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# Sensitivity studies of the recent new data on O(<sup>1</sup>D) quantum yields in O<sub>3</sub> Hartley band photolysis in the stratosphere

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## Abstract

The production yields of excited oxygen  $O(^1D)$  atoms from the near ultraviolet  $O_3$  photolysis are essential quantities for atmospheric chemistry calculations because of its importance as major sources of hydroxyl (OH) radicals and nitric oxide (NO). Recently, new  $O(^1D)$  quantum yields from  $O_3$  photolysis between 230 and 305 nm in the Hartley band region were reported, which are almost independent of the photolysis wavelength (0.88–0.93) and smaller than NASA/JPL-2000 recommendation (0.95 between 240 and 300 nm). In order to assess consequences of the new data of  $O(^1D)$  quantum yields on the stratospheric chemistry, the changes in stratospheric chemical partitioning and  $O_3$  concentration are examined using a one-dimensional atmospheric model. Our steady state model simulations for mid-latitude in March indicate that the smaller  $O(^1D)$  quantum yields result in increases of stratospheric  $O_3$  (up to  $\sim 2\%$  in the upper stratosphere), which are attributed to the changes in  $HO_x$ ,  $NO_x$ , and  $ClO_x$  abundance and their catalyzed  $O_3$  loss rates.

## 1. Introduction

Photodissociation by solar ultraviolet (UV) radiation drives much of the chemistry in the stratosphere and troposphere, since it contributes to the removal of many atmospheric trace gases by decomposition and generates highly reactive radicals. One of the important photochemical reactions is the photolysis of  $O_3$  in the UV region, which produces  $O(^1D)$  atoms. Then, the produced  $O(^1D)$  radicals react with water vapor and generate OH radicals which rule the oxidation capacity of the atmosphere (Brasseur et al., 1999; Finlayson-Pitts and Pitts, 1999):



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The chemical reactions of O(<sup>1</sup>D) play important roles in determining the chemical composition of the stratosphere. Figure 1 illustrates the principal chemical reactions involving O(<sup>1</sup>D) in the stratosphere. Most of the O(<sup>1</sup>D) atoms produced by the photolysis of O<sub>3</sub> are quickly deactivated by collisions with major atmospheric species (M = N<sub>2</sub> and O<sub>2</sub>) and then form O<sub>3</sub> molecules again:



The production rate of stratospheric OH depends on the O(<sup>1</sup>D) production from O<sub>3</sub> photolysis. The OH radicals formed by reaction (3) initiate the HO<sub>x</sub> catalytic cycle of O<sub>3</sub> loss, which is the main process for controlling O<sub>3</sub> loss in the lower and upper stratosphere. OH is directly involved in a HO<sub>x</sub> catalytic cycle and also controls the partitioning between active species such as nitrogen oxides and chlorine oxides and their reservoirs:



The O(<sup>1</sup>D) also produces the NO radical in the stratosphere due to the reaction with N<sub>2</sub>O:



NO is the major catalyst for O<sub>3</sub> loss of NO<sub>x</sub> in the middle stratosphere. NO<sub>x</sub> also suppresses the halogen catalytic destruction of O<sub>3</sub> by sequestering them in unreactive forms such as ClONO<sub>2</sub>:



The net effect on stratospheric O<sub>3</sub> depends on the relative contributions of these mechanisms at each altitude.

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The channel branching ratios between channels (1) and (2) from  $O_3$  photolysis have been examined extensively in the wavelength range  $\lambda > 306$  nm at 298 K and low temperature by various laboratories over the past two decades (Matsumi et al., 2002, and references therein), which are used in the model calculation for such a comparison of observed and modeled OH,  $HO_x$ , and  $O_3$  concentrations and photolysis rate of  $O_3$  (e.g. Wennberg et al., 1999; Pfister et al., 2000). The  $O(^1D)$  quantum yields in the photolysis of  $O_3$  at wavelengths shorter than 300 nm have not received much attention and JPL-2000 evaluations for atmospheric modeling by NASA panel recommended the constant value of 0.95 for the wavelength range of 240–300 nm (Sander et al., 2000). The experimental data for the  $O(^1D)$  quantum yields from  $O_3$  photolysis over the Hartley band (200–300 nm) are sparse, which may result in some notable uncertainties in the model calculation. Very recently, Taniguchi et al. (2000) and Takahashi et al. (2002) have published results of the precise  $O(^1D)$  quantum yield measurements in the photolysis of  $O_3$  between 230 and 308 nm. The latest NASA/JPL panel (Sander et al. 2003) adopted the new experimental results of Taniguchi et al., they have recommend  $\sim 0.90$  for  $\lambda < 306$  nm. In this study, the atmospheric impacts of their laboratory results of  $O(^1D)$  quantum yields from  $O_3$  photolysis on the stratospheric chemistry have been explored, in the framework of a one-dimensional dynamical-photochemical model.

