Shock-Tube Study of Vibrational Relaxation in Nitrous Oxide

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The vibrational relaxation of nitrous oxide has been investigated by following the density changes occurring behind incident shock waves using a Mach–Zehnder interferometer. Measurements made up to an equilibrium temperature of 1700°K (Mach 7) show that neither the symmetric stretching mode nor the asymmetric stretching mode has a significantly longer relaxation time than the bending mode. The rate of relaxation has been measured as the gas relaxes towards equilibrium. During this process, the translational temperature of the gas falls, and it has been found that this fall in temperature will account for the observed increase of the relaxation time. Relaxation times have been measured from 320° to 850°K.

I. INTRODUCTION

This investigation follows similar work on the vibrational relaxation of carbon dioxide.[1] Again, the objects of experiments were to provide reliable measurements of the relaxation times and to find out whether the different vibrational modes possess separate vibrational relaxation times and whether the relaxation time depends upon how far the system is from equilibrium. In Ref. 1, evidence was given that the different modes have the same relaxation time, at least within a factor of 5, and that the time does not depend upon how far the system is from equilibrium. Nitrous oxide has very similar physical properties to carbon dioxide, but whereas there is Fermi resonance between the bending and the symmetric stretching mode of carbon dioxide, in nitrous oxide there is a wavenumber difference of 107 cm⁻¹ between the second harmonic of the bending mode and the symmetric stretching mode. This will result in a slower transfer of energy to the symmetric stretching mode from the bending mode in nitrous oxide than in carbon dioxide. Furthermore, the excitation of the bending mode in nitrous oxide (vibrational wavenumber 589 cm⁻¹) is a faster process than in carbon dioxide (vibrational wavenumber of 667 cm⁻¹). Thus, with the bending mode being excited more rapidly than in carbon dioxide and the energy-transfer process being slower, it might be expected that nitrous oxide does have separate relaxation times for these two vibrational modes. On the other hand, it is possible that the energy-transfer process is so fast that both modes relax together.

Since this work was undertaken, a paper has been published by Bhangu[2] which contradicts the earlier findings of Griffith, Brickl, and Blackman[3] that nitrous oxide possesses separate relaxation times. Bhangu analyzed his results by the method developed by Johannesen, Zienkiewicz, Blythe, and Gerrard[4] and

concluded that the relaxation time depends upon the displacement of the system from equilibrium.

II. EXPERIMENTAL

The shock tube used has been described in Ref. 1. The low-pressure section is rectangular, of internal dimensions 5.1 by 7.6 cm and length 3.7 m. The tube was driven using helium, nitrogen, or sulfur hexafluoride (SF_6), with prescored aluminium or brass diaphragms bursting spontaneously under pressure.

The shock trajectories were calculated using 13 accurately positioned gauges and making time measurements to ± 0.1 μsec using a spiral time base.[5] Before carrying out any measurements on the vibrational relaxation, a series of experiments was done to determine what gas pressures and diaphragm opening times were required to give shock trajectories in which the shock velocity remains constant to within $\pm 1\%$ for at least 1 m before the measuring station (see Ref. 6). Experiments on the variation of the density behind the incident shock wave showed that under these conditions the density remains constant to within $\pm 2\%$ for at least 50 μsec apart from the first few microseconds during which vibrational relaxation occurs.

Density changes were measured using a Mach–Zehnder interferometer. The density ρ_x at a position x behind the shock front is related to the measured fringe shift ΔN by the equation

$$\rho_x - \rho_1 = \lambda \Delta N / Kt.$$

The initial density ρ_1 was calculated from the initial temperature and the initial pressure. The pressures used varied from 5 to 200 mbar and were measured on Wallace and Tiernan absolute pressure gauges which had been calibrated at the National Physical Laboratory. t is the width of the shock tube and K the specific refractivity, given by

$$K = (n_0 - 1)/\rho_0,$$

[1] C. J. S. M. Simpson, K. B. Bridgman, and T. R. D. Chandler, J. Chem. Phys. **49**, 513 (1968).

