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ScienceDirect
Advances in Space Research 47 (2011) 1937–1948
ADVANCES IN SPACE RESEARCH
(a COSPAR publication)
www.elsevier.com/locate/asr

Ozone trends in the mid-latitude stratopause region based on microwave measurements at Lindau (51.66° N, 10.13° E), the ozone reference model, and model calculations

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Received 22 September 2010; received in revised form 21 December 2010; accepted 14 January 2011
Available online 22 January 2011

Abstract

We compared 8 years of ozone measurements taken at Lindau (51.66° N, 10.13° E) at altitudes between 40 and 60 km using the microwave technique with the CIRA ozone reference model that was established 20 years ago (Keating et al., 1990). We observed a remarkable decrease in ozone density in the stratopause region (i.e., an altitude of 50 km), but the decrease in ozone density in the middle mesosphere (i.e., up to 60 km in altitude) is slight. Likewise, we observed only a moderate decrease in the atmospheric region below the stratopause. Other studies have found the strongest ozone decrease at 40 km and a more moderate decrease at 50 km, which is somewhat in contradiction to our results. This decrease in ozone density also strongly depends on the season. Similar results showed model calculations using the GCM COMMA-IAP when considering the increase in methane. In the lower mesosphere/stratopause region, the strongest impact on the concentration of odd oxygen (i.e., O_3 and O) was observed due to a catalytic cycle that destroys odd oxygen, including atomic oxygen and hydrogen radicals. The hydrogen radicals mainly result from an increase in water vapor with the growing anthropogenic release of methane. The finding suggesting that the stratopause region is apparently attacked more strongly by the water vapor increase has been interpreted in terms of the action of this catalytic cycle, which is most effective near the stratopause and amplified by a positive feedback between the ozone column density and the ozone dissociation rate, thereby chemically influencing the ozone density. However, the rising carbon dioxide concentration cools the middle atmosphere, thereby damping the ozone decline by hydrogen radicals.

Keywords: Ozone trend; Reference model; Microwave measurements; Stratopause; Catalytic cycles; Hydrogen radicals

1. Introduction

The first sign of a reduction in the ozone concentration in an investigation of the decline in the ozone layer due to the anthropogenic impact of ClO_x and NO_x was found via Umkehr measurements in the upper stratosphere (Reinsel et al., 1984, 1987). However, in the stratopause region, the influence of these compounds is extremely limited because the ozone chemistry in this domain is almost purely based on an odd oxygen-odd hydrogen (i.e., O, O_3 – H, OH, and HO_2) chemistry (Crutzen et al., 1995). Hydrogen radicals mainly result from water vapor. In the past, the concentration of the hydrogen radicals has increased due to the growing anthropogenic release of methane that was chiefly oxidized to water vapor in the stratosphere. However, the water vapor concentration of the middle atmosphere is also impacted by middle atmospheric dynamics, particularly by the Brewer–Dobson circulation (Foster and Shine, 1999; Randel et al., 2006; Scherer et al., 2008) and the planetary wave activity (Bittner et al., 2000; Höppner and Bittner, 2007). Consequently, one given year does not offer a representative sample for a trend that has lasted more than 20 years. The Ozone Reference Model (ORM) of Keating et al. (1990) is based on a very limited number of years, namely 1982 and 1983, which are years of mean solar

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doi:10.1016/j.asr.2011.01.010

activity. Also the eight year mean of the ozone measurements at Lindau correspond to solar mean conditions.

Keating et al. (1996) improved their model by extending the period of analyzed data. Also Wang et al. (1999) inferred a reference model for middle atmosphere ozone (from 100 to 0.1 hPa) from 80° N to 80° S on the basis of satellite data that considered observations from Stratospheric Aerosol and Gas Experiment (SAGE), the Halogen Occultation Experiment (HALOE), and the Microwave Limb Sounder (MLS) for the period from April 1992 to March 1993. They called their model “a reference model in 1992–1993,” indicating that the reference model will change when considering other years.

The ozone decline is a result of water vapor concentration growth and is somewhat dampened by the decreasing temperatures in the atmosphere due to an increase in CO_2, which cools this domain (e.g., Hauchecorne et al., 1991; Bremer, 1997; Keating et al., 2000; Bremer and Berger, 2002). The ozone formation sensitively depends on temperature. Specifically, ozone concentration increases as the temperature decreases.