## 2. $O(^1D)$ quantum yield data in the photolysis of $O_3$

The absolute quantum yields of  $O(^1D)$  formation from  $O_3$  photolysis between 306 and 328 nm have been evaluated by the Matsumi et al. (2002) with the detailed examination of recent experimental measurements as a joint activity of SPARC and IGAC. Very recently, Takahashi et al. (2002) have measured the  $O(^1D)$  quantum yields from  $O_3$  photolysis between 230 and 308 nm using a new experimental technique. Using the same technique, Taniguchi et al. (2000) have indicated that the  $O(^1D)$  quantum yield in the wavelength range of 297–306 nm is almost independent of the wavelength ( $\sim 0.89$ ). In Fig. 2, the yield values presented by Taniguchi et al. (2000) and Takahashi et al.

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(2002) are compared with both values previously reported by other different groups (Trolier and Wiesenfeld, 1988; Cooper et al., 1993; Talukdar et al., 1997, 1998) and JPL-2000 recommendations (Sander et al., 2000). Talukdar et al. (1998) reported that the  $O(^1D)$  quantum yield between 289 and 305 nm was  $0.89 \pm 0.02$ , which is in good agreement with results presented by Taniguchi et al. (2000) and Takahashi et al. (2002). The yield values reported by Trolier and Wiesenfeld (1988) and JPL-2000 recommendations in this wavelength region are larger than values reported by Talukdar et al. (1998), Taniguchi et al. (2000), and Takahashi et al. (2002). At shorter wavelengths, JPL-2000 panel has recommended a constant value of 0.95 for the  $O(^1D)$  quantum yield in the Hartley band photolysis of  $O_3$  between 240 and 300 nm. The  $O(^1D)$  quantum yields presented by Takahashi et al. (2002) are almost independent of the photolysis wavelengths ( $\sim 0.91$ ) between 230 and 300 nm, which are  $\sim 4$ –5% smaller than the JPL-2000 recommendation values and in good agreement with values determined by Cooper et al. (1993), except for 228.5 and 231 nm. Talukdar et al. (1997) reported the room temperature  $O(^1D)$  quantum yield of  $0.91 \pm 0.06$  at 248 nm, which is in good agreement with the value of  $0.914 \pm 0.019$  presented by Takahashi et al. (2002). Talukdar et al. (1998) showed that the  $O(^1D)$  quantum yields between 289 and 305 nm were independent of the temperature (203–320 K). Talukdar et al. (1997) and Takahashi et al. (1998) reported a negligible temperature dependence of  $O(^1D)$  quantum yields at 248 nm and 305 nm, respectively. We have focused on the difference in the wavelength range of 230–305 nm between the new quantum yield values (Taniguchi et al., 2000; Takahashi et al., 2002) and JPL-2000 recommendations, and examined the consequences of the difference in the chemical compositions in the mid-latitude stratosphere using a one-dimensional chemical model. The effect of the difference of the  $O(^1D)$  quantum yield values in the wavelength region of 230–305 nm should be significant in the stratosphere and very little in the troposphere, since the solar radiation at the wavelengths shorter than 305 nm mainly affects the stratospheric chemistry.

### 3. O(<sup>1</sup>D) production rates in the stratosphere

The total production rates of O(<sup>1</sup>D) atom from O<sub>3</sub> photolysis at several altitudes,  $P_{\text{total}}(\text{O}^1D)$ , were calculated by

$$P_{\text{total}}(\text{O}^1D) = \int P(\lambda) d\lambda = \int F(\lambda) \sigma(\lambda, T) \Phi_{1D}(\lambda, T) d\lambda, \quad (10)$$

where  $\lambda$  is the wavelength, and  $T$  is the temperature and  $F$  the actinic flux at the altitude.  $\sigma$  defines the absorption cross section of the O<sub>3</sub> molecule and  $\Phi_{1D}$  the O(<sup>1</sup>D) quantum yield from O<sub>3</sub> photolysis which is the probability for a process (1) to occur upon absorption of a photon. We calculated the  $P_{\text{total}}(\text{O}^1D)$  values for the altitudes of 15, 25, and 40 km. The numerical data of  $F$  at solar zenith angle of 40° were taken from Finlayson-Pitts and Pitts (1999) and  $\sigma$  at 228 and 263 K were taken from Malicet et al. (1995) (Fig. 3). It should be noted that the relative O(<sup>1</sup>D) production rate function,  $P(\lambda)$ , predominantly depends on the wavelength region ~230–320 nm, which is limited by the sunlight spectrum penetrating into the stratosphere and by the absorption properties of O<sub>3</sub> molecules. Therefore, the O(<sup>1</sup>D) quantum yield from O<sub>3</sub> photolysis in this wavelength region and its temperature dependence is a key input parameter for modeling calculations in the stratospheric chemistry since the predominant source of the O(<sup>1</sup>D) atoms in the stratosphere is the photolysis of O<sub>3</sub>. Due to the temperature dependence of  $\sigma$  and  $\Phi_{1D}$ , the ambient temperature influences the O(<sup>1</sup>D) production rate functions at each altitude. At  $\lambda > 310$  nm, the O(<sup>1</sup>D) formation via photodissociation of the vibrationally and rotationally excited O<sub>3</sub> and spin-forbidden process takes place (Matsumi et al., 2002). Since the population of the internally excited O<sub>3</sub> molecules is dependent on the temperature, the O(<sup>1</sup>D) quantum yields at  $\lambda > 310$  nm (up to ~325 nm) change as a function of the temperature (Talukdar et al., 1998; Takahashi et al., 1998; Smith et al., 2000). In the calculations for the wavelengths longer than 308 nm, the expression for the O(<sup>1</sup>D) quantum yields recommended by JPL-2000 (Sander et al., 2000) was used, which is a function of photolysis wavelength and temperature.

