THE PHOTODISSOCIATION COEFFICIENTS OF OZONE AND OXYGEN IN THE CLOUDY TURBID ATMOSPHERE

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ABSTRACT

In this paper, the effects of clouds with different albedos at different altitudes as underlying surface on the photodissociation coefficients of oxygen and ozone in the turbid atmosphere, where the multi-scattering of molecules and aerosols is considered, have been investigated. In addition, the effects of doubling the ozone concentration in the tropopause due to the atmospheric motion on the photodissociation coefficients of ozone and oxygen are also studied.

I. INTRODUCTION

At the earlier stage in the calculation of photodissociation coefficients in the atmospheric photochemical models only a purely absorbing atmosphere was considered. Later, the molecular scattering effects were considered by Luther et al[1]. Then Fiocco et al.[2] investigated the effects of aerosols on the photodissociation coefficients. In those works the cases at different solar zenith angles and surface albedos in a cloudless atmosphere were studied. In this paper, the effects of clouds as underlying surface at different altitudes on the photodissociation coefficients in the molecular and aerosol multi-scattering atmosphere have been discussed. In addition, the changes of the photodissociation coefficients caused by increasing ozone concentration or the existence of the secondary maximum of ozone concentration in the tropopause have been also explored.

II. RADIATIVE TRANSFER MODEL

For simplicity, we start with the azimuthally-averaged monochromatic radiative transfer equation in a plane-parallel atmosphere. For downward radiance $I(\tau,\mu)$, we have

$$I(\tau,\mu) = I(0,\mu)\exp(-\tau/|\mu|) + \int_0^\tau J(\tau',\mu)\exp[-(\tau-\tau')/|\mu|]\frac{d\tau'}{|\mu|}, \tag{1}$$

where

$$J(\tau,\mu) = \frac{\tilde{\omega}_0(\tau)}{2}\int_{-1}^1 P(\tau,\mu,\mu')I(\tau,\mu')d\mu' + \tilde{F}(\tau,\mu). \tag{2}$$

where τ is the optical depth from the top of the atmosphere to the level considered and it depends on wavelength, μ the cosine of the solar zenith angle θ, $I(\tau,\mu)$ the azimuthally-averaged monochromatic radiance in the direction μ at the level τ and the wavelength λ, $\tilde{\omega}_0(\tau)$ the single scattering albedo, $p(\tau,\mu,\mu')$ the azimuthally-averaged scattering phase function, and $\tilde{F}(\tau,\mu)$ the source term.

In the spectral region of interest (1850—8500Å), the thermal emission of the atmosphere and the surface is negligible. If the atmosphere is only illuminated at its upper boundary by a parallel beam of

radiation of net flux πF_s per unit area normal to itself in the direction μ_0, $\tilde{F}$ can be written as

$$\tilde{F}(\tau,\mu) = \frac{\tilde{\omega}_0(\tau)}{4\pi} p(\tau,\mu,\mu_0)\pi F_s \exp(-\tau/|\mu_0|). \tag{3}$$

For simplicity, the subscriptions λ in preceding formulae have been omitted.

The diffuse radiances can be obtained by means of the method of Gauss-Seidel iteration[3]. The atmosphere of optical depth τ_λ is divided into N layers, $\tau = \tau_0, \cdots, \tau_i, \cdots, \tau_N$. Here $\tau_0 = 0$, $\tau_N = \tau_\lambda$, $\tau_{i-1} < \tau_i$. In the interval $[\tau_i, \tau_{i+2}]$ the theorem of integral mean value and Gauss quadrature formula are respectively applied to the second term on the right side in Eq. (1) and the first term on the right side in Eq. (2). From Eqs. (1), (2) and (3) the following equation is approximately obtained

$$I(\tau_{i+2},\mu_j) = I(\tau_i,\mu_j)\exp(-2\Delta\tau_i/|\mu_j|)$$
$$+ [1 - \exp(-2\Delta\tau_i/|\mu_j|)] \cdot \left\{ \frac{1}{2} \sum_{j'=1}^{2M} a_{j'}\tilde{\omega}_0(\tau_{i+1}) \, p(\tau_{i+1}, \mu_j,\mu_{j'}) \cdot I(\tau_{i+1},\mu_{j'}) \right.$$
$$\left. + \frac{1}{4\pi}\tilde{\omega}_0(\tau_{i+1}) \, p(\tau_{i+1},\mu_j,\mu_0) \, \pi F_s \exp(-\tau_{i+1}/|\mu_0|) \right\}, \tag{4}$$
$$i = 0,1,\cdots,N-2,$$
$$j = M+1,\cdots,2M,$$
$$j' = 1,2,\cdots,2M,$$