The paper is organized as follows: In Section 2, we introduce the catalytic cycles that destroy the odd oxygen, thereby decreasing its concentration in the stratopause region. In Section 3, we present the ozone measurements that were gathered at Lindau using the microwave technique. Section 4 deals with the 3D-model calculations and compares them with the observations. In Section 5, the results will be discussed in terms of anthropogenic changes in the middle atmosphere, and Section 6 gives a brief summary of the entire work.

2. Ozone chemistry of the stratopause region

The ozone production by the photolysis of molecular oxygen is essentially balanced by four odd oxygen destructing schemes. The first process is the Chapman reaction:

$$O_3 + O \rightarrow 2O_2 \tag{1}$$

This process itself does not depend on the anthropogenic changes in the atmosphere. Atomic oxygen is mainly formed by the dissociation of ozone $O_3 + h\nu \rightarrow O_2 + O(1D)$, whereas the net production results from the dissociation of molecular oxygen (O_2). Excited atomic oxygen $O(^1D)$ is quickly quenched by collisions with air particles. In the first approximation, its equilibrium concentration is given by $[O(^1D)] = J_{O_3}[O_3]/\gamma[M]$ with J_{O_3} representing the dissociation rate of ozone, γ representing the quenching rate, and [M] representing the air concentration. The reaction rate of reaction (1) is highly temperature-dependent and increases with temperature.

The second reaction scheme reads as follows:

$$\begin{aligned} &OH + O \rightarrow H + O_2\\ &H + O_2 + M \rightarrow HO_2 + M\\ &HO_2 + O \rightarrow OH + O_2\\ &\text{net}: \quad O + O \rightarrow O_2 \end{aligned} \tag{2}$$

This reaction scheme depends on the concentration of the hydrogen radicals, i.e., H, OH, and HO_2, and the concentration of the atomic oxygen resulting from the photolysis of ozone. The hydrogen radicals stem mainly from water vapor, i.e., from its photolysis and, to a minor extent, from its oxidation by $O(^1D)$, which is represented in the following formula: $H_2O + O(1D) \rightarrow OH + OH$. An additional small amount results from the decomposition of methane and molecular hydrogen. A comparison of the reaction rates reveals that depending on temperature, the rates of O reacting with the hydrogen radicals are about four orders in magnitude larger than the rate for the reaction of O with ozone. Consequently, the first process becomes comparable with the second cycle when the ozone concentration is four orders in magnitude larger than, e.g., the hydroxyl concentration (OH). This may happen approximately below the stratopause.The third reaction scheme is given by:

$$\begin{aligned} &O_3 + OH \rightarrow HO_2 + O_2\\ &HO_2 + O \rightarrow OH + O_2\\ &\text{net}: \quad O_3 + O \rightarrow 2O_2 \end{aligned} \tag{3}$$

The reaction rate of the reaction of ozone with hydroxyl is comparably small (i.e., about three orders in magnitude smaller than that of atomic oxygen with hydroxyl and one order larger than that of ozone with atomic oxygen); thus, this reaction does not play a large role in the mesosphere. The second reaction is the same as one of the reaction involved in the previously detailed cycle. Atomic hydrogen is widely removed in the lower mesosphere by the strong three-body reaction, i.e., $H + O_2 + M \rightarrow HO_2 + M$, introduced in the second scheme, which depends quadratically on the air density. It forms peroxyhydrogen (HO_2), thereby making a fourth cycle of minor importance in the lower mesosphere due to the small content of atomic hydrogen available. Note that the current atomic hydrogen is mainly formed by the reaction $OH + O \rightarrow H + O_2$

$$\begin{aligned} &O_3 + H \rightarrow OH + O_2\\ &OH + O \rightarrow H + O_2\\ &\text{net}: \quad O_3 + O \rightarrow 2O_2 \end{aligned} \tag{4}$$

However, this cycle is dominant in the middle mesosphere due to the decreasing air density. Both the second and third cycles would occur at the same rate only if the O_3 concentration becomes three orders in magnitude larger than the O concentration. This may happen in the middle stratosphere but not in the stratopause region.

When comparing all cycles, the second cycle and then the first reaction are the most important in the stratopause, followed by the third and then the fourth cycle. Ozone decreases with increasing hydrogen radical concentration. However, the hydrogen radical concentration does not linearly increase as the water vapor mixing ratio increases because radical loss depends on the square of its concentration ($[OH] \times [HO_2]$), which slows down the effect with rising hydrogen radical concentration. In other words, as the