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Technical Notes

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Modeling of High-Temperature Air Species Nonequilibrium Spectral Radiation Properties

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Nomenclature

A_{ul} = Einstein spontaneous emission coefficient
B_{lu} = Einstein absorption coefficient
c = velocity of light
e = electron charge
g_e = degeneracy of electronic level of molecular
g_I = nuclear statistical weight
$g_{i,a}$ = degeneracy of the ith energy level of the atom
h = Planck constant
k = Boltzmann constant
m_e = electron mass
N = number density
n = principal quantum number
Q_V = vibrational partition function
T = translational temperature
T_e = electronic temperature
T_r = rotational temperature
T_V = vibrational temperature
T_0 = initial environmental temperature
Z = ion charge number
ε = energy of the vibrational level
ε_D = dissociation energy
ν = frequency
σ = symmetric factor

Subscripts

u = upper level
l = lower level

I. Introduction

THE phenomenon of high-temperature thermochemical nonequilibrium gas radiation is an important aspect of high-temperature aerodynamics and aerothermophysics research [1–3]. For example, the hypersonic reentry vehicle must experience a terrible thermal environment during the atmosphere passes, and the gas in the flowfield around the front of the reentry vehicle, especially in the head shock layer, has a very high temperature. Owing to the high temperature, the gas species in the shock layer, such as air species N_2, N_2^+, N, N^+, O_2, O_2^+, O, O^+, NO, NO^+, and e^-, will be excited with various thermochemical processes such as dissociation, ionization, and recombination, and will emit strong radiation. Because of the different thermochemical processes with different relaxation times [4–6], the gases are usually in a thermochemical nonequilibrium state. Thermal radiation is a manner of energy transmission, and so a nonequilibrium radiation problem is very important for studying nonequilibrium phenomena.

Since the 1960s, the theoretical [7] and experimental [8,9] investigation of air radiation properties under high temperature has been carried out. The previous theoretical work calculated the air absorption coefficient in thermal equilibrium, but few in nonequilibrium. Since the 1980s, the physical phenomenon of nonequilibrium gas radiation coupled with flowfield and chemical reaction has been a subject of interesting research in hypersonic vehicle reentry, and some algorithms have been developed. A nonequilibrium correction factor method [10] was developed using approximate correction factors for the calculation of nonequilibrium energy level populations and an eight-step model for absorption. Park [11] developed a nonequilibrium air radiation (NEQAIR) code, which includes detailed descriptions of the radiative transitions. The nonequilibrium populations of the energy levels are obtained by solving the energy levels' rate equations using the quasi-steady-state approximation and the detailed line-by-line approach is implemented to calculate absorption. Based on NEQAIR, Hartung [12] advanced Langley's optimized radiative nonequilibrium code by applying the smeared band approximation for molecular radiation. The direct simulation Monte Carlo (DSMC) [13] method is also used for radiation modeling. The power of DSMC lies in its direct modeling of the physical processes involved, and therefore suffers most from uncertainties in what these models and their parameters should be. Unfortunately, owing to the fact that many rate coefficients in energy level rate equations for calculating level population distributions are inadequate, current theoretical methods are often inadequate or too cumbersome for practical application [14].

In this paper, the correlated multitemperature coupled-vibration-dissociation (CMTCVD) model [15] is used to calculate the nonequilibrium population distribution of vibrational energy levels, then the CMTCVD model is combined with the three-temperature model [4] to calculate the nonequilibrium level distributions of a gas mixture with 11 air species. At the same time, the important absorption and emission band systems of the gas molecular, as well as the gas atomic, line and continuous spectrum absorption are considered. At last, a simple model to calculate the absorption and emission coefficient of 11 air species is established. This model can be applied to both the air equilibrium and nonequilibrium radiation calculation.

II. Model Description

A. CMTCVD Model

The main idea of the CMTCVD model [15] is as follows: The energy difference between neighboring vibrational levels decreases

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with the increase of the vibrational quantum number, because the practical vibration of the diatomic molecule is inharmonious [2], as depicted in Fig. 1. The harmonicity is better in the lower vibrational levels, whereas the energy difference is smaller in the higher vibrational levels. For this reason, the vibration–vibration (VV) energy exchange in the lower vibrational levels of molecules is rapid, and the vibration–translation (VT) energy exchange is also rapid in the higher vibrational levels and between the higher vibrational levels and free levels (dissociation) [16–19], as shown in Fig. 1. Therefore, the lower and higher vibrational levels can, respectively, reach quasi equilibrium quickly in relaxation processes. Whereas from the lower vibrational levels to the higher ones, the excitation process of the molecule needs to cover many VV and VT energy exchange processes between the middle vibrational levels. However, as some experiments and theories [20,21] revealed, the relaxation of the middle vibrational levels is slower than that of the lower and higher levels, because VV or VT energy exchange is inefficient due to the inharmonious vibration and large energy gaps between the middle vibrational levels. And so, the slower relaxation processes of the middle levels delay the energy transfer from the lower to higher levels. It is one of the most important reasons for non-Boltzmann distribution in vibrational levels.

