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The Multiple Quantum Jump Model for Vibrational Energy Relaxation

By

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ROYAL AIRCRAFT ESTABLISHMENT
BEDFORD.THE MULTIPLE QUANTUM JUMP MODEL
FOR VIBRATIONAL ENERGY RELAXATION**

- by -

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and
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An anomaly has existed for some years concerning the much faster vibrational energy relaxation rates observed for some gases in expanding flows than are inferred from data measured in shock-excited environments. An analysis is described for a simple diatomic gas in these situations in which multiple quantum jumps are allowed between vibrational states in an attempt to account for this anomaly. The relaxation rates are shown to depend upon the vibrational temperature as well as the translational temperature. Rates calculated for nitrogen show the de-excitation rates in a nozzle expansion to be faster than the excitation rates in a shock-excited environment at the same translational temperature, but by an amount far less than that observed experimentally.

Contents/

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1. Introduction

At moderate temperatures, when the contributions to the energy content of a molecular gas due to electronic excitation, ionisation and dissociation are negligibly small, the internal energy of a gas is made up of three parts: the kinetic energy of translation of the molecules; the energy of molecular rotation; and the energy of molecular vibration. At any temperature these energies have equilibrium values which can be calculated using quantum-statistical mechanics.

In hypersonic flow the changes of state imposed upon a gas are often very rapid. In many cases the time required for a gas to reach equilibrium in the equipartition of energy between the various degrees of freedom of its particles may be comparable to the particle transit time over some characteristic length in the flow. Under these circumstances the flow is said to be a "non-equilibrium" flow, and the time characterising the existence of a gas element in a non-equilibrium condition is called the "relaxation time". Under non-equilibrium conditions each degree of freedom may have an energy content which differs from its equilibrium value. Provided that the density of the gas is high enough, the energy modes will exchange energy by collision until they attain their equilibrium values. The translational and rotational energy modes usually adjust very quickly towards equilibrium with each other, only a few molecular collisions being required. These modes are therefore called the active energy modes, and their energy content is specified by one "active" temperature, T . The vibrational energy mode is relatively much more slowly adjusted. This slow adjustment, and the ease with which a vibrational non-equilibrium state can be produced under laboratory conditions, has

led to a great deal of experimental and theoretical attention being focussed upon it.

Landau and Teller (Ref. 1) were the first to derive a theoretical relation describing the vibrational relaxation of a gas system composed of diatomic molecules. They showed that the relaxation process may be described by the rate equation

$$\frac{dE_v}{dt} = ZP_{1,0} \{ 1 - \exp(-\theta_v/T) \} \{ E_v(T) - E_v \} \quad \dots \quad (1)$$

where E_v is the instantaneous vibrational energy of the gas, $E_v(T)$ is the vibrational energy that the system would have if it were in equilibrium at the local active temperature T , θ_v is the characteristic vibrational temperature, and Z is the bimolecular collision rate. The term $P_{1,0}$ is the probability per collision of transferring one quantum of energy from the vibrational mode to the active energy mode, the vibrator "jumping" from the first excited vibrational energy level to the ground state.

Equation (1) may be written in the form

$$\frac{dE_v}{dt} = \frac{E_v(T) - E_v}{\tau} \quad \dots \quad (2)$$

where τ is a characteristic vibrational relaxation time given by

$$\tau = \left\{ ZP_{1,0} \{ 1 - \exp(-\theta_v/T) \} \right\}^{-1} \quad \dots \quad (3)$$

The dependence of τ on the bimolecular collision rate Z shows that it is inversely proportional to the pressure p of the gas. It is usual when correlating vibrational relaxation data to define a napier time τ_N such that

$$\tau_N = \tau p \quad \dots \quad (4)$$

Using viscosity data, Landau & Teller derived an expression for $P_{1,0}$ as a function of the temperature T of the active modes as

$$\frac{1}{P_{1,0}} = A(T) \exp (B/T)^{1/3} \dots\dots\dots (5)$$

where $A(T)$ is a weak function of T and B is a constant both of which depend upon the properties of the molecule. Equations (3) and (5) provide the dependence of τ on T . Further details of the derivation of these equations are given in Ref. 2.

The limitations on the Landau-Teller rate equation and the relaxation time τ are set by the approximations in the thermodynamic model used to derive the equations and the accuracy of the viscosity data used. The dependence of $\ln \tau$ on $T^{-1/3}$ has been confirmed by more sophisticated theoretical arguments, for example those by Zener (Ref. 3) and by Schwartz and Herzfeld (Ref. 4) and also by experiments (Refs. 5 and 6). However, the values of A and B are controversial and these are normally determined by experiment. The Landau-Teller model predicts a variation of relaxation time with temperature which is in good agreement with measured values in shock-excited environments where the vibrational mode is excited by energy transfer from the active modes (Ref. 5). Using these measurements to determine values of $A(T)$ and B , the Landau-Teller rate equation may be applied in expansion environments, such as nozzle flows, where the vibrational mode is being de-excited by energy transfer to the active modes. For nitrogen the predicted rates of de-excitation are considerably lower than those measured in such circumstances (Refs. 7 and 8). Similar anomalous results have been reported for carbon monoxide (Ref. 9) though conflicting evidence is reported in Ref. 8. A summary of the current status of the measured vibrational

relaxation data for nitrogen is shown in Figure 1 taken from Ref. 10.* The functional dependence of τ on $\exp(T^{-\frac{1}{2}})$ is present in both cases, but the parameters A (T) and B of equation (5) are very different for the excitation and de-excitation cases.

