A-10 Researches on Elucidating Mechanisms of Ozone Layer Variations Using Satellite Data

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1. Introduction

After the discovery of the ozone hole in the Antarctica[1], several studies have been conducted in order to study the chemical/physical mechanisms of ozone depletion[2]. As a result, it was revealed that stratospheric ozone depletion is the result of catalytic chemistry involving man-made chlorofluorocarbons which is most evident in each austral spring in Antarctica, where about half of the total ozone column is depleted each September, forming the Antarctic ozone hole. Measurements of large amounts of ClO, a key ozone destruction catalyst, are among the fingerprints showing that human releases of chlorofluorocarbons are the primary cause of this change[3]. Enhanced ozone depletion in the Antarctic and Arctic regions is linked to heterogeneous chlorine chemistry that occurs on the surfaces of polar stratospheric clouds (PSCs) at cold temperature. As human use of chlorofluorocarbons continues to decrease, these changes throughout the ozone layer are expected to gradually reverse during the twenty-first century. However, comprehensive and quantitative understanding of the ozone-depletion mechanisms including the characterization of the PSCs has not yet been done.

2. Objectives

In order to contribute to the global monitoring of the ozone layer, the Ministry of the Environment decided to develop and launch a satellite sensor called the Improved Limb Atmospheric Spectrometer (ILAS). ILAS onboard the Advanced Earth Observing Satellite (ADEOS) was successfully launched on 17 August 1996, and made continuous measurement of ozone and its related gas species from November 1996 until June 1997. The purpose of this study is to contribute the further understanding of the chemical/physical mechanisms of the ozone depletion in the stratosphere. In order to achieve the purpose, we will conduct the study with six sub-themes as follows: 1) Research on improving retrieval algorithms for vertical profiles of trace gas species from remotely sensed spectral data from satellite sensors. 2) Research on the precise measurements of trace-gas spectra for the atmospheric remote sensing. 2-1) Experimental study on the temperature-dependence of absorption line parameters. 2-2) Study on experimental determination and reliability evaluation of absorption line parameters. 3) Evaluation of ground-based measurement and PSC observation data for validating satellite data. 4)

Research on scientific analysis and data evaluation using satellite data. 5) A quantification of chemical ozone destruction using a 3-dimensional chemical transport model. 6) Research on the polar stratospheric chemistry using a photochemical Lagrangian model.

3. Results

3.1. (Sub-theme 1) Research on improving retrieval algorithms for vertical profiles of trace gas species from remotely sensed spectral data from satellite sensors

Ministry of the Environment has developed atmospheric satellite sensors ILAS, ILAS-II. Another sensor SOFIS was planned to be developed in future. The research sub-theme 1 aims to develop useful data processing algorithms to estimate vertical profiles of minor constituents in the atmosphere from satellite remote sensing spectral data.

By using of the ILAS & ILAS-II observational data, and the ILAS-II & SOFIS synthetic data, the following items have been investigated. (1) Improvements and validation of the ILAS data retrieval algorithm, (2) Chlorine Nitrate retrieval method from the ILAS & ILAS-II data, (3) Development of a new micro-window selection method for SOFIS by considering clouds and aerosol effects, (4) Combined utilization of the several satellite sensor data which has an infrared spectrometer to retrieve a new physical parameter.

The ILAS Version 5.20 level 2 data products has been released to general users from January 2002 as a result of the algorithm refinement and data validation. As for Chlorine Nitrate ($ClONO_2$) retrieval from ILAS & ILAS-II data, it has been confirmed that the $ClONO_2$ can be retrieved with other species by applying a suitable algorithm, which has been established as the ILAS version 6.00 algorithm. A new method for micro-window selection method has been developed. This method selects several moderately-wide windows called "medium windows", which are useful under the situation of the aerosol effects on the infrared region. As a research for combined sensor data usage, three dimensional distribution feature of ozone have been derived by combining two types of ozone data observed by ILAS and IMG which provide longitudinal and latitudinal ozone cross section, respectively. These results showed that synergy datasets of various types of sensors are very useful to make clear the distribution feature of gaseous constituents in the atmosphere.