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We found that the total  $O(^1D)$  production rates  $P_{\text{total}}(O(^1D))$  estimated with the new  $O(^1D)$  quantum yields are smaller than those with the JPL-2000 recommendations by 2.5, 3.8 and 5.1%, at 15, 25 and 40 km, respectively. Atmospheric  $O_3$  is photolyzed mainly by the UV radiation wavelength  $\sim 295$ – $315$  nm at 25 km and  $\sim 250$ – $310$  nm at 40 km, respectively. Therefore, the decreases in  $O(^1D)$  production rates caused by the new  $O(^1D)$  quantum yields in the wavelength range of 230–305 nm change the  $P_{\text{total}}(O(^1D))$  more effectively at 40 km than that at 20 km. Comparisons of results obtained using the smaller values of  $O(^1D)$  quantum yields with those using the recommendations of JPL-2000 clearly suggest the significance of new  $O(^1D)$  yield data. Therefore, we examined the effects of the new  $O(^1D)$  yields on the stratospheric chemistry by model calculations, as described in the following section.

#### 4. One-dimensional atmospheric model calculations

We have examined the effect of the smaller values of  $O(^1D)$  quantum yields (Taniguchi et al., 2000; Takahashi et al., 2002) using a one-dimensional dynamical-photochemical model, in which all the chemical reactions related to  $O_3$  chemistry are reasonably represented and it is suitable for assessing the impact of the new  $O(^1D)$  quantum yield data on stratospheric chemistry. All chemical schemes in this one-dimensional model used here are the same as those used in the Garcia-Solomon two-dimensional (GS-2D) model (e.g. Solomon et al., 1996), which includes 90 kinetic reactions, 30 photolysis reactions, and 40 chemical species. Table 1 summarizes all 40 species included in this model. The model also includes actinic flux calculations. The reaction rate coefficients and absorption cross sections are updated to include NASA/JPL-1997 and -2000 recommendations (DeMore et al., 1997; Sander et al., 2000). Mixing ratios of 24 chemical species including  $O_3$  for middle latitude in March are initialized, using data sets given by Brasseur et al. (1999) (Table 1). The vertical profiles of all species including the other photochemical species and families are computed to be in steady state

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for the day-night average condition. Since model responses of chemical species due to the change in  $O(^1D)$  quantum yields represent the time-dependent propagation of infinitesimal perturbations, individual responses grow and converge on the time scale associated with that process. Therefore, calculations for all chemical species with the new values or JPL-2000 recommendations for the  $O(^1D)$  quantum yields were run long enough to ensure convergence ( $\pm 0.2\%$  in concentration of all chemical species). The vertical profiles of  $O_3$ ,  $HNO_3$ , and chemical families,  $HO_x$ ,  $ClO_x$ , and  $NO_x$ , predicted by the model are illustrated in Fig. 4, when the new quantum yield values are used. Here, the families are defined as  $HO_x = H + OH + HO_2$ ,  $ClO_x = Cl + ClO$ , and  $NO_x = NO + NO_2$ .

We have estimated how model concentration results for  $O_3$  and other chemical species are affected when a new set of model parameters, that is, the new  $O(^1D)$  quantum yields are adopted. The change in  $O_3$  concentration,  $\delta O_3$ , is the relative change in a predicted model concentration:

$$\delta O_3 \equiv \frac{[O_3]_{New} - [O_3]_{JPL}}{[O_3]_{JPL}}, \quad (11)$$

where  $[O_3]_{New}$  is concentration of  $O_3$  calculated with the new values of  $O(^1D)$  quantum yields from  $O_3$  photolysis between 230 and 308 nm (Taniguchi et al., 2000; Takahashi et al., 2002), while  $[O_3]_{JPL}$  is that using JPL-2000 recommendations as a standard model (Sander et al., 2000). Figure 5 shows the results of the diurnally averaged photochemical model calculations, which indicates the change of the  $O(^1D)$  and  $O_3$  concentrations,  $\delta O(^1D)$  and  $\delta O_3$ , versus altitude for latitudes of 20, 40, and 60° in March between the model runs with the new  $O(^1D)$  values and the JPL-2000 recommendations. The partitioning changes in the chemical families,  $NO_x$ ,  $HO_x$ , and  $ClO_x$ , predicted as a result of the parameter changes of  $O(^1D)$  quantum yields from JPL-2000 recommendations to the new values are shown in Fig. 6.

