Carbon Dioxide Density and $15\ \mu$ Band Radiation in the Mesosphere and Lower Thermosphere

Yasunobu IWASAKA and Haruo HORII

*Water Research Institute, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, Japan*

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The CO_2 density profile is decided using the photochemical-eddy diffusion model, and the cooling rate of CO_2 $15\ \mu$ band in the lower thermosphere is discussed. These results show that the cooling rate of $15\ \mu$ band decreases somewhat in comparison with the estimation using the assumption of constant mixing ratio of CO_2 . The $\text{O}_2(^1\Delta_g)$ density profile which is simultaneously calculated has small second peak near 85 km.

1. Introduction

Atmospheric carbon dioxide, CO_2 , plays an important role in cooling and heating of the upper atmosphere through radiative transfer of infrared radiation in the $15\ \mu$ band region. In this paper, we show a result of new calculation on the density profile of CO_2 and discuss the effect of this profile on cooling rate of $15\ \mu$ band in the lower thermosphere. The vertical distribution of CO_2 in the lower thermosphere has been theoretically estimated by WOFSY *et al.* (1972), and HAYS and OLIVERO (1970). HAYS and OLIVERO (1970) derived the model assuming O and OH density profiles proposed by HESSTVEDT (1967), however HESSTVEDT had estimated the densities of O and OH using different value of the eddy diffusion coefficient from HAYS and OLIVERO's. Many investigators pointed out that O density was strongly affected by eddy diffusion processes in the lower thermosphere (COLEGROVE *et al.*, 1966; SHIMAZAKI, 1967; HESSTVEDT, 1967; SHIMAZAKI and LAIRD, 1970, 1972; BOWMAN *et al.*, 1970; KENESEA and ZIMMERMAN, 1970; GEORGE *et al.*, 1972; IWASAKA, 1973). Therefore it seems necessary to calculate simultaneously the densities of CO_2 , O, OH and other constituents using same value of eddy diffusion coefficient. In the calculation by WOFSY *et al.* (1972), the profile of O density is adapted after CIRA 1965 model atmosphere. The density of O in CIRA 1965 has vagueness in the altitude range 80–120 km. Therefore their CO_2 density may be in error in the lower thermosphere. Instead, using the chemical-eddy diffusion model proposed by COLEGROVE *et al.* (1966) we calculate the distributions of constituents with

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long life time which are affected considerably by eddy diffusional transport. In addition to these facts, we consider the effect of solar emission lines such as H ly- α which are not previously taking into account. The solar UV radiation which dissociates CO₂ is absorbed by O₂, N₂, NO and O₂(¹ Δ_g), and the densities of these constituents need to be simultaneously determined in the lower thermosphere. Recently, HUFFMAN *et al.* (1971) estimate the photoionization rate of O₂(¹ Δ_g) assuming the constant mixing ratio of CO₂ in the lower thermosphere. Their results need some correction if a CO₂ density profile is used which is estimated by taking photodissociation and eddy diffusion processes in the lower thermosphere into consideration (IWASAKA, 1973).

2. Chemical Reactions and Basic Equations

Chemical reactions used in this calculation are listed in Table 1. The reactions in part 1 are main reactions which control the rates of production and loss of CO and CO₂ in the lower thermosphere and upper mesosphere. Reactions in part 2 are used to determine O and OH densities. In order to determine the distribution of O₂(¹ Δ_g), we need to consider the reactions in part 3 in addition to those in part 2. We consider that effective solar UV radiation which dissociates CO₂ in the region of wavelength 920 Å–2000 Å, and this solar UV is absorbed by N₂, NO, O₂ and O₂(¹ Δ_g). These processes are listed in part 4 of Table 1. In practice, the solar UV radiation in the spectral range 1200 Å–1700 Å can be considered as the most effective light source for dissociation of CO₂.

At zero optical depth, the photodissociative life time of CO₂ given by the reciprocal of the product of cross section and solar flux is about 10⁶ sec, and below 90 km this time becomes considerably longer. Similarly the eddy diffusional time constant, H_{ave}^2/K ; H_{ave} =average scale height and K =eddy diffusion coefficient, is approximately of the order of magnitude of one day using the average scale height in CIRA 1965. These conditions along with the extremely long life time of recombination of CO₂ in the lower thermosphere and upper mesosphere justify the ignorance of the diurnal variation in the atmospheric CO₂ density to first order approximation.

