# Measurement of the relaxation frequency of the asymmetric stretching mode of carbon dioxide

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The vibrational relaxation frequency of carbon dioxide has been determined by measuring the rate of change of thermal emission in shock waves near $4\cdot3\,\mu$. This method of measuring the relaxation frequency depends mainly on the degree of excitation of the asymmetric stretching mode of the molecule, and the results are compared with those of earlier density measurements made in the same shock tube. The gas samples used are not optically thin, and it is shown that self-absorption can be taken into account. The results imply that the relaxation frequency of the asymmetric stretching mode is about 70 % of that of the bending mode.

## 1. Introduction

Vibrational relaxation in carbon dioxide has been extensively studied during the last fifteen years. The Mach–Zehnder interferometer has been the main instrument during this period, and the details of shock wave structure have been determined from measurements of density.

Smiley & Winkler (1954), Griffith, Brickl & Blackman (1956), Johannesen, Zienkiewicz, Blythe & Gerrard (1962), and Johannesen, Zienkiewicz & Gerrard (1963) have obtained such experimental results.

All three groups found that the density varied exponentially with distance behind the shock front; but they disagreed on the value of the density far behind the shock wave. Griffith *et al.* found that only the bending mode had reached equilibrium and concluded that the stretching modes relaxed at least one order of magnitude more slowly than the bending mode. The other two groups found that the final value of the density corresponded to complete equilibrium. Greenspan & Blackman (1957) suggested that the three modes had three different relaxation frequencies. Since 1957 there has been much discussion on the relaxation rates of molecules with more than one mode of vibration with particular attention being paid to carbon dioxide.

The Fermi resonance between the vibrational energy levels of the bending and symmetric stretching modes is thought to provide a strong degree of coupling between these modes during relaxation. This idea was first formulated by Schwartz (1954), and it follows that the vibrational energy transfer between these two modes should be a fast process, so that the two modes should be

essentially in mutual equilibrium during the relaxation process. Thus the asymmetric stretching mode is expected to have a relaxation frequency different from the other two modes. There is thus disagreement between the theoretical conclusions of Schwartz and the experimental observations of Griffith et al. (1956) and Johannesen et al. (1962), which are themselves in conflict. It should be noted, however, that the interferometer experiments are sensitive mainly to the bending and symmetric stretching modes, since these have lower characteristic temperatures than the asymmetric stretching mode. In fact the latter mode contains only a small fraction of the total vibrational energy under the conditions of the experiments.

Recently Simpson, Bridgeman & Chandler (1967a) have performed Mach–Zehnder interferometer experiments in carbon dioxide. These results agree with those of Johannesen et al. (1962) in the value of the density ratio across the shock wave, though the way in which equilibrium was attained was found to be slightly different. The main feature of the results was that the relaxation frequency was found to depend on temperature only, whereas Johannesen et al. (1962) concluded that the relaxation frequency depended also on the vibrational energy.

The first important work on vibrational relaxation incorporating infra-red emission techniques was performed by Hooker & Millikan (1963). They measured the vibrational relaxation time of carbon monoxide both as a pure gas and in bimolecular mixtures with argon, nitrogen and hydrogen. The infra-red emission technique is a valuable method for determining the relaxation frequency of a particular mode of vibration of a complicated molecule. The emission from a fundamental band, related to a normal mode of vibration of the molecule, is observed and the rate of excitation of the mode can be determined.

The earliest measurements of the relaxation time of the asymmetric stretching mode of carbon dioxide by this method were reported by Borrell (1963). He found that the relaxation time at 600 °K was about twice the value calculated from the results of Johannesen et al. (1962).

Camac (1964) observed the emitted radiation from the $4 \cdot 3 \mu$ band in shock waves, while simultaneously monitoring the density with an electron beam technique. The experiments were carried out in a low density shock tube in the temperature range 2000–6000 °K. Camac's report is brief, and he has made only a preliminary analysis of his results, which show a scatter of a factor of about two. The two techniques did not reveal different relaxation times.

Since the experiments described in the present paper were performed, the results of experiments by Weaner, Roach & Smith (1967) have been reported. The experimental technique was similar to that of Camac, but covered a lower temperature range. There is, however, a considerable scatter in their results.

