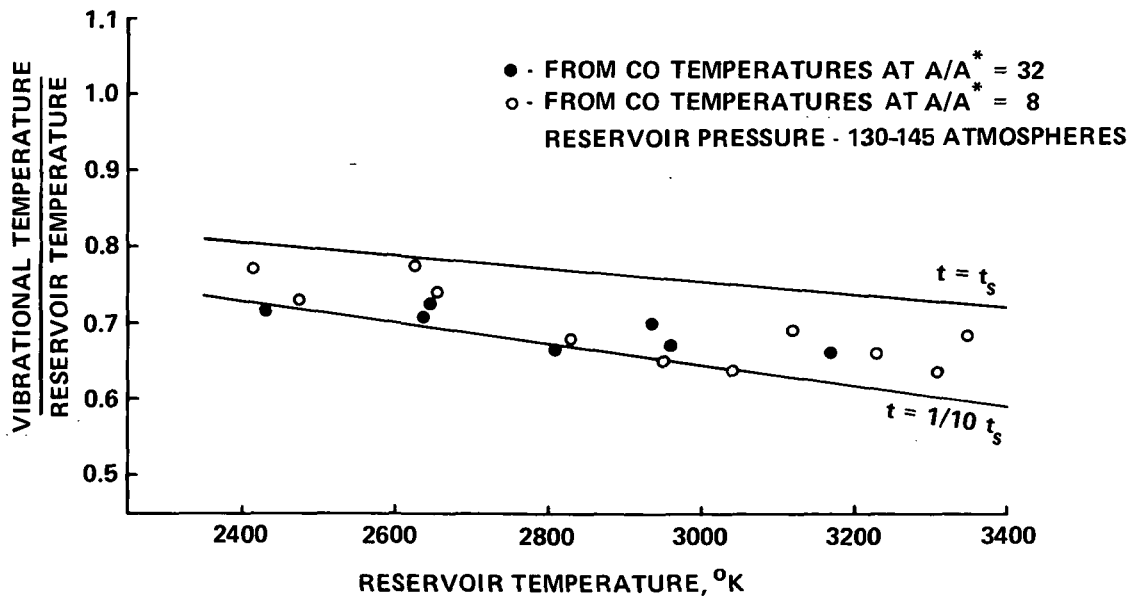
Figure 4 INFERRED N_2 VIBRATIONAL TEMPERATURES IN NOZZLE FLOWS
OF 5% CO - 95% N_2. THE LINES $t = t_s$ AND $t = 1/10$ t_s REPRESENT
CALCULATED VALUES BASED ON THE OBSERVED V - T RATES
IN SHOCK WAVE FLOWS AND TEN TIMES THESE RATES.

28