The gradient of density of n -th component is given (1) in steady state (COLEGROVE *et al.*, 1966):

$$\begin{aligned} \frac{d[n]}{dz} = & -\frac{[n]}{D_n + K} \left\{ \frac{D_n}{H_n} + \frac{K}{H_{ave}} \right\} - \frac{[n]}{T} \frac{dT}{dz} - \frac{\phi_n}{D_n + K} \\ & - \frac{[n]D_n}{[N](D_n + K)} \sum_m \frac{D_{n,m}}{\phi_m} \end{aligned} \quad (1)$$

where $[n]$ =number density of n -th component, D_n =effective molecular diffusion coefficient of n -th component, K =eddy diffusion coefficient, T =temperature,

Table 1. Reaction rate constants.

Part 1			
$\text{CO}_2 + h\nu$	$\longrightarrow \text{CO} + \text{O}(^1\text{D})$	R_1	
$\text{CO} + \text{O} + M$	$\longrightarrow \text{CO}_2 + M$	$K_1 = 10^{-34}$	a
$\text{CO} + \text{OH}$	$\longrightarrow \text{CO}_2 + \text{H}$	$K_2 = 1.5 \times 10^{-13}$	a
$\text{CO} + \text{HO}_2$	$\longrightarrow \text{CO}_2 + \text{OH}$	$K_3 = 10^{-10} \exp(-23000/RT)$	b
Part 2			
$\text{O} + \text{O} + M$	$\longrightarrow \text{O}_2 + M$	$K_4 = 2.7 \times 10^{-33}$	c
$\text{O} + \text{O}_2 + M$	$\longrightarrow \text{O}_3 + M$	$K_5 = 8 \times 10^{-35}(890/RT)$	d
$\text{O}_2 + h\nu$	$\longrightarrow \text{O} + \text{O}(^1\text{D})$	R_2	
$\text{O}_2 + h\nu$	$\longrightarrow \text{O} + \text{O}$	R_3	
$\text{O} + \text{O}_3$	$\longrightarrow 2\text{O}_2$	$K_6 = 5.6 \times 10^{-11}(-5700/RT)$	d
$\text{O}(^1\text{D}) + \text{O}_3$	$\longrightarrow 2\text{O}_2$	$K_7 = 10^{-11}$	e
$\text{O}(^1\text{D}) + M$	$\longrightarrow \text{O} + M$	$K_8 = 10^{-12}$	
$\text{O}(^1\text{D}) + \text{H}_2\text{O}$	$\longrightarrow 2\text{OH}$	$K_9 = 10^{-11}$	f
$\text{OH} + \text{O}_3$	$\longrightarrow \text{HO}_2 + \text{O}_2$	$K_{10} = 5 \times 10^{-13}$	g
$\text{HO}_2 + \text{O}_3$	$\longrightarrow \text{OH} + 2\text{O}_2$	$K_{11} = 10^{-14}$	h
$\text{OH} + \text{O}$	$\longrightarrow \text{O}_2 + \text{H}$	$K_{12} = 5 \times 10^{-11}$	a
$\text{HO}_2 + \text{O}$	$\longrightarrow \text{OH} + \text{O}_2$	$K_{13} = 10^{-11}$	a
$\text{OH} + \text{OH}$	$\longrightarrow \text{H}_2\text{O} + \text{O}$	$K_{14} = 2.8 \times 10^{-12}$	a
$\text{OH} + \text{HO}_2$	$\longrightarrow \text{H}_2\text{O} + \text{O}_2$	$K_{15} = 10^{-11}$	a
$\text{H} + \text{O}_2 + M$	$\longrightarrow \text{H}_2\text{O} + M$	$K_{16} = 3 \times 10^{-32}$	a
$\text{HO}_2 + \text{HO}_2$	$\longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$K_{17} = 5 \times 10^{-11} \exp(-800/RT)$	a
$\text{OH} + \text{H}_2\text{O}_2$	$\longrightarrow \text{H}_2\text{O} + \text{HO}_2$	$K_{18} = 4 \times 10^{-13}$	i
$\text{O}_3 + h\nu$	$\longrightarrow \text{O}(^1\text{D}) + \text{O}_2(^1\Delta_g)$	R_4	
$\text{H}_2\text{O}_2 + h\nu$	$\longrightarrow 2\text{OH}$	R_5	
Part 3			
$\text{O}_2(^1\Delta_g) + h\nu$	$\longrightarrow \text{O}_2 + h$	$A_1 = 2.58 \times 10^{-14} \text{ sec}^{-1}$	
$\text{O}_2(^1\Delta_g) + M$	$\longrightarrow \text{O}_2 + M$	$K_{19} = 4.4 \times 10^{-19}$	j
$\text{O}_2(^1\Delta_g) + \text{O}_3$	$\longrightarrow 2\text{O}_2 + \text{O}$	$K_{20} = 3.5 \times 10^{-15}$	k
$\text{O} + \text{O} + M$	$\longrightarrow \text{O}_2(^1\Delta_g) + M$	$K_{21} = 2.7 \times 10^{-33}$	l
Part 3			
$\text{O}_2 + h\nu$	$\longrightarrow \text{O}_2^*$	P_1	
	$\text{O}_2^+ + e$	P_1	
$\text{N}_2 + h\nu$	$\longrightarrow \text{N}_2^*$	P_2	
$\text{NO} + h\nu$	$\longrightarrow \text{NO}^+ + e$	P_3	
$\text{O}_2(^1\Delta_g) + h\nu$	$\longrightarrow \text{O}_2^+ + e$	P_4	
a: KAUFMAN, 1969 c: REEVES <i>et al.</i> , 1960 e: FITZSIMON and BAIR, 1964 g: KAUFMAN, 1964 i: FONER and HUDSON, 1962 k: CLARK <i>et al.</i> , 1970 Unit of rate constant: three-body recombination ($\text{cm}^6 \text{ sec}^{-1}$) two-body recombination ($\text{cm}^3 \text{ sec}^{-1}$) Photodissociation and photoionization (sec^{-1})			
b: BALDWIN <i>et al.</i> , 1970 d: BENSON and AXWORTHY, 1965 f: SCHIFF, 1969 h: HUNT, 1966 j: CLARK and WAYNE, 1969 l: EVANS and LLIWELLYN, 1972			

