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Master Equation Study and Nonequilibrium Chemical Reactions for $H + H_2$ and $He + H_2$

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Complete sets of state-to-state cross sections and rate coefficients for the transition of 348 (v,j) rotational and vibrational states of the electronic ground state of the hydrogen molecule for H and He collisions were evaluated using quasi-classical trajectory calculations based on the latest potential energy surfaces. The state-to-state cross sections for the rotational and vibrational energy transitions were validated by comparing the results with those of quantum mechanical calculations and other quasi-classical trajectory calculations. The state-to-state rate coefficients were fed into a master equation, and the rotational and vibrational number densities were numerically evaluated. In this master equation study, relaxation of the rotational and vibrational temperatures, number density relaxation, and average rotational and vibrational energy losses due to dissociation were examined in heating and cooling environments. From the results of the state-to-state rate coefficients and the master equation study, dissociation and recombination rate coefficients were calculated under a quasi-steady-state assumption for a temperature range between 1000 and 32,000 K. These rate coefficients were validated by comparing the results with existing experiments. The reaction rates expressed by a two-temperature model based on translational and vibrational temperatures were also proposed upon collision with H and He, respectively.

Nomenclature

$E(j)$ = energy of rotational level j, erg
E_{tr} = relative translational energy, erg
$E(v)$ = energy of vibrational level v, erg
E_0 = threshold energy, erg
e_r = average rotational energy, erg
e_v = average vibrational energy, erg
j = rotational energy level
K_f = dissociation rate coefficients, $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$
$K_{f\text{-two}}$ = dissociation rate coefficients of two-temperature model, $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$
K_r = recombination rate coefficients, $\mathrm{cm}^{-6}\ \mathrm{s}^{-1}$
$K(v, j; c)$ = bound–free transition rate coefficient for v, $j \to$ free, $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$
$K(v, j; v', j')$ = bound–bound transition rate coefficient for v, $j \to v'$, j', $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$
k = Boltzmann constant, erg/K
N_H = number density of atomic hydrogen, cm^{-3}
N_{H_2} = number density of molecular hydrogen, cm^{-3}
N_M = number density of collision partner, cm^{-3}
$N(v, j)$ = number density of (v, j) state of molecular hydrogen, cm^{-3}
Q_m = molecular partition function
$Q_{v,j}$ = partition function for (v, j) state
T = translational temperature, K
T_a = geometrical mean of temperature, K
T_v = vibrational temperature, K
t = time, s
t_c = elastic collision time, s
v = vibrational energy level
z = collision number
ε_r = average rotational energy loss, erg
ε_v = average vibrational energy loss, erg
η = viscosity, poise
ρ_H = normalized number density of atomic hydrogen
$\rho_{v,j}$ = normalized number density of molecular hydrogen for (v, j) state
$\sigma(v, j; v, j; E_{\mathrm{tr}})$ = state-to-state cross section for $v, j \to v', j'$, $\mathrm{Å}^2$
τ_L = vibrational relaxation time, s
$\Omega^{(2,2)}$ = viscosity type of collision integral
μ = reduced mass, g

Subscript

Eq = equilibrium state

I. Introduction

STATE-TO-STATE energy transfer processes are known to determine the macroscopic behavior of nonequilibrium phenomena of rotational and vibration energy relaxations and chemical reaction. For heavy particles, such as N_2, O_2, and NO, the state-to-state rate coefficients have been studied using analytic models, such as the Schwartz–Slawsky–Herzfeld theory [1], the Rapp–Englander-Gorden theory [2], the Sharma–Brau theory [3], and the forced harmonic oscillator model [4]. In these studies, vibration-translation transition or vibration-vibration-translation transition was considered, but rotation-vibration-translation (RVT) transition was ignored, because rotational energy relaxation occurs at a much faster rate than vibrational energy relaxation. However, in describing the nonequilibrium behavior of hydrogen molecules (H_2), those previous models have some limitations. In the case of H_2 molecules, RVT transition is important [5–7], because rotation changes the shape of the potential energy surface, and the magnitudes of the bound–bound and bound–free transition rates might be affected by the shape of the potential energy surface.

Several theoretical studies were previously conducted about the RVT transitions of $H + H_2$ and $He + H_2$ collisions. Roberge and Dalgarno [8], Lepp and Shull [9], and Martin et al. [10] have carried out master equation studies for $H + H_2$ collisions at all transitions of

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rotational and vibrational states. The state-to-state rate coefficients of $H + H_2$ collisions [11], which were used in the work by Martin et al. [10], were calculated using the quasi-classical trajectory (QCT) method based on the potential energy surface (PES) by Liu, Siegbahn, Truhlar, and Horowitz (LSTH) [12]. A nonequilibrium analysis by a master equation study for $He + H_2$ collision was made by Dove et al. [13] using the state-to-state rate coefficients [14], which were obtained from the QCT method based on the Wilson et al. PES [15]. However, to accurately describe nonequilibrium rotational and vibrational energy relaxations and chemical reaction, more detailed master equation studies are needed, because the effect of high temperature involving chemical reaction has not been previously investigated. Also, new PESs which include fits to over 8701 ab initio energy points for the interaction of $H + H_2$ by Boothroyd et al. (BKMP2) [16] and 20,000 ab initio energy points for the interaction of $He + H_2$ by Boothroyd et al. (BMP) [17] have become available for the interaction of H_2 collision with H and He atoms.

In the present study, complete sets of state-to-state cross sections and rate coefficients for the transition of 348 (v, j) states of $H + H_2$ and $He + H_2$ collisions were obtained using the QCT calculations based on the BKMP2 PES [16] and the BMP PES [17], respectively. Because the energy transition behaviors of reactive and nonreactive channels are different from each other, each corresponding channel was considered separately in these QCT calculations. The state-to-state cross sections for rotational and vibrational energy transitions were validated by comparing the results with those of the quantum mechanical calculations and other QCT calculations. The state-to-state rate coefficients were fed into a master equation, and the equation was numerically solved to determine the rotational and vibrational number densities. From this master equation study, relaxation of the rotational and vibrational temperatures, number density relaxation, and average rotational and vibrational energy losses due to dissociation were examined for both heating and cooling environments. By using the state-to-state rate coefficients and the results of the master equation study, the dissociation and recombination reaction rates were proposed for a temperature range between 1000 and 32,000 K. These rate coefficients were validated by comparing the results with existing experiments. The reaction rates for describing nonequilibrium chemical reaction were also proposed for a two-temperature model [18] based on translational and vibrational temperatures.

II. State-to-State Cross Sections and Rate Coefficients

A. Method of Calculation

In the present study, the state-to-state rate coefficients were calculated from the state-to-state cross sections evaluated by the QCT method. In these calculations, the BKMP2 PES [16] and the BMP PES [17] were used for the interactions of $H + H_2$ and $He + H_2$, respectively. All trajectories were initiated by the internal energies which correspond precisely to each of the 348 (v, j) states of H_2 molecules. To determine the initial coordinates and the conjugated momenta of H_2 given by the exact Schwenke PES [7], a fast Fourier transform method proposed by Eaker [19] was used with some modifications. In the present QCT calculations, stratified sampling was adopted to obtain the impact parameter, and all other parameters were Monte Carlo selected. The final rotational and vibrational energy levels were quantized by the Wentzel, Kramers, and Brillouin (WKB) approximation method [20]. Also, the quasi-bound states were determined from the effective potential method proposed by Kuntz [21], and the collisions were calculated in a classical manner. A total of 2000 trajectories were calculated per impact parameter at the batch size of 0.1 Å (*A*). To ensure the convergence of the cross sections, the calculations were repeated until all collisions became elastic. Reactive and nonreactive trajectories were treated separately in the calculations of the cross sections. The nonreactive trajectories were counted as described by Mandy et al. [22], while the reactive trajectories were counted twice: the first as orthostate with a weighting of three-quarters due to nuclear spin, and the second as parastate with a weighting of one-quarter. In the present QCT calculations, to obtain the accurate state-to-state cross sections, the statistical error was set less than 30%. Further details about the QCT calculations can be found in other literatures [20,21].

