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Rate Parameters for Coupled Vibration-Dissociation in a Generalized SSH Approximation

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We report a theoretical study of vibrational excitations and dissociations of nitrogen undergoing a nonequilibrium relaxation process upon heating and cooling. The rate coefficients for collisional induced vibrational transitions and transitions from a bound vibrational state into a dissociative state have been calculated using an extension of the theory originally proposed by Schwartz, Slawsky, and Herzfeld (SSH). High-lying vibrational states and dissociative states were explicitly included, but rotational energy transfer was neglected. The transition probabilities calculated from the SSH theory were fed into the master equation, which was integrated numerically to determine the population distribution of the vibrational states, as well as bulk thermodynamic properties. Our results show that 1) the transition rates have a minimum near the middle of the bound vibrational levels, causing a bottleneck in the vibrational relaxation and dissociation rates, 2) high vibrational states are always in equilibrium with the dissociative state, 3) for the heating case, only the low vibrational states relax, according to Landau-Teller theory, 4) for the cooling case, vibrational relaxation cannot be described by a rate equation, and 5) the average vibrational energy removed in dissociation is about 30% of the dissociation energy.

Nomenclature

A = parameter in Landau-Teller equation
D_0 = dissociation energy
$E(v)$ = energy of the vibrational level v measured from minimum of the vibrational potential
e_v = average vibrational energy per molecule
h = Planck's constant
K_f = forward (dissociation) reaction rate coefficient, in $\mathrm{cm^3 s^{-1}}$
K_{fE} = rate coefficient for equilibrium vibration in the CVD model, in $\mathrm{cm^3 s^{-1}}$
K_r = reverse (recombination) reaction rate coefficient, in $\mathrm{cm^3 s^{-1}}$
$K(v,c)$ = transition rate coefficient for $v \rightarrow c$ (continuum) transition, in $\mathrm{cm^3 s^{-1}}$
$K(v,v')$ = transition rate coefficient for $v \rightarrow v'$ transition, in $\mathrm{cm^3 s^{-1}}$
k = Boltzmann constant
$M(v)$ = second moment of vibrational transition rate, see Eq. (35)
m = number of vibrational levels
m_μ = reduced mass of colliding molecules
N = number density
n = temperature exponent in rate coefficient
$P^{v-v'}_{v_2-v_2'}$ = probability of collisional induced vibrational transition
p = pressure in atmosphere
$p^{v-v'}_{v_2-v_2'}$ = velocity-dependent probability of collisional induced vibrational transition
Q_{tA}, Q_{tb} = translational partition function for atoms A and B, respectively
Q_v = partition function for level v
q = the vibrational quantum number above which quasi-steady-state approximation holds
R = matrix element of relative motion
r = distance between the centers of mass of the colliding molecules
s = parameter in semiempirical rate equation of Park
s_1, s_2 = vibrational coordinates of molecules 1 and 2
T = translational temperature
T_a = geometrical mean temperature
T_d = characteristic temperature of dissociation
T_v = vibrational temperature
T_{v1}, T_{v2}, T_{v3} = three definitions of vibrational temperatures in a nonequilibrium flow
t = time
u_0, u_f = initial and final velocity of relative motion between two molecules
V = interaction potential between two colliding molecules
V_0, α, β = parameters in the interaction potential
$\mathcal{V}(v \rightarrow v')$ = matrix element for the vibrational transition of molecule 1, from an initial quantum state of v to v'
v = vibrational quantum number
Δv = change in v
ϵ = average vibrational energy removed from the molecule per each dissociation event
θ = characteristic vibrational temperature
μ = reduced mass of colliding particles in atomic mass units
ρ_A, ρ_B = normalized population density of atoms A and B, respectively
ρ_h, ρ_p = homogeneous and particular solutions of Eq. (26)
ρ_v = normalized population density at level v
τ_L = relaxation time deduced from the Landau-Teller equation
ψ_v = vibrational wavefunction of level v

Subscripts

A = atoms A
B = atoms B

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E = equilibrium
i = initial condition
v = vibrational level v
x = molecule

Introduction

VIBRATIONAL excitations in diatomic molecules play an important role in the aerothermodynamics of hypersonic flows. At temperatures typical of shock layers around a hypersonic vehicle, the kinetic energy of the gaseous particles is at least comparable to the excitation energy between the ground and first excited vibrational levels. Hence, a significant portion of the kinetic energy can be absorbed through vibrational excitation. This excitation process reduces the gas temperature and, thereby, also affects the pressure. Also, in the flight regimes of hypersonic vehicles, the air density is likely to be so low that the vibrational levels may not necessarily be in equilibrium. Such a reasoning prompted early investigators of hypersonic flows to study the nonequilibrium vibrational rate processes.

Early studies on this topic focused on the determination of vibrational relaxation rates. Millikan and White[1] collated the early results and showed that most existing experimental data on the vibrational relaxation times τ can be reproduced by an empirical formula derived by Landau and Teller[2] for harmonic oscillators

$$\tau_L = (1/p)\exp[A(T^{-1/3} - 0.015\mu^{1/4}) - 18.42] \tag{1}$$

where τ_L is in seconds. The quantity A is given by

$$A = 1.16 \times 10^{-3}\mu^{1/2}\theta^{4/3}$$

and

$$\theta = [E(1) - E(0)]/k$$

Here $E(0)$ and $E(1)$ are the energies of the ground and first excited vibrational levels. According to the Landau-Teller model $e_v(T_v)$ is given by

$$\frac{\partial e_v(T_v)}{\partial t} = \frac{e_{vE}(T) - e_v(T_v)}{\tau_L} \tag{2}$$

Equation (2) is known as the Landau-Teller relaxation equation. The Landau-Teller model entailed that the vibrational transitions can occur only between neighboring levels, and that their rates are proportional to the vibrational quantum numbers. Comparison with experimental data showed that Eqs. (1) and (2) are accurate at temperatures up to ≈ 5000 K, and hold approximately to ≈ 8000 K, although the equation tends to slightly underestimate the relaxation times at the higher temperature range.

In the meantime, several theoretical models have been developed to calculate the vibrational relaxation time. The most frequently applied is the treatment proposed by Schwartz, Slawsky, and Herzfeld,[3] commonly referred to as the SSH theory. In this theory, the vibrational transition probability is obtained by solving the Schrödinger equation for the colliding particles with the simplified assumptions of collinear collisions and separability of the vibrational and translational degrees of freedom in the interaction potential. These assumptions allow the efficient computation of vibrational relaxation time for a complete manifold of vibrational and dissociative levels at high temperatures. Contrary to the Landau-Teller model, vibrational transitions can occur between non-neighboring levels. It also allows equal treatment of vibration and dissociation.

More elaborate methods for solving the vibration-dissociation problem also are available. The classical, semiclassical, and quantal methods[4] have all been used to treat various aspects of the vibration-rotation-translation energy transfer problem. However, all these methods require the knowledge of a full potential energy surface for the nuclear motion. For the H_2-H_2 system, a full ab initio surface has been determined, and the coupled vibration-dissociation problem, including the effect of rotation, have been studied[5] using a quasiclassical trajectory method. However, for the N_2-N_2 system, a reliable potential energy surface is not presently available. Thus, in the present study, we choose to employ the SSH theory to study the vibrational excitations and dissociation of N_2. This can be considered as a first step in clarifying the problem of coupling vibration and dissociation.

Using shock tube experiments, numerous investigators studied the nonequilibrium kinetic processes behind a shock wave. For N_2, dissociation is the major energy-absorbing phenomenon at temperatures above ≈ 5000 K. These experiments revealed that a short time must pass before dissociation can begin (see, for example, Ref. 5). The length of this time period, commonly referred to as the incubation period, was found to be roughly equal to the vibrational relaxation time. It was reasoned that the molecules must first be vibrationally excited before they dissociate. At temperatures below ≈ 8000 K, the incubation time is usually much shorter than the time necessary for achieving dissociation equilibrium, and, therfore, vibrational equilibrium is reached before dissociation occurs. Above 8000 K, the dissociation time is so short that it becomes comparable to the vibrational relaxation. In such an environment, the number of vibrationally excited molecules that can dissociate are fewer, and the dissociation rate is slower than in the case when vibration is equilibrated.[6]

Since the maximum temperature encountered during a typical entry flight of a vehicle from an Earth orbit is over 30,000 K, keen interests have been aroused to determine the dissociation rate in such a regime. The first of such endeavors is the work of Hammerling et al.[7] They considered the simplest possible gas model: the molecules have no rotational motion, the vibrational motion is harmonic, the cross sections for the collision-induced dissociation from individual vibrational states are independent of their vibrational quantum numbers, and the vibrational states are populated according to a Boltzmann distribution corresponding to a vibrational temperature T_v. The model led to an expression for the dissociation rate coefficient K_f of the form

$$K_f(T,T_v) = K_{fE}(T)\frac{\theta}{T}\frac{1 - \exp(-T_d/T_v + T_d/T)}{\exp(\theta/T_v - \theta/T) - 1} \times \frac{\exp(\theta/T_v) - 1}{\exp(\theta/T) - 1} \tag{3}$$

where $T_d = D_0/k$, D_0 being the dissociation energy measured from the vibrational ground state. This analysis was named the CVD (coupled-vibration-dissociation) model.

Treanor and Marrone[8] pointed out that during such coupled processes, ϵ is larger than e_v (for the harmonic oscillator, $e_v = k\theta/[\exp(\theta/T_v) - 1]$). Under the assumptions made by Hammerling et al., it was shown that ϵ is equal to half the dissociation energy

$$\epsilon = D_0/2 \tag{4}$$

This modification of the CVD model was named the CVDV (coupled-vibration-dissociation-vibration) model.

