JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 18, No. 4, October–December 2004

# Rotational Relaxation of $N_2$ Behind a Strong Shock Wave

Chul Park*
*ELORET Corporation, Moffett Field, California 94035*

**Using an existing expression for the state-to-state rotational transition rate coefficients, which is derived from the experimental data taken at temperatures equal to or below 1500 K, the master equation for rotational states is integrated with time for $N_2$. The postshock temperature considered is from 400 to 128,000 K. From the numerical solutions of the master equation, the effective collision numbers and characteristic relaxation times are determined. The results show that the effective collision number varies from about 4 at 400 K to about 700 at 128,000 K. The product of the rotational relaxation time and pressure is determined to be $2.47 \times 10^{-14} T^{1.692}$ atm · s. The calculated rotational relaxation time is larger than the vibrational relaxation time at temperatures above 12,000 K, but is believed to be only hypothetical there because vibration-rotation coupling will pull the temperatures of these two modes together. The present model approximately reproduces the rotational temperature values measured in a shock tube by Sharma and Gillespie and by Fujita et al. up to a postshock temperature of 90,000 K.**

## Nomenclature

$E$ = energy level, $\text{cm}^{-1}$
$E_v$ = vibrational energy per particle, erg
$i, j$ = rotational quantum number
$K(i, j)$ = $i$-to-$j$ rotational transition rate coefficient, $\text{cm}^3/\text{s}$
$k$ = Boltzmann constant $1.3806 \times 10^{-16}$ erg/K
$k(i, j)$ = $K(i, j)$ divided by elastic collision rate coefficient
$m$ = mass of one $N_2$ molecule, g
$n$ = number density, $\text{cm}^{-3}$
$n_i$ = number density of state $i$, $\text{cm}^{-3}$
$n_k$ = number density of species $k$, $\text{cm}^{-3}$
$p$ = pressure, $\text{dyne/cm}^2$ or atm
$T$ = translational temperature, K
$T_r$ = rotational temperature, K
$t$ = time, s
$Z_1$ = characteristic collision number based on initial slope
$Z_2$ = characteristic collision number based on the $e$-folding point
$Z_3$ = characteristic collision number based on the 95%-approach point
$z$ = running collision number
$\mu$ = viscosity, poise
$\rho(i)$ = normalized nonequilibrium population of state $i$
$\tau$ = characteristic relaxation time, s

*Subscripts*

$c$ = elastic collision
$e$ = equilibrium
$r$ = rotation
$v$ = vibration

## Introduction

THE phenomenon of rotational relaxation in a diatomic gas has been described hitherto using the concept of effective, or characteristic, collision numbers. The pioneering works by Parker[1] and Lordi and Mates[2] led to the effective collision number of the order of 10. That is, within about 10 collisions the rotational mode is expected to equilibrate with the translational mode. Early experiments at temperatures below 1500 K confirmed this finding.[3,4] Numerous refined theoretical studies have been carried out in recent years to strengthen this finding (e.g., Ref. 5).

The limitation of the current state of knowledge of the subject is described well in Refs. 6 and 7. An important limitation is on the high-temperature behavior. The behavior of rotational relaxation in the high-temperature environment was studied spectroscopically in recent years by Sharma and Gillespie[8] and by Fujita et al.[9] If the effective rotational collision number were of the order of 10, then the measured rotational temperature was expected to be that of the calculated translational-rotational temperature at the points where the measurements were made, which would have been above 10,000 K. However, the measured rotational temperature was closer to the vibrational temperature of 5000 to 6000 K. Such a low rotational temperature implies an effective collision number much larger than 10.

Furudate and Sawada[10] observed that the shock stand-off distances for a sphere flying in a ballistic range are larger than those calculated by the multitemperature model in which rotational temperature is assumed to equilibrate instantly with the translational temperature, at flight speeds between 2.4 and 4 km/s. Agreement between the calculated and the measured shock standoff distance was obtained when the finite-rate rotational relaxation is accounted for using an effective rotational collision number much larger than the conventional value.

A large shock standoff distance results from a large rotational collision number because the latter implies that air behaves more as a monatomic gas (of specific heat ratio of $\frac{5}{3}$) than as a diatomic gas (of specific heat ratio $\frac{7}{5}$) immediately behind the shock wave. For a lifting body with a finite angle of attack, this will produce a relatively larger pressure in the forward region than in the rearward region, leading to a nose-up pitching moment.

One cause of uncertainty of rotational behavior at high temperature has hitherto been the lack of knowledge of the state-to-state transition rates for the rotational mode. Of all diatomic species, $N_2$ is the most important species regarding rotational nonequilibrium at high temperatures because it constitutes $\frac{4}{5}$ of air by volume and because $O_2$ tends to be fully dissociated at high temperatures. Recently, several experimental data have been obtained on the rotational transition rates of $N_2$ (Refs. 11–15). A detailed quantum mechanical calculation of the state-to-state rotational transition has also been made for $N_2$ (Ref. 16). It is now possible to predict the rotational relaxation behavior of $N_2$ at fairly high temperatures by extrapolating these existing data.

It is the purpose of the present work to derive the rotational relaxation parameters for $N_2$ from the existing data on state-to-state rotational transition rates.

---

Presented as Paper 2002-3218 at the AIAA/ASME 8th Joint Thermophysics and Heat Transfer Conference, St. Louis, Missouri, 24–26 June 2002; received 10 June 2004; revision received 9 June 2004; accepted for publication 14 June 2004.

*Senior Research Scientist; currently Professor, Department of Aerospace Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea; cpark216@kaist.ac.kr. Fellow AIAA.

## Transition-Rate Coefficients

In Fig. 1, the experimental data on the state-to-state transition-rate coefficient for $N_2$ obtained by Sitz and Farrow[13] and Sharafutdinov et al.[15] and the quantum mechanical calculation by Huo and Green[16] are plotted and compared with the expression proposed by Rahn and Palmer,[11]

$$K(i, j) = 1.757 \times 10^{-10}\left[\frac{1 + (1.5E_i/kT)/1.26}{1 + 1.5E_i/kT}\right] \times \left(\frac{295}{T}\right)^{1.346} \exp(-1.67\Delta E/kT)\ \mathrm{cm^3/s} \qquad (1)$$

Here $E_i$ is the energy level for rotational quantum number $i$, and $\Delta E$ is the difference in energy levels between the final state $j$ and the initial state $i$, where $j > i$. The expression is applicable only when $j - i$ is an even number: the odd-number jumps are quantum mechanically forbidden. A fairly good agreement is seen among the plotted values.

