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Electron-Impact Vibrational Relaxation in High-Temperature Nitrogen

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Vibrational relaxation process of N_2 molecules by electron-impact is examined for the future planetary entry environments. Multiple-quantum transitions from excited states to higher/lower states are considered for the electronic ground state of the nitrogen molecule $N_2(X^1\Sigma_g^+)$. Vibrational excitation and de-excitation rate coefficients obtained by computational quantum chemistry are incorporated into the "diffusion model" to evaluate the time variations of vibrational number densities of each energy state and total vibrational energy. Results show a nonBoltzmann distribution of number densities at the earlier stage of relaxation, which in turn suppresses the equilibration process, but affects little on the time variation of total vibrational energy. An approximate rate equation and a corresponding relaxation time from the excited states, compatible with the system of flow conservation equations, are derived for the first time. The relaxation time from the excited states indicates the weak dependency of the initial vibrational temperature, and is shorter than the previously obtained relaxation time in which only excitation from the ground state was considered. The empirical curve-fit formulas for the improved *e-V* relaxation time is obtained. The rate equation and the relaxation time, suited for the numerical simulation of the highly ionized planetary entry flowfields, are suggested.

Nomenclature

E_t = total energy
E_v = vibrational energy
E_v^* = equilibrium vibrational energy at T_e
f = correction factor
h = Planck's constant
J = rotational quantum number
K_0 = equivalent diffusivity
$k_{v,v'}$ = rate coefficients from vibrational state v to v'
M = second moment of vibrational transitions
m = highest vibrational state
m_e = electron mass
n_e = number density of electron
n_M = number density of molecule
n_v = number density of vth excited state
$n_{v'}$ = number density of v'th excited state
p_e = pressure of electron
s = arbitrary parameter in rate equation
T = translational temperature of heavy particle
T_e = electron temperature
T_v = vibrational temperature
t = time
v, v' = vibrational quantum number
θ_v = characteristic temperature for vibration
κ = Boltzmann constant
ν = frequency of oscillator
ρ_v = normalized number density of vth state
τ_e = vibrational relaxation time for *e-V* process

Introduction

RECENTLY, an intense worldwide interest has developed concerning the prospect of both unmanned and manned exploration of the Moon and the planet Mars. In order to reduce the weights of vehicles for such future missions, an aerobraking maneuver in the atmosphere is highly desirable. The aerobraking maneuver takes place in the upper atmosphere at very high velocity over extended periods of time. As a result, the flow around such vehicles is expected to be in both a thermal and chemical nonequilibrium state.

While the estimated entry velocity of the aeroassisted orbital transfer vehicle (AOTV) is about, or less than, 10 km/s, the Lunar-return entry velocity into the Earth's atmosphere is up to about 11 km/s. The proposed Mars-return entry velocity in manned mission is between 11.3–14 km/s.[1] Unlike the flow around the AOTV, the flow surrounding the future aeroassisted space transfer vehicle (ASTV) will be highly ionized because of higher entry velocities.[2]

Due to its light mass, electron-molecule collisions are much more frequent than heavy particle-molecule collisions. Thus, electrons are very efficient collision partners in causing vibrational energy transitions in molecules. In electron-vibration (*e-V*) energy exchange processes, the Landau-Teller conditions, in which only the transitions between adjacent levels are allowed, are violated.[3] Therefore, the multiple-level vibrational energy transitions must be considered in the *e-V* process.

For atmospheric molecules, the low-energy electron-impact vibrational excitation process is usually dominated by resonant mechanism.[4] That is, an incident electron is temporarily captured in the neighborhood of a target molecule, therefore forming a compound state. This resonance enhances the vibrational excitation cross sections by orders of magnitude. Lee[5] theoretically obtained the vibrational excitation cross sections and rate coefficients for the electronic ground state of the nitrogen molecule $N_2(X^1\Sigma_g^+)$ with the boomerang model of Dubé and Herzenberg.[6] Although this method is in principle a semi-empirical one, the obtained cross sections agree reasonably well with the experimental data of Schulz.[7]

Lee[5] obtained the analytical solution of the time variation of vibrational energy based on the "diffusion model[8]" at high-temperature regime. Subsequently, an approximate rate equation and a corresponding relaxation time, compatible with the system of flow conservation equations, were developed. Although the obtained relaxation time agrees substantially with experimental result, as pointed out by Hansen,[9] only the multiple-level excitation from the vibrational ground state is considered in the evaluation. This assumption is valid only for the flow in the vicinity of the shock wave around a

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vehicle, where most molecules are populated in the vibrational ground state ($v = 0$) at $t = 0$. However, if the flow leaves the shock wave, the contributions of the vibrational excited states ($v > 0$) become important, and the effects of excitation and de-excitation from these $v > 0$ states must be considered. This is especially true for the flow around ASTV in which the ionization level is much higher than that of AOTV.