Marrone and Treanor[9] examined the coupling process still further. Based on the argument that the cross sections for dissociation from various vibrational levels increase with the vibrational quantum number, they reasoned that dissociation must occur preferentially from the high vibrational states close to the dissociation limit. As a result, the average vibrational energy removed should be larger than that given by Eq. (4). At that time, they could not give the exact value for ϵ because the quantities needed for its calculation were not known. This theory is referred to as the preferential removal model.

In later papers,[10,11] Treanor and his associates pointed out another important aspect of the problem, namely, the effect of resonant energy transfer. A molecule is readily excited by colliding with an excited molecule wherein the latter transfers its vibrational energy to the former in a resonant energy exchange. This is called resonant V-V (vibration-to-vibration) energy transfer. Such resonant transitions occur selectively when the vibrational energy gaps of the two molecules are nearly the same. Due to the anharmonicity in the vibrational potential, the vibrational energy gap monotonically decreases with the vibrational quantum number. Since most of the colliding molecules are in the lowest few vibrational levels, the resonant transition process promotes rapid energy exchange among these levels. On the other hand, the energy mismatch prevents resonant energy transfer between the high and low vibrational levels, and the transitions between them are slow. Treanor and his associates applied the SSH theory to predict such a phenomenon. Their study considered both the shock-heated and the expanding (cooling) flows. By solving the conservation equations for individual vibrational levels, known as master equations, they obtained the number density distribution for the vibrational states of nitrogen up to $v = 40$. They showed that the combination of the anharmonicity and the V-V resonance phenomenon leads to a non-Boltzmann distribution among the vibrational states. The limitations of these early works were that 1) the vibrational potential for nitrogen was calculated using the first two terms of the Dunham expression and, thus, was valid only for the lowest few vibration levels, and 2) the bound-free transitions were not included. The two-term approximation of the potentials lead to the conclusion that the vibrational transition rates decrease monotonically with v. The impact of non-Boltzmann distribution on dissociation could not be determined because the bound-free transitions were not included.

The effect of the resonance-dominated V-V transfer on the vibrational population distribution in expanding flows has also been studied theoretically by Bray,[12] Rich and Rehm,[13] Bray and Pratt,[14] and Rush and Pritchard.[15] These studies predicted that the decrease in vibrational excitation rates with vibrational quantum number in an anharmonic oscillator can cause a bottleneck in the transition between the lower and the higher vibrational states, leading to an overpopulation of the high vibrational states during an expansion. Under certain conditions, the overpopulation is so large that a population inversion may occur. However, these theoretical analyses were only qualitative because numerical values of the transition rates among the high vibrational levels and the bound-free transition rates were unknown.

Only a very limited number of experimental data relating to these phenomena have been reported. The SSH theory was approximately validated[16,17] through measurements with a mixture containing two different diatomic gases, such as N_2 and CO. Appleton[18] confirmed that, for a flow behind a shock wave of nitrogen heavily diluted by argon, vibrational relaxation occurs according to the Landau-Teller model even at fairly high temperatures. For an expanding flow through a hypersonic nozzle, a series of experiments conducted at the Cornell Aeronautical Laboratory[19] showed that the vibrational relaxation rates are generally faster than predicted by the Landau-Teller model. This anomaly was later attributed to the presence of water vapor in the nozzle flow. The experiments by Blom et al.[20] and McLaren and Appleton[21] showed that, at least when the diatomic gas is diluted heavily by argon, vibrational relaxation in an expanding flow obeys the Landau-Teller model. McKenzie[22] showed experimentally that, in a flow mostly of carbon monoxide, the population inversion occurs as predicted, and he demonstrated a gasdynamic laser based on this principle. However, the details of the vibrational population distribution were not studied in his work.

Simultaneously with the aforementioned studies, experiments were conducted in shock tubes and ballistic ranges to determine the intensities of the radiation emanating behind shock waves at high flow velocities. The results of such experiments were never analyzed in detail at the time. In recent years, the vibration-dissociation coupling phenomenon drew renewed attention in connection with the chemico-kinetic phenomena at very high flight speeds, up to about 10 km/s, corresponding to a postshock temperature of the order of 50,000 K. According to Park,[23] the time scales of vibrational excitation and dissociation in such an environment are so closely matched that the vibrational nonequilibrium seriously slows down the rates of dissociation. The existing theoretical models, such as the CVD,[7] CVDV,[8] and preferential removal[9] models mentioned earlier, were found to be inadequate to describe the phenomena accurately. The reaction rates predicted by these models were still much faster than the observed rates. This prompted Park to propose a semiempirical model based on an average temperature

$$T_a = \sqrt{T_v T} \tag{5}$$

According to the model, the dissociation rates are determined by this average temperature via the conventional rate coefficient expression

$$K_f(T, T_v) = C T_a^n \exp(-T_d/T_a) \tag{6}$$

The vibrational temperature is determined in turn by a rate equation of the form

$$\frac{\partial e_v(T_v)}{\partial t} = \frac{e_{vE}(T) - e_v(T_v)}{\tau_L} \left(\frac{T_i - T_v}{T_i - T_{vi}} \right)^{s-1} \tag{7}$$

where the subscript i refers to the initial condition immediately behind the shock wave. The parameter s is an increasing function of T_i, the maximum value being 3.5. This model approximately reproduced the observed radiation characteristics for nitrogen and air at such high speeds.[24,25]

Up to the present, there is no firm rational foundation for the semiempirical model. The absence of a rational foundation prevents this model from being used in new untested flow regimes. Previous theoretical investigations cannot be used for this purpose because their calculations did not include transition rates among high vibrational states and between the vibrational bound states and free states. At the time those investigations were carried out, numerical difficulties in solving the Schrödinger equation for the realistic vibrational potential prevented such transition rates from being calculated reliably and efficiently. This situation has since been remedied. The present work is an effort to explain the vibration-dissociation coupling phenomena. Specifically, it intends to explore the following points:

1) How are the vibrational states populated and what are the corresponding characteristic vibrational temperatures during the relaxation period?

2) What are the relaxation rates for the characteristic vibrational temperatures? Which model is most accurate?

3) How are the dissociation and the recombination rates related to the characteristic vibrational temperatures? Which model is most accurate?

4) What is the value of the average vibrational energy removed during dissociation?

To answer these questions, we extend previous theoretical works by generalizing the SSH theory to include the high vibrational states and free states, and carry out calculations of transition rates among all vibrational and dissociative states of N_2. The vibrational potential for N_2 is approximated by a more realistic potential (Murrell-Sorbie potential[26]) than the two-term Dunham expansion used previously. Rotational energy transfer has been neglected. For resonant V-V energy transfer, this is probably a reasonable approximation. The transition probabilities in that case are very large and rotation tends to play a small role. In a nonresonant V-V or V-T energy transfer, rotation becomes important. The latter is analogous to atom-diatom energy transfer, where rotation and vibration are probably equally important. Under those circumstances, our result will no longer be valid. Although the neglect of rotation limits the utility of the present calculation, we still feel that an accurately soluble mathematical model serves the purpose in presenting an overall picture that can then be systematically improved in the future. Furthermore, in the case of a cooling flow where the translational and rotational temperatures already are down at room temperature but the vibrational temperature remains high, the present model becomes realistic.

To focus the study on the effect of the resonant V-V energy transfers, we assume both colliding partners are molecules (except for three-body recombination, where one of the colliding partners must be a molecule). The relaxation phenomena have been studied theoretically for two typical cases. The first is a heating case wherein the gas, initially in equilibrium at 4000 K, is heated suddenly to 8000 K. In the second case, the gas is cooled from the initial temperature of 6000 K to 4000 K. A constant-volume, isothermal condition was assumed during the relaxation process. The rate equations for the change of the vibrational state populations, that is, the master equations, are integrated in time for these two cases with the use of the computed transition rate coefficients.

The calculation yields a complete set of transition rate coefficients among all combinations of initial and the final vibrational and/or free states. The integration of the master equation yields the population distribution of all vibrational states as a function of time, as well as the number densities of the atoms and molecules. From these vibrational distributions, the vibrational temperature, the forward (dissociation) and reverse (recombination) rate coefficients, and the average transferred energy ϵ are calculated. The dissociation rate coefficients are also calculated, using Park's model, and comparison is made between these values and the results from the time integration. The transition rate coefficients calculated in the present work show a hitherto unknown phenomenon, namely, that the transitions are very fast among the high vibrational states and between the high vibrational states and the free state. This drives the population distribution into a distinct dual-mode, in which the lower and the higher states reach separate quasiequilibrium distributions. Because of this phenomenon, the bottleneck predicted by the early investigators occurs more prominently than previously envisioned. Park's two-temperature model is seen to agree with the detailed calculation to within an order of magnitude, provided T_a is redefined as

$$T_a = T_v^{0.3} T^{0.7} \tag{8}$$

The average vibrational energy transferred in dissociation ϵ is found to be only 30% of D_0, much less than predicted by the CVDV[8] and the preferential removal[9] theories.