[2] J. K. Bhangu, J. Fluid Mech. **25**, 817 (1966).

[3] W. Griffith, D. Brickl, and V. Blackman, Phys. Rev. **102**, 1209 (1956).

[4] N. H. Johannesen, H. K. Zienkiewicz, P. A. Blythe, and J. H. Gerrard, J. Fluid Mech. **13**, 213 (1962).

[5] A. G. Gaydon and I. R. Hurle, *The Shock Tube in High-Temperature Chemical Physics* (Chapman and Hall Ltd., London, 1963), p. 125.

[6] C. J. S. M. Simpson, T. R. D. Chandler, and K. B. Bridgman, Phys. Fluids **10**, 1894 (1967).
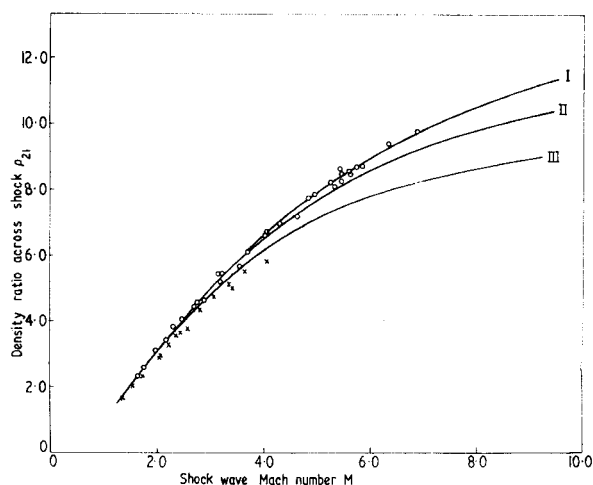
FIG. 1. Equilibrium density ratios for N_2O. Calculated curves: I, all modes excited; II, bending and symmetric stretching modes excited; III, bending mode only excited. Experimental points: O, present work; $\times$, Griffith et al. (Ref. 3).

where ρ_0 is the density of the gas at 0°C and 1.01 bar and n_0 its refractive index at the wavelength λ.

In order to find the final equilibrium density, measurements were made across the shock front under conditions at which vibrational relaxation occurred rapidly. The displacement of a given fringe was found using white light. When this technique is used, it must be remembered that as the fringe system is displaced dispersion effects will cause the brightest fringe to change its position from a given fringe to its neighbor for a jump of about 20 fringes.[7,8] The number of fringes after which this effect occurs depends upon the dispersion of the gas used in the shock tube and the mean wavelength of the light, but not upon its bandwidth. The latter quantity governs the magnitude of the relative intensity change but, at least within 0.01 of a fringe, not the fringe position. In order to avoid ambiguity due to dispersion, fringe jumps of less than 10 were used. Any further uncertainty of identification was eliminated by doing experiments with fringe jumps of only about 5 fringes. In such cases, selecting one fringe would give a result which agreed with that calculated for a change to an equilibrium condition to within 2%, whereas the choice of an adjacent fringe would give a difference of greater than 20%.

After each shock had been fired, a set of calibration fringes was taken on the same plate, or on the same film for drum camera experiments. For this purpose a narrow band filter centered at 4275 Å was used. The bandwidth was only 30 Å at 50% of peak height. For such a wavelength interval at 4275 Å, the response of the blue-sensitive Ilford L–N plates changes very

little and has a negligible effect in displacing the effective center of the filter. By measuring the fringe spacing for the brightest white light fringes, the effective wavelength of this light may be deduced as $\lambda_w F_w = \lambda_b F_b$, where F_w and F_b are the spacings in fringes per millimeter for the white and blue light. It was found to be 4400±70 Å. The uncertainty in λ_w gives an uncertainty in the specific refractivity K_w of ±0.1%. The measured displacement of a given white light fringe is given by $y = t(\rho_x - \rho_1)K_w/\lambda_w F_w$. The corresponding displacement of a monochromatic blue fringe for the same density change would be $y' = t(\rho_x - \rho_1)K_b/\lambda_b F_b$. Thus, y' can be found from y and the ratio of the specific refractivities, which is 1.002±0.001. F_b was measured from an average of 10 fringes and λ_b is known accurately, and so ρ_x can be calculated.