The purpose of this article is to numerically solve the master equation for vibrational transitions from the excited states, and to develop an appropriate rate equation and a relaxation time which approximately represent the rigorous solution of the master equation. The obtained rate equation and the vibrational time for *e-V* process will be suitable for the numerical simulation of ASTV flowfield, since they include the effects of multiple excitation/de-excitation from and to non-ground states.

Vibrational Rate Process

Master Equation for Vibrational Transitions

In the following analysis, several assumptions are made. First, the harmonic oscillator model is applied to describe the molecular vibration. Second, the effects of dissociation are neglected. These assumptions are valid rigorously only for the lower vibrational energy states. High-vibrational states deviate significantly from the harmonic oscillator assumption due to the anharmonic vibrational potential and the very small unequal energy gaps between the vibrational states.[10] Furthermore, dissociation of molecules depletes the population of upper vibrational states. In gas mixtures with electrons such as the case of planetary entry environments, T_e tends to equilibrate rapidly with T_v because of efficient vibrational transitions by electron collisions. When T_v becomes nearly equal to T_e, the electron collisions cause no further change in vibrational populations, even though these temperatures may be far out of equilibrium with T. After T_e becomes equal to T_v, heavy particle collisions promote T_e and T_v to equilibrate with T (translational-vibrational energy transfer).[9] Consequently, the above assumptions are validated at the initial stage of vibrational relaxation, where major transitions are confined to the relatively lower vibrational energy states, in gas mixtures by electron bombardment.

Assuming that the vibrational oscillators interchange their energies with an electron heat bath having a constant temperature T_e, the rate of change of n_v without dissociation is given by the master equation

$$\frac{\partial n_v}{\partial t} = \sum_{v'=0}^{m} (k_{v',v} n_{v'} - k_{v,v'} n_v) n_e \tag{1}$$

The principle of detailed balancing provides the condition

$$k_{v',v} n_{v'E} = k_{v,v'} n_{vE} \tag{2}$$

where n_{vE} is the equilibrium population in state v. Using the relation [Eq. (2)] and the normalized number density $\rho_v = n_v/n_{vE}$, one obtains the following normalized master equation:

$$\frac{1}{n_e}\frac{\partial \rho_v}{\partial t} = \sum_{v'=0}^{m} k_{v,v'}(\rho_{v'} - \rho_v) \tag{3}$$

At the high temperature regime where the kinetic energy κT_e is larger than the vibrational energy gap, collisional excitation and de-excitation of the vibrational states occur almost in accordance with the classical mechanics.[8] According to the classical analogy, the vibrational energy states are continuously distributed over energy state v, and the summations in Eq. (3) can be replaced by integrations

$$\frac{1}{n_e}\frac{\partial \rho_v}{\partial t} = \int_{v'=0}^{m} k_{v,v'}(\rho_{v'} - \rho_v)\,\mathrm{d}v' \tag{4}$$

If $k_{v,v'}$ in Eq. (4) is assumed to be large only for $|v' - v| \sim 1$, i.e., the transitions occur mostly between neighboring states, then the integration limits can be changed from $-\infty$ to ∞

$$\frac{1}{n_e}\frac{\partial \rho_v}{\partial t} = \int_{-\infty}^{\infty} k_{v,v'}(\rho_{v'} - \rho_v)\,\mathrm{d}v' \tag{5}$$

The right side of Eq. (5) is expanded in powers of $\partial^n \rho_v/\partial v^n$, and the terms only to second-order are retained, then, one obtains the following diffusion type equation[8,10]:

$$\frac{1}{n_e}\frac{\partial \rho_v}{\partial t} = \frac{\partial}{\partial v}\left(M\frac{\partial \rho_v}{\partial v}\right) \tag{6}$$

where

$$M = \frac{1}{2}\int_{-\infty}^{\infty} k_{v,v'}(v' - v)^2\,\mathrm{d}v' \tag{7}$$

is the second moment of vibrational energy transfer between vth state and v'th state. When $k_{v,v'}$ is given for discrete vibrational states v and v', the moment M can be determined by summing over the discrete states

$$M(v) = \frac{1}{2}\sum_{v'} (v' - v)^2 k_{v,v'} \tag{8}$$

The resulting Eq. (6) is a diffusion equation in the vibrational space v. This equation, together with the requirement that the sum of all n_v equals the given number density of molecules n_M

$$n_M = \sum_{v=0}^{m} n_v \simeq \int_0^m n_v\,\mathrm{d}v \tag{9}$$

give n_v, which is a function of time and energy state v.

Solution of Master Equation

Relaxation from Ground State (Case A)

This is the case wherein the flow immediately behind the shock wave is where most molecules are in the ground state at $t = 0$.

