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**SPECTROPHOTOMETRIC MEASUREMENTS OF THE
VIBRATIONAL RELAXATION OF CO IN SHOCK WAVE
AND NOZZLE EXPANSION-FLOW ENVIRONMENTS**

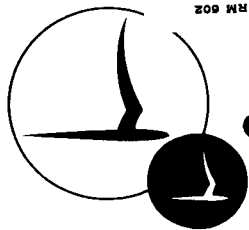
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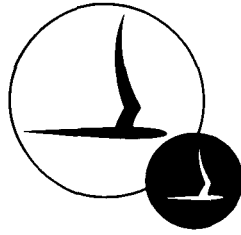
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ABSTRACT

Infrared and Na line-reversal spectrophotometric methods have been employed for the investigation of the vibrational relaxation of pure CO and 5% CO + 95% Ar test gas mixtures behind normal shock waves and in quasi-steady expansion flows. The shock-wave studies were conducted over a range of equilibrium shocked-gas temperatures of about 1400° to 3200° K and pressures of a few atmospheres. Vibrational relaxation times obtained by these two techniques were found to agree quite well and are consistent with other available shock-wave data for both test gas mixtures. The expansion-flow results for 5% CO + 95% Ar were obtained in a shock-driven conical nozzle for a range of reservoir temperatures of about 3500° to 5000° K and reservoir pressures of about 45 atm. For these experiments, the Na line-reversal and CO infrared diagnostic techniques indicated vibrational temperatures much lower than those predicted by the Landau-Teller theory using the shock-wave measured rate data. In addition, the infrared measurements indicated somewhat lower vibrational temperatures than the Na line-reversal results. In terms of vibrational relaxation rates, the expansion-flow data indicate that the deexcitation process in the nozzle proceeds about two orders of magnitude faster than anticipated on the basis of the rates measured behind shock waves. These observations are consistent with previous results obtained for N₂. While a conclusive explanation of these results is not presently available, the results of recent theoretical studies are discussed which suggest that the detailed mechanism of the relaxation process may depend on the gasdynamic environment.

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I INTRODUCTION

The excitation of the vibrational degrees of freedom of a wide variety of molecules has been the subject of considerable theoretical and experimental investigation¹. The work of Landau and Teller² has formed the basis upon which the rather extensive theory of vibrational relaxation has been developed. Coincident with the development of the theory, experimental investigators have used various diagnostic methods including pressure measurements, ultrasonic absorption, interferometry, schlieren and spectroscopy to determine vibrational relaxation rates. These relaxation-rate measurements have been obtained over a wide range of temperatures from ambient temperature up to several thousands of degrees Kelvin. For the high-temperature ranges, extensive use has been made of shock wave and flame environments (see e. g., Refs. 1 and 3). Consequently, these rate determinations have been obtained under conditions in which the predominant kinetic process is one of excitation of the vibrational mode to some final equilibrium distribution.

In contrast, many of the flows of current technical interest, such as propulsive, reentry and test-facility flows, involve expansion environments in which the predominant process with respect to vibration is one of deexcitation, corresponding to a flux of the distribution from upper to lower energy states. In kinetic processes, the assumption of local thermodynamic equilibrium is used to relate forward and reverse (excitation and deexcitation) rate constants. In this manner, relaxation rates obtained in shock-wave (excitation) environments have been extrapolated to expansion (deexcitation) environments with no experimental justification.

Recently, experimental measurements of the rates of vibrational relaxation of nitrogen have been obtained in expansion flows using spectroscopic line-reversal⁴⁻⁶ and electron beam techniques^{7, 8}. The relaxation rates inferred from these experiments indicate rates which are at least one order

of magnitude faster than similar measurements obtained in shock-wave flows. Despite the indirectness of these techniques for the measurement of vibrational relaxation, the good agreement^{9, 10} among the results obtained with these very different approaches lends considerable mutual support to the observations. The large difference between the shock-wave and expansion-flow results for the vibrational relaxation of N_2 reflects very strongly on the understanding of this basic relaxation process and has precipitated extensive theoretical study.

Concurrently, the need for a direct measurement of vibrational relaxation in the two flow environments was apparent and necessary. A further question of interest was whether N_2 is peculiar in exhibiting this difference between shock-wave and expansion flow vibrational relaxation or whether other molecules behave similarly. This has provided the motivation for the present experimental research.

The present work uses both the Na line-reversal technique and an extension of reversal methods using the fundamental, infrared vibration-rotation band (without the need for thermometric additive) to measure the vibrational relaxation of CO in both shock wave and nozzle expansion flows. Measurements have been obtained in pure CO and in a mixture of 5% CO + 95% Ar, both of which have been studied previously in shock-wave flows by other investigators¹¹⁻¹⁴, thus providing a comparison with the present results.

In the present studies, time-resolved emission and absorption were simultaneously recorded photometrically at either 5893 \AA or 4.55μ in the shock tube and/or nozzle. From these data and the assumption of Boltzmann-like distributions, the vibrational temperature history was obtained. Using these results together with the calculable gasdynamic environment, the vibrational relaxation rates defined by the first-order Landau-Teller equation are determined.

In the present paper, the experimental apparatus is briefly summarized in Sec. II-1 while the details of infrared diagnostic technique, and method for the determination of the vibrational temperatures are described in Secs. II-2 and II-3, respectively. The present line-reversal and infrared measurements of the vibrational relaxation of 100% CO and 5% CO + 95% Ar obtained

behind shock-wave flows are described and discussed in Sec. III-1; the present line-reversal and infrared measurements of the vibrational relaxation of 5% CO + 95% Ar obtained in the nozzle expansion flows are described and discussed in Sec. III-2. Finally, the combined results are discussed more fully in Sec. IV in the light of other experimental and theoretical studies.

II. EXPERIMENTAL METHOD

1. Apparatus

The experiments to be described below were conducted in the shock tube-supersonic nozzle apparatus which has been described in considerable detail in Ref. 4. The only significant modification to this apparatus was to increase the length of the driven tube from 20 ft. to about 36 ft. This tube extension had two purposes: first, to permit radiation measurements behind the incident shock wave at a near midtube location (~ 20 ft. from the driver diaphragm) without any influence due to radiation resulting from further heating of the test gas by the shock wave reflected at the nozzle entrance region, and secondly, to increase the available quasi-steady test flow duration in the nozzle. In addition, the quartz windows in the shock tube and nozzle were replaced with sapphire windows to permit the infrared measurements near 4.55μ . The measurements obtained in the nozzle were obtained at a geometric, local-to-throat area ratio (A/A^*) of 8.

