JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 14, No. 4, October–December 2000

Analytical Models for Electron-Vibration Coupling in Nitrogen Plasma Flows

A. Bourdon* and P. Vervisch†
Universite et Institut National des Sciences Appliquées de Rouen, 76821 Mont Saint Aignan CEDEX, France

A model for the electron-vibration energy exchange in nitrogen based on a Landau–Teller-type rate equation is presented. Analytical expressions of relaxation times are derived for cutoff harmonic oscillator and Morse oscillator approximations, assuming that the relaxation proceeds by way of a continuous series of Boltzmann distributions over the vibrational states. Comparisons with the direct numerical integration of the master equation have shown that the use of a two-temperature relaxation time allows accurate modeling of the nitrogen vibrational energy relaxation rate for various conditions encountered in high-enthalpy flows with electron and vibrational temperatures up to 40,000 K.

Nomenclature

a = constant in the analytical expression of rate coefficients for $v > 0 \longrightarrow w > v$ transitions
$\mathrm{d}E_v^n/\mathrm{d}t$ = nondimensional vibrational energy relaxation rate
E_v = vibrational energy per unit volume, J/m^3
E_v^* = vibrational energy calculated with vibrational levels in Boltzmann equilibrium at the electron temperature T_e, J/m^3
$E_{v,\mathrm{init}}$ = vibrational energy at 0-s time, J/m^3
J = rotational quantum number
k_B = Boltzmann constant, J/K
$k_{v,w}$ = electron-vibration (E-V) rate coefficient of the $v \longrightarrow w$ transition, m^3/s
N_t = total N_2 number density, $\sum N_v$, m^{-3}
N_v = number density of the vibrational level v of N_2, m^{-3}
n_e = electron number density, m^{-3}
p_e = electron partial pressure, $n_e k_B T_e$, atm
T_e = electron temperature, K
T_v, T_{exci} = vibrational temperature, K
t = time, s
t^n = nondimensional time
v_m = total number of excited vibrational levels
$\Delta\epsilon$ = constant of the Morse oscillator, cm^{-1}
$\epsilon(v)$ = energy of the vibrational level v of N_2, J
ϵ_1 = energy of the first vibrational level of N_2, J
$\sigma_{v,w}$ = E-V cross section of the $v \longrightarrow w$ transition, m^2
τ_e = E-V relaxation time, s

Supercripts

HO = truncated harmonic oscillator
MO = Morse oscillator

I. Introduction

THE computations of reentry flows require the modeling of numerous complex phenomena because these flows are generally in strong thermochemical nonequilibrium (vibrationally excited, dissociated, and even ionized). Different studies have shown that the rough modeling of one term (transport property, energy exchange term, etc.) could significantly affect the calculated flow.[1,2] Therefore, it is important to test and improve the accuracy of the thermochemical models used. In particular, concerning the vibrational energy relaxation in high-enthalpy flows, many models have been developed in the recent years for the coupling between vibration and chemistry. Conversely, only few studies have been devoted to the modeling of the electron-vibration energy exchange. So far, all of the models[3–5] use the approximation originally proposed by Lee[6–8] to express the vibrational energy relaxation rate as a Landau–Teller-type rate equation of the form

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = \frac{E_v^* - E_v}{\tau_e} \tag{1}$$

For the electron-vibration (E-V) relaxation time, Lee[8] derived an approximate analytical expression using a harmonic oscillator model and proposed an empirical curve-fit formula as a function of T_e for $1000 \leq T_e \leq 50{,}000$ K, easy to incorporate in flow codes. In agreement with the analysis carried out by Mertens,[4] in this work only Lee's 1992 results[8] will be used for comparison. The most exhaustive work on the determination of E-V relaxation times is the recent study carried out by Mertens.[4] This author integrated numerically the master equation using a complete database for E-V rate coefficients and an anharmonic oscillator approximation, to determine two-temperature relaxation times. For $0 \leq T_v$, $T_e \leq 5$ eV, results are given in the form of polynomial equations easy to implement in flow codes.

In the present work, we propose to study the direct analytical solution of the master equation for vibrational-level populations to derive a simple expression of the E-V relaxation time. An analytical approach makes possible easily testing the influence of the choice of the oscillator model for N_2, and the accuracy of the E-V rate coefficients on the derived relaxation times. In earlier works, E-V models have been mainly developed and tested in exciting conditions as shocks.[3,4,8] In this study, we also propose to investigate relaxing situations as in expanding flows.[5] Conditions encountered in high-enthalpy flows are studied, with electron and vibrational temperatures up to 40,000 K.

II. Problem Formulation

A. Oscillator Models

The N_2 molecule is well known to be anharmonic, and its potential has been determined accurately by Dmitrieva et al.[9] A truncated harmonic oscillator (HO) agrees with Dmitrieva's model[9] only up to $v \simeq 10$, whereas with a Morse oscillator approximation a good agreement is obtained up to $v \simeq 34$. For a Morse oscillator (MO), the vibrational energy of a level v is given by

$$\epsilon(v) = v\epsilon_1[1 - (\Delta\epsilon/\epsilon_1)(v - 1)] \tag{2}$$

Received 8 December 1999; revision received 26 May 2000; accepted for publication 30 May 2000. Copyright © 2000 by A. Bourdon and P. Vervisch. Published by the American Institute of Aeronautics and Astronautics, Inc., with permission.

[*] Research Scientist, Unite Mixte de Recherche No 6614, Complexe de Recherche Interprofessionnel en Aerothermochimie, Centre National de la Recherche Scientifique.

[†] Senior Scientist, Unite Mixte de Recherche No 6614, Complexe de Recherche Interprofessionnel en Aerothermochimie, Centre National de la Recherche Scientifique.

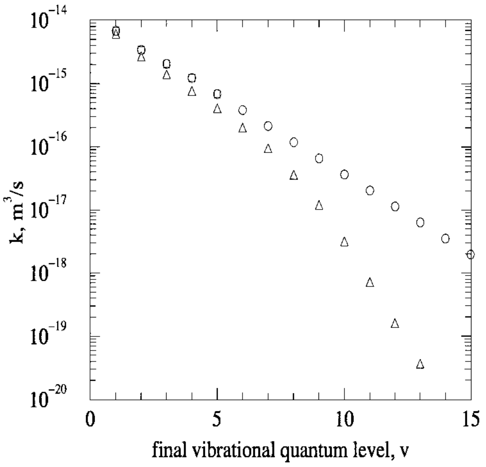

Fig. 1 Rate coefficients of 0→ v transitions for T_e = 1 eV: □, calculations from Huo et al.[10] up to v = 5; △, measurements from Allan[14] up to v = 13; and ○, database given by Huo et al.[10] and extension to 0→ v >5 transitions using the technique given by Mertens.[4]

