Parameterization of the Non-Local Thermodynamic Equilibrium Source Function with Chemical Production by an Equivalent Two-Level Model

Xun ZHU[*]

The Johns Hopkins University Applied Physics Laboratory, MD 20723-6099, *USA*

ABSTRACT

The classic two-level or equivalent two-level model that includes only the statistical equilibrium of radiative and thermal processes of excitation and quenching between two vibrational energy levels is extended by adding chemical production to the rate equations. The modifications to the non-local thermodynamic equilibrium source function and cooling rate are parameterized by ϕ_c, which characterizes the ratio of chemical production to collisional quenching. For applications of broadband emission of O_3 at 9.6 μm, the non-LTE effect of chemical production on the cooling rate and limb emission is proportional to the ratio of O to O_3. For a typical $[O]/[O_3]$, the maximum enhancements of limb radiance and cooling rate are about 15%–30% and 0.03–0.05 K day^{-1}, respectively, both occurring near the mesopause regions. This suggests that the broadband limb radiance above $\sim$80 km is sensitive to O_3 density but not sensitive to the direct cooling rate along the line-of-sight, which makes O_3 retrieval feasible but the direct cooling rate retrieval difficult by using the O_3 9.6 μm band limb emission.

Key words: non-LTE radiative transfer, ozone cooling, ozone retrieval, space weather

1. Introduction

Atmospheric radiative transfer sometimes involves non-local thermodynamic equilibrium (non-LTE) processes. The mathematical formulations of the non-LTE processes are composed of two sets of equations: a set of rate equations and a set of radiative transfer equations. The rate equations describe a localized statistical equilibrium at given states of molecules that correspond to certain energy levels, and the radiative transfer equations relate the non-localized radiative energy exchanges among different layers of atmosphere to the changes of populations at those states. In general, the coupled equations for the multi-states are nonlinear and need to be solved iteratively (e.g., Mihalas, 1978; Zhu and Strobel, 1990; Kutepov et al., 1998; Lopez-Puertas and Taylor, 2001).

Many applications of infrared radiative transfer in the middle atmosphere and planetary atmospheres utilize vibrational-rotational spectra of gas molecules and often require calculations of broadband radiation fields such as cooling rates or spectrally integrated limb radiances of radiatively active species (e.g., Goody and

Yung, 1989). A broadband usually consists of many sub-band transitions among many vibrational states. However, the fundamental band corresponding to the transition between the ground state and the first vibrationally excited state is far stronger than the hot bands and other minor isotope bands. The classic two-level model that includes only the fundamental band (e.g., Houghton, 1986) reduces the non-LTE system into one rate equation and one equation for radiative transfer. Most importantly, the system is linearized so that the solution of its source function and other radiation fields such as radiative heating/cooling rate can be expressed in closed matrix forms.

For an optically thick atmosphere, contributions from the hot bands and minor isotope bands become comparable to or more important than those from the fundamental band (e.g., Wehrbein and Leovy, 1982; Dickinson, 1984). To reduce the generally nonlinear multi-level system into a linear two-level system while still accounting for the non-LTE processes of various sub-bands, Zhu (1990) and Zhu and Strobel (1990) explicitly developed and tested an equivalent two-level

*E-mail: xun.zhu@jhuapl.edu

model for the middle atmosphere cooling rate calculations. Since a broadband cooling rate of an equivalent two-level model using a broadband Curtis matrix is efficient and accurate, it has been used in some radiation algorithms for middle atmosphere models (e.g., Zhu, 1994).

In addition to the common non-LTE processes of collisional pumping/quenching and radiative absorption/emission, the populations of different energy states may also be affected by chemical production/loss. Depending on the relative importance of different processes, chemical production could be a determining factor for source functions under certain circumstances. In this paper, the equivalent two-level model developed by Zhu (1990) for the broadband source function and cooling rate calculations is extended by including an additional term of chemical production in the rate equations. The model is used to evaluate the influence of chemical production of O_3 vibrational pumping by the three-body reaction $O+O_2+M \rightarrow O_3+M$ on the O_3 9.6 μm band cooling rate and limb emission in the mesosphere.

2. Parameterization of the non-LTE source function with chemical production

Considering two states j and $i = j-1$ of vibrational energies E_j and $E_i (= E_j - h\nu)$ with occupation number densities (populations) n_j and n_i (m^{-3}), where $h (= 6.626 \times 10^{-34}$ J s) is the Planck constant and ν (s^{-1}) the band frequency, we start with the following rate equation for an upper state j (e.g., Zhu, 1990; Lopez-Puertas and Taylor, 2001)

$$n_j(A_{ji} + B_{ji}\overline{L}_{\nu j} + k_j[M]) + n_j D_j = n_i(B_{ij}\overline{L}_{\nu j}$$
$$+ k_i[M]) + \sum_l P_{l \rightarrow j} + P_{cj}, \; j = 1,2,3,\dots \quad (1)$$

The notation in the above equation mostly follows Zhu (1990). B_{ji}, B_{ij} (m^2 J^{-1} s^{-1} sr), and A_{ji} (s^{-1}) are the Einstein coefficients for absorption, stimulated emission, and spontaneous emission, respectively, for the vibrational transition between j and i. [M] (m^{-3}) is the air number density, k_j and k_i (m^6 s^{-1}) the vibrational quenching ($k_j n_j$[M]) and excitation ($k_i n_i$[M]) rate coefficients, respectively, and $\overline{L}_{\nu j}$ (J m^{-2} sr^{-1}= W m^{-2} sr^{-1} Hz^{-1}) the mean radiance. The first two terms in the parentheses in (1) represent the rates of loss and production, respectively, for the state j that are usually included in a two-level model (e.g., Houghton, 1986). $n_j D_j$ and $\sum_l P_{l \rightarrow j}$ denote the rates of loss and production, respectively, by other collisional transitions not included in the first two terms (Zhu, 1990). The last term P_{cj} represents the added

chemical production generated by photochemical reactions for the state j.