Many reasons have been put forward to explain this anomaly, but the various models proposed have met with little success. In deriving the Landau-Teller rate equation governing the vibrational relaxation process, no account is taken of several phenomena which may have some effect on relaxation rates. Among these are:

- (a) molecular anharmonicity,
- (b) non-isothermal effects,
- (c) energy exchange between the vibrational and rotational modes,
- (d) coupling between vibrational relaxation and chemical reactions,
- (e) coupling between the vibrational mode and the electronically excited states of free atoms present as impurities,
- and (f) multiple quantum jumps between vibrational energy levels.

Each of these effects is discussed briefly.

(a) Molecular anharmonicity

The Landau-Teller model depends critically upon the assumption that the vibrational mode of molecules may be adequately represented as a simple harmonic oscillator. The simple harmonic oscillator approximation takes no account of the closely packed upper energy levels typical of a real gas near the dissociation limit. Energy

* The two curves \bar{A} and \bar{B} for the shock-excitation data in Figure 1 are correlations of the experiments of References 7 and 11, among others. Although curve \bar{B} has been accepted as representing the excitation rate data at moderately low temperatures, recent experimental work reported in Reference 12 suggests that curve \bar{A} may be a better fit to the data.

is exchanged relatively easily between these levels and the active energy mode, and such exchanges occur much more readily than active energy exchanges with the lower energy levels of the oscillators. In shock excitation environments the higher energy states of the vibrational mode have a small population during the initial stages of relaxation. Conversely, in expanding flow environments the upper states have a relatively large population which enhances the transfer of energy to the active mode via the higher vibrational levels.

Bray (Ref. 13) used a Morse oscillator model to account for the anharmonicity of a real gas. He found that, in an expanding flow, much faster de-excitation rates are predicted using his model than are predicted by the Landau-Teller rate equation using the same excitation data. This appeared to explain the anomaly. However for nitrogen, the conditions necessary for the faster rates implied by Bray's analysis are far removed from the actual conditions under which anomalous rates have been obtained experimentally.

(b) Non-isothermal effects

Inherent in most derivations of a vibrational relaxation rate equation is the assumption of a steady-state vibrational energy distribution function. In other words,

$$N_m = N_m(m, T, T_v) \dots\dots\dots(6)$$

where N_m is the population of the m^{th} vibrational energy level, T_v is the vibrational temperature specifying the energy in the vibrational mode and T is the active temperature. Thus changes in the active temperature with time will introduce dT/dt terms into the rate equation. These are usually assumed to be negligible and τ is regarded as a local relaxation time at the instantaneous

temperature T.

Conditions may arise however when such terms are not negligible, and in those circumstances the Landau-Teller rate equation among others, becomes invalid. Furthermore, it has been shown (see Ref.13) that a falling active temperature increases the transfer of vibrational energy to the active modes by increased transfer from the closely-packed upper energy levels, as mentioned previously.

In his anharmonic oscillator model, Bray also considers non-isothermal effects. He concludes that very large rates of change of temperature are required under extreme conditions of low temperature and pressure before these effects invalidate the assumption of a steady state distribution function and increases in vibrational relaxation rates occur.

(c) Energy exchange between the vibrational and rotational modes

There is a much smaller difference between a quantum of vibrational energy and a quantum of rotational energy than between vibrational and translational quanta, at least away from the dissociation limit. It is to be expected therefore that vibrational energy is transferred to the translational mode via the rotational mode as well as by direct transfer. It is this coupling of vibration and rotation which gives rise to the variation with temperature of the parameter A in equation (5). Stretton (Ref. 14) suggests that this coupling enhances the overall vibration-translation energy transfer by three to six-fold. This seems to be about the best assessment one may make at present and explains the need for experiments to obtain absolute values of vibrational rate parameters. However, although the rate of energy transfer from vibration to translation is increased via vibration-rotation coupling, there does not appear to be a mechanism whereby vibration-rotation exchanges are not equally effective in both

vibrational excitation and de-excitation environments. Very little experimental work has been reported on energy transfer from vibration to rotation (Ref. 15) so that few significant conclusions can be reached regarding this type of transfer process.

(d) Coupling between vibrational relaxation and chemical reactions

In principle experimental conditions may be chosen in such a way that chemical effects on the vibrational relaxation rate are negligible. However, impurities may have a marked effect on the vibrational relaxation rate of the test gas. Hydrogen is a typical example of an impurity which may affect the relaxation rates as measured in shock-tubes and shock tunnels. Hydrogen is often used as the driver gas in these devices, and unless precautions are taken molecules may remain in the test section from earlier shock-tube experiments. In addition, back streaming of pump oil is a source of hydrocarbons from which hydrogen atoms are easily stripped.

For excitation environments behind shock waves, little time is available for any hydrogen compounds present to dissociate and form atoms which will affect the relaxation rate of the shocked test gas. In shock tunnels, a high enthalpy reservoir of gas is obtained by shock heating, and the hot gas is then expanded into a nozzle. This high enthalpy region may exist for sufficient time to dissociate* any hydrogen molecules or hydrocarbons present in this region. The hydrogen atoms so formed expand through the nozzle with the test gas. Depending on their concentration, these highly mobile atoms

* Where direct dissociation is unlikely because the enthalpy of the test gas is too low, the presence of sodium atoms, which are often used as a trace material in vibrational relaxation experiments, could catalyse the breakdown of hydrogen molecules through the formation of NaH (Ref.16).