Formulation of the SSH Approximation

The SSH theory[3] assumes that the center-of-mass motion in the colliding system is one-dimensional. Rotation is neglected. V is further approximated by exponential repulsive potentials.

$$V = V_0 e^{-\alpha(r + \beta_1 s_1 + \beta_2 s_2)} \tag{9}$$

The parameters V_0 and α are determined by fitting $V_0 e^{-\alpha r}$ to the Lennard-Jones potential between the colliding partners, whereas β_1 and β_2 can be chosen to account for the collisional geometry, i.e., deviation from the optimal approach. With the interaction potential in Eq. (9), the transition probability for collisional induced vibrational transition or dissociation between two diatomic molecules can be expressed as products of transition probabilities for individual degrees of freedom

$$p_{v_2 \to v_2'}^{v \to v'}(u_0) = \frac{16\pi^2 V_0^2}{u_0 u_f h^2} \mathcal{V}^2(v \to v') \mathcal{V}^2(v_2 \to v_2') R^2$$

The macroscopic transition probability for molecule 1 excited/de-excited from v to v', and for molecule 2 excited/de-excited from v_2 to v_2' is obtained by averaging over the initial velocity u_0

$$P_{v_2 \to v_2'}^{v \to v'}(T) = 2\left(\frac{m_\mu}{2kT}\right)^2 \int_0^\infty u_0^3 p_{v_2 \to v_2'}^{v \to v'}(u_0) \times \exp(-m_\mu u_0^2/2kT)\, \mathrm{d}u_0 \tag{10}$$

In the present treatment, we follow the SSH's practice by setting the parameters V_0, β_1, and β_2 in the interaction potential to unity. The parameter α is chosen such that V and $\mathrm{d}V/\mathrm{d}r$ agree with the Lennard-Jones potential at the classical point of closest approach, with the relative velocity u_0 determined by the heat bath temperature.

The vibrational transition matrix element $\mathcal{V}(v \to v')$ is given by

$$\mathcal{V}(v \to v') = \int_{-\infty}^{\infty} \psi_v(s_1) e^{\frac{1}{2}\infty s_1} \psi_{v'}(s_1)\, \mathrm{d}s_1$$

The vibrational wavefunctions ψ_v and $\psi_{v'}$ are numerical solutions of the one-dimensional Schrödinger equation of vibrational motion. The analytic Murrell-Sorbie potential[26] was used in all our calculations. This potential has the form

$$U(s) = -D_0(1 + a_1 s + a_2 s^2 + a_3 s^3) e^{-a_1 s}$$

where the constants a_1, a_2, and a_3 are obtained from the harmonic, cubic, and quartic force constants. This potential has been shown to be superior to the Hulbert-Hisrchfelder potential.[26] The term values for the first 12 vibrational levels calculated with this potential are in good agreement with experiment. Larger deviations are obtained for higher vibrational levels. In total, we found 57 bound vibrational levels using this potential, vs the 66 bound vibrational levels calculated using the Rydberg-Klein-Rees (RKR) potential[27] extended with ab initio calculations.[28] We have chosen to use the Murrell-Sorbie potential instead of the extended RKR potential because the small discontinuity in matching the ab initio data to the RKR potential affected the calculations of the continuum wavefunctions. Both the bound and continuum vibrational wavefunctions have been calculated using the Numerov-Cooley technique.[29]

The vibrational excitation rate $K(v, v')$ is expressed in terms of $P_{v_2 \to v_2'}^{v \to v'}$

$$K(v, v') = \sum_{v_2, v_2'} \rho_{v_2} \sqrt{\frac{8kT}{\pi m_\mu}} \sigma_0 P_{v_2 \to v_2'}^{v \to v'}$$

where ρ_{v_2} is the normalized population density of molecule 2 in vibrational level v_2 (see the following section), and σ_0 is the effective hard sphere cross section. For the present calculations, σ_0 is chosen so that the calculated $K(v, v')$ for the lowest vibrational level matches with the empirical value of Millikan and White.[1] The dissociation rate $K(v, c)$ is obtained by replacing the final vibrational level v' by the continuum and integrating over the continuum up to 25,000 cm^{-1} above the dissociation limit. Notice that the summation over v_2', the final vibrational level of molecule 2, also includes the continuum

Formulation of Rate Equations

Temporal Variation in Vibrational State Populations

We will designate the N_2 molecule with the suffix x and the two atoms resulting from its dissociation by the suffixes A and B, even though they are identical. We consider that the mixture containing the species x, A, and B is confined in a box of unit volume. At times prior to $t = 0$, equilibrium existed at a specified temperature T_0. At time $t = 0$, the gas is suddenly heated or cooled by an unspecified means so that the translational temperature acquires a new value T. The box is then maintained at an isothermal condition. Due to the suddenly changed T, collisional processes occur to vibrationally excite or de-excite to relax to a condition appropriate to T. Some of the collisions lead to a free-bound (dissociation or recombination) transition $v \rightleftharpoons A + B$. The state $A + B$ will be designated by c (continuum). There are a total of $m = 57$ vibrational states starting from $v = 0$ to $v = 56$. As stated in the introduction, the collisional transitions are assumed to occur only when both colliding partners are molecules. (For the three-body recombination case, one of the colliding partners must be a molecule.) In this manner, we can focus our study to the effect of the resonance transitions in V-V energy transfer—a dominant process in the typical flow regime around a hypersonic vehicle.

The number density of those molecules in the vibration state v, or population N_v, is affected by the incoming and outgoing rates. An incoming rate is the rate of an individual transition from an initial vibrational state v' or a free state c via collisions with the colliding particle x. When the initial state is a bound vibrational state, the rate is given by $K(v',v)N_{v'}N_x$, where $K(v',v)$ is the rate coefficient for the vibrational transition given in units of cm^3 s^{-1}. When the initial state is the free state, its rate is given by $K(c, v)N_AN_BN_x$. An outgoing rate is its reverse, $K(v, v')N_vN_x$ or $K(v, c)N_vN_x$. The time rate of change of N_v is the difference between the sum of all incoming rates and the sum of all outgoing rates

$$\frac{\partial N_v}{\partial t} = N_x \sum_0^m K(v',v)N_{v'} + K(c,v)N_AN_BN_x$$
$$- N_x \sum_0^m K(v,v')N_v - K(c,v)N_vN_x \tag{11}$$

We introduce N_{vE}, the equilibrium population of the state v for a given total molecule density N_x

$$N_{vE} = N_x(Q_v/Q_x) \tag{12}$$

where Q_x is the vibrational partition function of the molecule x and Q_v is the contribution from the v-level. We further define the normalized population ρ_v by

$$\rho_v = (N_v/N_vE) \tag{13}$$

For the free state, we define the normalized density ρ_A and ρ_B by

$$\rho_A = (N_A/N_{AE}), \qquad \rho_B = (N_B/N_{BE}) \tag{14}$$

The equilibrium number densities, N_{AE} and N_{BE}, are given by

$$\frac{N_{AE}N_{BE}}{N_x} = \frac{Q_{At}Q_{Bt}}{Q_{xt}Q_xQ_r} \exp\left(-\frac{D_0}{kT}\right)$$

Here, Q denotes a partition function as before, and the subscripts t and r refer to the translational and the rotational modes. We invoke the principle of detailed balancing between a forward and its backward rates under the equilibrium, which leads to

$$K(v,v')N_{vE} = K(v',v)N_{v'E} \tag{15}$$

for the bound-bound transitions, and

$$K(v,c)N_{vE} = K(c,v)N_{AE}N_{BE} \tag{16}$$

for the bound-free transitions. By dividing Eq. (11) by N_{vE}, and using Eqs. (14-16), the master equation becomes

$$\frac{1}{N_x}\frac{\partial \rho_v}{\partial t} = \sum_0^m K(v,v')(\rho_{v'} - \rho_v) + K(v,c)(\rho_A\rho_B - \rho_v) \tag{17}$$

Here, the index m denotes the highest bound vibrational level.

The rate of change of the density of the atoms A and B and of the molecular density can be expressed as

$$\frac{\partial N_A}{\partial t} = \frac{\partial N_B}{\partial t} = -\frac{\partial N_m}{\partial t}$$
$$= \sum_0^m K(v,c)N_xN_v - \sum_0^m K(c,v)N_AN_BN_x$$

Using the detailed balancing relationship (15) and (16), we can rewrite the equation in the form

$$\frac{\partial N_A}{\partial t} = N_xN_m \sum_0^m K(v,c)\frac{Q_v}{Q_m} - N_xN_AN_B \sum_0^m K(v,c)\frac{N_{vE}}{(N_AN_B)_E} \tag{18}$$

Multiplication of Eq. (18) by $2N_A$ and division by $(N_AN_B)_E$ leads to

$$\frac{\partial(\rho_A\rho_B)}{\partial t} = 2\sqrt{\frac{\rho_A\rho_B}{(N_AN_B)_E}} \sum_0^m K(v,c)N_xN_{vE}(\rho_v - \rho_A\rho_B) \tag{19}$$

Equations (17) and (19) are integrated numerically to obtain ρ_v and $\rho_A\rho_B$ as functions of time. The equations are very stiff, and so a second-order implicit integrating technique is employed. The unoptimized version of the code typically required 10,000 s on the Cray X-MP computer.

Quasi-Steady-State Population Distribution

Except in the very early stage of relaxation, the sum of all incoming rates and the sum of all outgoing rates in Eq. (17) are nearly equal. As a result, the left-hand side of Eq. (17) is nearly zero. In this case, the population distribution can be determined by setting the left-hand side of Eq. (17) as zero for all values of v, except the ground state $v = 0$, and by solving the resulting system of simultaneous linear algebraic equations in ρ_v. For the ground state, it is unrealistic to set the left-hand side to zero, because the two rates are obviously not in balance. The ground state population can be determined by imposing the condition that the sum of all vibrational state populations equals the given number density of the molecules N_x, that is,

$$\sum N_v \equiv \sum N_{vE}\rho_v = N_x \tag{20}$$

This procedure is known as the quasi-steady-state (QSS) approximation. In the present study, the QSS equations are also solved for the purpose of comparing the ρ_v values so obtained with those obtained through time integration.