In Fig. 2, a similar comparison is made for the so-called total rotational transition rate coefficients,

$$\text{Total rotational transition rate coefficient} = 2\Sigma_j K(i, j) \qquad (2)$$

obtained by Rahn and Palmer[11] and Herring and South[14] and the theoretical value obtained by summing Eq. (1). The two sets of experimental data agree closely at 300 K. As seen, the Rahn–Palmer expression, Eq. (1), is satisfactory at temperatures at or above 300 K. At temperatures below 300 K, the expression does not reproduce the experimental data. Behind a strong shock wave, the flow temperature is never below 300 K. Therefore, the discrepancy at low temperature is irrelevant.

Under a Boltzmann distribution, the maximum contribution to the total number density occurs at the quantum number (Ref. 17, p. 15) $i_{\max} = 0.7\sqrt{(kT/B)}$, where $B$ is the rotational constant. To describe the rotational excitation phenomenon accurately at high temperatures, state-to-state rotational transition rate must be known to very high quantum numbers, for example, to about 100 for 10,000 K and 200 for 40,000 K. (The highest quantum number for the ground electronic state of $N_2$ is about 250.)

As seen in Fig. 2, the existing experimental data cover quantum numbers of up to 30 and temperature of up to 1500 K. The theoretical calculation by Huo and Green[16] accounted for quantum numbers of up to 18 and temperature of 300 K. These restrictions on quantum numbers and temperature imply that Eq. (1) is valid, in a strict sense, only to 1500 K.

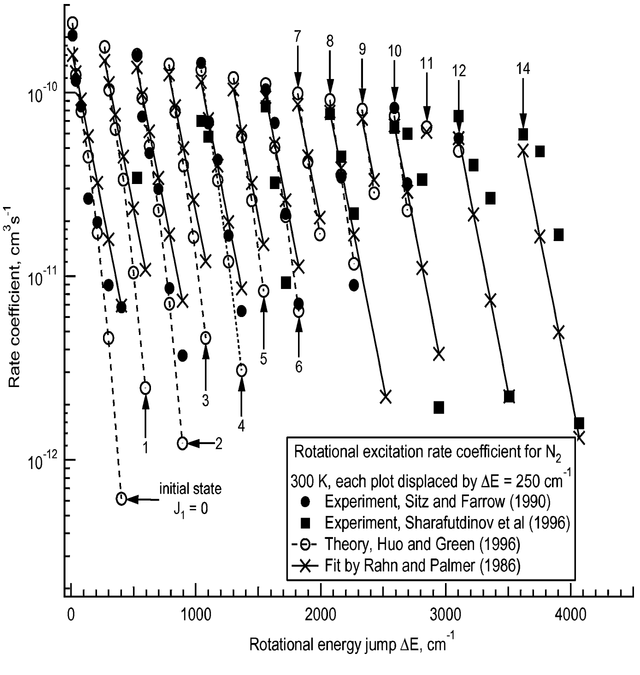

**Fig. 1 Comparison of the state-to-state rotational transition-rate coefficients for $N_2$.**

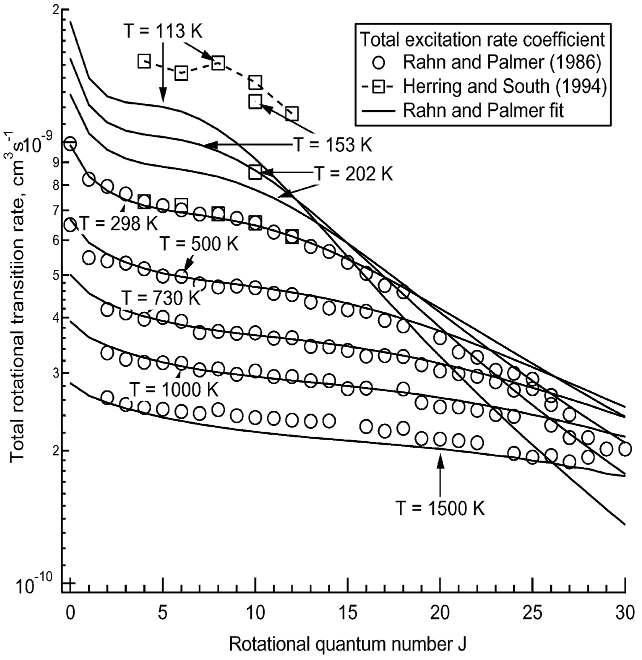

**Fig. 2 Comparison of the total rotational transition-rate coefficients for $N_2$.**

It is unrealistic at this time to expect experimental measurement of state-to-state rotational transition rates to a temperature much above 1500 K. Theoretical calculations accounting for quantum numbers up to 100 or 200, and temperatures up to 40,000 K, still remain to be done.

Therefore, Eq. (1) is used in the present work at temperatures far exceeding 1500 K, that is, to 128,000 K. This bold extrapolation is based on the observation that the values plotted in Figs. 1 and 2 behave smoothly at the higher limits of quantum numbers and temperature. The validity of Eq. (1) at very high temperatures will be tested by comparing the calculated rotational temperatures with the experimental data obtained in a shock tube[8,9] in the section titled Comparison with Shock-Tube Experiment.

A question is raised by Fujita and Abe[18] about the correct way of extrapolating Eq. (1) to temperatures above 1500 K. The question concerns the method of interpretation of the experiment by Rahn and Palmer.[11] Fujita and Abe[18] proposed in effect that a factor $(T/295)$ be multiplied to Eq. (1). When this factor is multiplied to Eq. (1), the resulting rotational relaxation rate at high temperatures becomes nearly the same as or faster than at the room temperature, and cannot reconcile with the experimental data of Sharma and Gillespie[8] or Fujita et al.[9] Therefore, $(T/295)$ was not multiplied to Eq. (1) in the present work.