Lee[3,5] obtained the analytical solution for Eq. (6) assuming that the variation of the second moment M with the vibrational space is small at $v = 0$. Then, the normalized number density ρ_v can be expressed as

$$\rho_v(v, t) = \rho_0\{1 - \mathrm{erf}[v/2(K_0 t)^{1/2}]\} \tag{10}$$

where $\rho_0 = (n_v/n_{vE})_{v=0}$ is the normalized number density at $v = 0$, and $K_0 = n_e(M)_{v=0}$ is the equivalent diffusivity at $v = 0$, and $\mathrm{erf}(z)$ is the error function defined by

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-\xi^2}\,\mathrm{d}\xi$$

The value of ρ_0 can be approximately assumed to be 1.

The total E_v per unit volume for harmonic oscillators is given by

$$E_v = \sum_{v=0}^{m} vh\nu n_{vE}\rho_v \simeq h\nu \int_0^m v n_{vE}\rho_v\,\mathrm{d}v \tag{11}$$

$$E_v(t) = A\left\{\frac{1}{a^2} - \frac{b}{a\sqrt{\pi}} - \left[1 - \mathrm{erf}\left(\frac{ab}{2}\right)\right] e^{a^2b^2/4}\left(\frac{1}{a^2} - \frac{b^2}{2}\right)\right\} \tag{12}$$

where $A = h\nu n_M(1 - e^{-a})$, $a = \theta_v/T_e$ and $b = 2(K_0 t)^{1/2}$.

The time derivative of $E_v(t)$ is given by

$$\frac{\mathrm{d}E_v(t)}{\mathrm{d}t} = AK_0\left\{\left[1 - \operatorname{erf}\left(\frac{ab}{2}\right)\right] e^{a^2b^2/4} \cdot \left(1 + \frac{a^2b^2}{2}\right) - \frac{ab}{\sqrt{\pi}}\right\} \tag{13}$$

For small t

$$E_v(t) = A(K_0t + \cdots) \tag{14}$$

$$\frac{\mathrm{d}E_v(t)}{\mathrm{d}t} = AK_0 \tag{15}$$

For large t

$$E_v(t) = A(1/a^2)[1 - (2/a\sqrt{\pi}\sqrt{K_0t}) + \cdots] \tag{16}$$

$$\frac{\mathrm{d}E_v(t)}{\mathrm{d}t} = \frac{2AK_0}{ab\sqrt{\pi}} \tag{17}$$

Relaxation from Excited State (Case B)

In the flow region away from the shock wave, the gas has already been excited to T_v. Therefore, to describe the relaxation process from this excited state, the excitation and de-excitation from/to all levels need to be considered. Since the M cannot be considered constant in this case, the diffusion Eq. (6) must be solved numerically. Once $n_v(t)$ is determined numerically, then, $E_v(t)$ and $\mathrm{d}E_v(t)/\mathrm{d}t$ are calculated.

Since the diffusion Eq. (6) is the one-dimensional parabolic partial differential equation, the Crank-Nicolson scheme is used to solve the equation numerically.

Rate Equation and Relaxation Time

In the actual numerical simulation, it is quite convenient to use an appropriate rate equation, which is compatible with the system of flow conservation equation, instead of using $E_v(t)$ or $\mathrm{d}E_v(t)/\mathrm{d}t$ obtained from the diffusion equation. This rate equation corresponds to the source term for vibrational energy equation for a flowing gas. The resulting vibrational energy equation is used in a computation of nonequilibrium multitemperature flow, along with the conservation equations of mass, momentum, and energy. Therefore, a modified Landau-Teller-type of rate equation, which approximates the rigorous solution of Eq. (6), is developed. In order to derive the rate equation and the relaxation time, an assumption of Boltzmann distribution is made. That is, the vibrational energy levels of molecules are assumed to be populated by a Boltzmann distribution with a unique T_v.

The rate equation for vibrational relaxation at any given instant may be defined in general as

$$\frac{\mathrm{d}E_v(t)}{\mathrm{d}t} = \frac{E_v^* - E_v}{\tau_e} f \tag{18}$$

where f is given by

$$f = \left(\frac{E_v^* - E_v}{E_v^* - E_{v,0}}\right)^{s-1} \tag{19}$$

where superscript * and subscript 0 refer to the equilibrium value and $t = 0$. In Eq. (19), s has a positive value between 1 (Landau-Teller model) and 3.5 (diffusion model). The value $s = 3.5$ corresponding to the diffusion model was chosen empirically to fit the results of the diffusion Eq. (6) and the rate Eq. (18) at high temperatures in Ref. 5. Park[10] analytically determined the value $s = 3.5$ for the diffusion model in the case of translation-vibration (T-V) relaxation process.