$[N]$ =total particle density, ϕ_n =particle flux of species n , $D_{n,m}$ =mutual molecular diffusion coefficient between n -th and m -th component, H_n =scale height of n -th component, H_{ave} =average scale height.

The continuity equation of species n is,

$$\frac{d\phi_n(z)}{dz} = Q_n(z) - L_n(z) \quad (2)$$

where $Q_n(z)$ and $L_n(z)$ are rate of production and loss of n -th component through photochemical reactions at z respectively. The temperature and total particle density are taken from CIRA 1965 model atmosphere. The data sources of absorption cross section and solar UV irradiance used in this calculation are listed in Table 2.

Table 2. Absorption cross sections and solar constant.

Cross sections of absorption and photoionization		
CO ₂	920~2000 Å	COOK <i>et al.</i> , 1966; OGAWA 1971; THOMPSON <i>et al.</i> , 1963; INN <i>et al.</i> , 1953
O ₂ (¹ Δ _g)	1028~1118 Å	HUFFMAN <i>et al.</i> , 1971
N ₂	920~1000 Å HLY-ε, -γ, -δ, CII, NII	HINTERGGER <i>et al.</i> , 1965
O ₂	1775~1325 Å HLY-β, NII, CII and other lines listed in Table 1 of HINTERGGER <i>et al.</i> (1965)	HINTEREGGER <i>et al.</i> , 1965; HUFFMAN <i>et al.</i> , 1971
NO	HLY-α	SCHOEN, 1969
O ₃	2000~3000 Å	INN and TANAKA, 1953
H ₂ O ₂	< 5650 Å	VOLMAN, 1963
Solar flux		
920~2000 Å HLY-ε, HLY-δ, HLY-γ, CII, NII, HLY-β, OVI, NI, SiII, HLY-α	HALL and HINTEREGGER, 1970	

The lower and upper boundaries of the solution are located at $z = z_1 = 50$ km and $z = z_2 = 130$ km. We assume the following boundary conditions:

The mixing ratio of CO at $z_1 = 0.001$ – 0.05 ppm;

The mixing ratio of CO₂ at $z_1 = 315$ ppm;

The ratio, $[O]/[O_2] = 1.7$ at 120 km.

