Vibrational Population Depletion in Thermal Dissociation for Nonequilibrium Energy Distribution

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Abstract. The generalized depletion equations, considering state-to-state kinetics of dissociating Nitrogen, are solved to predict the extent of vibrational depletion in the temperature range of 3000-10000 K. For the case of dissociation from the last vibrational quantum level, depletion of vibrational population is high. Vibration-translation (V-T) energy transfers make a major contribution to depletion whereas the effect of vibration-vibration (V-V) exchanges is minor. The dissociation rates predicted using the vibration-dissociation coupling model are significantly lower than the Park’s rates and helps explain the restricted success of the Park’s dissociation model in certain temperature ranges of hypersonic flow past a blunt body. Underprediction of shock-standoff distance of 17% by Park dissociation model for a Mach 11.18 flow past a blunt body is predicted well by the present model.

INTRODUCTION

The study of vibrational relaxation of diatomic molecules is fundamental to the evaluation of the kinetic properties of high temperature air associated with hypersonic flowfields [1, 2, 3]. Such studies are important not only for understanding the vibrational nonequilibrium process itself but also allow us to appropriately treat the strong coupling of vibrational relaxation with other processes in hypersonic flows: dissociation, ionization and radiation. The kinetics of thermal dissociation has long been a topic of theoretical research due to the difficulty of reconciling the measured rates within the framework of the flowfield. The theories are mainly involved with depletion effects from the upper vibrational levels, possible effects of rotational energy on the dissociation mechanism and how these aspects are related to the low activation energies.

Early attempts to model the vibration-dissociation coupling known as the CVD model by Hammerling, et al. [4] used a simple harmonic oscillator assumption of the vibrational energy relaxing in the quantum states through a series of Boltzmann distributions corresponding to a first level vibrational temperature. Thus the nonequilibrium dissociation rate was the equilibrium rate multiplied by a “factor” to account for the nonequilibrium distribution of the vibrational level populations. The coupled vibration-dissociation (CVD) model of Treanor and Marrone [5] extended the CVD model to account for the removal of vibrational energy by dissociation. Their analysis favored the weak bias mechanism to account for the incubation time that exists behind the shock front. Marrone and Treanor [6] introduced an additional factor in the CVDV model to make the probability of dissociation an increasing function of the vibrational quantum number. This preferentially weighted the dissociation from the upper vibrational levels.

Based partly on these studies, an empirical two-temperature vibration-dissociation model was proposed by Park [7]. Its ease of implementation in numerical codes and good agreement with experimental data for radiative energy flux [8] made the model very popular for vibration-dissociation coupling in hypersonic aerodynamic flows. In some recent studies, however, the treatment of vibration-dissociation coupling using Park’s two-temperature dissociation model yielded up to 20% lower shock-standoff distances compared to data for blunt body flows (see Refs. [9, 10]) in the Mach number range of 11-16. The physics of vibration-dissociation coupling has important implications in the accurate prediction of aerodynamic heating and drag on hypersonic vehicles and thrust in propulsive nozzles.

In the upper vibrational quantum levels, the vibration-translation (V-T) processes dominate the energy transfer. Dissociation is a reactive process with an activation energy typically over an order of magnitude greater than the energy associated with V-T exchange. Non-reactive kinetic processes tend to bring about an equilibrium distribution in the vibrational manifold, whereas, the dissociation process perturbs it [11]. The vibration-vibration (V-V) processes can
play an important role by accelerating the reaction rates. [12]. In the work of Josyula and Bailey [13], the generalized
depletion equations, considering the state-to-state kinetics of dissociating Nitrogen, were solved to predict the extent
of population depletion in the vibrational manifold. The present paper presents an generalized vibrational population
depletion analysis to include effects of V-V transfers in a dissociating medium. Vibrational-dissociation coupling is
investigated with an experimentally consistent set of V-V, V-T and dissociation rate coefficients. A sample calculation
of the shock-standoff distance for a blunt body is compared to experimental data to demonstrate the improvement of
the present model over the Park two-temperature dissociation model.

