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Technical Notes

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Nonequilibrium Vibration–Dissociation Properties of Diatomic Molecule Behind Shock Waves

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Nomenclature

a_1, a_2, a_3 = the coefficients in Eq. (7)
E = translational energy
e_V = average vibrational energy
F = function of vibrational population distribution
k = Boltzmann constant
k_f = dissociation rate coefficient
N = number density of the whole interesting system
N_a = number densities of N_2 atom
N_x = number densities of N molecule
Q_V = vibrational partition function
T = translational temperature
T_a = average temperature
T_V = vibrational temperature
T_0 = initial environmental temperature
t = time
ε = energy of the vibrational level
ε_D = dissociation energy of the studied electronic state
ρ = normalized vibrational population
μ = reduced mass
τ = vibrational relaxation time

I. Introduction

IT is necessary to study phenomena and mechanisms in conditions of high temperature, high velocity, and high enthalpy, because more problems appear along with the development of aeronautics and astronautics technique, plasma technique, and hypersonic combustion technique [1]. In those conditions, the energy levels of gas are excited with chemical reactions such as dissociation, ionization, and recombination. Therefore, the chemical reacting flow with several components is generated. Because of different reactions with different relaxation times [2,3], the gas is in the thermochemical nonequilibrium state, and the distribution of inner energy cannot be described by a single temperature. Therefore, classical equilibrious theory is unconformable to obtain the energy levels population distribution, which makes it difficult to describe various microcosmic processes. The population distribution of vibrational levels has an obvious impact on chemical reactions and characters of flow fields. So investigating the feature of vibrational levels population distribution from the structure of molecule and the energy transport mechanism is significant for understanding the nonequilibrium processes [4–7], and an appropriate thermophysical model describing the vibration–dissociation processes and a reasonable definition of vibrational temperature are needed.

Early studies on this topic focused on the relaxation rates. The Landau–Teller model [8]

$$\frac{\partial e_V(T_V)}{\partial t} = \frac{e_{VE}(T) - e_V(T_V)}{\tau} \tag{1}$$

is advanced, where e_V is average vibrational energy per particle, t and τ are time and vibrational relaxation time, respectively, and T_V and T are vibrational temperature and translational temperature, respectively. Millikan and White reproduced the vibrational relaxation times in Landau–Teller formulation by an empirical formula [9]. Park modified the relaxation times at higher temperature range [6]. Schwartz, Slawsky, and Herzfeld developed the SSH theory, which allows for vibrational transitions occurring between nonneighboring levels [10]. Landrum and Candler corrected the SSH theory by considering more physical processes impacting on the vibration–dissociation coupling [4]. Hammerling et al. were the first researchers interested in dissociation rate [11]. They considered the simplest possible gas model and advanced coupled-vibration–dissociation (CVD) model. Marrone and Treanor examined the coupling process further [12] and advanced coupled-vibration–dissociation-vibration (CVDV) model. But the reaction rates predicted by these models were still faster than the observed rates. So Park proposed a semiempirical two-temperature model [6] to determine the dissociation rates by average temperatures $T_a = \sqrt{TT_V}$ and $T_a = T_V^{0.3}T^{0.7}$. The rate equations adopted the average temperatures were used widely [4–6].

More elaborate methods such as classical, semiclassical, quantal method, and direct simulation Monte Carlo method for solving the vibration–dissociation problem also are available [3]. However, all these methods require the knowledge of a full potential energy surface of the nuclear motion, which is not presently available easily. Thus, building an empirical or semiempirical model of nonequilibrium vibrational relaxation through some reasonable analyses and simplifications is a feasible method for engineering needs.