The constituents which have short life time near lower boundary satisfy the chemical equilibrium condition.

It is assumed that the diffusive equilibrium is established for each constituents $z = z_2$. In addition to these boundary conditions, we assume the fractional content of hydrogen corresponds to water vapor mixing ratio of 5×10^{-6} by weight.

The eddy diffusion coefficient used in this calculation is shown in Fig. 1.

Fig. 1. The eddy diffusion coefficient in this calculation is curve c. Curve a is eddy diffusion coefficient given by JOHNSON and WILKINS (1965). Curve b is kinematic eddy viscosity used by MIDGLEY and LIEMON (1966), and this value is equal to eddy diffusion coefficient if turbulent field is completely homogeneous. The points are measured values by KENESEA and ZIMMERMAN (1970). Their measured values suggest the rapid decrease of eddy diffusion coefficient in the lower thermosphere.

Below 100 km, we determine this value considering the results by JOHNSON and WILKINS (1965) and MIDGLEY and LIEMON (1966). Above 100 km we choose the profile which rapidly decreases after KENESEA and ZIMMERMAN (1970). The points in the figure are measured values of diffusion coefficient by KENESEA and ZIMMERMAN (1970). The density and downward flux of O is noticeably depend on the value of eddy diffusion coefficient not only below but also above the turbopause. The models that extend turbulence beyond the turbopause, or lumped parameter models, reduce the effective curvature beyond that produced by the molecular diffusion-chemical equilibrium model and produce effective broadening of an O profile (KENESEA and ZIMMERMAN, 1970).

3. Results of Calculation

In Fig. 2, the result of calculation is shown in comparison with that by HAYS and OLIVERO (1970). In Fig. 3, curves show the results under the conditions that eddy diffusion coefficient is changed and other conditions are kept the same. Our mixing ratio of CO_2 considerably decreases above 80 km, and this tendency is roughly in agreement with HAYS and OLIVERO's (1970). But it can be easily found that our results of the lower thermosphere are certainly different from Hays and Olivero's in detailed points. We consider the following factors as the causes of this difference:

1. The emission lines, which were ignored by Hays and Olivero, contribute the photodissociation of CO_2 in the upper mesosphere. However, the dissociation rate due to H γ - α is about $3 \times 10^{-8} \text{ sec}^{-1}$ in the middle mesosphere and the value of K/H_{ave}^2 is $9 \times 10^{-7} \text{ sec}^{-1}$.

Fig. 2. The mixing ratio of CO_2 . Fig. 3. The CO_2 density profiles.

- curve (a): constant mixing ration model
 curve (b): eddy diffusion coefficient=1.5 X model of (c) in Fig. 1, and solar zenith angle=0.
 curve (c): eddy diffusion coefficient=1.5 X model of (c) in Fig. 1, and solar zenith angle=36°.
 curve (d): eddy diffusion coefficient=model of (c) in Fig. 1, and solar zenith angle=0.
 curve (e): eddy diffusion coefficient=model of (c) in Fig. 1, and solar zenith angle=36°.

These values show that the photodissociation of CO_2 does not become noticeable phenomena and the change of upward flux is strongly effective to variation of density of CO_2 above that height because the density profile rapidly decreases with the increase of height.

2. The eddy diffusion profile used in this calculation is different from that of Hays and Olivero somewhat. They consider the effect of the variation of eddy diffusion coefficient in the stratosphere, but our calculations are made for the change of eddy diffusion coefficient in the range 50–130 km. In addition to this, our calculation

simultaneously determines the density of O for values values of eddy diffusion coefficient. Therefore, the density variation of O affects the density profile of CO₂.

4. CO₂ Density and 15 μ Band Radiation

Few investigators have studied the radiative transfer process of 15 μ band considering CO₂ density which is decided using the photochemical-eddy diffusion model in the lower thermosphere. According to GOODY (1965), the heating function H has the following relation to J , the non-Planckian type source function, in the region where the radiative thermal equilibrium condition is not satisfied:

$$J = B + \frac{H}{2} \frac{\tau_e}{\tau_r} \quad (3)$$

where B is black body radiation intensity, and τ_e and τ_r are relaxation times of CO₂ through collision and radiation respectively. The value of τ_e is given by τ_0/p ; p =atmospheric pressure and τ_0 =relaxation time at STP.