GOVERNING EQUATIONS

The global conservation equations in mass-averaged velocity form to simulate a blunt body flow are presented in this
section. The inviscid Euler equations were used to assess a new vibration-dissociation coupling model by simulating
experimental flow conditions in the continuum regime. The models used to simulate the V-T and V-V processes and
the generalized depletion analysis for dissociating flows are then discussed. The depletion analysis and the vibration-
dissociation coupling model can be used in rarefied gas dynamic codes, as well.

\[
\frac{\partial}{\partial t} (\rho_n) + \nabla \cdot (\rho_n \mathbf{u}) = 0 \quad n=0,1,... \quad (1)
\]

\[
\frac{\partial}{\partial t} (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \mathbf{u} - \rho \mathbf{u}) = 0 \quad (2)
\]

\[
\frac{\partial}{\partial t} (\rho e) + \nabla \cdot \rho (e + p/\rho) \mathbf{u} = 0 \quad (3)
\]

Eqns. 1 to 3 describe the conservation of mass, momentum and energy in the flowfields of interest. Eqn. 1 is discussed
further in the following section. Eqn. 2 and 3 represent the conservation of total momentum and energy, respectively.
A microscopic kinetic approach was taken by treating the molecule as anharmonic oscillator, calculating the state
populations using the master equations. In the treatment of vibrational energy for the diatomic species in the master
equation code, a separate vibrational conservation equation is not necessary as the vibrational energy can be calculated
for each quantum level.

Anharmonic Oscillator (ANO)

The conservation Eqn. 1 is written for the mass density in quantum level \( n \). The source term \( \omega_n \) derived from the
vibrational master equations is made up of the relevant energy exchange processes consisting of the V-T, V-V and
dissociation processes. The mass density of the molecular species is the sum of the corresponding state densities in the
vibrational levels.

\[
\rho = \sum_{n=0}^{n_0} \rho_n \quad (4)
\]

The symbolic equations governing the V-T transitions responsible for the variation of the particles distributed in the
\( n^{th} \) vibrational level are:

\[
N_2(n) + N_2 \leftrightarrow N_2(n') + N_2 \quad (5)
\]

the equations governing the V-V process are:

\[
N_2(n) + N_2(m) \leftrightarrow N_2(n') + N_2(m') \quad (6)
\]

and the equations governing the dissociation process are:

\[
N_2(m_0) + N_2 \rightarrow 2N + N_2 \quad (7)
\]
The kinetics of the particle exchanges among the quantum states are simulated using the vibrational master equations, the population distributions are calculated with [14]:

\[
\omega_n = \frac{1}{M} \left\{ \sum_{n'} |k_{VT}(n' \rightarrow n)| \rho_{n'} - k_{VT}(n \rightarrow n') \rho_n \right\} + \sum_{m,m'} |r_{VT}(n,m' \rightarrow n,m)| \rho_m \rho_{m'} - r_{VT}(n,m \rightarrow n',m') \rho_n \rho_m \right\}
\]

(8)

In the present calculations, the exchanges are restricted to single quantum transitions. The V-T process is associated with the rate coefficient \( k_{VT} \) where the molecule loses or gains a vibrational quantum. The de-excitation rate from \( n' \) to \( n \) for colliding molecules is denoted by \( k_{VT}(n' \rightarrow n) \), the inverse collision from \( n \rightarrow n' \) by \( k_{VT}(n \rightarrow n') \). On the other hand, when considering V-V exchanges, the initial and final vibrational states of each collision partner must be identified; thus the transition rate from \( n' \) to \( n \) and \( m' \) to \( m \) is given by \( r_{VV}(n',m' \rightarrow n,m) \). Consistency of the rate coefficient with the principle of detailed balance is enforced.