Once the state-to-state cross sections are obtained, the state-to-state rate coefficients are evaluated as

$$K(v, j; v', j') = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \int_{E_0}^{\infty} \frac{E_{\mathrm{tr}}}{kT} \sigma(v, j; v', j'; E_{\mathrm{tr}}) \exp\left(-\frac{E_{\mathrm{tr}}}{kT}\right) \mathrm{d}\left(\frac{E_{\mathrm{tr}}}{kT}\right) \quad (1)$$

Because all (v, j) states are considered, the state-to-state rate coefficients for each transition become available for both directions of the transition. This indicates that the state-to-state rate coefficients in one direction of the transition are related to those in the reverse direction by the detailed balancing relation [18]. In the present study, the detailed balancing relation was considered in the transition of the exoergic direction.

B. Comparison of State-to-State Cross Sections

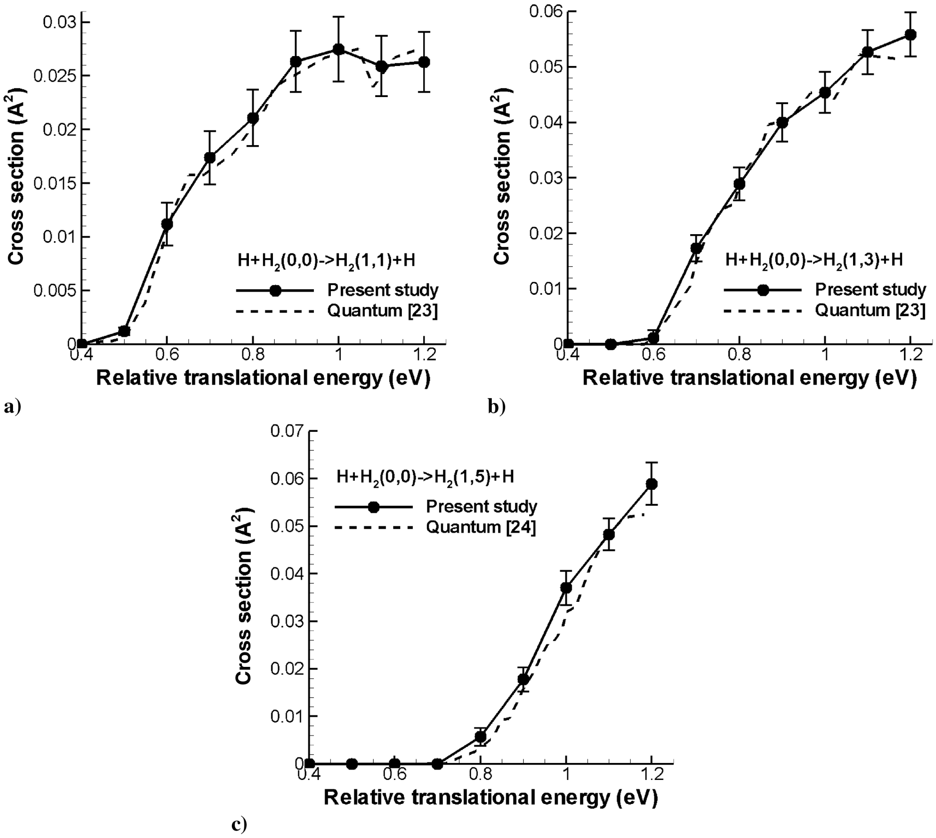
The state-to-state cross sections of $H + H_2$ and $He + H_2$ collisions obtained by the QCT method were compared with those calculated by a quantum mechanical method and other QCT methods [22–30].

In Fig. 1, the quasi-classical cross sections of the present study are compared with the quantum cross sections by other researchers. For the transitions of $H + H_2(0, 0) \rightarrow H_2(1, j = 1, 3) + H$, the results are compared with those of Zhang and Miller [23] calculated on the LSTH PES [12]. For the transition of $H + H_2(0, 0) \rightarrow H_2(1, 5) + H$, the comparison is made with the results of Manolopoulos and Wyatt [24] for the reactive channel based on the double many-body expansion (DMBE) PES [25]. The figure shows that the quasi-classical cross sections for exchange reactions calculated in the present study agree remarkably well with the quantum cross sections for all three cases, even in the threshold region. There is no evidence that tunneling significantly affects the cross sections near the threshold, even though this does not preclude the possibility of its effect at higher energy levels.

In Fig. 2, comparison of the state-to-state cross sections is made between the present results and the QCT results by Mandy et al. [22] for the transitions of $H + H_2(0, 2) \rightarrow H_2(1, j = 1, 3) + H$. In Mandy et al.'s study, the LSTH PES was used, whereas the BKMP2 PES was used in the present study. The results show that the discrepancy between the present results and Mandy et al.'s results is small. This is because no significant difference exists between the BKMP2 PES and the LSTH PES, except at low collision energies [26]. However, the results of the present study are supposed to be more accurate, because the BKMP2 PES describes the interaction of $H + H_2$ more accurately than the LSTH PES for all collision energies.

In Fig. 3, the quasi-classical cross sections of the present study for the transitions $He + H_2(1, 0) \rightarrow He + H_2(0, j = 0, 2, 4)$ are compared with those obtained from the quantum mechanical calculations by Alexander [27] on the modified Tsapline–Kutzelnigg (T-K) PES of Raczkowski and Lester [28], the QCT calculations by Dove et al. [14] on the WKB PES, and the distorted wave calculations [29]. The present quasi-classical cross sections are supposed to be more accurate than other calculations, because the BMP PES used in the present study is the most recent surface available for the interaction of $He + H_2$, which was obtained using a large number of ab initio energy points, compared to the WKB and T-K PESs. The figure shows that, compared to the present study, the distorted wave calculations significantly underpredicted the cross section values, whereas the QCT and quantum calculations show overpredicted results. This is because the behaviors of the WKB and T-K PESs are significantly different [30] from that of the BMP PES. The results of the exact quantum mechanical calculations on the BMP PES are not available for comparison.

In Fig. 4, the state-to-state cross sections of the present study for the states of $He + H_2(0, 0)$ and $He + H_2(12, 0)$ collisions are compared with those of the QCT results by Mandy and McNamara [30] evaluated on the same BMP PES used in the present study.