The heating function H is defined by

$$H = \frac{\int_{d\nu} h_\nu d\nu}{2\pi[\text{CO}_2] \int_{d\nu} k_\nu d\nu} = \frac{\int_{d\nu} h_\nu d\nu}{2\pi[\text{CO}_2]S} \quad (4)$$

where h_ν and k_ν are heating rate and absorption coefficient at frequency $=\nu$ respectively, and S is molecular band intensity.

In calculations of radiative transfer of 15 μ band of CO₂ in the upper atmosphere, many investigators pointed out that the dominant term was that which represent cooling to space (MURGATROYD and GOODY, 1958; RODGERS and WALSHAW, 1966; Leovy, 1969). In order to make assessment of the effect on the heating rate of CO₂ in the lower thermosphere, this dominant term only be considered. At altitude z , average heating rate is approximately expressed by

$$\begin{aligned} h(z) &= \int_{d\nu} h_\nu(z) d\nu \\ &= -2\pi[\text{CO}_2]J(z) \left(\int_{d\nu} k_\nu E_2(u_\nu(z, \infty)) d\nu \right) \end{aligned} \quad (5)$$

where

$$E_n(x) = \int_1^\infty \exp(-vx) v^{-n} dv \quad \text{and} \quad u_\nu(z, \infty) = \left| \int_z^\infty [\text{CO}_2(z)] k_\nu dz \right| \quad (6)$$

Substituting in (5) for J from (3), we have the following approximate form

$$h(z) = - \frac{2\pi[\text{CO}_2]B \int_{d\nu} k_\nu E_2(u_\nu(z, \infty)) d\nu}{1 + \frac{1}{2} \frac{1}{S} \frac{\tau_e}{\tau_r} \int_{d\nu} k_\nu E_2(u_\nu(z, \infty)) d\nu} \quad (7)$$

In this equation we can easily find that the heating rate is strongly depend on the number density of CO_2 and collisional relaxation time in the lower thermosphere since the transmission $\int k_\nu E_2(u_\nu(z, \infty)) d\nu$ shows little change above 80 km, and $\tau_r S$ is constant value $(c/8\pi\nu^3)(g_2/g_1)$: g_1 and g_2 are statistical weights of the lower and upper vibrational levels of CO_2 respectively. We show the value $\int E_2 d\nu$ in Fig. 4. The value $\int E_2 d\nu$ calculated using the newly estimated CO_2

Fig. 4. The ratio of $[\text{CO}_2] \int k_\nu E_2 d\nu$. $\int E_2 d\nu$ is unity about 73 km.

The ratio of $[\text{CO}_2] \int k_\nu E_2 d\nu$ is dependent only the density variation above 80 km.

density does not show noticeable difference from the value due to the CO_2 density estimated by constant mixing model above 80 km. Below 80 km, our $\int E_2 d\nu$ becomes large compared with the value estimated on the assumption of the constant mixing ratio CO_2 model. Therefore, the cooling rate to space becomes somewhat large in the mesosphere in comparison with that due to the model of constant mixing ratio of CO_2 .

The rate of temperature change is given by

$$\frac{\partial T(z)}{\partial t} = \frac{h(z)}{\rho(z)C_p} \quad (8)$$

where $\rho(z)$ is the atmospheric density at a level of z , and C_p is the specific heat of air at constant pressure.

The cooling rate stimulated by (7) and (8) are shown in Fig. 5 in comparison with other investigators' estimations. Curves A, B and C are approximatic estimation by (7) and (8). Curves a, b and c are estimated by KHUN and LONDON (1969). Curve d is shown by DRAYSON and EPSTEIN (1969). We compare the cooling rate by the emission of $\text{O } 62 \mu$ estimated by CRAIG and GILLE (1969).