A fundamental difficulty in determining the relaxation time of a single mode of a polyatomic molecule is that only average values for each shock wave can be determined. To determine local values of the relaxation time the vibrational energies of the other modes must be known, as these determine the density and translational temperature of the relaxing gas. If an assumption regarding the state of the other modes is made, then the local value of the relaxation time can be found using the Rayleigh-line technique devised by Johannesen (1961).

It can be shown quite simply that the emitted radiant power of a fundamental band of a sample of radiating gas is proportional to the vibrational energy of the mode associated with the band. Two main assumptions are involved: (i) that the gas sample is optically thin in the spectral region of the band, and (ii) that the harmonic oscillator approximation is valid. This proportionality relationship was used by Camac, for whose experiments assumption (ii) may be incorrect owing to the high temperature range of his experiments. It was also used by Weaner *et al.* under experimental conditions not very different from those described in §4 of the present paper, and the validity of assumption (i) must be in some doubt. The scatter of the results of Weaner *et al.* may be a consequence of these assumptions.

The samples of carbon dioxide available for our experiments were not optically thin near $4 \cdot 3 \mu$. Thus assumption (i) could not be made. Instead, a complete calculation of the integrated emissivity of the relaxing gas was required. The method used for this is due to Malkmus (1963), and was adapted to apply to gas samples not in vibrational equilibrium. An outline of the required modifications for application of this method is given in §2.

Owing to the lack of information as to the energy of the bending and symmetric stretching modes in the relaxation region, it was necessary, for both the emissivity calculation and the determination of the local relaxation frequency, to assume that all three modes were in mutual equilibrium at all times in the relaxation region. Failure of this assumption would be apparent from a comparison of these results with those of Johannesen *et al.* (1962), who also made this assumption. Such a comparison is given in §5.

## 2. Calculation of the emissivity, near 4.3 μ, of an optically thick sample of carbon dioxide not in vibrational equilibrium

The emissivity of the $4 \cdot 3 \mu$ band of carbon dioxide was calculated by Malkmus (1963) using the harmonic oscillator model to calculate the spectral line intensities, the anharmonic vibrator including the first-order rotation-vibration interaction approximation to calculate the spectral line positions, and the statistical model of a spectral band. Malkmus in fact used the statistical model according to several approximations and found best over-all agreement with earlier absorption measurements using the 'weak-strong approximation'. This approximation is particularly useful when studying gas samples which are neither optically thin nor very thick, and do not contain any strong spectral lines. Malkmus made calculations for equilibrium gas samples and the weak–strong approximation generally over-estimates the emissivity by about 20 %.

A few relatively simple modifications to the equilibrium calculations allow a determination of the emissivity of non-equilibrium samples. The emissivity depends on the temperatures of rotation, vibration and translation. All the temperature-dependent terms of the equilibrium calculation can be written in terms of these three temperatures. The pressure and optical path length are also required, together with the relevant spectroscopic parameters. Since we are interested in gas samples where the rotational and translational temperatures are essentially equal, only one extra temperature is required.

It was not possible, without major alterations to the method, to specify a separate vibrational temperature for each mode of vibration. This would in any case lead to serious complications in the interpretation of the experimental observations since we have no information on the rate of relaxation of the bending and symmetric stretching modes. These affect the density and translational temperature in the relaxation region. Since only de-excitation of the asymmetric stretching mode can lead to the emission of a photon near $4\cdot3\,\mu$, however, the quantity of emission is governed primarily by the temperature of this mode. Variations in other quantities have smaller effects on the emitted radiant power. We have assumed a vibrational temperature common to all the modes, but the technique depends primarily on the asymmetric stretching mode, just as the interferometer experiments depend primarily on the bending mode.

These calculations of the emissivity were made on the University of Manchester Atlas Computer. The calculated equilibrium radiant power reaching the infra-red detecting device was related to the equilibrium output signal of the detector. The vibrational temperature in the relaxation region was related to the time-scale of the oscillogram. Thus each experiment was used to calibrate the responsivity of the infra-red detector and at the same time annul the effects of the over-estimate in the emissivity calculation.