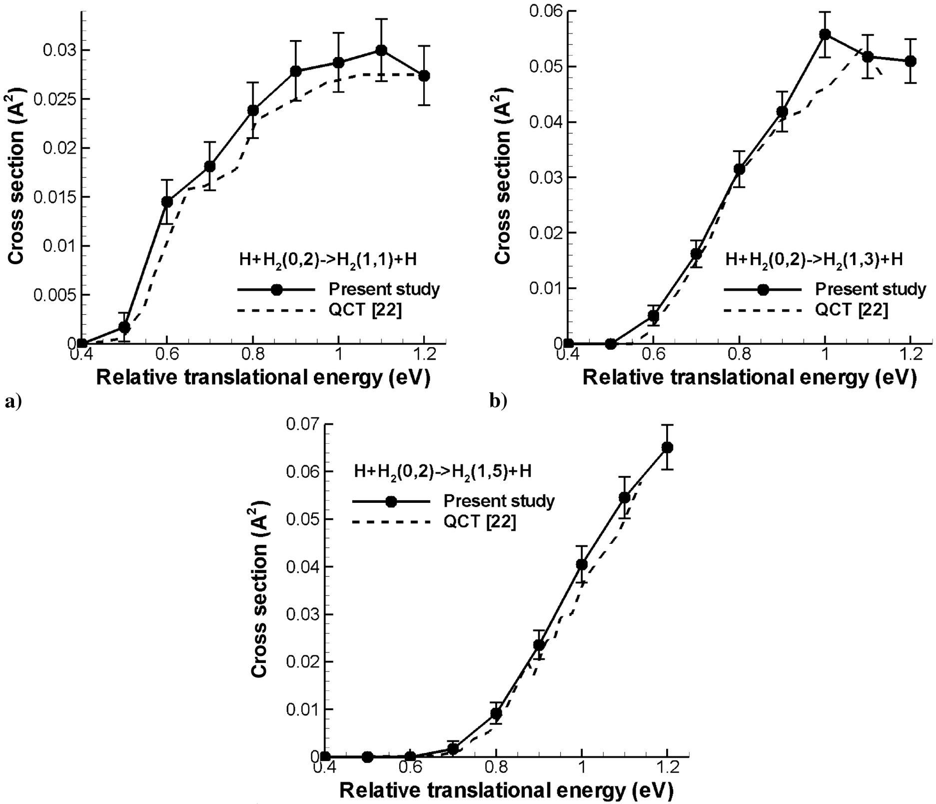


a)

b)

c)

Fig. 1 Comparison of state-to-state cross sections of $H + H_2$ in the reactive channel between the present study and quantum mechanical calculations: a) exchange reaction of $H + H_2(0, 0) \rightarrow H_2(1, 1) + H$ compared with quantum results of Zhang and Miller [23] on the LSTH PES, b) exchange reaction of $H + H_2(0, 0) \rightarrow H_2(1, 3) + H$ compared with quantum results of Zhang and Miller [23] on the LSTH PES, and c) exchange reaction of $H + H_2(0, 0) \rightarrow H_2(1, 5) + H$ compared with quantum results of Manolopoulos and Wyatt [24] on the DMBE PES.



a)

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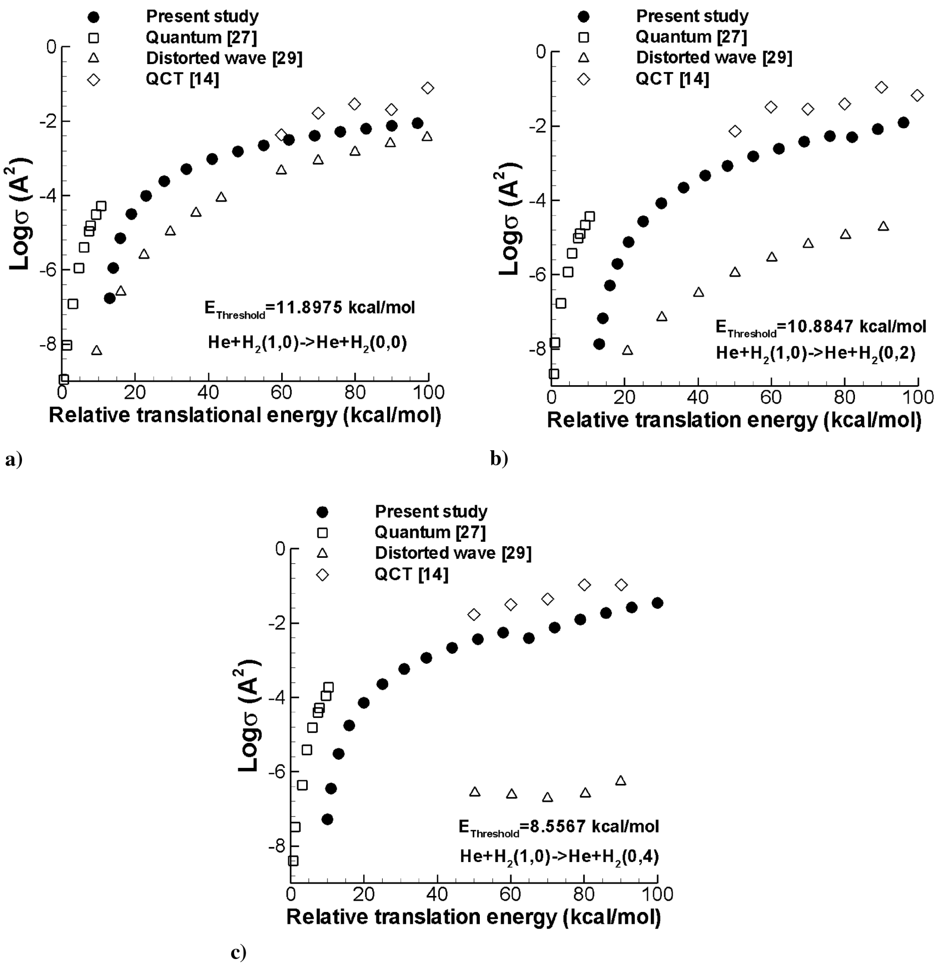
Fig. 2 Comparison of state-to-state cross sections of $H + H_2$ in the reactive channel between the present study and QCT calculations by Mandy et al. [22] on the LSTH PES: a) exchange reaction of $H + H_2(0, 2) \rightarrow H_2(1, 1) + H$, b) exchange reaction of $H + H_2(0, 2) \rightarrow H_2(1, 3) + H$, and c) exchange reaction of $H + H_2(0, 2) \rightarrow H_2(1, 5) + H$.



a) b) c)

Fig. 3 Comparison of state-to-state cross sections of He + H_2 between the present study and quantum mechanical calculations by Alexander [27] on T-K PES, distorted wave calculations by Dove et al. [29], and QCT calculations by Dove et al. [14] on WKB PES: a) bound–bound transition of He + $H_2(1,0)$ → He + $H_2(0,0)$, b) bound–bound transition of He + $H_2(1,0)$ → He + $H_2(0,2)$, and c) bound-bound transition of He + $H_2(1,0)$ → He + $H_2(0,4)$.

The figure shows that, for the complete range of the translational energy, the results of the present study are similar to those of the QCT calculations. However, in the present study, the complete set of 348 (v, j) states for He + H_2 collisions was evaluated, whereas only a limited number of states were calculated with the QCT method by Mandy and McNamara [30].