where μ_j are roots of Legendre function $p_M(\mu)$ as the quadrature points, a_j Gauss quadrature coefficients, and

$$\Delta\tau_i = \frac{1}{2}(\tau_{i+2} - \tau_i).$$

For the upward diffuse radiances ($\mu > 0$), the similar equation is deduced

$$I(\tau_{i-2},\mu_j) = I(\tau_i,\mu_j)\exp(-2\Delta\tau_i/|\mu_j|)$$
$$+ [1 - \exp(-2\Delta\tau_i/|\mu_j|)] \left\{ \frac{1}{2} \sum_{j'=1}^{2M} a_{j'}\tilde{\omega}_0(\tau_{i-1})p(\tau_{i-1},\mu_j,\mu_{j'}) \, I(\tau_{i-1},\mu_{j'}) \right.$$
$$\left. + \frac{1}{4\pi}\tilde{\omega}_0(\tau_{i-1})p(\tau_{i-1},\mu_j,\mu_0)\pi F_s \, \exp(-\tau_{i-1}/|\mu_0|) \right\}, \tag{5}$$
$$i = 2,3\cdots,N$$
$$j = 1,2,\cdots,M,$$
$$j' = 1,2,\cdots,2M.$$

At the top of the atmosphere, the downward diffuse radiances are zero. And it is assumed that the upward diffusely reflected radiances at the surface obey Lambert's law. Thus, the boundary conditions are

$$I(0,\mu_j) = 0, \qquad (\mu_j < 0) \tag{6}$$
$$I(\tau_N,\mu_j) = \frac{A_s}{\pi}[-\pi F_s\mu_0 \exp(-\tau_N/|\mu_0|) - 2\pi \sum_{j'=M+1}^{2M} a_{j'}\mu_{j'} I(\tau_N,\mu_{j'})],$$
$$(\mu_j > 0, \mu_{j'} < 0) \tag{7}$$

where A_s is the surface albedo. From Eqs. (4), (5), (6) and (7) the diffuse radiances at different levels in different directions can be solved by using Seidel iteration.

When the solar radiation of spectral flux density πF_s reaches on the top of the atmosphere in the direction μ_0 and no specular reflection at the earth's surface is considered, the spectral flux density of the

direct radiation with wavelength λ at level τ is

$$F_{\lambda,dir}(\tau) = \pi F_s \exp(-\tau/|\mu_0|). \tag{8}$$

Then the total flux density with wavelength λ at level τ is

$$F_\lambda(\tau) = \pi F_s \exp(-\tau/|\mu_0|) + 2\pi \sum_{j=1}^{2M} a_j I(\tau,\mu_j). \tag{9}$$

The photodissociation coefficient for transforming species A to B is given by

$$J_{A \to B} = \int_{\Delta\lambda} \sigma_\lambda(T) Q_\lambda(A \to B) F'_\lambda(\tau) d\lambda, \tag{10}$$

where $\sigma_\lambda(\tau)$ is absorption cross section, T is the temperature, $Q_\lambda(A \to B)$ is the quantum yield, F'_λ is the flux of photons and given by $F_\lambda' = \lambda F_\lambda/hc$, where h is the planck's constant and c the speed of light, $\Delta\lambda$ is the wavelength range and it changes with different species. For O_2, $\Delta\lambda$ is 1850—2424Å and for O_3, 2000—8500Å.

