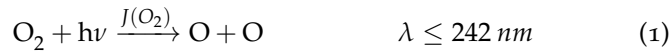# 1-D Photolysis Model

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Introduction

The ozone layer plays a key role in blocking harmful ultra-violet radiation from reaching the Earth's surface. Oxygen concentrations in the atmosphere have varied considerably during Earth's history. This has impacts on ozone through the Chapman reactions

$$O_2 + h\nu \xrightarrow{J(O_2)} O + O \qquad \lambda \leq 242\,nm \qquad (1)$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \qquad (2)$$

$$O_3 + h\nu \xrightarrow{J(O_3)} O_2 + O \qquad \lambda \leq 1180\,nm \qquad (3)$$

$$O_3 + O \xrightarrow{k_3} 2\,O_2 \qquad (4)$$

primarily in the stratosphere where there is sufficient shortwave radiation to photolyse O_2. In the steady state, the concentration of ozone is given by

$$[O_3] = \sqrt{\frac{J(O_2)\,k_3[M]}{J(O_3)\,k_4}}\,[O_2] \qquad (5)$$

which suggests that increasing O_2 leads to a corresponding increase in O_3, however the reaction rates aren't independent of O_2. Numerical simulations are required: the code for a simple 1-D photolysis model which includes Chapman chemistry can be found at `https://github.com/dcw32/oxygen`.

Rates of Reaction

Photolysis rates vary by altitude z according to the equation

$$J_X(z) = \int q_X(\lambda)\,\sigma_X(\lambda)\,I(z,\lambda)\,d\lambda \qquad (6)$$

where q_X is the quantum yield for the photolysis of X, σ_X is the absorption cross section[1] of X and I is intensity of radiation: all at wavelenth λ. I is given by

$$I(z,\lambda) = I(\infty,\lambda)e^{-\delta(z,\lambda)} \qquad (7)$$

[1] The absorption cross section depends not only on λ but is also temperature and pressure dependent, for instance O_2 can form the O_4 dimer.

where $I(\infty, \lambda)$ is the wavelength-dependent intensity of incoming solar radiation at the top of the atmosphere and δ is the optical depth

$$\delta(z, \lambda) = \int_z^\infty \left(\sigma_{O_2}(\lambda)\,[O_2](z') + \sigma_{O_3}(\lambda)\,[O_3](z')\right) dz' \tag{8}$$

which assumes that the majority of the absorption of radiation is due to O_2 and O_3. As oxygen can be considered fully mixed in the atmosphere $[O_2]$ can be approximated as

$$[O_2](z) = [M]_0 \exp(-z/H) \tag{9}$$

where H is some scale height, often taken to be 7 km, and $[M]_0$ is the surface gas concentration. As ozone is variable throughout the atmosphere the integral has to be determined numerically. When calculating the ozone column from first principles, such as using Equation 5, it is necessary to start at the top layer of the atmosphere as δ varies according to the ozone column.

The rates of gas phase reactions in the atmosphere vary with temperature. The rate of reaction k_4 is implemented in the code as

$$k_4(T) = 1 \times 10^{-11} \exp(-2100/T) \, \text{cm}^3 \, \text{s}^{-1} \tag{10}$$

exhibiting an Arrhenius temperature dependence. By contrast rate of reaction k_3 is implemented in the code as

$$k_3(T) = 6 \times 10^{-34} \, (300/T)^2 \, \text{cm}^6 \, \text{s}^{-1} \tag{11}$$

which decreases with temperature[2].

[2] This non-Arrhenius temperature dependence is due to the formation of a reactive intermediate between O_2 and O which is longer lived at low temperatures.