C. Reaction Rate Coefficients

The quasi-steady-state (QSS) reaction rate coefficients [18] were derived for the reaction $M + H_2(v, j) \rightarrow M + H + H$, where M is a colliding particle. The rate of change of density of H can be written as

$$\frac{\partial N_H}{\partial t} = N_{H_2} N_M \iint K(v, j; c) N(v, j) \, \mathrm{d}v \, \mathrm{d}j - N_H N_H N_M \iint K(c; v, j) \, \mathrm{d}v \, \mathrm{d}j \qquad (2)$$

The normalized number density ρ is defined as the ratio of the nonequilibrium number density divided by the equilibrium number density, and for a specific (v, j) state, it can be written as $\rho_{v,j} = N_{v,j}/N_{v,j;\mathrm{Eq}}$. The normalized number density for a hydrogen atom is $\rho_H = N_H/N_{H;\mathrm{Eq}}$. Then, Eq. (2) can be expressed as

$$\frac{\partial N_H}{\partial t} = N_{H_2} N_M \iint K(v, j; c) \frac{Q_{v,j}}{Q_m} [\rho(v, j) - \rho_H \rho_H] \, \mathrm{d}v \, \mathrm{d}j \qquad (3)$$

The normalized number density $\rho(v, j)$ is defined as $\rho_h + \rho_p \rho_H \rho_H$, where ρ_h and ρ_p are the homogeneous and particular solutions, respectively. Then Eq. (3) can be rewritten as

$$\frac{\partial N_H}{\partial t} = N_{H_2} N_M \iint K(v, j; c) \frac{Q_{v,j}}{Q_m} \rho_h \, \mathrm{d}v \, \mathrm{d}j - N_M N_H N_H \iint K(c; v, j) \frac{N_{H_2;\mathrm{Eq}}}{N_{H;\mathrm{Eq}} N_{H;\mathrm{Eq}}} (1 - \rho_p) \, \mathrm{d}v \, \mathrm{d}j \qquad (4)$$

Then, the dissociation and recombination rate coefficients are determined, respectively, as

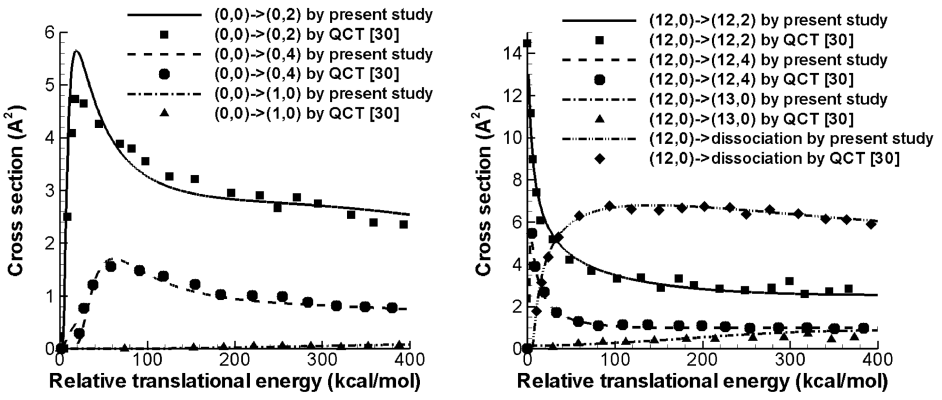
$$K_f = \iint K(v, j; c) \frac{Q_{v,j}}{Q_m} \rho_h \, \mathrm{d}v \, \mathrm{d}j \qquad (5)$$

$$K_r = \iint K(v, j; c) \frac{N_{H_2;\mathrm{Eq}}}{N_{H;\mathrm{Eq}} N_{H;\mathrm{Eq}}} \frac{Q_m}{Q_{v,j}} (1 - \rho_p) \, \mathrm{d}v \, \mathrm{d}j \qquad (6)$$

The rate of change of density of H can be expressed with K_f and K_r as

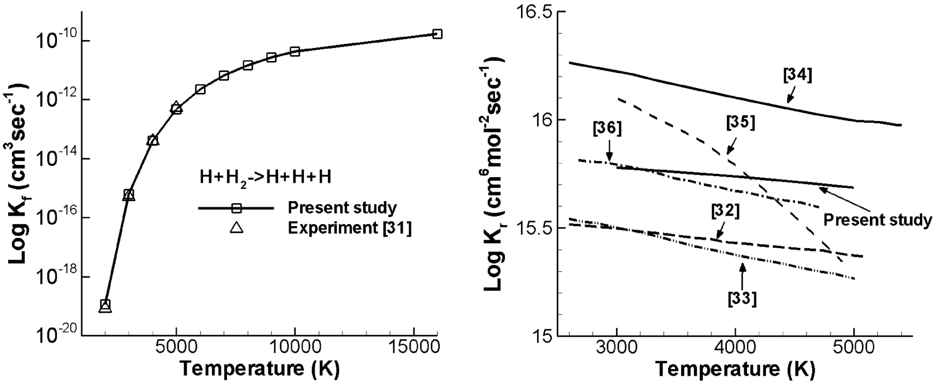
$$\frac{\partial N_H}{\partial t} = K_f(T) N_{H_2} N_M - K_r(T) N_H N_H N_M \qquad (7)$$

In Fig. 5, the dissociation and recombination rate coefficients calculated in the present study for $H + H_2 \leftrightarrow H + H + H$ are compared with the experiments by Cohen and Westberg [31] for dissociation and by Gardiner and Kistiakowsky [32], Rink [33], Patch [34], Sutton [35], and Jacob et al. [36] for recombination. In these calculations, the state-to-state rate coefficients evaluated by the QCT method were used, and the dissociation and recombination rate coefficients were determined as $K_f = 6.4757 \times 10^{-3} T^{-1.4484} e^{-55105/T}$ cm^3 s^{-1} and $K_r = 7.9637 \times 10^{-31}$



a) b)

Fig. 4 Comparison of state-to-state cross sections of He + H_2 between the present study and QCT calculations by Mandy and McNamara [30] on BMP PES: a) bound–bound transition of He + $H_2(0,0) \rightarrow$ He + $H_2(0,j' = 2,4)$ and He + $H_2(0,0) \rightarrow$ He + $H_2(1,0)$, and b) bound–bound transition of He + $H_2(12,0) \rightarrow$ He + $H_2(12,j' = 2,4)$ and He + $H_2(12,0) \rightarrow$ He + $H_2(13,0)$ and bound–free transition of He + $H_2(12,0) \rightarrow$ He + H + H.



a) b)

Fig. 5 Comparison of reaction rate coefficients between the present study and the experiments for H + $H_2 \leftrightarrow$ H + H + H: a) dissociation rate coefficients compared with the experiments by Cohen and Westberg [31], and b) recombination rate coefficients compared with the experiments by Gardiner and Kistiakowsky [32], Rink [33], Patch [34], Sutton [35], and Jacob et al. [36].

$T^{-0.37946}$ $\text{cm}^6\,\text{s}^{-1}$, respectively. For the dissociation rate coefficients, the experimental results are available only at the temperature range between 1000 and 5000 K. The figure shows that the present theoretical dissociation rate coefficients agree very well with the experiment and are available for higher temperatures. In the case of the recombination rate coefficients, the experimental results are shown to be scattered over a logarithmic range between 15.5 and 16.3 at temperatures between 3000 and 5000 K. The theoretical recombination rate coefficients by the present study compare very closely with the measurements by Jacob et al. [36].