The method of operation, as well as the shock tube and nozzle characteristics and flow calibration studies are also described in Ref. 4.

The test gases used consisted of 100% CO and a mixture of 5% CO + 95% Ar. The CO was Matheson CP grade with a minimum purity of 99.5%; the argon was produced by Linde and had a purity level of 99.996%. The 5% CO + 95% Ar mixture was always premixed in a stainless steel mixing tank and agitated by means of a magnetic stirrer for at least 1 hour prior to charging the driven tube. Charging pressures for both test gases were in the range of about 10 to 300 torr.

The incident shock speed was measured over five intervals by means of thin-film resistance gages whose output signals were used to start and stop electronic digital-counters of $1\mu s$ resolution. During a number of calibration experiments, the equilibrium gas temperature measured behind incident shock waves using the infrared technique were found to agree to within about $30^\circ K$ with those calculated on the basis of the measured wave speed over the temperature range of about 1400° to $2200^\circ K$.

The overall response time of the diagnostic techniques was in no case greater than about 4 μ s.

2. Diagnostic Technique

The principal diagnostic techniques used in the present studies for obtaining time resolved measurements of vibrational temperature consisted of simultaneous measurements of emission and absorption at a wavelength region centered near 5890 \AA of trace amounts of Na added to the CO test gas in the form of NaCl smoke, and of the CO itself in the infrared spectral region centered near 4.55 μ . The latter method (which will be referred to as the band-reversal technique) is essentially very similar to the Na line-reversal technique with the important difference that a direct measurement of the fundamental vibration-rotation transitions of CO is possible. In view of the basic similarity of the two techniques and in view of the detailed description of the Na line-reversal method in Ref. 4, only a brief description of the infrared band-reversal method will be given here.

The methods essentially consist of recording the relative emission and absorption of the test gas with reference to two background sources at different but known brightness temperatures in the wavelength region of interest. The optical apparatus used for the infrared studies is shown diagrammatically in the sketch in Fig. 1.

The background light source is encased in an external water jacket which is sealed at the ends by caps containing "O" rings. The radiation source consists of 1/4-in. O.D. x 3-in. long spectroscopic-carbon rod (National Carbon Co., Inc.) which is bored internally to about 1/8 in. The central inch of the element is further machined externally to give a wall thickness of 0.015-0.020 in. The element is heated resistively; the electrical connections are made through solid carbon pieces which are tightly fitted to each end of the 3-in. cylindrical element. The assembled three-piece element extends through the housing end caps through soapstone bushings and the exposed ends are fitted with finned aluminum caps to facilitate air cooling and to which electrical connections are made. One wall of the radiation element has about a 0.060-in. hole drilled radially at its midpoint to expose the inner core of the element. The radiation from this inner

cavity passes through the water jacket by means of a 1/2-in. tube. The entire region surrounding the element is continuously purged with argon. The power requirements for this lamp are in the range of about 100-180 amps at 12 volts giving brightness temperatures (as measured with an optical pyrometer at 6550 Å) of up to about 3000° K.

A magnified image of the cavity radiation source is formed by a spherical front-surface mirror at an image plane which contains two 2-mm diameter holes for the generation of two identical light beams. In this design, the beams are unidirectional in order to avoid any adverse effect on the signal-to-noise ratio of the detectors due to reflected radiation from the windows of the test section. Clearly, the two beams do not intercept identical volumes of test gas, though on the other hand, they do intercept geometrically similar volumes of test gas at the same time or at the same axial location. For the Na line-reversal studies, the two beams were located along the axis of the test section so that each beam would see the same volume of test gas as it is swept past the observation stations. This modification is necessary as a result of possible nonuniformities in the distribution of the NaCl smoke in the test gas.

The two small pencils of radiation are then refocussed at the center of the test section by means of mirrors. The emerging beams are then collected and refocussed onto the sensitive area of the two indium antimonide, photovoltaic, infrared detectors (Daverts Corp). A stop is used where the beams overlap, as shown, to define identical solid angles for the two beams. This stop is overfilled by the background source beams. Also located in this plane is the narrow-passband interference filter which provides the spectral resolution. In this manner, both beams (emission and absorption) pass through the same area of the filter.

The electrical signals from the detectors are then amplified and balanced by means of potentiometers in conjunction with load resistors. The balance procedure insures that for the same radiation intensity in the test section, both detectors give identical input signals to the dual beam oscilloscope. In practice, the absorption is measured with respect to the background source while the emission is measured with respect to the ambient

surroundings by masking one of the beams. Accordingly, biasing circuits are employed to null any radiation signals in both beams due to the surroundings.

In the present infrared studies, the interference filter is centered at 4.55μ and has a halfwidth of 0.05μ and a transmission coefficient of about 0.6. The interference filters were obtained from Eastman Kodak. With this filter a number of rotational lines in the R-branch of the CO fundamental transitions are monitored. The fundamental system consists of all one-quantum vibrational transitions and thus, in the absence of anharmonicity, a given wavelength interval will include contributions from all vibrational levels. However, on the assumption of a near-Boltzmann distribution of oscillators among the vibrational energy states the contributions to the radiation signals from higher vibrational levels will be exponentially diminished by the Boltzmann factor. At a vibrational temperature of 1000° K, for example, approximately 95% of the optical activity results from the $0 \longleftrightarrow 1$ transition. Thus, this diagnostic technique is mostly sensitive to the populations of only the lowest vibrational levels.

3. Determination of the Vibrational Temperature

The time-resolved vibrational temperatures can be determined from the photometric measurements of emission and absorption as follows. If T_s is the true thermodynamic temperature of the background source, and $T_{B\lambda}$ and $\epsilon_{s\lambda}$ are its brightness temperature and emissivity at wavelength λ , then from Planck's radiation law

$$i_\lambda = 2C_1 A \epsilon_\lambda \lambda^{-5} \left\{ \exp(C_2/\lambda T) - 1 \right\}^{-1} d\lambda$$

the radiant intensity, $I_{s\lambda}$, of the background continuum in the region of a spectrum line of wave length λ is given by

$$I_{s\lambda} = \epsilon_\lambda \left\{ \exp(C_2/\lambda T_s) - 1 \right\}^{-1} \equiv \left\{ \exp(C_2/\lambda T_{B\lambda}) - 1 \right\}^{-1}$$

where $I_\lambda = i_\lambda \lambda^5 / 2C_1 A d\lambda$.

Similarly, if subscript g refers to the test gas, then for any isolated spectrum line centered at wavelength λ

$$I_{g\lambda} = \epsilon_{g\lambda} \left\{ \exp(C_2/\lambda T_g) - 1 \right\}^{-1} .$$

When viewed against the background, the line will have an apparent intensity given by the sum of the spectral emission of the line and that portion of the background radiation which is transmitted through the gas.