Neglecting the correction factor in Eq. (18), which is only slightly different from unity, τ_e is given by

$$\tau_e = \frac{E_v^* - E}{\mathrm{d}E_v(t)/\mathrm{d}t} \tag{20}$$

Relaxation from Ground State (Case A)

Since the molecules are all in the ground state at $t = 0$, $E_{v,0}$ in Eq. (19) is zero, and, therefore, the solution of Eq. (18) is given by

$$E_v(t) = E_v^*\{1 - [1 + (s - 1)(t/\tau_e)]^{[1/(1-s)]}\} \tag{21}$$

In this case, τ_e can be approximately given as

$$\tau_e \simeq \left[\frac{E_v^* - E_v}{\mathrm{d}E_v(t)/\mathrm{d}t}\right]_{t=0} = \frac{1}{a^2K_0} = \frac{1}{(\theta_v/T_e)^2K_0} \tag{22}$$

Thus, τ_e is represented by

$$\tau_e = \left[1 \Big/ \left(\frac{\theta_v}{T_e}\right)^2 \left(\frac{1}{2}\right) n_e \sum_{v'=0}^{m} k_{0,v'}(v')^2\right] \tag{23}$$

and τ_e is independent of T_v.

τ_e in Eq. (23) may be rewritten in the form $p_e\tau_e$ (atm-s) as

$$p_e\tau_e = \left[\kappa T_e \Big/ \left(\frac{\theta_v}{T_e}\right)^2 \left(\frac{1}{2}\right) \sum_{v'=0}^{m} k_{0,v'}(v')^2\right] \tag{24}$$

Relaxation from Excited State (Case B)

Based on the assumption that the vibrational levels are occupied by a Boltzmann distribution with T_v, $E_{v,0}$ at $t = 0$ is given by

$$E_{v,0} = E_v|_{t=0} \equiv E_0 = [n_Mh\nu/(e^{\theta_v/T_e} - 1)]|T_{v(t=0)} \tag{25}$$

The solution of Eq. (18) is

$$E_v = (E_v^* - E_0)\{1 - [1 + (s - 1)(t/\tau_e)]^{[1/(1-s)]}\} + E_0 \tag{26}$$

The numerator of Eq. (20) is defined by

$$\begin{aligned} E_v^* - E_v &= E_v^*(T_e) - E_v^*(T_v) \\ &= n_Mh\nu\{[1/(e^{\theta_v/T_e} - 1)] - [1/(e^{\theta_v/T_v} - 1)]\} \end{aligned} \tag{27}$$

The rate of change of $\mathrm{d}E_v(t)/\mathrm{d}t$ is established by the excitation and de-excitation rates from/to all levels. For harmonic oscillators

$$\frac{\mathrm{d}E_v(t)}{\mathrm{d}t} = n_en_Mh\nu \sum_{v=1}^{m} \sum_{v'=0}^{m} |v - v'| \left[\left(\frac{n_v'}{n_M}\right) k_{v',v} - \left(\frac{n_v}{n_M}\right) k_{v,v'}\right] \tag{28}$$

Thus

$$\frac{\mathrm{d}E_v(t)}{\mathrm{d}t} = n_en_Mh\nu(1 - e^{\theta_v/T_v}) \sum_{v=1}^{m} \sum_{v'=0}^{m} |v - v'| \cdot (e^{-v'\theta_v/T_v}k_{v',v} - e^{-v\theta_v/T_v}k_{v,v}') \tag{29}$$

In compression flow (heating) case, the number density of v'th energy state is small compared with the one of vth state when $v' > v$, and the excitation rate coefficient $k_{v,v'}$ is much smaller than the de-excitation rate coefficient $k_{v',v}$ when $v \geq 1$. Thus, the sum over v' in Eq. (29) may be chosen as $v' = 0, 1, 2, \ldots, v - 1$. That is, the energy gains for all transitions to the state v comes from below, and the energy losses for all transitions from state v goes downward. Then

$$\frac{\mathrm{d}E_v(t)}{\mathrm{d}t} = n_e n_M h\nu(1 - e^{\theta_v/T_v}) \sum_{v=1}^{m} \sum_{v'=0}^{v-1} (v - v') \cdot (e^{-v'\theta_v/T_v} k_{v',v} - e^{-v\theta_v/T_v} k_{v,v'}) \tag{30}$$

τ_e is obtained from Eq. (20)

$$\tau_e = \frac{1}{n_e} D \left[1 \Big/ \sum_{v=1}^{m} \sum_{v'=0}^{v-1} (v - v')(e^{-v'\theta_v/T_v} k_{v',v} - e^{-v\theta_v/T_v} k_{v,v'}) \right] \tag{31}$$

where

$$D = [(e^{\theta_v/T_e} - 1)^{-1} - (e^{\theta_v/T_v} - 1)^{-1}/(1 - e^{-\theta_v/T_v})]$$

It must be noted that τ_e in this case is a function of both T_v and T_e.