The dissociation and recombination rate coefficients for He + $H_2 \leftrightarrow$ He + H + H can also be determined by using Eqs. (5) and (6), similar to H + H_2 collisions. The dissociation rate coefficients are evaluated as $K_f = 3.2003 \times 10^{-2} T^{-1.9265} e^{-55105/T}$ $\text{cm}^3\,\text{s}^{-1}$ for the temperature range between 1000 and 10,000 K and as $K_f = 6.7038 \times 10^{-5} T^{-1.2555} e^{-55105/T}$ for temperatures above 10,000 K. The recombination rate coefficients are evaluated as $K_r = 3.9816 \times 10^{-29} T^{-1.1404}$ $\text{cm}^6\,\text{s}^{-1}$. For this He + $H_2 \leftrightarrow$ He + H + H reaction, experimental results are not available for comparison.

III. Master Equation Study

A. Formulation of Master Equation

The number density of the molecules $N_{v,j}$ for a rotational and vibrational state (v, j) is affected by the incoming and outgoing rates. The incoming rate is the rate of individual transition from an initial vibrational and rotational state (v', j') or a free state c to a final vibrational and rotational state (v, j) by collisions with the colliding particle M. When the incoming rate is bound–bound transition, the number density is given by $K(v', j'; v, j) N_{v',j'} N_M$. When the incoming rate is free-bound transition, it is given by $K(c; v, j) N_H N_H N_M$. For the reverse process of outgoing rates, the number densities for bound–bound and bound–free transitions are $K(v, j; v', j') N_{v,j} N_M$ and $K(v, j; c) N_{v,j} N_M$, respectively. Then, the time rate of change of $N_{v,j}$ is the difference between the sum of all incoming rates and the sum of all outgoing rates:

$$\frac{\partial N_{v,j}}{\partial t} = \sum_{v'=0}^{\max v'} \sum_{j'=0}^{\max j'} K(v', j'; v, j) N_{v',j'} N_M - \sum_{v'=0}^{\max v'} \sum_{j'=0}^{\max j'} K(v, j; v', j') N_{v,j} N_M + K(c; v, j) \frac{N_H^2}{4} N_M - K(v, j; c) N_{v,j} N_M \tag{8}$$

The principle of the detailed balancing relation between the forward and backward rates is invoked under an equilibrium, which leads to

$$K(v, j; v', j') N_{v,j;\text{Eq}} = K(v', j'; v, j) N_{v',j';\text{Eq}} \tag{9}$$

for bound–bound transition, and

$$K(v, j; c) N_{v,j;\text{Eq}} = K(c; v, j) N_{H;\text{Eq}} N_{H;\text{Eq}} \tag{10}$$

for bound–free transition. By dividing Eq. (8) by $N_{v,j;\text{Eq}}$ and using Eqs. (9) and (10) with the normalized number densities, $\rho_{v,j} = N_{v,j}/N_{v,j;\text{Eq}}$ and $\rho_H = N_H/N_{H;\text{Eq}}$, the master equation becomes

Table 1 Initial conditions for the master equation study of H + H_2 and He + H_2 collisions in heating and cooling environments

	Heating environment		Cooling environment	
	$T_r = T_v$	T	$T_r = T_v$	T
Case 1	1000 K	2000 K	10,000 K	2000 K
Case 2	1000 K	3000 K	10,000 K	3000 K
Case 3	1000 K	5000 K	10,000 K	4000 K
Case 4	1000 K	7000 K	10,000 K	5000 K
Case 5	1000 K	10,000 K	10,000 K	6000 K
Case 6	1000 K	16,000 K	10,000 K	8000 K

$$\frac{\partial \rho_{v,j}}{\partial t} = \sum_{v'=0}^{\max v'} \sum_{j'=0}^{\max j'} N_M K(v,j;v',j')[\rho_{v',j'} - \rho_{v,j}] + N_M K(v,j;c)[\rho_H^2 - \rho_{v,j}] \tag{11}$$

The rates of change of density of the atom and of the molecular density can be expressed as

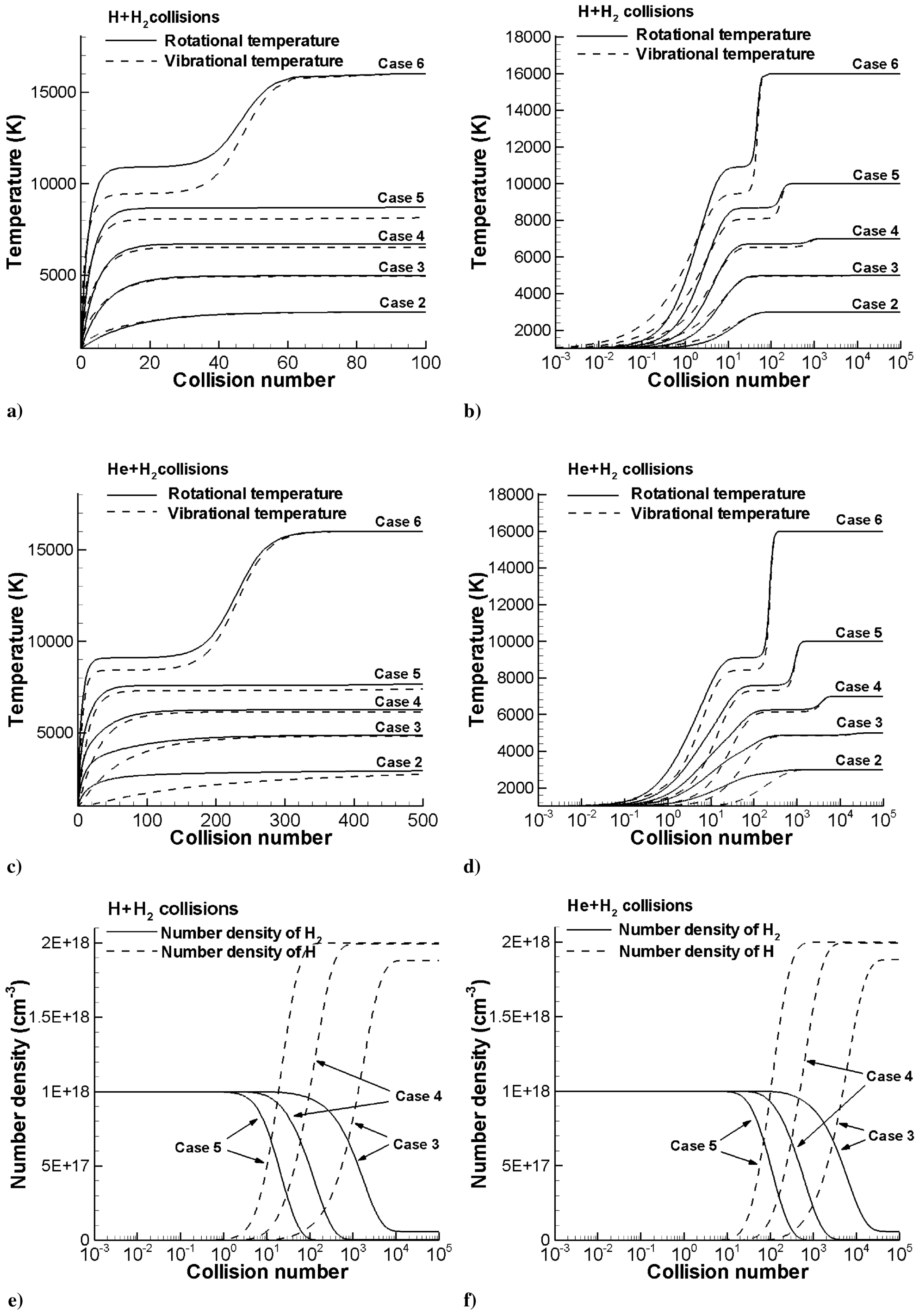


Fig. 6 Rotational and vibrational temperatures and number density for heating environment: a) H + H_2 collisions as a function of collision number, b) H + H_2 collisions as a function of logarithmic collision number, c) He + H_2 collisions as a function of collision number, d) He + H_2 collisions as a function of logarithmic collision number, e) number density relaxation of H + H_2 collisions, and f) number density relaxation of He + H_2 collisions.