The radiative transfer equation holds for monochromatic radiation. In practice, the calculation is made in a finite wavelength interval. Following Fiocco et al.[2] , the exponential sum fitting approximation is utilized to gain the averaged transmission function in a finite spectral interval and the spectral region 1850—8500Å is divided into 130 intervals. In the wavelength range 2000—7300Å, which overlaps with that of Fiocco's, Fiocco' fitting parameters of absorption of O_3 and H_2O are utilized . In the range 1850—2424Å, the absorption coefficients of O_2 are taken from Hudson et al.[4] In the range 7500—8500Å, the absorption coefficients in a wavelength interval of 100Å are obtained by means of the data of Lowtran 4 [5]. Because the absorption of O_3 is rather smooth in the visible range, the transmission of atmospheric absorption gases in the overlapping absorption region of O_3 and H_2O can be regarded as the product of their individual transmissions. In the ultraviolet range, where the absorption of O_3 overlaps with that of O_2, but ozone has no band structure comparable to oxygen's, the transmission of the atmosphere can be approximately regarded as the product of transmissions of O_3 and O_2. It is assumed that the transfer Eq. (1) holds in the small wavelength intervals and the average total transmission of absorption gases is the product of average transmissions of various absorption gases.

In addition to the calculations of the photodissociation coefficients of O_2 añd O_3, J_{O_2} (1850—2424Å) and J_{O_3} (2000—8500Å), the photodissociation coefficients corresponding to different absorption bands of O_3 are also seperately calculated. These bands are Hartley band ^1S ($\Delta\lambda_1$:2000--2360Å), Hartley band ^1D ($\Delta\lambda_2$: 2360—3100Å), Huggins band ($\Delta\lambda_3$: 3100—3600Å), and Chappuis band ($\Delta\lambda_4$:4100—8500Å). The corresponding photodissociation coefficients are denoted as $J_{O_3,a}$, $J_{O_3,b}$, $J_{O_3,c}$ and $J_{O_3,d}$, respectively.

III. ATMOSPHERE MODEL

In the wavelength range of interest the absorptions by O_2, O_3 and H_2O are taken into account. In addition, the multi-scattering of air molecules and aerosols and the diffuse reflection at the surface are also taken into account. The thermal emission of the atmosphere and the surface as well as the specular reflection of the surface are neglected.

In this model the distributions of O_2, H_2O and air density, O_3 concentration, temperature and pressure versus the altitude are taken from "U.S. Standard Atmosphere, 1976"[6].

The aerosols in the stratosphere (above 12 km) consist of one part of dust of refractive index $n = 1.65-i0$ and two parts of sulphuric acid droplets of $n = 1.65-i 0.001$ The aerosols in the troposphere

(below 12 km) are all composed of dust. The size distribution of aerosols is assumed to follow haze type H Deirmendjian distribution in the stratosphere and haze type L Deirmendjian distribution in the troposphere. The number density profile of aerosols is similar to that of McClatchey[7] for the visibility 23 km at the surface. Because the different size distributions are utilized in the two models, the total number of aerosols in our model is corrected to make the visibility at the surface also equal 23 km. Besides, a dense stratospheric aerosol layer after the volcanic eruption is also considered. In this case, a stratospheric aerosol layer between 13 and 24 km is added to the original aerosol model. The maximum value of number density at 18 km is ten times larger than the original value at that height.

In the calculation the atmosphere is divided into 42 layers. The thickness of each layer is 1 km between 0 and 40 km and 5 km between 40 and 50 km. Each layer is subdivided into sublayers depending on the optical depth at different wavelengths. The vertical optical depth of each sublayer is less than 0.024 in the spectral range longer than 3000Å and a little larger in the wavelength range shorter than 3000Å due to the strong absorption and the limited numbers of the sublayers restricted by the computer storage. The largest value in that range is less than 0.131.

IV. RESULTS

1. *Effect of Molecular Scattering*

As a criterion of comparison, the photodissociation coefficients of O_2 and O_3 in the purely absorbing molecular atmosphere at a solar zenith angle of 60 are given in Fig. 1. When the molecular
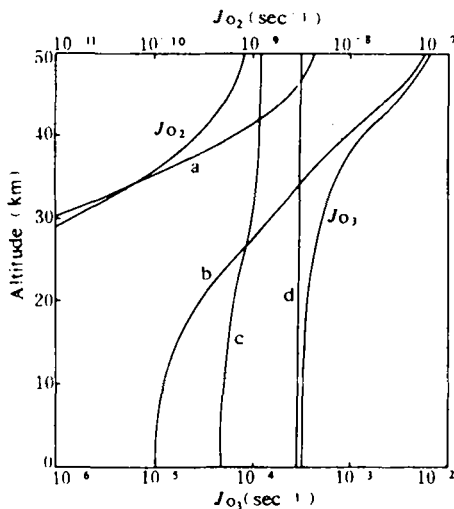

