# A Note of Vibrational Rate Equations for C02-N2 System Applied to C02 Gasdynamic Laser

# A Note of Vibrational Rate Equations for $CO_2-N_2$ System Applied to $CO_2$ Gasdynamic Laser

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## ABSTRACT

The detailed derivation of molecular vibrational rate equations in $CO_2-N_2$ (+He) system is presented, based on the assumption of three-mode model.  Also given is an improvement of the form of derived rate equations with temperature expression, which is convenient to time-dependent numerical analysis.  A quasi-onedimensional estimation of the characteristics of $CO_2$ gasdynamic laser by these equations was performed with the aid of mass, momentum, energy conservation, and equation of state.  Explicit time-dependent technique devised by MacCormack was employed.  The estimated performance of $CO_2$ gasdynamic laser shows reasonable agreement with the result from conventional $CO_2$ GDL analysis.

## NOMENCLATURE

$C_i$    : Mass fraction of $i$-th gas

$e_i^v$    : Vibrational energy per unit mass of $i$-th gas (mode)

$e_i^V$    : Vibrational energy per unit volume of $i$-th gas (mode)

$f$    : Activation factor, fraction of collisions that involves sufficient energy

$g_l$    : Statistical weight of $l$-th energy level

$h$    : Planck's constant, $h=6.6256\times10^{-34}$ Jsec

$k$    : Boltzmann constant, $k=1.38054\times10^{-23}$ J/K

$K_N, K_C$ : Rate constants for $T-V$ process defined by Eqs. (3-17) and (3-18)

$l$    : Quantum number of an energy level

$m_i$    : Molecular weight of $i$-th gas

$M$    : Collisional partner molecule

$N_i$    : Number (population) density of $i$-th gas per unit volume, $N_i=\sum_{l=0}^{\infty} N_{i,l}$

$N_{i,l}$    : Number density of $i$-th gas per unit volume in energy level $\varepsilon_l$

$N_{i,l}^{j,r}$    : Number density of $l$-th energy level in $i$-th mode with $r$-th level in $j$-th mode

$P$    : Steric factor, fraction of sufficiently energetic collisions for reaction

$P_C$    : rate constant of intramolecular $V-V$ process defined by Eq. (4-7)

$Q_i^v$    : Vibrational partition function of $i$-th gas

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$Q_{CN}$ : Rate constant of intermolecular $V-V$ process defined by Eq. (4-8)

$R_i$ : Gas constant of $i$-th gas, $R_i = k/m_i$

$r$ : Quantum number of a vibrational energy level

$T$ : Temperature, or translational temperature

$x_l, x_r$ : Normalized number densities defined by Eqs. (3-46)

$x_l^r$ : Normalized number density defined by Eqs. (3-46)

$X_i$ : Molar fraction of $i$-th gas

$Z$ : Number of molecular collisions per unit volume, per unit time

$z_{i,j}$ : Number of molecular collisions between $i$-th and $j$-th gases (modes)

$\nu_1, \nu_2, \nu_3, \nu_N$ : Symmetric, bending, asymmetric vibrational mode of $CO_2$, and vibrational mode of $N_2$, also denoting the energy frequencies of these modes

$\varepsilon_l$ : Vibrational energy of a molecule, $\varepsilon = lh\nu$, $l = 0, 1, 2, \ldots\ldots$

$\theta_1, \theta_2, \theta_3, \theta_N$ : Vibrational characteristic temperatures of modes $\nu_1, \nu_2, \nu_3$, and $\nu_N$

$\nu$ : Frequency of energy (radiated light), $c = \lambda\nu$

$\tau_{i,j}$ : Relaxation time of energy transfer between $i$-th and $j$-th gases (modes)

*Subscripts*

1, 2, 3, $N$ : Vibrational modes $\nu_1, \nu_2, \nu_3, \nu_N$

12 : The first mode of three-mode model, combined mode $\nu_1$ and $\nu_2$

C : $CO_2$

N : $N_2$

H, He : He

$l, r$ : Quantum numbers

# 1. INTRODUCTION

With the progress of investigations about $CO_2$ gasdynamic laser (GDL), new applications have been in our scope to technology such as isotope separation, space energy transmission, laser fusion, or material processing. Together with these applicational approach, the clarification of fundamental phenomena in $CO_2$ GDL is still of importance. As regards the general characteristics of gasdynamic lasers, the reviewed volumes by Anderson[1] and Losev[2] should be referred.

In analyzing the fundamental performance of $CO_2$ GDL, a system of vibrational relaxation equations that dominate energy transitions in laser gas system ($CO_2$-$N_2$) play a principal role. Several rate equations have been derived corresponding to the model of $CO_2$-$N_2$ vibrational relaxation processes[1,3,4]. Among others commonly employed are the

rate equations based on three-mode model, which were dissertated by Lee[5] or Anderson[6] in the standard formulation. The detailed deduction of these equations, however, is not so familiar to aerodynamicist who investigates $CO_2$ GDL from the fluid dynamical aspect, and some misunderstanding for rate equations may occur without regarding the difference of kinetic models, e. g. those of intramolecular processes.

Anderson[1] gave partly the information of these formulations following the work of Munjee[7], which is not enough to understand the intramolecular vibrational-vibrational energy transfer of $CO_2$. The derivation of these equations was given also by Suzuki[8] in detailed form.

This paper presents the detailed formulation of vibrational relaxation rate equations for $CO_2$-$N_2$ system, according to the method reported by Suzuki, with further refinement. Also an improvement of the form of rate equations is discussed in order to apply them with computational facility to the numerical time-dependent analysis of $CO_2$ GDL.

## 2. VIBRATIONAL KINETICS

Under the condition that dissociation or ionization of molecules are not prevailing, the probabilities of detailed energy transfer in $CO_2$-$N_2$ system are ultimately specified by the following vibrational kinetic reactions;
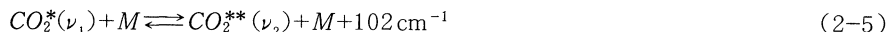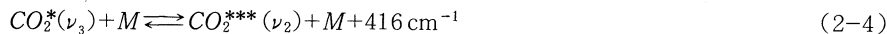
Translational-Vibrational ($T$-$V$) Processes

$$CO_2^*(\nu_2)+M \rightleftharpoons CO_2+M+667 \text{ cm}^{-1} \qquad (2-1)$$

$$N_2^*+M \rightleftharpoons N_2+M+2331 \text{ cm}^{-1} \qquad (2-2)$$

Intermolecular Vibrational-Vibrational ($V$-$V$) Processes

$$CO_2^*(\nu_3)+N_2 \rightleftharpoons CO_2+N_2^*+18 \text{ cm}^{-1} \qquad (2-3)$$

Intramolecular Vibrational-Vibrational ($V$-$V$) Processes

$$CO_2^*(\nu_3)+M \rightleftharpoons CO_2^{***}(\nu_2)+M+416 \text{ cm}^{-1} \qquad (2-4)$$

$$CO_2^*(\nu_1)+M \rightleftharpoons CO_2^{**}(\nu_2)+M+102 \text{ cm}^{-1} \qquad (2-5)$$

In these kinetic reactions, the asterisks denote the vibrational quantum level in a given mode, and $M$ represents a collisional partner which may be $CO_2$, $N_2$, (He). The intramolecular $V$-$V$ process given by Eq. (2-5) is well known as Fermi Resonance, where the energy transition is so fast that modes $\nu_1$ and $\nu_2$ can be reasonably assumed to relax in equilibrium. Though the reaction by Eq. (2-3) can also be supposed as near-resonance
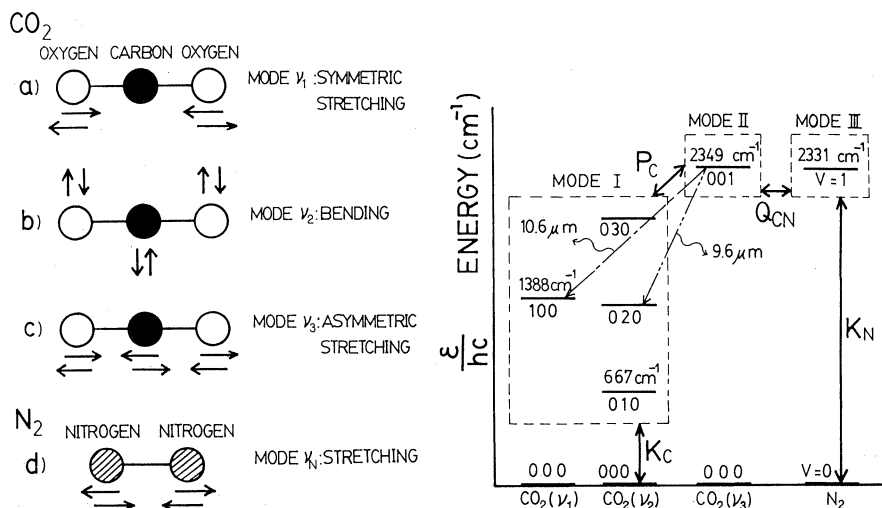
**Fig. 1**  Vibrational modes and energy levels of
$CO_2-N_2$ molecules. (three-mode model)

called "energy pumping", these modes are treated separately because of the intermo-
lecular effect and of the applicability of this analysis to laser energy extraction.    Ac-
cording to the conditions above mentioned, three-mode model can be assumed in vi-
brational kinetics of $CO_2-N_2$ (+He) system, which is shown in Fig. 1.