$$\frac{\partial N_H}{\partial t} = -\frac{\partial N_{H_2}}{\partial t} = 2\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} K(v,j;c)N_{v,j}N_M - 2\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} K(c;v,j)\frac{N_H^2}{4}N_M \tag{12}$$

Using the detailed balancing relation in Eq. (10), Eq. (12) can be rewritten in the following form after some manipulations:

$$\frac{\partial \rho_H}{\partial t} = 2\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} \frac{N_{v,j;\mathrm{Eq}}N_M}{N_{H;\mathrm{Eq}}} K(v,j;c)[\rho_{v,j} - \rho_H^2] \tag{13}$$

Equation (13) and a total of 348 equations in the form of Eq. (11) are to be integrated numerically to obtain $\rho_{v,j}$ and ρ_H as a function of time. For solving these 349 stiff equations, an implicit time integration algorithm [37] was used in the present study.

B. Average Rotational and Vibrational Energy Losses Due to Dissociation

When a gas molecule dissociates due to collision with other particles, the rotational and vibrational energy contents of the gas are reduced. This dissociation typically occurs at upper energy states. Thus, even a single dissociation depletes the rotational and vibrational energies by an amount nearly equivalent to the dissociation energy of the molecule. The rate of rotational energy loss due to the transition from a (v, j) state is $K(v, j; c)E(j)N_{v,j}N_M$, and the rate of vibrational energy loss is $K(v, j; c)E(v)N_{v,j}N_M$, where $E(j) = E(v, j) - E(v, 0)$ and $E(v) = E(v, 0)$ represent the rotational and vibrational energies, respectively. In the reverse process of recombination, these rotational and vibrational energies are added to the (v, j) state. Then, the average rotational energy loss ε_r can be defined as

$$-\varepsilon_r\frac{\partial N_{H_2}}{\partial t} = N_M\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} E(j)K(v,j;c)N_{v,j} - N_M\frac{N_H^2}{4}\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} E(j)K(c;v,j) \tag{14}$$

Using the detailed balancing relation in Eq. (10) and the rate of change of density of the atom in Eq. (12), the average rotational energy loss ε_r can be expressed as

$$\varepsilon_r = \frac{\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} E(j)K(v,j;c)(Q_{v,j}/Q_m)[\rho_{v,j} - \rho_H^2]}{\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} K(v,j;c)(Q_{v,j}/Q_m)[\rho_{v,j} - \rho_H^2]} \tag{15}$$

The average vibrational energy loss ε_v is defined in a similar manner as

$$\varepsilon_v = \frac{\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} E(v)K(v,j;c)(Q_{v,j}/Q_m)[\rho_{v,j} - \rho_H^2]}{\sum_{v=0}^{\max v}\sum_{j=0}^{\max j} K(v,j;c)(Q_{v,j}/Q_m)[\rho_{v,j} - \rho_H^2]} \tag{16}$$

C. Results and Discussion

The normalized number density $\rho_{v,j}$ for all 348 rotational and vibrational states and ρ_H were calculated for heating and cooling environments by the master equation in Eqs. (11) and (13). The initial conditions of six heating and cooling cases for $H + H_2$ and $He + H_2$ collisions are tabulated in Table 1. In these calculations, it was assumed that rotational and vibrational excitations and chemical reaction occur at constant volume and at isothermal condition. The initial number density of H_2 was set to a constant of 1.0×10^{18} cm^{-3}, and the atom number densities of H and He were set to 5.0×10^{17} cm^{-3}. To transfer the time domain to the effective collision number z domain, the collision time was used as

$$t = zt_c = z\frac{\pi}{4}\frac{\eta}{N_H kT} \tag{17}$$

where η is the viscosity, which can be expressed in terms of the collision integral for the energy transfer $\Omega^{(2,2)}$ as

$$\eta = \frac{5}{16}\frac{\sqrt{\pi\mu kT}}{\Omega^{(2,2)}} \tag{18}$$

The energy-equivalent rotational and vibrational temperatures can be determined by the average rotational energy e_r and the average vibrational energy e_v, respectively. These average energies are defined as

$$e_r = \frac{\sum_v\sum_j E(j)N_{v,j;\mathrm{Eq}}\rho_{v,j}}{\sum_v\sum_j N_{v,j;\mathrm{Eq}}\rho_{v,j}} \tag{19}$$

$$e_v = \frac{\sum_v\sum_j E(v)N_{v,j;\mathrm{Eq}}\rho_{v,j}}{\sum_v\sum_j N_{v,j;\mathrm{Eq}}\rho_{v,j}} \tag{20}$$

In Fig. 6, the calculated rotational and vibrational temperatures are presented as a function of effective collision number for heating environment. For both H and He collisions, a QSS period is observed above 5000 K for all test cases presented. During this QSS period, the rotational and vibrational temperatures are at almost constant values, and the number density of H is rapidly increased. For the temperature relaxation of H collisions, vibrational relaxation occurs slightly faster than rotational relaxation at the initial collision stage. However, this relaxation pattern is reversed ahead of the QSS period, and then rotational relaxation occurs faster than vibrational relaxation. These phenomena are more obvious for the cases with the initial temperature condition higher than 5000 K, even though overall relaxation patterns of the rotational and vibrational temperatures are similar for all test cases considered. In the case of He collisions, rotational relaxation occurs faster than vibrational relaxation at all collision numbers. However, this rotational relaxation occurs slow enough to be considered a nonequilibrium process. From these relaxation patterns of H and He collisions, it can be concluded that rotation-vibration-translation transition has a significant effect on the nonequilibrium phenomena of $H + H_2$ and $He + H_2$ collisions.

The vibrational energy relaxation can be described by the Landau–Teller equation [38] as

$$\frac{\partial e_v}{\partial t} = \frac{e_{v;\mathrm{Eq}}(T) - e_v(T_v)}{\tau_L} \tag{21}$$

By multiplying τ_L by pressure, one obtains the characteristic vibrational relaxation rate parameter $p\tau_L$, which is independent of