Lopez-Puertas and Taylor (2001, section 3.7) discussed the non-LTE source function for the following two special cases: (i) the classic two-level model that includes only the first two terms in (1); and (ii) the non-classical situations that neglect the absorption and stimulated emission ($B_{ji} = B_{ij} = 0$). In this paper, we consider the following case, which adds a term of chemical production to the classic two-level model ($i = j-1$)

$$n_j(A_{ji} + B_{ji}\overline{L}_{\nu j} + k_j[M]) = n_i(B_{ij}\overline{L}_{\nu j}$$
$$+ k_i[M]) + P_{cj}, \; j = 1,2,3,\dots \quad (2)$$

The rate equation (1) needs to be solved simultaneously together with the radiative transfer equation that relates the radiation field ($\overline{L}_{\nu j}$) to the source function (J_j: W m^{-2} sr^{-1} Hz^{-1}) determined by the ratio of the two occupation number densities (n_j/n_i). In general, the coupled equations are nonlinear and need to be solved iteratively (e.g., Mihalas, 1978; Zhu and Strobel, 1990; Kutepov et al., 1998; Lopez-Puertas and Taylor, 2001). The complete solution that explicitly takes into account the rate equations for many states and the radiative transfer equations for the corresponding transitions among those states is tremendously time consuming and impractical in many applications. The classic two-level model that includes only the fundamental band linearizes the system and expresses the non-LTE cooling rate in a closed matrix form (e.g., Houghton, 1986).

One source of nonlinearity in a multi-level system comes from the V-V energy transfer among different states during collisions within the absorbing molecules ($k_{\nu\nu}n_k n_l$). By establishing the rate equations for transitions rather than for states, Zhu (1990) showed that a multi-level system can be de-coupled into a set of linear two-level models for different sub-bands when the V-V transitions are absent, assuming LTE populations of different rotational states within a vibrational level. Neglecting V-V transitions induces noticeable errors in the source functions for different sub-bands. In addition, the source functions among different sub-bands differ significantly due to different band strengths and quenching rates. However, Zhu and Strobel (1990) found that a significant cancellation exists among those errors so that the broadband radiation field, such as the total cooling rate by all the sub-bands, was well approximated by an equivalent two-level model that adopted a mean quenching rate weighted by the sub-band strengths. A possible improvement was also proposed in Zhu (1989) in which the source function was parameterized as a linear combination of two limiting source functions with

an adjustable parameter that determines the relative contribution from the V-V transitions.

To derive an equivalent two-level model for the system (2) we first note the following relations among the different coefficients (e.g., Mihalas, 1978; Zhu, 1990; Lopez-Puertas and Taylor, 2001):

$$\frac{A_{ji}}{B_{ji}} = \frac{2h\nu^3}{c^2}, \ \frac{B_{ij}}{B_{ji}} = \frac{g_j}{g_i},$$
$$k_i = \frac{g_j}{g_i} \exp\left(-\frac{h\nu}{k_B T}\right) k_j , \quad (3)$$

where $c(= 2.998 \times 10^8 \text{ m s}^{-1})$ is the speed of light, $k_B(= 1.381 \times 10^{23} \text{ J K}^{-1})$ is the Boltzmann constant, T is the kinetic temperature, and g_j and g_i are the statistical weights of states j and i, respectively. To simplify the derivation we note that the stimulated emission is negligible in (1) and (2) for vibrational transitions

$$B_{ji}\overline{L}_{\nu j} \ll A_{ji} . \quad (4)$$

For example, neglecting $B_{ji}\overline{L}_{\nu j}$ in (2) produces a fractional error of about 0.25% for emissions at the 9.6 μm band. Under such an approximation, the source function (J_j) and the Planck blackbody function (B_ν: W m^{-2} sr^{-1} Hz^{-1}) can be expressed as (e.g., Mihalas, 1978; Zhu, 1990; Lopez-Puertas and Taylor, 2001)

$$J_j = \frac{2h\nu^3}{c^2}\frac{g_i n_j}{g_j n_i} , \ B_\nu = \frac{2h\nu^3}{c^2}\exp\left(-\frac{h\nu}{k_B T}\right) . \quad (5)$$

Substituting (3)-(5) into (2) we obtain the source function for the two-level model with chemical production

$$J_j = \frac{\overline{L}_{\nu j} + \phi_{tj}(1+\phi_{cj})B_\nu}{1+\phi_{tj}} , \ j = 1, 2, 3, \ldots \quad (6)$$

where $\phi_{tj} = k_j[\text{M}]/A_{ji}$ is a well-known parameter measuring the non-LTE effect in a two-level model (e.g., Houghton, 1986) whereas the non-LTE correction due to chemical production is determined by

$$\phi_{cj} = \frac{g_i P_{cj}}{g_j k_j[\text{M}]n_i}\exp\left(\frac{h\nu}{k_B T}\right) , \ j \to i = j - 1 . \quad (7)$$