When Eq. (1) is used to temperatures above 1500 K, one immediate question arises as to what is the effect of rotation-to-vibration energy transfer on rotational relaxation. There are as yet no data, theoretical or experimental, on this quantity. However, one expects that the transitions between the rotational and vibrational modes will occur efficiently through the so-called resonance exchange, if the energy gaps in the rotational level structure closely matched those in the vibrational level structure. Examination of the two energy level structures reveals that such a close energy level match exists at many level combinations. Another mechanism is a concerted rotational-vibrational energy transfer, that is, two $N_2$ molecules undergoing simultaneous rotational and vibrational excitation/deexcitation. Such fast rotation-to-vibration exchange will occur at high temperatures where the high vibrational and rotational levels are populated significantly.

Vibrational relaxation phenomenon is well known and can be described by the Landau–Teller equation. In reality, vibrational excitation of a molecule by the collisions with other molecules occurs partly by the transfer of translational energy of the colliding molecules, $1.5kT$, and partly by the transfer of rotational energy of the colliding molecules, $kT$. By representing the fractional contribution of the rotation-to-vibration energy transfer to the total (translation + rotation-to-vibration) energy transfer by $f$, one can rewrite the Landau–Teller equation into the form:

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = \frac{E_{\mathrm{ve}} - E_v}{\tau_v} = f\frac{E_{\mathrm{ve}}(T_r) - E_v}{\tau_v} + (1-f)\frac{E_{\mathrm{ve}}(T) - E_v}{\tau_v} \tag{3}$$

where $\tau_v$ is the characteristic vibrational relaxation time and $E_{\mathrm{ve}}(T_r)$ and $E_{\mathrm{ve}}(T)$ are the equilibrium values of vibrational energy evaluated at rotational temperature $T_r$ and at the translational temperature $T$, respectively. Equation (3) reduces to the conventional Landau–Teller equation when $T_r = T$ for any arbitrary value of $f$. If the probability of rotation-to-vibration energy transfer in a collision is the same as that of translation-to-vibration energy transfer, then $f$ becomes $f = kT/(kT + 1.5kT) = 0.4$.

The characteristic vibrational relaxation time $\tau_v$ for $N_2$ can be expressed using the correlation formula of Millikan and White[19] at temperatures of up to about 8000 K. At higher temperatures, one must account for the fact that the relaxation rate is limited by the rate of elastic collisions, that is, the so-called collision-limiting correction must be made.[20] Thus, the $\tau_v$ in the second term of Eq. (3) should be replaced in general by the sum of the Millikan–White value $\tau_{\mathrm{MW}}$ and the collision-limiting value $\tau_c$. However, for the $\tau_v$ in the first term of Eq. (3), one observes that, according to the experimental data of Refs. 8 and 9, vibration-to-rotation energy transfer occurs much faster than vibration-to-translation energy transfer at very high temperatures (presumably because of the fast rotation-to-vibration energy transfer mechanisms cited above). Therefore, adding $\tau_c$ to $\tau_{\mathrm{MW}}$ is not warranted in the first term of Eq. (3). The rate equation for vibration should thus read

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = 0.4\frac{E_{\mathrm{ve}}(T_r) - E_v}{\tau_{\mathrm{MW}}} + 0.6\frac{E_{\mathrm{ve}}(T) - E_v}{\tau_{\mathrm{MW}} + \tau_c} \tag{4a}$$

The numerical value of $\tau_c$ in this three-temperature (translation, vibration, and rotation) description becomes different from that used in the two-temperature (translation-rotation and vibration) description. To conserve total energy, the rate expression for rotation should be written

$$\frac{\mathrm{d}(kT_r)}{\mathrm{d}t} = \frac{kT - kT_r}{\tau_r} + 0.4\frac{E_v - E_{\mathrm{ve}}(T_r)}{\tau_{\mathrm{MW}}} \tag{4b}$$

The rotational relaxation time $\tau_r$ is being determined in the present work.

## Integration of Master Equation

The master equation for the rotational state $i$ is

$$\frac{1}{n}\frac{\mathrm{d}n_i}{\mathrm{d}t} = \Sigma_j K(j,i)n_j - \Sigma_j K(i,j)n_i$$

By dividing both sides by the equilibrium number density of state $i$, $n_{\mathrm{ie}}$, and introducing the normalized nonequilibrium population $\rho(i)$

$$\rho(i) = n_i/n_{\mathrm{ie}} \tag{5}$$

and invoking the detailed balance relationship between the forward and reverse transitions, one obtains (Ref. 17, p. 100)

$$\frac{1}{n}\frac{\mathrm{d}\rho(i)}{\mathrm{d}t} = \Sigma_j K(i,j)[\rho(j) - \rho(i)] \tag{6}$$

The effective collision number $z$ is the ratio between the real time $t$ and the elastic collision time $t_c$. The elastic collision time is defined customarily using viscosity $\mu$ (e.g., see Ref. 7) by

$$t_c = (\pi/4)(\mu/nkT)\ \mathrm{s} \tag{7}$$

Viscosity is expressible in general in terms of the collision integral for energy transfer $\Omega^{(2,2)}$ as

$$\mu = (5/16)\left(\sqrt{\pi mkT}\middle/\Omega^{(2,2)}\right)\ \text{poise} \tag{8}$$

Therefore the collision number becomes

$$\text{Collision number} = z = \frac{t}{t_c} = \frac{4}{\pi}\frac{16}{5}\frac{nkT\Omega^{(2,2)}}{\sqrt{\pi mkT}}t \tag{9}$$

Taken from Ref. 21, $\Omega^{(2,2)}$ is expressed as

$$\Omega^{(2,2)} = 5.974 \times 10^{-15}T^{-0.0203\ln T + 0.0683}\ \mathrm{cm}^2$$

At 300 K where this expression is not expected to be very accurate, the error in viscosity is only about 4%. The elastic collision rate $K_c$ is

$$K_c = 1/t_c n = (4/\pi)(kT/\mu)\ \mathrm{cm}^3\mathrm{s}^{-1} \tag{10}$$

By dividing the two sides of Eq. (6) by the elastic collision rate, Eq. (10), and defining the normalized rate coefficient $k(i,j)$ as

$$k(i,j) = K(i,j)/K_c \tag{11}$$

one obtains the normalized form of master equation as

$$\frac{\mathrm{d}\rho(i)}{\mathrm{d}z} = \Sigma_j k(i,j)[\rho(j) - \rho(i)] \tag{12}$$

Immediately behind a strong shock wave, $\rho(i)$ is calculable from the Boltzmann distribution corresponding to the preshock temperature. By integrating Eq. (12) with $z$, one obtains the rotational state distribution as a function of collision number $z$. Equation (12) does not enforce the mass conservation relation explicitly at each integrating steps, that is, the requirement that the sum of all states equals the given number density, which must remain unchanged: as the integration progresses, the total mass slowly deviates from the initial value because of the accumulation of truncation errors. Therefore, after each step of integration the calculated $\rho(i)$ values are modified to conserve mass by distributing the incurred error proportionately to their values.