Also

$$p_e\tau_e = \kappa T_e D \cdot \left[1 \Big/ \sum_{v=1}^{m} \sum_{v'=0}^{v-1} (v - v')(e^{-v'\theta_v/T_v} k_{v',v} - e^{-v\theta_v/T_v} k_{v,v'}) \right] \tag{32}$$

At T_e, $T_v \gg \theta_v$

$$D \simeq [T_v(T_e - T_v)/\theta_v^2]$$

Thus, $p_e\tau_e$ can be approximated by

$$p_e\tau_e \simeq \left\{ \kappa T_e \Big/ \left[\frac{\theta_v^2}{T_v(T_e - T_v)} \right] \cdot 1 \Big/ \sum_{v=1}^{m} \sum_{v'=0}^{v-1} \left[(k_{v',v} - k_{v,v'}) + \left(\frac{\theta_v}{T_v} \right) (v k_{v,v'} - v' k_{v',v}) \right] \right\} \tag{33}$$

Results and Discussion

The electronic ground state of the nitrogen molecule $N_2(X^1\Sigma_g^+)$ is considered in the present study, which is the dominant vibrationally excited molecular species expected in the Earth-return ASTV environment. Twelve initial vibrational states ($v = 0$–12) are included with 10 quanta change ($\Delta v = v' - v = \pm 10$). Vibrational excitation and de-excitation rate coefficients of N_2, based on computational quantum chemistry,[12] are used in the present calculation. These coefficients obtained by Huo et al.[12] provide only 5 quanta change ($\Delta v = \pm 5$) because of presumably precipitous dropping of the value for changes of 6 or more vibrational quanta. Hence, these rate coefficients are extrapolated to up to 10 quanta change by using the exponential curve fit formula $y = a \cdot \exp(-bx)$ in order to give sufficient convergence of the present calculation. $J = 50$ is considered here because only the rate coefficients with this value are available for the time being.

Figure 1 shows the comparison of Lee's theoretical rate coefficients[5] with theoretical values of Huo et al.[12] for $v = 0$–1, $v = 0$–3, $v = 0$–5, $v = 0$–7, $v = 0$–9 transitions. With the exception of the transition $v = 0$–9, of which value itself is negligibly small, the vibrational rate coefficients based on two theoretical methods exhibit excellent agreement for the entire electron energy range. This agreement justifies the extrapolation of the coefficients of Ref. 12 for quanta change larger than 5 by the exponential curve-fit formula.

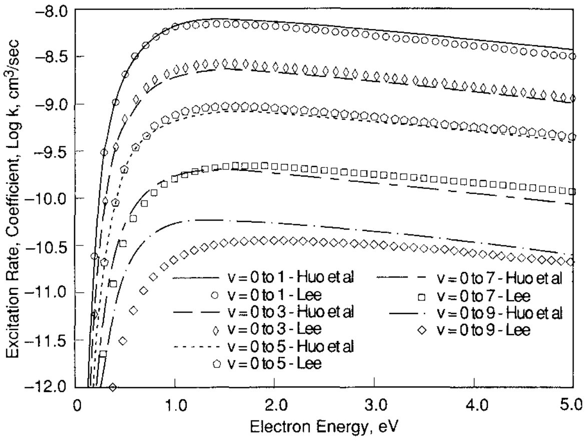

Fig. 1 ***e-V* Excitation rate coefficients for N_2.**

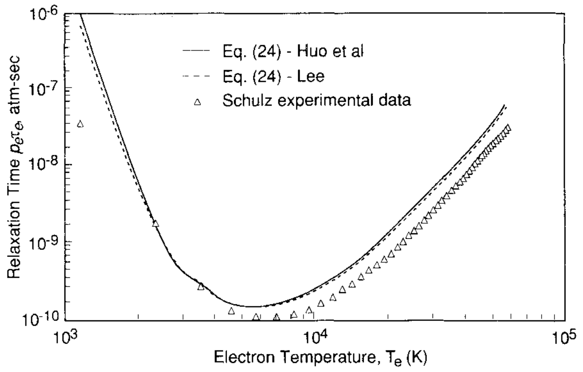

Fig. 2 Vibrational relaxation time for *e*-N_2 collision.

It must be noted that all rate coefficients are strongly energy-dependent at low energy, and increase sharply at the onset of the resonance, which is approximately 2.3 eV[5]. At the high-energy end, the rate coefficients decrease slowly because of an increasing portion of the Maxwellian electrons having energies above the resonance energy. The electron-impact vibrational rate coefficients have been caculated assuming that the electron velocity distribution is Maxwellian. The rate coefficients also sharply decrease with increasing Δv.