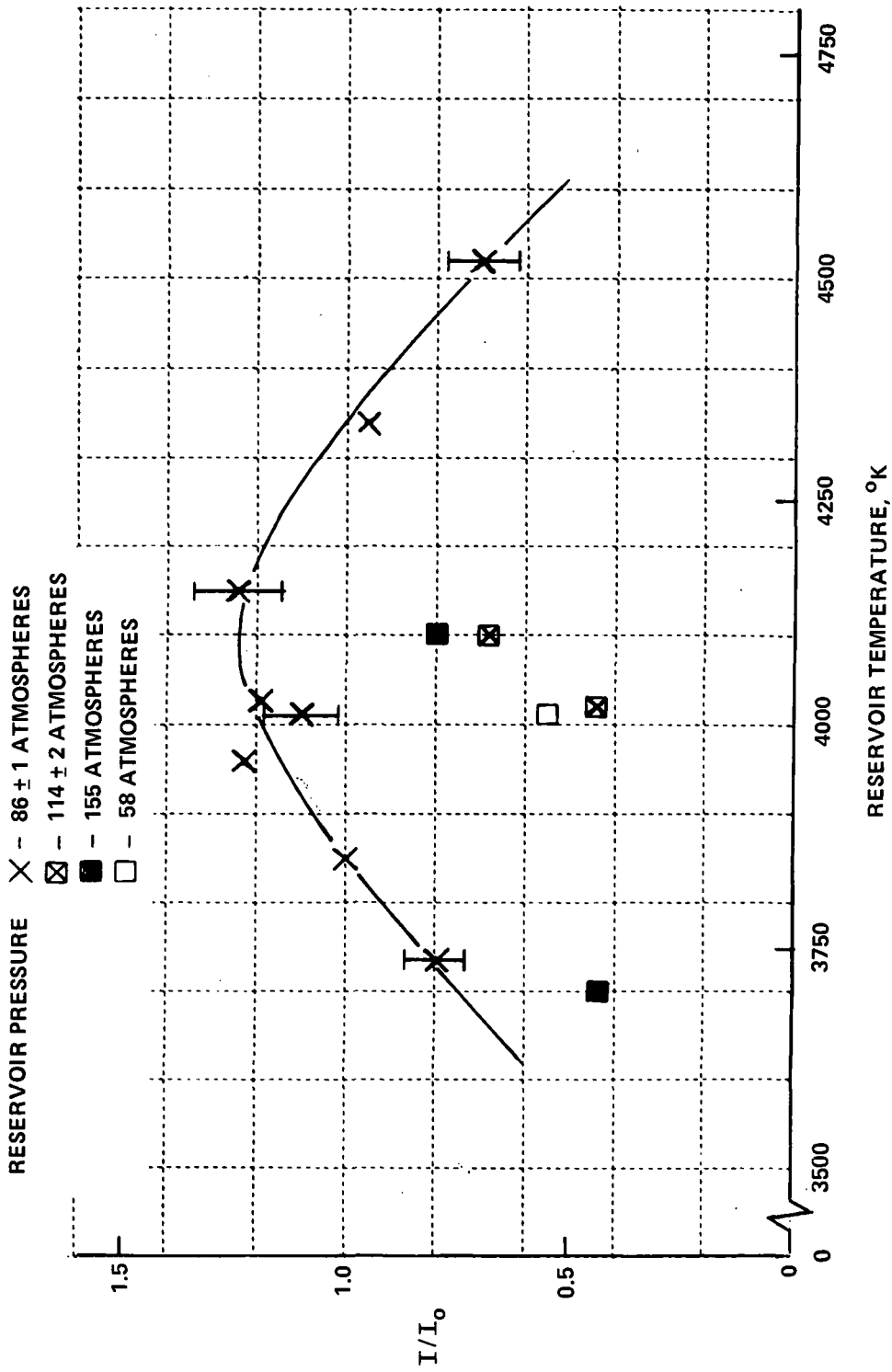
Figure 5   LASER AMPLIFICATION (I/I_o) AT $A/A^* = 32$, AS A FUNCTION OF RESERVOIR TEMPERATURE. AND PRESSURE. GAS MIXTURE: 5% CO - 15% N_2 - 80% ARGON

29
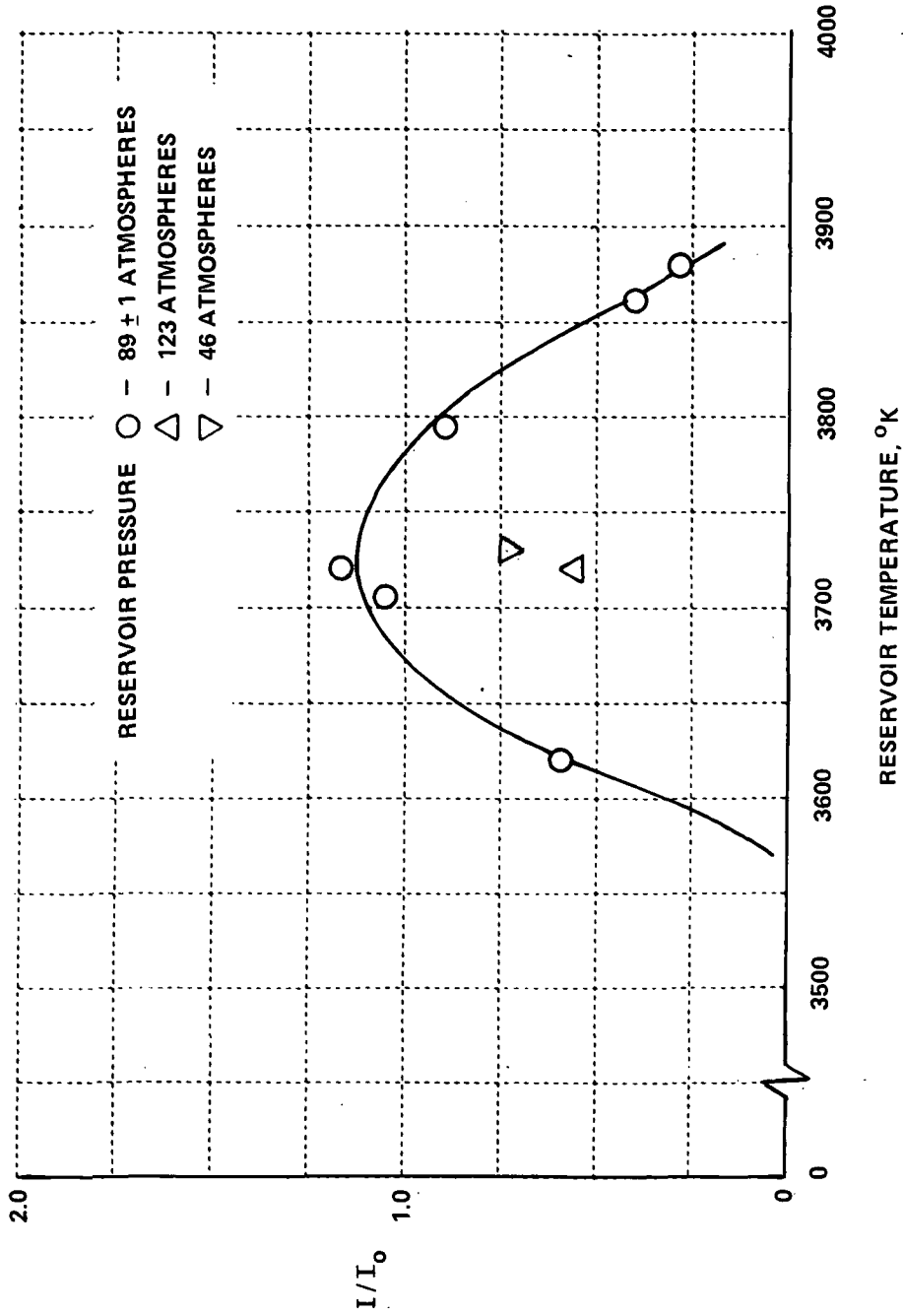
Figure 6   LASER AMPLIFICATION (I/I_o) AT $A/A^* = 