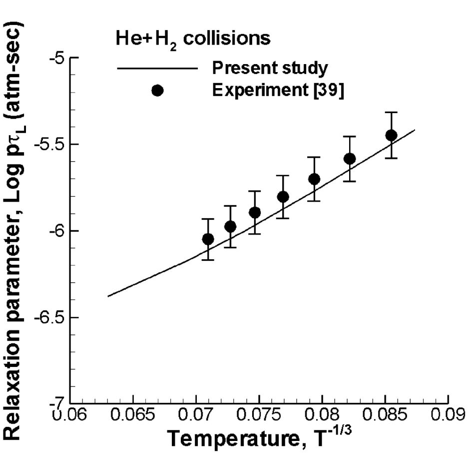
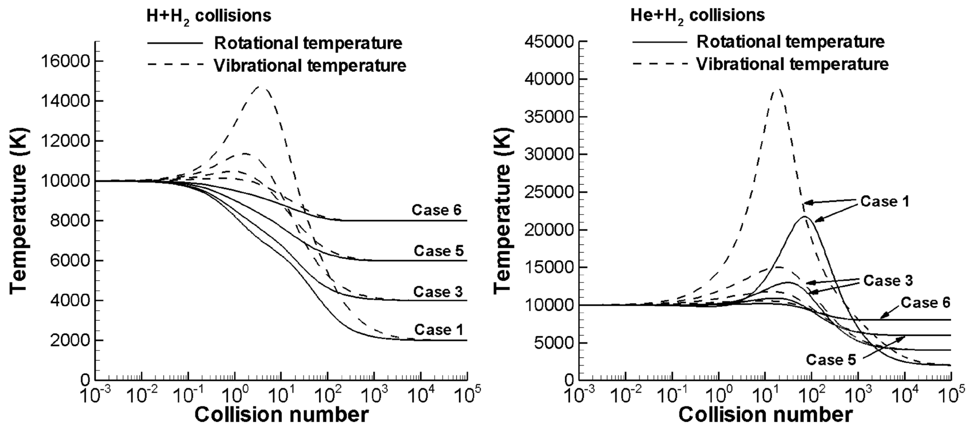


Fig. 7 Comparison of vibrational relaxation rate parameter $p\tau_L$ of $He + H_2$ between the present study and the experiment by Dove and Teitelbaum [39].



a) b)

Fig. 8 Rotational and vibrational temperatures for cooling environment as a function of logarithmic collision number: a) H + H_2 collisions, and b) He + H_2 collisions.

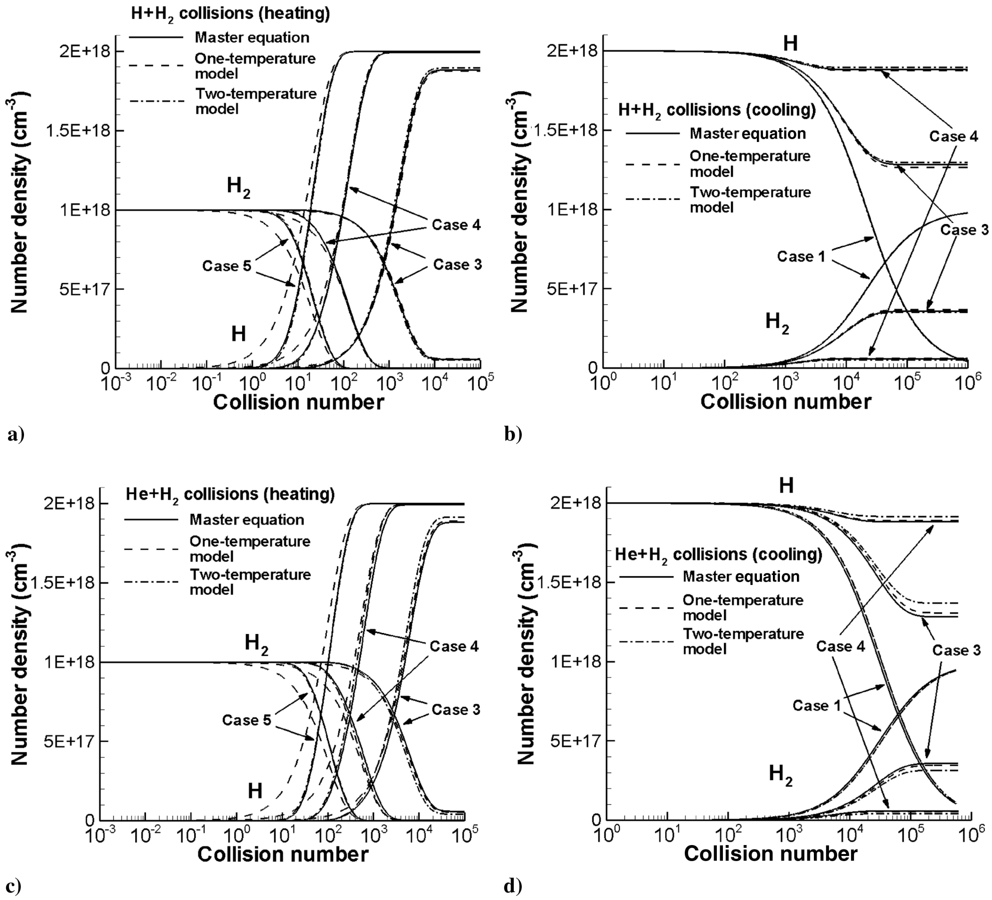
pressure. The vibrational relaxation rate parameter of gaseous H_2 in mixtures with He was obtained experimentally by Dove and Teitelbaum [39] using a laser schlieren technique by measuring the relaxation time of incident shock waves at a temperature range between 1350 and 3000 K. In Fig. 7, the theoretical vibrational relaxation rate parameter $p\tau_L$ for He collisions calculated by the present study is compared with the experimental results [39] determined by the *e*-folding collision number method. The figure shows that the present theoretical relaxation rate parameter compares well with the measurement within the experimental error bound. For H collisions, the vibrational relaxation parameter is

$$\begin{aligned} p\tau_L &= 1.3521 \times 10^{-6} T^{-0.6303} \qquad (\text{for } T < 4000\ \text{K}) \\ p\tau_L &= 6.4461 \times 10^{-9} T^{0.015634} \qquad (\text{for } T > 4000\ \text{K}) \end{aligned} \tag{22}$$

For He collisions, the vibrational relaxation parameter is

$$\begin{aligned} p\tau_L &= 10.522 \times 10^{-6} T^{-2.0660} \qquad (\text{for } T < 5000\ \text{K}) \\ p\tau_L &= 1.4259 \times 10^{-4} T^{-0.72711} \qquad (\text{for } T > 5000\ \text{K}) \end{aligned} \tag{23}$$

In Fig. 8, relaxations of the rotational and vibrational temperatures are presented as a function of effective collision number for selected



a) b) c) d)

Fig. 9 Comparison of number densities of H_2 and dissociated H between the master equation study and the one-temperature and two-temperature models: a) H + H_2 collisions for heating environment, b) H + H_2 collisions for cooling environment, c) He + H_2 collisions for heating environment, and d) He + H_2 collisions for cooling environment.

test cases of cooling environment. It was observed that, for the collision numbers between 1 and 100, the vibrational temperature for $H + H_2$ collisions, and both rotational and vibrational temperatures for $He + H_2$ collisions are locally increased. This is because, at this region, the number density of high-energy level molecules is increased due to recombination, and this recombination occurs at a much faster rate than the rotational and vibrational energy relaxations. These phenomena were also observed by the experiments [40,41] and the theoretical study [42]. The figure shows that rotational relaxation for this cooling environment also occurs slowly as a nonequilibrium process, and thus RVT transition has a significant effect for both H and He collisions.