Neglecting scattering, conservation requirements deem that

$$t \text{ (transmissivity)} + \alpha \text{ (absorptivity)} = 1.$$

The apparent, detectable, radiant intensity at the detector is thus

$$I = (1 - \alpha_{g\lambda}) I_{s\lambda} + I_{g\lambda} .$$

In view of Kirchoff's law

$$\epsilon_{g\lambda} = \alpha_{g\lambda}$$

it follows that

$$I = (1 - \epsilon_{g\lambda}) I_{s\lambda} + I_{g\lambda} .$$

For a spectral passband which contains η nonoverlapping spectrum lines, the total radiation signal is the sum of the contributions of each line

$$\mathcal{I} = \sum_{\eta} \left\{ (1 - \epsilon_{g\lambda\eta}) I_{s\lambda} + I_{g\lambda\eta} \right\}$$

and the net emission from the gas is

$$\mathcal{I}_{em} = \sum_{\eta} \left\{ (1 - \epsilon_{g\lambda\eta}) I_{s\lambda} + I_{g\lambda\eta} \right\} - I_{s\lambda}$$

When viewed against another background source of arbitrary intensity $I'_{s\lambda}$ corresponding to a source at temperature T' which is higher than the gas temperature, the net absorption for an isolated spectrum line is

$$I_{abs} = I'_{s_\lambda} - \left\{ (1 - \epsilon_{g_\lambda}) I'_{s_\lambda} + I_{g_\lambda} \right\}$$

Again, for a passband containing n nonoverlapping spectrum lines

$$I_{abs} = I'_{s_\lambda} - \sum_n \left\{ (1 - \epsilon_{g_{\lambda n}}) I'_{s_\lambda} + I_{g_{\lambda n}} \right\} .$$

Taking the ratio of net absorption to net emission and denoting this ratio by R gives

$$R = \frac{I_{abs}}{I_{em}} = \frac{\sum_n \epsilon_{g_{\lambda n}} I'_{s_\lambda} - \sum_n I_{g_{\lambda n}}}{\sum_n I_{g_{\lambda n}} - \sum_n \epsilon_{g_{\lambda n}} I_{s_\lambda}}$$

or

$$(R+1) \sum_n I_{g_{\lambda n}} = \sum_n \left\{ \epsilon_{g_{\lambda n}} (I'_{s_\lambda} + R I_{s_\lambda}) \right\} .$$

Using the previous definition of I_{g_λ} and substituting above gives

$$(R+1) \sum_n \epsilon_{g_{\lambda n}} \left\{ \exp (C_2 / \lambda T_g) - 1 \right\}^{-1} = \sum_n \epsilon_{g_{\lambda n}} (I'_{s_\lambda} + R I_{s_\lambda}) .$$

In view of the narrowness of the filter passband, I'_{s_λ} and I_{s_λ} corresponding to background sources at brightness temperature T'_{B_λ} and T_{B_λ} may be considered to be approximately constant over the wavelength passband of the filter. The wavelength λ in the exponential term may also be considered to be constant and equal to the wavelength at the center of the passband. With these assumptions, the last equation above becomes

$$(R+1) \left\{ \exp (C_2 / \lambda T) - 1 \right\}^{-1} \sum_n \epsilon_{g_{\lambda n}} = (I'_{s_\lambda} + R I_{s_\lambda}) \sum_n \epsilon_{g_{\lambda n}}$$

or

$$\left\{ \exp (C_2 / \lambda T_g) - 1 \right\} = \frac{R+1}{I'_{s_\lambda} + R I_{s_\lambda}} .$$

In the present studies, the emission is measured with respect to ambient surroundings whose effect is further biased to give zero signal so that T_{B_λ} and I_{s_λ} are zero. Hence,

$$\left\{ \exp \left(C_2 / \lambda T_g \right) - 1 \right\} = \frac{R+1}{I'_{s\lambda}} = (R+1) \left\{ \exp \left(C_2 / \lambda T_{B\lambda}' \right) - 1 \right\}$$

where $T_{B\lambda}'$ is the known brightness temperature of the background source at wavelength λ used for absorption and R is the ratio of the absorption to emission. This ratio is determined from the linear screen deflections on the oscilloscope with the channel sensitivities set equal as described above. The vibrational temperature history, $T_g(t)$, is thus uniquely related to the time-resolved radiation measurements, $R(t)$. Note that in the limit of short wavelength at moderate temperatures the exponential terms are large compared with unity and the last equation, to good approximation, can be written as

$$C_2 / \lambda T_g = C_2 / \lambda T_{B\lambda}' + \ln(R+1) .$$

This situation was found to be valid for the Na line-reversal measurements.

If the gas is at a higher temperature than the background source $T_{B\lambda}'$, the absorption channel will indicate a net emission. In this case, both channels indicate emission. If we define R as the absolute value of the ratio of the linear oscilloscope deflections for the absorption-to-emission intensities, the gas temperature may be determined from

$$\left\{ \exp \left(C_2 / \lambda T_g \right) - 1 \right\} = (1-R) \left\{ \exp \left(C_2 / \lambda T_{B\lambda}' \right) - 1 \right\} .$$

The determination of the vibrational relaxation rates from the vibrational temperature history proceeds in the manner described in detail in Refs. 4 and 15.

One of the assumptions in the foregoing analysis is the existence of isolated spectrum lines. The validity of this assumption can be readily evaluated by using the data for the CO infrared spectrum given in Ref. 16. Using these data, it is found that the rotational lines do not overlap provided that the static pressure is less than about 30 atm for a kinetic temperature of about 2000° K.

III. EXPERIMENTAL OBSERVATIONS

1. Shock-Wave Flow Experiments

One of the foremost considerations of the experimental program was the need for verification that for a convenient range of gasdynamic environments the infrared band-reversal technique would permit direct measurements of vibrational relaxation of CO. In addition, it was desirable to establish the resolution and reproducibility of this diagnostic technique. As a result, a number of experiments were conducted in shock-wave flows of 100% CO and 5% CO + 95% Ar, for which ample independent data¹¹⁻¹⁴ including previous Na line-reversal data⁹ were available for vibrational relaxation rates. These experiments were conducted over a range of equilibrium shocked-gas temperatures of about 1400° to 2500° K and pressures of a few atmospheres. The final equilibrium gas temperatures also provided a convenient means for calibrating the background radiation source used for the infrared absorption measurements and to calibrate the various optical losses.