Using the aforementioned analyses, the vibrational excitation and dissociation of diatomic molecules in a heating case is divided into two stages in the CMTCVD model. The first one is the incubation period, in which a quasi-equilibrium state is quickly reached independently in the lower and higher vibrational levels, and the dissociation is very slight in this stage. The second one is the stage after the incubation period (coupled-vibration-dissociation period), in which the energy relaxation process of the middle vibrational levels is the primary restricting process of the whole vibration-dissociation system, that is, the dissociation rate and equilibrium degree of the vibration system are controlled by the population distribution of the middle vibrational levels. In succession, the two different vibrational temperatures that correspond to these two stages are redefined by a modified Hammerling hypothesis [22]. In the incubation period the vibrational temperature $T_{v,\mathrm{inc}}$ is represented by the population distribution of the lower and higher vibrational levels, and in the coupled-vibration-dissociation period the vibrational temperature $T_{v,\mathrm{dis}}$ is represented by the population distribution of the middle vibrational levels. And so, the nonequilibrium vibrational level population distributions of a given electronic energy level in and after the incubation period can be presented [15] as follows:

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

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

where N and $N(\varepsilon)$ are the molecular number densities of the studied electronic energy level and that of the ε vibrational level, respectively.

Equations (1) and (2) are functions which correlate vibrational temperature, initial temperature, and environmental temperature to simulate diatomic molecular vibrational level population distributions in the thermodynamic nonequilibrium relaxing processes. When in an equilibrium state, $T_{v,\mathrm{inc}}$ and $T_{v,\mathrm{dis}}$ are equal to T_0 and T, then Eqs. (1) and (2) reduce to the Boltzmann distribution.

A heating case in a nonequilibrium state is taken into consideration. The gas mixture made up of N_2 and N is assumed to initially be in equilibrium at $T_0 = 4000$ K and instantaneously heated to 8000 K. Vibrational excitation and dissociation are specified to occur at a constant volume and in an isothermal condition. This process is qualitatively similar to that occurring behind a shock wave. According to Eqs. (1) and (2), the nonequilibrium vibrational level population distributions at different vibrational temperatures in and after the incubation period are shown in Fig. 2. The detailed deductions, comparisons, and analyses of the CMTCVD model are out of the scope of this paper and can be found in [15].

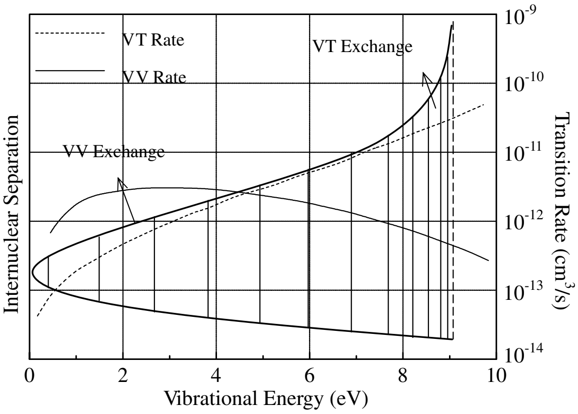

Fig. 1 Schematic of the vibrational potential well and VV and VT transition rates.

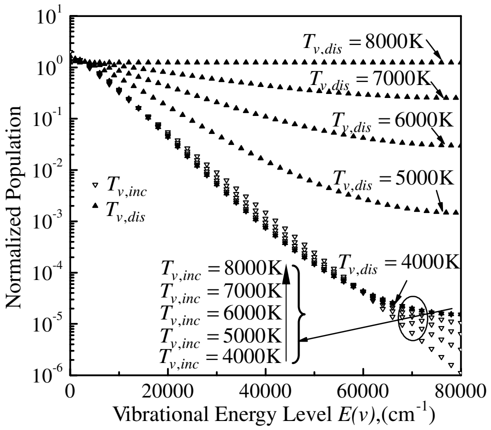

Fig. 2 Normalized vibrational population calculated by the CMTCVD model at different vibrational temperatures.