II. Analyses and Modeling

The energy difference between neighboring vibrational levels decreases with the vibrational quantum number increasing, because the practical vibration of diatomic molecules is inharmonious. The harmonicity is better in the lower vibrational levels whereas the energy difference is smaller in the higher vibrational levels. For this reason, in the heating process, vibration–vibration (V–V) energy exchange is rapid between the lower levels of molecules and translation–vibration (T–V) energy exchange is also rapid between the higher levels and between the higher levels and free levels

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[13,14]. Therefore, the lower and higher vibrational levels can, respectively, reach quasiequilibrium quickly. While from the lower vibrational levels to the higher ones, the excitation process of molecule needs to cover many T–V and V–V energy exchange processes between the middle vibrational levels, that is, the middle vibrational levels are the bridge of relaxation between the lower and higher vibrational levels. However, as some experiments and theories [15–17] revealed, the relaxation of middle vibrational levels is slower than that of lower and higher levels, because neither V–V nor T–V energy exchange is efficient due to the inharmonious vibration and large energy gaps between middle vibrational levels. The slower relaxation of middle levels delays the energy transfer from lower to higher levels. It is one of the most important reasons of non-Boltzmann distribution in vibrational levels. All above shows that the differences of vibrational relaxing rate and nonequilibrium distribution of vibrational levels are induced by the special energy level structure and collisional mechanism of diatomic molecules. Experiments of diatomic molecule's dissociation, such as N_2, revealed that a short time must be spent before dissociation in the heating case [18]. The length of this time period, commonly referred to as the incubation period, was found to be approximately equal to the vibrational relaxation time.

So the vibrationally excitation and dissociation of diatomic molecules in heating case can be divided into two stages: The first one is the incubation period, in which stage a quasiequilibrium state is quickly reached independently in the lower and higher vibrational levels through V–V energy exchange and T–V energy exchange, respectively, whereas the midlevels relax slowly because of their inefficient energy exchange. Therefore, the whole vibrational population distribution is mainly controlled by the lower and higher levels. However, in this stage, the number of molecules in higher levels that can easily dissociate is very small, and the dissociation probability of molecules in lower levels by direct collisions is also very small, and so the dissociation in this stage is very slight. After the incubation period is the second stage. The energy accumulation for dissociation through various energy exchanging also exists in this stage. Molecules in higher vibrational levels partially dissociating continuously causes a relative population density difference between vibrational levels, which is a generalized force leading to a redistribution of all vibrational levels and promoting relaxation of middle levels. As a result, the molecules in lower vibrational levels are excited to the higher levels through many middle levels continuously. So that, in this stage the energy relaxation process of the middle levels is the primary restricting process of the whole vibration–dissociation system, that is, the dissociation rate and equilibrium degree of the vibration system are controlled by the population distribution of the middle vibrational levels, and its variation can most closely describe the relaxing rule from nonequilibrium to equilibrium and the degree of nonequilibrium departing from equilibrium.

The relaxation processes can be denoted by the vibrational temperature varying from initial temperature T_0 to environmental temperature T. We modify the commonly used Hammerling hypothesis [11] and redefine the vibration temperature by the distribution of lower, middle, and higher vibrational levels, respectively, as follows:

$$T_{Vi} = -\frac{N(\varepsilon_i)}{k[\partial N(\varepsilon)/\partial\varepsilon]_{\varepsilon_i}} \qquad i=1, \qquad \varepsilon_i = 0; \qquad i=2 \qquad \varepsilon_i = \frac{\varepsilon_D}{2}; \qquad i=3, \qquad \varepsilon_i = \varepsilon_D \tag{2}$$

where ε is the energy of the vibrational level, and ε_D is the dissociation energy. The vibrational temperature of the incubation period $T_{V,\mathrm{inc}}$ is represented by the vibrational temperature defined by the lower and higher vibrational levels:

$$T_{V1} = T_{V3} = T_{V,\mathrm{inc}} \tag{3}$$

In the incubation period, the relaxation process is indicated by $T_{V,\mathrm{inc}}$ varying from T_0 to T, and the vibrational temperature T_{V2} defined by midlevels keeps the initial temperature T_0:

$$T_{V2} = T_0 \tag{4}$$

After the incubation period, T_{V1} and T_{V3} keep environment temperature T, and T_{V2} representing the vibrational temperature $T_{V,\mathrm{dis}}$ varies from T_0 to T, which indicates the relaxation process in this stage:

$$T_{V1} = T_{V3} = T \tag{5}$$

$$T_{V2} = T_{V,\mathrm{dis}} \tag{6}$$

Vibrational levels population distribution is according to Boltzmann rule in equilibrium state, and nonequilibrium state is a departure from normal equilibrium state, and so we construct the exponential form of the nonequilibrium vibrational levels population distribution which is similar to Boltzmann distribution:

$$N(\varepsilon) = \frac{N}{Q_V}\prod_{i=1}^{3}\exp(a_i\varepsilon^{\gamma_i}) \tag{7}$$

where N, $N(\varepsilon)$ are the molecular number density of the whole interested system and that of the ε vibrational level respectively; Q_V is the vibrational partition function, γ_i are empirically assumed to be 1, 1.5, and 2, respectively, and a_i are different functions of T_0, T, $T_{V,\mathrm{inc}}$, and $T_{V,\mathrm{dis}}$ in different stage.

The a_i during the incubation period can be worked out by replacing Eqs. (2–4) into Eq. (7):

$$a_1 = -\frac{1}{kT_{V,\mathrm{inc}}} \tag{8a}$$

$$a_2 = \frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T_{V,\mathrm{inc}}} - \frac{1}{T_0}\right) \tag{8b}$$

$$a_3 = \frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_0} - \frac{1}{T_{V,\mathrm{inc}}}\right) \tag{8c}$$

So

$$N(\varepsilon) = \frac{N}{Q_V}\exp\left\{-\frac{\varepsilon}{kT_{V,\mathrm{inc}}} + \frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T_{V,\mathrm{inc}}} - \frac{1}{T_0}\right)\varepsilon^{1.5} + \frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_0} - \frac{1}{T_{V,\mathrm{inc}}}\right)\varepsilon^2\right\} \tag{9}$$

The a_i after the incubation period can be worked out by replacing Eqs. (2), (5), and (6) into Eq. (7):

$$a_1 = -\frac{1}{kT} \tag{10a}$$

$$a_2 = \frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T} - \frac{1}{T_{V,\mathrm{dis}}}\right) \tag{10b}$$

$$a_3 = \frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_{V,\mathrm{dis}}} - \frac{1}{T}\right) \tag{10c}$$

So

$$N(\varepsilon) = \frac{N}{Q_V}\exp\left\{-\frac{\varepsilon}{kT} + \frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T} - \frac{1}{T_{V,\mathrm{dis}}}\right)\varepsilon^{1.5} + \frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_{V,\mathrm{dis}}} - \frac{1}{T}\right)\varepsilon^2\right\} \tag{11}$$

Equations (9) and (11) are new functions of diatomic molecular vibrational levels population distribution in and after incubation period, respectively, which correlate vibrational temperature, initial temperature, and environmental temperature to simulate the whole relaxing processes in thermodynamic nonequilibrium states. So the model advanced in this paper is called the correlated multi-temperature coupled-vibration-dissociation model (CMTCVD).

The normalized population can be got through dividing functions of population distribution by the equilibrium population distribution function:

$$\rho(\varepsilon) = \frac{N(\varepsilon)}{N_E(\varepsilon)} \tag{12}$$

III. Results and Comparisons

To compare the CMTCVD model with other methods mentioned in [4,5], a heating case in nonequilibrium is taken into consideration. To obtain a better comparison, Landau–Teller equation [Eq. (1)] modified by Park [6,19–21] is used to correlate vibrational temperature with time. The gas mixture made up of N_2 and N is assumed to initially be in equilibrium at $T_0 = 4000$ K, and instantaneously heated to 8000 K. Vibrational excitation and dissociation are specified to occur at a constant volume and in isothermal condition. This process is qualitatively similar to that occurring behind a shock wave.