## 3.   FORMULATION OF RATE EQUATIONS

### 3-1.   Vibrational Energy, Transition Probability, and General Rate Equation

As for the processes shown in Fig. 1, vibrational rate equations can be derived in  corre-
spondence with Eqs. (2-1) to (2-4).    Before  penetrating  into  the  each  detailed  rate
process, several fundamental relations of molecular statistics are outlined.

The vibrational energy of unit mass of $i$-th gas, $e_i^v$, is given by

$$e_i^v = \frac{e_i^V}{N_i m_i} = \frac{1}{N_i m_i} \sum_{l=0}^{\infty} N_{i,l} \varepsilon_l = \frac{1}{N_i m_i} \sum_{l=0}^{\infty} N_{i,l} lh\nu , \tag{3-1}$$

where number density per unit volume, $N_i$, is defined by the number (population) density
of $i$-th gas, $N_{i,l}$, in energy level $\varepsilon_l$ as

$$N_i = \sum_{l=0}^{\infty} N_{i,l} , \qquad \varepsilon_l = lh\nu .$$

From local thermodynamic equilibrium (Treanor Equilibrium) defined by temperature

$T$, Boltzmann distribution in $l$-th energy level can be formed as

$$N_{i,l} = N_i \frac{g_i \exp\left(-\frac{\varepsilon_l}{kT}\right)}{Q_i^v} \qquad (3-2)$$

The statistical weight $g_l$ of $l$-th level is regarded as unity, and $Q_i^v$ is partition function of $i$-th gas to give

$$Q_i^v = \sum_{l=0}^{\infty} \exp\left(-\frac{lh\nu}{kT}\right) = \frac{1}{1-\exp\left(-\frac{h\nu}{kT}\right)}, \qquad (3-3)$$

for the system of harmonic oscillators. In terms of the combination $h\nu/k$ called characteristic temperature, $\theta_\nu$, Eqs. (3-2) and (3-3) become

$$\left. \begin{aligned} N_{i,l} &= N_i \exp\left(-\frac{l\theta_\nu}{T}\right)\left\{1-\exp\left(-\frac{\theta_\nu}{T}\right)\right\}, \\ Q_i^v &= \frac{1}{1-\exp\left(-\frac{\theta_\nu}{T}\right)}, \end{aligned} \right\} \qquad (3-4)$$

and vibrational energy $e_i^v$ of Eq. (3-1) is expressed as follows[9],

$$e_i^v = RT^2 \frac{\partial}{\partial T} \ln Q_i^v = \frac{\theta_\nu R}{\exp\left(\frac{\theta_\nu}{T}\right)-1}. \qquad (3-5)$$

These relations are applied to the gas of diatomic molecule. For poliatomic molecules the relations can be extended, and the following equations are obtained about $CO_2$ under the assumptions of local equilibriums;

$$e_c^v = (e_1^v + 2e_2^v + e_3^v) = \frac{R_c\theta_1}{\exp\left(\frac{\theta_1}{T_{12}}\right)-1} + \frac{2R_c\theta_2}{\exp\left(\frac{\theta_2}{T_{12}}\right)-1} + \frac{R_c\theta_3}{\exp\left(\frac{\theta_3}{T_3}\right)-1}, \qquad (3-6)$$

$$Q_c^v = \left\{1-\exp\left(-\frac{\theta_1}{T_{12}}\right)\right\}^{-1}\left\{1-\exp\left(-\frac{\theta_2}{T_{12}}\right)\right\}^{-2}\left\{1-\exp\left(-\frac{\theta_3}{T_3}\right)\right\}^{-1}, \qquad (3-7)$$

where $T_{12} \equiv T_1 = T_2$, $T_3$ are vibrational temperatures that define the local equilibrium vibrational energies, $R_c$ is the gas constant of $CO_2$, and $\theta_1$, $\theta_2$, $\theta_3$ denote vibrational characteristic temperature for each mode in Fig. 1, $\theta_1 = 1997\,K$, $\theta_2 = 960\,K$, $\theta_3 = 3380\,K$, $(\theta_N = 3353\,K)$. The energy $e_i^v$ is extended to the local vibrational energy in $i$-th mode of $CO_2$. The factor 2 of the second term in the right-hand side of Eq. (3-6) represents the degeneracy in $\nu_2$ mode.

In the process of vibrational energy transfer by molecular collision, the rate of a reaction is presented in the following general expression[10];

$$
\begin{pmatrix}
\text{Number of collisions} \\
\text{which take transition} \\
\text{per unit volume, per} \\
\text{unit time.}
\end{pmatrix}
=
\begin{pmatrix}
\text{Number of collisions} \\
\text{per unit volume, per} \\
\text{unit time.} \\
\text{[collision rate]} Z
\end{pmatrix}
\times
\begin{pmatrix}
\text{Fraction of collisions} \\
\text{that involve sufficient} \\
\text{energy.} \\
\text{[activation factor]} f
\end{pmatrix}
$$

$$
\times
\begin{pmatrix}
\text{Fraction of sufficiently energetic} \\
\text{collisions resulting in actual reaction,} \\
\text{defined by quantum mechanics.} \\
\text{[steric factor]} P
\end{pmatrix}
\qquad (3\text{--}8)
$$

The combination $fP$ is usually considered as transition probability. Activation factor $f$ can be evaluated from equilibrium kinetic theory[10] or simply from the principle of detailed balancing[1] to give

$$
\left.
\begin{aligned}
f\left[\genfrac{}{}{0pt}{}{l,\,l+1}{i}\right] &= \exp\left(-\frac{\theta_\nu}{T}\right) &&\text{for}\quad l \to l+1, \\[1em]
f\left[\genfrac{}{}{0pt}{}{l+1,\,l}{i}\right] &= 1 &&\text{for}\quad l+1 \to l.
\end{aligned}
\right\}
\qquad (3\text{--}9)
$$

Using the terms above mentioned, obtained is the general rate equation that represents the change per unit time of number density of harmonic oscillators in $l$-th vibrational energy level as follows;

$$
\frac{dN_{i,l}}{dt} = z_{iM} N_M N_{i,l+1} f\left[\genfrac{}{}{0pt}{}{l+1,\,l}{i}\right] P\left[\genfrac{}{}{0pt}{}{l+1,\,l}{i}\right] - z_{iM} N_M N_{i,l} f\left[\genfrac{}{}{0pt}{}{l,\,l+1}{i}\right] P\left[\genfrac{}{}{0pt}{}{l,\,l+1}{i}\right]
$$

$$
- z_{iM} N_M N_{i,l} f\left[\genfrac{}{}{0pt}{}{l,\,l-1}{i}\right] P\left[\genfrac{}{}{0pt}{}{l,\,l-1}{i}\right] + z_{iM} N_M N_{i,l-1} f\left[\genfrac{}{}{0pt}{}{l-1,\,l}{i}\right] P\left[\genfrac{}{}{0pt}{}{l-1,\,l}{i}\right], \qquad (3\text{--}10)
$$

where $z_{iM}$ is collision frequency between $i$-th gas and $M$, and the bracket $\left[\genfrac{}{}{0pt}{}{l,\,l+1}{i}\right]$ denotes the transition of $l$-th quantum level of $i$-th molecule to $l+1$ level.

## 3-2. *T-V* Energy Transfer

Regarding the transition probability, Landau-Teller's condition in quantum mechanics gives the following relations for steric factor,

$$
\left.
\begin{aligned}
P\left[\genfrac{}{}{0pt}{}{l,\,l+1}{i}\right] &= P\left[\genfrac{}{}{0pt}{}{l+1,\,l}{i}\right], \\[1em]
P\left[\genfrac{}{}{0pt}{}{l+1,\,l}{i}\right] &= (l+1) P\left[\genfrac{}{}{0pt}{}{1,\,0}{i}\right].
\end{aligned}
\right\}
\qquad (3\text{--}11)
$$