Rate coefficients for the V-T and V-V transitions were used in earlier studies of Refs. [14] and [15]: (a) V-T de-excitation rate coefficients calculated according to expressions proposed by Capitelli, et al. [16] and Billing and Fisher [17] and (b) V-V transfer rates by Doroshenko, et al. [18]. The vibrational energy of the diatomic molecules N\(_2\), treated as anharmonic oscillators, is given in terms of the quantum level energies by,

\[
e_{\text{vib}} = \sum_{n=0}^{\infty} \frac{\rho_{\text{n}}}{\rho} e_n
\]

(9)

where the index \( n \) enumerates the vibrational quantum level. In this equation, \( \rho_{\text{n}}/\rho \) is the fractional population of the \( n^\text{th} \) vibrational level and \( e_n \) the quantum level energy given by the third-order approximating formula:

\[
\frac{e_i}{hc} = \omega_i(i - \frac{1}{2}) - \omega_{i+1}i(i - \frac{1}{2})^2 + \omega_{i+2}(i - \frac{1}{2})^3 \quad i=1,2,\ldots
\]

(10)

where \( h \) is the Planck’s constant and \( c \) is the speed of light. Here, \( \varepsilon_1 \) denotes ground state vibrational energy, \( \varepsilon_2 \) denotes first excited state, and so on. The spectroscopic constants are given by [19], \( \omega_e=2358.57 \text{ cm}^{-1} \), \( \omega_{e+1}=14.324 \text{ cm}^{-1} \), and \( \omega_{e+2}=-0.00226 \text{ cm}^{-1} \). When \( n_0=47 \), the value of energy exceeds the \( N_2 \) dissociation energy, 9.86 eV.

### Dissociation Kinetics

The vibration-dissociation coupling model presented in the earlier study [10, 20] is solved in its generalized form [13] in the present paper. The analysis introduces a parameter, \( \varphi \), to characterize the deviation of the perturbed quasisteady distribution from an equilibrium Boltzmann distribution. That is, if the equilibrium distribution is denoted by \( \rho_{\text{n}}^{\text{eq}} \) and the quasisteady distribution by \( \rho_{\text{n}}(t) \), then \( \rho_{\text{n}}(t) = \rho_{\text{n}}^{\text{eq}} (1 + \varphi_{\text{n}}) \). It is seen that when \( \varphi < 0 \), the level population decreases relative to the equilibrium population. The generalized vibration-dissociation coupling model with the parameter \( \varphi \) is discussed in the following section.

### Generalized Depletion Equations for V-T and V-V Systems

This section presents the kinetic equations describing the dissociative-relaxation coupling considering the balance equations for the numbers of particles in each vibrational level. The equilibrium value of the total dissociation rate was taken from Park [21]. The approach, in an approximate form, is outlined in Refs. [11, 12]. The rate equation for change in vibrational population accounting for V-T and V-V transfers with dissociation is given by,

\[
\frac{d\rho_j}{dt} = \frac{d\rho_j^{\text{eq}}}{dt} \left\{ 1 + \varphi_j(t) \right\} + \rho_j(t) \dot{\varphi}_j(t) = \gamma_j \nu (1 + \varphi_j)
\]

(12)
Following Osipov and Stupochenko [11, 12],
\[
\frac{dp}{dt} = v = -\sum_{i=0}^{m} \left( k_{d,i} \rho_i \right)
\]  
(13)

Here \( \rho_j \) is the mass density associated with the vibrational population in state \( j \). The superscript “0” denotes equilibrium conditions. In Eqn. 11, \( k_{j+1,j} \) is the V-T rate coefficient for vibrational transitions to occur from \( j + 1 \rightarrow j \). The variables \( n_{j+1,j}^{n+1} \) and \( n_{j+1,j}^{-j} \) are the V-V rate coefficients for vibrational exchanges between two molecules from/with \( j + 1 \rightarrow j \), \( n \rightarrow n + 1 \). The rate constant for dissociation from vibrational state \( j \) is \( k_{d,j} \). Note that \( \sum_{n=0}^{m} \rho_n = \rho \).