By multiplying $\rho(i)$ with the energy level of the state $i$ and summing over all $i$, one obtains the rotational energy content. The temperature that gives the rotational energy so calculated under a Boltzmann distribution is defined as the rotational temperture of the nonequilibrium distribution. That is, the rotational temperature adopted in the present work is the so-called energy-representative temperature. In the calculations, the starting rotational temperature is assumed to be 300 K, except for a few test cases made at higher temperatures (see the following).

The solution of the master equation (12) depends on the translational temperature $T$, which is in general a function of time. Two hypothetical cases are considered for this model calculation, isothermal and adiabatic, as was done in other works (e.g., see Ref. 6). In the isothermal case, $T$ remains unchanged during integration. In the adiabatic case, the sum of the translational and rotational energies remains unchanged. Vibration is neglected for this model calculation.

## Results

In Fig. 3, the rotational temperature obtained by integrating the master equation is shown for the isothermal case of postshock temperature $T = 8000$ K. The calculated rotational temperature values are compared with those obtained by integrating the Landau–Teller equation:

$$\frac{\mathrm{d}T_r}{\mathrm{d}z} = \frac{T - T_r}{Z_2} \tag{13}$$

Three characteristic rotational collision numbers $Z_1$, $Z_2$, and $Z_3$ are identified in the figure from the results of master equation integration. They are as follows:

1) $Z_1$ = the collision number at which $T_r$ would equal $T$ if the slope of increase of $T_r$ remains fixed at the initial value (initial slope

**Table 1 Characteristic rotational collision numbers $Z_1$, $Z_2$, and $Z_3$ calculated by integrating master equation for fixed postshock translational bath temperatures $T$**

| $T$ | $Z_1$[a] | $Z_2$[a] | $Z_3$[a] |
|---|---|---|---|
| 400 | 3.71 | 4.20 | 19.6 |
| 1,000 | 8.72 | 9.85 | 49.2 |
| 2,000 | 17.3 | 19.7 | 102 |
| 4,000 | 35.1 | 40.1 | 213 |
| 8,000 | 71.2 | 81.6 | 440 |
| 16,000 | (144) | (165) | (834) |
| 32,000 | (288) | (277) | (1100) |
| 64,000 | (635) | (409) | (1460) |
| 128,000 | (1810) | (682) | (2350) |

[a] The $Z$ values at temperatures above 8000 K are in parentheses to indicate that they are hypothetical; see text.

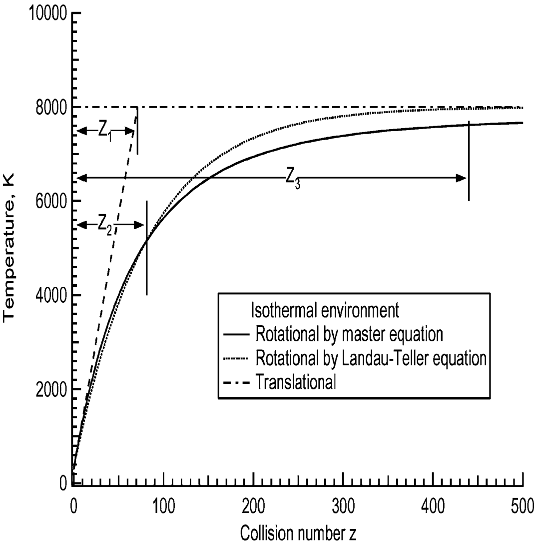

**Fig. 3 Comparison between the master equation integration and Landau–Teller equation for the isothermal case.**

collision number). The initial slope is determined here arbitrarily from the $z$ value at which $T - T_r$ is 90% of the $T - T_{r0}$, that is, where $T_r$ has made 10% of the total change. (Theoretically it should be evaluated at a point infinitesimally close to the shock wave. However, doing so introduces a numerical error. See a later discussion in this section.)

2) $Z_2 =$ the collision number at which $T - T_r$ becomes $1/e = 0.3679$ of the value immediately behind the shock wave ($e$-folding collision number).

3) $Z_3 =$ the collision number at which $T - T_r$ becomes 0.05 of the value immediately behind the shock wave (95% approach collision number).

The quantity $Z_1$ characterizes the early phase of rotational relaxation. In the past, $Z_1$ was used commonly to represent the rotational relaxation time (e.g., see Refs. 6 and 7), even though $Z_2$ is associated more closely with the rate of energy transfer. If rotational relaxation occurs according to the Landau–Teller equation, rotational temperature will vary following an exponential function in $z$, and so $Z_1$ and $Z_2$ become the same, and therefore, the choice of $Z_1$ over $Z_2$ becomes immaterial. However, as will be shown, $Z_2$ is different from $Z_1$ in the present work.

The quantity $Z_3$ characterizes the later phase of rotational relaxation. In a Landau–Teller relaxation, $Z_3$ becomes $2.996 \times Z_2$. The quantity $Z_3$ is calculated here in order to show that the later phase of rotational relaxation is also different from that described by the Landau–Teller equation.

The calculated three $Z$ values are presented in Table 1. As mentioned, the starting postshock rotational temperature was assumed to be 300 K. However, calculations made at different starting rotational temperatures produced no discernible difference in the calculated $Z_1$, $Z_2$, and $Z_3$ values.