Changes in the reactive families influence  $O_3$  loss rates via the catalytic cycles involving those families. Figure 7 shows the  $O_3$  loss rates by the three principal reactive

families,  $\text{NO}_x$ ,  $\text{HO}_x$ , and  $\text{ClO}_x$ , versus altitude for latitude of 40 degree in March, which were calculated based on the new  $\text{O}(^1D)$  quantum yield values.

## 5. Discussions

The steady-state  $\text{O}(^1D)$  concentration for latitude of  $40^\circ$  becomes smaller by  $\sim 2\text{--}6\%$  with a negative peak at 35 km due to the smaller  $\text{O}(^1D)$  quantum yields from  $\text{O}_3$  photolysis between 230 and 308 nm (Fig. 2), depending on altitude in the stratosphere as shown in Fig. 5. This result is consistent with our evaluation of the altitudinal changes in the total  $\text{O}(^1D)$  production rate  $P_{\text{total}}(\text{O}(^1D))$ . This indicates the consistency between the simple calculation with Eq. (10) and the one-dimensional chemical calculation, and that the concentration of  $\text{O}(^1D)$  is influenced only by the production process of  $\text{O}(^1D)$ . The loss process of  $\text{O}(^1D)$  is determined by the quenching process (4) which is not affected by the changes of the concentrations of minor species in the atmosphere. The  $\text{O}_3$  concentration calculated with the new  $\text{O}(^1D)$  quantum yields is higher than that with the JPL-2000 recommendations throughout the stratosphere. It should be noted that the change in the  $\text{O}(^1D)$  concentration influences  $\text{O}_3$  abundance even though atmospheric concentration of  $\text{O}(^1D)$  atoms is much lower than  $\text{O}_3$  concentration, since the  $\text{O}(^1D)$  reactions (3) and (8) are the direct source for stratospheric  $\text{HO}_x$  and  $\text{NO}_x$  molecules which control the stratospheric radical partitioning and  $\text{O}_3$  abundance through catalytic reactions (Fig. 1). The calculated response of  $\text{O}_3$  concentration from these changes in the concentration of  $\text{HO}_x$  and  $\text{NO}_x$  is different between the upper, middle, and lower stratospheres because of the interdependence of the  $\text{O}_3$  loss catalytic cycles.

As shown in Figs. 5 and 6, the absolute change in the stratospheric  $\text{O}_3$  concentration is the largest at  $\sim 40\text{--}45$  km (increase up to  $\sim 2\%$ ). This results from effect of the suppression of  $\text{O}_3$  loss by the decrease of the  $\text{NO}_x$ ,  $\text{HO}_x$ , and  $\text{ClO}_x$  concentrations in their catalytic  $\text{O}_3$  loss cycles (Fig. 6). Figure 7 shows that total  $\text{O}_3$  loss rate, that is, the sum of the  $\text{O}_3$  loss rates in  $\text{NO}_x$ ,  $\text{HO}_x$ , and  $\text{ClO}_x$  catalytic cycles has a peak around 40 km. Changes in  $\text{O}_3$  loss rates in  $\text{NO}_x$ ,  $\text{HO}_x$ , and  $\text{ClO}_x$  catalytic cycles, which were calcu-

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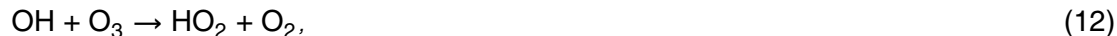
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lated from model runs with the new O(<sup>1</sup>D) quantum yields and with the JPL-2000 recommendations, were similar to changes in NO<sub>x</sub>, HO<sub>x</sub>, and ClO<sub>x</sub> concentrations which are shown in Fig. 6. Above this region, the contribution of the HO<sub>x</sub> cycle becomes predominant drastically as the altitude increases (Fig. 7). The HO<sub>x</sub> concentration in the upper stratosphere is decreased by the decrease of the OH formation through reaction (3) due to the smaller O(<sup>1</sup>D) quantum yield (Fig. 6). In the upper stratosphere, atomic O(<sup>3</sup>P) constitutes efficiently the following catalytic cycle in which the rate-limiting step in the cycle is reaction (12):



Therefore, the decrease in HO<sub>x</sub> concentration in the upper stratosphere caused by the smaller O(<sup>1</sup>D) quantum yields results in the O<sub>3</sub> concentration increase most effectively in this region. On the other hand, HO<sub>x</sub> concentration increases in the middle and lower stratosphere (Fig. 6). The NO<sub>x</sub> concentration is reduced by the decrease of the O(<sup>1</sup>D) formation via reaction (8). This reduction of the NO<sub>x</sub> concentration takes place throughout the stratosphere. The increase of HO<sub>x</sub> concentration in the middle and lower stratosphere may be attributed to the decrease of the rate of reaction (6) due to the smaller concentration of NO<sub>x</sub>. Since the contribution of three-body reaction (6) becomes more significant at lower stratospheric altitudes, HO<sub>x</sub> increases in the lower stratosphere as shown in Fig. 6.