From Eqs. (3–9) and (3–11), the general rate equation (3–10) becomes in the following form,

$$\frac{dN_{i,l}}{dt}=z_{iM}N_MP[\overset{1,0}{i}]\Big[(l+1)N_{i,l+1}-lN_{i,l}+\exp\Big(-\frac{\theta_\nu}{T}\Big)\Big\{lN_{i,l-1}-(l+1)N_{i,l}\Big\}\Big).$$

$$(3\text{--}12)$$

As the vibrational energy $e_i^v$ is expressed by Eq. (3–1), the rate of energy change is obtained by multiplying $lh\nu$ to Eq. (3–12) and summing them over to give

$$\frac{de_i^v}{dt}=\frac{1}{N_im_i}z_{iM}N_MP[\overset{1,0}{i}]h\nu\sum_{l=0}^{\infty}\Big[l(l+1)N_{i,l+1}-l^2N_{i,l}+\exp\Big(-\frac{\theta_\nu}{T}\Big)\Big\{l^2N_{i,l-1}-l(l+1)N_{i,l}\Big\}\Big].$$

$$(3\text{--}13)$$

In the bracket of right-hand side of this equation, we have

$$\sum_{l=0}^{\infty}\{l(l+1)N_{i,l+1}-l^2N_{i,l}\}=\sum_{l=0}^{\infty}(l-1)lN_{i,l}-\sum_{l=0}^{\infty}l^2N_{i,l}=-\sum_{l=0}^{\infty}lN_{i,l},$$

$$(3\text{--}14)$$

and

$$\sum_{l=0}^{\infty}\{l^2N_{i,l-1}-l(l+1)N_{i,l}\}=\sum_{l=0}^{\infty}lN_{i,l}+\sum_{l=0}^{\infty}N_{i,l}.$$

$$(3\text{--}15)$$

With these relations, Eq. (3–13) is rewritten as

$$\frac{de_i^v}{dt}=\frac{1}{N_im_i}z_{iM}N_MP[\overset{1,0}{i}]\Big[-\sum_{l=0}^{\infty}lh\nu N_{i,l}+\exp\Big(-\frac{\theta_\nu}{T}\Big)\Big(\sum_{l=0}^{\infty}lh\nu N_{i,l}+h\nu\sum_{l=0}^{\infty}N_{i,l}\Big)\Big]$$

$$=\frac{1}{N_im_i}z_{iM}N_MP[\overset{1,0}{i}]\Big\{-e_i^V+\exp\Big(-\frac{\theta_\nu}{T}\Big)(e_i^V+k\theta_\nu N_i)\Big\}$$

$$=z_{iM}N_MP[\overset{1,0}{i}]\Big\{1-\exp\Big(-\frac{\theta_\nu}{T}\Big)\Big\}\Big\{\frac{R_i\theta_\nu}{\exp\Big(\frac{\theta_\nu}{T}\Big)-1}-e_i^v\Big\}.$$

$$(3\text{--}16)$$

This is the rate equation for $T$-$V$ process, and applying this relation to $N_2$ and $\nu_2$ mode of $CO_2$ (Eqs. (2–1) and (2–2)), following rate equations are represented;

$$\Big(\frac{de_N^v}{dt}\Big)_{T-V}=z_{NM}N_MP[\overset{1,0}{N}]\Big\{1-\exp\Big(-\frac{\theta_N}{T}\Big)\Big\}\Big\{\frac{R_N\theta_N}{\exp\Big(\frac{\theta_N}{T}\Big)-1}-e_N^v\Big\}$$

$$=K_N\Big\{\frac{R_N\theta_N}{\exp\Big(\frac{\theta_N}{T}\Big)-1}-e_N^v\Big\},$$

$$(3\text{--}17)$$

$$\Big(\frac{de_2^v}{dt}\Big)_{T-V}=z_{CM}N_MP[\overset{1,0}{\nu_2}]\Big\{1-\exp\Big(-\frac{\theta_2}{T}\Big)\Big\}\Big\{\frac{R_C\theta_2}{\exp\Big(\frac{\theta_2}{T}\Big)-1}-e_2^v\Big\}$$

$$=K_C\Big\{\frac{R_C\theta_2}{\exp\Big(\frac{\theta_2}{T}\Big)-1}-e_2^v\Big\},$$
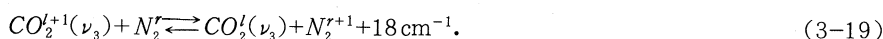
$$(3\text{--}18)$$

where $R_N$ is the gas constant of $N_2$, and $K_N, K_C$ denote the rate constants for $T$-$V$ pro-

cesses.

## 3-3.  Intermolecular $V$-$V$ Energy Transfer

As for the intermolecular process in $CO_2$–$N_2$, following kinetic reaction should be considered;

$$CO_2^{l+1}(\nu_3)+N_2^r \rightleftarrows CO_2^l(\nu_3)+N_2^{r+1}+18\,\text{cm}^{-1}. \tag{3-19}$$

Equation (2–3) corresponds to the case of the lowest quantum level of this equation, and it presents the model to determine the kinetic rate constant associated with transition probability in undermentioned procedure.  Similar to Eq. (3–9) from the principle of detailed balancing, activation factor $f$ for this intermolecular reaction can be obtained as

$$\left.\begin{aligned}
f\left[\overset{l,l+1}{\nu_3}\,;\,\overset{r+1,r}{N_2}\right]&=\exp\left(-\frac{\theta_3-\theta_N}{T}\right),\\[2mm]
f\left[\overset{l+1,l}{\nu_3}\,;\,\overset{r,r+1}{N_2}\right]&=1
\end{aligned}\right\} \tag{3-20}$$

and the relations between steric factors are given by

$$\left.\begin{aligned}
P\left[\overset{l+1,l}{\nu_3}\,;\,\overset{r,r+1}{N_2}\right]&=(l+1)(r+1)P\left[\overset{1,0}{\nu_3};\overset{0,1}{N_2}\right],\\[2mm]
P\left[\overset{l+1,l}{\nu_3}\,;\,\overset{r,r+1}{N_2}\right]&=P\left[\overset{l,l+1}{\nu_3}\,;\,\overset{r+1,r}{N_2}\right]
\end{aligned}\right\} \tag{3-21}$$

A)   Intermolecular Transition Rate for Mode $\nu_3$ of $CO_2$

With the aid of relations aforementioned, the energy transferred into mode $\nu_3$ of $CO_2$ can be estimated.  In the similar manner as Eq. (3–10), general intermolecular rate equation from Eq. (3–19) has the following summed form,

$$\begin{aligned}
\frac{dN_{3,l}}{dt}=&\sum_{r=0}^{\infty}z_{CN}N_{3,l+1}N_{N,r}f\left[\overset{l+1,l}{\nu_3}\,;\,\overset{r,r+1}{N_2}\right]P\left[\overset{l+1,l}{\nu_3}\,;\,\overset{r,r+1}{N_2}\right]\\[1mm]
&-\sum_{r=0}^{\infty}z_{CN}N_{3,l}N_{N,r+1}f\left[\overset{l,l+1}{\nu_3}\,;\,\overset{r+1,r}{N_2}\right]P\left[\overset{l,l+1}{\nu_3}\,;\,\overset{r+1,r}{N_2}\right]\\[1mm]
&-\sum_{r=0}^{\infty}z_{CN}N_{3,l}N_{N,r}f\left[\overset{l,l-1}{\nu_3}\,;\,\overset{r,r+1}{N_2}\right]P\left[\overset{l,l-1}{\nu_3}\,;\,\overset{r,r+1}{N_2}\right]\\[1mm]
&+\sum_{r=0}^{\infty}z_{CN}N_{3,l-1}N_{N,r+1}f\left[\overset{l-1,l}{\nu_3}\,;\,\overset{r+1,r}{N_2}\right]P\left[\overset{l-1,l}{\nu_3}\,;\,\overset{r+1,r}{N_2}\right].
\end{aligned} \tag{3-22}$$

Substituting Eqs. (3–20) and (3–21), and with rearrangement we have

$$\begin{aligned}
\frac{dN_{3,l}}{dt}=z_{CN}P\left[\overset{1,0}{\nu_3};\overset{0,1}{N_2}\right]&\left[\left\{(l+1)N_{3,l+1}-lN_{3,l}\right\}\sum_{r=0}^{\infty}(r+1)N_{N,r}\right.\\[1mm]
&\left.-\left\{(l+1)N_{3,l}-lN_{3,l-1}\right\}\exp\left(-\frac{\theta_3-\theta_N}{T}\right)\sum_{r=0}^{\infty}(r+1)N_{N,r+1}\right]. 
\end{aligned} \tag{3-23}$$

The summation terms can be modified as

$$\sum_{r=0}^{\infty}(r+1)N_{N,r}=\sum_{r=0}^{\infty}rN_{N,r}+\sum_{r=0}^{\infty}N_{N,r}=\frac{1}{h\nu_N}\sum_{r=0}^{\infty}h\nu_N rN_{N,r}+N_N$$

$$=N_N\left(\frac{e_N^V}{N_N\theta_N k}+1\right), \tag{3-24}$$

and

$$\sum_{r=0}^{\infty}(r+1)N_{N,r+1}=\sum_{r=0}^{\infty}rN_{N,r}=\frac{e_N^V}{k\theta_N}, \tag{3-25}$$

to give

$$\frac{dN_{3,l}}{dt}=z_{CN}N_N P[\overset{1,0}{\nu_3};\overset{0,1}{N_2}]\left[\left\{(l+1)N_{3,l+1}-lN_{3,l}\right\}\left(\frac{e_N^V}{N_N\theta_N k}+1\right)\right.$$

$$\left.-\left\{(l+1)N_{3,l}-lN_{3,l-1}\right\}\exp\left(\frac{\theta_N-\theta_3}{T}\right)\frac{e_N^V}{N_N\theta_N k}\right]. \tag{3-26}$$