B. Modified Three-Temperature Model

The nonequilibrium population densities of energy levels are the result of various energy relaxation processes. The three-temperature model advanced in [4] assumed that each relaxation process rapidly reached an equilibrium state corresponding to the controlled temperature of each energy mode. That is to say, the population of electronic energy levels, vibrational energy levels, and rotational energy levels number densities are in agreement with the Boltzmann distribution, respectively, which is marked by electronic temperature T_e, vibrational temperature T_v, and rotational temperature T_r. At the same time, the translational temperature of a free electron is assumed to be equal to the electronic temperature, and the translational temperature of the heavy particle is assumed to be equal to the rotational temperature. And so the degree of nonequilibrium can be characterized by the departure degree of these three temperatures. If these three temperatures are equal to one another, then the equilibrium number densities are obtained. In this paper, the three-temperature model is modified by the CMTCVD model to calculate the nonequilibrium vibrational level population distributions of a diatomic molecule.

1. Electronic Excitation of Atoms

In an equilibrium state, the energy levels are populated according to the Boltzmann distribution and characterized by a uniform kinetics temperature. In a nonequilibrium state, from the assumption of the three-temperature model, the relationship between the electronic level population densities and the total number densities also follows the Boltzmann distribution, but is characterized by the electronic level temperature and electronic translational temperature T_e:

$$\frac{N_{i,a}}{N_{\mathrm{tot},a}}=\frac{g_{i,a}}{Q_{\mathrm{tot},a}}\exp\left(-\frac{\Delta E_i}{kT_e}\right) \tag{3}$$

$$Q_{\mathrm{tot},a}=\sum_i g_{i,a}\exp\left(-\frac{\Delta E_i}{kT_e}\right) \tag{4}$$

where ΔE_i is the energy differential of the ith energy level to ground level ($i=1$), $N_{i,a}$ is the number density of the ith level of the atom, $N_{\mathrm{tot},a}$ is the total number density, and $Q_{\mathrm{tot},a}$ is the atomic internal partition function.

2. Molecular Excitation

It is well known that the internal energy of a molecule consists of electronic energy, vibrational energy, and rotational energy. And so one can make an assumption in the same way that the excitation mechanisms of these three energy modes are independent of one another and each energy mode will quickly relax from nonequilibrium to equilibrium marked by each characteristic temperature. And so the electronic level and the rotational level are populated according to the Boltzmann distribution dominated by T_e and T_r, respectively. The vibrational level is populated according to the CMTCVD model dominated by T_v.

The electronic level (e) population is as follows:

$$\frac{N_e}{N_{\mathrm{tot}}}=\frac{g_e[Q_v^{(e)}Q_r^{(e,v)}]\exp[\frac{-hcT(e)}{kT_e}]}{Q_{\mathrm{tot}}}\frac{(2I_1+1)(2I_2+1)}{\sigma} \tag{5}$$

The vibrational level (e, v) population in and after the incubation period according to Eqs. (1) and (2) is as follows:

$$\frac{N_{e,v}}{N_e}=\frac{Q_r^{(e,v)}\exp\{-\frac{\varepsilon}{kT_{v,\mathrm{inc}}}+\frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}(\frac{1}{T_{v,\mathrm{inc}}}-\frac{1}{T_0})\varepsilon^{1.5}+\frac{\sqrt{2}+1}{k\varepsilon_D}(\frac{1}{T_0}-\frac{1}{T_{v,\mathrm{inc}}})\varepsilon^2\}}{[Q_v^{(e)}Q_r^{(e,v)}]_{\mathrm{inc}}} \tag{6}$$

$$\frac{N_{e,v}}{N_e}=\frac{Q_r^{(e,v)}\exp\{-\frac{\varepsilon}{kT}+\frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}(\frac{1}{T}-\frac{1}{T_{v,\mathrm{dis}}})\varepsilon^{1.5}+\frac{\sqrt{2}+1}{k\varepsilon_D}(\frac{1}{T_{v,\mathrm{dis}}}-\frac{1}{T})\varepsilon^2\}}{[Q_v^{(e)}Q_r^{(e,v)}]_{\mathrm{dis}}} \tag{7}$$