128$, AS A FUNCTION OF RESERVOIR TEMPERATURE
AND PRESSURE. GAS MIXTURE: 5% CO - 15% N_2 - 80% ARGON

30
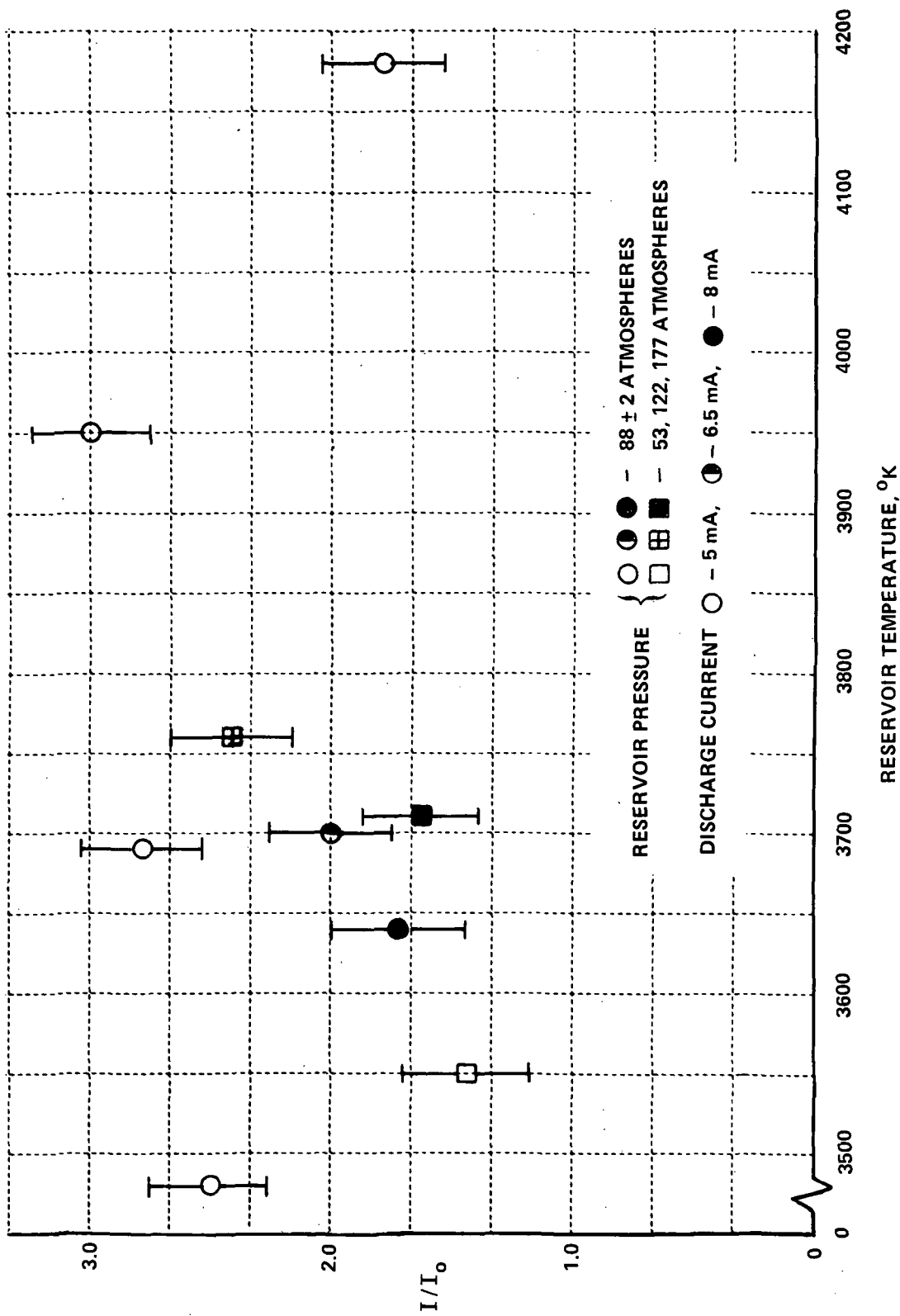
Figure 7 LASER AMPLIFICATION (I/I_o) AT $A/A^* = 512$, AS A FUNCTION OF RESERVOIR TEMPERATURE (T_o) AND PRESSURE (P_o). GAS MIXTURE: 