As seen in Table 1 and Fig. 3, $Z_1$ is smaller than $Z_2$, signifying that initially rotational relaxation is faster than that under Landau–Teller relaxation. Table 1 shows that $Z_3$ is larger than $2.996 Z_2$, signifying that, in the later phase, rotational relaxation is slower than that under Landau–Teller relaxation.

At temperatures above about 12,000 K, the rotational collision numbers become only hypothetical. This is because, at 12,000 K, the rotational relaxation time and vibrational relaxation time become approximately equal, as will be shown later. Also, at that temperature, the vibration-rotation energy exchange will begin to occur efficiently because the high vibrational and rotational levels are significantly excited. As a result, at temperatures above 12,000 K rotational temperature will equilibrate with vibrational temperature, and rotational relaxation will become indistinguisable from vibrational relaxation. At this time, it is impossible to determine the relaxation rate of the combined vibration-rotation mode because, among others, the additive collision-limiting time $\tau_c$ is not known. However, the rotational collision numbers above 12,000 K will still be meaningful very early in the excitation process where the high levels are not excited.

Though not shown, the solutions of master equation can be reproduced more closely by the Landau–Teller equation in the temperature regime from 2000 to 16,000 K by replacing $Z_2$ in Eq. (13) by

$$Z_2' = Z_1[(T - T_{r0})/(T - T_r)]^{0.4} \tag{14}$$

where $T_{r0}$ is the rotational temperature immediately behind the shock wave. This expression correctly describes the early phase of relaxation, and slows down the rate of approach to equilibrium at large times to agree approximately with the master-equation solution. The form of this expression is the same as that for vibrational relaxation and is attributable to the so-called diffusive nature of the ladder-climbing process [that the maser equation, Eq. (12), is reducible to a diffusion equation, see Ref. 17, pp. 108–111].

The $e$-folding $Z$, $Z_2$, which characterizes the energy transfer rate between the translational and rotational modes best among the three $Z$, is shown in Fig. 4 and compared with the works of others.[1–7] As seen in Fig. 4, at temperatures below 500 K the present work tends to underestimate the collision number slightly. The effective collision number values at temperatures above 12,000 K are shown with a dashed line to indicate that they are only hypothetical; the calculated rotational relaxation time becomes longer than the known

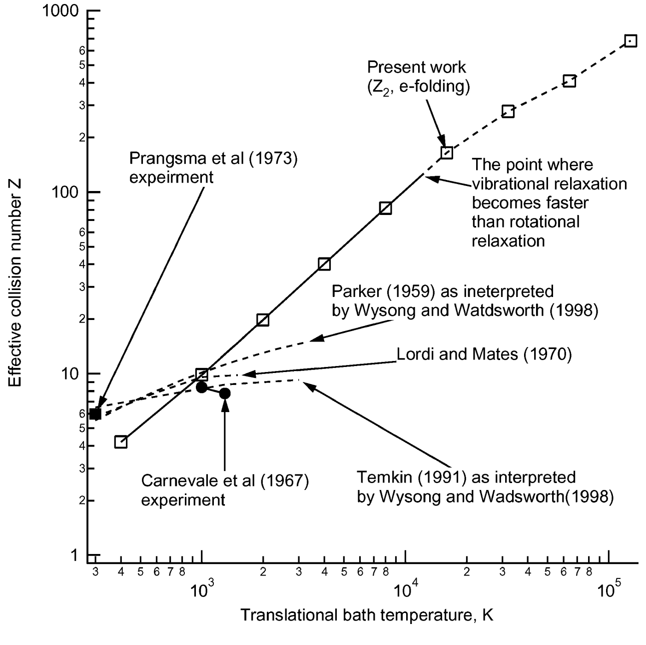

**Fig. 4 Characteristic rotational collision numbers.**

vibrational relaxation time, which is not possible because of the coupling between the rotational and vibrational modes.

The main feature of Fig. 4 is that the effective collision number from the present work increases steadily with temperature, while the other works asymptote to a value less than about 20. Three possible causes can be cited for this difference. The first is the factor $(295/T)^{1.346}$ in Eq. (1), which is based on the observed decrease of measured state-to-state transition rates with temperature (see Fig. 2).

Secondly, the energy gap $\Delta E$ in Eq. (1) becomes large for large rotational quantum numbers. At high temperatures, the contribution to the energy-representative temperature adopted in the present work comes mostly from the high rotational quantum number states. The large $\Delta E$ for high rotational levels reduces $K(i, j)$ for these levels. This is a quantum-mechanical effect and is not accounted for in the classical treatments used in Refs. 1 and 2.

Third and most importantly, at high temperatures the rates of the reverse transitions, that is, the deexcitation transition rates, become nearly equal to the forward transition rates. At high temperatures, the Boltzmann factor between the lower and upper states of a transition, which specifies the ratio between the forward and reverse rates, becomes nearly unity. Therefore the net excitation rates (the difference between the forward and reverse rates) become substantially smaller than the sum of all forward rates. This depression of net transition rates can be accounted for correctly only by performing a master equation integration such as that made here. In the master equation (12) this phenomenon appears in the form of $\rho(i)$ and $\rho(j)$ becoming nearly equal to each other. In other works, this aspect has not been accounted for, at least for the high-temperature regime treated here. For instance, the theoretical collision times of Temkin et al.,[5] shown in Fig. 4, as interpreted by Wysong and Wadsworth,[7] are derived using the same state-to-state transition rate values as the present work, and yet are smaller than the present results at high temperatures because that work did not resort to master equation integration.

At the beginning of relaxation, theoretically this behavior should be absent. Therefore, the $Z_1$ value calculated in the present work should be the same as the collision number values obtained by others neglecting this phenomenon. In the present work, the $Z_1$ value was calculated from the $z$ and $T_r$ values at the point where $T_r$ has gone 10% of the overall change $T - T_{r0}$. By this time, the said depression of net transition rates has already taken place.

Landau–Teller calculation is made using $Z_2$ as the effective $Z$ value for the adiabatic case for the postshock translational temperature of 8000 K. The result is shown in Fig. 5 and compared with the master equation solution. The two solutions agree fairly well. Though not shown, $Z_2'$, Eq. (14), results in a slightly better agreement. But the degree of improvement was not deemed worthy of its general use.

