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Chemical Rate Constants in Nonequilibrium Flows

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A new method of determination of dissociation and recombination rate constants in a vibrationally nonequilibrium diatomic gas is proposed. This method is based on a hierarchy of characteristic times of elementary collisional processes including translation–rotation–vibration exchanges and chemical transformations. The corresponding Boltzmann equations are solved by a generalized Chapman–Enskog technique. Among the considered situations, the case of a relatively weak vibrational nonequilibrium combined with an arbitrary (equilibrium or nonequilibrium) chemical regime may be treated completely, and explicit relations for the rate constants and vibration energy removed in dissociation may be obtained. These results are then generalized to any type of regime, excluding, however, very strong gradient zones. Examples of the computation of rate constants are presented for various flows: Behind strong shock waves, in supersonic expansion, and in a shock-tube end-wall boundary layer. These example cases all exhibit a non-Arrhenius behavior of rate constants. For the strong shock case, the calculated values of dissociation rates are compared to results obtained from other models.

Nomenclature

A, B, D, F, G, H = coefficients of Chapman–Enskog expansions
a, b, d, f, g, h = coefficients of Chapman–Enskog expansions
C = specific heat
c = velocity of molecules relative to the flow, v-u
E = mean energy per molecule
E_{v_D} = vibrational energy lost per dissociation act
$\dot{e}$ = vibration energy source term
f = distribution function
g_{ij} = relative velocity of molecules i and j
g_{ir} = rotational statistical weight
I = differential cross section
i, j = quantum numbers (i_r, i_v), (j_r, j_v)
i_r, i_v = rotational, vibrational quantum numbers
J = collisional term of the Boltzmann equation
K = chemical rate constant
k = without subscript, Boltzmann constant; with subscript, rate constant of dissociation from a specific vibrational level
M = Mach number
m = mass of a molecule
N = number of levels
n = density
P = Wang Chang–Uhlenbeck polynomial
p = pressure
Q = partition function
R = ratio of collisional integrals, $\gamma_R/\gamma_{\mathrm{trv}}$
r = general spatial coordinate
S = Sonine polynomial
t = time
u = macroscopic velocity
v = molecular velocity
ε = ratio of characteristic times
ε_i = internal energy per molecule on level i
θ = reference flow time
ξ = molar concentration
τ = characteristic or relaxation time
φ = perturbation function
ψ = transverse coordinate through the boundary layer

Subscripts

c = chemical
D = dissociation
e = boundary-layer edge
i = internal level, i_r, i_v
m, n, p = order of polynomials
o = stagnation conditions
p = molecules p
q = atoms q
R = recombination
t, r, v = translation, rotation, vibration
tr, trv = translation–rotation, translation–rotation–vibration

Superscripts

0 = zeroth order of the distribution function expansion
1 = first order of the distribution function expansion
$*$ = nondimensional quantity
– = denotes an equilibrium quantity

Introduction

VIBRATION–DISSOCIATION and vibration–recombination coupling has been the subject of a great number of studies, and an extensive review has been presented.[1] The main problem consists in determining the influence of molecular vibrational distribution on the values of dissociation and recombination rate constants. The secondary, but very important, problem is the reciprocal influence of dissociation and recombination on vibration, particularly on vibrational temperature, when it is possible to define this quantity.

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The numerous methods used to model vibration–dissociation coupling may be generally classified into two categories. First, there are physicochemical studies that, based on a more or less detailed analysis of dissociative collisions, deduce statistical properties like dissociation constants, vibrational energy lost per dissociation act, etc.[2–6] The second category includes semiempirical models leading to simple formulas for rate constants as functions of vibrational temperature.[7–9] The models from the latter category, because of their simplicity, are of an obvious practical interest for computations of hypersonic flows. Physicochemical nonempirical models can be more or less physically realistic in spite of frequent restrictive assumptions. However, these models are generally more difficult to incorporate into practical computations.

In this paper we develop a model of a completely different type, because it is based on a kinetic approach to the problem and on the Chapman–Enskog method of solving the Boltzmann equation, taking into account a hierarchy of characteristic times of various processes.[10] Because of variable time scales of these processes, the Chapman–Enskog procedure is nonunique, and it must be applied for each particular case.[11] First, we analyze different solutions of the Boltzmann equation covered by a classical Chapman–Enskog method. These solutions correspond to weak or strong nonequilibrium situations with regard to vibration and chemistry. To relax the assumptions and to widen the applicability range of the solutions, a generalized Chapman–Enskog method is then constructed, allowing the description of general cases of vibrational and chemical nonequilibrium. The only assumptions remaining are 1) that the characteristic time of vibrational relaxation remains shorter than or equal to the chemical time, and 2) that excluded from consideration are strong gradient zones. Explicit formulas for rate constants and vibrational energy consumption are derived and incorporated into general conservation equations for species and vibrational energy, thus closing the Navier–Stokes set of equations for nonequilibrium flow. Practical examples of nonequilibrium flows, including flow behind shocks, expansion nozzle flow, and end-wall boundary layer illustrate the vibration-reaction coupling and non-Arrhenius behavior of rate constants.