The rate of energy change of $e_3^V$ per unit volume is now obtained by multiplying $lh\nu_3$ to both sides of this equation and summing them over,

$$\sum_{l=0}^{\infty}lh\nu_3\frac{dN_{3,l}}{dt}=z_{CN}N_N P[\overset{1,0}{\nu_3};\overset{0,1}{N_2}]\sum_{l=0}^{\infty}lh\nu_3\left[\left\{(l+1)N_{3,l+1}-lN_{3,l}\right\}\left(\frac{e_N^V}{N_N\theta_N k}+1\right)\right.$$

$$\left.-\left\{(l+1)N_{3,l}-lN_{3,l-1}\right\}\exp\left(\frac{\theta_N-\theta_3}{T}\right)\frac{e_N^V}{N_N\theta_N k}\right], \tag{3-27}$$

then we have

$$\frac{de_3^V}{dt}=z_{CN}N_N P[\overset{1,0}{\nu_3};\overset{0,1}{N_2}]h\nu_3\left[\left(\frac{e_N^V}{N_N\theta_N k}+1\right)\sum_{l=0}^{\infty}\left\{l(l+1)N_{3,l+1}-l^2N_{3,l}\right\}\right.$$

$$\left.-\frac{e_N^V}{N_N\theta_N k}\exp\left(\frac{\theta_N-\theta_3}{T}\right)\sum_{l=0}^{\infty}\left\{l(l+1)N_{3,l}-l^2N_{3,l-1}\right\}\right]. \tag{3-28}$$

The summation terms in the right-hand side are replaced as

$$\sum_{l=0}^{\infty}\left\{l(l+1)N_{3,l+1}-l^2N_{3,l}\right\}=\sum_{l=1}^{\infty}(l-1)lN_{3,l}-\sum_{l=0}^{\infty}l^2N_{3,l}=-\frac{e_3^V}{k\theta_3}, \tag{3-29}$$

and

$$\sum_{l=0}^{\infty}\left\{l(l+1)N_{3,l}-l^2N_{3,l-1}\right\}=\sum_{l=0}^{\infty}l(l+1)N_{3,l}-\sum_{l=-1}^{\infty}(l+1)^2N_{3,l}$$

$$=-\sum_{l=1}^{\infty}(l+1)N_{3,l}$$

$$=-\left(\frac{e_3^V}{\theta_3 k}+N_C\right). \tag{3-30}$$

Equation (3-28) thus has the form

$$\frac{de_3^V}{dt}=z_{CN}N_N P[\overset{1,0}{\nu_3};\overset{0,1}{N_2}]\left[\frac{e_N^V}{N_N\theta_N k}\exp\left(\frac{\theta_N-\theta_3}{T}\right)\left(e_3^V+N_C k\theta_3\right)-\left(\frac{e_N^V}{N_N\theta_N k}+1\right)e_3^V\right]. \tag{3-31}$$

Using the equations for energies per unit mass and gas constants,

$$e_3^v = \frac{e_3^V}{N_C m_C}, \qquad e_N^v = \frac{e_N^V}{N_N m_N}, \qquad R_C = \frac{k}{m_C}, \quad \text{and} \quad R_N = \frac{k}{m_N}, \tag{3-32}$$

the equation of intermolecular $V$-$V$ energy transfer rate per unit mass into $\nu_3$ mode of $CO_2$ is transformed as follows,

$$\left(\frac{de_3^v}{dt}\right)_{V-V}^{INT} = z_{CN} N_N P[\overset{1,0}{\nu_3}; \overset{0,1}{N_2}] \left[\frac{e_N^v}{R_N \theta_N} \exp\left(\frac{\theta_N - \theta_3}{T}\right)(e_3^v + R_C \theta_3) - \left(\frac{e_N^v}{R_N \theta_N} + 1\right)e_3^v\right]. \tag{3-33}$$

B)   Intermolecular Transition Rate for $N_2$

Similar to Eq. (3-10), the general rate equation of $r$-th energy level of $N_2$ has the form;

$$\frac{dN_{N,r}}{dt} = \sum_{l=0}^{\infty} z_{CN} N_{3,l} N_{N,r+1} f[\overset{l,l+1}{\nu_3}; \overset{r+1,r}{N_2}] P[\overset{l,l+1}{\nu_3}; \overset{r+1,r}{N_2}]$$

$$- \sum_{l=0}^{\infty} z_{CN} N_{3,l+1} N_{N,r} f[\overset{l+1,l}{\nu_3}; \overset{r,r+1}{N_2}] P[\overset{l+1,l}{\nu_3}; \overset{r,r+1}{N_2}]$$

$$- \sum_{l=0}^{\infty} z_{CN} N_{3,l} N_{N,r} f[\overset{l,l+1}{\nu_3}; \overset{r,r-1}{N_2}] P[\overset{l,l+1}{\nu_3}; \overset{r,r-1}{N_2}]$$

$$+ \sum_{l=0}^{\infty} z_{CN} N_{3,l+1} N_{N,r-1} f[\overset{l+1,l}{\nu_3}; \overset{r-1,r}{N_2}] P[\overset{l+1,l}{\nu_3}; \overset{r-1,r}{N_2}]. \tag{3-34}$$

Through the same procedure, following relations are obtained;

$$\frac{dN_{N,l}}{dt} = z_{CN} P[\overset{1,0}{\nu_3}; \overset{0,1}{N_2}] \left[\exp\left(\frac{\theta_N - \theta_3}{T}\right)\{(r+1)N_{N,r+1} - rN_{N,r}\}\sum_{l=0}^{\infty}(l+1)N_{3,l}\right.$$

$$\left. - \{(r+1)N_{N,r} - rN_{N,r-1}\}\sum_{l=0}^{\infty}(l+1)N_{3,l+1}\right], \tag{3-35}$$

$$\left.\begin{aligned}\sum_{l=0}^{\infty}(l+1)N_{3,l} &= \frac{e_3^V}{k\theta_3} + N_C, \\[2mm] \sum_{l=0}^{\infty}(l+1)N_{3,l+1} &= \frac{e_3^V}{k\theta_3}\end{aligned}\right\} \tag{3-36}$$

$$\sum_{r=0}^{\infty} rh\nu_N \frac{dN_{N,r}}{dt} = \frac{de_N^V}{dt}$$

$$= z_{CN} N_C P[\overset{1,0}{\nu_3}; \overset{0,1}{N_2}]\left[\exp\left(\frac{\theta_N - \theta_3}{T}\right)\left(\frac{e_3^V}{N_C \theta_3 k} + 1\right)h\nu_N\left\{\sum_{r=0}^{\infty} r(r+1)N_{N,r+1} - \sum_{r=0}^{\infty} r^2 N_{N,r}\right\}\right.$$

$$\left. - \frac{e_3^V h\nu_N}{N_C \theta_3 k}\left\{\sum_{r=0}^{\infty} r(r+1)N_{N,r} - \sum_{r=0}^{\infty} r^2 N_{N,r}\right\}\right], \tag{3-37}$$

$$\left.\begin{aligned}\sum_{r=0}^{\infty}\left\{r(r+1)N_{N,r+1} - r^2 N_{N,r}\right\} &= -\frac{e_N^V}{\theta_N k}, \\[2mm] \sum_{r=0}^{\infty}\left\{r(r+1)N_{N,r} - r^2 N_{N,r}\right\} &= -\left(\frac{e_N^V}{\theta_N k} + N_N\right),\end{aligned}\right\} \tag{3-38}$$

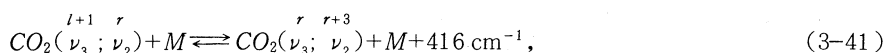and finally for the energy transferred into $N_2$ per unit mass,

$$\left(\frac{de_N^v}{dt}\right)_{V-V}^{INT}=z_{CN}N_C P\overset{1,0\ \ 0,1}{[\ \nu_3;\ N_2]}\left[(e_N^v+R_N\theta_N)\frac{e_3^v}{R_C\theta_3}-e_N^v\exp\left(\frac{\theta_N-\theta_3}{T}\right)\left(\frac{e_3^v}{R_C\theta_3}+1\right)\right]\ (3\text{–}39)$$

$$=-\frac{C_C\theta_N}{C_N\theta_3}\left(\frac{de_3^v}{dt}\right)_{V-V}^{INT},\tag{3–40}$$

where $C_C$ and $C_N$ are mass fractions of $CO_2$ and $N_2$.