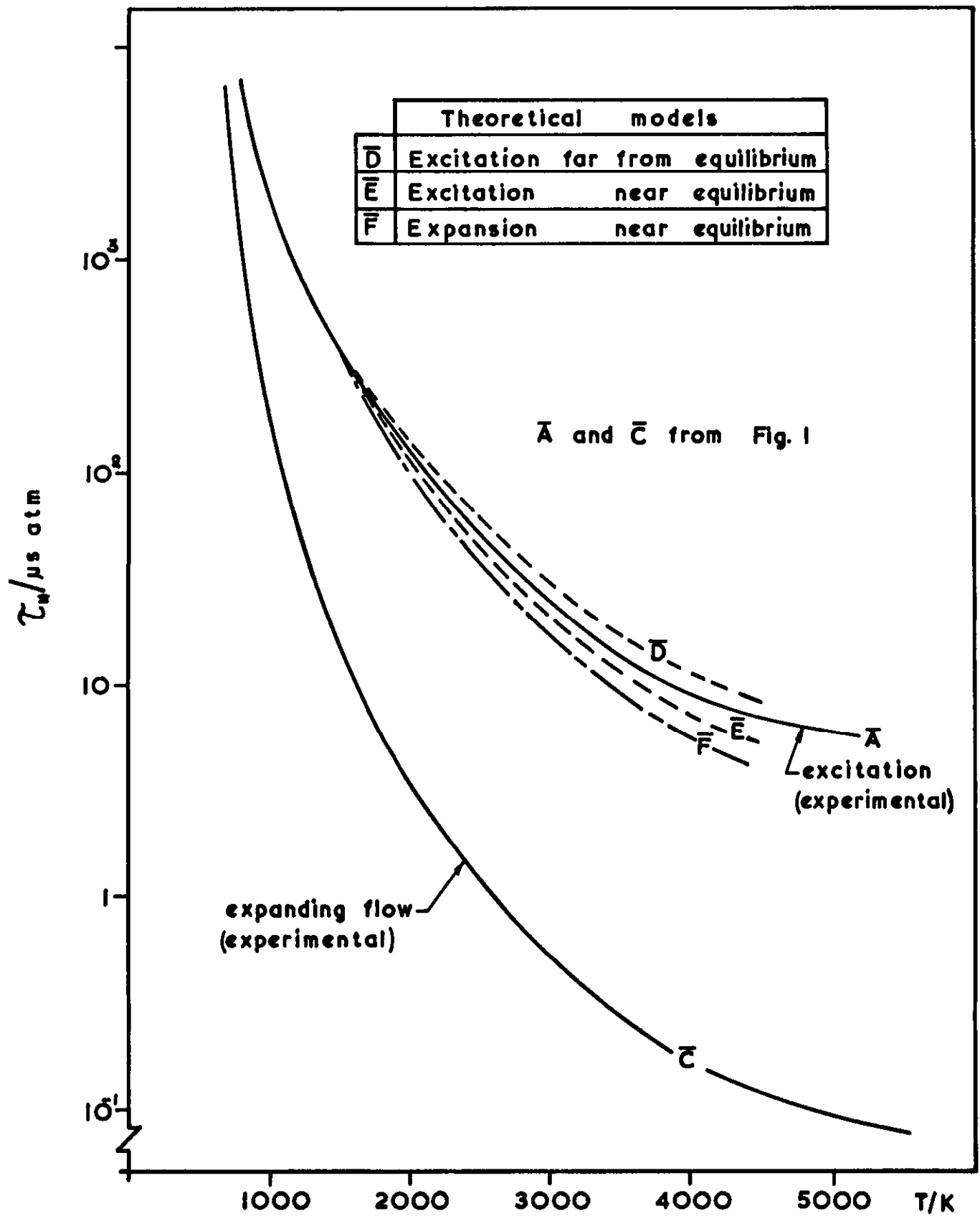


Fig. 2 Comparison of calculated results with empirical correlations of Figure 1

between these modes. The light emitted by the metallic atoms is thus an indirect measure of the energy content of a particular vibrational energy level. The transfer of energy between the active modes of the test gas and the electronic energy of the metallic atoms is negligible compared with the vibrational energy transfer. Provided the molecules of the test gas have a Boltzmann distribution of their vibrational energy, the electronic temperature of the metallic atoms present is indicative of the test gas vibrational temperature. This resonant energy exchange has been verified experimentally for sodium and nitrogen (Ref. 18). The main doubt in line-reversal experiments is whether in expansion flow environments, a Boltzmann population of the vibrational energy levels exists.

This is discussed by Bray (Ref.12) who concluded that very extreme conditions are necessary before the steady state distribution function ceases to apply. The thermodynamic effects of seeding a test gas are discussed in Ref. 12.