General Equations for Nonequilibrium Flows

For a pure diatomic gas flow in a continuum regime, and simultaneously in a vibrational and dissociation-recombination nonequilibrium, the Boltzmann equation for the molecules p on a quantum level i, including rotational i_r and vibrational i_v levels, may be written as

$$\frac{\mathrm{d}f_{ip}}{\mathrm{d}t} = J_{\mathrm{tr}p} + J_{vp} + J_{cp} \tag{1}$$

Here, the translation–rotation tr, vibration v, and chemical c collisional exchanges proceed on different time scales: τ_{tr}, τ_v, and τ_c, respectively. For atoms q produced by the dissociation, we have

$$\frac{\mathrm{d}f_q}{\mathrm{d}t} = J_{tq} + J_{cq} \tag{2}$$

Conventional macroscopic conservation equations are deduced from Eqs. (1) and (2) in a standard manner, by multiplying the equations by collisional invariants of translation–rotation collisions, integrating over velocities, and summing over internal levels. Thus, in particular, species conservation and vibrational energy relaxation equations can be written as follows:

$$\frac{\partial n_p}{\partial t} + \frac{\partial \cdot n_p u}{\partial r} = \dot{W}_p \tag{3}$$

$$\frac{\mathrm{d}E_v}{\mathrm{d}t} + \frac{\partial \cdot q_v}{\partial r} = \dot{e}_p \tag{4}$$

Here, $\dot{W}_p$ and $\dot{e}_p$ are source terms for molecular species and their vibrational energy, respectively.

Considering, for example, the case of a dissociation with no recombination, combined with harmonic oscillator model, we have simply

$$W_p = K_D n_p^2 \tag{5}$$

$$\dot{e}_p = [(\bar{E}_v - E_v)/\tau_v] - (E_{vD} - E_v)K_D n_p \tag{6}$$

where the subscript p has been omitted for simplicity in the expression for vibrational energy.

The second term of Eq. (6) represents the influence of dissociation on vibrational energy evolution.

More complicated expressions would be obtained when considering recombination, anharmonic oscillators, several reactions etc. However, in the general development of the method, presented next, these complicating factors are disregarded.

Thus, the expressions for K_D and E_{vd} have to be determined to close the set of equations. Similarly, transport terms that appear in other conservation equations have to be defined, which is beyond the scope of this paper. The closure of these equations is achieved by a Chapman–Enskog procedure.

Chapman–Enskog Procedure

Let τ_{tr} be the characteristic time of the translation–rotation exchanges, τ_v the characteristic time of vibrational relaxation, τ_c the characteristic time of the chemical exchanges, and θ the characteristic time of the flow. Then, the Boltzmann equation for the molecules p has the nondimensional form:

$$\frac{\mathrm{d}f_{ip}^*}{\mathrm{d}t^*} = \frac{1}{\varepsilon_{\mathrm{tr}}} J_{\mathrm{tr}}^* + \frac{1}{\varepsilon_v} J_v^* + \frac{1}{\varepsilon_c} J_c^* \tag{7}$$

with

$$\varepsilon_{\mathrm{tr}} = \tau_{\mathrm{tr}}/\theta, \qquad \varepsilon_v = \tau_v/\theta, \qquad \varepsilon_c = \tau_c/\theta$$

From a physical point of view $\tau_{\mathrm{tr}} < \tau_v \leq \tau_c$ (Figs. 1 and 2) and, $\tau_{\mathrm{tr}} << \theta$ or $\varepsilon_{\mathrm{tr}} << 1$ (continuum regime).

Equation (1) may be solved by a Chapman–Enskog procedure when assuming a certain hierarchy of the characteristic times. This procedure is nonunique because of the different possible nonequilibrium regimes. However, defining a small

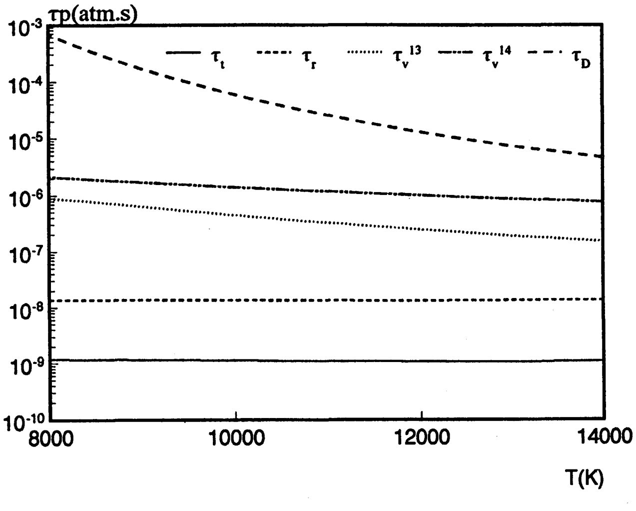

Fig. 1 Nitrogen characteristic times.