The V-T terms may be re-grouped and the populations written in terms of \( \varphi_j \) and the equilibrium population resulting in:
\[
k_{j+1,j}\rho_{j+1}\rho - k_{j,j+1}\rho_j\rho - k_{j-1,j}\rho_j\rho + k_{j-1,j}\rho_j\rho \{ (\varphi_{j+1} - \varphi_j) \} - k_{j-1,j}\rho_j\rho (\varphi_j - \varphi_{j-1})
\]  
(14)

Similarly the V-V terms, in Eqn. 11, may be grouped and recast in a form convenient for the depletion analysis:
\[
\sum_{n=0}^{m-1} \left\{ r_{j+1,j}^{n+1} \rho_{j+1}^{n+1} \rho_{n+1}^{n+1} [(1 + \varphi_{j+1})(1 + \varphi_n) - (1 + \varphi_j)(1 + \varphi_{n+1})] - \right\}
\]  
(15)

Collecting the V-V and V-T terms, the rate equation can now be re-assembled and expressed in terms of the equilibrium population and state depletion factor, \( \varphi_j \):
\[
\gamma_j v (1 + \varphi_j) = k_{j+1,j} \rho_j^{n+1} \rho \left\{ \frac{\gamma_j}{\gamma_j} (\varphi_{j+1} - \varphi_j) \right\} - k_{j-1,j} \rho_j^{n+1} \rho (\varphi_j - \varphi_{j-1}) + \sum_{n=0}^{m-1} \left\{ r_{j+1,j}^{n+1} \rho_{j+1}^{n+1} \rho_{n+1}^{n+1} [(1 + \varphi_{j+1})(1 + \varphi_n) - (1 + \varphi_j)(1 + \varphi_{n+1})] - v\right\}
\]  
(16)

These cascade equations can be combined to relate \( \varphi_{j+1} \) to \( \varphi_j \). Relating the factors of \( \varphi_j \) and \( \varphi_{j+1} \):
\[
\varphi_j (1 + \sum_{n=0}^{m-1} \left\{ r_{j+1,j}^{n+1} \rho_{j+1}^{n+1} \rho_{n+1}^{n+1} (1 + \varphi_n) \right\}) = \varphi_j + \sum_{n=0}^{m-1} \left\{ r_{j+1,j}^{n+1} \rho_{j+1}^{n+1} \rho_{n+1}^{n+1} (\varphi_{n+1} - \varphi_n) \right\} + \]
\[
\varphi_j \sum_{n=0}^{m-1} \left\{ r_{j+1,j}^{n+1} \rho_{j+1}^{n+1} \rho_{n+1}^{n+1} (1 + \varphi_{n+1}) \right\} = \frac{D_j}{k_{j+1,j} \rho_{j+1}^{n+1} \rho}
\]  
(17)

where we have used:
\[
v = -\sum_{j=0}^{m} k_{d,j} \gamma (1 + \varphi_j)
\]  
(18)

and defined
\[
D_j = -\sum_{j=0}^{m} \left\{ \sum_{n=0}^{m} k_{d,n} \gamma (1 + \varphi_n) \right\} - k_{d,j} \gamma (1 + \varphi_j)
\]  
(19)

The coupled rate equations, Eqn. 17 was linearized and an iterative solution achieved. The solution was validated against a solution of the Master Equations. Deviations of the two solutions of less than 2% were achieved over the temperature range of 3000 to 10,000 K. Figure 1a shows the term \( 1 + \varphi \) and its inverse which gives the dissociation reduction factor from Park’s equilibrium rates plotted as a function of temperature. Note that when \( \varphi < 0 \), the effect is to deplete the population in the vibrational states. The reduction factor, \( \frac{1}{1+\varphi} \), is the ratio of the level population distribution at equilibrium to the nonequilibrium state. The reduction factor which accounts for the deviation from the quasi-steady state distribution can range from 1 to 3 orders of magnitude between the temperatures of 5,000 K to 10,000 K at which there is considerable nitrogen dissociation. This factor was applied as a correction to the Park’s dissociation rates to account for the depletion effects in the vibrational levels. Although the reduction factor is the highest below 2,000 K there is negligible nitrogen dissociation at this temperature. The reduction factor again peaks at about 6,000 K and remains large till 12,000 K, a region of significant nitrogen dissociation, and then decreases.
approaching a factor of 1 at the highest temperature of 15,000 K shown in the Figure 1a. This behavior helps in explaining the validity of Park’s rates only in certain temperature ranges.