ClO<sub>x</sub> concentration also decreases in the upper-middle stratosphere with the smaller O(<sup>1</sup>D) quantum yields, and a little increases in the lower stratosphere. The behavior of ClO<sub>x</sub> concentration change is similar to that of HO<sub>x</sub> concentration. The chlorine reservoir compound HCl is probably activated to ClO<sub>x</sub> by reaction (7), that is, the reaction between OH and HCl (Fig. 1). The decreased OH production rate due to the smaller O(<sup>1</sup>D) quantum yield results in the smaller ClO<sub>x</sub> concentration. In the lower stratosphere, the decrease of the third body reaction (9) with smaller NO<sub>x</sub> concentra-

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tion may lead to the increase of  $\text{ClO}_x$ .  $\text{ClO}_x$  cycle is important especially around 45 km and accounts for about  $\sim 35\%$  of the total  $\text{O}_3$  loss rate in this region (Fig. 7).

As shown in Fig. 6,  $\text{NO}_x$  concentration is decreased throughout the stratosphere by the smaller  $\text{O}(^1D)$  quantum yields, while the enhancement of  $\text{O}_3$  takes place around 20–25 km (up to  $\sim 1\%$ ), but slightly less around 30 km. In the middle stratosphere, the  $\text{NO}_x$  catalytic cycle has the largest effect on the  $\text{O}_3$  reduction (Fig. 7). The enhancements of  $\text{O}_3$  concentration around 20–25 km with the new  $\text{O}(^1D)$  quantum yields should be attributed to the decrease of  $\text{NO}_x$  catalytic  $\text{O}_3$  loss.

In the upper stratosphere and mesosphere, a number of models cause an under-prediction of  $\text{O}_3$  concentrations at 40–50 km altitude compared to observations, with magnitude of the discrepancy increasing with altitude (Eluszkiewicz and Allen, 1993). This has been known as the “ozone deficit” problem. In the upper stratosphere, the chemical composition is determined by chemical processes that are faster than the relevant dynamical processes. Crutzen et al. (1995) and Grooß et al. (1999) have investigated the  $\text{O}_3$  budget in the upper stratosphere in comparison with observations and photochemical modeling. They have pointed out that the uncertainty in the model parameters is a large source of the discrepancy although improvement of the observation quality and updated the latest model parameters decreases a significant ozone deficit. Smith et al. (2001) estimated  $\text{O}_3$  uncertainties near 12% modeled in the middle and upper stratosphere, increasing in the lower stratosphere, from the JPL-2000 recommendations which significantly reduced several key reaction uncertainty values by laboratory measurements, that is, total catalytic photochemical uncertainty in model  $\text{O}_3$  compared with a previous modeling. The enhancement of  $\text{O}_3$  concentration in our chemical model calculations around 40–50 km altitude may contribute to precise assessment of the photochemical  $\text{O}_3$  budget including the “ozone deficit” problem.

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## 6. Conclusions

Consequences of the new data of  $O(^1D)$  quantum yields from  $O_3$  photolysis between 230 and 305 nm in the Hartley band region on the stratospheric chemistry are examined using a one-dimensional atmospheric model. Our sensitivity studies for mid-latitude in March indicate that the smaller  $O(^1D)$  quantum yields increase the  $O_3$  concentration throughout stratosphere via a decrease in the importance of  $NO_x$  concentration in the middle stratosphere and the  $HO_x$  in the upper stratosphere.

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**Table 1.** List of chemical species used in the one-dimensional dynamical-photochemical model calculations

Initially set by Brasseur et al. (1999)					
O <sub>3</sub>	H	OH	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	N
NO	NO <sub>2</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>4</sub>	HNO <sub>3</sub>	H <sub>2</sub> O
CH <sub>4</sub>	N <sub>2</sub> O	Cl	ClO	HOCl	ClONO <sub>2</sub>
HCl	CCl <sub>4</sub>	CFCl <sub>3</sub>	CF <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> Cl	CO
Calculated to be in steady state					
O( <sup>3</sup> P)	O( <sup>1</sup> D)	NO <sub>3</sub>	Cl <sub>2</sub>	Cl <sub>2</sub> O <sub>2</sub>	OCIO
HBr	Br	BrO	HOBr	BrONO <sub>2</sub>	CO <sub>2</sub>
H <sub>2</sub>	ClOO	CHClF <sub>2</sub>	CH <sub>3</sub> Br		