Free atoms which take no part in the vibrational energy exchange but merely provide a "heat bath", have been used in vibrational relaxation experiments to ensure that the relaxation process takes place under isothermal conditions (Ref. 17). Vibrational relaxation rate data obtained from such experiments using a mixture of nitrogen and argon agree with the results for pure nitrogen. In view of the wide range of nitrogen concentrations used, these results suggest that the relaxation rate anomaly is not associated with atom-exchange processes of the type proposed by Bauer & Tsang (Ref.19).

(f) Multiple quantum jumps between vibrational energy levels

The calculation of transition probabilities for energy exchanges between the vibrational and the active modes of a molecular system may be divided into two distinct parts: low active temperatures and

high active temperatures. At low temperatures, the time of interaction between molecules is large compared with the vibrational period of the molecules. In this case most collisions lead to transitions between low lying vibrational levels. This is called "almost adiabatic" energy transfer and it leads to the prediction of single quantum jumps between neighbouring vibrational levels during the relaxation process. This gives the Landau-Teller type of relaxation equation presented earlier.

As the active temperature of the gas increases, the assumption of almost adiabatic energy transfer between the active and vibrational modes becomes less justifiable and the first-order perturbation analyses used to derive transition probabilities are no longer valid. When the active temperature of the gas is sufficiently large, the active energy of the molecules may be considered as unchanged during a collision which involves an exchange of vibrational quanta. This is the "impulsive" interaction theory proposed by Bak & Fisher (Ref.20); it leads to the prediction that vibrational quantum jumps to any level are equally probable.

Between these extremes are the numerical calculations of Shuler & Zwanzig (Ref. 21) and Rapp & Sharp (Ref. 22). By their nature these calculations cannot provide an analytical description of the vibrational energy relaxation process.

If transitions between other than neighbouring vibrational levels are allowed, a mechanism exists whereby the de-excitation may be faster than the excitation of the vibrational mode. This is because the energy required to transfer quanta into the vibrational mode must be available in the active mode. This introduces an effective collision term into the excitation terms in the master equation controlling the relaxation process. Conversely, the vibrational

de-excitation terms do not have this effective collision term if it is assumed that the active mode of a molecule can absorb any amount of vibrational energy during a collision. This point is clarified in Section 2 where this mechanism is examined in detail.

A numerical calculation of the effects of multiple quantum jumps on the vibrational relaxation rate has been carried out by Northup & Hsu (Ref. 23).

They used the machine calculations of Rapp & Sharp (Ref. 22) to evaluate the transition probabilities in the master equations for vibrational relaxation. They then solved the equations for shock excited nitrogen and compared the resulting energy distribution with experimental values obtained by Hurle & Russo (Ref. 17). Their results show that multiple quantum jumps have little or no effect on the vibrational relaxation rate of nitrogen up to a temperature of 7000 K, and that the Landau-Teller type of analysis is adequate up to this temperature. Unfortunately, Northup and Hsu did not extend their calculations to expanding flow environments. Such a calculation is described in this paper.

2. The multiple quantum jump model

Of the theoretical models whose implications have been fully investigated none has explained the anomalous vibrational de-excitation rate of nitrogen. However the effects of allowing multiple quantum jumps between vibrational energy levels has not been examined for an expanding gas, and a model is proposed here to do so. The assumptions embodied in this model are aimed at simplicity in order to obtain an analytic form for the rate equation. Complications such as anharmonicity and non-Boltzmann populations of vibrational energy levels are ignored, and in general at low temperatures, active to vibrational mode transition probabilities are overestimated. The results of the analysis justify these assumptions to some extent, as will be demonstrated. The assumptions are listed below.

- (1) The gas system is composed of N simple harmonic oscillators which can only exist at a very large number (assumed infinite for the purpose of calculation) of discrete energy levels, the m^{th} energy level having a population N_m .
- (ii) A Boltzmann distribution of vibrational energy exists at all times and is characterised by one vibrational temperature T_v .
- (iii) V-V collisions, which only involve exchanges of vibrational energy, are far more probable than T-V collisions which involve exchanges of energy between the active and vibrational modes. The V-V collisions maintain the Boltzmann population distribution among the vibrational energy levels.
- (iv) T-V transitions probabilities are of the impulsive interaction type as given by Bak & Fisher (Ref. 20).
- (v) A Boltzmann population of the active energy modes exists

at all times and is characterised by one temperature T. The energy in the rotational mode is accounted for by T, but the effect of rotational energy on T-V collisions is ignored to avoid further complexity.

- (vi) During collision, a vibrator can take up any number of quanta of vibrational energy provided this energy is available in the active mode.
- (vii) During a collision, a vibrator can lose any number of quanta of vibrational energy to the active mode, and this exchange is only limited by the energy in the vibrator.
- (viii) The principle of detailed balancing is valid during collisions which involve a transfer of more than one quantum of vibrational energy.

For assumption (iv) the transition probabilities for T-V energy transfer become,

$$\begin{aligned}
 P_{m, m-n} &= P_{m, m-1} & ; & \quad (n = 1, 2 \dots m) \\
 P_{m, m+n} &= P_{m, m+1} & ; & \quad (n = 1, 2 \dots \infty) \\
 P_{m+n, m} &= P_{m+1, m} & ; & \quad (n = 1, 2 \dots \infty) \\
 P_{m-n, m} &= P_{m-1, m} & ; & \quad (n = 1, 2 \dots m)
 \end{aligned}
 \tag{7}$$

where $P_{m, m-n}$ is the probability of a molecule jumping from level m to level m-n during a T-V collision, and similarly for $P_{m, m+n}$, etc.