5% CO - 15% N_2 - 80% ARGON. THE EFFECT OF THE LASER DISCHARGE CURRENT IS SHOWN FOR $T_o \approx 3700$ °K AND $P_o \approx 88$ ATMOSPHERES.
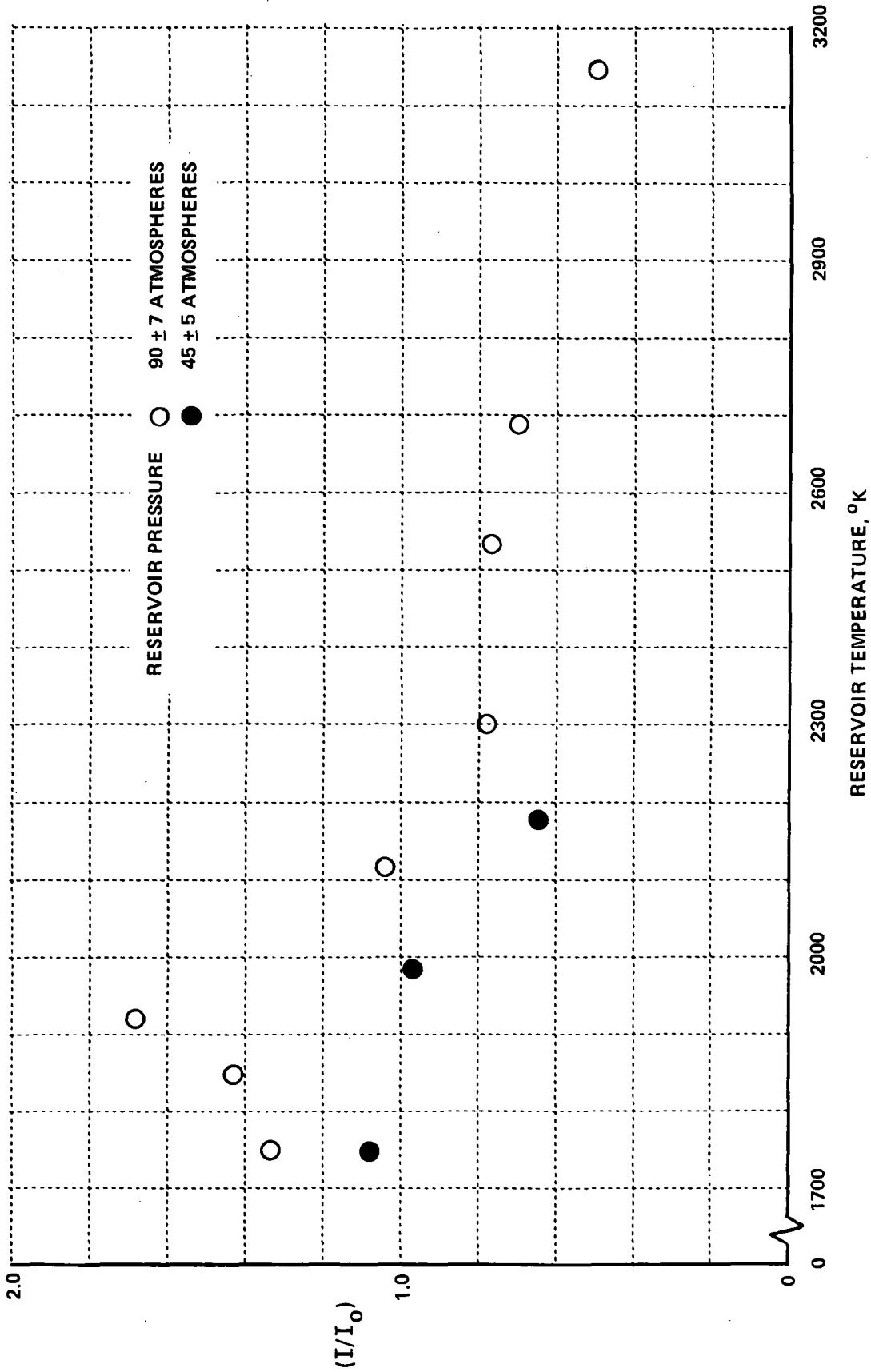
Figure 8 LASER AMPLIFICATION (I/I_o) AT $A/A^* = 512$, AS A FUNCTION OF RESERVOIR TEMPERATURE AND PRESSURE. GAS MIXTURE: 5% CO - 95% N_2.