The effective brightness temperature of the lamp in the center of the shock tube in the wavelength range of interest ($4.55 \pm 0.05 \mu$) was determined by applying the method of analysis described above to the equilibrium region behind incident shock waves for a number of runs. That is, the brightness temperature, resulting from all of the optical losses, is determined from the emission and relative absorption, and the equilibrium shocked-gas temperature calculated from the wave speed history. The measured effective temperature as a function of lamp current and observed optical pyrometer temperature at 6550 Å then serves as the calibration. Thus, a desired lamp temperature is prescribed by a known electrical current and/or a known pyrometer temperature. In the experiments described in this report it was required that the electrical current and pyrometer temperature agree with respect to the infrared temperature of the lamp in order for the data to be considered usable. This precaution insured that the resistivity of the radiation element, and hence its temperature vs. current characteristics, did not change due to erosion of the element itself.

The net transmission (including reflection losses) of the sapphire windows were calibrated in order to correct the lamp brightness temperature for the thinner windows present in the nozzle apparatus. For this purpose, the windows in the shock tube were at first removed and the response of the *InSb* detector to the chopped and filtered (at $4.55 \pm 0.05 \mu$) radiation from the background source was measured. Next, single sapphire windows of 1/8-, 1/4-, and 1/2-inch thicknesses were introduced into the beam at a location corresponding to the actual window location and the signals were measured again. The absorption coefficient for the sapphire windows was thus found to be about 0.27 cm^{-1} for this wavelength interval.

The rise time of the infrared detection system was also assessed from the shock-wave relaxation data and found to be about $4 \mu\text{s}$. This rise time is a result of the particular load resistor used for the detector in order to obtain suitable signal-to-noise levels for data acquisition. A second check of the rise time of the infrared system was obtained by simultaneously monitoring the chopped radiation of the background source using both an EMI 9558 photomultiplier and at 4.55μ using the *InSb* detector. A comparison of the data indicated virtually the same rise time, which was limited by the mechanical chopping arrangement. The observed rise time for both detectors ($\sim 7 \mu\text{s}$) agreed well with that calculated from the mechanical properties of the chopping system.

Upon completion of the calibration studies, radiation data were obtained for the purpose of calculating relaxation rates for CO behind incident shock waves. Typical emission and absorption data are shown in Fig. 2, together with the vibrational temperature history calculated from the data. It will be noted that for this run the absorption channel first indicates absorption and then emission. That is, the vibrational temperature of the test gas is lower than the effective brightness temperature of the lamp initially and, as the relaxation process proceeds, the vibrational temperature increases and eventually exceeds the lamp temperature. The vibrational temperature history obtained from the radiation data as shown in the lower portion of the figure clearly shows a monotonic rise in temperature with elapsed time in laboratory coordinates. It can also be noted from the radiation data and the

resultant temperature profile that the response time of the optical instrumentation is about 4 μ s.

A vibrational relaxation rate is obtained from such data by first calculating the vibrational energy, E , on the basis of a simple harmonic oscillator and then plotting $\ln \frac{E_{eq} - E(t)}{E_{eq} - E(t_0)}$ versus $P_2 \frac{\rho_2}{\rho_1} t$ where

P_2 = equilibrium pressure behind the shock wave
measured in atmospheres

ρ_2 / ρ_1 = equilibrium density ratio across the shock wave

t = time measured from passage of the shock wave past
the observation station in laboratory coordinates

$E = R \theta (e^{\theta/T_v} - 1)^{-1}$; θ = characteristic vibrational temperature,
 T_v = measured vibrational temperature

E_{eq} = value of E when the gas has achieved thermal equilibrium.

Note that the shock density ratio converts the laboratory coordinate time to the correct time in shock-fixed coordinates during which the relaxation process actually occurs. The data in such a plot were fitted by a straight line over the usable range of the data. Such a straight line fit indicates that the relaxation process proceeds at a constant rate whose value is given by the slope of the line. In principle, a constant rate could only be obtained if the translational-rotational temperature did not vary over the period of vibrational relaxation. For the incident shock waves used in the present work, the largest decrease in translation temperature occurred for 100% CO and was about 10% over the measurable relaxation period. For the 5% CO mixtures, it was less than 1% for all cases. In the interpretation of the present experiments, no account was taken of this variation; rather, the heat bath temperature was taken to be the final equilibrium, translational temperature.

The results of the shock-wave studies are presented in Fig. 3. In this figure, the vibrational relaxation times calculated from the radiation data (both Na line- and infrared band- reversal) within the framework outlined above are plotted as a function of shocked-gas temperature. For pure CO, two data points, connected by a bar, are shown for each experiment. The left-hand symbol corresponding to the lower temperature represents the

relaxation time plotted as a function of the equilibrium shocked-gas temperatures. The right-hand symbol represents the same relaxation times plotted as a function of the arithmetic mean of the equilibrium and frozen shocked-gas temperatures. The temperature difference between data points is seen to be largest ($\sim 7\%$) for the highest shocked-gas temperatures. The remaining data* are for the most part plotted as a function of the average shocked-gas temperature. The solid curves are those derived in Ref. 14 by fitting an analytic expression to available experimental data. In view of the high dilution there is considerably less ambiguity for the 5% CO + 95% Ar studies in the value of the kinetic temperature during the relaxation process so that only single data points are plotted.

Two observations can be made from these data: first, the Na line-reversal and infrared band-reversal data are consistent even though little overlap of the experimental conditions was achievable; secondly, the present data are in fair agreement with the experimental results available from other investigators. From these data, it appears that the infrared band-reversal technique offers a convenient method for obtaining vibrational relaxation data for CO.

2. Nozzle Expansion-Flow Experiments

Previously, Na line-reversal data for the vibrational relaxation of 5% CO + 95% Ar had been obtained in the quasi-steady expansion flow environment of the conical nozzle apparatus⁹. These data indicate, as for the case of N₂^{4, 9}, that the vibrational deexcitation of CO in the expansion flow appears to proceed at a rate between one and two orders of magnitude faster than predicted by rates based on shock-wave results. One of the main objectives of the present work was to obtain an independent measurement of these rates using a more direct spectroscopic technique. Such experiments have been performed in the present study using the infrared band-reversal apparatus as the diagnostic method. These experiments were again conducted for 5% CO + 95% Ar test gas mixtures for a range of nozzle reservoir (reflected shock) temperatures of about 3500° to 5000° K and reservoir pressures of about 45 atm.

*A tabulation of this data was kindly supplied by R. C. Millikan.