Characteristic Vibrational Temperatures

In a nonequilibrium flow, there is no unique vibrational temperature. However, one can define a vibrational temperature arbitrarily for a specific purpose. Three such vibrational temperatures are defined in the present work.

The first is the vibrational temperature based on the ratio of the number densities among the low vibrational states. We arbitrarily chose the $v = 0$ and $v = 4$ states for this purpose. The vibrational temperature, designated T_{v1}, is defined as

$$\frac{N(4)}{N(0)} \equiv \frac{N_E(4)}{N_E(0)}\frac{\rho(4)}{\rho(0)} = \exp\left[-\frac{E(4) - E(0)}{T_{v1}}\right]$$

In most experiments, vibrational temperature is deduced from the ratios of the number densities among the low vibrational states. In such experiments, the measured vibrational temperature would be T_{v1}.

The second is the vibrational temperature that characterizes the energy contained in the vibrational mode. Using the conventional harmonic oscillator expression, the temperature T_{v2} is defined from the average vibrational energy e_v as

$$e_v = \frac{k\theta}{\exp(\theta/T_{v2}) - 1} \tag{21}$$

The energy e_v is determined in turn from the computed ρ_v by

$$e_v = \frac{\Sigma E(v) N_{vE} \rho_v}{\Sigma N_{vE} \rho_v}$$

The temperature is useful in displaying the amount of energy contained in the vibrational mode.

The third vibrational temperature T_{v3} is that based on the ratio of the number densities between the highest vibrational state, $v = 56$, and the ground state, $v = 0$, that is,

$$\frac{N(56)}{N(0)} \equiv \frac{N_E(56)}{N_E(0)} \frac{\rho(56)}{\rho(0)} = \exp\left[-\frac{E(56) - E(0)}{T_{v3}} \right] \tag{22}$$

This temperature characterizes the behavior of the high vibrational states.

Reaction Rate Coefficients

For relaxing gases, it is customary to express the rate of change of number density in terms of bulk rate coefficients K_f for the forward (dissociation) and K_r for the reverse (recombination) processes.

$$\frac{\partial N_{A,B}}{\partial t} = K_f N_x N_x - K_r N_x N_A N_B \tag{23}$$

When the gas is in a highly nonequilibrium condition, one of the two terms of Eq. (23) is dominant over the other. In such a case, K_f or K_r can be determined approximately from

$$K_f \approx \frac{\partial N_{A,B}}{\partial t} \frac{1}{(N_x^2)} \tag{24}$$

or

$$K_r \approx \frac{\partial N_{A,B}}{\partial t} \frac{1}{(N_A N_B N_x)} \tag{25}$$

Eq. (24) is used in determining the K_f in the present work.

In general, K_f and K_r are functions of time because ρ_v varies with time. If the ρ_v distribution is uniquely determined by T and T_{v1}, K_f and K_r can be expressed as functions of T and T_{v1} only. Such condition can exist if the high vibrational states are populated according to the QSS condition, that is, the left-hand side of Eq. (17) is negligibly small in comparison with either of the two rates affecting ρ_v, namely, the sum of all incoming rates or the sum of all outgoing rates. Suppose that the QSS condition exists for the states above $v = q$. Then, for these states, the master equation can be written as

$$\begin{aligned} &\sum_q^m K(v,v')\rho_{v'} - \sum_0^m K(v,v')\rho_v - K(v,c)\rho_v \\ &\quad = -K(v,c)\rho_A\rho_B - \sum_0^q K(v,v')\rho_{v'} \end{aligned} \tag{26}$$

If the states below $v = q$ are populated according to the Boltzmann distribution at a vibrational temperature T_{v1}, then the second term on the right-hand side becomes a function only of T and T_{v1}. In that case, the solution to the algebraic Eq. (26) can be written as

$$\rho_v = \rho_h(T) + \rho_A \rho_B \rho_p(T, T_{v1}) \tag{27}$$

where ρ_h is the homogeneous solution of Eq. (26) and ρ_p is a particular solution.

Using the detailed balance relationship, Eqs. (15) and (16), the overall reaction rate can now be written as

$$\begin{aligned} \frac{\partial N_A}{\partial t} &= N_x \sum_q^m K(v,c) N_{vE} \rho_v - N_x (N_A N_B) \sum_q^m K(c,v) \\ &= N_x^2 \sum_q^m K(v,c) \frac{Q_v}{Q_x} \rho_h - N_x N_A N_B \sum_q^m \frac{N_x}{N_{AE} N_{BE}} (1 - \rho_p) \end{aligned} \tag{28}$$

By comparing Eq. (28) with Eq. (23), one finds

$$K_f = \sum_q^m K(v,c) \frac{Q_v}{Q_x} \rho_h \tag{29}$$

$$K_r = \sum_q^m K(v,c) \frac{N_x}{N_{AE} N_{BE}} \frac{Q_v}{Q_x} (1 - \rho_p) \tag{30}$$

Equations (29) and (30) are valid even when the flow is close to or at equilibrium. These equations are used in the present work whenever appropriate.

Average Vibrational Energy Loss Due to Dissociation

When a gas molecule with the vibrational energy $E(v)$ dissociates by collision with another particle, the vibrational energy content of the gas is reduced by an amount equal to $E(v)$. As pointed out by Marrone and Treanor,[9] dissociation occurs preferentially from the upper vibrational states. Thus, even a single dissociation depletes the vibrational energy by an amount nearly equal to the dissociation energy of the molecule. The rate of energy loss by a transition from the vibrational level v is $K(v,c)E(v)N_v N_x$. Conversely, the reverse process of recombination into the vibrational level v adds a vibrational energy equaling $K(c,v)E(v)N_A N_B N_x$. The average vibrational energy loss ϵ can be defined by

$$\begin{aligned} -\epsilon \frac{\partial N_x}{\partial t} &= \sum_0^m E(v) K(v,c) N_v N_x - \sum_0^m E(v) K(c,v) N_A N_B N_x \\ &= N_x^2 \sum_0^m E(v) K(v,c) \frac{Q_v}{Q_x} (\rho_v - \rho_A \rho_B) \end{aligned} \tag{31}$$

In terms of ρ_v, the average vibrational energy loss rate is

$$\epsilon = \frac{\Sigma_0^m E(v) K(v,c) (Q_v/Q_x)(\rho_v - \rho_A \rho_B)}{\Sigma_0^m K(v,c)(Q_v/Q_x)(\rho_v - \rho_A \rho_B)} \tag{32}$$

Diffusion Approximation

At the high-temperature regime where the kinetic energy kT is larger than the vibrational energy gap, collision excitation and de-excitation of the vibrational states occur almost in accordance with the classical mechanics. According to the classical concept, the vibrational levels are considered to be continuously distributed. The quantities v and v', in suitable units, are considered to represent the continuously distributed vibrational energies. The summation in Eq. (17) is then replaced by an integration

$$\frac{1}{N_x} \frac{\partial \rho_v}{\partial t} = \int_0^m K(v,v')(\rho_{v'} - \rho_v)\, dv' + K(v,c)(\rho_A \rho_B - \rho_v) \tag{33}$$

Keck and Carrier[30] have shown that this equation can be converted into a diffusion equation. Since their original paper does not show the details of the derivation, the diffusion equation is derived below.

In general, the vibrational level v' can be expressed as $v' = v + \Delta v$. If the transitions occur mostly between neighboring states, then the integrating limits can be changed from $\Delta v = -\infty$ to $\Delta v = +\infty$

$$\begin{aligned} \frac{1}{N_x} \frac{\partial \rho(v)}{\partial t} &= \int_{-\infty}^{+\infty} K(v, v + \Delta v)\{\rho(v + \Delta v) - \rho(v)\} \mathrm{d}(\Delta v) \\ &\quad + K(v,c)\{\rho_A \rho_B - \rho(v)\} \end{aligned}$$

The quantity $\rho(v + \Delta v)$ can be expanded in a power series in Δv. To the second order in Δv, we can write

$$\rho(v + \Delta v) = \rho(v) + \frac{\partial \rho(v)}{\partial v}(\Delta v) + \frac{1}{2} \frac{\partial^2 \rho(v)}{\partial v^2}(\Delta v)^2 + \cdots$$

so that the equation can be modified as

$$\frac{1}{N_x}\frac{\partial \rho(\nu)}{\partial t} = \frac{\partial \rho(\nu)}{\partial \nu}\int_{-\infty}^{+\infty} K(\nu,\nu+\Delta\nu)(\Delta\nu)\,\mathrm{d}(\Delta\nu)$$
$$+\frac{1}{2}\frac{\partial^2\rho(\nu)}{\partial \nu^2}\int_{-\infty}^{+\infty} K(\nu,\nu+\Delta\nu)(\Delta\nu)^2\,\mathrm{d}(\Delta\nu)$$
$$+K(\nu,c)\{\rho_A\rho_B-\rho(\nu)\}$$

The quantity $K(\nu,\nu+\Delta\nu)$ is then expanded in a power series in $\Delta\nu$. The series will converge if the transitions occur preferentially between neighboring states. In expansion, the linear term in $\Delta\nu$ is zero because $K(\nu,\nu+\Delta\nu)$ is maximum when $\Delta\nu$ is zero. Retaining terms only to second order of accuracy, using the simplification

$$\left[\frac{\partial^2 K}{\partial \Delta\nu^2}\right]_{\Delta\nu=0}(\Delta\nu) = \left[\frac{\partial K}{\partial \nu}\right]_{\Delta\nu=\Delta\nu}, \text{ etc.}$$

we can write

$$\frac{1}{N_x}\frac{\partial \rho(\nu)}{\partial t} = \frac{\partial}{\partial \nu}\left(M\frac{\partial \rho(\nu)}{\partial \nu}\right) + K(\nu,c)\{\rho_A\rho_B-\rho(\nu)\} \tag{34}$$

where M, the second moment of vibrational transition, is defined as

$$M = \frac{1}{2}\int_{-\infty}^{+\infty} K(\nu,\nu+\Delta\nu)(\Delta\nu)^2\,\mathrm{d}(\Delta\nu) \tag{35}$$

The resulting equation, Eq. (34), is a diffusion equation in the vibrational space ν. This diffusion equation is solved in the present work for the purpose of determining the validity of the diffusion concept.