Fig. 1. Photodissociation coefficients of O_2 and O_3, J_{O_2} and J_{O_3}, versus altitude in a purely absorbing atmosphere at a solar zenith angle of 60°.
Curves a,b,c, and d represent the photodissociation coefficients corresponding to Hartley band ^1S (2000—2360Å), Hartley band ^1D (2360—3100Å), Huggins band (3100—3600Å) and Chappuis band (4100—8500Å) of ozone, respectively.
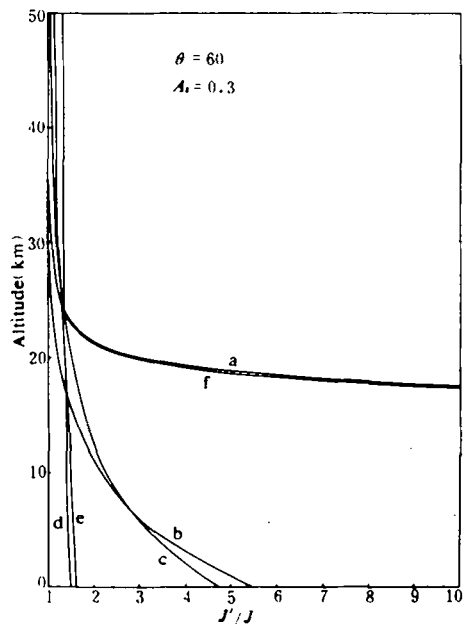

Fig. 2. Ratios of photodissociation coefficients of O_2 and O_3, $J(m)$, in a molecular scattering atmosphere to those, $J(p)$, in a purely absorbing atmosphere versus altitude.
Curves e and f are for O_3 and O_2, respectively. Curves a, b, c, and d, are for different absorbing bands of O_3; see the note in Fig. 1.

scattering is considered, the diffuse radiation increases with descent of altitude. The molecular multi-scattering radiation is inversely proportional to the fourth power of wavelength. Therefore, the photodissociation coefficient corresponding to the shorter wavelength radiation increases with descent of altitude obviously. The ratios of the photodissociation coefficients of O_2 and O_3 in the molecular scattering atmosphere to those in the purely absorbing molecular atmosphere at the solar zenith angle of 60^c and with the albedo of 0.3 are given in Fig. 2, respectively. It can be clearly seen that the coefficients below 25 km increase obviously, especially, J_{O_2} and $J_{O_3,a}$ show a variation of an order of magnitude. Therefore, if the molecular scattering is not taken into account in the calculation, the photodissociation coefficients related to the shorter wavelength radiation will have large errors below 25 km.

2. *Effects of Aerosol*

In the real atmosphere, besides the molecular scattering, there is the extinction due to aerosol. The percentage deviations of the photodissociation coefficients of O_3 and O_2 for the turbid atmosphere and
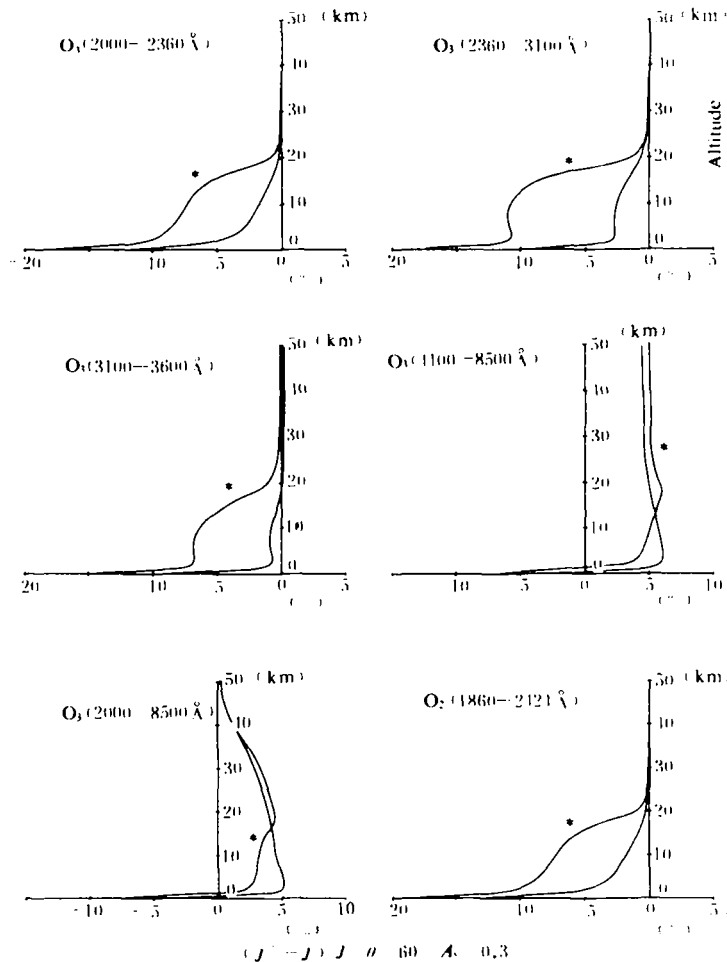
Fig. 3. Percentage deviation of photodissociation coefficients of O_2 and O_3, J', for a turbid atmosphere to those, J, for a molecular scattering atmosphere.