In these expansion flow experiments, rise time of the instrumentation was of no consideration since the nozzle starting time was of the order of 200 μ s with a usable flow duration of about 1-2 ms. Thus, despite the low vibrational temperatures anticipated on the basis of the previous Na line-reversal results and the low static pressures in view of the supersonic expansion to an area ratio of $A/A^* = 8$, suitable signal-to-noise ratios could be obtained by increasing the load resistance of the infrared detector by about one order of magnitude.

The measured vibrational temperatures from a number of nozzle-flow experiments are shown in Fig. 4. The measured temperatures are normalized by the reservoir temperatures and include slight corrections for reservoir pressure variations in some of the experiments. Also shown in this figure for comparison are the experimental data obtained from the Na line-reversal measurements. The curves represent the ratios of vibrational-to-reservoir temperature predicted by approximate solutions⁴ of the Landau-Teller relaxation equation using the relaxation time determined from shock-wave experiments ($\tau = \tau_s$ as given in Fig. 3) and for times faster by one ($\tau = \frac{1}{10} \tau_s$), two ($\tau = \frac{1}{100} \tau_s$), and three ($\tau = \frac{1}{1000} \tau_s$) orders of magnitude than the shock-wave values. These curves were calculated by assuming that the vibrational relaxation only slightly perturbed the equilibrium solution so that the linear, vibrational relaxation equation could be solved by a finite-difference method based on equilibrium properties of the flow. The experimental data and calculations are given for a nozzle geometric area ratio of $A/A^* = 8$.

At this area ratio, the translational temperature of the gas mixture has decreased to a value of about 1/7th of the reservoir value. (That is, the local translational temperatures lie in the range of about 500° to 750° K.) Under the conditions of rapidly decreasing kinetic temperature during the supersonic expansion, the rate of collisional deexcitation of vibration rapidly decreases, resulting in freezing of the vibrational population distribution. In the present studies, this freezing is calculated to occur upstream of the nozzle observation station. Although collisional deexcitation of vibration has effectively ceased, the populations of excited vibrational levels can continue to be altered by radiative processes.

A conservative estimate of the magnitude of the effect of radiative depopulation on the infrared measurements can be obtained by considering the following process



where k is the reciprocal of the infrared radiative lifetime ($\tau_r = 0.033$ sec). If the gas is assumed to be in thermal equilibrium at the nozzle throat (denoted by superscript *) and if k is a constant, then

$$\left\{ \frac{(\text{CO})_{v=1}}{(\text{CO})_{v=0}} \right\}_{A/A^*} = \left\{ \frac{(\text{CO})_{v=1}^*}{(\text{CO})_{v=0}^*} \right\} e^{-t/\tau_r}$$

where t is the flight time of a molecule from the nozzle throat to any area ratio, A/A^* . Such an estimate has been obtained for the case of 5% CO + 95% Ar at reservoir conditions of 4500° K and 45 atm pressure. The results indicate that the radiative depopulation ($1 \rightarrow 0$) up to the observation station amounts to only about 0.1% of the initial value whereas the infrared measurements indicate that the overall change in population ratio of the first to the zeroth vibrational level is about 75%.

Any significant excitation of vibration by the absorption of infrared radiation from the background source is precluded on the basis of an optically thin gas. The optical thickness of the gas was checked during the pure CO shock-wave studies. In this check, the equilibrium shocked-gas temperature was maintained constant, but the pressure was increased by a factor of two. The corresponding infrared emission data similarly indicated a twofold increase in signal indicating that the test gas was indeed optically thin. The vibrational temperatures in the nozzle-flow experiments were similar to these shock-wave experiments, but the static pressure of the CO at the observation station was much lower and the physical gas thickness at the observation station was less than half of the shock tube dimension so that the thin gas approximation is equally valid for the nozzle-flow experiments.

The foregoing considerations indicate that the effects of radiative processes on the infrared measurements are negligible. The effect of radiative processes due to Na have also been shown⁴ to be negligible.

It is immediately obvious from Fig. 4 that both the infrared and Na line-reversal data indicate CO vibrational relaxation rates which are considerably faster in the expansion flow than in shock-wave flows. The Na line-reversal data indicate vibrational deexcitation rates between one and two orders of magnitude faster while the CO data indicate rates almost three orders of magnitude faster. It is emphasized that both of these techniques yielded results behind shock waves in agreement with other available data and, moreover, in agreement with each other. The expansion flow results, as shown in Fig. 4, present an entirely different comparison. It is interesting to note that the present nozzle-flow results, while indicating much faster vibrational deexcitation than predicted using shock wave relaxation data, differ somewhat in the extent to which the rate is faster. This point is further discussed in the following section.

IV. DISCUSSION

The observations presented in this report indicate two important results:

- (i) Both the Na line-reversal and CO infrared band-reversal diagnostic techniques follow the vibrational temperature history in the flows of CO behind normal shock waves;
- (ii) Both the Na line-reversal and CO infrared band-reversal diagnostic techniques yield vibrational temperatures in nozzle expansion flows of CO which are much lower than those predicted from the Landau-Teller theory using shock-wave measured rate data.

These observations are not unique for CO. Similar low vibrational temperatures in expansion flows have been obtained previously for N₂ using Na line-reversal⁴⁻⁶ and an electron beam fluorescence method^{7, 8}. Recent comparisons of these data for N₂ are presented in Refs. 9 and 10. In the latter reference, the author has also employed a boundary layer analysis to correct the nozzle data for any possible viscous effects.

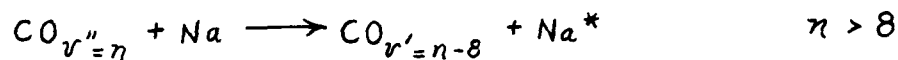
The effects of impurities on the vibrational relaxation of N₂ were studied^{17, 18} and were not found to significantly affect the expansion-flow results for the respective operating conditions. In Ref. 4 the authors discuss a number of other possible mechanisms which might compromise the

validity of the line-reversal measurements, but find no suitable explanation for the observed results.

In the present infrared studies, the impurity content of the test gases is somewhat higher than that of Ref. 4 due primarily to the purity level of the CO which was used without further processing and without a detailed knowledge of the nature of the impurities. However, the same test gases were used for both the shock-wave and expansion-flow studies. In the expansion-flow experiments, impurities would be expected to be less important since these impurities (e. g., H_2O) would be largely dissociated in the equilibrium region behind the reflected shock wave. The subsequent freezing of recombination processes during the rapid nozzle expansion would then result in greatly reduced molecular impurity content. On the other hand, the molecular impurity content is a maximum during the vibrational relaxation process behind normal shock waves since, of course, dissociation processes require larger collision numbers. Despite the unknown nature of the possible impurities, it is evident from the correlation of the shock-wave data that they exert a rather small influence on the experimental observations behind the shock waves in the present study. The effect of the impurities is accordingly also considered to be small in the present experiments.