Fig. 5. The cooling rate by CO_2 $15\ \mu$ band in the lower thermosphere. Curves A, B and C are the results of this study. Curves a, b and c are after KUHN and LONDON (1969). Curve d is after DRAYSON and EPSTEIN (1969). The cooling rate by O $62\ \mu$ is estimated by CRAIG and GILLE (1969). The conditions for estimation of these curves:

- a: CO_2 density due to constant mixing ratio, $\tau_0 = 2 \times 10^{-5}$ sec.
- b: CO_2 density due to constant mixing ratio, $\tau_0 = 10^{-5}$ sec.
- c: CO_2 density due to constant mixing ratio, $\tau_0 = 10^{-6}$ sec.
- d: CO_2 density due to constant mixing ratio, $\tau_0 = 2 \times 10^{-5}$ sec.
- A: CO_2 density due to constant mixing ratio, $\tau_0 = 10^{-5}$ sec.
- B: CO_2 density due to constant mixing ratio, $\tau_0 = 10^{-6}$ sec.
- C: CO_2 density in this calculation, $\tau_0 = 10^{-6}$ sec.

The curves with the exception of C are estimated using the density of CO_2 calculated on the assumption of constant mixing ratio. Curve C is calculated using the newly estimated CO_2 density. Curve A and B are in good agreement with the accurate integration of radiative transfer equation, curves b and c respectively, above 95 km. When τ_0 is 10^{-6} sec, the cooling rate due to infrared radiation of CO_2 $15\ \mu$ becomes comparable with the heating rate by absorption of solar UV by molecular oxygen and thermal conduction process is negligible. Curve C shows some decrease of cooling rate in the lower thermosphere. In the present stage, the parameter τ_0 has not been made clear. We conclude that the decrease of CO_2 density through photodissociation of CO_2 causes the decrease of cooling rate by CO_2 $15\ \mu$ band in the lower thermosphere, and in the mesosphere the change of transmission may affect thermal balance.

5. Density Profile $\text{O}_2(^1\Delta_g)$

The density profile of $\text{O}_2(^1\Delta_g)$ in this calculation is shown in Fig. 6. The results do not fully agree with the observational results by EVANS *et al.* (1968, 1969). Our results indicate the existence of the second small peak of $\text{O}_2(^1\Delta_g)$ profile which is pointed out by EVANS *et al.* (1968, 1969, 1970). SHIMAZAKI

Fig. 6. The density profile of $O_2(^1\Delta_g)$. Curve a is the observational value by EVANS *et al.* (1968). Curve b, c, d and e show the estimated values and each profiles are corresponding to the density profiles of CO_2 b, c, d and e.

and LAIRD (1970) pointed out that the second small peak of $O_2(^1\Delta_g)$ density is accounted for by the reaction of $O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O$ and $O_3 + O \rightarrow O_2 + O_2(^1\Delta_g)$ for the large concentration of O_3 estimated by them. In this calculation, the density of O_3 near 85 km is $\sim 7 \times 10^7/\text{cm}^3$ and not the value of 10^8 – $10^9/\text{cm}^3$ estimated by SHIMAZAKI and LAIRD (1970), because the density of O becomes noticeably small compared with the SHIMAZAKI and LAIRD model (1970) and this results in a small production rate of O_3 by $O + O_2 + M \rightarrow O_3 + M$. Our calculation suggests that the second small peak of $O_2(^1\Delta_g)$ density is produced by reaction $O + O + M \rightarrow O_2(^1\Delta_g) + M$ in addition to ozone photolysis.

6. Summary and Discussion

The emission rate of CO_2 $15\ \mu$ band decreases in the lower thermosphere in comparison with the estimation using the constant mixing ratio CO_2 assumption, since CO_2 is dissociated by solar UV above 85 km. In the upper atmosphere the collisional relaxation time of CO_2 is an important parameter which controls the radiative transfer of $15\ \mu$ band. But this value has many points which are uncertain.

We estimate the density profile $O_2(^1\Delta_g)$ using the value of $2.7 \times 10^{-33}\ \text{cm}^6\ \text{sec}^{-1}$ as the reaction rate constant of $O + O + M \rightarrow O_2(^1\Delta_g) + M$ after EVANS *et al.* (1972). This value is equal to the rate constant of $O + O + M \rightarrow O_2 + M$, and may be overestimated. The rate constant has not been accurately measured in laboratory. Some other excitational reactions are suggested (EVANS *et al.*, 1970, 1972; WOOD, 1972):

But more detailed research is required in order to make clear the $O_2(^1\Delta_g)$ distribution of the lower thermosphere.

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