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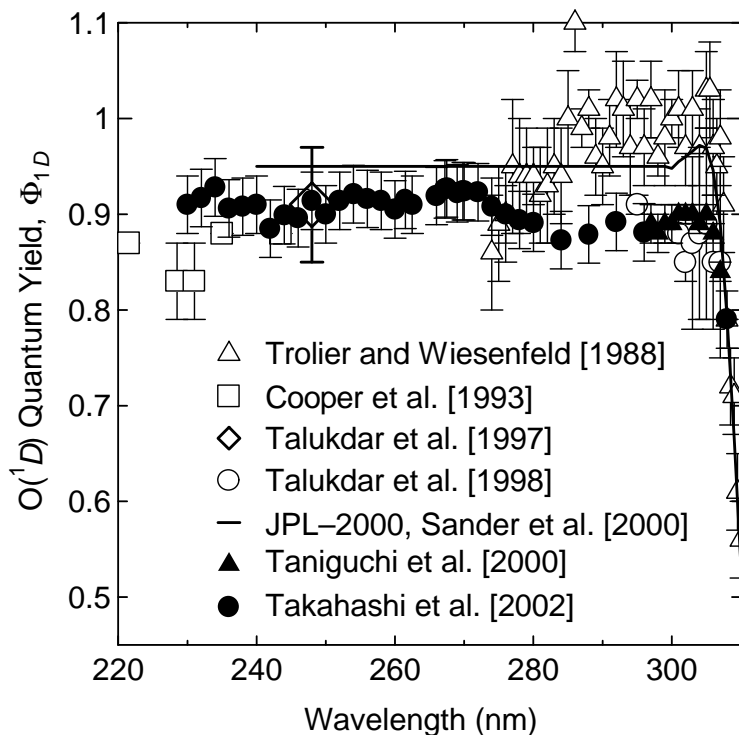




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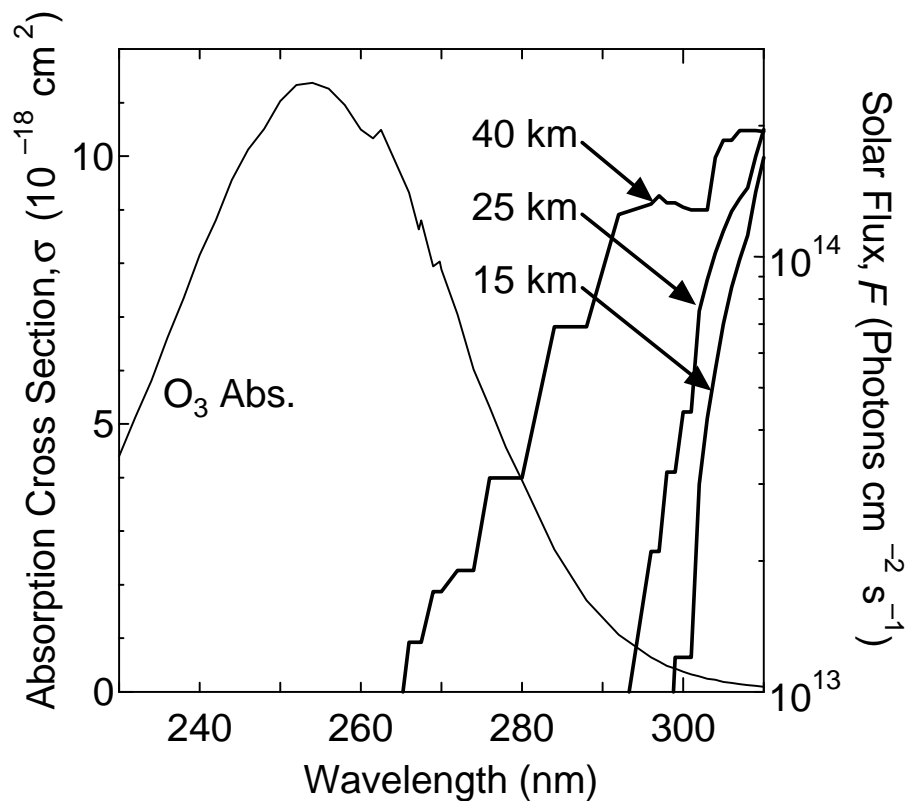


**Fig. 2.** The quantum yields for  $O(^1D)$  formation in the Hartley band photolysis of  $O_3$  obtained by Taniguchi et al. (2000) and Takahashi et al. (2002). For comparison, the yield values reported by other groups are also shown (Troler and Wiesenfeld, 1988; Cooper et al., 1993; Talukdar et al., 1997, 1998). Solid line indicates the yield values recommended by JPL-2000 evaluations for atmospheric modeling by NASA panel (Sander et al., 2000), which are constant (0.95) between 240 and 300 nm.