A more detailed account of the modifications to the method of Malkmus is to be reported separately (Hodgson 1969).

## 3. Calculation of the relaxation frequency

The Rayleigh-line procedure was first used to analyse shock-wave relaxation regions by Johannesen *et al.* (1962), who applied the method to carbon dioxide. Since then, Bhangu (1966) (nitrous oxide), Lutz & Kieffer (1966) (oxygen) and Simpson, Bridgeman & Chandler (1967a,b) (carbon dioxide and nitrous oxide) have utilized the technique.

The method varies slightly depending on the observed thermodynamic variable. The relaxation frequency $\phi$, as defined by the well-known equation

$$d\sigma/dt = \rho\phi(\bar{\sigma} - \sigma) \tag{1}$$

can be calculated as a function of the translational temperature of the relaxing gas in a shock wave. Here $\sigma$ is the vibrational energy, $\bar{\sigma}$ its local equilibrium value and $\rho$ the density. $\phi$ is expected to vary through the shock wave since the translational temperature varies.

The timescale in (1) can quite simply be related to the timescale on the oscillogram ($t'$) by the equation

$$dt'/dt = v/u_s, \tag{2}$$

where $u_s$ is the shock wave velocity relative to the shock tube and $v = v(t)$ is the velocity of the shocked gas relative to the wave.

In these experiments the measured thermodynamic variable was the vibrational temperature $T_V$, and the vibrational modes were assumed to be in mutual equilibrium.

It follows that
$$\phi = \frac{v}{\rho u_s (\overline{\sigma} - \sigma)} \left(\frac{d\sigma}{dT_V}\right)\left(\frac{dT_V}{dt'}\right).$$
(3)

The shock velocity $u_s$ was determined experimentally, and from the initial conditions the velocity $v$, density $\rho$ and vibrational energies $\overline{\sigma}$ and $\sigma$ were found from the Rayleigh-line equations. The vibrational specific heat $(d\sigma/dT_V)$ can be found from thermodynamic tables (Hilsenrath *et al.* 1955). The rate of change of the vibrational temperature can be found from the experimental observations.

## 4. Experimental equipment and procedure

The 8 in. by 2 in. shock tube in these experiments has been described by Johannesen *et al.* (1962). The only significant modification made to the shock tube was the replacement of the optically flat interferometer windows by infra-red transmitting ones. These were 2 cm diameter sapphire disks, 0·2 cm thick, mounted in metal cells so that they were flush with the inside walls of the shock tube.

The infra-red radiation detector was a Mullard RPY 36 indium antimonide device, and had a nominal responsivity of 3 mV/$\mu$W at 4·3 $\mu$. Its response time, measured using a pulsed gallium arsenide recombination lamp radiating at 0·92 $\mu$, was less than 2 $\mu$sec. The detector had a sensitive area of 0·6 cm by 0·05 cm, which was focused into the centre of the shock tube by a front-silvered concave mirror of focal length 16·5 cm, so that the longest side of the image was vertical. The optical axis, which passed through the 8 in. width of the shock tube, was made perpendicular to the axis of the shock tube. A vertical aperture stop was used at the mirror to reduce the width of the pencil of rays emanating from the detector and passing through the shock tube. No optical stops were used at any other point on the optical axis, since these reduced the over-all sensitivity of the detecting system by a larger fraction than the reduction of the response time. The single aperture stop reduced the sensitivity and response time of the system to practical values for the experiment. A secondary effect of having aperture stops at places other than at the mirror was to distort the volume of the shock tube from which emitted photons could reach the detector. This causes complications in calculating the emissivity of an optically thick sample of gas.

The pencil of rays emanating from the detecting element had a geometric width of 0·18 cm in the shock tube. Diffraction effects at 4·3 $\mu$ broadened the image of the detector by about 0·02 cm. Care was taken to restrict the upper and lower portions of this pencil of rays to the sapphire windows, so that no part of the shock tube walls was in the line of sight of the detector. This was a necessary precaution to reduce the amount of radiation scattered into the field of view of the detector prior to the arrival of the shock front.