In an equivalent two-level model developed by Zhu (1990) and tested by Zhu and Strobel (1990) the parameters ϕ_{tj} for different sub-bands ($j \to i$, $j = 1, 2, 3, \ldots$) were averaged over sub-band strengths to yield an equivalent ϕ_t

$$\phi_t = \sum_j S_j\phi_{tj}/S , \ j = 1, 2, 3, \ldots \quad (8)$$

from which a single source function (J_ν) for the broadband emission was derived. Here, we introduce an equivalent ϕ_c using a similar approach by averaging the chemical correction factor ϕ_{cj} over $S_j\phi_{tj}$

$$\phi_c = \sum_j S_j\phi_{tj}\phi_{cj}/(S\phi_t) , \ j = 1, 2, 3, \ldots \quad (9)$$

In (8) and (9), S_j (m^2 kg^{-1} s^{-1}) is the band strength for sub-band j and $S = \sum_j S_j$ the total band strength for the broadband. Replacing ϕ_{tj} and ϕ_{cj} in (6) with their equivalent values ϕ_t and ϕ_c, we obtain the broadband source function

$$J_\nu = \frac{\overline{L}_\nu + \phi_t(1+\phi_c)B_\nu}{1+\phi_t} , \quad (10)$$

where $\overline{L}_\nu$ is the broadband mean radiance and is related to the heating/cooling rate (Q: K s^{-1}) through a formal solution of the radiative transfer equation (e.g., Zhu, 1990)

$$Q = \frac{4\pi r_{\text{air}}S}{c_p}\left(\overline{L}_\nu - J_\nu\right) , \quad (11)$$

where c_p (J kg^{-1} K^{-1}) is the atmospheric specific heat at constant pressure and r_{air} the air mass mixing ratio. Eliminating $\overline{L}_\nu$ between (10) and (11) yields the broadband source function for an equivalent two-level model

$$J_\nu = \frac{c_p}{4\pi r_{\text{air}}S\phi_t}Q + (1+\phi_c)B_\nu . \quad (12)$$

The above equation represents a localized relationship between the source function and the cooling rate that holds at every spatial point (z_k) in the vertical. It can be written in the following matrix form:

$$\boldsymbol{J} = \boldsymbol{E}\boldsymbol{Q} + \boldsymbol{B}' , \quad (13)$$

where the non-zero diagonal matrix $\boldsymbol{E}$ that measures the non-LTE effect of vibrational quenching is given by (Zhu, 1990)

$$(\boldsymbol{E})_k = (c_p/[4\pi r_{\text{air}}\sum_j S_j\phi_{tj}])_k , \quad (14)$$

and the vector $\boldsymbol{B}'$ is the modified Planck blackbody function that includes the non-LTE effect of chemical production

$$(\boldsymbol{B}')_k = ([1+\phi_c]B_\nu)_k . \quad (15)$$

When $\boldsymbol{E}=0$ and $\phi_c = 0$ we recover the LTE source function of $\boldsymbol{J} = \boldsymbol{B}$.

Solving the radiative transfer equation for a given broadband source function we can express $\boldsymbol{Q}$ in terms of $\boldsymbol{J}$ and a contribution from boundary flux ($\boldsymbol{q}$) through the broadband Curtis matrix ($\boldsymbol{C}$) that also easily takes into account the overlapping absorption among different sub-bands (e.g., Houghton, 1986; Zhu 1990, 1994)

$$\boldsymbol{Q} = \boldsymbol{C}\boldsymbol{J} + \boldsymbol{q} . \quad (16)$$

Combining (13) and (16) we finally arrive at the following set of equations of an equivalent two-level model for the non-LTE source function and the heating/cooling

rate with chemical production

$$J = (I - EC)^{-1}(B' + Eq), \qquad (17a)$$

$$Q = (I - CE)^{-1}(CB' + q), \qquad (17b)$$

where I is the identity matrix.

The strength of the fundamental band between the ground state and the first vibrationally excited state of a major isotope is far greater than those of hot bands and minor isotope bands (Rothman et al. 1992). Therefore, the mean values of ϕ_t and ϕ_c specified by (8) and (9) are mainly contributed from the fundamental band of the major isotope. Note that contributions to the broadband cooling rate by hot bands and minor isotope bands sometimes are comparable to that by the fundamental band (e.g., Wehrbein and Leovy, 1982; Dickinson, 1984). However, the effect of non-LTE processes on the broadband radiation fields, such as the broadband cooling rate or the broadband limb emission, becomes important only when the emissions by the majority of the sub-bands become non-LTE. Therefore, the equivalent two-level model as suggested by (8), (9), and (17) is expected to be a good approximation for the broadband radiation fields, as demonstrated in Zhu and Strobel (1990). In addition, Zhu et al. (1992) showed that the line overlap effect among different sub-bands could be a significant source of errors in cooling rate calculations. The fact that a broadband Curtis matrix can easily take into account this overlapping effect automatically removes the hurdle in all existing non-LTE models that can only be applied to the special case of weak absorption when the overlapping effect can be neglected (e.g., Lopez-Puertas et al., 1986; Wintersteiner et al., 1992; Lopez-Puertas and Taylor, 2001, p. 162).