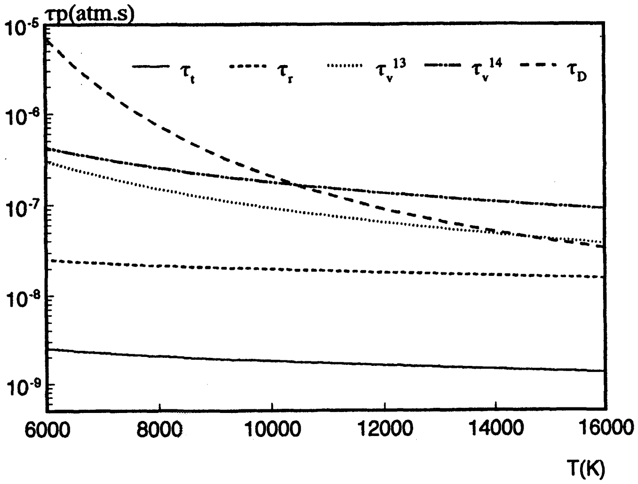

Fig. 2 Oxygen characteristic times.

parameter ε, one may conventionally expand the distribution function to the first order

$$f_{ip} = f^0_{ip}(1 + \varphi_{ip}) \tag{8}$$

Now, taking into account the assumption $\varepsilon = \varepsilon_{tr} << 1$, it is necessary to specify the relative magnitude of the other two parameters, ε_v and ε_c, excluding frozen regimes, $\varepsilon_v >> 1$, $\varepsilon_c >> 1$, which present no significant interest. Thus, three possible cases are possible in the classical Chapman–Enskog procedure:

Case 1 = $\varepsilon_v << 1$ and $\varepsilon_c << 1$: So that $\varepsilon = \varepsilon_{tr}, \varepsilon_v, \varepsilon_c << 1$.

All characteristic times are smaller than θ, so that the zeroth-order distribution function is in complete, but coupled, vibrational, and chemical equilibrium. A weak nonequilibrium (WNE) appears in the first order (φ_i). This case, $(\mathrm{WNE})_v$ + $(\mathrm{WNE})_c$, is relevant only to flows close to equilibrium, and may cover in the zeroth order the quasisteady state defined by Park[12]:

$$J^0_v + J^0_c = 0 \tag{9}$$

This case is of rather limited interest, and it will not be further considered in this paper.

Case 2 = $\varepsilon_v << 1$ and $\varepsilon_c \sim 1$: Then the small parameter would be $\varepsilon = \varepsilon_{tr}, \varepsilon_v$.

The dissociation–recombination regime is out of equilibrium [strong nonequilibrium regime (SNE)] but, in the zeroth order, the vibrational population remains in equilibrium. A weak vibrational nonequilibrium (WNE) appears in the first order. This case, which we call $(\mathrm{WNE})_v$ + $(\mathrm{SNE})_c$, corresponds to zones for which $\tau_v << \tau_c$, excluding regions with strong gradients ($\tau_v \sim 0$).

Case 3 = $\varepsilon_v \sim 1$ and $\varepsilon_c \sim 1$: In this case the processes of vibrational and chemical relaxation proceed simultaneously. The small parameter of the expansion is $\varepsilon = \varepsilon_{tr}$. This case, covering the zones of strong nonequilibrium, will be called $(\mathrm{SNE})_v$ + $(\mathrm{SNE})_c$. f^0_{ip} is out of equilibrium and an additional, essentially translational–rotational, nonequilibrium appears in the first order.

Cases 2 and 3 seem to be the most interesting cases to analyze in practical situations, as can be seen in Figs. 1 and 2, which show the relaxation times of various processes, τ_t, τ_r, τ_v, and τ_D, for N_2 and O_2 as functions of temperature. It is clear that case 2 is realized for N_2 in a very wide temperature range, and 3 is more restrictively valid for O_2.

In Figs. 1 and 2, two different calculations of vibrational relaxation time τ_v are represented.[13,14] Overall, the comparison of characteristic times shows that τ_v and τ_c have the same order of magnitude beyond 10–12.10³ K.

Examining case 3, we have the following system giving the zeroth-order distribution function f^0_{ip} and the correction φ_i:

$$J^0_{tr} = 0 \tag{10a}$$

$$\frac{\mathrm{d}f^0_{ip}}{\mathrm{d}t} = J^1_{tr} + J^0_v + J^0_c \tag{10b}$$

The nonequilibrium is simultaneously present for vibration and chemistry in the zeroth order, so that the coupling only appears in the definition of rate constants for each level k_{D_i} and k_{R_i}. These state-specific rate constants cannot be determined by the Chapman–Enskog procedure. Therefore, no new information may be expected from the present method in the zeroth order.

To define k_{D_i} and k_{R_i}, any appropriate model may be used. In particular, taking into account the definition of K^0_D and K^0_R, and assuming a dissociation probability independent of the vibrational level, the nonpreferential model of Marrone and Treanor[8] is reproduced. In the first order the Chapman–Enskog solution gives the tr-c coupling term of the order of τ_{tr}/τ_c, as expected, this ratio being generally very small.

Thus, case 2 seems the most interesting to examine using the Chapman–Enskog method.

Case $(\mathrm{WNE})_v$ + $(\mathrm{SNE})_c$

f^0_{ip} and φ_{ip} are successively given by the following system:

$$J^0_v = 0 \tag{11a}$$

$$\frac{\mathrm{d}f^0_{ip}}{\mathrm{d}t} = J^1_v + J^0_c \tag{11b}$$

Accounting for only translation–rotation–vibration collisions, f^0_{ip} is equal to

$$f^0_{ip} = n_p\left(\frac{m_p}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m_p c^2}{2kT}\right)\frac{g_{ir}\exp(-\varepsilon_i/kT)}{Q_r(T)Q_v(T)} \tag{12}$$

with $n = n_p + n_q$.