The critical assumption is now made that the ratio of transition probabilities between two levels is proportional to the ratio of the corresponding vibrational energy levels. Strictly this assumption only applies to adiabatic collisions between simple harmonic oscillators in an exponential force field. In the absence of better

information this assumption is made for non-adiabatic collisions. Thus,

$$\begin{aligned}
 P_{m, m-1} &= m P_{1,0} \\
 P_{m, m+1} &= (m+1) P_{0,1} \\
 P_{m+1, m} &= (m+1) P_{1,0} \dots\dots\dots(8) \\
 P_{m-1, m} &= m P_{0,1}
 \end{aligned}$$

The master equation (see Ref. 24) which describes the rate of change of population of the mth level with time $\frac{dN_m}{dt}$, and which allows for multiple quantum jumps during a collision is given by:

$$\begin{aligned}
 \frac{dN_m}{dt} &= \sum_{n=1}^m Z' P_{m-n,n} N_{m-n} - \sum_{n=1}^{\infty} Z' P_{m,m+n} N_m \\
 &+ \sum_{n=1}^{\infty} Z' P_{m+n,m} N_{m+n} - \sum_{n=1}^m Z' P_{m,m-n} N_m + (V-V)\text{-terms} \dots\dots(9)
 \end{aligned}$$

where Z' is the number of collisions per time during which energy is exchanged between the active and vibrational modes. The "(V-V)-terms" account for collisions which involve only an exchange of vibrational quanta during a collision.

In order for n quanta to be transferred from the active mode to the vibrational mode in one collision, only a collision pair with a relative active energy greater than or equal to $nh\nu$ will be effective in a collision. Here, h is Planck's constant and ν is the vibrational frequency of the oscillator. Conversely, for the transfer of vibrational energy to the active mode, all collisions are assumed effective. Under these circumstances, equation (9) becomes

$$\begin{aligned}
 \frac{dN_m}{dt} &= Z \left\{ \sum_{n=1}^m e^{n\alpha} P_{m-n,m} N_{m-n} - \sum_{n=1}^{\infty} e^{n\alpha} P_{m,m+n} N_m \right. \\
 &+ \left. \sum_{n=1}^{\infty} P_{m+n,m} N_{m+n} - \sum_{n=1}^m P_{m,m-n} N_m \right\} + (V-V)\text{-terms} \dots (10)
 \end{aligned}$$

where Z is the bimolecular collision rate and

$$\alpha = -\frac{\Theta_v}{T} \dots\dots\dots(11)$$

In equation (10), $e^{n\alpha}$ is an effective collision parameter derived from classical mechanical considerations (Ref. 2).

Multiplying equation (10) by m and summing over the vibrational energy levels gives -

$$\begin{aligned} \frac{d}{dt} \left\{ \sum_{m=0}^{\infty} m N_m \right\} &= Z \sum_{m=0}^{\infty} \sum_{n=1}^m e^{n\alpha} P_{m-n,m} N_{m-n} \\ &- Z \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} e^{n\alpha} P_{m,m+n} N_m \\ &+ Z \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} P_{m+n,m} N_{m+n} \\ &- Z \sum_{m=0}^{\infty} \sum_{n=1}^m P_{m,m-n} N_m \quad \dots \quad (12) \end{aligned}$$

and the (V-V) terms in equation (10) sum to zero, as they neither add to nor subtract from the vibrational energy of the system.

Assumptions (ii) and (v) give

$$E_v = \frac{Nh\nu}{\{ \exp(\theta_v/T_v) - 1 \}} \quad \dots \quad (13)$$

and

$$E_v(T) = \frac{Nh\nu}{\{ \exp(\theta_v/T) - 1 \}} \quad \dots \quad (14).$$

Two parameters, S and R related to the vibrational partition functions at temperatures T_v and T respectively are defined for convenience as

$$S = \{ 1 - \exp(-\alpha/T_v) \}^{-1} \quad \dots \quad (15)$$

and

$$R = \{ 1 - \exp(-\alpha) \}^{-1} \quad \dots \quad (16).$$

Using the principle of detailed balancing, and substituting from equations (7) to (16), equation (12) is reduced to

$$\frac{dE_v}{dt} = Z P_{1,0} G(T, T_v) \{ E_v(T) - E_v \} \quad \dots \quad (17)$$

where

$$G = 2R^2 + 4S^2 + 4SR - 5R - 8S + 4 \quad \dots \quad (18).$$

Comparison with equation (2) gives the relaxation time as

$$\tau(T, T_v) = \{ Z P_{1,0} G \}^{-1} \dots (19)$$

Equation (17) is the rate equation governing vibrational relaxation when multiple quantum jumps are allowed.

3. Discussion

Two significant points are immediately obvious from the form of the rate equation (17) governing the relaxation process. At low temperatures, T and T_v much less than Θ_v , the rate equation reduces to the Landau-Teller equation, i.e. equation (1). This shows that the exaggerated impulsive interaction transition probabilities at low temperatures have little effect on vibrational energy transfer due to the small population of the higher vibrational levels at these low temperatures. At temperatures of order Θ_v the impulsive interaction assumption becomes more valid, and the effect of this assumption is embodied in the term G of the rate equation. The relaxation time is now a function of both T and T_v because G is a function of these parameters. This appears to be the only model of vibrational relaxation in which a dependence of τ on T_v has been found.