3. Applications of the equivalent two-level model to the ozone 9.6 μm emission

One important example showing that chemical production may play a major role is the O_3 9.6 μm emissions in the mesosphere (Mlynczak and Drayson, 1990). To apply the equivalent two-level model (8), (9), and (17) to this case and to quantitatively evaluate the effect, we note that the major chemical production of the excited vibrational states is the following three-body reaction (Mlynczak and Drayson, 1990):

$$k_3, k_{cj} : O + O_2 + M \rightarrow O_3(v_1, v_2, v_3) + M, \qquad (18)$$
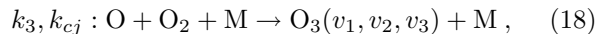
where (v_1, v_2, v_3) denotes various vibrational quantum numbers, k_3 the loss rate coefficient, and k_{cj} the production rate coefficient of an excited vibrational state. $k_{cj}(= q_v k_3)$ is related to k_3 by the quantum yields (q_v) of different vibrational states. Based on the analysis

in the previous section we have ($g_j/g_i = 1$)

$$\phi_c = \frac{k_c[O_2]}{k_t} \exp\left(\frac{h\nu}{k_B T}\right) f_{13}, \qquad (19)$$

where $f_{13}=[O]/[O_3]$. Because the fundamental band is far stronger than other sub-bands, we have replaced n_i in (7) with the total O_3 number density ($n_0 \approx [O_3]$) while deriving (19). In addition, we have also approximated the average over ϕ_{cj} by replacing k_{tj} and k_{cj} with the band-strength weighted mean values of k_t and k_c, respectively.

Equations (12) and (19) suggest that the effect of chemical production always enhances the localized source function ($\phi_c > 0$) by increasing relative populations at higher energy levels. A strong effect of chemical production, i.e., $\phi_c \gg 1$ due to a very small k_t, means that the energy acquired and stored in a vibrationally excited state through chemical reaction (18) is lost by non-localized radiative emission before being thermalized by localized collisions.

It is known that both [O] and [O_3] change significantly with altitude, latitude, and local time in the mesosphere. Equation (19) suggests that the effect of chemical production is proportional to their ratio f_{13}. The daytime f_{13} varies less dramatically in space than [O]. On the basis of chemical equilibrium, it can be approximated by (e.g., Brasseur and Solomon, 1984)

$$f_{13} = \frac{J_{O_3}}{k_3[M][O_2]}, \qquad (20)$$

where J_{O_3} is the O_3 photolysis rate coefficient for $O_3 + h\nu \rightarrow O + O_2$ and k_3 is defined in (18). Substituting (20) into (19) we obtain the daytime modification to the source function due to chemical production

$$\phi_c(\text{day}) = \frac{k_c J_{O_3}}{k_t k_3[M]} \exp\left(\frac{h\nu}{k_B T}\right). \qquad (21)$$

The nighttime f_{13} in the mesosphere has to be determined by more complicated chemical-transport modeling since it usually depends on more than one process.

In Fig. 1, we show two f_{13} profiles, at the equator and at 84°N, on 15 January, as functions of altitude (z) derived from the Johns Hopkins University Applied Physics Laboratory (JHU/APL) two-dimensional (2D) dynamical-photochemical coupled model (Zhu et al., 1999). The equatorial profile represents a daytime condition whereas the profile at 84°N represents a polar night condition where the upper mesosphere [O] is primarily determined by transport processes. The figure shows that f_{13} at the equator is greater than at the polar night at most altitudes because an efficient conversion of O_3 to O by the daytime photolysis reaction $O_3 + h\nu \rightarrow O + O_2$ maintains a great [O] even in the stratosphere. Around the winter mesopause region, the meridional transport of O from

the high altitude and the summer hemisphere coupled with the catalytic destruction of O_3 by HO_x leads to a greater ratio of O to O_3 than at the equator. In calculating the two corresponding ϕ_c profiles by (19), we have also adopted the global mean temperature and $[O_2]$ profiles derived from the JHU/APL 2D model.

The chemical pumping rate coefficient used in the calculations is $k_c = 0.2 \times [6 \times 10^{-46}(300/T)^{2.3}]$ m^6 s^{-1} (Rawlins, 1985; Mlynczak and Drayson, 1990). For the collisional quenching rate coefficient k_t, we use the following formula that fits the temperature-dependence to recent measurements (Menard et al., 1992)

$$k_t = \begin{cases} 1.2 \times 10^{-18} \exp(-1800/T) \, \text{m}^3 \, \text{s}^{-1}, & T \geqslant 220 \, \text{K}; \\ 3.3 \times 10^{-22} \, \text{m}^3 \, \text{s}^{-1}, & T < 220 \, \text{K}. \end{cases} \tag{22}$$

Figure 1 shows that the effect of chemical production in terms of ϕ_c is negligible ($\phi_c \ll 1$) below ∼60 km but becomes important ($\phi_c \gg 1$) above ∼80 km. Also shown in the figure are the global mean O_3 and ϕ_t profiles derived from the JHU/APL 2D model. Note from (10) that $J_\nu \to \overline{L}_\nu$ as $\phi_t \to 0$, which corresponds to a scattering-determined source function. According to (11), the cooling rate also vanishes under this circumstance even though scattered radiance is still coming from the region ($J_\nu \neq 0$). To quantitatively examine the effects of chemical production on the broadband radiation fields, we calculate cooling rates and limb emissions of the O_3 9.6 μm band in the mesosphere.

