

Chemical ozone formation- and destruction pathways in Mars' atmosphere

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Abstract

Ozone is a species of central interest on the Mars, since it has a significant impact on the photochemical stability of the atmosphere and is furthermore a suitably observable species. The abundance of ozone is controlled by chemical pathways. In this contribution we apply a unique algorithm, called the Pathway Analysis Program - PAP to the results of the JPL/Caltech photochemical column model of the Martian atmosphere to investigate the chemical pathways producing and consuming ozone as functions of height.

1. Introduction

On Mars, ozone is a trace gas of major significance. It has been observed not only in the infrared from ground-based telescopes e.g. [1, 2, 3] but also in the ultraviolet by space telescopes e.g. [4] and orbiters e.g. [5, 6, 7]. Additionally there exist also some in situ measurements e.g. [8, 9, 10].

Ozone is related to the photochemical stability of the main atmospheric constituent, CO_2 in two ways. Firstly its abundance is anticorrelated to the abundance of HO_x (see [11, 12]), which catalytically destroys ozone. Note that HO_x is also the family including the major catalyst species acting in chemical CO_2 formation pathways e.g. [13, 14, 16, 17]. Secondly, it can be directly involved in those pathways either by providing atomic oxygen via photolysis or by acting as catalyst species [16, 17, 18].

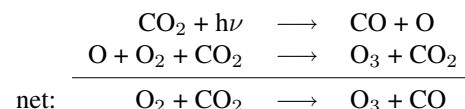
From both, modeling and observations, it has been shown, that the concentration of ozone varies with altitude. The Martian atmosphere exhibits two ozone layers, one near the surface and the other one around 40 km altitude. It is therefore desirable to identify the chemical pathways acting at different heights and to quantify their efficiency by calculating the rates of different pathways.

2. Method

Finding chemical pathways in complex reaction networks is generally a challenging task. In this study, we use an automated computer algorithm, the Pathway Analysis Program (PAP, [19]) and apply it to the results of the updated JPL/Caltech photochemical column model of the Martian atmosphere which is based on [15] in order to address this problem. Rates of individual ozone production and destruction pathways are computed for different altitudes, by analyzing each vertical layer from the surface up to 80 km of the column model separately with the PAP.

3. Results and Conclusions

In this contribution we identify all dominant pathways responsible for ozone production and consumption. Furthermore, we determine their efficiency by calculating altitude dependent pathway rates. Our results suggest, that in the lower altitudes ozone is mainly produced by a Chapman-like mechanism involving CO_2



In the upper ozone layer ($40 \text{ km} < z < 60 \text{ km}$), downwards-diffusion by atomic oxygen plays the dominant role for ozone production. Ozone is mainly destroyed by photolysis, leading to the conversion of CO to CO_2 and/or O_2 via $\text{O}_x\text{-HO}_x$ -pathways in all heights in the considered altitude range.

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References

- [1] Espenak, F., Mumma, M.J., Kostiuk, T., Zipoy, D.: Ground-based infrared measurements of the global distribution of ozone in the atmosphere of Mars, *Icarus*, Vol. 92, 252–262, 1991.
- [2] Fast, K., Kostiuk, T., Espenak, F. et al.: Ozone abundance on Mars from infrared heterodyne spectra. I. Acquisition, retrieval, and anticorrelation with water vapor, *Icarus*, Vol. 181, 419–431, 2006.
- [3] Fast, K.E., Kostiuk, T., Lefèvre, F. et al.: Comparison of HIPWAC and Mars Express SPICAM observations of ozone on Mars 2006-2008 and variation from 1993 IRHS observations, *Icarus*, Vol. 203, 20–27, 2009.
- [4] Clancy, R.T., Wolff, M.J., James, P.B. et al.: Mars ozone measurements near the 1995 aphelion: Hubble space telescope ultraviolet spectroscopy with the faint object spectrograph, *Journal of Geophysical Research*, Vol. 101, 12777–12784, 1996.
- [5] Barth, C.A., Hord, C.W., Steward, A.I. et al.: Mariner 9 Ultraviolet Spectrometer Experiment: Seasonal Variation of Ozone on Mars, *Science*, Vol. 179, 795–796, 1973.
- [6] Lane, A.L., Barth, C.A., Hord, C.W., Stewart, A.I.: Mariner 9 Ultraviolet Spectrometer Experiment: Observations of Ozone on Mars (A. 5.4), *Icarus*, Vol. 18, 102, 1973.
- [7] Wehrbein, W.M., Hord, C.W. Barth, C.A.: Mariner 9 ultraviolet spectrometer experiment - Vertical distribution of ozone on Mars, *Icarus*, Vol. 38, 288–299, 1979.
- [8] Krasnopol'sky, V.A. and Parshev, V.A.: Ozone and photochemistry of the Martian lower atmosphere, *Planetary and Space Science*, Vol. 27, 113–120, 1979.
- [9] Blamont, J.E. and Chassefière, E.: First detection of ozone in the middle atmosphere of Mars from solar occultation measurements, *Icarus*, Vol. 104, 324–336, 1993.
- [10] Owen, T., Biemann, K., Biller, J.E., et al.: The composition of the atmosphere at the surface of Mars, *Journal of Geophysical Research*, Vol. 82, 4635–4639, 1977.
- [11] Clancy, R.T. and Nair, N.: Annual (perihelion-aphelion) cycles in the photochemical behavior of the global Mars atmosphere, *Journal of Geophysical Research*, Vol. 101(E5), 12785–12790, 1996.
- [12] Lefèvre, F., Lebonnois, S., Montmessin, F., Forget, F.: Three-dimensional modeling of ozone on Mars, *Journal of Geophysical Research (Planets)*, Vol. 109(E18), 7004, 2004.
- [13] McElroy, M.B. and Donahue, T.M.: Stability of the Martian atmosphere, *Science*, Vol. 177, 986–988, 1972.
- [14] Parkinson, T.M. and Hunten, D.M.: Spectroscopy and aeronomy of O₂ on Mars, *Journal of Atmospheric Science*, Vol. 29, 1380–1390, 1972.
- [15] Nair, H., Allen, M., Anbar, A.D., Yung, Y.L.: A Photochemical Model of the Martian Atmosphere, *Icarus*, 111, 124–150, 1994.
- [16] Stock, J.W., Boxe, C.S., Lehmann, R. et al.: Chemical pathway analysis of the Martian atmosphere: CO₂-formation pathways, *Icarus*, Vol. 219, 13–24, 2012.
- [17] Stock, J.W., Grenfell, J.L., Lehmann, R., et al.: Chemical pathway analysis of the Martian atmosphere: The CO₂-stability problem, *Planetary and Space Science*, Vol. 68, 18–24, 2012.
- [18] Yung, Y.L. and DeMore, W.B.: *Photochemistry of Planetary Atmospheres*, Oxford University Press, 1999.
- [19] Lehmann, R.: An Algorithm for the Determination of All Significant Pathways in Chemical Reaction Systems, *Journal of Atmospheric Chemistry*, Vol. 47, 45–78, 2004.