For the measurement of vibrational relaxation times, no question of identifying fringes arose, as the final equilibrium densities were calculated from the shock speeds and the relaxation process was investigated by making measurements of the displacements of a given fringe from its final equilibrium position.

The light source used in this work was either the "argon jet" source developed by North[9] with a duration at half-intensity of about 300 nsec or a spark source with a similar light output, but a duration at half-intensity of only 80 nsec.[10] The latter source was developed in order to try to get records with narrower shock fronts and a better time resolution than with the argon jet source. However, the improved time resolution did not lead to a decrease in the apparent shock-front thickness of about 0.2 mm. It seems this shock thickness is due to curvature of the shock front, as the result is consistent with estimates made using the
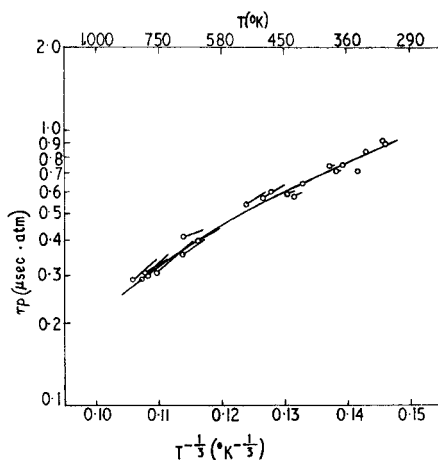

FIG. 2. Present experimental results for the vibrational relaxation times of N_2O. ——, over-all relaxation time; O—, relaxation time versus temperature for one experiment.

[7] H. K. Zienkiewicz, N. H. Johannesen, and J. H. Gerrard, J. Fluid Mech. 17, 267 (1963).
[8] H. K. Zienkiewicz, Aeronautical Research Council Rept. 26635 (1964).

[9] R. J. North, J. Soc. Motion Picture Television Engrs. 69, 711 (1960).
[10] C. J. S. M. Simpson, K. B. Bridgman, and T. R. D. Chandler, J. Sci. Instr. 1, 568 (1968).

formulas given by de Boer.[11] The fringe displacements were measured photoelectrically to 0.01 of a fringe.[12]

The nitrous oxide used was supplied and analyzed by the British Oxygen Company. The chief impurity was about 25 ppm of water vapor, which was reduced to a few parts per million using a Linde molecular sieve, Type 5A.

In experiments using carbon dioxide, it was found that a water content of about 30 ppm had a small but measurable effect on the relaxation rate.[1] Relaxation in nitrous oxide is less affected by water vapor than in carbon dioxide,[13] and so an impurity of a few parts per million will have a negligible effect. A further contamination of the gas might arise from leaking or degassing from the shock-tube wall. However, this could not be a serious source of water vapor as the tube was evacuated to 1×10^{-2} μbar for at least 2 h before each experiment, only dry gas was admitted into the shock tube, which has a leaking and degassing rate of about 10^{-3} mbar/min, and the shock was fired within 3 min of putting in the test gas.

III. RESULTS AND DISCUSSION

A. Possible Existence of Separate Relaxation Times for the Different Vibrational Modes

If all the vibrational modes have the same relaxation times to within a factor of about 5, then the density immediately following the relaxation region will correspond to the value for complete equilibrium. However, if the times differ by about 10, the curve of density against distance behind the shock front will show a
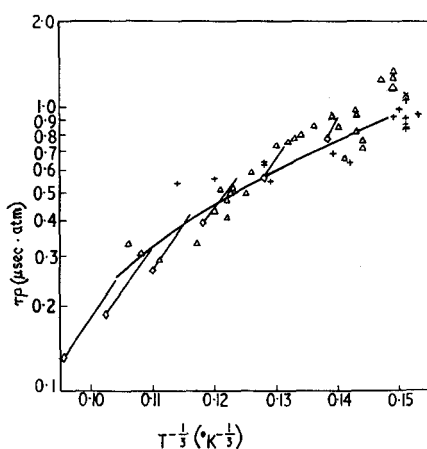

