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## Tropospheric O<sub>3</sub> from photolysis of O<sub>2</sub>

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[1] Photolytic dissociation of molecular oxygen (O<sub>2</sub>) at wavelengths about 205 nm produces ozone (O<sub>3</sub>) in the upper tropical troposphere. In tropospheric chemistry models that ignore this process, the O<sub>3</sub> abundance above 14 km in the tropics (a.k.a. Tropopause Transition Layer) is underestimated by 5 to 20 ppb. Even for models including O<sub>2</sub> photolysis, uncertainty in the O<sub>2</sub> cross sections yields similar uncertainty in TTL O<sub>3</sub>. The related impact on global atmospheric chemistry is small, i.e., ±0.2% in CO and CH<sub>4</sub> budgets, but the change in the O<sub>3</sub> column, ±1.6 DU in the tropics, may be important in calculating heating rates and climate forcing. **Citation:** Prather, M. J. (2009), Tropospheric O<sub>3</sub> from photolysis of O<sub>2</sub>, *Geophys. Res. Lett.*, *36*, L03811, doi:10.1029/2008GL036851.

[2] A key process generating ozone (O<sub>3</sub>) in the lower stratosphere is photolytic dissociation of molecular oxygen (O<sub>2</sub>) at wavelengths between 195 nm (Schumann-Runge bands) and 215 nm (Herzberg continuum). Shortward of 195 nm sunlight is absorbed by the overhead column of O<sub>2</sub>, and longward of 215 nm, by that of O<sub>3</sub>. A small fraction of sunlight at wavelengths from 195 to 215 nm penetrates into the tropical troposphere (e.g., 0.25% reaches 16 km altitude), where the most important photolytic rate for atmospheric chemistry is that of O<sub>2</sub> (J-O<sub>2</sub>). The wavelength dependence of J-O<sub>2</sub> is shown in Figure 1a. Noontime photolysis of O<sub>2</sub> produces several ppb (nanomoles per mole) of O<sub>3</sub> per day, increasing the abundance above 14 km altitude by 5 to 20 ppb. The inclusion of O<sub>2</sub> photolysis from the Schumann-Runge bands through the Herzberg continuum is standard in stratospheric chemistry models [Horowitz *et al.*, 2003; Chipperfield, 2006; Lamarque *et al.*, 2008], but it is often neglected in tropospheric chemistry models where wavelengths less than 290 nm are assumed to be absorbed in the stratosphere [Bey *et al.*, 2001; Wild *et al.*, 2003; Ito *et al.*, 2007]. One photolysis program used in many tropospheric chemistry-transport models (CTMs) addressed these O<sub>2</sub> photolysis rates in the text, but not as part of the code [Wild *et al.*, 2000, pp. 249–250].

[3] Using a radiative transfer code, the JPL-2006 O<sub>2</sub> cross sections [Sander *et al.*, 2006; Yoshino *et al.*, 1988, Table 2], and updated solar fluxes [Hsu and Prather, 2009], we calculate the J-O<sub>2</sub> profile (see Figure 1b) for a tropical atmosphere and solar zenith angle of 15°. High-sun J-O<sub>2</sub>

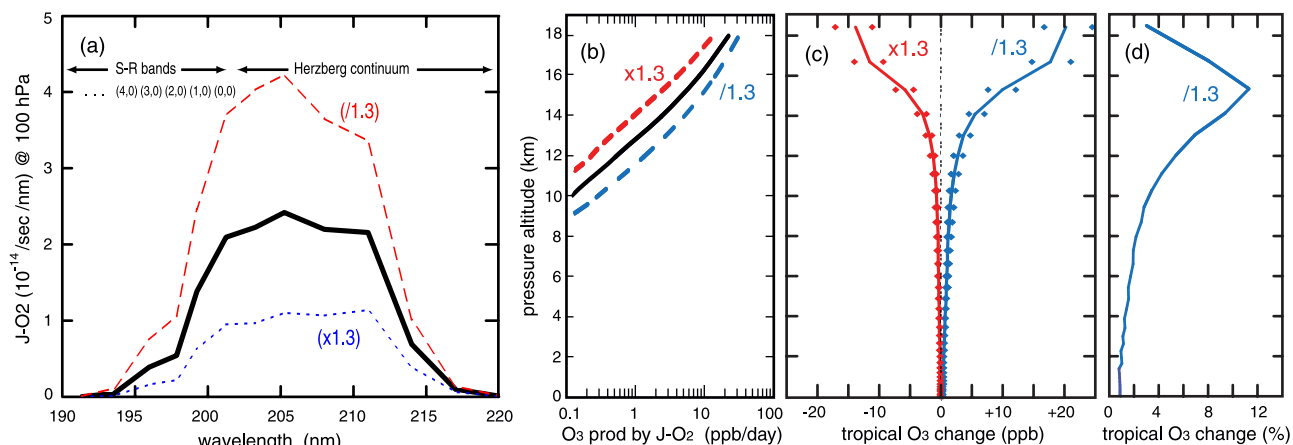
produces O<sub>3</sub> at an instantaneous rate of tens of ppb per day above 16 km in the troposphere, but is negligible, <0.1 ppb/day, below 10 km. The overhead O<sub>2</sub> column controls penetration of solar UV and near the tropopause has an optical depth of about 3 at 205 nm. Thus, solar UV in the upper troposphere is reduced by about 3% for every 1% increase in the O<sub>2</sub> cross section, resulting in the counterintuitive outcome of Figure 1b that reducing the O<sub>2</sub> cross section by a factor of 1.3 (labeled ‘/1.3’) increases tropospheric J-O<sub>2</sub> by about factor of 2, and vice versa for increasing (labeled ‘x1.3’). These bounding cases are slightly larger than the factor of 1.2 “reliability of the data” from the JPL-2006 assessment [Sander *et al.*, 2006], and provide a magnitude-estimate for those chemical models not including this process.