The rotational level (e, v, j) population is as follows:

$$\frac{N_{e,v,j}}{N_{e,v}}=\frac{(2J+1)g_I\exp[-hcF(e,\mathrm{v},j)/kT_r]}{Q_r^{(e,v)}(2I_1+1)(2I_2+1)/\sigma} \tag{8}$$

where Q_{tot}, Q_e, $Q_v^{(e)}$, and $Q_r^{(e,v)}$ are molecular, electronic, vibrational, and rotational partition functions, respectively, and given by

$$Q_{\mathrm{tot}}=\frac{(2I_1+1)(2I_2+1)}{\sigma}[Q_eQ_v^{(e)}Q_r^{(e,v)}] \tag{9}$$

$$\begin{aligned}[Q_eQ_v^{(e)}Q_r^{(e,v)}]_{\mathrm{inc}}=\sum_e\Bigg(\sum_v\Bigg\{\exp\Bigg[-\frac{\varepsilon}{kT_{v,\mathrm{inc}}}\\ +\frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T_{v,\mathrm{inc}}}-\frac{1}{T_0}\right)\varepsilon^{1.5}\\ +\frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_0}-\frac{1}{T_{v,\mathrm{inc}}}\right)\varepsilon^2\Bigg]\sum_J\left[(2J+1)\exp\left(-\frac{hcF(e,v,j)}{kT_r}\right)\right]\Bigg\}\\ \times g_e\exp\left[-\frac{hcT(e)}{kT_e}\right]\Bigg)\end{aligned} \tag{10a}$$

$$\begin{aligned}[Q_eQ_v^{(e)}Q_r^{(e,v)}]_{\mathrm{dis}}=\sum_e\Bigg(\sum_v\Bigg\{\exp\Bigg[-\frac{\varepsilon}{kT}\\ +\frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T}-\frac{1}{T_{v,\mathrm{dis}}}\right)\varepsilon^{1.5}\\ +\frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_{v,\mathrm{dis}}}-\frac{1}{T}\right)\varepsilon^2\Bigg]\sum_J\left[(2J+1)\exp\left(-\frac{hcF(e,v,j)}{kT_r}\right)\right]\Bigg\}\\ \times g_e\exp\left[-\frac{hcT(e)}{kT_e}\right]\Bigg)\end{aligned} \tag{10b}$$

$$\begin{aligned}[Q_v^{(e)}Q_r^{(e,v)}]_{\mathrm{inc}}=\sum_v\Bigg\{\exp\Bigg[-\frac{\varepsilon}{kT_{v,\mathrm{inc}}}+\frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T_{v,\mathrm{inc}}}-\frac{1}{T_0}\right)\varepsilon^{1.5}\\ +\frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_0}-\frac{1}{T_{v,\mathrm{inc}}}\right)\varepsilon^2\Bigg]\\ \times\sum_J\left[(2J+1)\exp\left(-\frac{hcF(e,v,j)}{kT_r}\right)\right]\Bigg\}\end{aligned} \tag{11a}$$

$$\begin{aligned}[Q_v^{(e)}Q_r^{(e,v)}]_{\mathrm{dis}}=\sum_v\Bigg\{\exp\Bigg[-\frac{\varepsilon}{kT}+\frac{4(\sqrt{2}+1)}{3k\sqrt{\varepsilon_D}}\left(\frac{1}{T}-\frac{1}{T_{v,\mathrm{dis}}}\right)\varepsilon^{1.5}\\ +\frac{\sqrt{2}+1}{k\varepsilon_D}\left(\frac{1}{T_{v,\mathrm{dis}}}-\frac{1}{T}\right)\varepsilon^2\Bigg]\\ \times\sum_J\left[(2J+1)\exp\left(-\frac{hcF(e,v,j)}{kT_r}\right)\right]\Bigg\}\end{aligned} \tag{11b}$$

$$Q_r^{(e,v)}=\sum_J(2J+1)\exp\left[-\frac{hcF(e,v,j)}{kT_r}\right] \tag{12}$$

where $T(e)$ is the electronic term of the eth electronic level; I is the spin quantum number; $G(e,v)$ is the vibrational term of the vth vibrational level of the eth electronic level; $F(e,v,j)$ is the rotational term of the jth rotational level, vth vibrational level, and eth electronic level. The subscripts inc and dis denote the parameters in and after incubation period.

From Eqs. (3) and (5–8), it can be seen that the present model will become an equilibrium distribution when $T_e=T_V=T_r=T$. The method for calculating nonequilibrium population densities proposed in this paper is called the CMTCVD3T model.