The spectral region of the 4·3 $\mu$ band was bounded at the short wavelength end by a low-pass filter and at the long wavelength end by the spectral limit of response of the detector. The 3 db points of the detecting system were at 3·9 $\mu$ and 5·7 $\mu$. The integrated band intensities of absorption of the three very weak

combination bands also within these spectral limits are less than 0·1 % of that of the 4·3 $\mu$ fundamental band (Weber, Holm & Penner 1952).

The indium antimonide detector, operated in the photo-conducting mode, was driven by a dry battery of 63 V, in series with two 27 k$\Omega$ resistors. The terminals of the detector were connected to a Tektronix 585 oscilloscope via differential plug-in unit $D$, so that in-phase noise was eliminated from the oscilloscope trace. The cell current was found to be constant from day to day at 1·02 mA.

In a preliminary experiment using a furnace-type radiator the detector was found to have a linear response to radiation (when used under the conditions specified above) for detector output voltages up to 60 mV. Thus the oscilloscope trace gave a proportional representation of the incident radiant intensity.

## 5. Observations and results

Shock waves with Mach numbers in the range 2·5–5·4 were fired into initial pressures of carbon dioxide of 0·5–10 mm of mercury. A typical oscilloscope trace is shown in figure 1.

It can be seen that a small amount of radiation reaches the detector prior to the arrival of the shock front. This radiation had been transmitted by the shock wave and reflected from the window on the opposite side of the shock tube to the detector. Later, when calcium aluminate glass windows with antireflecting coatings were fitted, the signal prior to the arrival of the shock front was reduced by about 60 %. A second feature of the trace is the slowly rising voltage long after the shock wave has passed the observation window. This may be associated with a small amount of attenuation of the shock wave as it is transmitted down the shock tube. Such effects have been discussed in detail by Gaydon & Hurle (1963) and Holbeche & Spence (1966).

Between the two very nearly horizontal parts of the oscilloscope trace is the more rapidly changing signal emitted by the vibrationally relaxing gas.

Measurement of the shock velocity near the working section of the shock tube allows a calculation of pairs of values of vibrational and translational temperatures in the relaxation region, using the Rayleigh-line technique. For emissivity calculations the pressure in the relaxation region was taken as constant, since it does not vary by more than about 1 %; and, as the gas samples were optically thick, the effect on the emissivity is less than 1 %. The radiant power reaching the detector could then be calculated for samples of gas all relaxing to the same equilibrium conditions. The equilibrium radiant power was then related to the equilibrium voltage on the oscilloscope record, and the time-scale of the relaxation process could be defined in terms of the time-scale on the oscillogram. Since there was no final equilibrium voltage, this was taken to be that voltage associated with the element of gas which had been shocked at the point midway between the two timing stations. Several variations on this were tried, including an attempt to account for the increasing equilibrium radiation from the fully relaxed gas, but in all cases the values of the relaxation frequency, as measured on the oscilloscope time-scale, differed by less than 2 % for the same experimental result.

Calculations of the vibrational temperature of the gas immediately behind the shock front could not be made because of interference with the radiation received prior to the arrival of the shock front. The attenuation effect led to errors at the near equilibrium end of the relaxation region. In between, the vibrational temperature could be determined with some accuracy.
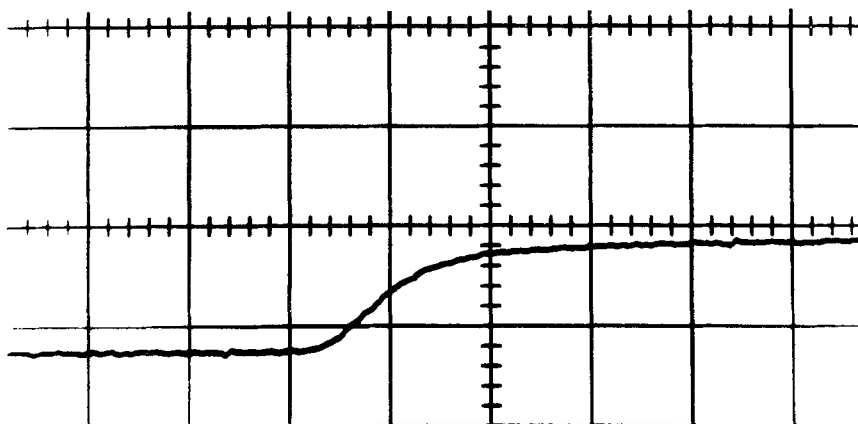


FIGURE 1. The oscilloscope record of the infra-red detector output signal during the passage of a shock wave. Shock Mach number 3·56, initial pressure 1·01 mm of mercury. Sweep rate 20 $\mu$sec/square, sensitivity 2·5 mV/square.