## 3–4. Intramolecular $V$-$V$ Energy Transfer

The intramolecular reaction between $\nu_3$ and $\nu_2$ modes of $CO_2$ is specified as

$$CO_2(\overset{l+1}{\nu_3};\overset{r}{\nu_2})+M\rightleftharpoons CO_2(\overset{r}{\nu_3};\overset{r+3}{\nu_2})+M+416\ cm^{-1},\tag{3–41}$$

where Eq. (2–4) stands for the lowest reaction level to determine the rate constant. The principle of detailed balancing is extended to $r\to r+3$ change of quantum number, and activation factor is given by

$$\left.\begin{aligned}f\overset{l,l+1\ \ r+3,r}{[\ \nu_3;\ \ \nu_2\ ]}&=\exp\left(-\frac{\theta_3-3\theta_2}{T}\right),\\[4pt]f\overset{l+1,l\ \ r,r+3}{[\ \nu_3;\ \ \nu_2\ ]}&=1\end{aligned}\right\}\tag{3–42}$$

Also extended is Landau-Teller's condition to $r\to r+3$ change, and from quantum mechanics the relations of steric factors are

$$\left.\begin{aligned}P\overset{l+1,l\ \ r,r+3}{[\ \nu_3\ ;\ \nu_2\ ]}&=\frac{1}{6}(l+1)(r+1)(r+2)(r+3)P\overset{1,0\ \ 0,3}{[\nu_3;\ \nu_2]},\\[4pt]P\overset{l+1,l\ \ r,r+3}{[\ \nu_3\ ;\ \nu_2\ ]}&=P\overset{l,l+1\ \ r+3,r}{[\ \nu_3\ ;\ \nu_2\ ]}.\end{aligned}\right\}\tag{3–43}$$

A) Intramolecular Transition Rate for Mode $\nu_3$ of $CO_2$

Corresponding to Eq. (3–10), general rate equation for $l$-th level of mode $\nu_3$ can be written as

$$\begin{aligned}\frac{dN_{3,l}}{dt}=&\sum_{r=0}^{\infty}z_{CM}N_M N_{3,l+1}^{2,r}\,f\overset{l+1,l\ \ r,r+3}{[\ \nu_3\ ;\ \ \nu_2\ ]}P\overset{l+1,l\ \ r,r+3}{[\ \nu_3\ ;\ \ \nu_2\ ]}\\[4pt]&-\sum_{r=0}^{\infty}z_{CM}N_M N_{3,l}^{2,r+3}\,f\overset{l,l+1\ \ r+3,r}{[\ \nu_3\ ;\ \ \nu_2\ ]}P\overset{l,l+1\ \ r+3,r}{[\ \nu_3\ ;\ \ \nu_2\ ]}\\[4pt]&-\sum_{r=0}^{\infty}z_{CM}N_M N_{3,l}^{2,r}\,f\overset{l,l-1\ \ r,r+3}{[\ \nu_3\ ;\ \ \nu_2\ ]}P\overset{l,l-1\ \ r,r+3}{[\ \nu_3\ ;\ \ \nu_2\ ]}\\[4pt]&+\sum_{r=0}^{\infty}z_{CM}N_M N_{3,l-1}^{2,r+3}\,f\overset{l-1,l\ \ r+3,r}{[\ \nu_3\ ;\ \ \nu_2\ ]}P\overset{l-1,l\ \ r+3,r}{[\ \nu_3\ ;\ \ \nu_2\ ]},\end{aligned}\tag{3–44}$$

where $N_{3,l}^{2,r}$ is the number density of $CO_2$ in mode $\nu_3$ with $l$-th level and in mode $\nu_2$ with $r$-th quantum level. Substituting Eqs. (3–42) and (3–43) into Eq. (3–44), we obtain,

$$\frac{dN_{3,l}}{dt}=\frac{1}{6}z_{CM}N_M P[\overset{1,0}{\nu_3};\overset{0,3}{\nu_2}]\sum_{r=0}^{\infty}\Big[(l+1)(r+1)(r+2)(r+3)N_{3,l+1}^{2,r}-l(r+1)(r+2)(r+3)N_{3,l}^{2,r}$$

$$+\exp\Big(\frac{3\theta_2-\theta_3}{T}\Big)\Big\{l(r+1)(r+2)(r+3)N_{3,l-1}^{2,r+3}-(l+1)(r+1)(r+2)(r+3)N_{3,l}^{2,r+3}\Big\}\Big].$$

$$(3-45)$$

In this step introduced are the normalized number densities defined by following relations;

$$x_l=\frac{N_{3,l}}{N_C},\qquad x_r=\frac{N_{2,r}}{N_C},\qquad x_l^r=\frac{N_{3,l}^{2,r}}{N_C},\qquad x_l^r=\frac{N_{3,l}}{N_C}\cdot\frac{N_{2,l}}{N_C}=x_l x_r.$$

$$(3-46)$$

In terms of these variables Eq. (3-45) can be rewritten as

$$\frac{dN_{3,l}}{dt}=\frac{1}{6}z_{CM}N_M P[\overset{1,0}{\nu_3};\overset{0,3}{\nu_2}]N_C\sum_{r=0}^{\infty}\Big[(l+1)(r+1)(r+2)(r+3)x_{l+1}x_r-l(r+1)(r+2)(r+3)x_l x_r$$

$$+\exp\Big(\frac{3\theta_2-\theta_3}{T}\Big)\Big\{l(r+1)(r+2)(r+3)x_{l-1}x_{r+3}-(l+1)(r+1)(r+2)(r+3)x_l x_{r+3}\Big\}\Big].$$

$$(3-47)$$

Multiplying Eq. (3-47) by $lh\nu_3$ and summing over all energy levels, energy transfer rate of mode $\nu_3$ in the process of Eq. (3-41) can be written by

$$\frac{de_3^V}{dt}=\sum_{l=0}^{\infty}lh\nu_3\frac{dN_{3,l}}{dt}$$

$$=\frac{1}{6}z_{CM}N_M N_C h\nu_3 P[\overset{1,0}{\nu_3};\overset{0,3}{\nu_2}]\Big[\sum_{l=0}^{\infty}\sum_{r=0}^{\infty}\Big\{l(l+1)x_{l+1}-l^2 x_l\Big\}x_r(r+1)(r+2)(r+3)$$

$$+\exp\Big(\frac{3\theta_2-\theta_3}{T}\Big)\sum_{l=0}^{\infty}\sum_{r=0}^{\infty}\Big\{l^2 x_{l-1}-l(l+1)x_l\Big\}x_{r+3}(r+1)(r+2)(r+3)\Big].\qquad(3-48)$$

The first summation term in the bracket of this equation becomes

$$\sum_{l=0}^{\infty}\sum_{r=0}^{\infty}\Big\{l(l+1)x_{l+1}-l^2 x_l\Big\}x_r(r+1)(r+2)(r+3)$$

$$=\sum_{r=0}^{\infty}x_r(r+1)(r+2)(r+3)\Big\{\sum_{l=0}^{\infty}(l-1)lx_l-\sum_{l=0}^{\infty}l^2 x_l\Big\}$$

$$=-\sum_{l=0}^{\infty}lx_l\sum_{r=0}^{\infty}(r^3+6r^2+11r+6)x_r,\qquad(3-49)$$

and the second summation term is, without exponential factor,

$$\sum_{l=0}^{\infty}\sum_{r=0}^{\infty}\Big\{l^2 x_{l-1}-l(l+1)x_l\Big\}x_{r+3}(r+1)(r+2)(r+3)$$

$$=\sum_{r=0}^{\infty}x_{r+3}(r+1)(r+2)(r+3)\Big\{\sum_{l=0}^{\infty}(l+1)^2 x_l-\sum_{l=0}^{\infty}l(l+1)x_l\Big\}$$

$$=\sum_{r=0}^{\infty}(r^3 x_r-3r^2 x_r+2rx_r)\Big(1+\sum_{l=0}^{\infty}lx_l\Big).\qquad(3-50)$$

Substituting Eqs. (3-49) and (3-50) into Eq. (3-48), obtained is

$$\frac{de_3^V}{dt}=\frac{1}{6}z_{CM}N_M P\left[\overset{1,0}{\nu_3};\overset{0,3}{\nu_2}\right]\left[-e_3^V\sum_{r=0}^{\infty}(r^3+6r^2+11r+6)x_r\right.$$

$$\left.+\exp\left(\frac{3\theta_2-\theta_3}{T}\right)\left(N_c h\nu_3+e_3^V\right)\sum_{r=0}^{\infty}(r^3-3r^2+2r)x_r\right].\qquad(3-51)$$

To evaluate summation terms in Eq. (3-51), a Boltzmann distribution function is introduced. Without taking into account other modes, mode $\nu_2$ of $CO_2$ is assumed to be in a local vibrational equilibrium specified by a temperature $T$. Note that the partition function is different from what defined by Eq. (3-7) because of omitting other modes in $CO_2$. According to this assumption, following relations are obtained;

$$x_r=\frac{N_{2,r}}{N_C}=\frac{\exp\left(-\dfrac{rh\nu_2}{kT}\right)}{Q^v}=\{1-\exp(h\nu_2\beta)\}\exp(rh\nu_2\beta),\qquad(3-52)$$

$$\beta\equiv-\frac{1}{kT}\,,$$

where partition function $Q^v$ is given by Eq. (3-3), and vibrational energy per unit volume $e_2^V$ is represented from Eqs. (3-1) and (3-5),

$$e_2^V=N_c m_C e_2^v=\sum_{r=0}^{\infty}rh\nu_2 N_C x_r=\frac{N_c h\nu_2}{\exp(-h\nu_2\beta)-1}\,.\qquad(3-53)$$

From Eq. (3-53), the summation of $rx_r$ is given by

$$\sum_{r=0}^{\infty}rx_r=\frac{1}{\exp(-h\nu_2\beta)-1}=\frac{e_2^V}{N_c h\nu_2}\equiv A\,.\qquad(3-54)$$

Also from the first differentiation of this equation by $\beta$, following relation is obtained;

$$\frac{\partial}{\partial\beta}\left(\sum_{r=0}^{\infty}rx_r\right)=\frac{h\nu_2\exp(-h\nu_2\beta)}{\{\exp(-h\nu_2\beta)-1\}^2}=\frac{(e_2^V)^2\exp(-h\nu_2\beta)}{(N_C)^2h\nu_2}$$

$$=\frac{e_2^V}{N_C h\nu_2}h\nu_2\left(1+\frac{e_2^V}{N_C h\nu_2}\right)=h\nu_2 A(1+A)\,.\qquad(3-55)$$