The new data provided by the present experiments together with the results of previous experiments thus provide very strong evidence in total that vibrational relaxation rates measured behind shock waves cannot generally be extrapolated to nozzle expansion-flow environments within the framework of the Landau-Teller relaxation theory. In addition to the relaxation rate data per se, the comparison of the infrared and Na line-reversal results indicates that the infrared temperature measurements correspond to even faster relaxation rates than the line-reversal temperatures for the same expansion flows.

The excitation energy of the Na (2P level) is about 2.1 ev which corresponds to approximately 8 quanta of vibrational energy of CO. The emission of radiation by the excited Na is proportional to the number density of excited Na present, which in turn is interpreted to be approximately proportional to the number of CO molecules in the 8th vibrational level (which can excite the Na). Contributions to the excited-Na population due to higher vibrational levels which can excite the Na via the mechanism



are significantly decreased as a result of the rapidly decreasing population distribution among the oscillators.

Clearly, if the oscillators were distributed according to the Boltzmann prescription, i. e., a unique distribution function corresponding to a complete Boltzmann distribution throughout, then the infrared- and Na-determined temperatures would be identical. Such a distribution is typically predicted theoretically for the case of simple harmonic oscillators where the spacing of the vibrational energy levels is constant. For the case of anharmonic oscillators, it has been shown in Ref. 19 that a non-Boltzmann steady-state distribution of the molecular vibration exists during the relaxation process when a rapid exchange of vibrational energy among the molecules is the predominant mechanism. The results of this theoretical analysis can be used to estimate the difference between the Na and infrared temperatures for the 5% CO + 95% Ar flows to be expected on the basis of anharmonicity. Such an estimate has been made for the present data for a reservoir temperature of 4500° K. The temperature which is associated with about the 8th vibrational level is calculated to be about 10% higher than that for the first vibrational level, while the temperature inferred from the Na measurements is about 20% higher than the infrared value. Thus, the effect of anharmonicity could account for approximately 50% of the temperature difference obtained with the Na and infrared methods.

This same analysis was applied to the case of pure N₂ in expansion flows⁴, where both Na and Cr line-reversal measurements had been obtained at the same nozzle location. The Cr excitation was interpreted to be resonant with about the 10th vibrational level of N₂ while the Na excitation was interpreted to be resonant with about the 7th vibrational level. The temperatures defined by the population ratios for Na and for Cr were found to be the same, which was taken in Ref. 4 to be indicative of a Boltzmann distribution among the oscillators. However, applying the results of Ref. 19 to these flows also, it is found that anharmonicity results in only about a 1% difference

in vibrational temperatures of the 7th and 10th levels. On the other hand, the reliability of the line-reversal measurements was estimated to be about $\pm 2\%$ ⁴ which precluded any measurement of the effect of anharmonicity in those flows. The N₂ results thus do not necessarily obviate the existence of a non-Boltzmann distribution due to anharmonicity, as is suggested by the present CO results.

A most significant question is the discrepancy among the vibrational relaxation rates inferred from shock-wave and expansion-flow studies using the same diagnostic techniques. In a recent theoretical study²⁰, the authors have further considered the effects of nonresonant vibrational-vibrational collisions for an anharmonic oscillator system on the overall relaxation of the vibrational energy. It is significant that these authors conclude that the rate of relaxation of vibrational energy can be enhanced in a gas system in which vibration-vibration exchange is a dominant mechanism when the following conditions are satisfied:

1. The vibrational temperature is a considerable fraction of the characteristic vibrational temperature.
2. The vibrational temperature is greater than the translational temperature.

This mechanism clearly distinguishes between the gasdynamic environments associated with shock-wave and expansion flows; the enhancement of the rate of energy relaxation is only associated with the expansion flows.

While this mechanism predicts an enhancement of the rate of relaxation of anharmonic oscillators in expansion flows, estimates of the rate of enhancement require as yet unavailable data concerning the detailed rate constants for vibration-vibration exchange events. On the other hand, experimental verification of the significance of this mechanism is necessary in any attempt to reconcile the shock-wave and expansion-flow data. If vibration-vibration exchanges are not predominant, then no enhancement of the vibrational relaxation process due to nonresonant events will result. Thus, one need only obtain vibrational temperature measurements for expansion flows in which vibration-vibration collisions do not predominate, i. e., in very dilute oscillator-heat bath flows. If the nonresonant exchange

mechanism is indeed important for the available expansion flow data, then the vibrational relaxation rate will not be enhanced in the dilute flows due to this mechanism and the measured vibrational temperatures should be indicative of relaxation rates approaching those obtained from shock-wave studies.

V. CONCLUDING REMARKS

The present experiments were undertaken to observe thermal nonequilibrium effects in shock wave and nozzle-expansion flows of CO, characterized by vibrational relaxation, using the line-reversal method and, more directly, by using infrared radiation measurements to monitor the vibrational temperature. In this manner, it was hoped to investigate further the occurrence of faster vibrational deexcitation in expansion flows than predicted on the basis of shock wave data, as was previously observed for N₂. The present results indeed indicate that the vibrational deexcitation of CO in the nozzle-expansion flows proceeds about two orders of magnitude faster than predicted by the Landau-Teller theory using vibrational relaxation rates obtained by the same diagnostic techniques behind shock wave flows.

Thus, available spectroscopic data for the vibrational relaxation of N₂ obtained from Na and Cr line-reversal measurements, and from electron beam fluorescence measurements, as well as the present data for the vibrational relaxation of CO obtained from Na line-reversal measurements, and infrared radiation measurements indicate that the relaxation rates measured in shock wave flows cannot generally be extrapolated to nozzle-expansion flows within the framework of the Landau-Teller theory. While an enhancement of the rate of deexcitation of vibrational energy has been suggested on the basis of nonresonant exchange processes in recent theoretical work, there is a need for considerably more experimental data before the vibrational relaxation process can be accurately predicted for expansion flow environments.