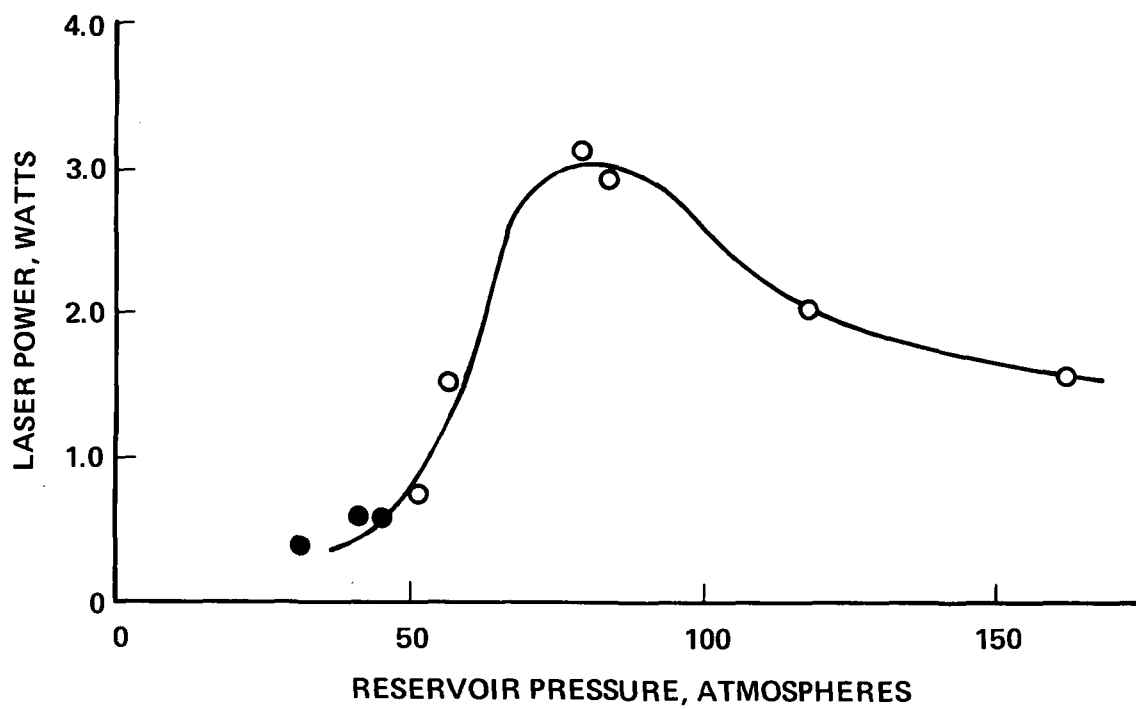
Figure 9 LASER POWER AT A/A* = 512 AS A FUNCTION OF RESERVOIR PRESSURE. RESERVOIR TEMPERATURE WAS 3860 ± 100 °K. O LASING OBSERVED THROUGHOUT THE TEST FLOW. ● - LASING PULSE ONLY DURING FLOW INITIATION.