Equation (19) shows that multiple quantum jumps provide a mechanism whereby a faster relaxation rate can occur in an expansion environment than in a shock excitation environment. By way of illustration consider the case where T is approximately equal to Θ_v . In an excitation environment T_v will be less than T . Thus only terms in G containing R will be significant in evaluating τ . In an expansion environment at the same value of T , T_v will be greater than T , and terms containing both R and S will be significant in evaluating G and hence τ . Depending on the values of R and S obtained in both environments, τ in the excitation case will be greater than τ in the expansion case. The question is: how much greater?

Because of the dependence of τ on T_v , its evaluation as a function of T is impossible without solving the rate equation simultaneously with the gas dynamic equations, and using the resulting vibrational

energy distribution to evaluate local values of τ by integrating equation (2).

The results of Northup & Hsu (Ref. 23) show that multiple quantum jumps have little effect on the dependence of τ on T for shock excitation environments. This enables the term $ZP_{1,0}$ to be evaluated in equation (19). The dependence of $ZP_{1,0}$ on T is chosen as

$$\frac{P}{ZP_{1,0}} = A \exp(B/T)^{\frac{1}{3}} \dots\dots (20)$$

and the rate equation (17) for quasi-steady one-dimensional flow conditions becomes

$$\frac{dE_v}{dx} = \frac{pG\{E_v(T) - E_v\}}{uA \exp(B/T)^{\frac{1}{3}}} \dots\dots (21)$$

where u is the local particle velocity and x is distance.

In equation (20), A and B are assumed constant. In practice, A is a weak function of T but may be considered constant to a good approximation.

Initial values of A and B were chosen and equation (21) was solved numerically together with the equations of continuity, momentum, energy and state for nitrogen in a shock excitation environment. The relevant equations for the shock excited case and the expansion flow environment are given in the Appendix. From the resulting vibrational and translational energy distributions, local relaxation times are evaluated by integrating equation (2). The calculated values of τ are then plotted as a function of active temperature. New values of A and B are chosen until the values of τ as calculated above, match the

experimental data presented in Figure 1 for curve \bar{A} . Curve \bar{A} is chosen rather than \bar{B} because of the experimental data presented in Ref. 12.

The results of this calculation are shown in Figure 2; and the values of A and B finally assumed give the functional dependence of τ on T and T_v for the excitation case as

$$\frac{\tau_p}{(\mu s \text{ atm})} = \frac{3.8 \times 10^{-7} \exp(658500K/T)^{1/3}}{G} \dots\dots\dots (22).$$

In figure 2, two curves are presented for $\tau = \tau(T)$ calculated from the above model. This is because τ is also a function of T_v and the value of τ evaluated at any particular temperature depends upon how far from equilibrium the vibrational mode is at that instant. The upper curve D represents data for the system away from equilibrium and the lower curve \bar{E} data evaluated near equilibrium.

With the rate equation (22) the gas dynamic equations were solved using the computer programme of Ref. 25 for the steady expansion in a convergent-divergent conical expansion nozzle of 12° half angle. The resulting vibrational and translational energy distributions have been used to calculate local values of τ as was done previously. The results of these calculations are represented in Figure 2 by curve \bar{F} . The vibrational energy in the nozzle is frozen before large departures from equilibrium are obtained. Hence, only vibrational relaxation times near equilibrium are represented by curve \bar{F} which is plotted as the envelope of the shortest relaxation times obtained from the analysis. Other relaxation times tended to fall between curves \bar{F} and \bar{E} , but these are only of academic

interest.

The data presented in Figure 2 suggest that the theoretical relaxation rate increases as the molecules approach equilibrium. This is expected because of the dependence of τ on the vibrational temperature T_v . In shock excitation environments, T is falling relatively slowly whilst T_v is increasing rapidly as the gas tends to equilibrium. The net effect is an increase in G which gives an increase in relaxation rate. Conversely, for the expanding flow in a nozzle both T and T_v are falling as the molecules flow down the nozzle, but the gas molecules are moving away from equilibrium. Thus curve F represents relaxation rates calculated near the nozzle throat where non-equilibrium phenomena are first apparent.

The effect of multiple quantum jumps on the relaxation rate in an expansion environment is shown in Figure 2 to be small. Multiple quantum jumps do increase this relaxation rate compared with similar data in shock excited flows, as predicted. However, this increase is not sufficient to explain the rates observed experimentally.

4. Conclusions.

The Landau-Teller rate equation for vibrational relaxation successfully describes the general behaviour of diatomic gases in environments in which the vibrational mode is being excited. Using experimental data to evaluate the absolute relaxation rates in such circumstances the unknown constants particular to each gas may be determined. When the resulting rate equation is used to describe the relaxation process in circumstances where the vibrational mode is being de-excited, it predicts rates at least an order of magnitude smaller than those measured for nitrogen. None of the theoretical models previously proposed have been able to explain this anomaly.

A simple model in which multiple quantum jumps between vibrational levels are allowed has been examined here, and while relaxation times in a nozzle are found to be smaller than those in a shock excited environment at any given active mode temperature, the difference is far less than that observed experimentally.