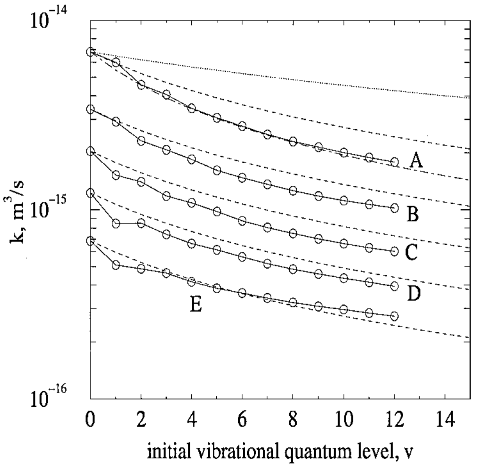

Fig. 2 Rate coefficients of v→ v+n transitions for fixed n at T_e = 1 eV: solid line with circles is database from Huo et al.[10]; A, n = 1; B, n = 2; C, n = 3; D, n = 4; and E, n = 5. Other lines are database from Huo et al.[10] for 0 ↔ v transitions and Eq. (4) with different values of a: - - -, a = 0.15; – -, a = 0.25; and · · ·, a = 0.05.

for $0 \leq v \leq v_m$, where $\epsilon_1 = 2330.26$ cm^{-1} and $\Delta\epsilon = 14.66$ cm^{-1}. In this case, 47 excited vibrational levels lie under the dissociation limit (33 for the truncated HO and 65 for the Ref. 9 model).

B. E-V Rate Coefficients

In this study, the influence of dissociation and recombination is neglected, and we consider only vibrational excitation and deexcitation processes by electron impact.[4,5] The E-V excitation rate coefficients $k_{v,w>v}$ (T_e) for $v \rightarrow w > v$ transitions are obtained by numerical integration of the excitation cross sections over a Maxwellian distribution function for the electrons. The associated deexcitation rates are derived using the detailed balance relationships. The vibrational excitation of the nitrogen molecule by electron impact has been studied extensively experimentally and theoretically in the past decades.[10–13] However, only few studies pertain to the accurate determination of absolute integral cross sections that are necessary to determine E-V rate coefficients. For $0 \rightarrow v$ transitions, Huo et al.[10] carried out ab initio calculations of cross sections and tabulated E-V rate coefficients up to $v = 5$ for N_2 rotational quantum numbers of $J = 0$, 50, and 150 and electron temperatures of 0.1–5.0 eV. In previous studies on E-V coupling in nitrogen,[4,8] the rate coefficients given by Huo et al.[10] for $J = 50$ have been used to take into account an average rotational excitation of N_2 in high-enthalpy flows. Measurements of $0 \rightarrow v$ transition cross sections are generally carried out at room temperature and are in fairly good agreement with the calculations from Huo et al. for $J = 0$ (Ref. 13). However, as shown by Fig. 1 for $T_e = 1$ eV, the discrepancy remains small between theoretical rate coefficients given by Huo et al.[10] for $0 \rightarrow v \leq 5$ transitions with $J = 50$ and those calculated using the cross sections measured by Allan.[14] For $0 \rightarrow v > 5$ transitions, Mertens[4] proposed to expand the rate coefficients given by Huo et al.[10] to include all v greater than 5 using a linear curve fit of a semilog plot of k vs v. The circles in Fig. 1 show that the rate coefficients calculated with this technique are much higher than those derived from the cross sections measured by Allan[14] up to $v = 13$.

In the present work, two sets of rate coefficients are used for $0 \rightarrow v$ transitions: the database given by Huo et al.[10] and expanded to higher vibrational levels with the technique proposed by Mertens[4] (denoted set 1 in the following sections) and the set of rate coefficients derived from Allan's measurements[14] up to $v = 13$ and expanded to higher vibrational levels with the technique proposed by Mertens[4] (set 2). For $w \neq 0 \rightarrow v > w$ transitions, no experimental information is available, and the most complete set of rate coefficients is the one calculated by Huo et al.[10] for $J = 50$ and initial vibrational quantum number up to 12 with changes in vibrational quantum numbers of -5 to $+5$. To study the relaxation of the vibrational energy, E-V rate coefficients are required for all transitions. Therefore, Mertens[4] has proposed to extend the database given by Huo et al.[10] for $J = 50$ to include all transitions between vibrational quantum levels 0–50 for $T_e = 0.1$–5 eV. To avoid calculations with a large rate constant database, in this work, following Gordiets et al.,[15] an analytical expression is used to derive $w \neq 0 \rightarrow v > w$ rate coefficients from $0 \rightarrow v$ coefficients. These authors[15] proposed to take into account the decrease of the $w \neq 0 \rightarrow v > w$ transition cross sections as w increases with the following expression:

$$\sigma_{v \neq 0 \rightarrow v+n} = \sigma(0 \rightarrow n)(1 + av)^{-1} \tag{3}$$

The corresponding excitation rate coefficient is

$$k_{v,v+n}(T_e) = \frac{k_{0,n}(T_e)}{1 + av} \tag{4}$$

with $a = 0.05$ (Ref. 15). In the present work, a new value of a is determined using Eq. (4) and the rate coefficients calculated by Huo et al.[10] for $1 \leq n \leq 5$. For $3000 \leq T_e \leq 40{,}000$ K, we have noted that the value of a varies slightly with temperature between 0.05 and 0.25, and in the following sections, most results will be presented for an average value of 0.15. As an example, Fig. 2 shows at $T_e = 1$ eV that the discrepancy between the rate coefficients given by Huo et al.[10] and Eq. (4) with $a = 0.15$ remains small. In the following sections, the influence of the value of a on the results will be discussed.

C. Master Equation

We consider a collection of N_2 molecules that start at $t = 0$ s to interchange energy with an electron heat bath having a constant temperature T_e. The resulting master equation is given by

$$\frac{\mathrm{d}N_v}{\mathrm{d}t} = n_e \sum_{w=0}^{v_m} [k_{w,v}(T_e)N_w - k_{v,w}(T_e)N_v] \tag{5}$$

for $0 \leq v \leq v_m$. Here T_e, n_e, and N_t are considered to be constant.[5] Considering the energy of the vibrational level $w = 0$ as a reference, the vibrational energy of the studied system is

$$E_v = \sum_{w=1}^{v_m} N_w \epsilon(w) \tag{6}$$

Then the rate of change of the vibrational energy is

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = \sum_{w=1}^{v_m} \frac{\mathrm{d}N_w}{\mathrm{d}t} \epsilon(w) \tag{7}$$

In Sec. III we propose to study the analytical solution of Eq. (7) using different oscillator models to determine $\epsilon(w)$ and a set of E-V rate coefficients consisting of given rate coefficients for $0 \leftrightarrow v > 0$ transitions and an analytical expression for other transitions.