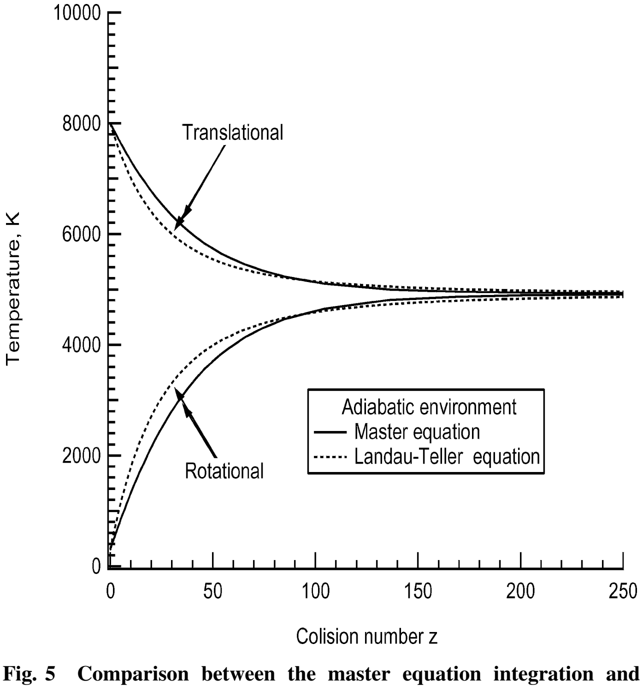

**Fig. 5 Comparison between the master equation integration and Landau–Teller equation for the adiabatic case.**

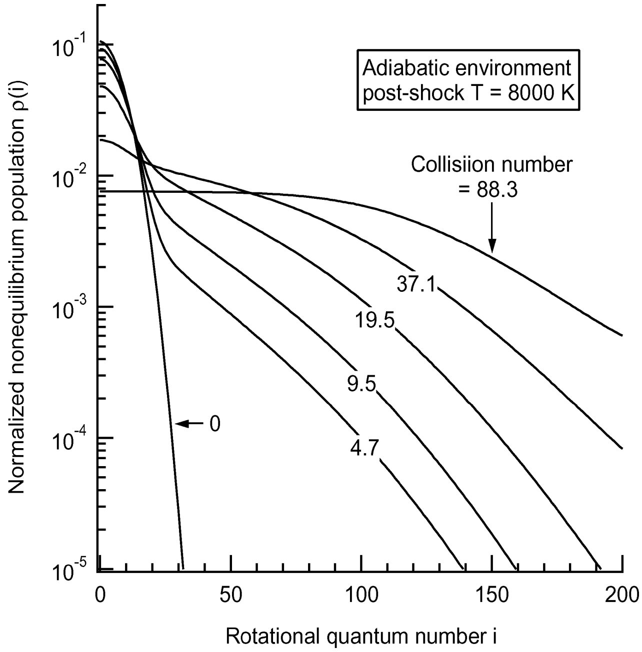

**Fig. 6 Evolution of nonequilibrium population distribution with time.**

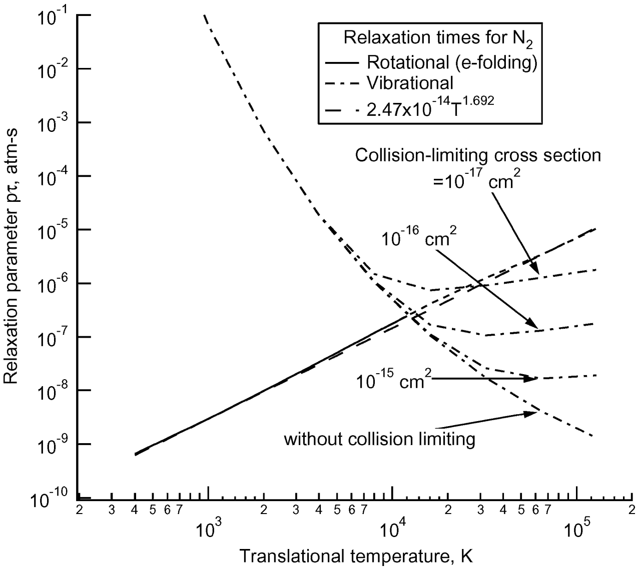

**Fig. 7 Characteristic relaxation time parameter for rotation compared with that for vibration.**

In Fig. 6, the normalized nonequilibrium population $\rho(i)$ is shown for the isothermal case of Fig. 3. The diffusion-like behavior of $\rho$, alluded to earlier, can be seen here. At large collision numbers, the $\rho$ values become nearly constant at low $i$. This effect depresses the magnitude of Eq. (12) and thereby the overall rate of rotational relaxation, as alluded to earlier also.

The macroscopic rotational relaxation time $\tau_r$ is obtained by multiplying $Z_2$ by $t_c$ given by Eq. (7):

$$\tau_r = Z_2 t_c \tag{15}$$

By multiplying $\tau_r$ by pressure, one obtains the characteristic rotational relaxation rate parameter $\tau_r p$, which is independent of pressure. The parameter is shown in Fig. 7. A close fit to the calculated

$p\tau_r$ is found to be

$$p\tau_r = 2.46 \times 10^{-14} T^{1.692} \text{ atm-s} \tag{16}$$

The corresponding $p\tau_v$ values of Millikan and White for vibration are shown for comparison for three different collision-limiting cross-section values. As seen in the figure, at temperatures below about 12,000 K, rotational relaxation is faster than vibrational relaxation. However, at higher temperatures, rotational relaxation is slower than vibrational relaxation. In reality, at high temperatures exchange of rotational and vibrational energies will occur almost as a resonant phenomenon. Therefore, rotational temperature will approach vibrational temperature, and the relaxation of the two modes will become indistinguishable. To indicate this behavior, the $p\tau$ values above 12,000 K are shown with a dash curve connecting the points.

## Comparison with Shock-Tube Experiments

In addition to Eqs. (4a) and (4b), which describe the interactions between rotation and vibration and between translation and rotation, two more parameters must be specified to apply the present model to a high-temperature environment. First, the effect of dissociation on rotational energy, the so-called energy feedback phenomenon, must be accounted for, because dissociation occurs through rotational ladder climbing as well as vibrational ladder climbing. Following Eq. (3.42c) of Ref. 17, which is for the vibrational mode, 30% of the dissociation energy of $N_2$ is assumed to be removed from the rotational mode during dissociation.