It is possible that the difference could be narrowed by taking account of effects such as anharmonicity, but the added complication seems unwarranted. The anomaly is not observed for all gases, while any explanation on the lines suggested here would be applicable to a greater or lesser extent for all gases. One is led to conclude that the anomaly is probably due to impurities in the test gases.

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Nomenclature

$A(T)$	slowly varying function of temperature T
\bar{A}	cross sectional area
B	constant
E_v	vibrational energy/mass
$E_v(T)$	vibrational energy/mass at temperature T
G	function defined by equation (19)
h	Planck's constant
H_0	total enthalpy/mass
m	vibrational energy level: $m = 0, 1, 2$ etc.
\dot{m}	mass flow rate
n	vibrational energy level: $n = 0, 1, 2$ etc.
N	total population of vibrational energy levels
N_m	population of level m
N_n	population of level n
p	pressure
$P_{m,n}$	probability of a molecule changing from level m to level n during a T-V collision
R	function defined by equation (16)
\bar{R}	specific gas constant
S	function defined by equation (15)
t	time
T	active temperature
T_v	vibrational temperature
u	velocity
x	distance
Z	bimolecular collision rate
Z'	collision rate for T-V energy transfer

α	$= -\theta_v / T$
γ	ratio of principal specific heat capacities for active modes only
θ_v	characteristic vibrational temperature
ν	oscillator frequency
ρ	density
τ	relaxation time
τ_N	napier time

Abbreviations

T-V	Collisions which only involve transfer of energy between the translational mode and the vibrational mode
V-V	Collisions which only involve exchange of vibrational energy

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A P P E N D I X

The Gas Dynamic Equations

The equations for steady one-dimensional flow of a relaxing gas are:-

$$\rho \bar{A}u = \dot{m} \quad \dots\dots\dots A1$$

$$\frac{\gamma RT}{\gamma - 1} + E_v + \frac{1}{2}u^2 = H_0 \quad \dots\dots\dots A2$$

$$\frac{udu}{dx} = -\frac{1}{\rho} \frac{dp}{dx} \quad \dots\dots\dots A3$$

where \bar{A} is the local cross sectional area, ρ is the density of the gas, u the velocity of the gas, H_0 the stagnation enthalpy/mass, γ the ratio of the principal specific heat capacities of the active modes and \bar{R} is the gas constant. In equation A2, the vibrational energy has been explicitly included as a separate term, and γ is to be regarded as 7/5 for linear molecules and 4/3 otherwise.

For the shock excitation case, u is the velocity of the gas relative to shock fixed co-ordinates, and the above equations are solved numerically together with the equation of state

$$p = \rho \bar{R}T \quad \dots\dots\dots A4$$

and an assumed form for the vibrational energy rate equation. Initial values for p, T and u are taken from tabulated data for the relevant value of γ , and an assumed shock Mach number.

The solution of the equations for an expanding flow is described in Ref.25.