The depleted vibrational state populations in N₂ resulting from the ladder climbing dissociation model with the dissociation loss to the continuum restricted to the last discrete vibrational level, are presented in Figure 1b. The ratio of state density variation is shown only for certain representative temperatures for clarity. The population density, shown as a factor of the equilibrium population undergoes a reduction in the highly excited vibrational states. The loss is significant in the upper levels shown for the temperatures between 3,000 K and 6,000 K. At higher temperatures, the depletion extends to lower levels also as can be seen for 11,000 K where the depletion occurs in the level range of 10 to 45. Above 11,000 K, however, the reduction in the vibrational level population diminishes and at the highest temperature of 14,000 K, the reduction is small. The varying loss in quantum level vibrational population at different temperatures was discussed earlier in Figure 1a.

In high temperature hypersonic blunt body flows or expansion nozzles, the process of dissociation influences flow characteristics and alters chemistry and relaxation times. The nonequilibrium dissociation rate can differ substantially from the equilibrium rate. The extent of this departure is determined by a complex interplay of the relative values of
the energy transfer rates, V-V and V-T, the dissociation rate and vibrational bias of the dissociation reaction. Here, using the generalized depletion analysis, we analyzed the role of V-T transfer and V-V exchange in nonequilibrium dissociation of Nitrogen using the standard “ladder model” of dissociation. Fig. 2 for Nitrogen at 4000 K. The rate (cm$^3$/s) of the V-V and V-T rates are presented in Figs. 2 at 4000 K. The V-T rate corresponds to $j + 1 \rightarrow j$ and increases monotonically with the quantum level vibrational energy. Two relevant V-V exchanges are presented, both weighted by the relative equilibrium population of the vibrational state of the collision partner: (1) the weighted V-V exchange with the ground state increases with quantum level vibrational energy and then decreases due to increasing disparity of the energy being exchanged, (2) population-weighted resonant exchange increases with vibrational quantum number initially and then decreases due to the reduced population associated with the excited state of the collision partner.

Also, shown is the equilibrium dissociation rate. This is the value required to support the equilibrium dissociation rate from a single, given vibrational state. In the “ladder model” the state of interest is the last bound vibrational state. For a given set of V-V and V-T transition rates, the relative kinetic importance of the V-V terms, $j, n$, the V-T term, $k, j+1, j$, and the dissociation term, $D_j$, appearing in Eqn. 17 can be assessed. It can be concluded that for Nitrogen at these temperatures, the dissociation probability for the last state is high relative to both the weighted V-V and V-T rates and that V-T is more important than V-V. Regarding depletion of the dissociating state, one would anticipate that depletion will be significant because the dissociation rate exceeds the V-T rate considerably. Since the V-T probabilities are higher than those of weighted V-V energy transfers, the effect of V-V on the population depletion is negligible.

**Conditions of Numerical Simulation**

A set of dissociation rates based on the present vibration-dissociation coupling model was used in the prediction of shock-standoff distance for a Mach 11.18 air flow past a blunt body. The blunt body air flow was chosen, particularly because of the inability of the Park two-temperature dissociation model to predict the shock-standoff distance correctly [9, 10]. Since the maximum temperature behind the shock wave is less than 7,000 K at which the dissociation of Oxygen is high, the dissociation rates obtained by applying the vibration-dissociation coupling model to the Oxygen molecule [20] was used in the present study. The numerical algorithm employed to solve the coupled set of equations is the Roe Flux Difference method described in Ref. [14]. Convergence to a steady state solution was monitored by the $L_2$ Norm.