III. Radiation Calculation

There are many transition mechanisms of atomic and molecular energy levels that should be taken into account to calculate gas absorption and emission coefficients. The absorption coefficient κ_ν and the emission coefficient j_ν at wave number ν imply the spectral feature of gas.

A. Atomic Radiation Calculation

The absorption and emission coefficient of bound–bound, bound–free, and free–free transitions including induced emission is [12]

$$\kappa_{bb,v} = N_l B_{lu} h v_{ul} F(v) \tag{13a}$$

$$j_{bb,v} = N_u h v_{ul} A_{ul} F(v)/4\pi \tag{13b}$$

$$\kappa_{bf,v} = \sum_n N_n \frac{64\pi^4}{3\sqrt{3}} \frac{m_e Z^4 e^{10}}{c h^6 n^5 v^3} g_{bf,v} \tag{14a}$$

$$j_{bf,v} = \frac{128\pi^4}{3\sqrt{3}} \frac{Z^4 e^{10}}{m_e^2 c^3 h^2} N_+ N_e \left(\frac{m_e}{2\pi k T_e}\right)^{3/2} \sum_{n_{\min}}^{n_{\max}} \frac{1}{n^3} \exp\left(-\frac{hv - I + E_l}{kT_e}\right) \tag{14b}$$

$$\kappa_{ff,v} = N_+ N_e \frac{4}{3} \left(\frac{2\pi}{3 m_e k T_e}\right)^{1/2} \frac{Z^2 e^6}{h c m_e v^3} g_{ff,v} \tag{15a}$$

$$j_{ff,v} = \frac{8}{3} \left(\frac{2\pi}{3 m_e k T_e}\right)^{1/2} \frac{Z^2 e^6}{c^3 m_e} N_+ N_e \exp\left(-\frac{hv}{kT_e}\right) \tag{15b}$$

where $F(v)$ is the line shape function, and here the Voigt line shape function is adopted; $g_{bf,v}$ is the Gaunt factor of photoionization; N_+ and N_e are the concentrations of the appropriate ions and of electrons, respectively; $g_{ff,v}$ is the Gaunt factor of braking radiation; and I is the threshold [23].

B. Molecular Radiation Calculation

Only the consideration of transition band systems with enough contribution to the total absorption and emission is required for the treatment of molecular radiation. More important band systems include the first negative band system of N_2^+, the first and second band systems of N_2, the β and the γ band systems of NO, and the Shumann–Runge band system of O_2.

From the molecular radiative theory, the absorption coefficient and emission coefficient of a certain transition is [12]

$$\begin{aligned}\kappa_{m,v} &= B_{lu} N_l h v_{ul} F(v) \\ &= N_{(e,v,j)_l} \frac{g_{(e,v,j)_u}}{g_{(e,v,j)_l}} \frac{8\pi^3}{3hc} v_{(e,v,j)_u \to (e,v,j)_l} |R_e|^2 q_{v^u v^l} S_{j^u j^l} F(v)\end{aligned} \tag{16a}$$

$$\begin{aligned}j_{m,v} &= \frac{1}{4\pi} A_{ul} N_u h v_{ul} F(v) \\ &= N_{(e,v,j)_u} \frac{16\pi^3}{3c^3} v^4_{(e,v,j)_u \to (e,v,j)_l} |R_e|^2 q_{v^u v^l} S_{j^u j^l} F(v)\end{aligned} \tag{16b}$$

where (e, v, j) denote the jth rotational level of the vth vibrational level of the eth electronic level. $N_{(e,v,j)_l}$ and $N_{(e,v,j)_u}$ are the number density of the lower and upper states, whereas $g_{(e,v,j)_u}$ and $g_{(e,v,j)_l}$ are the degeneracy of the upper and lower states. $|R_e|^2$ is the matrix element of electronic transition moments, $q_{v^u v^l}$ is the Franck–Condon factor for the probability of a vibrational transition, and $S_{j^u j^l}$ is the probability of a rotational transition.

The aforementioned expressions for the emission coefficient do not include the induced or simulated emission. This emission is proportional to the radiative intensity and is therefore commonly included as a correction to the absorption coefficient [12].

$$\kappa'_v = \kappa_v - j_v \frac{c^2}{2hv^3} \tag{17}$$

C. Results and Analysis

Based on the CMTCVD3T model Eqs. (1–12), the equilibrium and nonequilibrium number densities are calculated. The line-by-line method is used to obtain the equilibrium and nonequilibrium emission coefficient and the absorption coefficient based on Eqs. (13–17). The comparisons between calculated results and experiment results are carried out in Figs. 3–5. The related parameters can be found in [24].