The corresponding macroscopic set of equations, giving n, T, and $u = v - c$ in the zeroth order, includes Euler equations and a dissociation–recombination equation for n_p that does not modify the Boltzmann distribution [Eq. (12)]. Considering only the dissociating regime, we have from Eq. (3)

$$\frac{\partial n_p}{\partial t} + \frac{\partial \cdot n_p u}{\partial r} = K^0_D n^2_p \tag{13}$$

K^0_D and K^0_R are given by conventional Arrhenius expressions depending only on T. On the other hand, they can be expressed as sums of state-specific rates

$$K^0_D = \sum_{ip} k_{D_{ip}}\xi^0_{ip} \tag{14}$$

with $\xi^0_{ip} = n^0_{ip}/n_p$.

The first-order solution given by Eq. (11b) allows one to calculate the perturbation φ_{ip} to the Boltzmann distribution and, consequently, the rate constants in this order. Thus

$$K^1_D = \sum_{ip} k_{D_{ip}}\xi^1_{ip} \tag{15}$$

with $\xi^1_{ip} = n^1_{ip}/n_p$.

These values of rate constants are to be included in the Navier–Stokes equations with the other transport and relaxation terms computed from φ_{ip}. This computation may be performed from Eq. (11b), i.e.,

$$\varphi_{ip} = A_{ip}c\cdot\frac{\partial T}{\partial r} + B_{ip}cc\cdot\frac{\partial u}{\partial r} + D_{ip}\frac{\partial\cdot u}{\partial r} + G_{ip} + H_{ip}c\cdot \mathrm{d}p \tag{16}$$

where $X_i = A_i, B_i, D_i, G_i, H_i$ are unknown scalar functions of r, t, c, ε_i; and dp is proportional to pressure and concentration gradients.

Each X_i term is expanded in Sonine–Wang Chang–Uhlenbeck polynomials[11]:

$$X_i = \sum x_{mnp} S_t^m P_r^n P_v^p \tag{17}$$

with $x = a, b, d, h$.

Only zeroth- and first-order terms are retained in expansion (17), i.e., x_{000}, x_{100}, x_{010}, and x_{001}, where each subscript corresponds, respectively, to the order of expansion for translation, rotation, and vibration.

It is easily verified that only D_i and G_i terms that correspond to bulk viscosity and relaxation pressure, respectively, contribute to the value of ξ_{ip}^1 and, therefore, to K_D^1. Thus, we have $d_{000} = g_{000} = 0$

$$D_i = d_{100}\left(\frac{3}{2} - \frac{m_p c^2}{2kT}\right) + d_{010}\left(\frac{\varepsilon_{ir} - \bar{E}_r}{kT}\right) + d_{001}\left(\frac{\varepsilon_{iv} - \bar{E}_v}{kT}\right)$$

$$G_i = g_{100}\left(\frac{3}{2} - \frac{m_p c^2}{2kT}\right) + g_{010}\left(\frac{\varepsilon_{ir} - \bar{E}_r}{kT}\right) + g_{001}\left(\frac{\varepsilon_{iv} - \bar{E}_v}{kT}\right)$$

where g and d terms include collisional integrals γ_{trv} and γ_c usually found in expansions like that of Eq. (17).

By using Mason and Monchick simplifications,[15] and assuming that $\tau_v >> \tau_r$ (Figs. 1 and 2), one obtains

$$d_{100} = d_{100} = -\frac{C_v^2 n_p}{C_{\mathrm{trv}}^2 \gamma_{\mathrm{trv}}}, \qquad d_{001} = -\frac{C_v C_{\mathrm{trv}}}{C_{\mathrm{trv}}^2}\frac{n_p}{\gamma_{\mathrm{trv}}}$$

$$g_{100} = g_{010} = 0, \qquad g_{001} = N/\gamma_{\mathrm{trv}}$$

γ_{trv}, accounting for translation–rotation–vibration exchanges only, may be expressed in terms of phenomenological vibrational relaxation time τ_v, i.e.,[15]

$$\gamma_{\mathrm{trv}} = -(C_v n_p / k\tau_v) \tag{18}$$

N is also connected to the chemical (dissociation) time $\tau_D \sim (n_p K_D^0)^{-1}$, and one finds

$$N = \frac{K_D^0 n_p^2}{kT}\left[\left(\bar{E}_r + \bar{E}_v - \frac{3}{2}kT\right)\frac{C_v}{C_{\mathrm{trv}}} + \bar{E}_{vD} - \bar{E}_v\right] \tag{19}$$

Then, taking into account Eq. (15), one obtains for K_D^1

$$K_D^1 = K_D^0\left[1 - \left(g + d\frac{\partial\cdot u}{\partial r}\right)\frac{(\bar{E}_v - \bar{E}_{vD})}{kT}\right] \tag{20}$$

with the simplified notation

$$g = g_{001} \quad \text{and} \quad d = d_{001} = \frac{C_{\mathrm{tr}}k}{C_{\mathrm{trv}}^2}\tau_v \tag{21}$$

In the same way it is possible to compute, in the first-order, vibrational energy E_v^1

$$E_v^1 = \bar{E}_v + \left(g + d\frac{\partial\cdot u}{\partial r}\right)C_v T \tag{22}$$

It is easy to verify that the nonequilibrium terms in K_D^1 and E_v^1 depend on the deviation from the Boltzmann distribution (g term $\sim\tau_v/\tau_D$) and on the aerodynamic perturbation (d term $\sim\tau_v/\theta$), which is expected within the present method.