It was found that, relative to the oscilloscope time-scale, the vibrational temperature approached its equilibrium value exponentially in the central part of the relaxation region. A characteristic frequency (A) for each shock wave could then be found from this time-scale. The actual arrival time of the shock front was not required for this to be accomplished. A typical semi-log plot is shown in figure 2. These relaxation frequencies were normalised to standard density by dividing by the equilibrium density and plotted logarithmically against the reciprocal of the cube root of the equilibrium temperature ($T_2$). These points on the Landau–Teller diagram had a good least squares straight-line fit as shown in figure 3.

In that part of the relaxation region, in which ($T_2 - T_V$) was found to be exponential,

$$\log (T_2 - T_V) = At' + B, \tag{4}$$

where $A$ and $B$ are constants for each shock wave. Thus

$$\frac{dT_V}{dt'} = A(T_2 - T_V). \tag{5}$$

The value of $A$ is given by the straight line of figure 3,

$$\log (A/\rho_2) = aT_2^{-\frac{1}{3}} + b. \tag{6}$$

Equation (3) becomes $\quad \phi = \dfrac{vA(\rho_2, T_2)}{\rho u_s} \left( \dfrac{d\sigma}{dT_V} \right) \dfrac{T_2 - T_V}{\bar{\sigma} - \sigma}. \tag{7}$
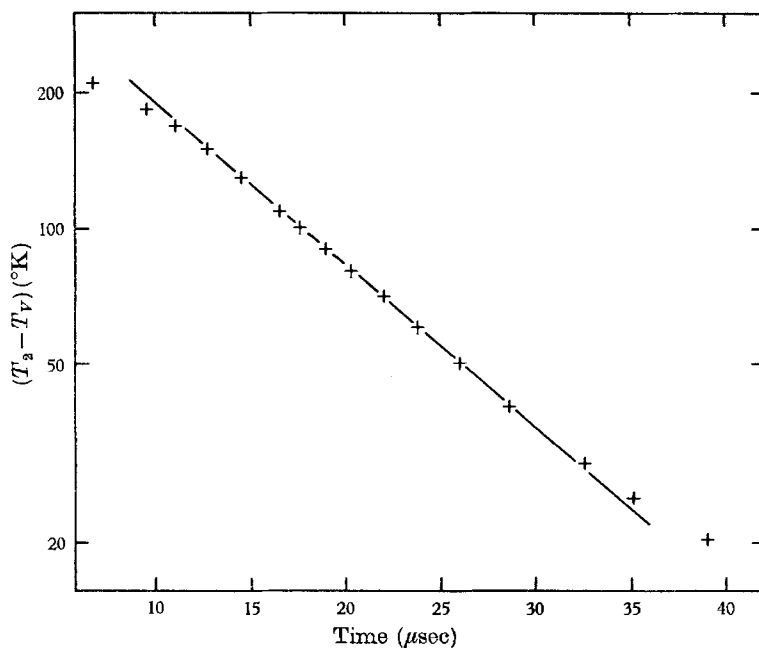
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FIGURE 2. Semi-log plot showing the departure from equilibrium of the vibrational
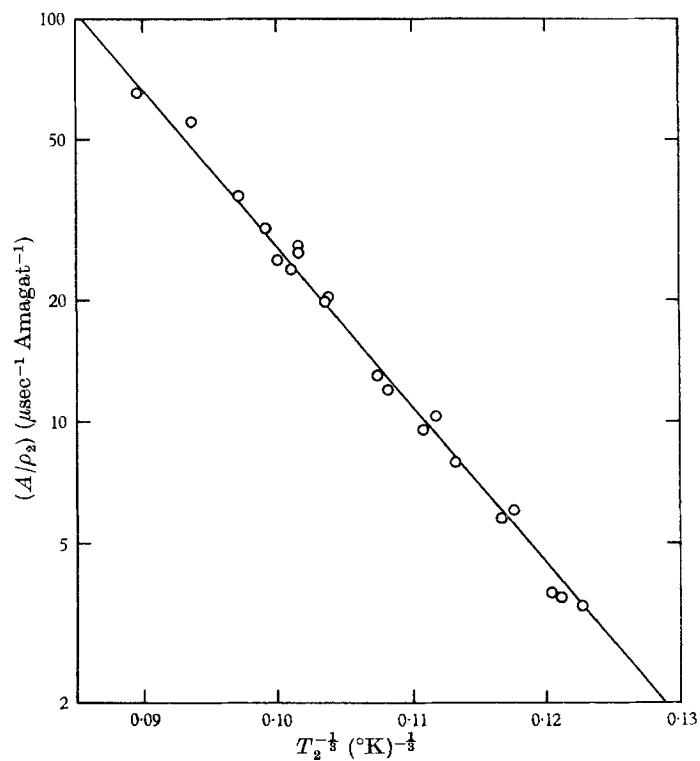temperature on the oscilloscope timescale (arbitrary zero).