Figure 2 shows O_3 9.6 μm band cooling rates (Q_{O_3}) for the O_3 profile shown in Fig. 1 under three different

specifications of ϕ_c : ϕ_c=0 and the ϕ_c values taken from the two profiles shown in Fig. 1, respectively. The cooling rate algorithm has been adopted from Zhu (1994), where the correlated-k distribution method was used for calculating the Curtis matrices. A negative cooling rate indicates that the radiative heating from the underlying warmer stratopause overcompensates the local cool-to-space cooling rate. Note that the radiative heating near the mesopause without chemical production (ϕ_c=0) is much smaller than those derived from previous calculations (e.g., Zhu, 1994). This is due to the quenching rate coefficient (22) adopted in this study, which is much smaller than the one suggested by Rawlins (1985). A much smaller k_t produces a vanishing ϕ_t near the mesopause (Fig. 1) so that O_3 molecu-
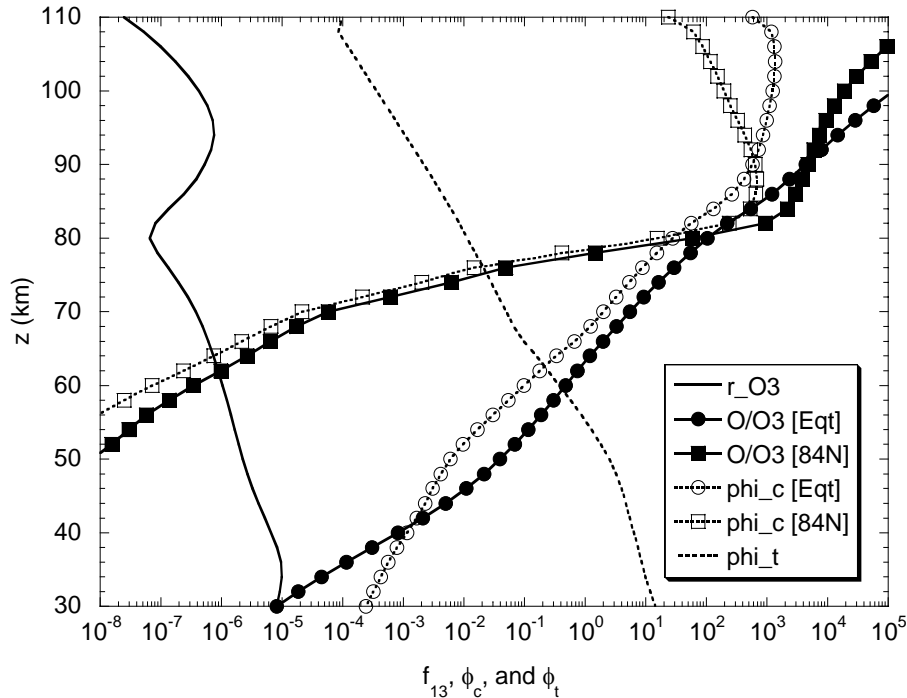

Fig. 1. Vertical profiles of a global mean O_3 volume mixing ratio, f_{13} and ϕ_c, at the equator and at 84°N, and ϕ_t derived from the JHU/APL two-dimensional dynamical-photochemical coupled model for the date of 15 January.
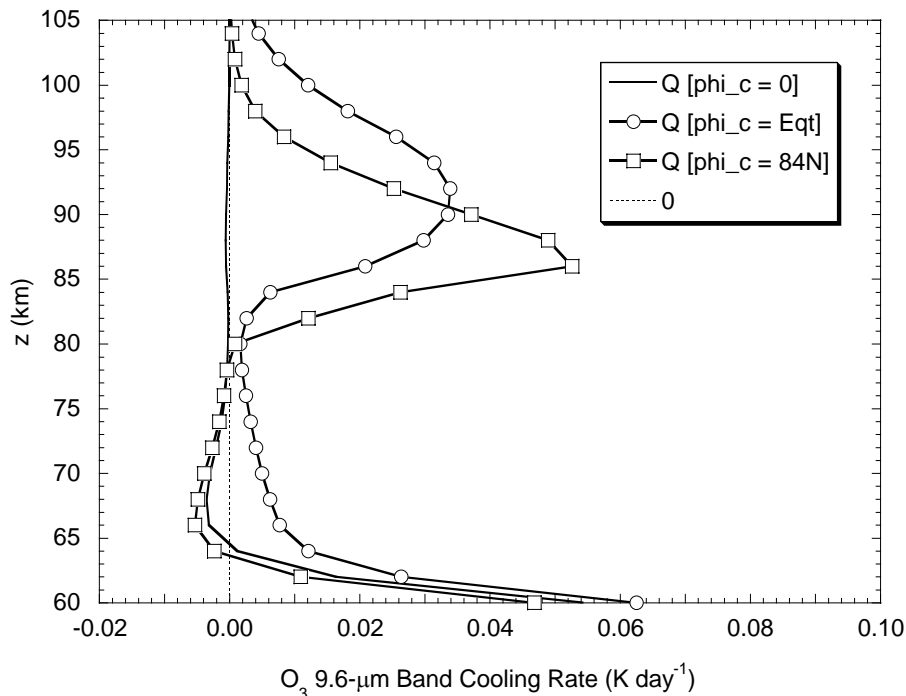
Fig. 2. Vertical profiles of O_3 9.6 μm band cooling rates (K day^{-1}) under three different specifications of chemical production of ϕ_c : $\phi_c = 0$ and ϕ_c values taken from the two profiles shown in Fig. 1, respectively.

les scatter most radiation energy emitted from the stratopause without going through a collisional thermalization process. In terms of relative magnitude, Fig. 2 shows a significant effect of chemical production on the radiative cooling rate above 80 km, where the sign of the cooling rate is reversed due to significant enhancement by chemical production. However, radiative cooling in the region between 70 and 100 km is primarily contributed by the CO_2 15 μm band. The overall magnitude of cooling by the O_3 9.6 μm band ($Q_{O_3} \leqslant 0.06$ K day^{-1}) is much smaller than that by CO_2 (Zhu 1994, Q_{CO_2}: 5–20 K day^{-1}). Therefore, the effect of modification in Q_{O_3} by chemical production on the mesospheric energy budget and the dynamics is expected to be minor.