* denotes the case of adding the stratospheric aerosol layer.

the molecular scattering atmosphere are shown in Fig. 3, where two aerosol models are involved. The extinction of aerosols affects the radiation reaching the ground so that the photodissociation coefficients near the ground are smaller than those for taking no account of the extinction of aerosols. But in the upper altitudes the results are different. Because of the upward scattering by the aerosols and the diffuse reflection by the surface, the photodissociation coefficients related to the radiation in the transparent wavelength range increase as compared with those in the molecular scattering atmosphere. The albedo of the surface is of significant to the photodissociation coefficients related to the visible radiation. However, for the middle ultraviolet region, the radiation is weak in low altitudes and the upward radiation scattered by aerosols is even much weaker. It is strongly absorbed once again by O_2 and O_3 when it goes up. Consequently, the photodissociation coefficients corresponding to the middle UV radiation are smaller than those in the molecular scattering atmosphere either in upper altitudes or near the ground. For the stratospheric aerosol model the extinction of the stratospheric aerosols leads to the reduction of the radiation arriving at low altitudes, so that the photodissociation coefficients near the ground will decrease as compared with those for the case of absence of the stratospheric aerosol layer. As a result of the increase of upward diffuse radiation scattered by the increased stratospheric aerosols, the photodissociation coefficients related to visible radiation increase in the upper atmosphere.

3.   *Effects of Clouds of Different Albedos at Different Altitudes*

The calculations above are made for the cloudless sky. However, over fifty percent of area of the earth are covered with clouds. In this section the effects of clouds as an underlying surface on the photodissociation coefficients are considered. It is assumed that the cloud at certain altitude reflects a part of the radiation which reaches on the top of the cloud and absorbs all of the rest. This assumption is reasonable for low or middle clouds, because the transmittance of low or middle clouds is very low. The radiation transmitting downward through the cloud, reflected by the surface and transmitting upward through the cloud again is quite small. For the high clouds of high transmittance, the situation is different from that of low or middle clouds. It is unreasonable to neglect the radiation penetrating the clouds upward. However, such radiation could be treated as a part of the reflected radiation by the clouds, so that the function of the surface and the atmosphere under the clouds could be regarded as increasing the cloud albedo. Hence, the high cloud could be taken as an underlying surface having a corrected albedo. The percentage deviation of the photodissociation coefficients of O_2 and O_3 for the cloudy turbid atmosphere at different cloud albedos and different cloud altitudes and for the cloudless turbid atmosphere at the surface albedo of 0.3 and solar zenith angle of 60° are shown in Fig. 4. Three cases for low, middle and high clouds have been considered. The altitudes of cloud top are 3 km, 5 km, and 8 km, respectively.

First, the cases for the same underlying surface albedo of 0.3 are compared. As a result of the rising of the underlying surface, the upward diffuse radiation scattered by molecules and aerosols below the underlying surface has no longer contributed to the photodissociation coefficients above the underlying surface. From Fig. 4 it could be clearly seen that when the albedos have the same value, the photodissociation coefficients in the clear sky are lower than those in the cloudy sky. The higher the altitudes of the cloud top, the lower the photodissociation coefficients. For the radiation which can not reach the lower altitudes, it is not important whether the clouds exist or how high the altitudes of cloud top are. The decreases of $J_{O_3,u}$ and J_{O_2} are very small.