[4] The sensitivity of tropospheric O<sub>3</sub> to J-O<sub>2</sub> is evaluated with the UCI CTM using ECMWF forecast meteorology at T42L40 resolution [Wild *et al.*, 2003; Neu *et al.*, 2008], comparing a typical year (2005) using standard O<sub>2</sub> cross sections and the two bounding cases (‘x1.3’ and ‘/1.3’). Changes in the annual average tropical tropospheric O<sub>3</sub> profiles relative to the reference case are shown in Figure 1c, where symbols denote the range in monthly means. At some locations the troposphere reaches up to 18 km [e.g., Takashima and Shiotani, 2007]. In these calculations stratospheric chemistry is fixed (Linoz v2 of Hsu and Prather [2009]), and only the tropospheric chemistry considers the range in O<sub>2</sub> cross sections. The impact of the bounding cases is substantial and nearly symmetric: uncertainties in O<sub>3</sub> abundance in the upper tropical troposphere are as large as ±20 ppb and extend into the lower troposphere at ±1 ppb. The decrease in O<sub>2</sub> cross sections (‘/1.3’) provides an estimate of the error in tropospheric CTMs not including J-O<sub>2</sub>. The relative change in mean tropical O<sub>3</sub> for ‘/1.3’ peaks between 14 and 16 km at nearly 12% (Figure 1d), falling above because of the rapid increase in O<sub>3</sub> abundance near the tropopause.

[5] Tropospheric J-O<sub>2</sub> has greatest impact in the tropical (tropopause) transition layer (TTL), a region distinct from either the lower troposphere or the stratosphere [Highwood and Hoskins, 1998]. TTL O<sub>3</sub> controls photochemistry and heating rates that in turn control the fluxes of water, aerosols, and trace gases into the stratosphere [Marcy *et al.*, 2007; Gettelman and Birner, 2007; Gao *et al.*, 2008]. Accurate photochemical modeling is critical in deciphering the source of measured O<sub>3</sub> as being produced locally or transported from the stratosphere [Takashima and Shiotani, 2007].

[6] An integrative measure of J-O<sub>2</sub> in the troposphere is the change in the column of tropospheric O<sub>3</sub>: +1.6 DU

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**Figure 1.** (a) Photolysis rate of O<sub>2</sub> (/sec/nm) as a function of wavelength (nm) for a solar zenith angle of 15° at 100 hPa with clear sky in the tropics (238 DU overhead O<sub>3</sub> column). (b) O<sub>3</sub> production (ppb/day) from O<sub>2</sub> photolysis, as in Figure 1a, plotted as a function of pressure altitude ( $z^* = 16 \times \log_{10}[1000/p(\text{hPa})]$  km). Total O<sub>3</sub> column is 260 DU. These instantaneous rates are about six times larger than the 24-hour averages. Results show recommended O<sub>2</sub> cross sections (solid line), those increased (x1.3) and decreased (/1.3) by a factor of 1.3. (c) Change in tropical tropospheric O<sub>3</sub> (ppb) for increased/decreased O<sub>2</sub> cross sections. Solid line is annual zonal tropical mean profiles with the minimum and maximum range for the monthly means shown as symbols. (d) Relative change (%) in tropical O<sub>3</sub> for decreased O<sub>2</sub> cross sections (/1.3).

(milli-cm amagat) for ‘/1.3’, or about 6% of the tropical tropospheric burden. This difference comes largely from increases in the upper troposphere where O<sub>3</sub> is particularly effective as a greenhouse gas [Lacis *et al.*, 1990] and may affect heating rates. Failure to accurately include J-O<sub>2</sub> in climate models would give a systematic bias of order 0.03 W m<sup>-2</sup> that would vary with climate change according to TTL mixing. Global impacts on atmospheric chemistry are apparent but limited, because tropospheric chemical budgets for gases like carbon monoxide (CO) and methane (CH<sub>4</sub>) are dominated by reactions in the lower troposphere. With ‘/1.3’, additional O<sub>3</sub> in the upper tropics reduces NO<sub>x</sub>, thus reducing OH and increasing CO and other hydrocarbons in the TTL. On a global, annual average, CO abundances increase by 0.25%, driving OH down globally, and thus CH<sub>4</sub> loss by reaction with hydroxyl (OH) radicals decreases by 0.22% (i.e., CH<sub>4</sub> abundance would increase).

[7] The photochemical balance of O<sub>3</sub> in the upper tropical troposphere is highly sensitive to J-O<sub>2</sub>. To reduce modeling uncertainty to less than ±5 ppb, we require knowledge of O<sub>2</sub> cross sections to a factor of 1.1. UCI has corrected the omission of J-O<sub>2</sub> in its first-generation tropospheric photolysis module fast-J [Wild *et al.*, 2000] by incorporating stratospheric photolysis [Bian and Prather, 2002] and merging to the fast-JX module that includes optimization for tropospheric CTMs [e.g., Duncan *et al.*, 2008] (see <http://www.ess.uci.edu/~prather/fastJX.html> and auxiliary material).<sup>1</sup>

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2008GL036851.

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