In Figs. 1 and 2, the normalized vibrational populations $\rho(\varepsilon)$ in different relaxing stages are compared with [4,5]. The SSH method is used in [5]. It can be seen in Fig. 2 that there are an obvious bottleneck in [5] because it only takes molecule–molecule collisions into account and molecule is thought rotationless. These assumptions are suitable for slight dissociation only and lead to the normalized vibrational population in higher levels smaller. The assumptions also lead to the time relaxing to equilibrium longer. More physical processes such as molecule–atom collisions are considered in [4], and so its results vary slightly and have no bottleneck at all. The model in this paper can be compared with [4] well except at the highest levels. The shapes of this model are similar to [5], but have no obvious bottleneck.

Variations of vibrational temperatures characterizing the low vibrational levels, high vibrational levels, and vibrational energy in [5] and the vibrational temperatures defined by the middle vibrational levels and by lower and higher vibrational levels in this model are compared in Fig. 3. The ratio of atom to molecule densities N_a/N_x which represents the degree of dissociation in a heating environment varying with time, is also shown for comparison. Significant dissociation does not occur until 10^{-4} seconds, shown in the N_a/N_x curve. The vibrational temperature T_{VL} characterizing low levels in [5] rises earlier, and relaxes to the environment temperature before significant dissociation. It illuminates that the lower vibrational levels relax to equilibrium faster, which is the same as the analyses above. The vibrational temperature T_{VH} characterizing high levels in [5] rises earlier too, but more gently, and reaches the environment temperature till the end of the dissociation. It also illuminates that the higher vibrational levels relax to quasiequilibrium earlier. The vibrational temperature $T_{V,\mathrm{inc}}$ defined in this paper varies with T_{VL} synchronously but more sharply because it is controlled by both lower and higher vibrational levels. The vibrational temperature $T_{V,\mathrm{dis}}$ advanced in this paper defined by middle levels rises later, but relaxes to environment temperature faster than T_{VH}. The $T_{V,\mathrm{dis}}$ varies with N_a/N_x synchronously. It maintains the initial temperature before the significant dissociation, and its curve has the same shape with T_{VL}. It shows that the relaxation of the middle levels and dissociation of the molecules are synchronous. The characteristics of different vibrational temperatures are consistent with analyses mentioned above. However, the vibrational temperature T_{VE} in [5] defined by vibrational energy does not reach the environment temperature ultimately, which can be explained from Fig. 4.

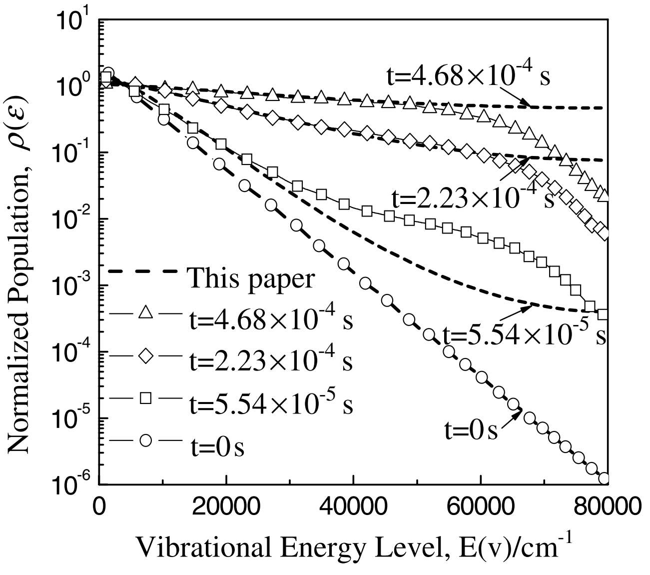

Fig. 1 Normalized vibrational population calculated by this model and [4] in a heating environment at $T = 8000$ K.