Another important quantity of broadband radiation fields is the spectrally integrated limb radiance L (W m^{-2} sr^{-1}) that is the integrated source function emission attenuated by the transmission function along a limb path (e.g., Lopez-Puertas and Taylor, 2001, p.260)

$$L = \int_{\triangle\nu} d\nu \int_{-\infty}^{\infty} [k_\nu(s)\rho_a(s)J_\nu(s)]\,\tau_\nu(s)ds , \quad (23)$$

where ρ_a (kg m^{-3}) is the absorber density, k_ν (m^2 kg^{-1}) the absorption coefficient, s the limb distance, and τ_ν

the limb transmission function given by

$$\tau_\nu(s) = \exp\left[-\left|\int_s^{\infty} k_\nu(s')\rho_a(s')ds'\right|\right] . \quad (24)$$

The source function J_ν in (23) is shown in (17a) and has been derived by solving the non-LTE radiative transfer equation in a plane-parallel atmosphere. The term in the brackets of (23) is the source function emission so that $k_\nu\rho_a ds$ can be defined as the monochromatic emissivity for an infinitesimal element of ds. Equation (23) also provides a physical justification for introducing ϕ_c by (9) in the equivalent two-level model. At high altitudes, say, above 80 km, where $\phi_c \gg 1$, $\phi_t \ll 1$ (Fig. 1), and $\tau_v(s) \approx 1$, the limb radiance contributed by the source function due to chemical production is $L_c \propto S\phi_t\phi_c$. According to (6) and (23), this is also applicable to individual sub-bands: $L_{cj} \propto S_j\phi_{tj}\phi_{cj}$. Equating L_c to $\sum_j L_{cj}$ for non-overlapping sub-bands yields (9) for the definition of an equivalent ϕ_c.

In Fig. 3, we show O_3 limb radiance as a function of tangent altitude (z) that is integrated over a wavenumber band of 980–1180 cm^{-1} under the same three specifications of ϕ_c as in Fig. 2. The overall magnitude of limb radiance decreases with the tangent al-
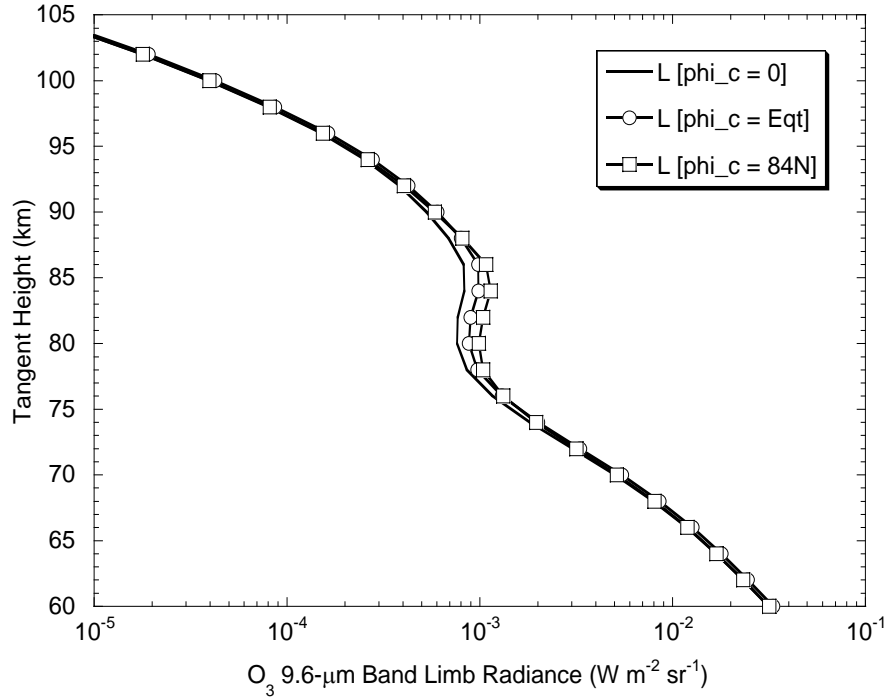
Fig. 3. Same as Fig. 2 except for O_3 limb radiance (W m^{-2} sr^{-1}) integrated over a wavenumber band of 980–1180 cm^{-1}.

titude exponentially because of the decreasing emissivity. We see that the largest enhancement of $\sim 35\%$ in limb radiance by chemical production occurs near 85 km. According to (23), a change in limb radiance will translate into approximately the same magnitude of change in O_3 number density for a given source function. Therefore, when the 9.6 μm band limb emissions are used to retrieve mesospheric O_3 profiles (e.g., Edwards et al., 1994; Mlynczak and Zhou, 1998) it is necessary to have an accurate and efficient parameterization of the source function with chemical production in a non-LTE radiative transfer model.