III. Analytical Approach

A. Harmonic Case

For an HO, the vibrational energy $\epsilon(w)$ of a level w is proportional to ϵ_1, and then Eq. (7) can be written as

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = n_e\epsilon_1 \sum_{w=1}^{v_m}\left[\sum_{j>w} w k_{j,w} N_j - \sum_{j>w} w k_{w,j} N_w + \sum_{j<w} w k_{j,w} N_j - \sum_{j<w} w k_{w,j} N_w\right] \tag{8}$$

By the use of the analytical expression of $w \neq 0 \leftrightarrow v > w$ rate coefficients as a function of $0 \leftrightarrow v$ ones, this equation becomes

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = n_e\epsilon_1 \sum_{w=1}^{v_m}\left[\sum_{j>w} w \frac{k_{j-w,0}}{1+aw} N_j - \sum_{j>w} w \frac{k_{0,j-w}}{1+aw} N_w + \sum_{j<w} w \frac{k_{0,w-j}}{1+aj} N_j - \sum_{j<w} w \frac{k_{w-j,0}}{1+aj} N_w\right] \tag{9}$$

which simplifies to

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = n_e\epsilon_1 \times \left[\sum_{w=1}^{v_m} w k_{0,w} \sum_{j=0}^{v_m - w} \frac{N_j}{1+aj} - \sum_{w=1}^{v_m} w k_{w,0} \sum_{j=w}^{v_m} \frac{N_j}{1+a(j-w)}\right] \tag{10}$$

The next step requires knowing the vibrational distribution. In Ref. 5, using slightly different E-V rate coefficients, temporal evolutions of vibrational distributions have been studied for different exciting and relaxing conditions. This study[5] has shown that, for conditions where low vibrational levels remained much more populated than high ones, deviations of the vibrational distribution from a Boltzmann distribution have a small influence on the vibrational energy relaxation rate. Therefore, to simplify Eq. (10), we propose to consider that the relaxation proceeds by way of a continuous series of Boltzmann distributions over the vibrational states. In this case, the number density of a vibrational level w is

$$N_w = N_{v=0} \exp\left[-\frac{\epsilon(w)}{k_B T_v(t)}\right] \tag{11}$$

where $T_v(t)$ is an effective vibrational temperature. Then the vibrational energy of the system at a given t is

$$E_v(t) = \epsilon_1 N_t L(T_v) \tag{12}$$

with

$$L(T_v) = \frac{1}{\exp(\epsilon_1/k_B T_v) - 1} - \frac{v_m + 1}{\exp[(v_m+1)\epsilon_1/k_B T_v] - 1} \tag{13}$$

At the final equilibrium, all vibrational levels are in Boltzmann equilibrium at the electron temperature T_e, and then

$$E_v^*(T_e) = \epsilon_1 N_t L(T_e) \tag{14}$$

By the use of Eq. (11), Eq. (10) simplifies to

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = n_e\epsilon_1 N_t \frac{1 - \exp[-(\epsilon_1/k_B T_v)]}{1 - \exp\{-[(v_m+1)\epsilon_1/k_B T_v]\}} \times \sum_{j=1}^{v_m} j k_{0,j}\left\{1 - \exp\left[\frac{j\epsilon_1}{k_B}\left(\frac{1}{T_e} - \frac{1}{T_v}\right)\right]\right\} \times \sum_{w=0}^{v_m - j} \frac{\exp[-(w\epsilon_1/k_B T_v)]}{1+aw} \tag{15}$$

With the expressions of $E_v(t)$ and $E_v^*(T_e)$, Eq. (15) can be easily expressed as a Landau–Teller-type rate equation with a relaxation time denoted $\tau_e^{\mathrm{HO}}(T_e, T_v)$ given by

$$\frac{1}{\tau_e^{\mathrm{HO}}(T_e, T_v)} = \frac{n_e}{L(T_e) - L(T_v)} \frac{1 - \exp[-(\epsilon_1/k_B T_v)]}{1 - \exp\{-[(v_m+1)\epsilon_1/k_B T_v]\}} \times \sum_{j=1}^{v_m} j k_{0,j}\left\{1 - \exp\left[\frac{j\epsilon_1}{k_B}\left(\frac{1}{T_e} - \frac{1}{T_v}\right)\right]\right\} \times \sum_{w=0}^{v_m - j} \frac{\exp[-(w\epsilon_1/k_B T_v)]}{1+aw} \tag{16}$$

In the limit case where $T_v \longrightarrow 0$, the expression of $\tau_e^{\mathrm{HO}}(T_e, T_v)$ simplifies to

$$\frac{1}{\tau_{e,T_v\rightarrow 0}^{\mathrm{HO}}(T_e)} = \frac{n_e}{L(T_e)} \sum_{j=1}^{v_m} j k_{0,j} \tag{17}$$

As expected, the latter expression is independent of the value of a.

B. Anharmonic Case

In this section, to take into account analytically the influence of the anharmonicity of N_2 on the vibrational energy relaxation rate, an MO approximation is used. In this case, the vibrational energy of a level w of N_2 is given by Eq. (2), and then Eq. (7) can be written as

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} = \epsilon_1 \sum_{j=1}^{v_m} j \frac{\mathrm{d}N_j}{\mathrm{d}t} - \Delta\epsilon \sum_{j=1}^{v_m} j(j-1)\frac{\mathrm{d}N_j}{\mathrm{d}t} \tag{18}$$

Using the analytical expression of $w \neq 0 \leftrightarrow v > w$ rate coefficients as a function of $0 \leftrightarrow v$ ones, we find that the two terms on the right-hand side of Eq. (18) become

$$\sum_{j=1}^{v_m} j \frac{\mathrm{d}N_j}{\mathrm{d}t} = \sum_{w=1}^{v_m} w k_{0,w} \sum_{j=0}^{v_m - w} \frac{N_j}{1+ja} - \sum_{w=1}^{v_m} w k_{0,w} \sum_{j=w}^{v_m} \frac{N_j}{1+(j-w)a} \exp\left[\frac{\epsilon(j) - \epsilon(j-w)}{k_B T_e}\right] \tag{19}$$

$$\sum_{j=1}^{v_m} j(j-1) \frac{\mathrm{d}N_j}{\mathrm{d}t} = 2\sum_{w=1}^{v_m} w k_{0,w} \sum_{j=1}^{v_m - w} \frac{jN_j}{1+ja} - 2\sum_{w=1}^{v_m} w k_{0,w} \sum_{j=w}^{v_m} \frac{jN_j}{1+(j-w)a} \exp\left[\frac{\epsilon(j) - \epsilon(j-w)}{k_B T_e}\right] + \sum_{w=1}^{v_m} w(w-1) k_{0,w} \sum_{j=0}^{v_m - w} \frac{N_j}{1+ja} + \sum_{w=1}^{v_m} w(w+1) k_{0,w} \times \sum_{j=w}^{v_m} \frac{N_j}{1+(j-w)a} \exp\left[\frac{\epsilon(j) - \epsilon(j-w)}{k_B T_e}\right] \tag{20}$$