Second, the translational-rotational temperature controlling chemical reaction rates must be defined. The effective translational-rotational temperature $T$ is defined here to be the energy-averaged temperature:

$$(1.5\Sigma_{k=\text{atom}} n_k + 2.5\Sigma_{k=\text{molecule}} n_k) kT$$
$$= \Sigma_{k=\text{all}} 1.5 n_k kT + \Sigma_{k=\text{molecule}} n_k k T_r \tag{17}$$

The present rotational nonequilibrium model is tested first against the experimental data obtained by Sharma and Gillespie.[8] For that shock-tube experiment, the ambient pressure was 1 torr, and shock velocity was 6200 m/s. The translational temperature behind the shock wave prior to excitation of rotational or vibrational modes or chemical reaction was 24,540 K.

The collision-limiting crosssection for vibrational excitation is varied to bring about agreement with the measured vibrational temperature. The value so chosen was $10^{-17}(50{,}000/T)^2$ cm$^2$. The exponent for the diffusion correction, the so-called $s$, was calculated using Eq. (3.55) of Ref. 17. All other parameters are those in Ref. 17.

In Fig. 8, the results of the calculation are shown and compared with the experimental data. The experimental values are those determined from the second positive system of $N_2$. The values determines by the first negative system of $N_2^+$ are not used because the excitation mechanisms for molecular ions are believed to be different from those of neutral molecules. As seen here, a fairly good agreement is seen between the rotational temperature calculated by the present model and the measured value.

Next, comparison is made between the present model and the experimental data by Fujita et al.[9] The ambient pressure was 0.3 torr, and shock velocity was 11.9 km/s for this case. The postshock translational temperature was 90,040 K. The same collision limiting cross section used for the Sharma and Gillespie's case was used here. The comparison is shown in Fig. 9. To within about 20%, the present model reproduces the measured rotational temperature.

## Discussion

As just seen, even though the present model was derived from the experimental and theoretical data on state-to-state rotational transitions obtained at temperatures equal to or below 1500 K, it seems to be valid to a post-shock temperature of 90,000 K. From Figs. 8 and 9, it is apparent that the conventional two-temperature model assuming the rotational temperature to be the same as the translational temperature is grossly in error at high temperatures.

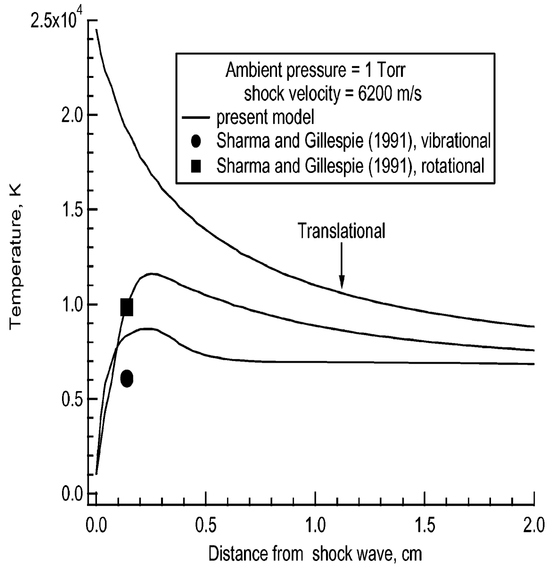

**Fig. 8 Comparison between the present method and the shock-tube data of Sharma and Gillespie.[8]**

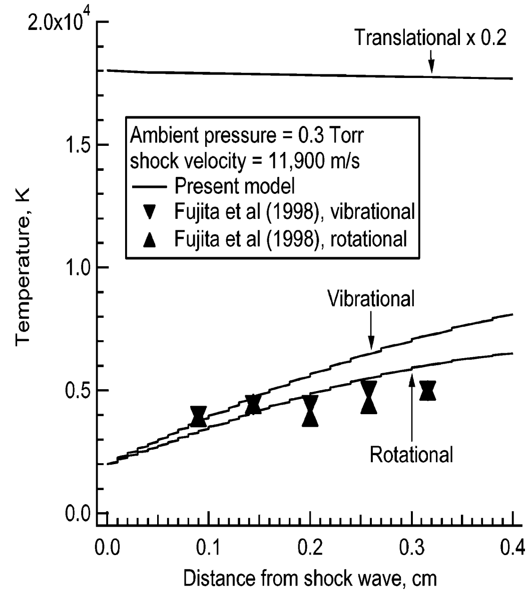

**Fig. 9 Comparison between the present method and the shock-tube data of Fujita et al.[9]**

In the experiment of Sharma and Gillespie shown in Fig. 8, the measured rotational temperature seems to be sufficiently high to possibly induce vibration-rotation coupling. However, in the experiment by Fujita et al. shown in Fig. 9, the observed rotational temperture is definitely too low for the vibration-rotation coupling to occur. Therefore, for this case the low rotational temperature must be attributed to the slow rotational relaxation at high translational temperatures.

As mentioned in the section titled Transition-Rate Coefficients, a question was raised by Fujita and Abe[18] as to whether the state-to-state transition rate coefficient given by Eq. (1) should be multiplied by $(T/295)$. If the multiplication is made, the rotational relaxation parameter $p\tau$ will not increase with temperature. In Ref. 22, coupled rotational-vibrational relaxation behavior of $H_2$ was studied theoretically. For this case, there was no uncertainty involving the factor $(T/295)$. According to that study, $p\tau$ for $H_2$ increases about 10-fold between $T = 1000$ and 5000 K. In the present work, $p\tau$ for $N_2$ increases about 15-fold between these two temperatures, in a reasonable agreement with the $H_2$ case. This agreement lends support to the present work over the work in Ref. 18.