In practice, the albedos of low and middle clouds are larger than those of land, sea water, and forests, therefore an albedo of 0.8 is taken for low and middle clouds. In this case the percentage deviations of the photodissociation coefficients for the cloudy atmosphere and cloudless atmosphere are also given in Fig. 4.
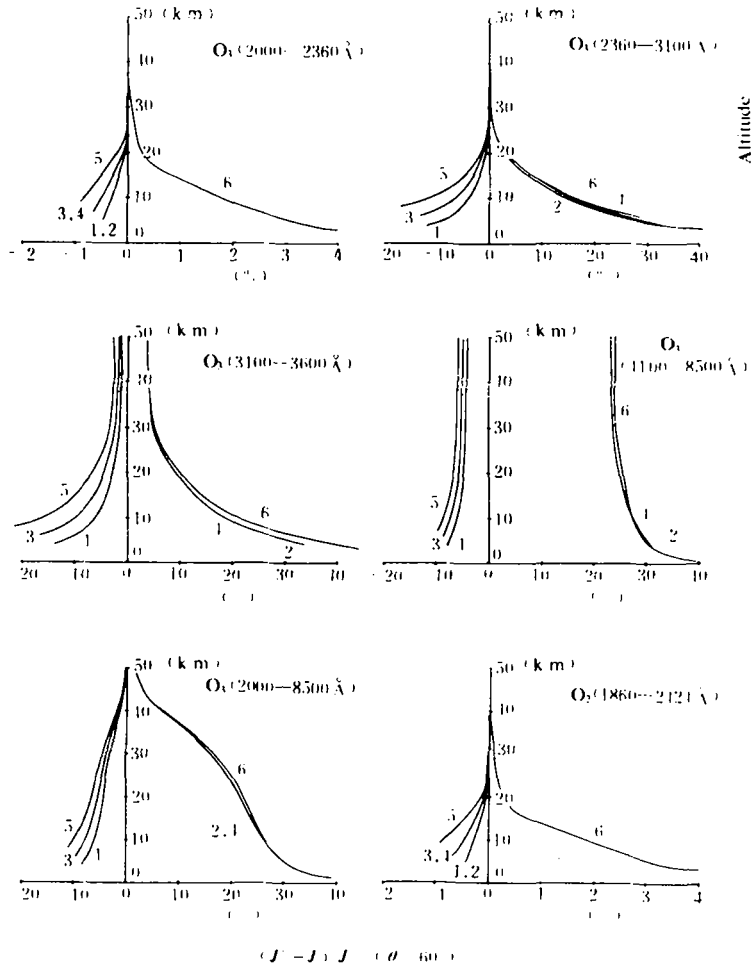
Fig. 4   Percentage deviation of the photodissociation coefficients of O₂ and O₃, J', for a cloudy turbid atmosphere of different underlying surface albedos at different altitudes to those, J, in a cloudless turbid atmosphere of surface albedo of 0.3.
Curve 1:(3,0.3), 2:(3,0.8), 3:(5,0.3), 4:(5,0.8), 5:(8,0.3), 6:(0,0.8)**. The values in the parentheses are in turn the underlying surface altitudes (km) and its albedos. ** denotes the case in a molecular scattering atmosphere.

For the transparent wavelength range under the condition of high underlying surface albedo, the radiation reflected by the underlying surface constitutes a large part of the total upward diffuse radiation. In this case, the differences of the radiations scattered by the underlying surface at different altitudes are relatively small. Hence for the albeso of 0.8, the differences of the photodissociation coefficients for the underlying surface at 3 km and 5 km are very small. Although the radiation scattered by molecules and aerosols below the cloud almost has no contribution to·the photodissociation coefficients when the cloud of high albedo presents, the high albedo of the underlying furface causes more upward scattering radiation. The effect of cloud of high albedo far exceeds that of aerosols. The comparison between the results for the molecular scattering atmosphere and the turbid atmosphere at underlying surface albedo of 0.8 also shows this tendency (see Fig. 4).