The upstream and farfield boundary conditions were prescribed as the undisturbed freestream values. At the downstream boundary, the no-change condition is imposed for the predominantly supersonic flowfield. On the body surface, $n \cdot \mathbf{u}$ is zero, where $n$ is the surface normal vector. The finite volume formulation of the present work allows fluxes at the singular line of symmetry to be set to zero because the control surface of the elementary cell at the axis of symmetry merges to a point.

The population densities were set to values corresponding to a Boltzmann distribution at the temperature $T_{V\infty}$ on the first $i$ levels of the spectrum produced by Eqn. 10. See Table 1 for the freestream flow conditions.

Initial conditions were set to freestream uniform flow conditions for the vibrational heating cases. Other cases were started from these converged solutions.

**RESULTS AND CONCLUSIONS**

A shock-standoff distance comparison of the experimental data and computational predictions is shown in Fig. 3. The computations without depletion effects are presented here for comparison and were discussed in an earlier paper [10]. The trace corresponding to the idealized conditions of equilibrium and $\gamma = 7/5$ are also presented for reference. The shock-standoff distances at velocities less than 3000 m/s are close to frozen flow conditions and the predictions using existing vibration-dissociation models without depletion effects are close to those with depletion effects. Hence, the computational results with depletion effects are not shown in the figure for velocities less than 3000 m/s. However
at higher flow velocities, the departure of the computation from data is about 17% due to faster dissociation rates predicted by the Park two-temperature dissociation model. The present computation which includes the depletion effects and a consequent reduction in the dissociation rate predicts a shock-standoff distance very close to data, Fig. 3.

In conclusion, the present study presents a generalized depletion analysis of vibration-translation (V-T) and vibration-vibration (V-V) systems and a new vibration-dissociation coupling model. The model finds use in nonequilibrium hypersonic dissociating flows of aerospace vehicles. The new model lowers Park’s dissociation rates and helps demonstrate the limited applicability of Park’s dissociation model in certain temperature ranges of hypersonic flow past a blunt body.

**NOMENCLATURE**

ANO  Anharmonic Oscillator Model  
SHO  Simple Harmonic Oscillator Model  
e  total energy per unit mass  
$e_n$  quantum level energy  
k  Boltzmann constant  
k_d  dissociation rate from state n [cm$^3$/s]  
M  Mach number, Molecular weight  
p  pressure  
P_{n+1,n}  V-T probability, $P_{n+1,n} = P_{n,n+1}/s_{n+1}$  
$Q_{m,n}^{s,l}$  V-V exchange probability, $s \rightarrow l, m \rightarrow n$  
$s_n$  Boltzmann factor, $\exp[-(e_n - e_{n+1})/kT]$  
T  translational temperature  
$T_v$  vibrational temperature  
$T_{vl}$  first level vibrational temperature  
$\mathbf{u}$  velocity vector  
n, m  vibrational quantum numbers  
n$_0$  last bound state, vibrational quantum number  
$Z_{vib}$  vibrational partition function  
$\tau$  relaxation time  
v  dissociation rate, $\frac{dn}{dt}$
$\Theta_d$ characteristic temperature of dissociation

$\Theta_v$ characteristic temperature of vibration

$\varphi_n$ depletion factor for state $n$, deviation of quasi-steady distribution from equilibrium Boltzmann

$\rho_n = \rho_n^0 (1 + \varphi_n)$

$k_{j,j-1}$ V-T rate [cm$^3$/s] for $j \rightarrow (j-1)$

$\equiv Z_{coll} P_{j,j-1}$

$r_{m-n-1}^{m-n}$ V-V rate [cm$^3$/s] for $m \rightarrow m, n \rightarrow (n-1)$

$Z_{coll}$ collision frequency

$\rho_n^0$ state density in the $n$th vibrational level

$\rho$ total density, total molecular population

$\gamma_n$ equilibrium fractional population in state $n$

$\equiv \exp(-\varepsilon_n/kT)/\{\sum_{m=0}^{n} \exp(-\varepsilon_m/kT)\}$

$\equiv \exp(-\varepsilon_n/kT)/Z_{vib}$

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