Now, if g and d are eliminated from Eqs. (20) and (22), a direct relation between K_D^1 and E_v^1 (or T_v) may be obtained, that is,

$$\frac{K_D^1 - K_D^0}{K_D^0} = \left(\frac{\bar{E}_{vD} - \bar{E}_v}{kT}\right)\left(\frac{E_v - \bar{E}_v}{C_v T}\right) \tag{23}$$

Thus, this expression represents the closing expression for K_D in Eq. (5).

Case (WNE)$_v$ + (GCE)$_c$

The previous method may not be applied close to chemical equilibrium because it assumes an SNE for chemistry. However, an extension of the method that would include chemical equilibrium may be developed using a generalized Chapman-Enskog method for chemistry (GCE)$_c$.[16–18] Specifically, this is done simply by adding a first-order chemical collisional term J_c^1 in Eq. (11b). Thus, the system [Eq. (11)] becomes

$$J_v^0 = 0 \tag{24a}$$

$$\frac{\mathrm{d}f_{ip}^0}{\mathrm{d}t} = J_v^1 + J_c^0 + J_c^1 \tag{24b}$$

In Eq. (24b), the unknown φ_i is included in J_v^1 and also in J_c^1 terms, which assures the matching between nonequilibrium and equilibrium solutions.

The procedure of solving Eq. (24b) is similar to that of Eq. (11b). The only difference comes from reactive collisional integrals γ_c, which must be added to γ_{trv}. These integrals may also be expressed in terms of chemical times, τ_c or K_D (and K_R). Thus,

$$g = N/(\gamma_{\mathrm{trv}} + \gamma_c) \tag{25}$$

$$d = \frac{n_p C_v C_{\mathrm{tr}}}{C_{\mathrm{trv}}^2}\frac{1}{(\gamma_{\mathrm{trv}} + \gamma_c)} \tag{26}$$

γ_c may also be expressed in terms of phenomenological chemical time τ_c, and through macroscopic thermal reaction rate. Thus, for dissociation, one finds

$$\gamma_c = -n_p^2 K_D^0\left(\frac{\bar{E}_v - \bar{E}_{vD}}{kT}\right)^2 \tag{27}$$

with $\tau_D \sim (n_p K_D^0)^{-1}$.

Equations (20) and (22) for K_D^1 and E_v^1 remain valid, but g and d must be replaced by Eqs. (25) and (26), so that the difference between the corresponding values coming from γ_c terms is mainly significant close to equilibrium, when $\tau_v/\tau_D \sim 1$.

The mean vibrational energy removed in the dissociation act, $\bar{E}_{vD} = E_{vD}^0$, may be computed from its definition. When the equiprobable (nonpreferential) model is used for the state-specific dissociation rate constants, then the $\bar{E}_{vD} = E_{vD}^0$ is equal to $0.5E_D$ for a harmonic oscillator and $0.4E_D$ for an anharmonic oscillator (see Appendix).

Finally, Eq. (23) for K_D obtained from the previous case, (W.N.E)$_v$ + (S.N.E)$_c$, remains valid. Thus, we obtain a generalization of Eq. (23) for virtually any interesting nonequilibrium case.

Examples of the variation of $\log(K_D^1/K_D^0) = \log V(T, T_v)$ as a function of T_v at a constant T are presented in Figs. 3 and 4. Similar formulas are obtained for the recombination rate constant K_R^1 involving $\bar{E}_{vR}$ instead of $\bar{E}_{vD}$.

As for the expression for E_{vD} that is necessary for the closure of Eqs. (1) and (2), and more generally, Navier–Stokes equa-

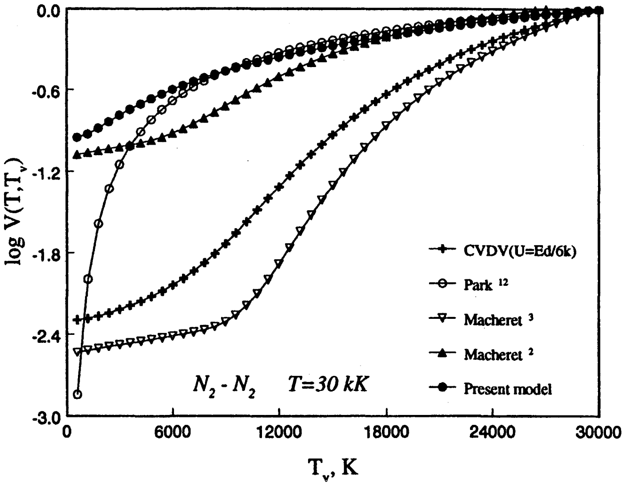

Fig. 3 $\log(K_D^1/K_D^0) = F(T_v)$ for $T = 3 \times 10^4$ K, nitrogen.