For the wavelength range in which the atmospheric absorption is strong, the value of the

underlying surface albedo, as well as the altitude of the underlying surface has little effect on the photodissociation coefficients related to this range, but the effect of aerosols is considerable.

The land surfaces at different elevations would have the same effects.

4. Effect of the Increase of Ozone in the Tropopause

In the preceding discussion, the ozone concentration distribution is assumed to follow a standard vertical profile. Sometimes the atmospheric motion leads to the increase of ozone concentration and formation of a secondary maximum of ozooe concentration in the troposphere. This could be observed in routine measurements. Consequently another ozone profile is considered in which the ozone concentration is double at 10 12 km above the ground and remains the same as the original one in the rest parts of the atmosphere. The percentage deviations of the photodissociation coefficients for both ozone distributions are shown in Fig. 5.
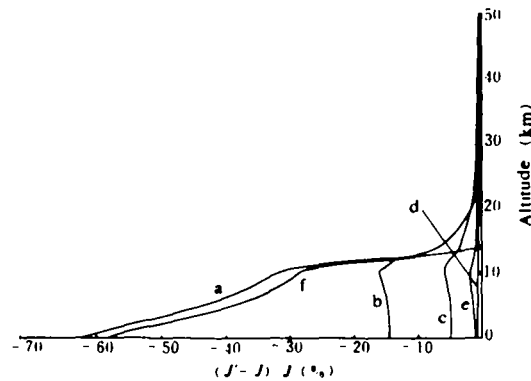

Fig. 5. Percentage deviations of photodissociation coefficients of O₂ and O₃ in a turbid atmosphere due to doubling ozone concentration in the tropopause The meanings of symbols a, b, c, d, e and f are the same as those in Fig. 2

The increment of ozone concentration at 10—12 km level results in a reduction of direct and diffuse radiation in the troposphere. The photodissociation coefficients corresponding to various radiation are reduced. J_{O_2} and J_{O_3} markedly decrease below 12 km owing to the strong absorption by O_2 and O_3 in Hartley band ^1S.

Above the tropopause the direct radiation unchanges and the upward diffuse radiation from the troposphere reduces. Because the contribution of radiation from the troposphere in the strong absorption wavelength range is very small, the effect of the variation of O_3 concentration at the tropopause on the photodissociation coefficients J_{O_2} and $J_{O_3,a}$ in the troposphere is negligible. But in the stratosphere, $J_{O_3,b}$ and $J_{O_3,c}$ corresponding to Hartley band ^1D and Huggins band of ozone, respectively, are decreased. Only at the altitude, where the radiation from the lower atmosphere is small, the change of these photodissociation coefficents is relatively small. In the visible range the scattering radiation from the lower part of the atmosphere can reach the upper atmosphere, the photodissociation coefficients in all altitudes are reduced but not too much. Although $J_{O_3,a}$ and $J_{O_3,b}$ change obviously in the troposphere and lower stratosphere due to doubling the ozone concentration in the tropopause, the total J_{O_3} changes only a little because the proportions of $J_{O_3,a}$ and $J_{O_3,b}$ in the total J_{O_3} are very small (see Fig. 1). J_{O_2}, which is only related to the short wave radiation, decreases a lot in the troposphere.

It could be inferred that the photodissociation coefficients of the other trace elements which are

only related to the short wave radiation will change greatly when the ozone concentration increases in the tropopause.

V. CONCLUSION

Some conclusions have been inferred from the calculation.

Above 20 km the photodissociation coefficients of O_2 and those of the trace species only related to the strongly absorbed short wave radiation have little relation to the altitude and albedo of the underlying surface and the aerosols. Below 20 km they have little relation to the altitude and albedo of underlying surface but relate to the column number density and distribution of aerosols.

The photodissociation coefficients of O_3 and those of the trace species corresponding to the radiation reaching the ground are in relation to the albedo of underlying surface. When the albedo is high, the effects of the aerosols and the altitude of underlying surface are small. When the albedo is low, the photodissociation coefficients below 20 km are affected by the altitude of underlying surface and the distribution and density of aerosols.

The appearance of the secondary maximum of ozone concentration at the tropopause leads to the decrease of photodissociation coefficients of O_2 and trace species which are only related to the strongly absorbed short wave radiation.

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