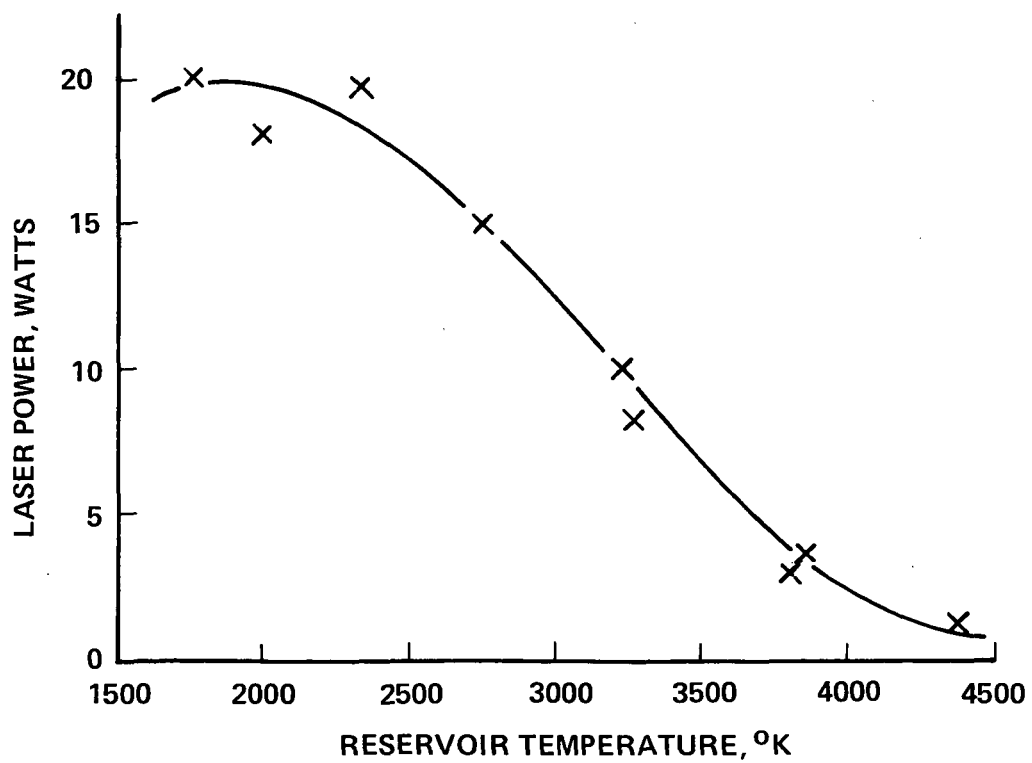
33

Figure 10   LASER POWER AT A/A* = 512 AS A FUNCTION OF RESERVOIR TEMPERATURE. RESERVOIR PRESSURE WAS 83 ± 6 ATMOSPHERES.
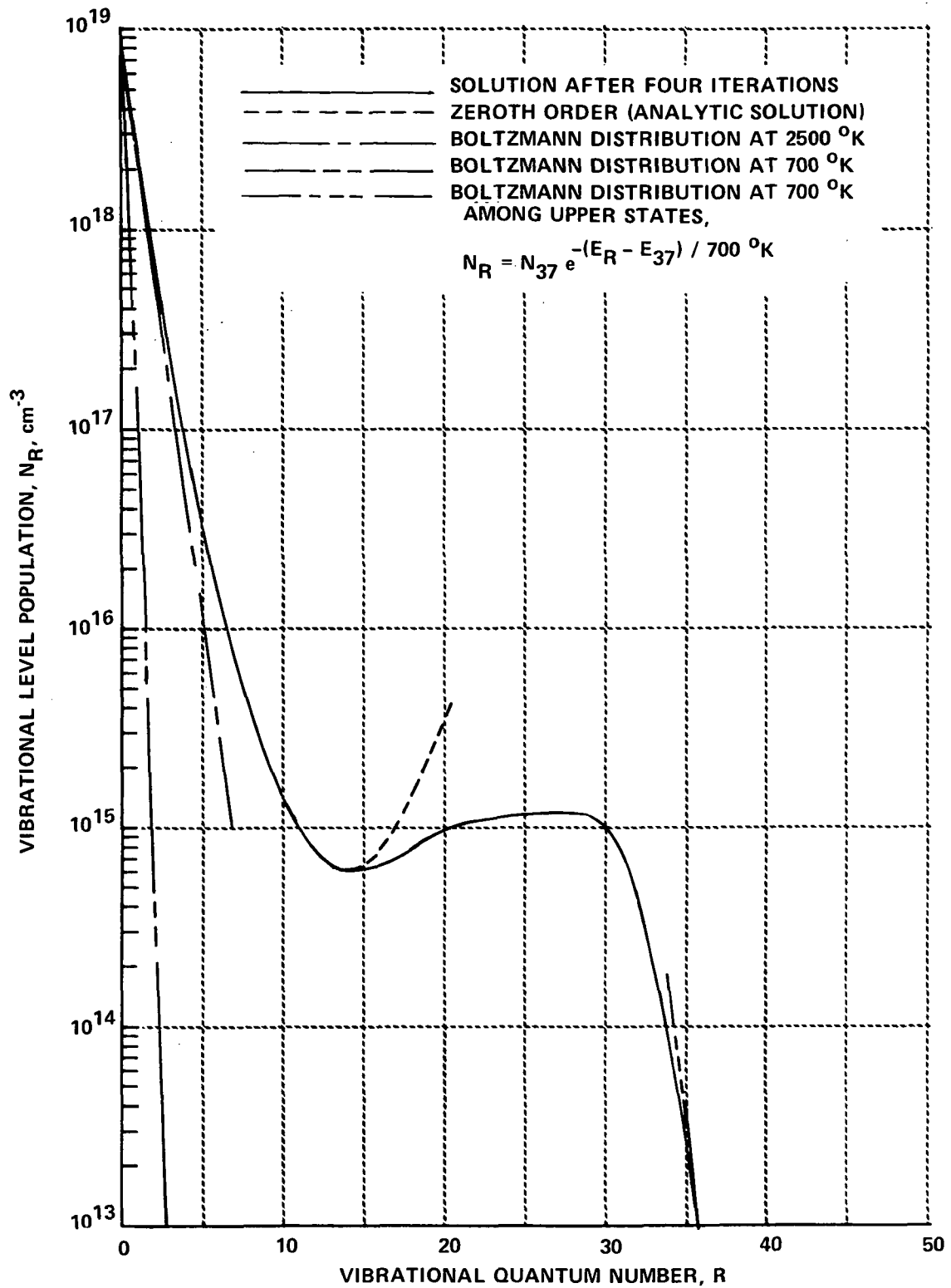