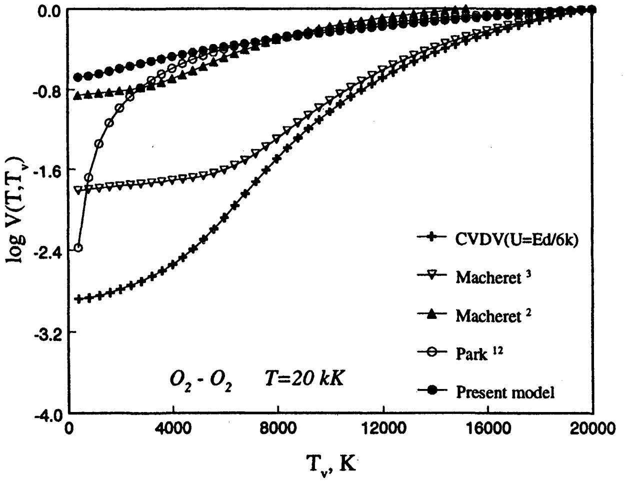

Fig. 4 $\log(K_D^1/K_D^0) = F(T_v)$ for $T = 2 \times 10^4$ K, oxygen.

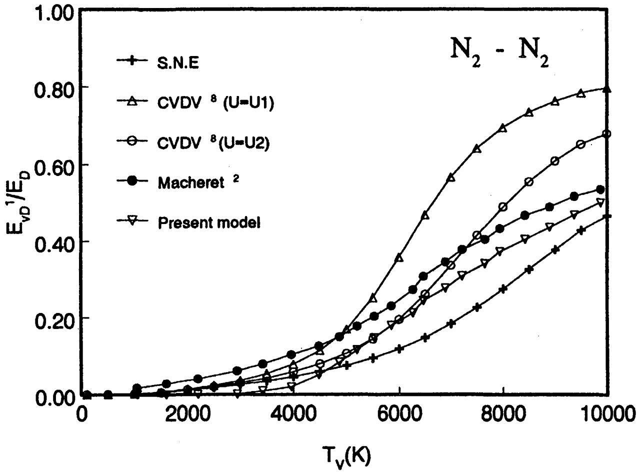

Fig. 5 Vibration energy lost per dissociation (fraction of dissociation energy). $T = 10^4$ K. Nitrogen, $U1 = E_D/6k$, $U2 = E_D/3k$.

tions, it may be obtained from its definition using appropriate models of state-specific rates and of the oscillator (see Appendix). In Fig. 5, the variation of E_{vD}^1 for N_2, assuming the equiprobable dissociation from all vibrational levels, is presented as a function of T_v for a grain value of T and compared with values given by other models. There are quantitative differences between the results but the trend is similar. Results obtained from coupled vibration–dissociation–vibration (CVDV) models[8] give higher values, and those computed with the SNE model described earlier are identical to the nonpreferential CVDV model, as in the case for values of K_D^1.

Applications

The newly developed method of computation of dissociation and recombination rate constants has been successively implemented in three cases: 1) In a flow behind a normal shock wave where dissociation dominates over recombination, 2) in a supersonic nozzle where the recombination is the main phenomenon, and 3) in the boundary layer of the end-wall of a shock tube where complex nonequilibrium situation is the cause of a pronounced non-Arrhenius behavior of rate constants.

Normal Shock Waves

The evolution of K_D^1 calculated from Eq. (23) for N_2 behind shock waves at Mach 25 is represented in Fig. 6. This prediction is compared to those given by other methods. The values of K_D^1 are always smaller than K_D^0 because of the coupling of vibrational and chemical relaxation. It is seen in Fig. 6 that at the beginning of the relaxation, when $T_v << T$, the rate constants calculated by different methods are very different from each other. In this zone, where $T_v << T$, the present method is, strictly speaking, invalid, because the assumption of (WNE)$_v$ was made in our derivations. However, because the dissociation rate in this zone is very low, the absolute values of K_D have no great importance for the overall dissociation process. As the relaxation proceeds, close to vibrational equilibrium, all

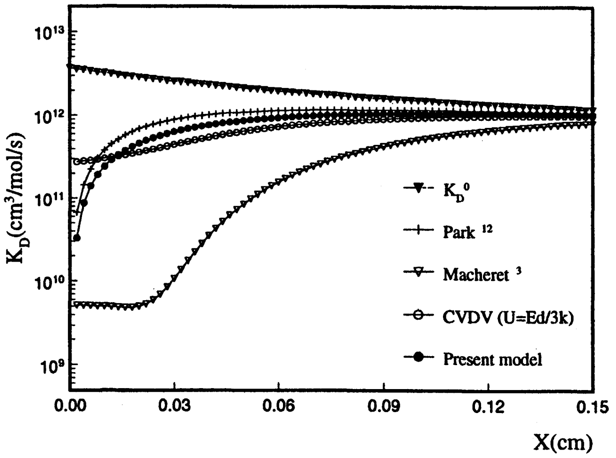

Fig. 6 Dissociation rate constant behind a shock wave. Nitrogen, $M = 25$, $p = 8.5$ Pa, $T = 205$ K.