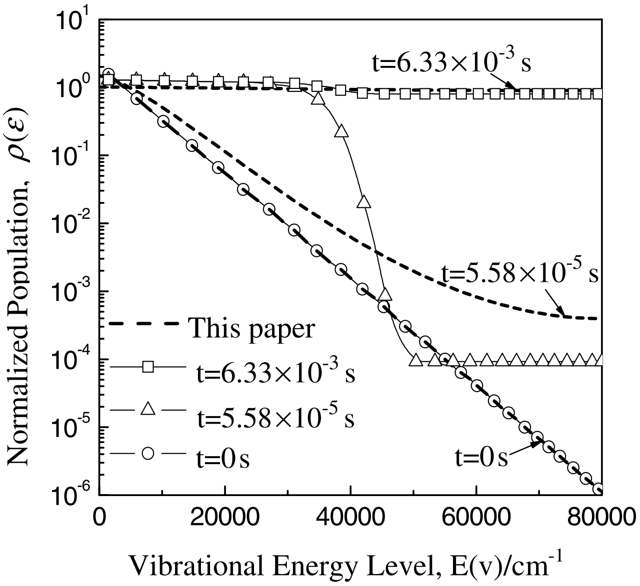

Fig. 2 Normalized vibrational population calculated by this model and [5] in a heating environment at $T = 8000$ K.

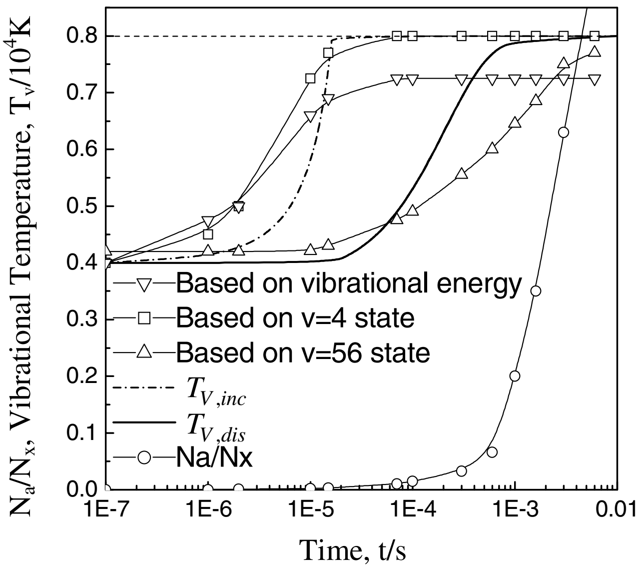

Fig. 3 Temporal variations of various vibrational temperatures and the ratio of atom to molecule densities in a heating environment.

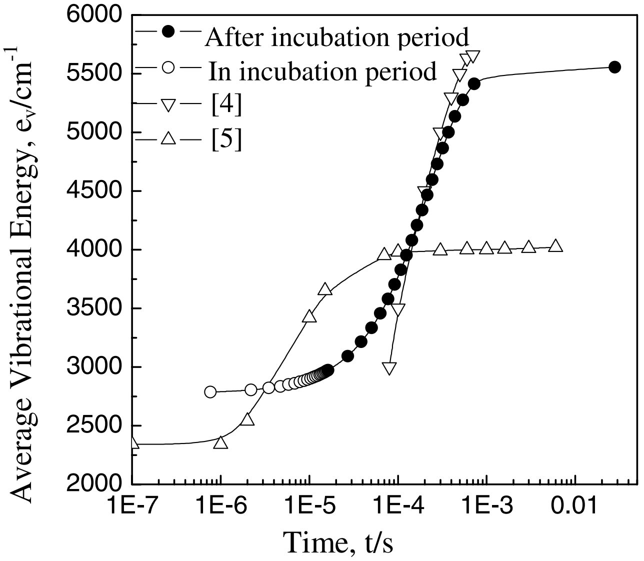

Fig. 4 Temporal variations of the average vibrational energy per particle e_V.