To describe the nonequilibrium chemical reaction, a two-temperature model based on translational and vibrational temperatures was previously proposed by Park [18]. In the present study, the two-temperature rate expression was derived from the results of the master equation study for both H and He collisions. For H collisions, the forward rate coefficient of the two-temperature model is given as

$$K_{f\text{-two}} = 3.1840 \times 10^{-4} T_a^{-1.0735} e^{-55105/T_a} \tag{24}$$

For He collisions, the forward rate coefficient can be described as

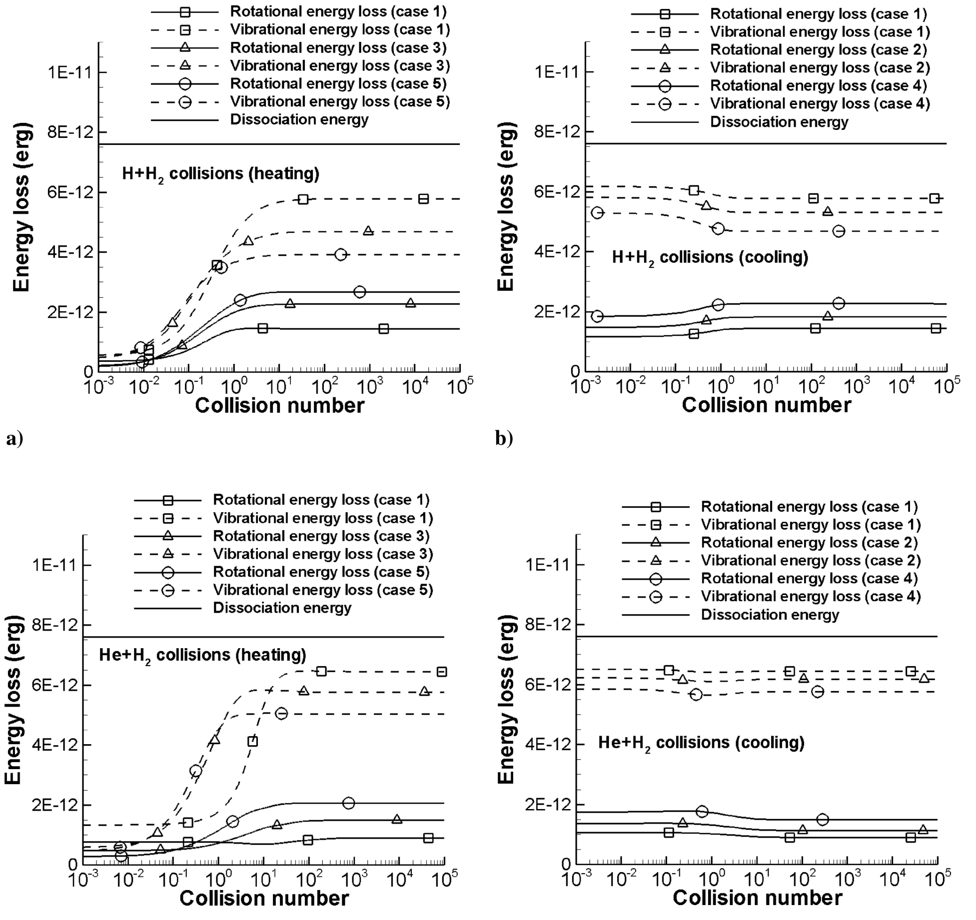
$$\begin{aligned} K_{f\text{-two}} &= 9.2719 \times 10^{-4} T_a^{-1.4773} e^{-55105/T_a} \quad (\text{for } T_a < 10{,}000\ \text{K}) \\ K_{f\text{-two}} &= 1.4568 \times 10^{-7} T_a^{-0.50175} e^{-55105/T_a} \quad (\text{for } T_a > 10{,}000\ \text{K}) \end{aligned} \tag{25}$$

where T_a is the geometrical mean $\sqrt{TT_v}$. In these expressions, the RVT transition effects of $H + H_2$ and $He + H_2$ collisions are already accounted for, because the results of the master equation study are used in determining these parameters. Using Eqs. (24) and (25), the time rate of change of N_H can be expressed as

$$\frac{\partial N_H}{\partial t} = K_{f\text{-two}}(T_a) N_{H_2} N_M - K_r(T) N_H^2 N_M \tag{26}$$

In Fig. 9, the behaviors of the number densities of H_2 and dissociated H calculated by the two-temperature model in Eq. (26), the one-temperature model in Eq. (7), and the master equation in Eqs. (11) and (13) are compared for H and He collisions as a function of logarithmic collision number for both heating and cooling environments. Comparison of the results between the one-temperature model and the master equation study shows that the change of the number density is not accurately simulated by the one-temperature model. The results of the two-temperature model are very similar to those of the master equation study for both heating and cooling environments, except case 3 of the cooling environment. This indicates that nonequilibrium chemical reactions can be simulated more accurately by using the two-temperature model than the one-temperature model for both H and He collisions. However, for most of the relaxation process, the difference between the one-temperature model and the master equation study is small, and thus the one-temperature model may also be used to describe nonequilibrium chemical reactions.

In Fig. 10, the average rotational and vibrational energy losses given by Eqs. (15) and (16) are presented for both H and He collisions for various initial temperature conditions. The results show that the average rotational energy loss is approximately half of the average vibrational energy loss for H collisions, and approximately one-third for He collisions. This indicates that the average rotational energy of chemically dissociating molecules is high enough and should be



a) b) c) d)

Fig. 10 Comparison of average rotational and vibrational energy losses as a function of logarithmic collision number: a) $H + H_2$ collisions for heating environment, b) $H + H_2$ collisions for cooling environment, c) $He + H_2$ collisions for heating environment, and d) $He + H_2$ collisions for cooling environment.

considered in chemical reaction, and that RVT transition should not be ignored in $H + H_2$ and $He + H_2$ collisions. In the case of the vibrational energy removal, the average vibrational energy losses for H and He collisions are approximately 50–75% and 65–80% of H_2 dissociation energy, respectively. These average vibrational energy losses are considerably larger than half of the dissociation energy predicted by the coupled-vibration-dissociation-vibration theory [43]. Similar results about the high average vibrational energy losses of activation for collisions leading to complete dissociation of H_2 were previously reported by Truhlar et al. [44] for $Ar + H_2$ collisions.

IV. Conclusions

In the present study, complete sets of state-to-state cross sections and rate coefficients for the transition of 348 (v, j) states for $H + H_2$ and $He + H_2$ collisions were calculated using the quasi-classical trajectory method. In these calculations, the latest potential energy surfaces were used to describe the interactions of the collisions. The transition cross sections were validated by comparing the results with those of quantum mechanical calculations and other QCT calculations. From the state-to-state rate coefficients, the dissociation and recombination rate coefficients were calculated based on a quasi-steady-state assumption, and the results were validated against existing experiments. The full 348 (v, j) state-to-state rate coefficients were fed into the master equation, and the nonequilibrium relaxations of the rotational and vibrational temperatures and the number densities of H_2 molecule and dissociated H atom were simulated. It was found that the relaxation pattern of rotational temperature is similar to that of vibrational temperature for H collisions. For He collisions, the relaxation process is slow enough to be considered as nonequilibrium in heating environments. In the case of cooling environments, local increase of the rotational and vibrational temperatures was observed for both H and He collisions. From these relaxation patterns, it was concluded that the nonequilibrium effect of the rotation-vibration-translation transition is important for both $H + H_2$ and $He + H_2$ collisions. To describe these nonequilibrium chemical reactions, the rate parameters for the two-temperature model including the RVT transition effect were proposed for both H and He collisions. Comparison of the number density relaxations showed that nonequilibrium chemical reactions can be assessed more accurately by using the two-temperature model than the one-temperature model. From the results of the average rotational and vibrational energy losses, it was found that the average rotational energy of the chemically dissociated molecules for both H and He collisions is high enough and should be considered in chemical reaction. It was also found that the average vibrational energy loss is considerably larger than half of the dissociation energy predicted by the coupled-vibration-dissociation-vibration theory.

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