SMILES measurements of diurnal variations of hydroperoxyl radical (HO$_2$) in the stratosphere and mesosphere

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1 Introduction

HO$_2$ radical is among the most important oxidants for atmospheric chemical compositions in the upper atmosphere. The accurate measurement of HO$_2$ turned out to be an extremely difficult problem because HO$_2$ volume mixing ratios are about a few parts per billion by volume. No significant measurement was reported so far to evaluate the atmospheric chemistry of HO$_2$ such as its diurnal variations and behaviors in stratosphere and mesosphere.

In this study, we report the first wide altitude range observations from stratospheric to mesospheric HO$_2$ diurnal variations, the measurements of which were previously considered to be difficult, by Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES). We discuss hydrogen chemistry in the stratosphere and mesosphere.

SMILES is a part of Japanese Experiment Module (JEM) onboard International Space Station (ISS).

2 Dataset and Analysis of SMILES HO$_2$ measurements

ISS which has SMILES platform orbits at an altitude of 320-340 km above the surface and completes a single earth orbit in about 90 minutes. SMILES observed about 1630 points per day over the Earth during September 2009-April 2010, and produce a global map everyday for each composition. The latitudinal range of the observation covers from 65° N to 38° S.

SMILES detects thermal emission from chemical substances contained in the atmosphere and obtains the emission signal from atmospheric compositions at the several height in the atmosphere. HO$_2$ transition frequency is 649.70 GHz.

We have used HO$_2$ data from SMILES NICT products. We selected the data into three parts of latitude. These parts are equator (20° N-20° S), mid-latitude (20° N-50° N) and north polar (50° N-65° N), respectively. And we selected HO$_2$ vertical profiles at 20-95 km at night and in the daytime and HO$_2$ diurnal variations as a function of solar zenith angle (SZA) at 10° intervals in the stratosphere (29.0-49.0 km) and mesosphere (53.0-74.5 km), in each region of latitude.

3 Results and Discussions

HO$_2$ vertical profiles at 20-95 km are obtained. HO$_2$ volume mixing ratios generally increase with the altitude above 20 km and the appearance of the maximum (peak) volume mixing ratio in the profile is evident in the mesosphere, near 79.5 km at about 3ppbv at night and near 74.5 km at about 5.5ppbv in the daytime. We confirmed that the altitude of daytime peak in the shape of HO$_2$ profiles is lower than that of nighttime peak in all parts of latitude.

The diurnal variation of HO$_2$ through in the stratosphere and mesosphere was obtained for the first time (Figure 1). HO$_2$ volume mixing ratios at the all altitude are enhanced during the daytime due to photochemical reaction. The largest source of HOx (H + OH + HO$_2$) radicals in the stratosphere are provided from reaction O($^1$D) atoms, which are generated predominantly from O$_3$ photolysis, with H$_2$O.

The increase of HO$_2$ mixing ratios in the stratosphere with altitude can largely be attributed to an increased formation rate due to the large increase in the abundance of O($^1$D) at high altitude in the stratosphere. On the other hand, the production processes for mesospheric HOx during the daytime involve the photodissociation reaction of water vapor, which plays an important role in HO$_2$ production additionally in the mesosphere.

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Figure 1. HO₂ diurnal variations from SMILES observations for equatorial region in the stratosphere (left panel) and mesosphere (right panel) at the altitude from 29.0 km up to 74.5 km.