In a similar manner the second derivative of Eq. (3-54) with respect to $\beta$ becomes as

$$\frac{\partial^2}{\partial\beta^2}\left(\sum_{r=0}^{\infty}rx_r\right)=\frac{\partial}{\partial\beta}\left[\frac{h\nu_2\exp(-h\nu_2\beta)}{\{\exp(-h\nu_2\beta)-1\}^2}\right]$$

$$=(h\nu_2)^2 A(1+A)(1+2A)\,.\qquad(3-56)$$

On the other hand the summation of $rx_r$ is also obtained from multiplying Eq. (3-52) by $r$ and taking their summation over $r$ as follows,

$$\sum_{r=0}^{\infty}rx_r=\sum_{r=0}^{\infty}r\{1-\exp(h\nu_2\beta)\}\exp(rh\nu_2\beta)\,.\qquad(3-57)$$

Taking the first derivative of this equation with $\beta$ yields

$$\frac{\partial}{\partial \beta}\left(\sum_{r=0}^{\infty} r x_r\right) = \sum_{r=0}^{\infty}\left[r^2 h\nu_2\{1-\exp(h\nu_2\beta)\}\exp(rh\nu_2\beta)-rh\nu_2\exp(h\nu_2\beta)\exp(rh\nu_2\beta)\right]$$

$$= \sum_{r=0}^{\infty} r^2 h\nu_2 x_r - \sum_{r=0}^{\infty} rh\nu_2 \frac{x_r}{\exp(-h\nu_2\beta)-1}$$

$$= h\nu_2 \sum_{r=0}^{\infty} r^2 x_r - h\nu_2 A^2,$$

and the summation of $r^2 x_r$ can be obtained from this relation together with Eq. (3–55) as

$$\sum_{r=0}^{\infty} r^2 x_r = \frac{1}{h\nu_2}\frac{\partial}{\partial \beta}\left(\sum_{r=0}^{\infty} r x_r\right) + A^2 = A + 2A^2. \tag{3–58}$$

The second differentiation of Eq. (3–57) with respect $\beta$ similarly becomes;

$$\frac{\partial^2}{\partial \beta^2}\left(\sum_{r=0}^{\infty} r x_r\right) = \frac{\partial}{\partial \beta}\sum_{r=0}^{\infty}\left[r^2 h\nu_2\{1-\exp(h\nu_2\beta)\}\exp(rh\nu_2\beta)-rh\nu_2\exp(h\nu_2\beta)\exp(rh\nu_2\beta)\right]$$

$$= \sum_{r=0}^{\infty}\left\{r^3 h^2\nu_2^2 x_r - 2r^2 h^2\nu_2^2 \frac{x_r}{\exp(-h\nu_2\beta)-1} - rh^2\nu_2^2 \frac{x_r}{\exp(-h\nu_2\beta)-1}\right\}$$

$$= h^2\nu_2^2 \sum_{r=0}^{\infty} r^3 x_r - 2e_2^V\frac{h\nu_2}{Nc}\left\{\frac{1}{h\nu_2}\frac{\partial}{\partial \beta}\left(\sum_{r=0}^{\infty} r x_r\right) + A^2\right\} - h^2\nu_2^2 A^2,$$

which gives the summation of $r^3 x_r$, along with Eq. (3–55),

$$\sum_{r=0}^{\infty} r^3 x_r = \frac{1}{(h\nu_2)^2}\frac{\partial^2}{\partial \beta^2}\left(\sum_{r=0}^{\infty} r x_r\right) + \frac{2e_2^V}{N_C(h\nu_2)^2}\cdot\frac{\partial}{\partial \beta}\left(\sum_{r=0}^{\infty} r x_r\right) + A^2 + A^3$$

$$= 6A^3 + 6A^2 + A. \tag{3–59}$$

Using Eqs. (3–54), (3–58), and (3–59), the summation terms in Eq. (3–51) can be evaluated to give;

$$\left.\begin{aligned}
\sum_{r=0}^{\infty}(r^3 x_r + 6r^2 x_r + 11r x_r + 6x_r) &= 6\left(\frac{e_2^V}{N_C h\nu_2}+1\right)^3,\\
\sum_{r=0}^{\infty}(r^3 x_r - 3r^2 x_r + 2r x_r) &= 6\left(\frac{e_2^V}{N_C h\nu_2}\right)^3.
\end{aligned}\right\} \tag{3–60}$$

Substituting these equations into Eq. (3–51), obtained is

$$\frac{de_3^V}{dt} = z_{CM}N_M P[\,_{\nu_3}^{1,0};\,_{\nu_2}^{0,3}]\left[\left(\frac{e_2^V}{N_C h\nu_2}\right)^3(e_3^V + N_C h\nu_3)\exp\left(\frac{3\theta_2-\theta_3}{T}\right) - e_3^V\left(\frac{e_2^V}{N_C h\nu_2}+1\right)^3\right]. \tag{3–61}$$

Finally the equation of intramolecular $V$-$V$ energy transfer rate per unit mass into $\nu_3$ mode of $CO_2$ is represented as follows;

$$\left(\frac{de_3^v}{dt}\right)_{v-v}^{ITR}=z_{CM}N_M P\left[\begin{smallmatrix}1,0\\\nu_3\end{smallmatrix};\begin{smallmatrix}0,3\\\nu_2\end{smallmatrix}\right]\left[\left(\frac{e_2^v}{R_C\theta_2}\right)^3(e_3^v+R_C\theta_3)\exp\left(\frac{3\theta_2-\theta_3}{T}\right)-e_3^v\left(1+\frac{e_2^v}{R_C\theta_2}\right)^3\right].$$

$$(3\text{-}62)$$

B)  Intramolecular Transition Rate for Mode $\nu_2$ of $CO_2$

Similar consideration can be applied to the mode $\nu_2$ of $CO_2$, and the equivalent rate equation to Eq. (3-44);

$$\frac{dN_{2,r}}{dt}=\sum_{l=0}^{\infty}z_{CM}N_M N_{3,l}^{2,r+3}f\left[\begin{smallmatrix}l,l+1\\\nu_3\end{smallmatrix};\begin{smallmatrix}r+3,r\\\nu_2\end{smallmatrix}\right]P\left[\begin{smallmatrix}l,l+1\\\nu_3\end{smallmatrix};\begin{smallmatrix}r+3,r\\\nu_2\end{smallmatrix}\right]$$

$$-\sum_{l=0}^{\infty}z_{CM}N_M N_{3,l}^{2,r}f\left[\begin{smallmatrix}l,l+1\\\nu_3\end{smallmatrix};\begin{smallmatrix}r,r-3\\\nu_2\end{smallmatrix}\right]P\left[\begin{smallmatrix}l,l+1\\\nu_3\end{smallmatrix};\begin{smallmatrix}r,r-3\\\nu_2\end{smallmatrix}\right]$$

$$-\sum_{l=0}^{\infty}z_{CM}N_M N_{3,l+1}^{2,r}f\left[\begin{smallmatrix}l+1,l\\\nu_3\end{smallmatrix};\begin{smallmatrix}r,r+3\\\nu_2\end{smallmatrix}\right]P\left[\begin{smallmatrix}l+1,l\\\nu_3\end{smallmatrix};\begin{smallmatrix}r,r+3\\\nu_2\end{smallmatrix}\right]$$

$$+\sum_{l=0}^{\infty}z_{CM}N_M N_{3,l+1}^{2,r-3}f\left[\begin{smallmatrix}l+1,l\\\nu_3\end{smallmatrix};\begin{smallmatrix}r-3,r\\\nu_2\end{smallmatrix}\right]P\left[\begin{smallmatrix}l+1,l\\\nu_3\end{smallmatrix};\begin{smallmatrix}r-3,r\\\nu_2\end{smallmatrix}\right]\qquad(3\text{-}63)$$

is transformed into

$$\frac{dN_{2,r}}{dt}=\frac{1}{6}z_{CM}N_M N_C P\left[\begin{smallmatrix}1,0\\\nu_3\end{smallmatrix};\begin{smallmatrix}0,3\\\nu_2\end{smallmatrix}\right]\left[\sum_{l=0}^{\infty}(l+1)x_l\left\{(r+1)(r+2)(r+3)x_{r+3}-r(r-1)(r-2)x_r\right\}\right.$$

$$\left.\times\exp\left(\frac{3\theta_2-\theta_3}{T}\right)-\sum_{l=0}^{\infty}(l+1)x_{l+1}\left\{(r+1)(r+2)(r+3)x_r-r(r-1)(r-2)x_{r-3}\right\}\right].$$

$$(3\text{-}64)$$

Making use of the following equations;

$$\left.\begin{aligned}&\sum_{l=0}^{\infty}x_l=1,\\[4pt]&\sum_{l=0}^{\infty}(l+1)x_l=\frac{e_3^V}{h\nu_3 N_C}+1,\\[4pt]&\sum_{l=0}^{\infty}(l+1)x_{l+1}=\frac{e_3^V}{h\nu_3 N_C},\end{aligned}\right\}\qquad(3\text{-}65)$$