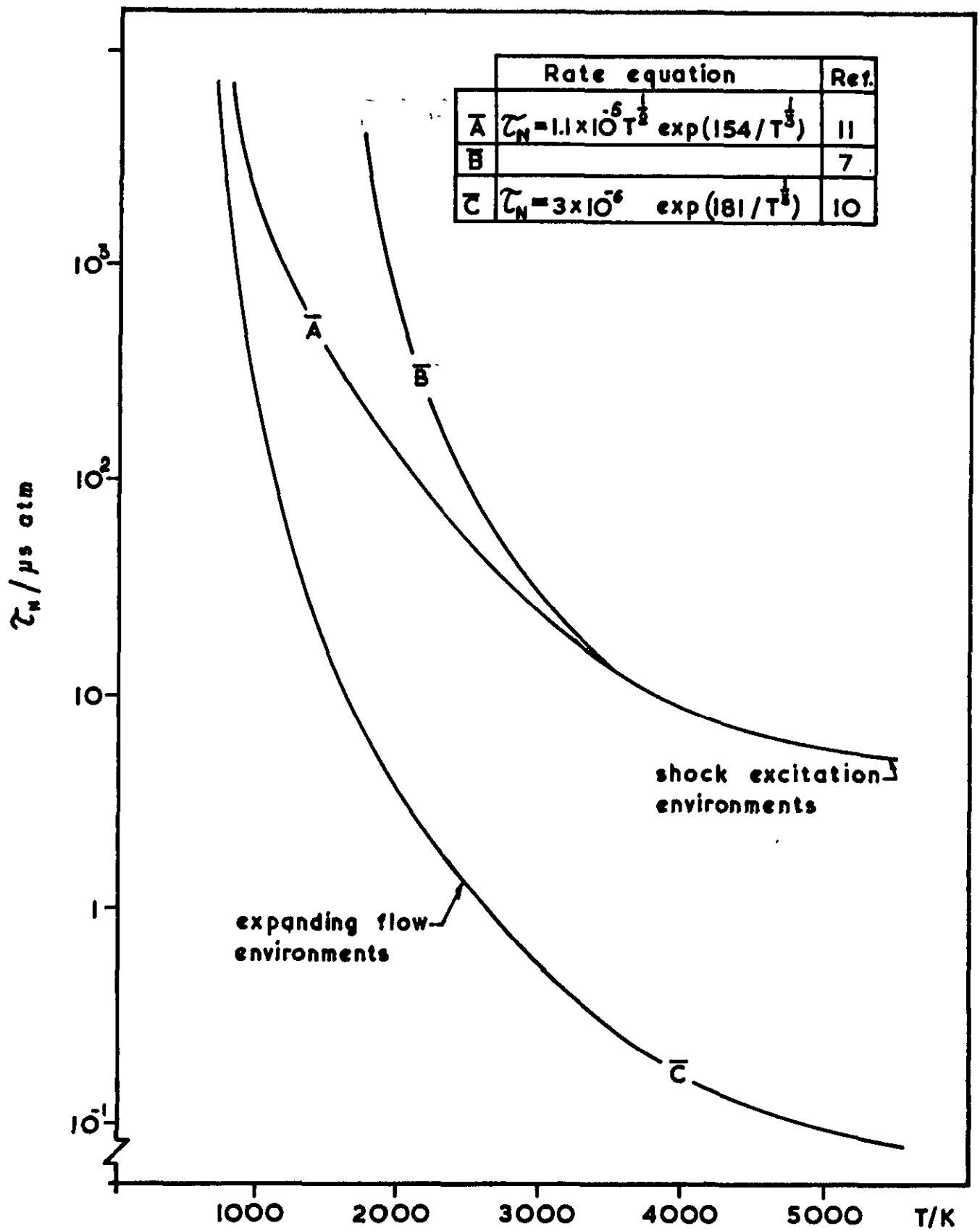


Fig. 1 Correlation of experimental results for vibrational relaxation of nitrogen

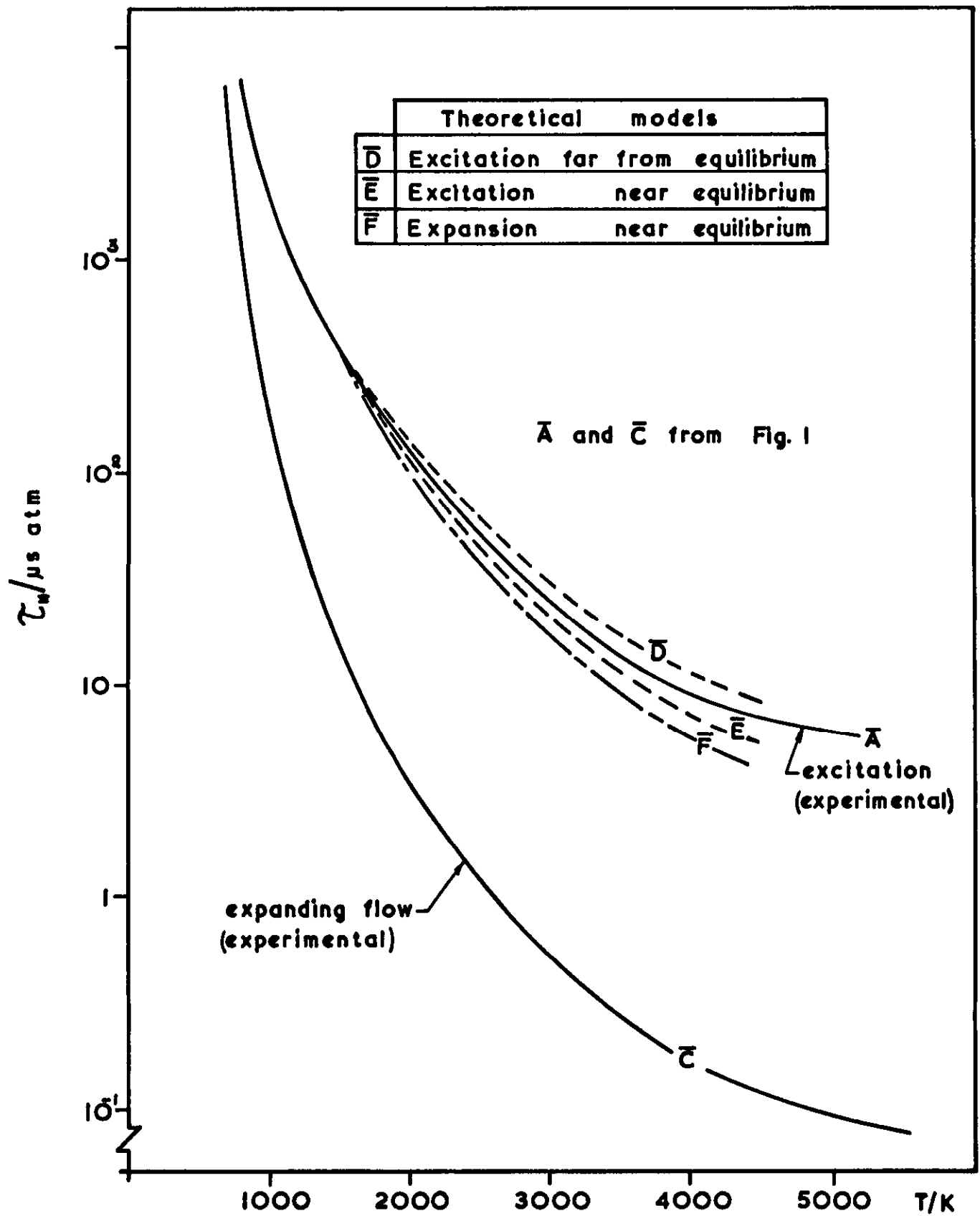


Fig. 2 Comparison of calculated results with empirical correlations of Figure 1

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