## Conclusions

Using the expression of Rahn and Palmer for the state-to-state rotational transition-rate coefficients, which was derived from the experimental data taken at temperatures equal to or below 1500 K, the rotational relaxation time parameter for $N_2$ behind a strong shock wave is derived as $2.47 \times 10^{-14} T^{1.692}$ atm · s, over the temperature range from 400 to 128,000 K. The effective collision number corresponding to this expression is less than 10 at temperatures below 1500 K, in agreement with the earlier works of others, and increases with temperature. At temperatures above 12,000 K, the calculated relaxation time is longer than the vibrational relaxation time, which is considered hypothetical because vibration-rotation coupling will force these two modes to relax together. The present model approximately reproduces the rotational temperatures measured in shock tubes, up to a postshock temperature of 90,000 K. The temperature dependence of the present relaxation parameter is in a reasonable agreement with that for $H_2$ determined theoretically.

## Acknowledgments

The author acknowledges the support provided for this work by NASA Ames Research Center through the Contract NAS2-99092 to ELORET Corporation. The author expresses his sincere thanks to Ingrid Wysong of European Office of Aerospace Research and Development for her valuable suggestions.

## References

[1] Parker, J. G., "Rotational and Vibrational Relaxation in Diatomic Gases," *Physics of Fluids*, Vol. 2, No. 4, 1959, pp. 449–462.

[2] Lordi, J. A., and Mates, R. E., "Rotational Relaxation in Nonpolar Diatomic Gas," *Physics of Fluids*, Vol. 13, No. 2, 1970, pp. 291–308.

[3] Carnevale, E. H., Carey, C., and Larson, G., "Ultrasonic Determination of Rotational Collision Numbers and Vibrational Relaxation Times of Polyatomic Gases at High Temperatures," *Journal of Chemical Physics*, Vol. 47, No. 8, 1967, pp. 2829, 2835.

[4] Prangsma, G. J., Alberga, A. H., and Beenakker, J. J. M., "Ultrasonic Determination of the Volume Viscosity of $N_2$, CO, $CH_4$, and $CD_4$ Between 77 and 300 K," *Physica*, Vol. 64, No. 2, 1973, pp. 278–288.

[5] Temkin, S., Thuet, J. M., Bonamy, L., Bonamy, J., and Robert, D., "Angular Momentum and Rotational Energy Relaxation in $N_2$-$N_2$ Collisions Calculated from Coherent and Stimulated Raman Specroscopy Data," *Chemical Physics*, Vol. 138, No. 1, 1991, pp. 89–104.

[6] Wysong, I. J., and Wadsworth, D. C., "Assessment of Direct Simulation Monte Carlo Phenomenological Rotational Relaxation Models," *Physics of Fluids*, Vol. 10, No. 11, 1998, pp. 2983–2994.

[7] Wysong, I. J., and Wadsworth, D. C., "Assessment of Rotational Collision Number of Nitrogen at High Temperature and Its Possible Effect on Modeling of Reacting Shocks," *Proceedings of the 21st International Symposium on Rarefied Gas Dynamics*, Vol. 2, Pergamon, New York, 1998, pp. 321–328.

[8] Sharma, S. P., and Gillespie, W., "Nonequilibrium and Equilibrium Shock Front Radiation Measurement," *Journal of Thermophysics and Heat Transfer*, Vol. 5, No. 3, 1991, pp. 257–265.

[9] Fujita, K., Sato, S., Abe, T., and Ebinuma, Y., "Experimental Investigation of Air Radiation Behind a Strong Shock Wave," *Journal of Thermophysics and Heat Transfer*, Vol. 16, No. 1, 2002, pp. 77–82.

[10] Furudate, M., and Sawada, K., "Effect of Rotational Nonequilibrium on Shock Standoff Distances in Intermediate Hypersonic Range," AIAA Paper 01-0813, Jan. 2001.

[11] Rahn, L. A., and Palmer, R. E., "Studies of Nitrogen Self-Broadening at High Temperature with Inverse Raman Spectroscopy," *Journal of Optical Society of America*, Vol. 3, No. 9, 1986, pp. 1164–1169.

[12] Koszykowski, M. L., Rahn, L. A., and Palmer, R. E., "Theoretical and Experimental Studies of High-Resolution Inverse Raman Spectra of $N_2$ at 1-10 Atm," *Journal of Physical Chemistry*, Vol. 91, No. 1, 1987, pp. 41–46.

[13] Sitz, G. O., and Farrow, R. L., "Pump-Probe Measurements of State-to-State Rotational Energy Transfer Rates in $N_2(v = 1)$," *Journal of Chemical Physics*, Vol. 93, No. 11, 1990, pp. 7883–7893.

[14] Herring, G. C., and South, B. W., "Pressure Broadening of Vibrational Raman Lines in $N_2$ at Temperatures Below 300 K," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 52, No. 6, 1994, pp. 835–840.

[15] Sharafutdinov, R. G., Belikov, A. E., Strekalov, M. L., and Storozhev, A. V., "State-to-State Rate Constants and Rotational Relaxation Time in Nitrogen," *Chemical Physics*, Vol. 207, No. 1, 1996, pp. 193–201.

[16] Huo, W. M., and Green, S., "Quantum Calculations for Rotational Energy Transfer in Nitrogen Molecule Collisions," *Journal of Chemical Physics*, Vol. 109, No. 19, 1996, pp. 7572–7589.

[17] Park, C., *Nonequilibrium Hypersonic Aerothermodynamics*, Wiley, New York, 1990.

[18] Fujita, K., and Abe, T., "Coupled Rotation-Vibration-Dissociation Kinetics of Nitrogen Using QCT Models," AIAA Paper 2003-3799, 2003.

[19] Millikan, R. C., and White, D. R., "Systematics of Vibrational Relaxation," *Journal of Chemical Physics*, Vol. 39, No. 12, Dec. 1963, pp. 3209–3213.

[20] Park, C., "Assessment of Two-Temperature Kinetic Model for Ionizing Air," *Journal of Thermophysics and Heat Transfer*, Vol. 3, No. 3, 1989, pp. 233–244.

[21] Gupta, R. N., Yos, J. M., Thompson, R. A., and Lee, K.-P., "A Review of Reaction Rates and Thermodynamic and Transport Properties for an 11-Species Air Model for Chemical and Thermal Nonequilibrium Calculations to 30,000 K," NASA RP 1232, Aug. 1990.

[22] Furudate, M., Fujita, K., and Abe, T., "Coupled Rotational-Vibrational Relaxation of Molecular Hydrogen at High Temperature," AIAA Paper 2003-3780, June 2003.