3.2. (Sub-theme 2) Research on the precise measurements of trace-gas spectra for the atmospheric remote sensing

3.2.1. (Sub-sub-theme 2-1) Experimental study on the temperature dependence of the absorption line parameters

The objective of this study is to determine the accurate absorption line parameters, such as the line position, the line strength, the half-width, and their temperature dependence of trace gases required in the data analysis of ILAS-II through the laboratory measurements. The main targets of experiments are the absorption bands of N_2O, CO_2, and CH_4 in the spectral region of Ch.2 which is newly installed in ILAS-II.

All the spectra of N_2O, CO_2, and CH_4, which were obtained at room temperature, were re-analyzed to improve the accuracies and precisions of the line strengths and half-widths. The revised values were reported for five bands (the ν_3, $\nu_1+2\nu_2$, and $2\nu_1$ bands of N_2O; the ν_3 band of CO_2; the ν_3 band of CH_4).

<N_2O>

The line strengths and the squared transition dipole moments of the ν_3 and $2\nu_1$ bands of

N_2O were determined at 240K and 180K. The values obtained at low temperatures agreed with the values obtained at room temperature within the experimental errors. The vibrational transition dipole moments for these bands were in agreement with the latest HITRAN database (HITRAN2K). N_2- and O_2-broadened half-widths were determined for the ν_3 and $2\nu_1$ bands of N_2O at 240K and 180K. Using the N_2- and O_2-broadened half-widths, the air-broadened half-widths were calculated. The temperature dependent exponents of the air-broadened half-widths were close to the result of the recent high-resolution experiment.

<CO_2>

The line strengths and the squared transition dipole moments of the ν_3, $\nu_1+\nu_3$, and $2\nu_2+\nu_3$ bands of CO_2 were determined at 240K and 180K. The vibrational transition dipole moments of these bands in this study agreed with the values of HITRAN2K within the experimental errors. The temperature dependent exponents of the air-broadened half-widths of the ν_3 band of CO_2 were in good agreement with the HITRAN2K values.

<CH_4>

The experimental spectra measured at low temperatures agreed well with the calculated spectra at low pressures. At high pressures (approximately 1 atmosphere), the differences between the measured and calculated spectra were found. The discrepancies would be caused by the line mixing effect.

3.2.2. (Sub-sub-theme 2-2) Study on experimental determination and reliability evaluation of absorption line parameters

Precise spectroscopic line parameters have to be determined in order to obtain correct retrieval of the trace gas compositions from the spectroscopic data obtained from a satellite-based sensor, such as ILAS-II, which was launched in 2002. For this purpose we have carried out the following studies together with the group of Meteorological Research Institute.

The subjects of this project are as follows.

(i) We measure, in collaboration with the Meteorological Research Institute, the infrared and far-infrared absorption spectra of CO_2 and N_2O with high resolution and high precision, and determine the intensity parameters, as well as the Herman-Wallis factors, and evaluate their reliability.

(ii) We develop the procedure to analyze line profiles precisely, and investigate the vibrational dependence of the broadening parameters.

(iii) We develop a method to measure the intensity of unstable chemical species.

The products of this project in the last years are as follows:

(i) The precise calculation of the partition function is required to obtain the absorption line intensity. In the present study we have evaluated the calculation procedures of the partition functions for linear molecules such as N_2O and CO_2.

(ii) The origin of the apparent temperature dependence of Herman-Wallis factors has been identified.

(iii) Using the pure rotational spectra of N_2O, CO, HCl, and SO_2, we have tested the reliability of the line parameters determined from the line profile measurements. A new program based of the Galatry profile has been developed for a special line profile due to the Dicke Narrowing effect. The traditional Voigt function, which is a convolution of a Gaussian and a Lorentzian function, cannot take care of such effect.