Figure 11 N_2 POPULATIONS VS. VIBRATIONAL QUANTUM NO.

$$"T"_{V_{N_2}} = 2500 \,^{\circ}K; \quad T = 700 \,^{\circ}K, \quad \gamma' = -3.48$$
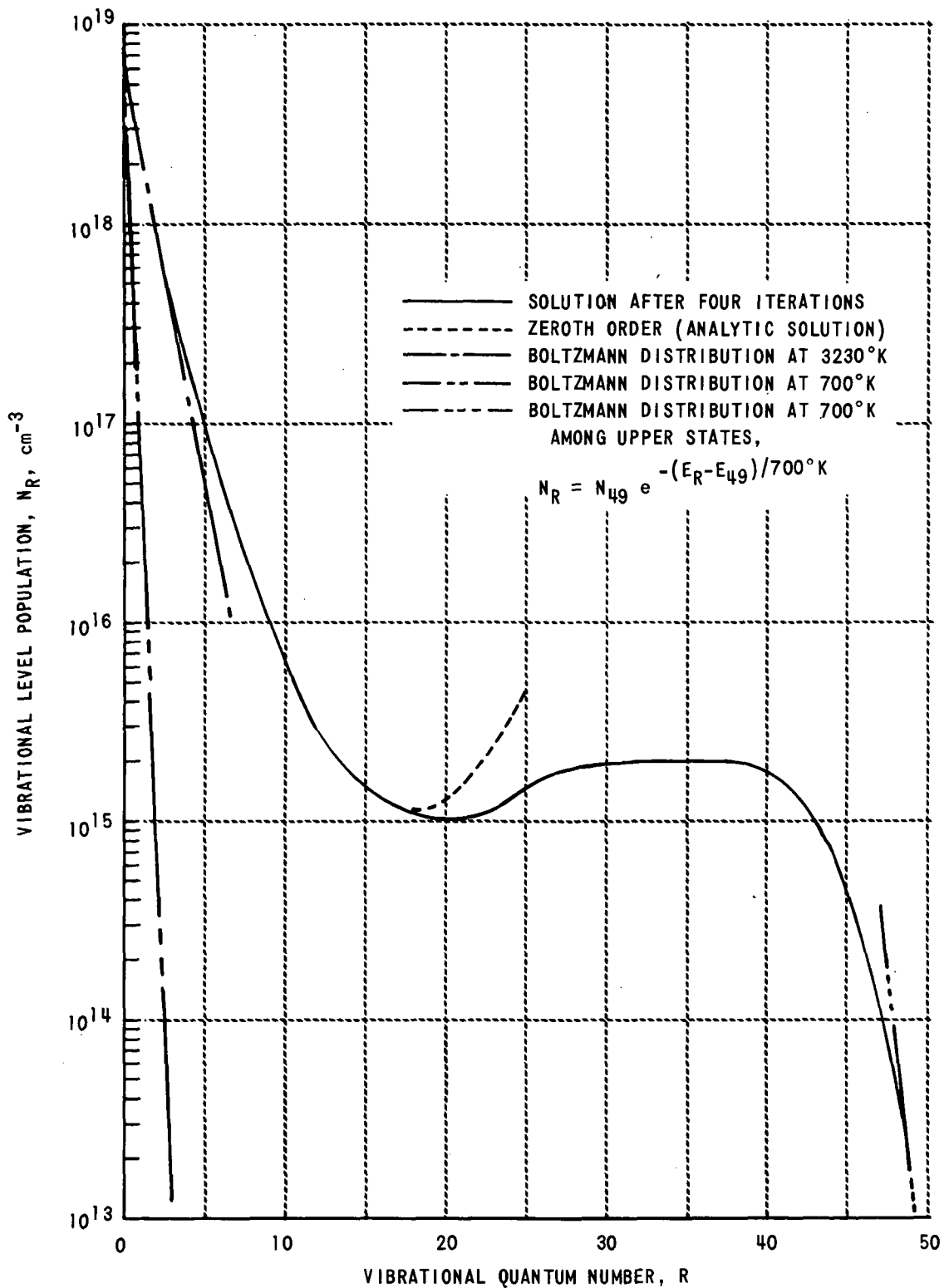