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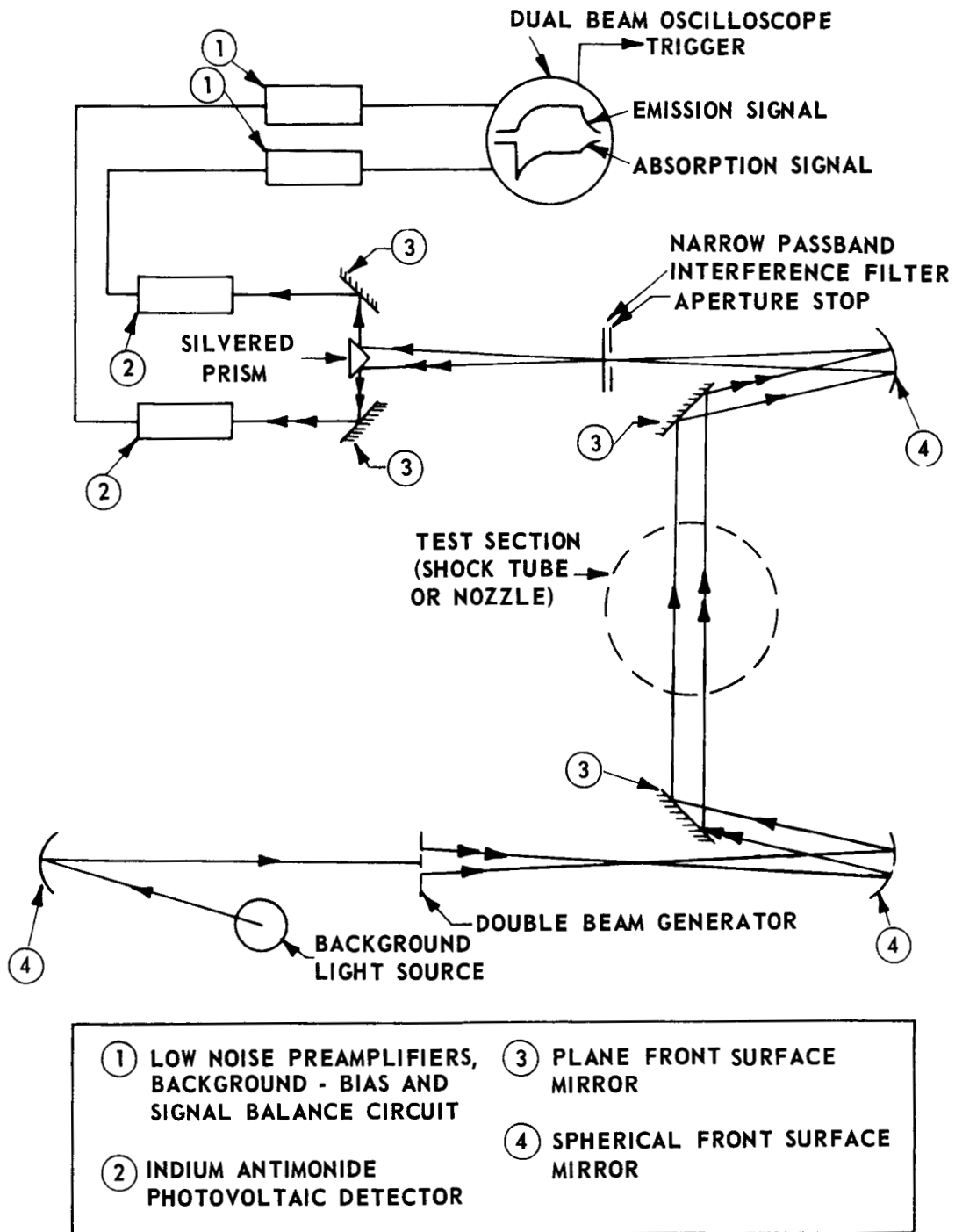


Fig. 1 Schematic diagram of the infrared optical apparatus

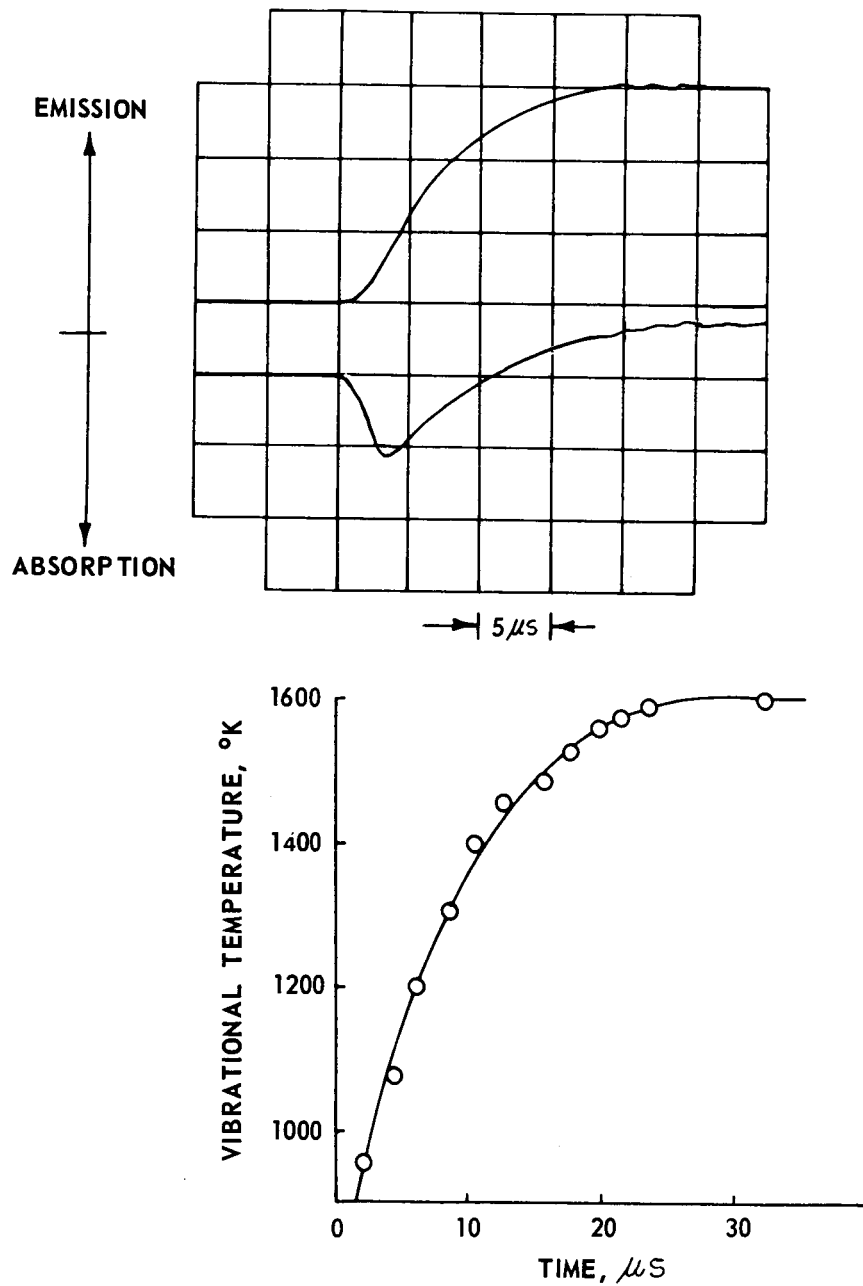


Fig. 2 Oscillograph traces of infrared emission and absorption intensities measured behind a shock wave including the time-resolved vibrational temperatures obtained from this radiation data