(iv) The vibrational dependence of the broadening parameters has been found to be

small.

(v) We have found the rational expression (Pade Approximant) can be used for representing the rotational dependence of the pressure broadening coefficients. We have applied this method to the N_2O data and published the results in the Journal of Molecular Spectroscopy.

3.3. (Sub-theme 3) Evaluation of ground-based measurement and PSC observation data for validating satellite data

The objective of this study is to contribute to validation of space-borne observations such as ILAS/ILAS-II, by developing techniques to obtain vertical profiles of atmospheric trace gas concentrations from ground-based infrared spectra, documenting time-height variations of the gas abundance, as well as by clarifying PSC characteristics and related micro-physical processes from satellite, balloon, and ground-based observations. The retrieval of a trace gas profile from infrared solar-absorption spectrum is increasingly used widely in the international science community but still needs improvement, and this study is targeting verifying and improving it. The results is as follows.

(1) Data analysis of the ILAS data set combined with a chemical box model and trajectory analysis could reveal :1. PSC composition. The aerosol extinction coefficient and nitric acid data were compared with the theoretically predicted values at thermodynamic equilibrium to classify PSC types. Many PSC events were categorized as the supercooled ternary solution (STS) in mid-January. Most of the PSCs observed late in the PSC season had features of nitric-acid-containing hydrates. 2. Chemical ozone loss amanount. The maximum ozone loss rate was estimated from a chemical model as about 34 ppbv/day in late February. The integrated ozone loss from 13 January to 31 March was 41%, averaged over the entire polar vortex. 3. An inter-hemispheric contrast in ClONO2 behavior during recovery from polar ozone depletions. The temporal enhancement of ClONO2 was apparent in the Arctic spring, while the ClONO2 mixing ratios were extremely low in the Antarctic polar vortex in November 1996,

(2) Ground-based observation of trace gases such as ozone and nitric acid etc. has been obtained successfully at Alaska, where is one of the best location for ILAS/ILAS-II validation. Ozone mixing ratio retrieved for 2000-2003 showed peak height of ~30km with seasonal variation, which agreed with other observations. Nitric acid observed in 2000-2003 showed peak at ~20km and seasonal variation with winter maximum. Error analysis temperature, a priori, Sa, and SN, on nitric acid height suggests 20% error or less, which enables us to argue the 50% seasonal changes.

(3) The SFIT2 height retrieval program was applied to ground-based infrared solar spectra observed at Tsukuba, Japan (36.0N , 140.1E) with a high-resolution Fourier transform spectrometer. The derived ozone spectra were compared with the ozonesonde measurements to validate the retrieval method so as to use it for the validation of ILAS and ILAS-II data. The instrumental line shape has been determined from the HBr and N_2O cell measurements and the correction was performed for the ozone analysis. The setting of the optics was not perfect and temporal variations of the instrumental line shape are also seen. Correction of the instrumental line shape in SFIT2 analysis for ozone works fairly well. The modulation correction is more effective than the phase correction. The correction do not work well when the instrumental line shape is in bad condition. The adjustment of the optics, the correction of the instrumental line shape, and the optimization of the fitting parameters will improve the accuracy of the retrieved profile.

(4) Balloon borne observations of Arctic stratospheric aerosols were performed at

Ny-Aalesund (79N, 12E). Aerosol size distributions with radius between 0.056 and 3.5 μm were observed with two types of balloon borne optical particle counter. Detail size distributions of stratospheric aerosols up to 25 km in the winter Arctic polar vortex were obtained through observations in winters of 2003 and 2004. Comparisons with lidar observations suggest that contribution of aerosols with radius of 0.056 - 0.1 μm on backscattering at wavelength of 532 nm is at least 10 % below 20 km in altitude, and becomes almost 100 % above 20 km. They show that observation of size distributions less than 0.1 μm in radius are important to understand optical property of stratospheric aerosols.