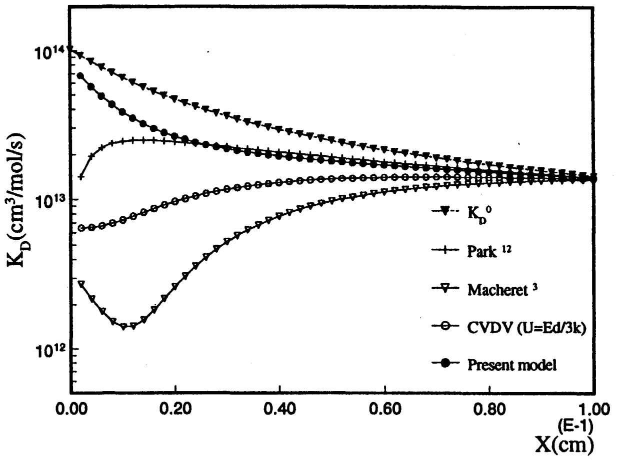

Fig. 7 Dissociation rate constant behind a shock wave. Oxygen, $M = 25$, $p = 8.5$ Pa, $T = 205$ K.

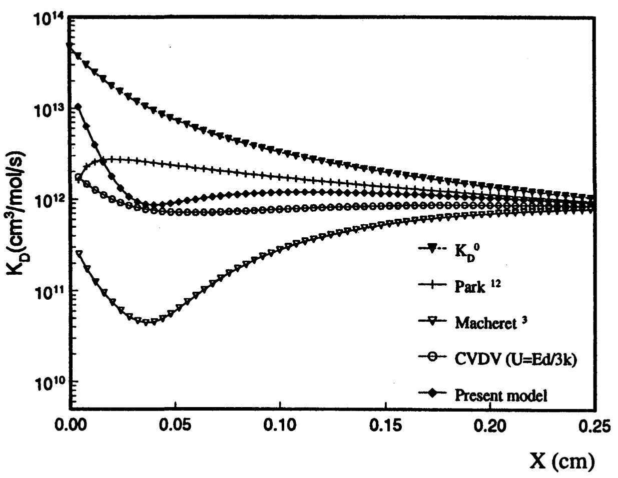

Fig. 8 Dissociation rate constant behind a shock wave. Oxygen, $M = 19, p = 9.9$ Pa, $T = 235$ K.

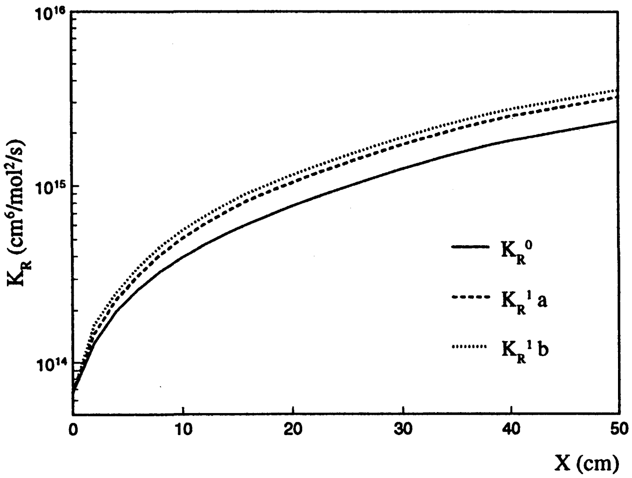

Fig. 9 Recombination rate constant K_R^1 along a supersonic nozzle. Nitrogen, $T_0 = 6500$ K, $P_0 = 1.53 \times 10^8$ Pa, divergent angle = 10 deg. a, harmonic oscillator; b, anharmonic oscillator.

models converge to the thermal dissociation rate, making the difference between the models small. The discrepancies between different models also decrease as the Mach number increases (Figs. 7 and 8), but the disagreement still reaches up to several orders of magnitude during most of the relaxation.

The evolution of K_D^1 in O_2, represented in Fig. 8 for Mach 19, presents a minimum similar to that found with another model[3], but the absolute values of the rate are different.

Nozzle Expansion

In this case recombination is the prevalent chemical process. Starting from reservoir conditions for which a diatomic gas A_2 is partially dissociated (Fig. 9), the two recombination processes are

$$A + A + A \overset{K_{R1}}{\Leftrightarrow} A_2 + A, \qquad A_2 + A + A + \overset{K_{R2}}{\Leftrightarrow} A_2 + A_2$$

Considering the previous analysis, only the recombination rate constant of the second reaction K_{R2} is essentially affected by the vibrational nonequilibrium, and this rate constant is

$$K_{R2} = K_{R2}^0 \left[1 - \left(\frac{E_v - \bar{E}_v}{C_v T} \right) \left(\frac{\bar{E}_v - \bar{E}_{vR}}{kT} \right) \right]$$

where $\bar{E}_{vR}$ $(=\bar{E}_{vD})$ is the vibrational energy gained in the recombination.

Assuming a one-dimensional nitrogen flow in the nozzle, the values of K_{R2} may be easily computed and their evolution along the nozzle is shown in Fig. 9. These values are greater than the equilibrium rate constant K_{R2}^0, because of the freezing of the vibration in the expansion resulting in overpopulation of upper levels. However, the quantitative effect of vibrational nonequilibrium on the recombination rate constant is not as important as that behind a shock.