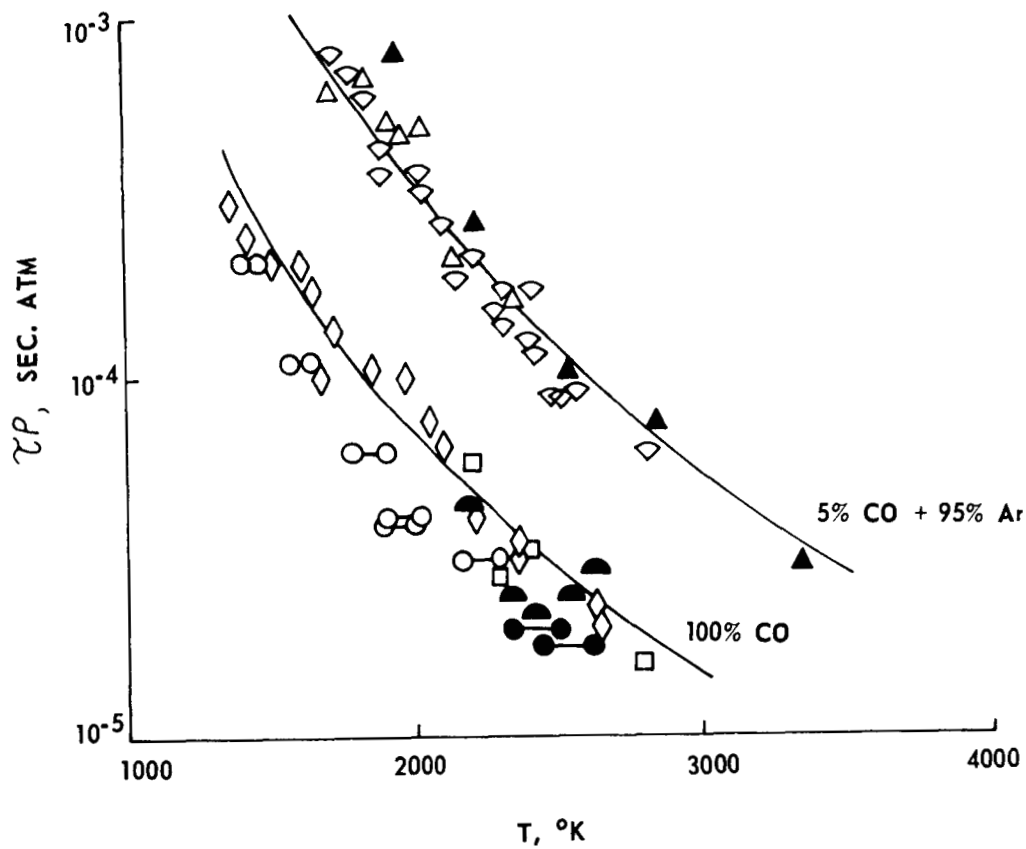


Fig. 3 Vibrational relaxation times, τ_P , for pure CO and 5% CO + 95% Ar from shock-wave experiments. 100% CO: \diamond Hooker and Millikan¹⁴, \square Matthews¹², \bullet Gaydon and Hurlle¹³, \circ present results-infrared, \bullet present Na results. 5% CO + 95% Ar: \diamond Hooker and Millikan¹⁴, \triangle present infrared results, \blacktriangle present Na results. Curves from Ref. 14

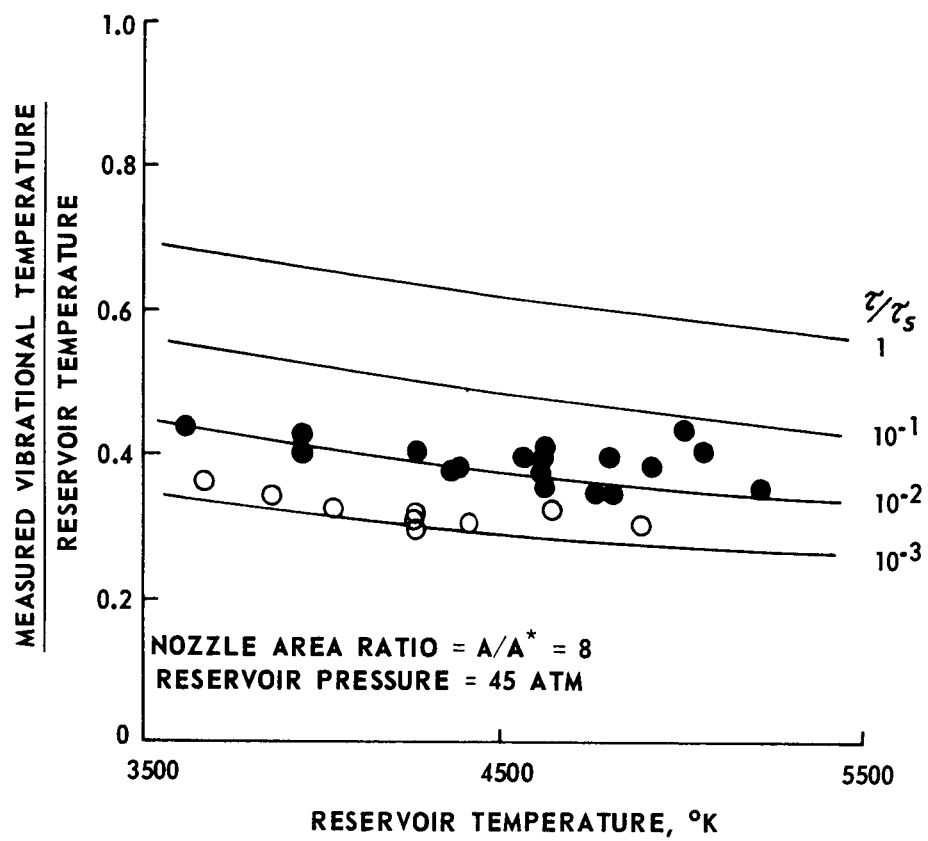


Fig. 4 Experimental vibration temperatures for 5% CO + 95% Ar measured in expansion flows: ○ infrared results, ● Na results