Results

Behavior of Transition Rate Coefficients

The calculated values of the bound-bound transition rate coefficient $K(\nu,\nu')$ cannot be shown in a single figure because there are $57 \times 57 = 3249$ such values. However, there are only 57 values each for the second moment of transition rate coefficient $M(\nu)$ and the bound-free transition rate coefficient $K(\nu,c)$. These two quantities are shown in Fig. 1 for the case where $T = 4000$ K and the vibrational states of the colliding particles are assumed to be populated according to a Boltzmann distribution at $T_\nu = 6000$ K. Since $M(\nu)$ is the sum of the rates from all states, it is a better indicator of the overall rate of transition. The $M(\nu)$ values for the Landau-Teller model are also shown in the figure for comparison.

As seen from the plot, the transition moment $M(\nu)$ based on the Landau-Teller model increases monotonically with the vibrational levels. This is due to the fact that $K(\nu,\nu+1)$ is proportional to $\nu+1$ in the Landau-Teller model. The transition moments $M(\nu)$ based on the SSH theory are identical to the Landau-Teller values for the low vibrational states, $E(\nu) \leq 10{,}000$ cm^{-1}, corresponding to $\nu \leq 5$. For these low-lying states, the vibrational transition processes are nearly resonant, and, hence, the Landau-Teller theory is expected to be a good approximation. For $E(\nu)$ between 10,000 and 45,000 cm^{-1}, $M(\nu)$ decreases, reaching a minimum approximately at the midpoint of the bound vibrational levels $\nu = 22$. This is a result of the anharmonic vibrational potential such that the energy gaps between the adjacent vibrational states in this region of ν are significantly smaller than the values for low ν. Earlier investigations,[11,12,22] which accounted for the anharmonicity in the vibrational potential using a two-term Dunham expansion, also showed the same trend.

At still higher vibration levels, the energy gaps are much smaller than the thermal energy kT. The collisions become nearly classical. As a result, there is no selection rule, and multiple quantum jumps can occur with almost equal probability as single quantum jumps. Because there are so many states within a small energy range, the sum of all these jumps produces a large value of $M(\nu)$. Also, $M(\nu)$ increases with ν in this region. This behavior was not found in any of the previous investigations, because they did not study the behavior of the transition rates among high-lying states. Instead, they claimed the transition rates to decrease steadily toward the dissociation limit, contrary to the present result.

As the result of the decrease of $M(\nu)$ between 10,000 to $45{,}000^{-1}$ and subsequent increase, the $M(\nu)$ curve in Fig. 1 has a minimum $M(\nu)$ around 45,000 cm^{-1}. At the minimum, $M(\nu)$ is nearly two orders of magnitude smaller than the peak value at $\nu = 5$. There is a second, shallower minimum around 72,000 cm^{-1}. Beyond this minimum, $M(\nu)$ increases steeply. This second minimum and the ensuing rise depends strongly on the curvature of the vibrational potential used. During the course of this work, calculations have also been made with an RKR potential extended by ab initio calculations. Although both calculations show the first peak and subsequent deep minimum, we found the secondary structures at higher energies differ for the two calculations. We conclude that these structures are quite sensitive to the curvature of the vibrational potential near the dissociation limit. Since we do not have reliable knowledge of the potential in this region and the secondary minimum is significantly weaker than the first, at this point we disregard these structures and concentrate on the significance of the primary minimum.

The primary minimum has a profound effect on the behavior of vibrational relaxation. As shown previously in the section on diffusion approximation, vibrational relaxation occurs in a manner similar to diffusion. When the excitation diffuses from the lower levels into the higher levels and vice versa, the minimum will act as a bottleneck. This bottleneck decouples the lower vibrational levels from the higher levels in the vibrational relaxation process.

The bound-free transition rate coefficient $K(\nu,c)$ generally increases with the quantum number. Beyond the first minimum, $K(\nu,c)$ attains a large, almost constant, value. The small oscillation around the constant value is probably due to computational inaccuracies, and should be considered inconsequential. In the high ν range, the values of $K(\nu,c)$ are roughly the same as $M(\nu)$. This agreement serves as a check of

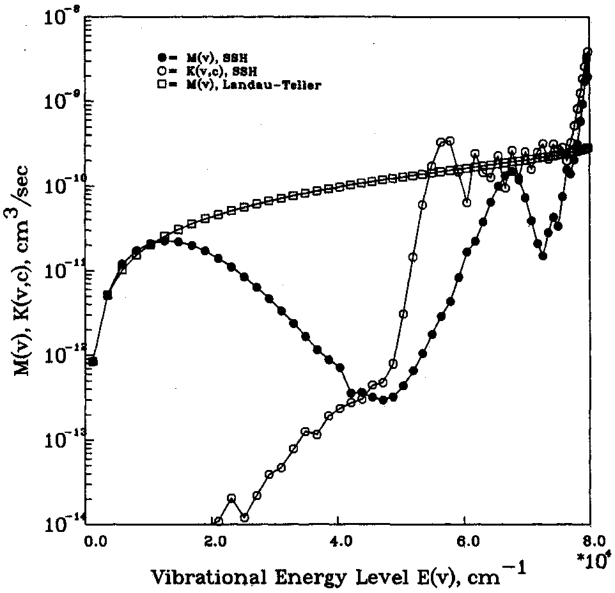

Fig. 1 Second moment of vibrational transition rate coefficients $M(\nu)$ and the bound-free transition rate coefficient $K(\nu,c)$, compared with $M(\nu)$ for the Landau-Teller model; $T = 4000$ K. The vibrational states of the colliding molecules are assumed to be populated according to a Boltzmann distribution corresponding to a vibrational temperature of 6000 K.

our calculation, since the bound-free transition can be considered as an analytical continuation of the bound-bound transition phenomenon. The fact that both $M(v)$ and $K(v,c)$ are large beyond the minimum point suggests that the states beyond the minimum point are likely to be in equilibrium with the free state.

Relaxation Behavior in Heating Case

The master equation [Eq. (17)] and the accompanying differential equation for $\rho_A \rho_B$ [Eq. (19)] were integrated in time to determine the normalized population ρ_v in all 57 vibrational states and all bulk flow properties as a function of time. As mentioned in the introduction, our calculations have been carried out for two cases, a heating and a cooling case. In the heating case, the gas was assumed to be in equilibrium initially at $T = 4000$ K. The number densities of N_2 molecules and N atoms under this equilibrium condition are 10^{17} and $2.19 - 10^{14}$ cm^{-3}, respectively. At time $t = 0$, the gas mixture is heated to $T = 8000$ K. Vibrational excitations and dissociations are allowed to occur at a constant-volume, isothermal condition thereafter. This process is qualitatively similar to that occurring behind a shock wave.

The calculated values of the normalized atomic number density N_A/N_x, average dissociation energy loss ϵ, average vibrational energy content e_v, and the vibrational temperature based on the ratio between the populations at $v = 4$ and $v = 0$ (T_{v1}) are plotted as functions of time in Fig. 2. The translational temperature T is also shown for comparison. As seen in the figure, the vibrational temperature equilibrates with the translational temperature $T = 8000$ K before significant dissociation begins. That is, the dissociation is dormant during the incubation period. This point agrees with the experimentally observed behavior behind a shock wave.[6] The increase of the average vibrational energy e_v is approximately proportional to the vibrational temperature. During the period in which significant dissociation occurs, that is, for $t > 10^{-4}$ s, the average energy loss due to the dissociation process, ϵ, is around 27,000 cm^{-1}, which is about 33% of the dissociation energy of the molecule. This ϵ value is considerably smaller than the $D_0/2$ value predicted by the CVDV theory[8] [see Eq. (4)] and, therefore, certainly smaller than the prediction of the preferential removal theory.[9]

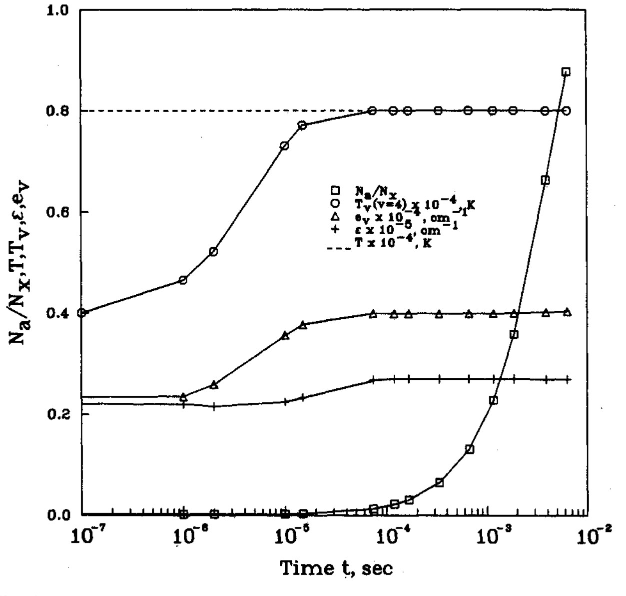

Fig. 2 Temporal variations of the bulk thermodynamic properties in a heating environment: the ratio of atom to molecule densities N_a/N_x, vibrational temperature characterizing the low vibrational states $T_v(v = 4)$, average vibrational energy per particle e_v, and the average vibrational energy removed in dissociation ϵ.