Shock-Tube End-Wall Boundary Layer

We performed computations of vibrationally relaxing and dissociating diatomic gas behind a reflected shock at the end-wall of a shock tube. The time evolution of the end-wall boundary layer was analyzed and, as previously observed,[11] the vibrational nonequilibrium through the boundary layer decreases monotonically between the shock and the wall during the early stages of the relaxation following the reflection. Then, as time goes on, a minimum appears close to the wall (Fig. 10), so that in the outer part of the boundary layer $T_v < T$, as is usual behind a shock, while in the inner part there is a freezing zone, where $T_v > T$. This behavior of vibrational temperature results in a maximum of the dissociation rate, because $K_D^1 > K_D^0$, where $T_v > T$ and $K_D^1 < K_D^0$, where $T_v < T$ (Fig. 11). To conclude this section, we note that in this case, the wall was assumed fully catalytic for vibration and chemistry. For a noncatalytic wall, there may be an increase of K_D^1 close to the wall.[19]

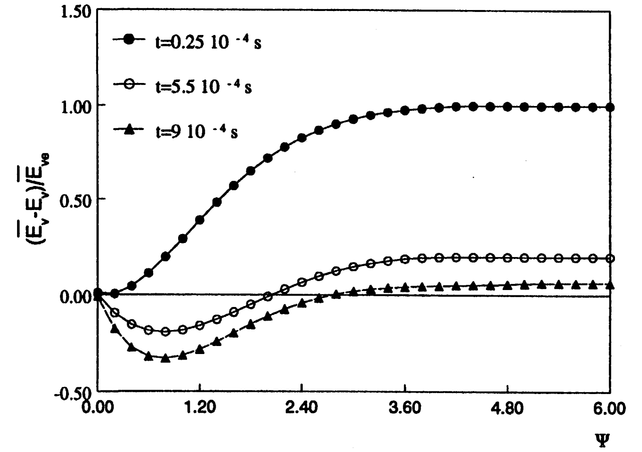

Fig. 10 Relative deviation from equilibrium vibrational energy across the end-wall boundary layer behind a reflected shock. Nitrogen, incident shock Mach number = 6. Initial temperature and pressure: $T = 295$ K, $p = 22 \times 10^{-4}$ bar. t is the time after reflection, in seconds.

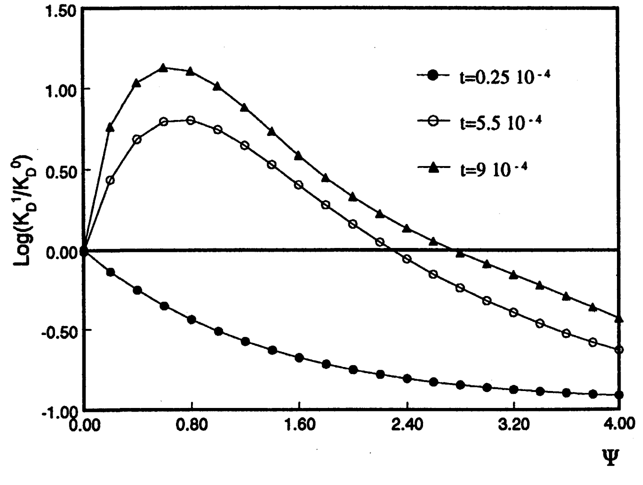

Fig. 11 Behavior of rate constant in the boundary layer. Same conditions as in Fig. 10.

Appendix: Computation of Vibrational Energy Lost per Dissociation

The definition of E_{vd} is

$$E_{vD} = \frac{\sum_i \int J_D \varepsilon_{iv}\, \mathrm{d}c}{\sum_i \int J_D\, \mathrm{d}c}$$

At the zeroth order of the distribution function, one has

$$J_D^0 = -\sum_j \int f_i^0 f_j^0 g_{ij} I_d\, \mathrm{d}\Omega\, \mathrm{d}c$$

An explicit model for k_{Di} is needed to calculate E_{vD}. If the nonpreferential CVDV mdoel is adopted, with an assumption of harmonic oscillator, one finds

$$E_{vD}^0 = \bar{E}_{vD} = \frac{k\theta(N-1)}{2}$$

which is practically equal to $0.5E_D$ for O_2 and N_2. For anharmonic oscillator models, one finds:

$$E_{vD}^0 = 0.42E_D \quad \text{for} \quad N_2, \qquad E_{vD}^0 = 0.45E_D \quad \text{for} \quad O_2$$

In the first order of the distribution function

$$J_D = -\sum_j \int f_i^0 f_j^0 (1 + \varphi_i + \varphi_j) g_{ij} I_d\, \mathrm{d}\Omega\, \mathrm{d}c$$

Finally

$$E_{vD}^1 = E_{vD}^0 \frac{K_D^0}{K_D^1} \left\{ 1 + \frac{E_v - \bar{E}_v}{C_v T} \left[\frac{(2N-1)}{3} \frac{\theta_v}{T} - \frac{\bar{E}_v}{kT} \right] \right\}$$

Conclusions

The development of a GCE method combined with the hierarchy of characteristic time scales makes a new approach to the vibration–dissociation coupling possible. In this paper, explicit formulas for rate constants and vibrational energy consumption have been derived that are valid in most nonequilibrium situations. In the future, applications to flows more sophisticated than those in the present paper, and to gas mixtures like air, could be considered.

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