The average vibrational energy per particle e_V calculated by this model is compared with [4,5] in Fig. 4. The e_{V1} calculated in [5] varies earlier and more gently. The e_{V2} calculated in [4] varies later and has a higher scope. In this model, the e_{V3} and e_{V4} calculated, respectively, in and after the incubation period smoothly combine to form an integrated curve of e_V. Its shape is similar to e_{V1} and its varying scope is the same with e_{V2}. As [6] illuminating, some physical processes impacted on the vibration–dissociation coupling were not included in [5] leading to the unsatisfactory population distribution. So the e_V and T_{VE} calculated in [5] through the population distribution depart from the real case.

Dissociation rate coefficient of diatomic molecule can be derived from the refined collision theory [22,23] using the vibrational population distribution of CMTCVD model in nonequilibrium:

$$k_f = \iint_{E+\varepsilon>\varepsilon_D} Z(E)F(\varepsilon)\,\mathrm{d}E\,\mathrm{d}\varepsilon \tag{13}$$

$$Z(E)\,\mathrm{d}E = Z_{AB}\exp(-E/kT)\,\mathrm{d}E/kT \tag{14}$$

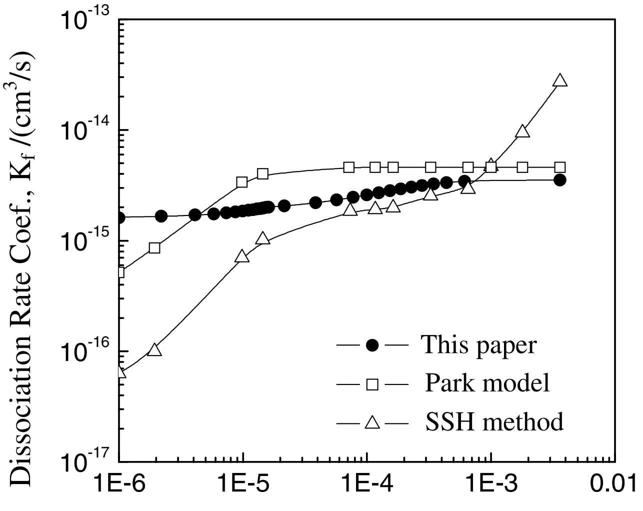

Fig. 5 Dissociation rate coefficient K_f for the vibrational relaxation of N_2.

$$Z_{AB} = \frac{\pi d_{AB}^2}{2}\left(\frac{8kT}{\pi\mu}\right)^{1/2} \tag{15}$$

$$F(\varepsilon)\,\mathrm{d}\varepsilon = \frac{\prod_{i=1}^{3}\exp\left(a_i\varepsilon^{\gamma_i}\right)}{Q_V}\,\mathrm{d}\varepsilon \tag{16}$$

where E is the translational energy, $F(\varepsilon)\,\mathrm{d}\varepsilon$ is the function of vibrational population distribution, and μ is the reduced mass of colliding particles. a_i and γ_i are determined in and after the incubation period, respectively, as above. The dissociation rate coefficients calculated by Eq. (13) in this paper, and by Park's average temperature model and by SSH method in [5] are compared in Fig. 5. It shows that the rate coefficient in this paper agree well with other two rate coefficients especially after the incubation period.

IV. Conclusion

Based on the idea of the multitemperature model, the characteristic information of distribution of vibrational levels and the vibration–dissociation coupling characteristics of diatomic molecules in nonequilibrium relaxing process are investigated and analyzed. The vibrational temperature $T_{V,\mathrm{inc}}$ and $T_{V,\mathrm{dis}}$ are redefined by lower and higher vibrational levels and by middle vibrational levels, which controls the relaxing process in and after the incubation period, respectively. Then a new distribution model (CMTCVD) of molecular vibrational levels population distribution correlated vibrational temperature, initial temperature and translational temperature is advanced. The simulation results of the nonequilibrium nitrogen species relaxation process behind a shock wave show that this model can exactly predict the incubation period and the relaxation time characteristics of average vibrational energy and vibrational temperature. It is also found that the relative population density difference between the vibrational levels, which caused by the partial dissociation of the higher levels, could lead to the redistribution of all vibrational levels, and molecule-atom collisions have a significant impact on vibrational excitation and dissociation.

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