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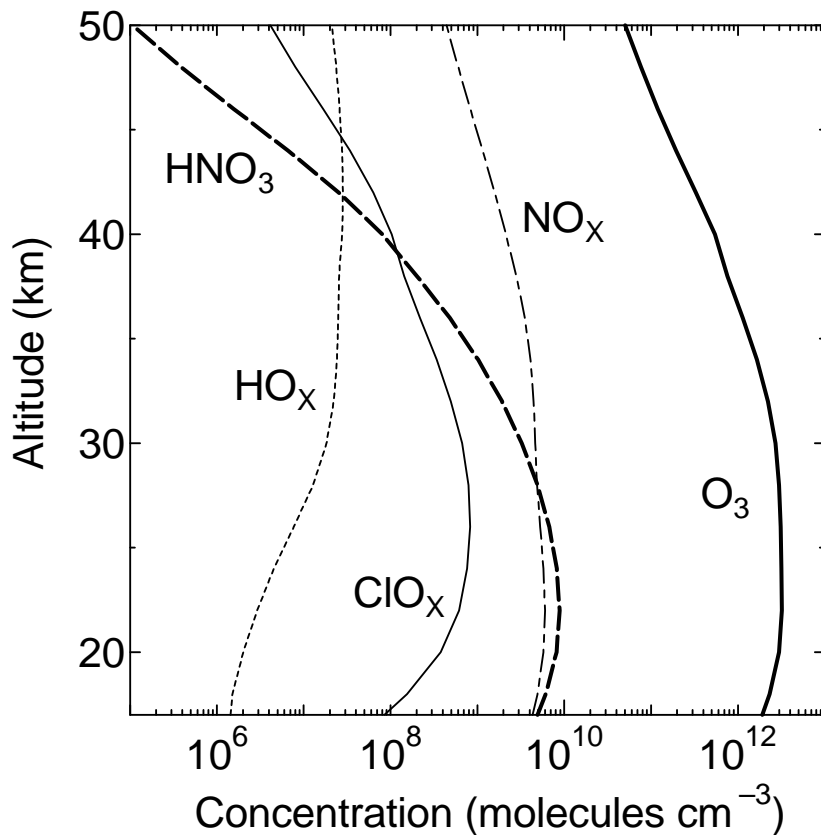
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**Fig. 3.** Ultraviolet absorption spectrum of  $O_3$  in the Hartley band at 263 K (Malicet et al., 1995) and actinic fluxes as a function of altitudes of 15, 25, and 40 km when the solar zenith angle is  $40^\circ$  (Finlayson-Pitts and Pitts, 1999).

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**Fig. 4.** Results of the one-dimensional chemical model calculations. Diurnally averaged vertical profiles of  $\text{NO}_x$ ,  $\text{HO}_x$ ,  $\text{ClO}_x$ ,  $\text{HNO}_3$  and  $\text{O}_3$  (dot-dash, dot, solid, thick dash, and thick solid lines, respectively) predicted for latitude of  $40^\circ$  in March using the  $\text{O}(^1D)$  quantum yield values measured by Taniguchi et al. (2000) and Takahashi et al. (2002).

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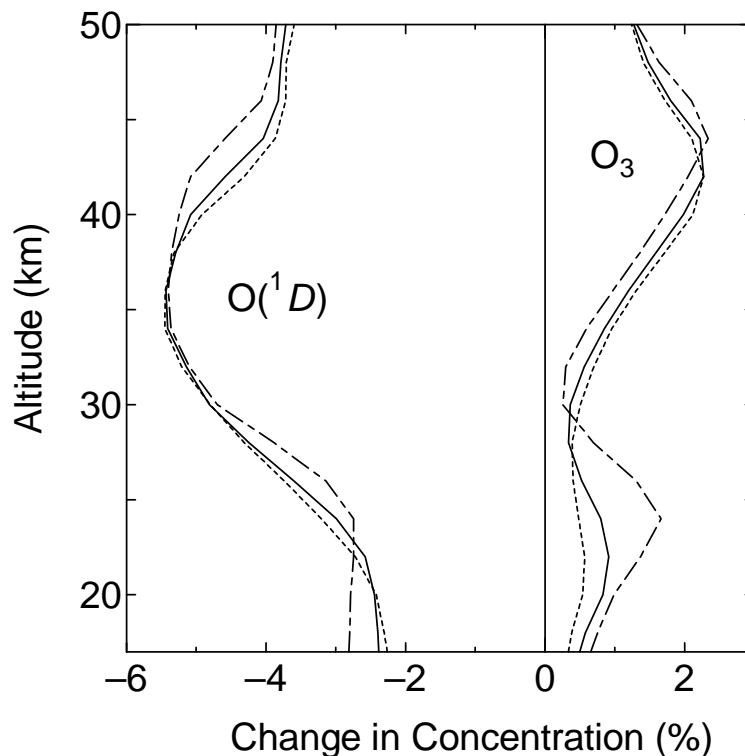
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**Fig. 5.** Results of the one-dimensional chemical model calculations. The percentage changes in diurnally averaged  $O(^1D)$  and  $O_3$  concentrations predicted for latitude of 20, 40, and 60° (dot, solid, and dot-dash lines, respectively) in March as a function of altitude using the  $O(^1D)$  quantum yield values measured by Taniguchi et al. (2000) and Takahashi et al. (2002), relative to those predicted using JPL-2000 recommendations for atmospheric modeling by NASA evaluation panel (Sander et al., 2000), that is,  $\delta O(^1D)$  and  $\delta O_3$  defined by Eq. (11) in the text.