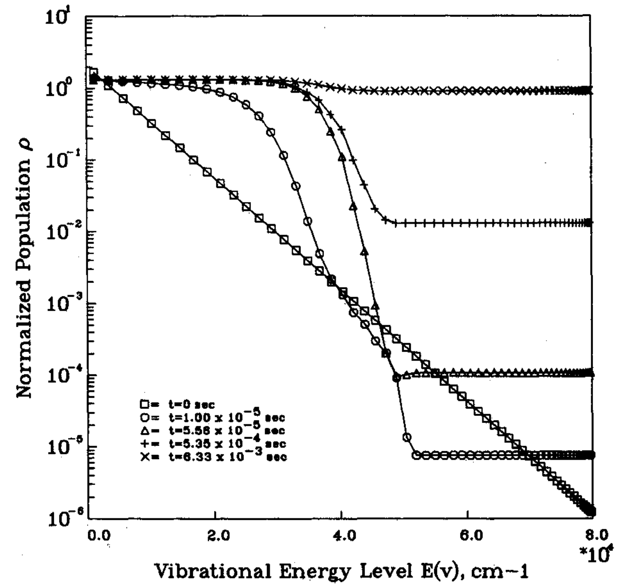

Fig. 3 Normalized vibrational population ρ_v as a function of time, in a heating environment.

The reason for such a small value for ϵ may be understood by studying Fig. 3, which shows the normalized population ρ_v at selected times. As the figure shows, the states below and above 42,000 cm^{-1}, the minimum point in the transition rate, relax differently. The lower states quickly reach a constant ρ value near unity. From the shape of the ρ values at $t = 10^{-5}$ s, we conclude that the approach to constant ρ is diffusion-like, as predicted by diffusion theory (see section on diffusion approximation). The fact that ρ is independent of v for the low-lying states implies that the vibrational temperature characterizing these low states, T_{v1}, is equal to T. Thus, one sees that the lower lying states equilibrate with T quickly. The upper level populations are nearly constant over the v range, but its value increases with time. The constant value of ρ at a given t means that the characteristic vibrational temperature defined among the upper levels themselves [in an equation similar to Eq. (22)] is also equal to T. Though not shown, the ρ value for $v = 56$ is nearly the same as $\rho_A \rho_B$ at all times. This means that the upper states are in equilibrium with the free state. The seeming discord between the lower and the upper states is a result of the minimum in transition rates seen in Fig. 1. The rate of increase of the upper state populations is dictated by the rate of the transition from the lower states across the bottleneck. Since the free state is in equilibrium with the upper states, the flow through the bottleneck also controls the rate of dissociation. The figure suggests that the vibrational temperature based on the ratio of the populations at $v = 56$ and $v = 0$ (T_{v3}) varies rather slowly, and is not equal to T until the free state reaches equilibrium. Overall, the distribution is quite different from a pure Boltzmann distribution. Hence, the early theoretical models, CVD,[7] CVDV,[8] and the preferential removal model,[9] can be considered invalid.

For further understanding of the relaxation process, the three vibrational temperatures defined in the section on vibrational temperatures have been plotted in Fig. 4. For the purpose of comparison, Fig. 4 also presents the vibrational temperature predicted by the Landau-Teller theory (calculated using the relaxation time formula of Millikan and White[1]). The three vibrational temperatures from the present study have different physical meanings: T_{v1} characterizes the lower states, T_{v3} characterizes the higher states, and T_{v2} characterizes the vibrational energy content. Figure 4 shows that the vibrational temperature based on the lower state populations, T_{v1}, varies approximately in accordance with the Landau-Teller theory.[2] In this temperature regime, Park's model for vibrational relaxation [Eq. (7)] is nearly identical to the

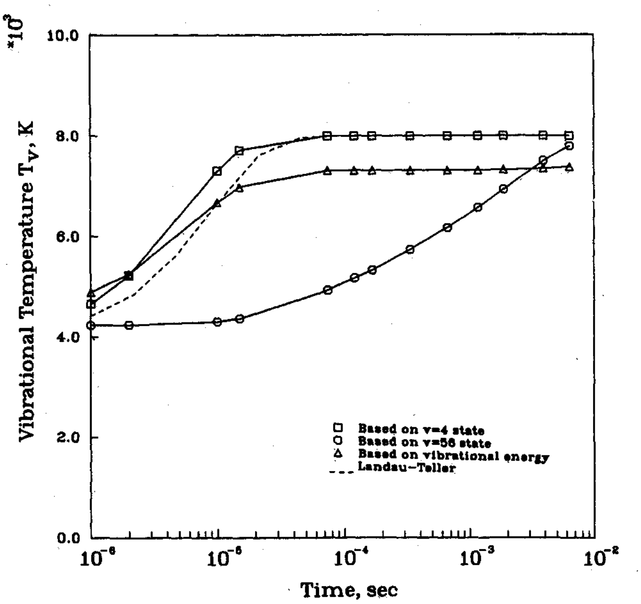

Fig. 4 Variations of the vibrational temperatures characterizing the low vibrational states ($v = 4$), high vibrational states ($v = 56$), and vibrational energy content, compared with the Landau-Teller prediction, in a heating environment.

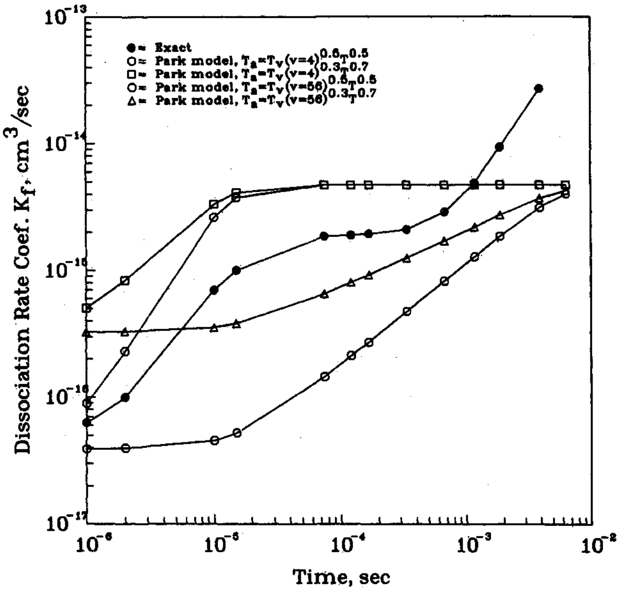

Fig. 5 Dissociation rate coefficient K_f calculated through the detailed time integration compared with Park's model [Eq. (6)] in a heating environment.

Landau-Teller model because the exponent s is nearly unity. Hence, we can say Park's model is also valid here. The vibrational temperature based on the vibrational energy, T_{v2}, varies with t at the same rate as T_{v1}. Note that T_{v2} does not approach 8000 K because it is calculated from e_v using a harmonic oscillator formula [Eq. (21)] that is inaccurate at 8000 K. The vibrational temperature based on the population ratio between $v = 56$ and $v = 0$, T_{v3}, varies very slowly with time. Its rate of change is between those of T_{v1} and atom density (see Fig. 2). From this, we surmise that T_{v3} is related to the dissociation phenomenon.

The forward (dissociation) rate K_f has been calculated for the heating case using Eq. (24). In Fig. 5, the calculated K_f values are compared with those obtained from Park's two-temperature rate model [Eq. (6)]. The parameters C and n in Eq. (6) are taken from Ref. 29: $C = 0.0116$ cm^{3}s^{-1} and $n = -1.6$. Two different vibrational temperatures—those characterizing the lower states (T_{v1}) and those characterizing the higher states (T_{v3})—are tested. Most of them agree with the exact calculation to within an order of magnitude. The best agreement with T_{v3} is obtained if the average temperature T_a is redefined as

$$T_a = T_v^{0.3}T^{0.7} \tag{36}$$

When T_{v3} is inserted for T_v in Eq. (36), the exact calculated K_f values are reproduced within a factor of about three over most of the relaxing range.

In Fig. 6, we test the validity of the diffusion approximation and the QSS assumption by comparing $\rho(v)$ with the exact values. The diffusion model results in the correct lower state population distribution. But it underestimates the rate of ap-

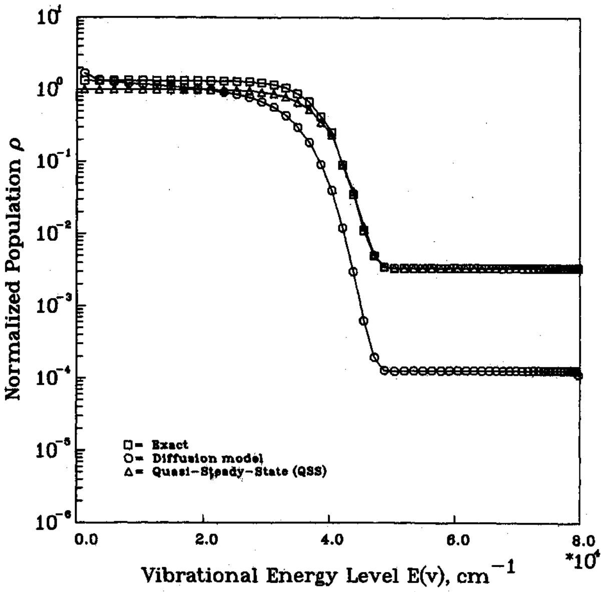

Fig. 6 Normalized vibrational population ρ_v calculated by the time integration compared with the diffusion approximation and the quasi-steady-state (QSS) approximation, in a heating environment, at time $t = 2.76 \times 10^{-4}$ s.