FIG. 3. Comparison between present and previous experimental results for the vibrational relaxation of N_2O. $\times$, spectrophone (Ref. 14); $+$, velocity of sound (Ref. 21); $\triangle$, Griffith et al. (Ref. 3); $\diamond$—, Bhangu (Ref. 2); ——, present work.
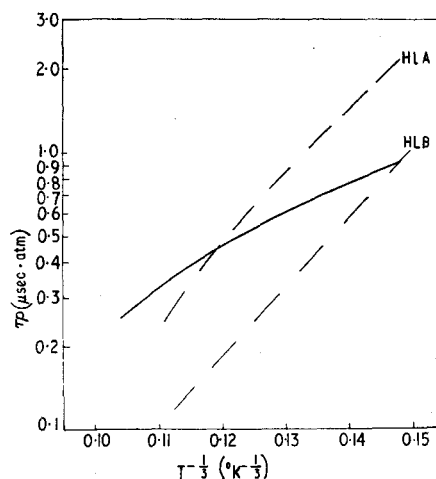

FIG. 4. Comparison between experimental and theoretical results for the vibrational relaxation of N_2O. HLA, Herzfeld and Litovitz Method A (Ref. 13); HLB, Herzfeld and Litovitz Method B (Ref. 13); ——, present work.

small step, and if the times differ very considerably, relaxation will occur to a condition where only some modes are excited, followed by a distinct, slower process. Griffith, Brickl, and Blackman[3] give results which are consistent with relaxation to such a state of partial excitation, though in the observation times available to them they found no evidence for the slower excitation to complete equilibrium. In this work we observed relaxation to the equilibrium value following the relaxation period of a few microseconds, with no evidence for a further change on a long time scale. Our results are given in Fig. 1 together with those of Griffith, Brickl, and Blackman. There is a very marked difference for which we have no satisfactory explanation. (It is not a case of the relaxation rate of the stretching modes being increased by impurities in our case since we used more carefully dried gas and have a shock tube which has a smaller leak rate and which was more carefully evacuated than that used by the Princeton workers.) Our results agree closely with those obtained recently by Bhangu.[2] They show that neither the symmetric stretching mode nor the asymmetric stretching mode relaxes much more slowly than the bending mode. Evidence for a small difference in relaxation times (1.6 and 1.1 μsec·atm) has been given from spectrophone experiments at room temperature by Cottrell, Macfarlane, Read, and Young.[14] No difference in times has been suggested from ultrasonic experiments.

B. Possible Dependence of the Relaxation Time on How Far the System is from Equilibrium

Before attempting a detailed analysis of the relaxation region, one must know the importance of the effect

[11] P. C. T. de Boer, Phys. Fluids 6, 962 (1963).
[12] G. D. Dew, J. Sci. Instr. 41, 160 (1964).
[13] K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic Press Inc., New York, 1959).

[14] T. L. Cottrell, I. M. Macfarlane, A. W. Read, and A. H. Young, Trans. Faraday Soc. 62, 2655 (1966).

of factors other than the relaxation on the fringe shift and flow variables behind the shock front. Imperfections in the optics may give random deviations of about 0.02 of a fringe. Howes and Buchele[15] have pointed out that the density gradient behind the shock can cause significant distortions to the fringe pattern observed across the shock tube for steep gradients using a wide shock tube. However, in this instance the correction is only about 0.01 of a fringe. Lapp[16] has considered the effect of infrared radiation causing excitation of the gas before the arrival of the shock wave. We have calculated the number of molecules excited in this way to be a very small fraction of those excited after the shock wave and find no experimental evidence for any change in density before the arrival of the shock wave.