Further simplifications require knowing the shape of the vibrational distribution. By the use of slightly different oscillator models and E-V rate coefficients, temporal evolutions of vibrational distributions have been studied for different exciting[4,5] and relaxing conditions[5] in previous works. For exciting conditions, we have noted in Ref. 5 that there were only slight deviations from the results obtained in the harmonic case close to the final equilibrium. In relaxing conditions,[5] due to anharmonicity, we have observed that high vibrational levels relax much more slowly than low ones. Then high vibrational levels remain overpopulated during the whole relaxation and may have an influence on the relaxation of the vibrational energy at high vibrational excitation temperatures. Neglecting this influence, to simplify Eqs. (19) and (20), we have assumed that the relaxation proceeds by way of a continuous series of Boltzmann distributions over the vibrational states. In this case, the number density of a vibrational level w is given by Eq. (11) and the vibrational energy of the system at a given t is

$$E_v(t) = \frac{N_t G(T_v)}{K(T_v)} \tag{21}$$

where

$$K(T_v) = \sum_{j=0}^{v_m} \exp\left[-\frac{\epsilon(j)}{k_B T_v}\right] \tag{22}$$

$$G(T_v) = \sum_{w=1}^{v_m} w\epsilon_1 \exp\left[-\frac{\epsilon(w)}{k_B T_v}\right]\left[1 - \frac{\Delta\epsilon}{\epsilon_1}(w-1)\right] \tag{23}$$

At the final equilibrium, all vibrational levels are in Boltzmann equilibrium at the electron temperature T_e, and then

$$E_v^*(T_e) = \frac{N_t G(T_e)}{K(T_e)} \tag{24}$$

By the use of Eq. (11) and the expressions of $E_v(t)$ and $E_v^*(T_e)$, the rate of change of the vibrational energy [Eq. (18)] can be expressed as a Landau–Teller-type rate equation with a relaxation time denoted $\tau_e^{\mathrm{MO}}(T_e, T_v)$ and given by

$$\frac{1}{\tau_e^{\mathrm{MO}}(T_e, T_v)} = \frac{n_e[\epsilon_1 T_1(T_e, T_v) - \Delta\epsilon T_2(T_e, T_v)]}{Den(T_e, T_v)} \tag{25}$$

where

$$T_1 = \sum_{w=1}^{v_m} w k_{0,w} \sum_{j=0}^{v_m - w} \frac{(B_j - B_{j+w})}{1 + ja} \exp\left[-\frac{\epsilon(j)}{k_B T_e}\right] \tag{26}$$

$$T_2 = 2\sum_{w=1}^{v_m} w k_{0,w} \sum_{j=1}^{v_m - w} \frac{j}{1 + ja} \exp\left[-\frac{\epsilon(j)}{k_B T_e}\right](B_j - B_{j+w}) \tag{27}$$

$$+ \sum_{w=1}^{v_m} w^2 k_{0,w} \sum_{j=0}^{v_m - w} \exp\left[-\frac{\epsilon(j)}{k_B T_e}\right] \frac{(B_j - B_{j+w})}{1 + ja} \tag{28}$$

$$+ \sum_{w=1}^{v_m} w k_{0,w} \sum_{j=0}^{v_m - w} \exp\left(-\frac{\epsilon(j)}{k_B T_e}\right) \frac{(B_{j+w} - B_j)}{1 + ja} \tag{29}$$

with

$$B_j = \exp\left[\frac{\epsilon(j)}{k_B}\left(\frac{1}{T_e} - \frac{1}{T_v}\right)\right] \tag{30}$$

$$Den = \frac{\sum_{w=1}^{v_m} \sum_{j=0}^{v_m} \epsilon(w) \exp\{-[\epsilon(w) + \epsilon(j)/k_B T_e]\}(B_j - B_w)}{K(T_e)} \tag{31}$$

where $K(T_e)$ is given by Eq. (22). In the limit case where $T_v \rightarrow 0$, Eq. (25) simplifies to

$$\frac{1}{\tau_{e,T_v \rightarrow 0}^{\mathrm{MO}}(T_e)} = \frac{n_e\left[\epsilon_1 \sum_{j=1}^{v_m} j k_{0,j} - \Delta\epsilon \sum_{j=1}^{v_m} j(j-1) k_{0,j}\right] K(T_e)}{G(T_e)} \tag{32}$$

As in the harmonic case, the latter expression is independent of the value of a.

IV. Comparison with Numerical Results

To validate the analytical expressions of the relaxation times derived in the preceding section, we propose to carry out comparisons with the direct numerical integration of the master equation. Further details on the numerical method used may be found in Ref. 5. The vibrational energy and its rate of change are calculated at each time step using Eqs. (6) and (7), respectively. Effective nitrogen vibrational temperatures T_v are determined by comparing the instantaneous value of E_v to the vibrational energy that would result from an equivalent Boltzmann vibrational temperature. The numerically calculated vibrational energy rate of change is compared to the one calculated using Eq. (1), where E_v is derived from numerical calculations and $E_v^*(T_e)$ and $\tau_e(T_e, T_v)$ are calculated analytically using the values of T_e and T_v.

A. Harmonic Case

First, we have considered the classical situation of a shock at $t = 0$ s, with all N_2 molecules populated in the ground state. Figure 3 shows, for example, for $T_e = 30{,}000$ K, the evolution of the normalized vibrational energy relaxation rate

$$\frac{\mathrm{d}E_v^n}{\mathrm{d}t} = \frac{\mathrm{d}E_v}{\mathrm{d}t} \frac{\tau_{e,T_v \rightarrow 0}^{\mathrm{HO}}(T_e)}{\left(E_v^* - E_{v,\mathrm{init}}\right)} \tag{33}$$

as a function of the normalized time

$$t^n = t \Big/ \left[\tau_{e,T_v \rightarrow 0}^{\mathrm{HO}}(T_e)\right] \tag{34}$$

With this normalization, results are independent of n_e and N_t. In Eq. (33), $\mathrm{d}E_v/\mathrm{d}t$ is either derived from the numerical integration of the master equation or calculated with a Landau–Teller-type law and different expressions for the relaxation time. For the E-V rate coefficients, set 2 and Eq. (4) with $a = 0.15$ have been used. As expected, Fig. 3 shows that the use of $\tau_{e,T_v \rightarrow 0}^{\mathrm{HO}}(T_e)$ allows accurate description

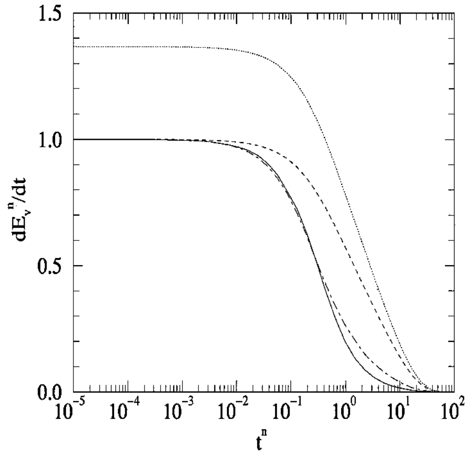

Fig. 3 For a truncated harmonic oscillator, temporal evolution of the normalized vibrational energy relaxation rate for an exciting condition with $T_e = 30{,}000$ K and at $t = 0$ s all N_2 molecules on the ground state: ——, numerical results with set 2 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0.15$; · · ·, Landau–Teller-type rate equation with Lee's relaxation time[8]; – – –, Landau–Teller-type rate equation with $\tau_{e,T_v \rightarrow 0}^{\mathrm{HO}}(T_e)$; and – · –, Landau–Teller-type rate equation with $\tau_e^{\mathrm{HO}}(T_e, T_v)$.