The emission spectrum of air at 9650 K in equilibrium calculated in this paper is in good agreement with the data obtained in Avco Research Laboratory's shock-tube experiment (R-156) [9] shown in Fig. 3. It indicates that the present calculation is reasonable because, in an equilibrium state, the population distribution calculated in the present three-temperature model would transfer to the Boltzmann distribution, according to which the emission spectrum is calculated reliably.

The nonequilibrium air emission spectrum calculated in this paper is compared with the R-156 experiment and Sharma's experiment [25] in Fig. 4. The translational temperature, vibrational temperature, and electron temperature are 18,000, 14,000, and 12,000 K, respectively. The results of this paper compared well with the R-156 experiment except in visible band, and compared well with Sharma's experiment except in ultraviolet band. The deviations may result from the inaccurate spectroscopic database.

In Fig. 5, the nonequilibrium air absorption coefficient calculated in this paper and that of NEQAIR in [4] are plotted. They are in good agreement except in ultraviolet band. The difference of the results should be due to the fact that the present model's calculation of

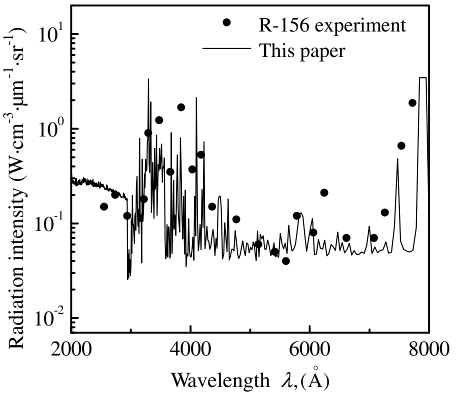

Fig. 3 Equilibrium radiation intensity comparison with experiment.

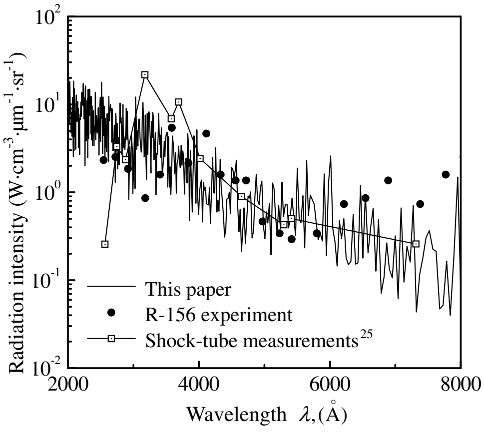

Fig. 4 Nonequilibrium radiation intensity comparison with experiments.

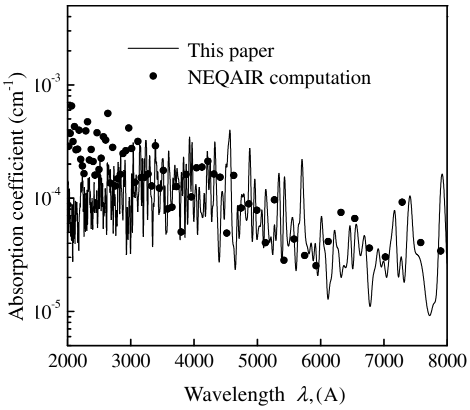

Fig. 5 Nonequilibrium absorption coefficient comparison with NEQAIR.

nonequilibrium energy level population is too rough. But it is simple and efficient.

IV. Conclusions

The high-temperature equilibrium or nonequilibrium air species absorption coefficient is an important parameter for the calculation of reentry vehicle radiation properties, heat shielding, and aerodynamic flowfield. For the calculation of the absorption coefficient of nonequilibrium air species, the key is how to deal with the nonequilibrium population of atomic and molecular energy levels.

In this paper, the correlated multitemperature coupled-vibration-dissociation model is used to calculate the nonequilibrium population distribution of vibrational energy levels. Then the CMTCVD model is combined with the three-temperature model to estimate nonequilibrium population distribution, and the contribution of various radiation transition processes of 11 species in air is directly calculated based on the atomic and molecular theory. The comparisons with experimentally measured data and NEQAIR's result indicate that the present model is applicable when calculating air radiation properties of thermal equilibrium or nonequilibrium. The inaccurate spectroscopic database and rough nonequilibrium energy level population model cause the deviations, but the model in this paper is simple and efficient, and is useful for engineering.

Acknowledgments

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