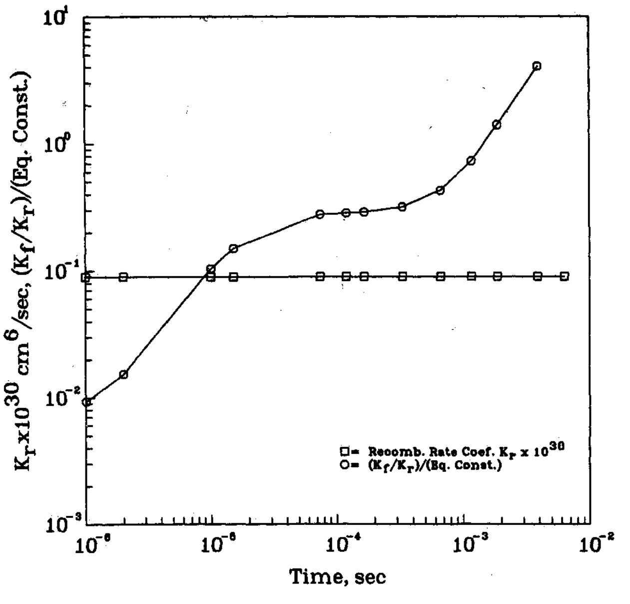

Fig. 7 Recombination rate coefficient K_r and the ratio between the forward and the reverse rates, divided by the equilibrium constant, for a heating environment. The equilibrium constant is calculated using $T_a = T_v(v = 4)^{0.3}T^{0.7}$.

proach of the upper states. The QSS assumption is seen to be fairly reasonable, at least at the particular value of t used.

In Fig. 7, the recombination rate K_r, calculated using Eq. (25), is shown in two different forms. The absolute value of K_r is constant, indicating that it is a function of T alone and is unaffected by the vibrational distribution. When the ratio of the forward rate coefficient K_f is divided by K_r and by the equilibrium constant $N_{AE}N_{BE}/N_x$, the result will be unity only if T is the controlling temperature. Under the two-temperature environment, it will be different from unity. Figure 7 shows this ratio. Here, the equilibrium constant is obtained using $T_a = T_{vl}^{0.3}T^{0.7}$. As seen here, the ratio deviates from unity by only an order of magnitude over most of the range of interest, a small deviation considering how widely it can vary.

Relaxation Behavior in Cooling Case

The foregoing calculations are repeated for a cooling case. In this case, the gas is assumed to be in equilibrium in the beginning, at $T = 6000$ K. The number densities of N_2 and N are 10^{17} and 2.35×10^{16} cm^{-3}, respectively, in the beginning. At time $t = 0$, the gas is cooled to 4000 K with an imaginary method, and is held at a constant-volume, isothermal condition thereafter. This process is qualitatively similar to that occurring in an expanded nozzle. The bulk properties, N_a/N_x, ϵ, e_v, T_v, characterizing the lower states, and T for this case, are plotted in Fig. 8 as functions of time. As expected, a recombination occurs in this case, and the atomic number density decreases with time. Interestingly, the vibrational temperature overshoots, that is, increases rapidly initially, achieving a maximum of over 14,000 K in about 10 μs before it decreases. Even at 20 μs, it is still over 10,000 K. The vibrational energy content e_v undergoes a mild overshoot also. The average dissociation energy loss ϵ approaches a value of 22,000 cm^{-1}, which is about 27% of the dissociation energy of the molecule, again much smaller than predicted previously.[8,9]

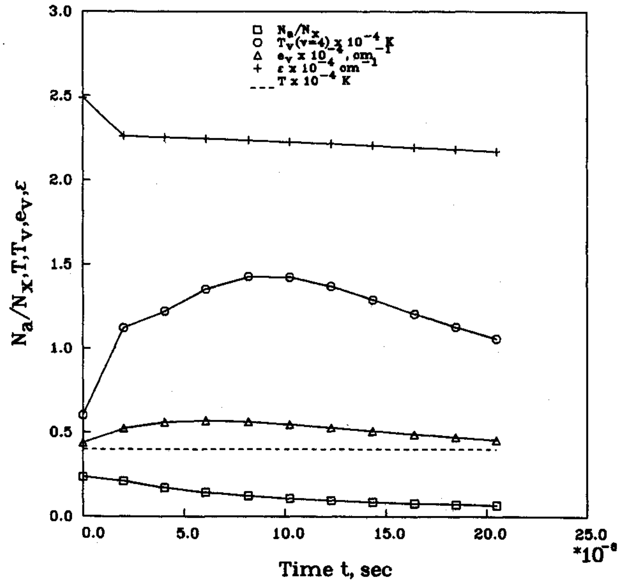

Fig. 8 Temporal variation in bulk thermodynamic properties in a cooling environment: the ratio of atom-to-molecule densities N_a/N_x, vibrational temperature characterizing the low vibrational states $T_v(v = 4)$, average vibrational energy per particle e_v, and the average vibrational energy removed in dissociation ϵ.

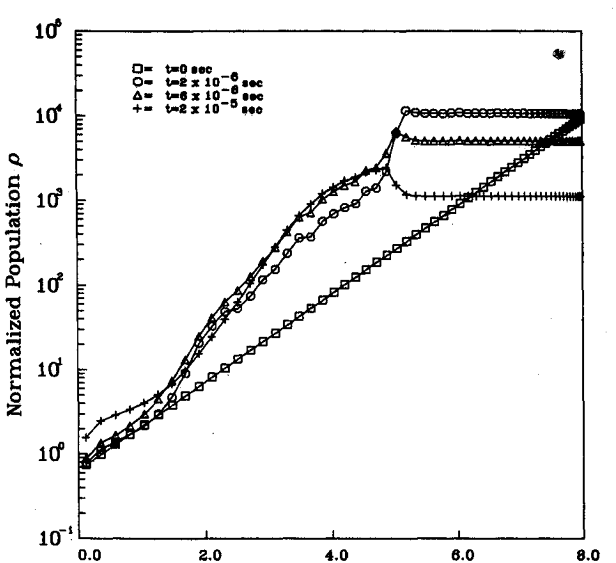

Fig. 9 Normalized vibrational population ρ_v as a function of time, in a cooling environment.

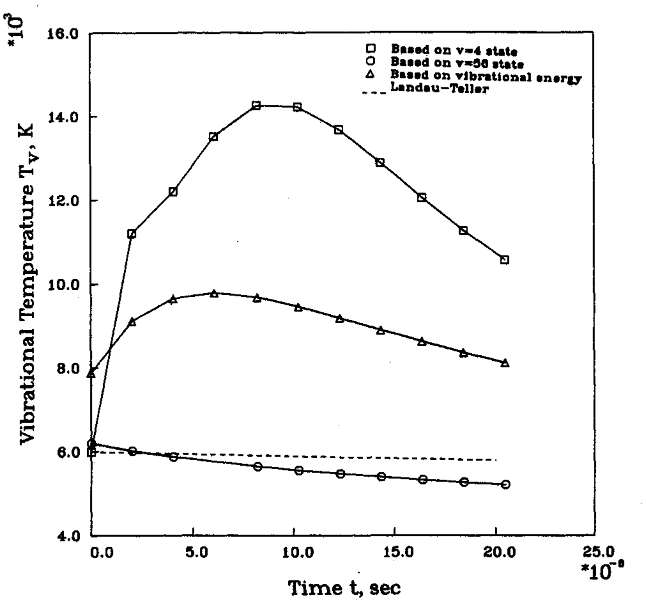

Fig. 10 Variations of the vibrational temperatures characterizing the low vibrational states ($v = 4$), high vibrational states ($v = 56$), and vibrational energy content, compared with the Landau-Teller prediction, in a cooling environment.

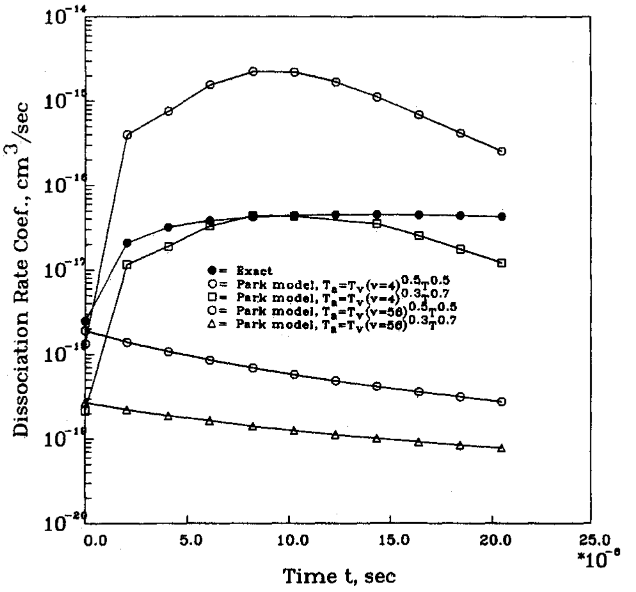

Fig. 11 Dissociation rate coefficient K_f calculated through the detailed time integration compared with Park's model [Eq. (6)] in a cooling environment.

Figure 9 depicts the time history of ρ for the cooling case. In this case, the upper states reach equilibrium with the free state quickly, and the lower levels tend to remain out of equilibrium longer throughout the time range shown. The shape of the distribution of ρ for the lower states hardly varies at all during this time period.