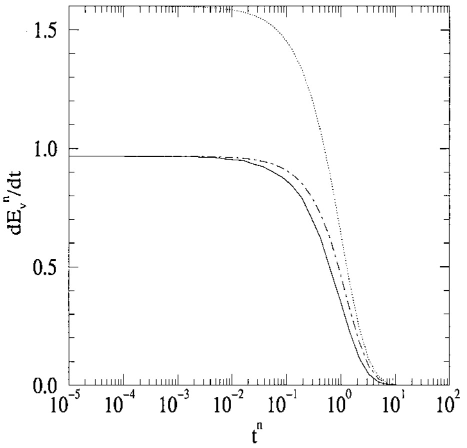

Fig. 4 For a truncated harmonic oscillator, the temporal evolution of the normalized vibrational energy relaxation rate for a relaxing condition with $T_{\text{exci}} = 15{,}000$ K at $t = 0$ s and $T_e = 5000$ K: ——, numerical results with set 2 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0.15$; · · ·, Landau–Teller-type rate equation with Lee's relaxation time[8]; and - -, Landau–Teller-type rate equation with $\tau_e^{\text{HO}}(T_e, T_v)$.

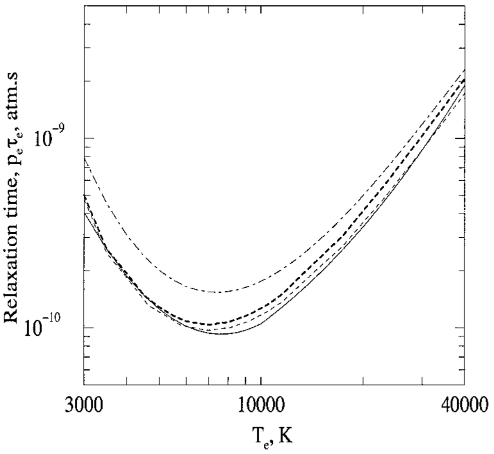

Fig. 5 Variations of $\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ as a function of T_e: ——, $p_e\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ with set 1 for $0 \leftrightarrow v$ transitions; - -, $p_e\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ with set 2 for $0 \leftrightarrow v$ transitions; ——, Lee's model[8]; and - - -, $p_e\tau^{\text{MO}}_{e,T_v\to 0}(T_e)$ with set 1 for $0 \leftrightarrow v$ transitions.

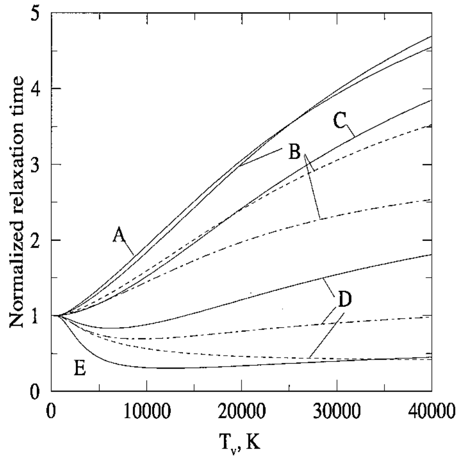

Fig. 6 Variations of $\tau_e^{\text{HO}}(T_e, T_v)/\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ as a function of T_v for different values of T_e: solid lines set 2 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0.15$; A, $T_e = 40{,}000$ K; B, $T_e = 20{,}000$ K; C, $T_e = 10{,}000$ K; D, $T_e = 5000$ K; and E, $T_e = 3000$ K. Other lines are results for $T_e = 20{,}000$ K and $T_e = 5000$ K only; - - -, set 1 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0.15$, and - -, set 2 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0$.

of the vibrational energy rate equation for short times, but overestimates it as the vibrational energy starts to increase. When the more general expression of the relaxation time $\tau_e^{\text{HO}}(T_e, T_v)$ is used, the agreement between the computations and a Landau–Teller-type law is significantly increased. However, because in this case the electron temperature is relatively high, discrepancies are observed close to the final equilibrium where the population of high vibrational levels becomes nonnegligible. Note that this discrepancy remains relatively small up to $T_e = 40{,}000$ K and decreases as the electron temperature decreases. Figure 3 also shows the results obtained with the approximate relaxation time proposed by Lee.[8] This model overestimates up to a factor of four the vibrational energy relaxation rate during the excitation process. Note that we have also obtained a good agreement between computations and a Landau–Teller-type rate equation with $\tau_e^{\text{HO}}(T_e, T_v)$, for exciting conditions with at $t = 0$ s, all vibrational levels in Boltzmann equilibrium at $300\text{ K} \leq T_{\text{exci}} < T_e$ for $3000 \leq T_e \leq 40{,}000$ K.

In previous studies, the validity of E-V models has been mainly tested in exciting conditions.[3,4,8] In relaxing conditions such as encountered in expanding flows, due to the recombination processes into high vibrational states, the vibrational distribution may deviate significantly from a Boltzmann distribution (see Ref. 16). However, as a first step, we have neglected this influence, and we have considered the rate of change of the vibrational energy in relaxing conditions, where at $t = 0$ s, the vibrational distribution is characterized by a vibrational temperature $T_{\text{exci}} > T_e$. Figure 4 shows, for example, the results obtained for $T_{\text{exci}} = 15{,}000$ K and $T_e = 5000$ K with for E-V rate coefficients, set 2, and Eq. (4) with $a = 0.15$. We note that a Landau–Teller-type rate equation with $\tau_e^{\text{HO}}(T_e, T_v)$ slightly overestimates the E-V energy transfer, but is much more accurate than using the approximate relaxation time proposed by Lee.[8] Similar results have been obtained for various other relaxing conditions with $3000 \leq T_{\text{exci}}$, $T_e \leq 40{,}000$ K and $T_{\text{exci}} > T_e$.