Figure 2 represents the *e-V* relaxation time in the form $p_e\tau_e$ (atm-s) for the case A (excitation only from the ground state) given by Eq. (24). As may be seen in Fig. 2, there is virtually no difference between the result based on Lee's semi-empirical rate coefficients[5] (dotted curve) and the one based on more rigorous coefficients of Huo et al.[12] (solid curve). These theoretical relaxation times agree substantially with the result based on the experimental values of the cross sections of Schultz,[7] except at very low electron temperature ($T_e \simeq 1000$ K). It must be emphasized that Schulz's experiment was conducted at room temperature, leading to the corresponding $J \sim 5$, and that both theoretical curves in Fig. 2 are for $J = 50$. At low electron temperature, because of the small number density of the electrons with sufficient energy to cause resonant excitation, the contribution of nonresonant excitation (direct excitation) is dominant.[5] In both Lee[5] and Huo et al.[12] calculations, this nonresonant direct excitation is neglected because of small effects on the excitation mechanism at moderate electron temperatures. Therefore, the experimental result is much more realistic at very low electron temperature.

The *e-V* relaxation time for case B (excitation/de-excitation from the excited states) given by Eq. (32) is shown in Fig. 3. The relaxation time in this case is a function of both T_e and T_v [see Eq. (32)]. T_v dictates the initial excited state with a Boltzmann distribution, and the molecules commence to equil-

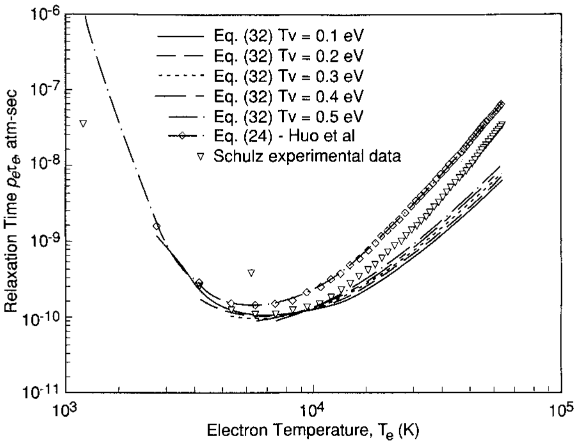

Fig. 3 *e-V* Relaxation time for N_2.

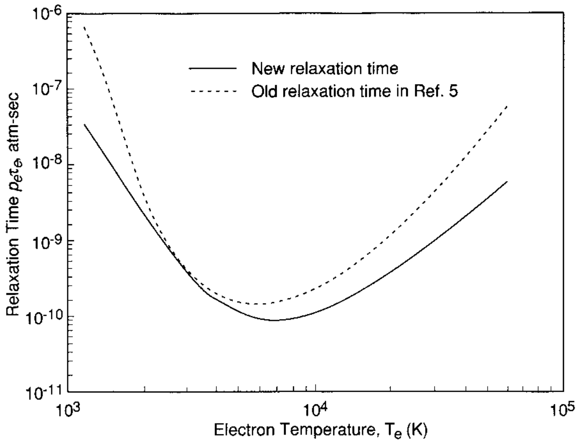

Fig. 4 Newly proposed *e-V* relaxation time for N_2.

ibrate from T_v to T_e. As can be seen in Fig. 3, the relaxation times for case B depend only weakly on T_v. The relaxation times become slightly longer with the increase of T_v, but the general tendency is the same. The effects of multiple excitation/de-excitation from the excited states contribute to shortening the relaxation times noticeably in the entire temperature range, as seen in Fig. 3. The *e-V* relaxation has a minimum value at $T_e \simeq 7000$ K due to the strong resonance at this temperature. On either side of this temperature, τ_e increases because of diminishing contribution of resonant excitation.

It may be concluded from the above-mentioned results, that the *e-V* relaxation time can be well represented by combining Schulz's experimental data at very low temperature and Eq. (32) with a specific value of T_v (e.g., $T_v = 0.1$ eV) at moderate and high temperatures. The resulting relaxation time will be a function of T_e only, and applicable to the temperature range of $1000 \text{ K} \le T_e \le 50{,}000$ K. In Fig. 4, a newly proposed *e-V* relaxation time, which is obtained from Eq. (32) with $T_v = 0.1$ eV for $0.2 \le T_e \le 5.0$ eV and Schulz's experimental value at $T_e = 0.1$ eV, is compared with Lee's relaxation time shown in Ref. 5. As can be seen in Fig. 4, the new relaxation time is much shorter than the previously proposed relaxation time[5] for the entire temperature range. This suggests stronger coupling between the electron and vibration modes for case B. Since molecules, in general, are considered to be vibrationally excited in the flow at given time, the improved relaxation time in Fig. 4 must be used in the future AOTV/ASTV flowfield calculations.