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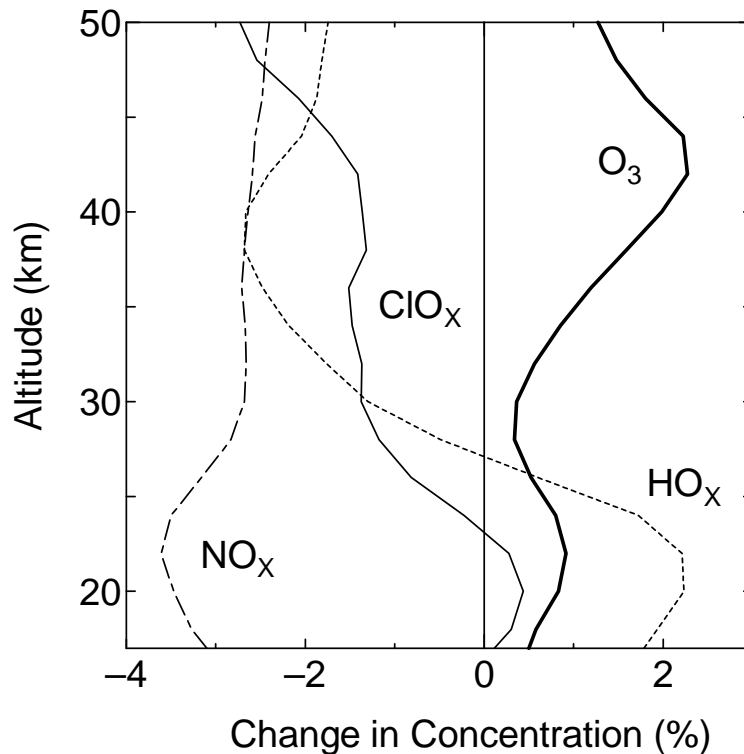
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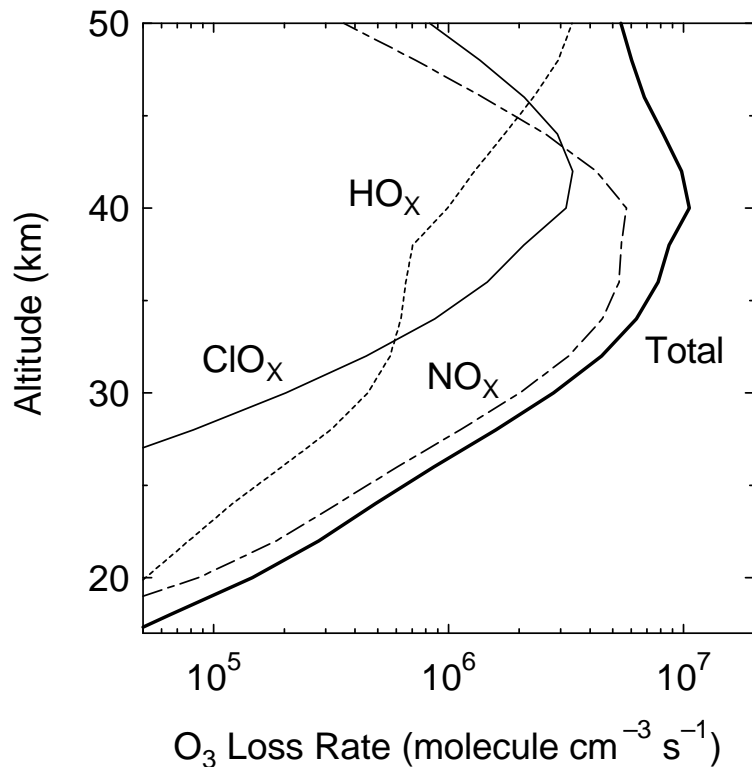


**Fig. 6.** Results of the one-dimensional chemical model calculations. The percentage changes in durnally averaged  $NO_x$ ,  $HO_x$ ,  $ClO_x$ , and  $O_3$  concentrations (dot-dash, dot, solid, and thick lines, respectively) predicted for latitude of  $40^\circ$  in March as a function of altitude using the  $O(^1D)$  quantum yield values measured by Taniguchi et al. (2000) and Takahashi et al. (2002), relative to those predicted using JPL-2000 recommendations for atmospheric modeling by NASA evaluation panel (Sander et al., 2000).

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**Fig. 7.** Results of the one-dimensional chemical model calculations. Diurnally averaged  $O_3$  loss rates due to  $NO_x$ ,  $HO_x$ , and  $ClO_x$  chemistry (dot-dash, dot, and solid lines, respectively) predicted for latitude of  $40^\circ$  in March using the  $O(^1D)$  quantum yield values measured by Taniguchi et al. (2000) and Takahashi et al. (2002). Thick line shows the total  $O_3$  loss rate which is the sum of the  $O_3$  loss rates in  $NO_x$ ,  $HO_x$ , and  $ClO_x$  catalytic cycles.

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