All of these comparisons with the direct numerical solution of the master equation validate the analytical expression of the E-V relaxation times derived in Sec. III.A for an HO approximation. In Figs. 5 and 6, we study more in detail the influence of the E-V rate coefficients and of the temperatures on the calculated relaxation times. Figure 5 shows the variations of $\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ as a function of the electron temperature with sets 1 and 2 for $0 \leftrightarrow v$ transition rate coefficients. Note that whatever set is used, the relaxation time is the smallest at 6000–7000 K and increases rapidly on either side of this temperature range. In the whole temperature range studied, the discrepancy between both relaxation times, which is an estimate of the accuracy of E-V relaxation times, is nearly constant and is about a factor of two. Figure 5 shows that the average value proposed by Lee[8] is very close to the relaxation time $\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ calculated with set 1. Figure 6 shows the variations of $\tau_e^{\text{HO}}(T_e, T_v)/\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ calculated with set 2 and Eq. (4) with $a = 0.15$ as a function of T_v for different values of T_e. We note that, depending on the nonequilibrium of the flow, the relaxation time $\tau_e^{\text{HO}}(T_e, T_v)$ may be greater or less than $\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$. The E-V relaxation time increase with increasing electron temperature is not linear, and for $T_e \geq 20{,}000$ K, the ratio $\tau_e^{\text{HO}}(T_e, T_v)/\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$ reaches an upper limit. Note that for the exciting conditions with $T_e \leq 10{,}000$ K, $\tau_e^{\text{HO}}(T_e, T_v)$ remains nearly equal to $\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$. For the exciting conditions with higher electron temperatures, the vibrational relaxation time increases with T_e and T_v and is up to a factor of four greater than $\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$. For the relaxing conditions ($T_v > T_e$), the relaxation time may be either shorter or longer than $\tau^{\text{HO}}_{e,T_v\to 0}(T_e)$. This result was already observed by Bourdon and Vervisch[5] but in the present work, it is put forward analytically. For $T_e = 20{,}000$ and 5000 K, we have also presented the results obtained with set 2 and Eq. (4) with $a = 0$, which corresponds to the situation where $w \neq 0 \to v > w$ transition rate coefficients are equal to $0 \to v - w$ coefficients.[17] In this case, at high T_e and T_v, the relaxation time is less than the one obtained for $a = 0.15$, and the discrepancy decreases with decreasing T_v and T_e. Figure 6 also shows for these two temperatures the evolution of $\tau_e^{\rm HO}(T_e, T_v)/\tau^{\rm HO}_{e,T_v\to 0}(T_e)$ calculated with set 1 and $a = 0.15$. Because of Eq. (4), the choice of the rate coefficients for $0 \to v$ transitions also has an influence on the ratio $\tau_e^{\rm HO}(T_e, T_v)/\tau^{\rm HO}_{e,T_v\to 0}(T_e)$. We note that the discrepancy with the results obtained with set 2 increases with increasing T_v and decreasing electron temperature.

B. Anharmonic Case

To test the validity of an MO approximation to model the E-V energy exchange in N_2, we have compared the vibrational energy relaxation rate computed using an MO with the one computed using the accurate potential given by Dmitrieva et al.[9] In the whole temperature range of our study, $3000 \le T_e, T_v \le 40{,}000$ K, we have observed a maximum discrepancy of ±3%. This result allows, for example, direct comparison of the analytical expression of the relaxation time derived for an MO in this work with those proposed by Mertens[4] for a more accurate anharmonic oscillator model. As in the harmonic case, to validate the analytical expressions of the relaxation times obtained in Sec. III.B, different exciting and relaxing conditions have been studied. Figure 7 presents the evolution of the normalized vibrational energy relaxation rate

$$\frac{\mathrm{d}E_v^n}{\mathrm{d}t} = \frac{\mathrm{d}E_v}{\mathrm{d}t}\,\frac{\tau^{\rm MO}_{e,T_v\to 0}(T_e)}{\left(E_v^* - E_{v,\rm init}\right)} \tag{35}$$

as a function of the normalized time

$$t^n = t\big/\left[\tau^{\rm MO}_{e,T_v\to 0}(T_e)\right] \tag{36}$$

for the same condition as Fig. 3. In this case, for E-V rate coefficients, set 1 and Eq. (4) with $a = 0.15$ is used. As in the harmonic case, at short times, good agreement is obtained with a Landau–Teller-type law and the relaxation time $\tau^{\rm MO}_{e,T_v\to 0}(T_e)$. However, as the vibrational energy increases, this model tends to overestimate the vibrational energy relaxation rate. Better agreement is obtained using the general expression of the relaxation time $\tau_e^{\rm MO}(T_e, T_v)$. Discrepancies close to the final equilibrium are observed only for $T_e > 20{,}000$ K and are due to the contribution of high vibrational level populations. In Fig. 7 we have also presented the results obtained using the polynomial expressions proposed by Mertens[4] for exciting conditions. As expected, with this model we obtain fairly good agreement with computations. The slight discrepancies observed are due to the small differences in the E-V rate coefficients used in the two studies for $v > 0 \leftrightarrow w > v$ transitions. Note that we have also obtained good agreement between computations and a Landau–Teller-type rate equation with $\tau_e^{\rm MO}(T_e, T_v)$ for the exciting conditions with, at $t = 0$ s, all vibrational levels in Boltzmann equilibrium at $300\ {\rm K} \le T_{\rm exci} < T_e$ for $3000 \le T_e \le 40{,}000$ K.

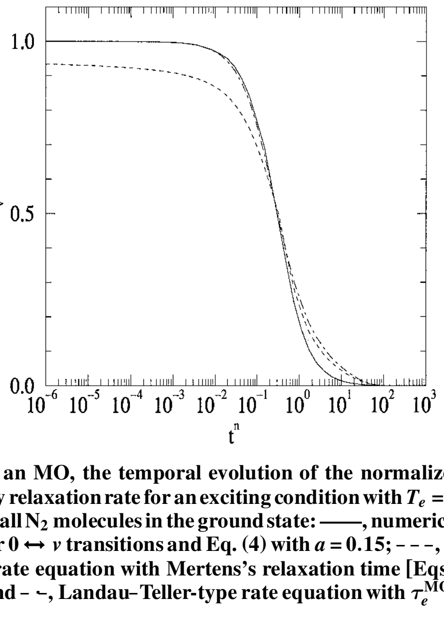

Fig. 7 For an MO, the temporal evolution of the normalized vibrational energy relaxation rate for an exciting condition with T_e = 30,000 K and at t = 0 s all N_2 molecules in the ground state: ——, numerical results with set 1 for 0 ↔ v transitions and Eq. (4) with a = 0.15; - - -, Landau–Teller-type rate equation with Mertens's relaxation time [Eqs. (11–14) in Ref. 4]; and - -, Landau–Teller-type rate equation with $\tau_e^{\rm MO}(T_e, T_v)$.