and multiplying by $rh\nu_2$, the summed rate of energy transfer becomes as;

$$\frac{de_2^V}{dt}=\sum_{r=0}^{\infty}rh\nu_2\frac{dN_{2,r}}{dt}$$

$$=\frac{1}{6}z_{CM}N_M N_C P\left[\begin{smallmatrix}1,0\\\nu_3\end{smallmatrix};\begin{smallmatrix}0,3\\\nu_2\end{smallmatrix}\right]\left[h\nu_2\left(\frac{e_3^V}{N_C h\nu_3}+1\right)\exp\left(\frac{3\theta_2-\theta_3}{T}\right)\left\{\sum_{r=0}^{\infty}r(r+1)(r+2)(r+3)x_{r+3}\right.\right.$$

$$-\sum_{r=0}^{\infty}r^2(r-1)(r-2)x_r\Big\}-h\nu_2\left(\frac{e_3^V}{N_C h\nu_3}\right)\Big\{\sum_{r=0}^{\infty}r(r+1)(r+2)(r+3)x_r$$

$$-\sum_{r=0}^{\infty}r^2(r-1)(r-2)x_{r-3}\Big\}\Big].\qquad(3\text{-}66)$$

The summation terms in bracket are estimated by

$$\sum_{r=0}^{\infty} r(r+1)(r+2)(r+3)x_{r+3}-\sum_{r=0}^{\infty} r^2(r-1)(r-2)x_r=-18\left(\frac{e_2^V}{Nch\nu_2}\right)^3,$$

$$\sum_{r=0}^{\infty} r(r+1)(r+2)(r+3)x_r-\sum_{r=0}^{\infty} r^2(r-1)(r-2)x_{r-3}=-18\left(\frac{e_2^V}{Nch\nu_2}+1\right)^3.$$

$$(3-67)$$

And finally obtained is the rate equation of intramolecular $V$-$V$ energy transfer per unit mass to mode $\nu_2$ of $CO_2$ as follows;

$$\left(\frac{de_2^v}{dt}\right)_{V-V}^{ITR}=z_{CM}N_MP\left[\begin{smallmatrix}1,0 & 0,3\\ \nu_3 & ; & \nu_2\end{smallmatrix}\right]\frac{3\theta_2}{\theta_3}\left[-\left(\frac{e_2^v}{R_C\theta_2}\right)^3(e_3^v+R_C\theta_3)\exp\left(\frac{3\theta_2-\theta_3}{T}\right)+e_3^v\left(1+\frac{e_2^v}{R_C\theta_2}\right)^3\right].$$

$$(3-68)$$

## 4. COMBINED RATE EQUATIONS FOR $CO_2$-$N_2$ SYSTEM

According to the three-mode model shown in Fig. 1, summarized energy rate equations for modes of energies $e_{12}^v=e_1^v+2e_2^v$, $e_3^v$, and $e_N^v$ can be given by the following relations;

$$\frac{de_{12}^v}{dt}=2\left(\frac{de_2^v}{dt}\right)_{T-V}+2\left(\frac{de_2^v}{dt}\right)_{V-V}^{ITR},$$

$$\frac{de_3^v}{dt}=\left(\frac{de_3^v}{dt}\right)_{V-V}^{INT}+2\left(\frac{de_3^v}{dt}\right)_{V-V}^{ITR},$$

$$\frac{de_N^v}{dt}=\left(\frac{de_N^v}{dt}\right)_{T-V}+\left(\frac{de_N^v}{dt}\right)_{V-V}^{INT}.$$

$$(4-1)$$

Substituting Eqs. (3-17), (3-18), (3-33), (3-40), (3-62), and (3-68) into these terms yields the final form of Eqs. (4-1) as;

$$\frac{de_{12}^v}{dt}=-\varDelta e_2^v+\frac{3\theta_2}{\theta_3}\varDelta e_{32}^v,$$

$$(4-2)$$

$$\frac{de_3^v}{dt}=-\varDelta e_{32}^v+\varDelta e_{3N}^V,$$

$$(4-3)$$

$$\frac{de_N^v}{dt}=-\varDelta e_N^v-\frac{C_C\theta_N}{C_N\theta_3}\varDelta e_{3N}^v,$$

$$(4-4)$$

where

$$\varDelta e_2^v=2K_C\left\{e_2^v-\frac{R_C\theta_2}{\exp\left(\frac{\theta_2}{T}\right)-1}\right\},$$

$$(4-5)$$

$$\varDelta e_N^v=K_N\left\{e_N^v-\frac{R_N\theta_N}{\exp\left(\frac{\theta_N}{T}\right)-1}\right\},$$

$$(4-6)$$

$$\Delta e_{32}^{v}=2P_C\left\{\left(\frac{e_2^v}{R_C\theta_2}+1\right)^3 e_3^v-(e_3^v+R_C\theta_3)\left(\frac{e_2^v}{R_C\theta_2}\right)^3\exp\left(\frac{3\theta_2-\theta_3}{T}\right)\right\}, \qquad (4-7)$$

$$\Delta e_{3N}^{v}=Q_{CN}\left\{(e_3^v+R_C\theta_3)\frac{e_N^v}{R_N\theta_N}\exp\left(\frac{\theta_N-\theta_3}{T}\right)-\left(\frac{e_N^v}{R_N\theta_N}+1\right)e_3^v\right\}. \qquad (4-8)$$

These relations are what are called vibrational rate equations for $CO_2-N_2$ (+He) system

employed in the analysis of $CO_2$ GDL. Here rate constants $P_C$ and $Q_{CN}$ are defined by

$$P_C=z_{CM}N_M P[\overset{1,0}{\nu}_3;\overset{0,3}{\nu}_2],$$

$$Q_{CN}=z_{CN}N_N P[\overset{1,0}{\nu}_3;\overset{0,1}{N_2}],$$

and each of these constants is the reciprocal of vibrational relaxation time $\tau$, so that the

parallel resistance rule for $\tau$ can be applied to the constants to give,

$$\left.\begin{aligned}
K_C&=\frac{X_N}{\tau_{2N}}+\frac{X_C}{\tau_{2C}}+\frac{X_{He}}{\tau_{2He}},\\[4pt]
K_N&=\frac{X_{He}}{\tau_{NHe}},\\[4pt]
P_C&=\frac{X_N}{\tau_{3N}}+\frac{X_C}{\tau_{3C}}+\frac{X_{He}}{\tau_{3He}},\\[4pt]
Q_{CN}&=\frac{X_N}{\tau_{NC}},
\end{aligned}\right\} \qquad (4-9)$$

with neglecting small terms. Relaxation times can be practically determined by empirical

data, e. g. from Taylor and Bittermann[11]. The data for relaxation times used in our in-

vestigation of $CO_2$ GDL are examplified as follows;

$$\left.\begin{aligned}
&\log(p\tau_{2C})=-0.7636-30.94\alpha+599.1\alpha^2-2123\alpha^3,\\[2pt]
&\log(p\tau_{2N})=-2.475+41.43\alpha-94.36\alpha^2,\\[2pt]
&\log(p\tau_{2He})=1.673-72.31\alpha+635.9\alpha^2-1667\alpha^3,\\[2pt]
&\log(p\tau_{NHe})=-2.179+34.6\alpha,\\[2pt]
&\log(p\tau_{NC})=-0.7297+19.03\alpha-170.4\alpha^2+159.7\alpha^3,\\[2pt]
&\log(p\tau_{3C})=-0.9207-89.93\alpha+1433\alpha^2-5114\alpha^3,\\[2pt]
&\log(p\tau_{3N})=-20.73+412.9\alpha-2681\alpha^2+5988\alpha^3,\\[2pt]
&\log(p\tau_{3He})=3.360-160.8\alpha+1821\alpha^2-5699\alpha^3,
\end{aligned}\right\} \qquad (4-10)$$

where $T(K)$, $p(\text{atm})$, and $\tau(\mu\,\text{sec})$ are employed and

$$\alpha=T^{-1/3}.$$

For example, the relaxation constants obtained from Eqs. (4-9) and (4-10) are shown

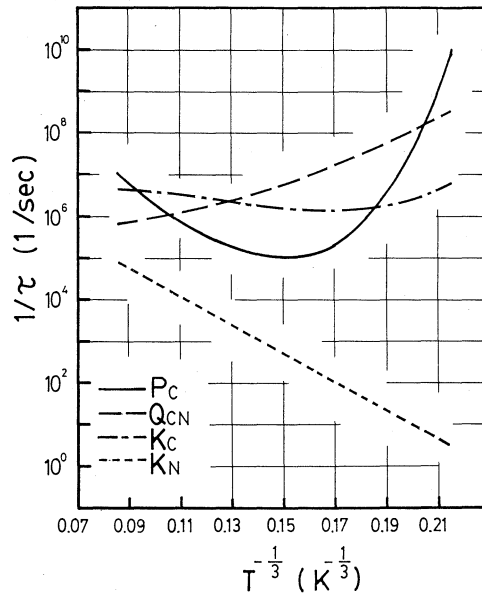in Fig. 2, in the case of $(X_C, X_N, X_{He})=(0.1, 0.4, 0.5)$.