More serious than these effects may be those caused by boundary layer growth. A slight compensation of having to make measurements within a few millimeters of the shock front as we have had to in studying this fast relaxation process is that the boundary layer has developed very little and so has only a small effect on the flow variables. Using equations given by Mirels,[17] we estimate that the higher density in the boundary layer may cause a fringe shift of about 0.02 of a fringe towards the end of our observation time.

Fox, McLaren, and Hobson[18] have pointed out that data on relaxation rates may need correcting due to the change in flow velocity behind the shock front caused by boundary layer growth. They made some experimental tests of equations developed by Mirels.[19] However, these corrections only become important for experiments concerned with gas at distance l behind the shock front when l is an appreciable fraction of l_m, the calculated maximum separation between the shock front and the contact surface. In our case l is only about 0.001 l_m, and the possible correction to the time scale behind the shock front is about 2% towards the end of our observation time. This has a negligible effect on our calculated relaxation times.

That our observed density changes are due to the relaxation process is shown by the fact that the fringe field becomes flat to 0.05 of a fringe over the relaxation region if the relaxation rate is increased. This occurs if the temperature is raised so that the relaxation rate is made fast or if this rate is increased by increasing the pressure. It might be objected that the latter test also causes the boundary layer to become thinner. However, if a gas is substituted which has similar physical properties to the test gas except for a faster relaxation time, then it can be used to show how flat the fringe field is under the actual test conditions for studying relaxation. In this way, nitrous oxide has been used to test the conditions for carbon dioxide, as it relaxes about 10 times as fast, and sulfur dioxide has been used for those for nitrous oxide, as it relaxes about another order of magnitude faster.

The relaxation times have been calculated by the same method as were those for carbon dioxide.[1] The conservation equations, the equation of state, and the relaxation equation, $d\sigma/dt = (\bar{\sigma} - \sigma)/\tau$, were solved to give a relation between the rate of relaxation, the initial conditions, the shock velocity, and the local values of the density and the density gradient behind the shock front. Here σ is the vibrational energy the molecule actually possesses at a position x behind the shock front when the translational temperature is T and $\bar{\sigma}$ is the vibrational energy which the molecule would possess in equilibrium at that temperature. τp is the relaxation time, which is expressed in microseconds·atmospheres. The necessary thermodynamic data were taken from the tables by McBride, Heimel, Ehlers, and Gordon.[20]

In order to find the values of ρ and $d\rho/dx$, the measured fringe displacements y were fitted by a curve $y = (a + bx + cx^2) \exp(kx)$ which was differentiated to give dy/dx. ρ and $d\rho/dx$ were then calculated from y and dy/dx. When the results were calculated in this way it was found that the relaxation time does not depend upon how far the system is from equilibrium, at least within an experimental error of ± 0.05 of a fringe, which was taken as the uncertainty on the final density reading. The results for the variation of relaxation time for a given shock are less certain than those measured for carbon dioxide, owing to the greater difficulty of following the faster relaxation process. The values of τp are plotted against $T^{-1/3}$ in Fig. 2. Each line represents the result from one run; for results near room temperature only one point is given, as the change in temperature during the relaxation process is very small and τp varies very little.

These results may be contrasted with those of Bhangu, who considers that the relaxation time is not simply a function of the translational temperature. The cause of this difference seems to be due to the assumption that the fringe displacement varies exponentially with the distance behind the shock front.

C. Comparison between the Present Results and Those Obtained by Other Workers

Figure 3 shows a comparison between our results, those obtained by Griffith, Brickl, and Blackman, by

15 W. L. Howes and D. R. Buchele, J. Opt. Soc. Am. 56, 1517 (1966).
16 M. Lapp, Phys. Fluids 7, 1233 (1964).
17 H. Mirels, National Advisory Committee for Aeronautics, Tech. Note 3712 (1956).
18 J. N. Fox, T. I. McLaren, and R. M. Hobson, Phys. Fluids 9, 2345 (1966).
19 H. Mirels, Phys. Fluids 6, 1201 (1963).