FIGURE 3. Experimental values of the empirical constant $A$, normalized to standard den-
sity. The least squares straight-line fit is given by equation (6) with $a = -39 \cdot 36$ $(^{\circ}\text{K})^{\frac{1}{3}}$
and $b = 5 \cdot 398$.

Outside the region where $(T_2 - T_V)$ was found to be exponential, it was not possible to determine $\phi$, since the measurements were inaccurate, and we have no experimental information on the value of $(T_2 - T_V)$.

The values of $\phi$ for several shock wave Mach numbers are shown in figure 4. Each different shock wave gives rise to a separate line segment in this plot.
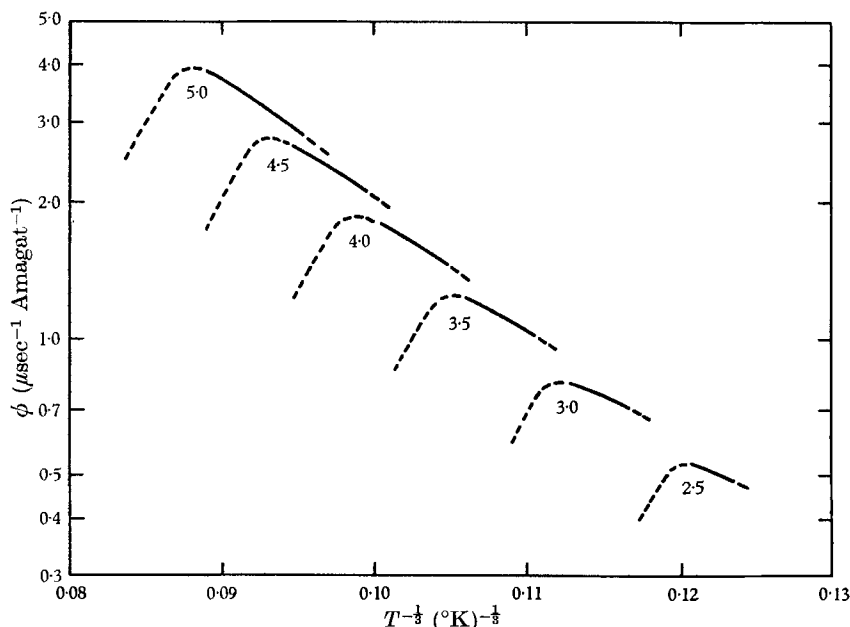


FIGURE 4. The relaxation frequency $\phi$ as a function of translational temperature for shock waves with the Mach numbers indicated.

The solid part of each segment corresponds to that part of the relaxation region for which $(T_2 - T_V)$ was found to be exponential. The broken lines at each end of the line segments represent the values of $\phi$, assuming that $(T_2 - T_V)$ is exponential throughout the relaxation region on the oscilloscope timescale. There is no experimental justification for consideration of the broken lines. Considering only the solid line segments, the relaxation frequency as measured by the infra-red emission techniques is a single-valued function of the translational temperature, to within the experimental error.