It is well known in a classic two-level model for parameterizing non-LTE processes that the departure of a source function from the Planck blackbody function depends not only on the localized ratio of $\phi_{tj}(= k_j[\text{M}]/A_{ji})$ but also on the atmospheric opacity (e.g., Houghton 1986; Dickinson et al. 1987; Strobel et al., 1996). Specifically, even if the occupation number densities (n_j) depart from the Boltzmann distribution, the radiance emerged from an optically thick atmosphere may still show an LTE source function distribution as photons experience absorption and re-emission many times through the atmosphere. Mathematically, this can also be understood from (17) that the localized non-LTE effects as defined by $\boldsymbol{E}$ are modified by the Curtis matrix $\boldsymbol{C}$ that describes the non-localized photon exchanges among different layers of atmosphere.

There is a similar situation in the modification effect of chemical production on the source function. Although the parameter ϕ_c measures the effect of chemical production based on the localized rate equation (2) or (10), its ultimate effects on the source function and cooling rate also depend on the energy exchanges among different layers of atmosphere. Note that the mesospheric radiance in the O_3 9.6 μm band is mainly contributed by the thermal radiation emitted from the stratopause (e.g., Zhu et al., 1991). Hence, the non-localized effect of energy exchange on modifying the source function is especially important. Figure 1 shows that $\phi_c > 10^2$ in the altitude region between 90 km and 105 km and $\phi_c \gg 1$ when $z > 80$ km. However, the effect of chemical production on the source function in the region between 90 km and 105 km is negligible (Fig. 3). Figure 3 shows that the maximum enhancement of L by chemical production that occurs near 85 km is only $\sim 35\%$. According to (10), this suggests that the first term in the numerator originating from $n_i B_{ij} \overline{L}_{\nu j}$ in (2) is much greater than the second term. To include the absorption term $(n_i B_{ij} \overline{L}_{\nu j})$ in (2) implies that one has to solve a non-localized radiative transfer equation in order to determine the non-LTE source function.

It is worthwhile examining the implications of limb measurements of (23) on the retrievals of O_3 and the cooling rate in regions of $\phi_c \gg 1$ (Fig. 1: $z > 80$ km

and $\phi_t \ll 1$). Substituting (19) into (10) and using (3) and (5) lead to the broadband source function

$$J_\nu = \overline{L}_\nu + \phi_t \phi_c B_\nu = \overline{L}_\nu + \frac{k_c[\text{O}][\text{O}_2][\text{M}]}{B_{lv}[\text{O}_3]}, \qquad (25)$$

where B_{lv} denotes the broadband Einstein coefficient for absorption averaged over all the sub-bands. The fact that the radiance is not greatly sensitive to chemical production suggests that the second term in (25) is much smaller than the first one:

$$\frac{k_c[\text{O}][\text{O}_2][\text{M}]}{B_{lv}\overline{L}_\nu[\text{O}_3]} \ll 1 . \qquad (26)$$

On the basis of (23), this makes the O_3 retrieval above 80 km possible because the limb radiance will be sensitive to the O_3 density along the line-of-sight (LOS): $L \sim [\text{O}_3]J_\nu \sim [\text{O}_3]\overline{L}_\nu$. At the same time, this also implies that the measured L contains little information on the O_3 cooling rate along the LOS because the source function ($J_\nu \sim \overline{L}_\nu$) represents primarily the scattered radiance originally emitted from the stratopause.

It is interesting to point out a complementary limiting case of (26). Had the second term in (25) been the predominant contribution to the source function, the measured limb radiance would be sensitive to the O density along the LOS:

$$L \sim [\text{O}_3]J_\nu \sim k_c[\text{O}][\text{O}_2][\text{M}]/B_{lv} , \qquad (27)$$

from which a direct O retrieval above 80 km based on the measurements of the 9.6 μm band would be possible. In addition, the direct cooling rate retrieval would be feasible because L would be predominantly contributed by the cooling rate emissions along the LOS.

Finally, it should be pointed out that the uncertainties of more than 30% in quenching rate coefficients are not unusual (e.g., Menard et al., 1992). Therefore, our rationale of developing the equivalent two-level model of (17) together with (7)–(9), (14) and (15) for the source function and cooling rate calculations of a broadband is well initiated on the basis of an overall balance between computational speed and accuracy.

4. Conclusions

In this paper, we extend the equivalent two-level model developed by Zhu (1990) to include an additional source term of chemical production generated by photochemical reactions for the upper-level energy states of gas molecules. The closed formulations of (17) for the source function and the cooling rate are similar to those of a previous equivalent two-level model except that the blackbody function B_ν is modified by a factor $(1 + \phi_c)$, with ϕ_c characterizing the ratio of chemical production to collisional quenching.

By applying the model to the broadband O_3 9.6 μm band emission, it is found that the modification parameter ϕ_c of chemical production by $\text{O}+\text{O}_2+\text{M}\rightarrow \text{O}_3(v_1, v_2, v_3)+\text{M}$ on the source function is proportional to the ratio of O to O_3. Using the critical quenching rate coefficient based on recent measurements by Menard et al. (1992) it is found that the broadband source function near the mesopause is predominantly determined by the absorption of radiance from the underlying atmosphere. The effect of localized chemical production on the O_3 9.6 μm band cooling rate produces an enhancement of about 0.05 K day^{-1} in the upper mesosphere. The maximum enhancement in the broadband limb radiance for the O_3 9.6 μm band is about 35% and occurs near 85 km.

By analyzing the relative importance of contributions to the source function from non-LTE scattering versus non-LTE emission, two complementary limiting cases are discussed. When non-LTE scattering is dominant over non-LTE emission, which approximately corresponds to the case of actual conditions near the mesopause, the O_3 retrieval is feasible but the direct cooling rate retrieval is not practical. In the other limiting case, retrievals of O and the direct cooling rate would be possible were the non-LTE emission dominant over non-LTE scattering.