(5) An ozonesonde campaign observation at Fairbanks, Alaska was carried out in August 2002, which revealed detailed ozone variation in the upper troposphere and lower stratosphere (UTLS). Frequent balloon launches every 3 hrs enables to deduce the wavelike structures both in ozone and winds showed downward phase progression with time, which is the first direct observation of stratospheric ozone fluctuations modulated by an atmospheric gravity wave. It is suggested that this short-vertical scale ozone variation is formed by not only vertical but also horizontal advections caused by the gravity wave. This result is expected in future to contribute to study of gas transport and mixing processes by gravity waves in the stratosphere.

3.4. (Sub-theme 4) Research on scientific analysis and data evaluation using satellite data

Assessment of ILAS version 6.0 data products were performed through comparisons with validation data as listed below:

- O_3, CH_4, H_2O measured by NASA's HALOE
- NO_2, HNO_3, N_2O, $ClONO_2$, CFC-11 measured by large balloon borne-sensors, which were financially supported by the Ministry of the Environment.
- Aerosol extinction coefficient measured by NASA's SAGE II

We have found that the version 6.0 data products have a quality that is comparable to the former version 5.2 data products, which were published in J. Geophys. Res. The version 6.0 data products also include new data such as $ClONO_2$ and CFC-12, not in the version 5.2. The version 6.0 data set is used for scientific studies in the stratosphere, since it is recognized as a high quality data set by researchers of the stratospheric science.

This study showed that the patterns of high PSC probabilities corresponded to those of high ozone loss rates. Also, it assessed the impact of increases of PSCs to ozone loss rate using the results of six winters. It is well known that increased greenhouse gasses warm the atmosphere near the Earth's surface and also radiatively cool the stratosphere. The stratospheric cooling has a potential to produce much more PSCs. The result from this study proposes the observational evidence of the response of Arctic ozone loss to changes in the number of PSCs. This provides great confidence in our knowledge of impact of climate change and contributes to the studies on prediction of future climate and ozone layer.

The ILAS HNO_3 data obtained in the Arctic vortex in January and February 1997 were used in identifying the mechanism of denitrification. The permanent loss of HNO_3 was estimated by a box model in which NAT particles form inside ternary droplets via NAD and NAT nucleation. The losses of HNO_3 calculated from the model along back trajectories were tightly correlated with those observed, although the model underestimated the degree of denitrification by ~20%. The agreement between the model and observations was significantly improved by taking into account the NAT particle sedimentation from

above locations along trajectories. These results provide evidence that the formation of NAT through the nucleation of NAD and NAT inside droplets was the major cause of observed denitrification.

Total reactive nitrogen (NOy) in the Arctic lower stratosphere was measured from the NASA DC-8 aircraft during the SAGE III Ozone Loss and Validation Experiment (SOLVE) in the winter of 1999/2000. NOy-N_2O correlations obtained at altitudes of 10–12.5 km in December 1999 and January 2000 are comparable to the reported reference correlation established using the MkIV balloon measurements made during SOLVE prior to the onset of denitrification. Between late February and mid-March, NOy values obtained from the DC-8 were systematically higher than those observed in December and January by up to 1 part per billion by volume, although a compact correlation between NOy and N_2O was maintained. Greater increases in NOy were generally observed in air masses with lower N_2O values. The daily minimum temperatures at 450–500 K potential temperature (~20–22 km) in the Arctic fell below the ice saturation temperature between late December and mid-January. Correspondingly, intense denitrification and nitrified air masses were observed from the ER-2 at 17–21 km and below 18 km, respectively, in January and March. The increases in NOy observed from the DC-8 in late February/March indicate that influence from nitrification extended as low as 10–12.5 km over a wide area by that time. We show in this paper that the vertical structure of the temperature field during the winter was a critical factor in determining the vertical extent of the NOy redistribution. The REPROBUS three-dimensional chemistry transport model reproduced the observed general features only when the NOy redistribution process is included.