## 6. Conclusion

In that part of the relaxation regions where we have confidence in our results, the vibrational temperature of carbon dioxide was found to approach the equilibrium temperature exponentially relative to the oscilloscope timescale. Johannesen *et al.* (1962) found that the density approached its equilibrium value exponentially relative to the distance behind the shock front. Since (i) the density measurements were most accurate near the shock front, (ii) the oscilloscope timescale is linearly related to the distance behind the shock front, and (iii) the

assumption that $(\rho_2 - \rho)$ and $(T_2 - T_V)$ are exponential are not compatible, it follows that $(T_2 - T_V)$ is not exponential near the shock front.

In the temperature range, in which our experiments overlap those of Johannesen *et al.* (1962), the values of the vibrational relaxation frequency are compared in figure 5. The results obtained using the infra-red technique lie below those obtained from the density measurements, indicating that the relaxation frequency
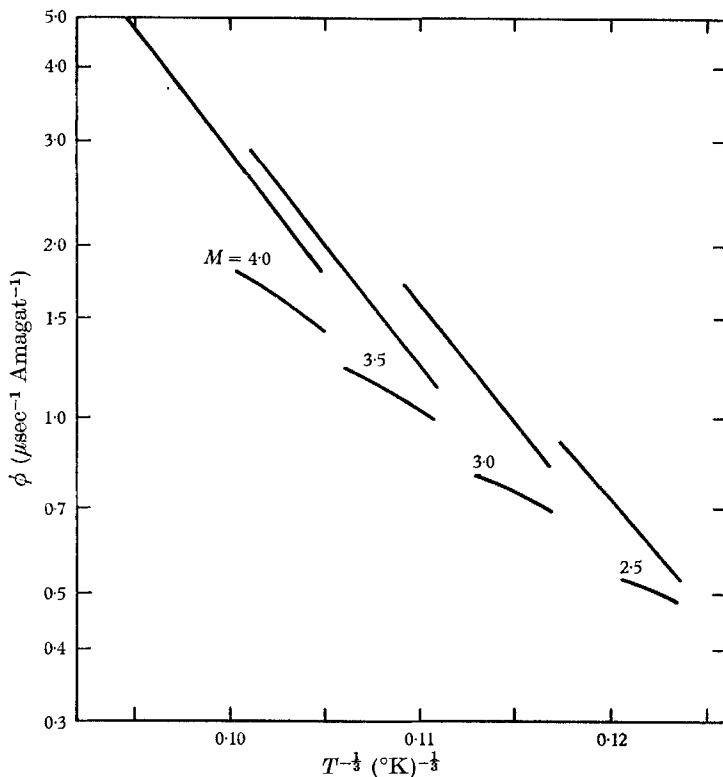


FIGURE 5. Comparison of the relaxation frequency obtained using the emission technique (lower line segments) with the results of the density measurements of Johannesen *et al.* (1962). Only the results for those parts of the relaxation region where the measurements were accurate are displayed.

of the asymmetric stretching mode is of the order of 30 % smaller than that of the bending mode. The exact relationship between the two single-mode relaxation frequencies is complicated, because neither series of observations depends entirely on the individual modes, and both sets of results were evaluated according to a single relaxation equation for the whole molecule.

In the light of recent theoretical investigations prompted by the publication of the work done by Simpson *et al.* (1967 *a*, *b*), it seems that the inclination of the line segments derived from the density measurements is a very sensitive function of the density and it is possible that the relaxation frequency as calculated from the density measurements is a single-valued function of temperature.