Candler and Park[13] obtained the empirical formulas for the *e-V* relaxation time by curve-fitting Lee's theoretical results[5] using two quadratics in the logarithm (base 10) of T_e. The same procedure is repeated here to derive the following expression for the new *e-V* relaxation time in Fig. 4:

$$\log(p_e\tau_e) = 3.91(\log T_e)^2 - 30.36(\log T_e) + 48.90, \quad 1000 \text{ K} \le T_e \le 7000 \text{ K} \tag{34}$$

$$\log(p_e\tau_e) = 1.30(\log T_e)^2 - 9.09(\log T_e) + 5.58, \quad 7000 \text{ K} \le T_e \le 50{,}000 \text{ K} \tag{35}$$

Figure 5 shows the comparison of the approximate solutions [Eq. (21) with $s = 3.5$] with rigorous solution [Eq. (12)] for $T_e = 1.0$ eV and for $n_e = 10^{19}$ 1/cm³. The abscissa in Fig. 5 is the time normalized by the relaxation time for case A [Eq. (23)]. $E_v(t/\tau_e)$ in the ordinate is normalized by E_v^*. In this case, the vibrational energy equilibrates from zero value since all molecules are in the ground state at $t = 0$. As can be seen in Fig. 5, the approximate rate Eq. (21) with $s = 3.5$, remarkably represents the diffusion characteristic of the electron-impact vibrational excitation process. This agreement also implicitly validates the assumption of Boltzmann distribution during the relaxation process for case A (relaxation from the ground state).

The second moment of vibrational transition $M(v)$ is shown in Fig. 6 for case B (relaxation from the excited states) where $T_e = 0.4$ eV. Since $M(v)$ is the sum of the rates from all states, its value is a good indicator of the overall rate of transition. The $M(v)$ increases rapidly from the ground state value $M(0)$ and remains nearly constant over the range of $v = 1$–12. This trend is in contrast to the Landau-Teller model in which $M(v)$ increases monotonically.[11] In the Landau-Teller model, only the transitions between adjacent energy levels are allowed, and $k_{v,v+1}$ is proportional to $v + 1$. Therefore, the behavior of the second moment $M(v)$ in Fig. 6 indicates the dominant effects of multiple-level transitions in the *e-V* relaxation process.

The integration of the master Eq. (1) or its equivalent diffusion Eq. (6) yields the population distribution of all vibrational states as a function of time. In order to solve the dif-

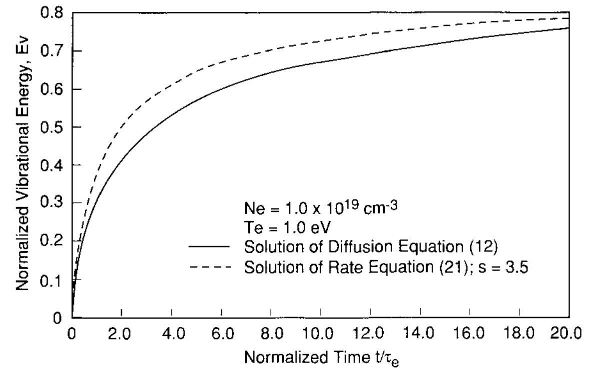

Fig. 5 Solution of vibrational energy equation (case A).

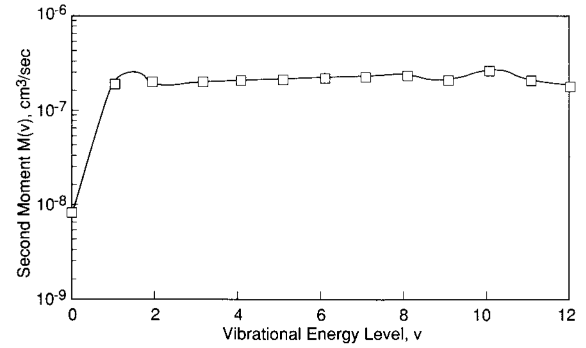

Fig. 6 Second moment of vibrational transition $M(v)$: $Te = 0.4$ eV.

fusion Eq. (6), the initial population distribution at $t = 0$ and the boundary conditions at $v = 0$ (the ground state) and $v = m$ (the highest state to be considered) must be given. The initial condition is set to be a Boltzmann distribution; i.e., the molecules are in equilibrium with given initial temperature at $t = 0$. At each integration time step, the ground state population ($v = 0$) is determined by the total population constraint [Eq. (9)], and the final state population ($v = m$) is determined by a local Boltzmann distribution at the uppermost levels ($v = m - 2, m - 1, m$). It must be noted that imposing this local Boltzmann distribution at the final state is somewhat arbitrary and is not mathematically compatible with the diffusion Eq. (6), except for $t = \infty$ where $\partial\rho_v/\partial t = \partial\rho_v/\partial v = \partial \log(\rho_v)/\partial v = 0$. This boundary condition, therefore, still remains to be addressed more rigorously.