Figure 12 CO-POPULATIONS VS. VIBRATIONAL QUANTUM NO.
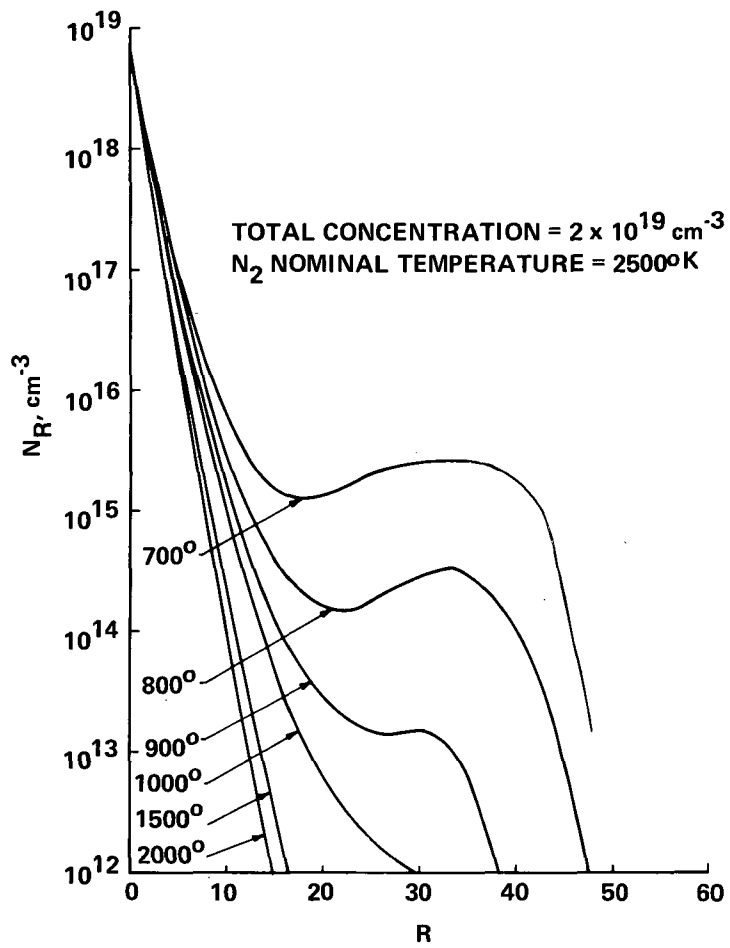"T"$_{V_{CO}}$ = 3230°K; T = 700°K

γ = -3.48

36

Figure 13 CO POPULATIONS, N_R, AS A FUNCTION
OF TRANSLATIONAL TEMPERATURE.

CAL