In order to determine a more exact relationship between the vibrational relaxation frequencies of the individual modes it is necessary to make a third set of observations. The experiment should be chosen so that the measured relaxation frequency is weighted differently towards each mode. Preferably the observed quantity should depend mainly on the symmetric stretching mode, but, since this mode does not exhibit in the emission spectrum of the molecule, such
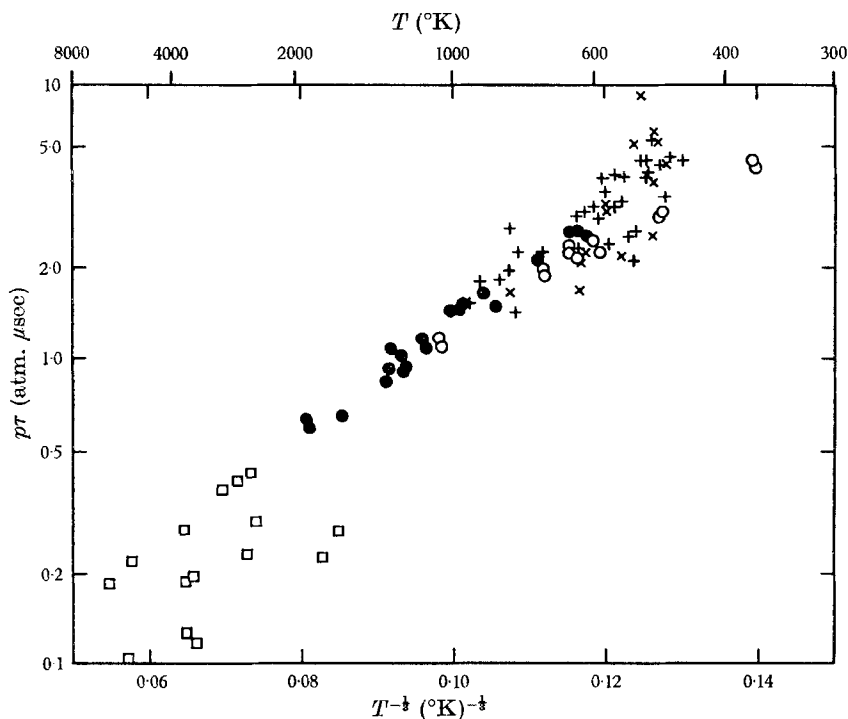


FIGURE 6. Over-all vibrational relaxation times at one atmosphere plotted against the mean translational temperature in the relaxation region. ●, present results (vibrational temperature); ○, Johannesen *et al.* (1962) (density); □, Camac (product of the density and specific vibrational energy of the asymmetric stretching mode); ×, Weaner *et al.* (density); +, Weaner *et al.* (product of density and specific vibrational energy of the asymmetric stretching mode).

a quantity would be difficult to isolate. For different weight factors it seems that the emission from the $2 \cdot 7 \mu$ combination band offers the best possibility experimentally, since this band is optically thin under the conditions necessary for shock tube measurement of the relaxation frequency of carbon dioxide. However, the integrated band intensity of combination bands is not a simple function of temperature (Malkmus 1964), so that the emitted radiant intensity is not proportional to the product of the density and specific vibrational energy of the modes involved, as for fundamental bands.

In order to compare these results and the density measurements of Johannesen *et al.* (1962) with those of Camac (1964) and Weaner *et al.* (1967), who calculated over-all relaxation times for each shock wave, the Manchester results were evaluated by the method used by Hooker & Millikan, and plotted in figure 6.

In this case there appears to be agreement between the present results and those of Johannesen *et al.* (1962); but it must be remembered that different quantities were observed in each case. Camac and Weaner *et al.* observed radiation emitted at $4 \cdot 3 \mu$ from gas samples assumed to be optically thin and described by the harmonic oscillator model. The variable measured was then the product of the density and the specific vibrational energy of the asymmetric stretching mode. Since both quantities in this product increase towards equilibrium the values of the relaxation times obtained would be expected to be smaller than those given by the density measurement.

The results of the infra-red emission experiments confirm the conclusion drawn by Johannesen *et al.* (1962) that all the vibrational modes have similar relaxation frequencies. This is opposed to the conclusion of Griffith *et al.* (1956), but the theoretical idea of Schwartz, that the bending and symmetric stretching modes have identical relaxation frequencies, may still be valid. All three vibrational relaxation frequencies are so similar that no single experiment is sufficiently accurate at present to detect the actual differences, though in principle three carefully chosen experiments should be sufficient to allow this.

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