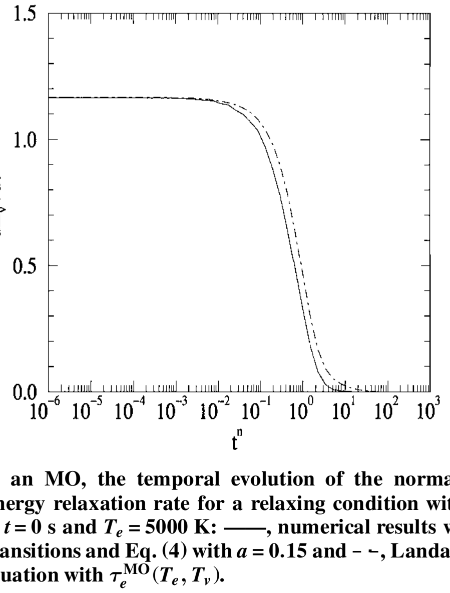

Fig. 8 For an MO, the temporal evolution of the normalized vibrational energy relaxation rate for a relaxing condition with $T_{\rm exci}$ = 15,000 K at t = 0 s and T_e = 5000 K: ——, numerical results with set 1 for 0 ↔ v transitions and Eq. (4) with a = 0.15 and - -, Landau–Teller-type rate equation with $\tau_e^{\rm MO}(T_e, T_v)$.

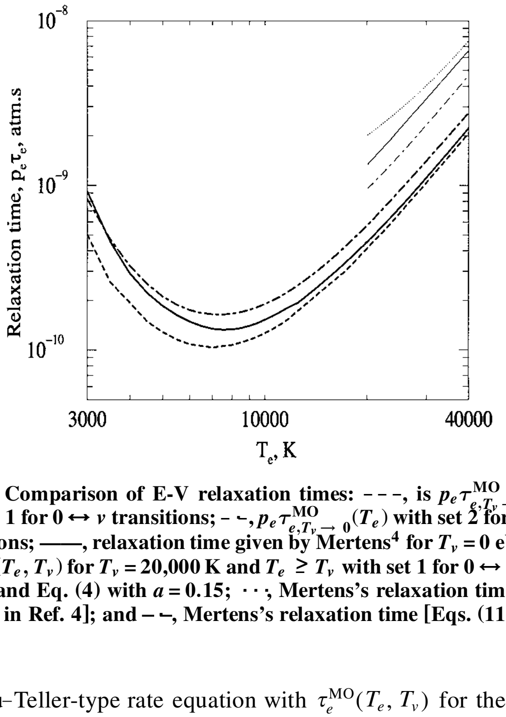

Fig. 9 Comparison of E-V relaxation times: - - -, is $p_e\tau^{\rm MO}_{e,T_v\to 0}(T_e)$ with set 1 for 0 ↔ v transitions; - -, $p_e\tau^{\rm MO}_{e,T_v\to 0}(T_e)$ with set 2 for 0 ↔ v transitions; ——, relaxation time given by Mertens[4] for T_v = 0 eV; ——, $p_e\tau_e^{\rm MO}(T_e, T_v)$ for T_v = 20,000 K and $T_e \ge T_v$ with set 1 for 0 ↔ v transitions and Eq. (4) with a = 0.15; · · ·, Mertens's relaxation time [Eqs. (11–14) in Ref. 4]; and – -, Mertens's relaxation time [Eqs. (11–13) in Ref. 4].

As in the harmonic case, we have also carried out comparisons for different simplified relaxing conditions, where at $t = 0$ s the vibrational distribution is characterized by a vibrational temperature $T_{\rm exci} > T_e$. As shown in one example in Fig. 8, we have observed that the use of a Landau–Teller-type equation with $\tau_e^{\rm MO}(T_e, T_v)$ allows an accurate description of the vibrational energy relaxation rate for relaxing conditions with $3000 \le T_e \le 40{,}000$ K and $T_e < T_{\rm exci} \le 40{,}000$ K. To study more in detail the influence of the anharmonicity on the calculated relaxation time, we have presented $\tau^{\rm MO}_{e,T_v\to 0}(T_e)$ calculated with set 1 in Fig. 5. As expected, we note that anharmonicity effects have only a small influence on relaxation times at high electron temperatures. Figure 9 shows the variation of $\tau^{\rm MO}_{e,T_v\to 0}(T_e)$ as a function of T_e for sets 1 and 2. We note that the discrepancy between both relaxation times remains nearly the same as in the harmonic case. The relaxation time proposed by Mertens[4] for $T_v = 0$ eV is in good agreement with our results with set 1 at high temperatures and is much closer to the results obtained using set 2 at low electron temperatures. To compare our results with Mertens,[4] we have presented the relaxation time $\tau_e^{\rm MO}(T_e, T_v)$ calculated for

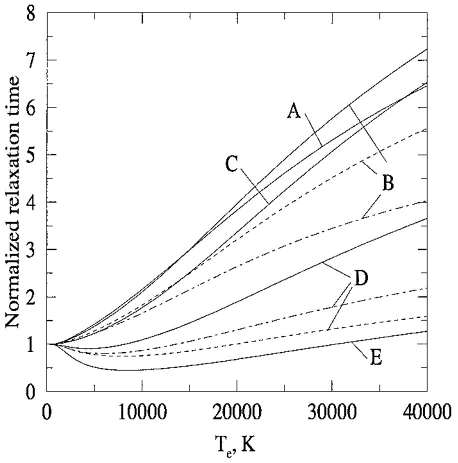

Fig. 10 Variations of $\tau_e^{\mathrm{MO}}(T_e, T_v)/\tau_{e,T_v\to 0}^{\mathrm{MO}}(T_e)$ as a function of T_v for different values of T_e: ——, set 2 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0.15$; A, $T_e = 40{,}000$ K; B, $T_e = 20{,}000$ K; C, $T_e = 10{,}000$ K; D, $T_e = 5000$ K; and E, $T_e = 3000$ K. Other lines are results for $T_e = 20{,}000$ K and $T_e = 5000$ K only; - - -, set 1 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0.15$ and - -, set 2 for $0 \leftrightarrow v$ transitions and Eq. (4) with $a = 0$.

the exciting conditions with $T_v = 20{,}000 \leq T_e \leq 40{,}000$ K. In agreement with Mertens,[4] the relaxation time is shown to increase at high vibrational temperatures in the exciting conditions. We note that our model is very close to the two sets given by Mertens. Similar results have been obtained for other exciting conditions with $2000 \leq T_v \leq 40{,}000$ K and $T_v \leq T_e$. Figure 10 is the same as Fig. 6 in the anharmonic case. In comparison to Fig. 6, we note that the relaxation time increases slightly more rapidly with T_v at high T_e than in the harmonic case. However, the discrepancy between the relaxation times obtained in the harmonic and anharmonic case remains small. The influence of the value of a and the choice between sets 1 and 2 is also shown in Fig. 10 and is very similar to the harmonic case. In the harmonic and anharmonic cases, the tests of the influence of the E-V rate coefficients have shown that the accuracy of the derived relaxation time is only of a factor of two. Therefore, further studies on the determination of E-V rate coefficients, in particular for $w \neq 0 \leftrightarrow v > w$ transitions, would be of great interest to improve the accuracy of the E-V relaxation times. In the anharmonic case, the expression of the relaxation time [Eq. (25)] is more intricate than in the harmonic case [Eq. (16)] and, therefore, requires more computation time. However, for a given set of $0 \leftrightarrow v$ transition rate coefficients and a value of a, the relaxation time can be tabulated easily for the electron and vibrational temperature range of interest before the computation of the flow. For the exciting conditions, we recommend the use of the polynomial equations given by Mertens, which are easy to implement directly in flow codes.