**Fig. 2** Variation of rate constants with temperature.

$(X_C,\ X_N,\ X_{He})=(0.1,\ 0.4,\ 0.5)$

## 5.  AN IMPROVED FORM OF RATE EQUATIONS

Owing to the assumption of 3-mode model in $CO_2$–$N_2$ system, modes $\nu_1$ and $\nu_2$ are specified by a single vibrational temperature $T_{12}$. When this model is applied to the numerical analysis such as time-dependent method for quasi-onedimensional nozzle flow of $CO_2$–$N_2$, algebraic equation with respect to $T_{12}$ must be numerically solved at each step to obtain the energies $e_1^v$ and $e_2^v$ separately.  To avoid this numerical inefficiency, the rate equations are transformed into the improved expression with vibrational temperatures.

Since the vibrational energy in each mode is a function of single vibrational temperature, following derivatives with respect to the temperatures can be derived;

$$\frac{de_{12}^v}{dT_{12}}=R_C\left[\frac{\exp\left(\frac{\theta_1}{T_{12}}\right)}{\left(\frac{T_{12}}{\theta_1}\right)^2\left\{\exp\left(\frac{\theta_1}{T_{12}}\right)-1\right\}^2}+2\,\frac{\exp\left(\frac{\theta_2}{T_{12}}\right)}{\left(\frac{T_{12}}{\theta_2}\right)^2\left\{\exp\left(\frac{\theta_2}{T_{12}}\right)-1\right\}^2}\right], \tag{5-1}$$

$$\frac{de_3^v}{dT_3}=R_C\,\frac{\exp\left(\frac{\theta_3}{T_3}\right)}{\left(\frac{T_3}{\theta_3}\right)^2\left\{\exp\left(\frac{\theta_3}{T_3}\right)-1\right\}^2}, \tag{5-2}$$

$$\frac{de_N^v}{dT_N} = R_N \frac{\exp\left(\frac{\theta_N}{T_N}\right)}{\left(\frac{T_N}{\theta_N}\right)^2 \left\{\exp\left(\frac{\theta_N}{T_N}\right)-1\right\}^2} . \tag{5-3}$$

The Rate Equation (4-2) for mode I in Fig. 1 can be arranged as

$$\frac{de_{12}^v}{dT_{12}} \frac{dT_{12}}{dt} = -\Delta e_2^v + \frac{3\theta_2}{\theta_3} \Delta e_{32}^v , \tag{5-4}$$

and with the aid of local equilibrium together with Eq. (5-1), the expression with $T_{12}$ transformed from Eq. (5-4) is obtained as

$$\frac{d}{dt}\left(\frac{T_{12}}{\theta_2}\right) = \left[\frac{\exp\left(\frac{\theta_1}{T_{12}}\right)}{\left(\frac{T_{12}}{\theta_1}\right)^2\left\{\exp\left(\frac{\theta_1}{T_{12}}\right)-1\right\}^2} + 2\frac{\exp\left(\frac{\theta_2}{T_{12}}\right)}{\left(\frac{T_{12}}{\theta_2}\right)^2\left\{\exp\left(\frac{\theta_2}{T_{12}}\right)-1\right\}^2}\right]^{-1} (-\Delta T_2^v + 3\Delta T_{32}^v), \tag{5-5}$$

where $\Delta T_2^v$ and $\Delta T_{32}^v$ are defined by

$$\Delta T_2^v = 2K_C\left\{\frac{1}{\exp\left(\frac{\theta_2}{T_{12}}\right)-1} - \frac{1}{\exp\left(\frac{\theta_2}{T}\right)-1}\right\}, \tag{5-6}$$

$$\Delta T_{32}^v = 2P_C \frac{\left\{\exp\left(\frac{\theta_2}{T_{12}}\right)\right\}^3 - \exp\left(\frac{\theta_3}{T_3}\right)\exp\left(\frac{3\theta_2-\theta_3}{T}\right)}{\left\{\exp\left(\frac{\theta_2}{T_{12}}\right)-1\right\}^3\left\{\exp\left(\frac{\theta_3}{T_3}\right)-1\right\}} . \tag{5-7}$$

In the similar procedure to obtain Eq. (5-5), expressions of Eq. (4-3) by $T_3$ and Eq. (4-4) by $T_N$ can be transformed as follows;

$$\frac{d}{dt}\left(\frac{T_3}{\theta_3}\right) = \frac{\left(\frac{T_3}{\theta_3}\right)^2\left\{\exp\left(\frac{\theta_3}{T_3}\right)-1\right\}^2}{\exp\left(\frac{\theta_3}{T_3}\right)}(-\Delta T_{32}^v + \Delta T_{3N}^v) , \tag{5-8}$$

$$\frac{d}{dt}\left(\frac{T_N}{\theta_N}\right) = \frac{\left(\frac{T_N}{\theta_N}\right)^2\left\{\exp\left(\frac{\theta_N}{T_N}\right)-1\right\}^2}{\exp\left(\frac{\theta_N}{T_N}\right)}\left(-\Delta T_N^v - \frac{C_C R_C}{C_N R_N}\Delta T_{3N}^v\right), \tag{5-9}$$

where $\Delta T_{3N}^v$ and $\Delta T_N^v$ are given by

$$\Delta T_{3N}^v = Q_{CN}\frac{\exp\left(\frac{\theta_3}{T_3}\right)\exp\left(\frac{\theta_N-\theta_3}{T}\right) - \exp\left(\frac{\theta_N}{T_N}\right)}{\left\{\exp\left(\frac{\theta_3}{T_3}\right)-1\right\}\left\{\exp\left(\frac{\theta_N}{T_N}\right)-1\right\}} , \tag{5-10}$$

$$\Delta T_N^v = K_N\left\{\frac{1}{\exp\left(\frac{\theta_N}{T_N}\right)-1} - \frac{1}{\exp\left(\frac{\theta_N}{T}\right)-1}\right\}. \tag{5-11}$$

Equations (5-5), (5-8) and (5-9) are the temperature expression of rate equations, which can be employed to numerical analysis without solving them to obtain vibrational temperatures in each numerical step.　　The similar consideration can be applied also to the vibrational energy expression of rate equations, and both expressions are utilized according to numerical demand.

# 6.　CONCLUSION

According to the assumption of three-mode model in $CO_2$–$N_2$ (+He) system, the detailed derivations of molecular vibrational rate equations are presented. An improvement of the form of these equations convenient to time-dependent numerical　analysis　is　also made to be present.

Along with this system of rate equations, mass, momentum, and energy equations and equation of state are employed to estimate the performance of $CO_2$ GDL.　A quasi-onedimensional calculation of these equation was applied to a nozzle shown in Fig. 3 by explicit time-dependent numerical method devised by MacCormack as an example.　　The typical result for the distributions of temperatures $T$, $T_2$, $T_3$, and $T_N$ is represented in Fig. 4. As can be seen in this figure, the present method by the system of rate equations with temperature expressions predicts reasonable performance of conventional $CO_2$ GDL.

$A^* = 200 \ (mm^2)$
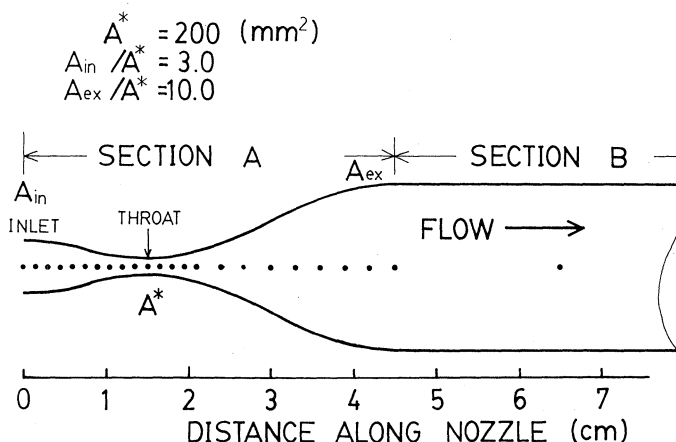$A_{in}/A^* = 3.0$
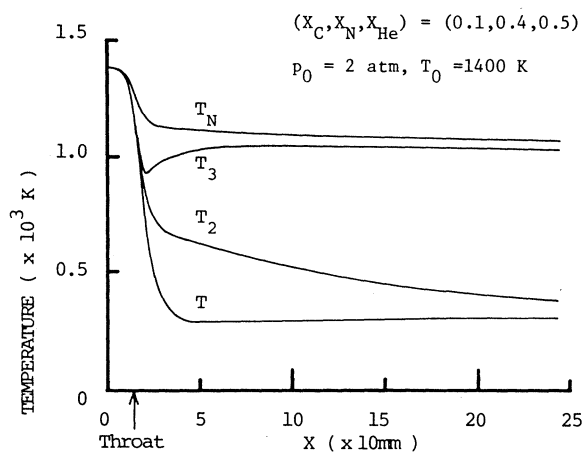$A_{ex}/A^* = 10.0$



**Fig. 3** Nozzle configuration



**Fig. 4** Distributions of translational and vibrational
temperatures along the nozzle.

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