REFERENCES

Brasseur, G., and S. Solomon, 1984: *Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere.* D. Reidel Publishing Company, Boston, 441pp.

Dickinson, R. E., 1984: Infrared radiative cooling in the mesosphere and lower thermosphere. *J. Atmos. Terres. Phys.*, **46**, 995–1008.

Dickinson, R. E., R. G. Roble, and S. W. Bougher, 1987: Radiative cooling in the NLTE region of the mesosphere and lower thermosphere Global energy balance. *Adv. Space Res.*, **7**(10), 5–15.

Edwards, D. P., M. Lopez-Puertas, and M. G. Mlynczak, 1994: Non-local thermodynamic equilibrium limb radiance from O_3 and CO_2 in the 9–11 mm spectral region. *J. Quant. Spectrosc. Radiat. Transfer*, **52**, 389–407.

Goody, R. M., and Y. L. Yung, 1989: *Atmospheric Radiation: Theoretical Basis.* Second Edition. Oxford Univ. Press, New York and Oxford, 519pp.

Houghton, J. T., 1986: *The Physics of Atmospheres.* 2nd ed. Cambridge Univ. Press, New York, 271pp.

Kutepov, A. A., O. A. Gusev, and V. P. Ogibalov, 1998: Solution of the non-LTE problem for molecular gas in planetary atmospheres: Superiority of accelerated lambda iteration. *J. Quant. Spectrosc. Radiat. Transfer*, **60**, 199–220.

Lopez-Puertas, M., R. Rodrigo, A. Molina, and F. W. Taylor, 1986: A non-LTE radiative transfer model for infrared bands in the middle atmosphere. I. Theoretical basis and application to CO_2 15 μm bands. *J. Atmos. Terres. Phys.*, **48**, 729–748.

Lopez-Puertas, M., and F. W. Taylor, 2001: *Non-LTE Radiative Transfer in the Atmosphere.* World Scientific Pub. Co., Singapore, 487pp.

Menard, J., L. Doyennette, and F. Menard-Bourcin, 1992: Vibrational relaxation of ozone in O_3-O_2 and O_3-N_2 gas mixtures from infrared double-resonance measurements in the 200–300 K temperature range. *J. Chem. Phys.*, **96**, 5773–5780.

Mihalas, D., 1978: *Stellar Atmospheres.* 2nd ed. W. H. Freeman and Company, San Francisco, 632pp.

Mlynczak, M. G., and S. R. Drayson, 1990: Calculation of infrared limb emission by ozone in the terrestrial middle atmosphere. 1. Source function. *J. Geophys. Res.*, **95**(D10), 16 497–16 511.

Mlynczak, M. G., and D. K. Zhou, 1998: Kinetic and spectroscopic requirements for the measurement of mesospheric ozone at 9.6 mm under non-LTE conditions. *Geophys. Res. Lett.*, **25**, 639–642.

Rawlins, W. T., 1985: Chemistry of vibrationally excited ozone in the upper atmosphere. *J. Geophys. Res.*, **90**, 12 283–12 292.

Rothman, L. S., and Coauthors, 1992: The Hitran molecular database: Editions of 1991 and 1992. *J. Quant. Spectrosc. Radiat. Transfer,* **48**, 409–507.

Strobel, D. F., X. Zhu, M. E. Summers, and M. H. Stevens, 1996: On thevertical thermal structure of Pluto's atmosphere. *Icarus*, **120**, 266–289.

Wehrbein, W. M., and C. B. Leovy, 1982: An accurate radiative heating and cooling algorithm for use in a dynamical model of the middle atmosphere. *J. Atmos. Sci.*, **39**, 1532–1544.

Wintersteiner, P. P., R. H. Picard, R. D. Sharma, J. R. Winick, and R. A. Joseph, 1992: Line-by-line radiative excitation model for the non-equilibrium atmosphere: Application to CO_2 15 μm emission. *J. Geophys. Res.*, **97**, 18,083–18,117.

Zhu, X., 1989: A parameterization of cooling rate calculation under the non-LTE condition: Multi-level model. *Advance in Atmospheric Sciences*, **6**, 403–413.

Zhu, X., 1990: Carbon dioxide 15 μm band cooling rates in the upper middle atmosphere calculated by Curtis matrix inte rpolation. *J. Atmos. Sci.*, **47**, 755–774.

Zhu, X., 1994: An accurate and efficient radiation algorithm for middle atmosphere models. *J. Atmos. Sci.*, **51**, 3593–3614.

Zhu, X., and D. F. Strobel, 1990: On the role of vibration-vibration transitions in radiative cooling of the CO_2 15 μm band around the mesopause. *J. Geophys. Res.*, **95**(D4), 3571–3577.

Zhu, X., M. E. Summers, and D. F. Strobel, 1991: Analytic models for the ozone radiative absorption rate at 9.6 in the mesosphere. *J. Geophys. Res.*, **96**(D10), 18 551–18 559.

Zhu, X., M. E. Summers, and D. F. Strobel, 1992: Calculation of CO_2 15 μm band atmospheric cooling rates by Curtis matrix interpolation of correlated-k coefficients. *J. Geophys. Res.*, **97**(D12), 12 787–12 797.

Zhu, X., J. -H. Yee, S. A. Lloyd, and D. F. Strobel, 1999: Numerical modeling of chemical-dynamical coupling in the upper stratosphere and mesosphere. *J. Geophys. Res.*, **104**(D19), 23 995–24 011.