20 B. J. McBride, S. Heimel, J. G. Ehlers, and S. Gordon, NASA SP3001 (1963).

Bhangu, and from ultrasonic and spectrophone experiments. The over-all values given by Bhangu differ slightly from our results, and each of his individual runs has a different temperature coefficient. By driving shocks with SF_6 we were able to make measurements quite close to room temperature, and here our results agree well with what are considered the most reliable values obtained from ultrasonic experiments (see Cottrell and McCoubrey[21] for references and a discussion of these results) and with the spectrophone result for the relaxation of the bending and symmetric stretching modes given by Cottrell et al.[14]

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[21] T. L. Cottrell and J. C. McCoubrey, *Molecular Energy Transfer in Gases* (Butterworths Scientific Publications Ltd., London, 1961).

D. Comparison between the Present Experimental Results and Calculated Results

Two different calculations for the relaxation times in nitrous oxide are given by Herzfeld and Litovitz[13] which differ only in the way in which the potential function is chosen. Both calculated curves are fairly close to the experimental results, but have too steep a temperature coefficient. This is similar to the situation found for the relaxation in carbon dioxide. The results are shown in Fig. 4.

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Shock-Tube Study of Vibrational Relaxation in Carbon Dioxide

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Measurements of the variation of density behind incident shock waves in carbon dioxide have been made using a Mach–Zehnder interferometer at shock speeds of up to Mach 9 (2500°K). The results show that vibrational relaxation occurs to a state in which all the vibrational modes are excited to their equilibrium values with neither the symmetric stretching nor the asymmetric stretching modes having significantly longer relaxation times than the bending mode. It has been found that the density does not change exactly exponentially with distance behind a shock front as has been assumed in the past. It has been shown that it is this assumption which led to the idea that the rate of vibrational relaxation depends not only on temperature, but also on the departure of the system from equilibrium. The present results can be accounted for if the relaxation time is a function of temperature alone. Relaxation times have been calculated taking account of the changes in the translational temperature which occur during the relaxation process. The results cover the temperature range 330°–1600°K.

I. INTRODUCTION

This study gives further evidence on three questions connected with the vibrational relaxation of carbon dioxide. The first is whether there are separate relaxation times for the different vibrational modes. The second is whether the vibrational relaxation time depends upon how far the system is from equilibrium as well as being a function of temperature. The third is which amongst the many measurements gives the correct relaxation times for pure carbon dioxide. In this investigation the relaxation process has been studied by measuring the density changes occurring behind incident shock waves.

II. EXPERIMENTAL

The shock tube used has a high-pressure section of internal diameter 10.8 cm and length 1.9 m. It was honed and chrome plated. This is followed by a 15-cm long stainless-steel transition section, leading to the 5.1×7.6-cm rectangular low-pressure section. This section is formed from four bars which are approximately 3 cm thick and 3.7 m long. Each bar was ground and plated together with all the fittings for the windows, thin-film gauges, and pressure gauges so that these can be fitted flush with the inner surface of the shock tube. The bars are bolted together in the form of a box and sealed with O rings. The tube can be evacuated to 1×10^{-5} torr and has a combined leaking and degassing rate of 2×10^{-4} torr/min. The shock trajectory was measured from thin-film gauges located to 0.1 mm every 30 cm along the length of the low-pressure section and the time intervals measured to 0.1 μsec using an oscilloscope with a spiral time-base generator.[1,2]

The diaphragms were made of brass, copper, or

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[1] A. G. Gaydon and I. R. Hurle, *The Shock Tube in High-Temperature Chemical Physics* (Chapman and Hall Ltd., London, 1963), p. 125.
[2] C. J. S. M. Simpson, T. R. D. Chandler, and K. B. Bridgman, Phys. Fluids **10**, 1894 (1967).