The three vibrational temperatures, those characterizing the lower states (T_{v1}), upper states (T_{v3}), and the vibrational energy (T_{v2}), are plotted in Fig. 10 for the cooling case and are compared with the Landau-Teller values. The overshoot occurs only for T_{v1} and T_{v3}. The calculated vibrational temperatures totally disagree with the Landau-Teller theory, and, therefore, by implication, with Park's model [Eq. (7)]. This point agrees with the previous theoretical[11-15] and experimental[22] results. Only the vibrational temperature characterizing the vibrational energy resembles that of the Landau-Teller model, if at all.

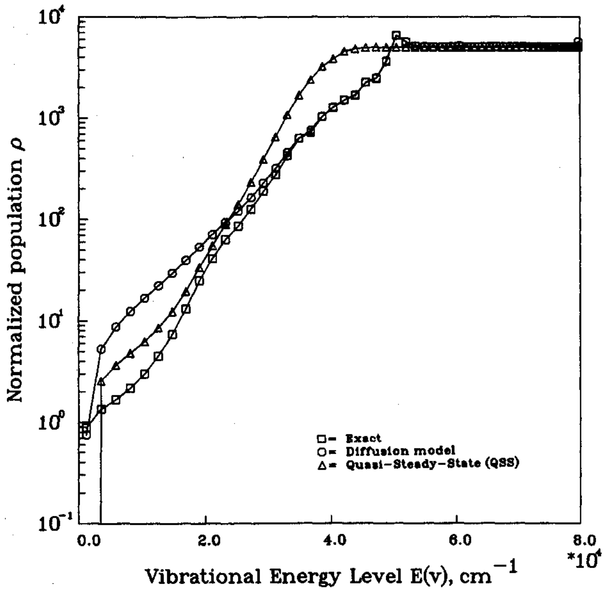

Fig. 12 Normalized vibrational population ρ_v calculated by the time integration compared with the diffusion approximation and the QSS approximation, in a cooling environment, at time $t = 6 \times 10^{-6}$ s.

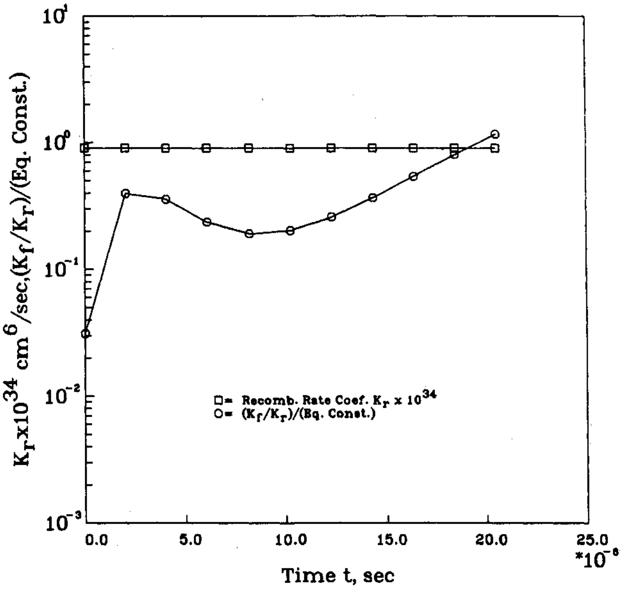

Fig. 13 Recombination rate coefficient K_r and the ratio between the forward and reverse rates, divided by the equilibrium constant, for a cooling environment. The equilibrium constant is calculated using $T_a = T_v(v = 4)^{0.3}T^{0.7}$.

The dissociation rate coefficient K_f is calculated using Eq. (29) for the cooling case, and the results are shown in Fig. 11 to compare with Park's model. In this case, the closest agreement between the exact calculation and Park's model is obtained with $T_a = T_{v1}^{0.3}T^{0.7}$. The agreement is quite close in this case.

Figure 12 compares the ρ_v distribution between the exact solution and the diffusion formulation, and the solution obtained assuming a QSS condition. All three are fairly similar, indicating the validity of the diffusion model and the assumption of the QSS condition, at least for the time point chosen. An anomaly exists for the QSS value at $v = 0$, where ρ_v is negative. This is caused by the inaccuracy in the model, and is a direct consequence of the mass conservation requirement [Eq (20)].

In Fig. 13, the recombination rate coefficient K_r, and the ratio K_f/K_r normalized by the equilibrium constant, are shown for the cooling case. As before, the equilibrium constant is determined using $T_a = T_{v1}^{0.3}T^{0.7}$. As seen here, K_r is a function only of T. The calculated ratio deviates from the ideal value of unity only within an order of magnitude, except in the very beginning where the gas is severely out of equilibrium.

Discussions

The most striking feature in the present calculation is the deep minimum in the vibrational transition rates (see Fig. 1). This minimum acts as a bottleneck in the transfer of vibrational energies between the lower and the upper vibrational states, leading to a bimodal distribution of the vibrational state populations. For the heating case, the lower states relax according to the Landau-Teller equation. But the upper states relax at a much slower rate due to the bottleneck. Since the percentage of dissociation is determined by the upper state population, the bottleneck effectively controls the net rate of dissociation. For the cooling case, the distribution of the lower states cannot be determined by Landau-Teller or Park's model at all. The vibrational population distribution departs severely from the Boltzmann distribution in both heating and cooling cases. This invalidates CVD and CVDV models proposed by the early investigators.

For both the heating and cooling environments, the dissociation rate coefficient can be approximated to within an order of magnitude by Park's two-temperature model, using a geometrically average temperature. The accuracy can be improved somewhat if the average temperature is redefined with a greater weight on T, at least for the temperature range studied. The recombination rate coefficient is independent of the nonequilibrium population distribution of vibrational states. The ratio of the forward and reverse rates is roughly (to within an order of magnitude) equal to the equilibrium constant based on the average temperature.

The average vibrational energy removed by the dissociation process is ≈ 30% of the dissociation energy (33% for heating case and 27% for cooling case), which is much smaller than predicted by the CVD and CVDV models. This is a consequence of the severe departure of the vibrational distribution from the Boltzmann distribution.

It is important to consider how much of the bottleneck phenomenon may be due to the approximations used in the calculations of the transition rates. Two approximations have been used here: the use of the SSH theory to determine the transition rates and the neglect of rotational energy transfer. The simplified interaction potential used in the SSH theory, as well as the assumption of collinear collisions, may produce transition rates that are skewed towards particular transitions and, thus, accentuate the bottleneck phenomenon. The neglect of rotational energy transfer may also produce error in the same direction. Here the rotational mode acts both as an energy reservoir and sink. As mentioned in the introduction, the neglect of the rotational energy transfer should not cause significant changes in the resonant V-V transitions, but the effect on nonresonant V-V and V-T transitions will be stronger. In a recent study of the H_2-H_2 system using a quasi-classical trajectory technique and including V-R-T transfer, Sharma and Schwenke[5] did not find a bottleneck for that system. However, the rotational energy transfer in H_2 is a good energy sink because of the large rotational constant. Whether their result is particular to the H_2-H_2 system remains to be tested. An additional effect of rotation is the change of the shape of the vibrational potential curve. In the temperature range of 4000–8000 K considered here, the majority of the molecules are at a rotational quantum number of the order of 50. Thus, the effective potential is shifted upwards, reducing the effective dissociation energy and introducing a rotational barrier. The transition rates $K(v,v')$, $M(v)$, and $K(v,c)$ will be affected quantitatively, though their general behavior will remain the same. We do not believe that this aspect of rotational motion will have strong effects on the bottleneck behavior.

A more elaborate study of the bottleneck behavior, using either classical or semiclassical methods and incorporating rotational degrees of freedom, requires the knowledge of a full potential energy surface. As pointed out in the introduction, this is not yet available for the N_2-N_2 system. Furthermore, the rotational manifold of N_2 is very dense, and a study of the coupled vibration-dissociation problem, including rotation, will be a very costly endeavor. Thus, we do not consider it worthwile to carry out such a study on more approximate surfaces, such as used by Billing in the HF-HF system.[31] However, ab initio calculations on the N_2-N_2 surface are underway, and we plan to return to this problem in the future.

Finally, the present work assumes that the vibrational transitions occur only through collisions with molecules. This assumption is valid only when the degree of dissociation is low. When the degree of dissociation is significant, collisions with atoms contribute significantly to the overall transition rates. The rates of such transitions do not have the bottleneck phenomena seen in molecules. Therefore, most of the phenomena shown in the present work will be moderated by the presence of the atoms. Under those circumstances, the present work will exaggerate the effect of the molecule-molecule collisions in vibrational transitions.

Toward the end of this discussion it should be pointed out that this study is only a first step in a process that will lead to a better understanding of the coupling between vibration and dissociation. Use of empirical models during this process to describe the phenomena will be only a stepping-stone towards the final goal of a good physical model.

Conclusions

The vibrational excitation rates have a minimum at a midpoint of the bound vibrational levels. This causes a bottleneck in the transfer of vibrational energy between the lower and the upper states and in dissociation. In a heating environment, the lower vibrational states relax in accordance with the Landau-Teller equation, but the upper states relax much more slowly. In a cooling environment, the upper states are in equilibrium with the free state, but the lower states are severely out of equilibrium. The relaxation behavior of the lower vibrational states cannot be described by the Landau-Teller model or its variation, Park's model. Dissociation rate coefficient, for the cases under study, is determined using Park's two-temperature model to within an order of magnitude, the accuracy being improved if the translational temperature is weighed more heavily in the expression for the average temperature used in the model. The average vibrational energy removed by dissociation is about 30% of the dissociation energy.

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