Figure 7 shows ρ_v at selected times. This is a case wherein the molecules, initially in equilibrium at 0.4 eV with a Boltzmann distribution, is heated suddenly by an electron heat bath having a constant $T_e = 1.0$ eV, which is corresponding to a phenomenon in the compression flow. As can be seen in Fig. 7, the population distribution is quite different from a pure Boltzmann distribution in the early stage of relaxation process. Although the populations at $v = 0$–3 levels always maintain a Boltzmann distribution [a straight line in the $v - \log(\rho_v)$ plot], the populations at $v \geq 4$ deviate considerably from a Boltzmann distribution until at $t = 5.48 \times 10^{-11}$ s. This underpopulation leads to the suppression of the equilibrium process at the earlier stage of relaxation.

The time variation of $E_v(t)$ given by Eq. (11) is compared with the solution of rate Eq. (26) in Fig. 8 for the case of $T_{v(t=0)} = 0.4$ eV, $T_e = 1.0$ eV, and for $n_e = 10^{19}$ 1/cm^3. The abcissa in the figure is the time normalized by τ_e [Eq. (31)]. The ordinate is $E_v(t/\tau_e)$ normalized by E_v^*. In this case, the vibrational energy starts from the given nonzero value [the excited state with $T_{v(t=0)}$]. As expected, the solid curve [solution of Eq. (6)] reveals a different feature from the dashed curve [Eq. (26) with $s = 3.5$], due to the suppression phenomenon caused by a nonBoltzman population distribution.

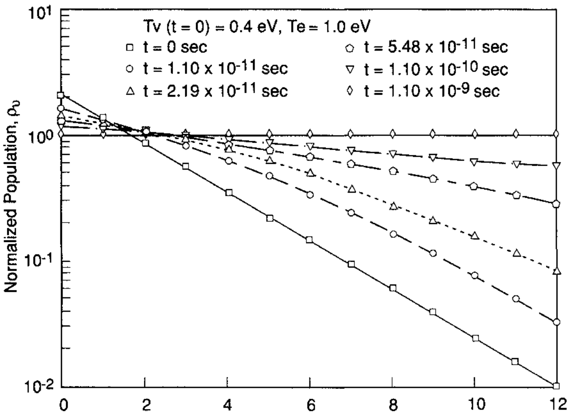

Fig. 7 Normalized vibrational population ρ_v.

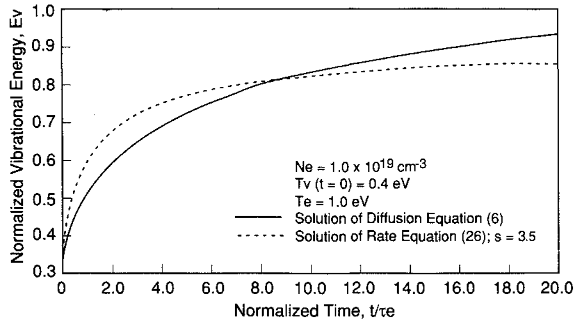

Fig. 8 Solution of vibrational energy equation (case B).

As evident in Fig. 7, the number densities of vibrational levels are underpopulated until $t = 5.48 \times 10^{-11}$ s, which is corresponding to $t/\tau_e = 5$ in Fig. 8. Because of this underpopulation, the vibrational energy is always smaller than the one predicted by a Boltzmann distribution during the early stage of relaxation. However, during this period of time, mainly the lower energy levels ($v \leq 5$) are significantly populated, and these lower levels locally maintain a Boltzmann distribution. Thus, the deviation of the total $E_v(t)$ from the value corresponding to a true Boltzmann distribution is not so large. After $t = 5.48 \times 10^{-11}$ s, the number densities of vibrational levels maintain a pure Boltzmann distribution throughout the rest of the relaxation process. As a result, the solution of the approximate rate Eq. (26) with $s = 3.5$ and the new relaxation time defined by Eq. (31), gives a good agreement with the solution of diffusion Eq. (6) in spite of the nonBoltzmann behavior at the earlier stage of relaxation.

It should be emphasized that the aforementioned discussion is confined only to the heating case (compression flow). Consequently, there is still a requirement for study of *e-V* transitions in the cooling case (expansion flow) in the future.

Conclusions

A study was made of the electron-impact vibrational rate processes expected in the future planetary entry flowfields. Multiple-quantum transitions from the excited states to higher/lower states were considered for the electronic ground state of the nitrogen molecule $N_2(X^1\Sigma_g^+)$. The relaxation time from the vibrational excited states was evaluated for the first time. The obtained relaxation time shows the weak dependency of the initial vibrational temperature, and the effects of multiple excitation/de-excitation from the excited states contribute noticeably to shortening the relaxation time in the entire temperature range. The empirical curve-fit formulas for the new relaxation time was also obtained. Based on the "diffusion model," the master equation for the *e-V* transitions was numerically solved for a heating case (a compression flow case). Results show a nonBoltzmann distribution of number densities at the earlier stage of relaxation, which, however, affects little on the time variation of total vibrational energy. Finally, the approximate rate equation and the corresponding relaxation time, which take account of the excitation/de-excitation effects, are suggested.

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