V. Conclusions

In this work, a Landau–Teller-type model for the E-V coupling in nitrogen is derived. In agreement with the most recent studies on absolute integral E-V cross sections, the database used in this work is made up of given rate coefficients for $0 \leftrightarrow v > 0$ transitions and an analytical expression for other transitions. Note that the method proposed can be easily adapted to take into account a more complex analytical expression of $v \neq 0 \leftrightarrow w > v$ transition rate coefficients. By the considering of harmonic and anharmonic oscillator models, analytical expressions of relaxation times are presented assuming that the relaxation proceeds by way of a continuous series of Boltzmann distributions over the vibrational states. This model has been validated by comparisons with the direct numerical integration of the master equation for vibrational level populations for various conditions encountered in high-enthalpy flows with electron and vibrational temperatures up to 40,000 K. Note that this model can be used to model accurately the E-V energy transfer even in situations where the vibrational distribution deviates from a Boltzmann distribution. In exciting conditions, the E-V relaxation time derived in this study for an MO is in good agreement with the recent results obtained by Mertens.[4] For the exciting conditions, to model the E-V coupling in flow codes, it is recommended to use the polynomial equations proposed by Mertens.[4] In this work, an attempt to model the E-V coupling in relaxing flows is also presented. The simplified case where, at $t = 0$ s, the vibrational distribution is characterized by a vibrational temperature $T_{\mathrm{exci}} > T_e$ has been studied. Further work in this direction should take into account a more realistic shape of the vibrational distribution in relaxing conditions.

Acknowledgment

The authors are grateful to Michael Allan for providing us his data files of experimental electron-vibration cross sections.

References

[1] Bourdon, A., Leroux, A., Domingo, P., and Vervisch, P., "Experiment–Modeling Comparison in a Nonequilibrium Supersonic Air Nozzle Flow," *Journal of Thermophysics and Heat Transfer*, Vol. 13, No. 1, 1999, pp. 68–75.

[2] Knab, O., Frühauf, H. H., and Messerschmid, E. W., "URANUS/CVCV-Model Validation by Means of Thermo-Chemical Nonequilibrium Nozzle Airflow Calculations," *Proceedings of the Second European Symposium on Aerothermodynamics for Space Vehicles*, SP-367, ESA Publication Div., Noordwijk, The Netherlands, 1994, pp. 129–134.

[3] Hansen, C., "Vibrational Relaxation in Very High Temperature Nitrogen," AIAA Paper 91-0465, Jan. 1991.

[4] Mertens, J. D., "Computational Model of Nitrogen Vibrational Relaxation by Electron Collisions," *Journal of Thermophysics and Heat Transfer*, Vol. 13, No. 2, 1999, pp. 204–209.

[5] Bourdon, A., and Vervisch, P., "Electron-Vibration Energy Exchange Models in Nitrogen Plasma Flows," *Physical Review E*, Vol. 55, No. 4, 1997, pp. 4634–4641.

[6] Lee, J. H., "Basic Governing Equations for the Flight Regimes of Aeroassisted Orbital Transfer Vehicles," *Thermal Design of Aeroassisted Orbital Transfer Vehicles*, edited by H. F. Nelson, Vol. 96, Progress in Astronautics and Aeronautics, AIAA, New York, 1985, pp. 3–53.

[7] Lee, J. H., "Electron-Impact Vibrational Excitation Rates in the Flowfield of Aeroassisted Orbital Transfer Vehicles," *Thermochemical Aspects of Re-entry Flows*, edited by J. N. Moss and C. D. Scott, Vol. 103, Progress in Astronautics and Aeronautics, AIAA, New York, 1986, pp. 197–224.

[8] Lee, J. H., "Electron-Impact Vibrational Relaxation in High-Temperature Nitrogen," AIAA Paper 92-0807, Jan. 1992.

[9] Dmitrieva, I. K., Pogrebnya, S. K., and Porshnev, P. I., "V-T and V-V Rate Constants for Energy Transfer in Diatomics. An Accurate Analytical Approximation," *Chemical Physics*, Vol. 142, No. 1, 1990, pp. 25–33.

[10] Huo, W. M., McKoy, V., Lima, M. A. P., and Gibson, T. L., "Electron-Nitrogen Molecule Collisions in High Temperature Nonequilibrium Air," *Thermochemical Aspects of Re-entry Flows*, edited by J. N. Moss and C. D. Scott, Vol. 103, Progress in Astronautics and Aeronautics, AIAA, New York, 1986, pp. 152–196.

[11] Brennan, M. J., Alle, D. T., Euripides, P., Buckman, S. J., and Brunger, M. J., "Elastic Electron Scattering and Rovibrational Excitation of N_2 at Low Incident Energies," *Journal of Physics B: Atomic, Molecular and Optical Physics*, Vol. 25, No. 11, 1992, pp. 2669–2682.

[12] Vićić, M., Poparić, G., and Belić, D. S., "Large Vibrational Excitation of N_2 by Low-Energy Electrons," *Journal of Physics B: Atomic, Molecular and Optical Physics*, Vol. 29, No. 6, 1996, pp. 1273–1281.

[13] Huo, W. M., and Thümmel, H. T., "Electron–Air Molecule Collisions in Hypersonic Flows," *Molecular Physics and Hypersonic Flows*, edited by M. Capitelli, Vol. 482, Kluwer, Dordrecht, The Netherlands, 1996, pp. 115–137.

[14] Allan, M., "Excitation of Vibrational Levels up to $v = 17$ in N_2 by Electron Impact in the 0–5 eV Region," *Journal of Physics B: Atomic, Molecular and Optical Physics*, Vol. 18, No. 22, 1985, pp. 4511–4517.

[15] Gordiets, B. F., Ferreira, C. M., Guerra, V. L., Loureiro, J. M. A. H., Nahorny, J., Pagnon, D., Touzeau, M., and Vialle, M., "Kinetic Model of a Low-Pressure N_2–O_2 Flowing Glow Discharge," *IEEE Transactions on Plasma Science*, Vol. 23, No. 4, 1995, pp. 750–768.

[16] Colonna, G., and Capitelli, M., "Electron and Vibrational Kinetics in the Boundary Layer of Hypersonic Flow," *Journal of Thermophysics and Heat Transfer*, Vol. 10, No. 2, 1996, pp. 406–412.

[17] Capitelli, M., and Dilonardo, M., "Non-Equilibrium Dissociation of Nitrogen," *Revue de Physique Appliquée*, Vol. 13, 1978, pp. 115–123.