We analyzed long-lived chemical constituents observed by the Improved Limb Atmospheric Spectrometer (ILAS) on board the Advanced Earth Observing Satellite (ADEOS) to study stratospheric descent in the Southern Hemisphere polar vortex. The ILAS N_2O distribution inside the polar vortex shows clear downward motion in February-June 1997. Average descent for the 5 months is estimated to be ~2.1-1.7 km/month in the middle stratosphere. In late April-May when planetary waves are relatively active, the vertical velocity shows time variations with a period of about 10 days. These time variations also synchronize with a both time variations of temperature time change and the Eliassen-Palm flux divergence (DF) in high latitudes.

Moreover, a correlation map in the latitude-height cross section between the vertical velocity and the temperature time change shows the following interesting feature. It shows a 4-box pattern, suggesting warming below 10 hPa and cooling above 10 hPa in the polar region (70°S- 90°S) and an opposite distribution in mid-latitudes (40°S- 70°S), when large descent is observed inside the polar vortex. It is just like the meridional circulation in response to DF induced by planetary waves, which was first illustrated by the Matsuno's stratospheric sudden warming theory.

The high vertical resolution atmospheric temperature profiles can be retrieved with GPS occultation measurements up to 35 km altitude. The accuracy and precision of these temperature profiles is very well and comparable to those of radiosonde measurements. These GPS temperature profiles are very good validation data for ILAS-II temperature profiles. In addition, the GPS temperature can be used for studies in tropospheric and stratospheric temperature structures globally.

3.5. (Sub-theme 5) A quantification of chemical ozone destruction using 3-dimensional chemical transport model

In order to analyze the amount of the transport of the air between inside and outside of

the polar vortex, a new method of the time threshold diagnostics (TTD) method was developed. In the winter through 1996 to 1997, trajectories of many air parcels were calculated in the Northern polar vortex in the lower stratosphere using the wind velocity data of ECMWF. The TTD method was used for investigating the northward and southward transport thorough the equivalent latitudes. The sum of northward and southward traffic showed a minimum value at the equivalent latitude on the polar vortex. The traffic shows the isolation of the polar vortex increased gradually from the end of 1996, and reached a maximum isolation in March 1997. From April to May in 1997, the isolation became weaker and this is consistent with the collapse of the polar vortex.

A CCSR/NIES nudging chemical transport model (CTM) has been developed. The model was used to calculate N2O and ozone concentrations for the period of the ILAS operation. The model simulates well the distributions of these species observed by ILAS: Before the Arctic polar vortex breakup, the N2O concentration shows a clear concentration difference between the inside and outside of the polar vortex. The concentration shows low values inside the Arctic vortex and high values outside. After the Arctic polar vortex breakup, a mixing process of the polar air with the midlatitude air was successfully simulated. The model calculations also show that the lower stratospheric ozone concentration in spring reflects a complicated process of ozone destruction through the heterogeneous reactions inside the Arctic polar vortex and through a NOx catalytic cycle activated in the spring of the polar region, and mixing processes of the polar air with the midlatitude air.

The amount of chemical ozone destruction inside the Arctic polar vortex was estimated by a CTM calculation with a full stratospheric chemistry and a calculation with an ozone tracer, where ozone was assumed to be a passive tracer that was not affected by any chemical reactions. The result shows that ozone in the north of 70N of the equivalent latitude, which corresponds to the region inside the Arctic polar vortex, was destroyed intensively from the end of February to the beginning of April, 1997. A TTD analysis showed that the air transport between the inside and outside of the polar vortex was extremely inhibited by a stable polar vortex at this period. These results indicates that the air was hardly transported between the inside and outside of the polar vortex at this time, which caused a very low temperature in the Arctic lower stratosphere, then Polar Stratospheric Clouds (PSCs) were formed and ozone was destroyed through the heterogeneous reactions on the PSCs and the denitrification process.

3.6. (Sub-theme 6) Research on the polar stratospheric chemistry using a photochemical Lagrangian model

Denitrification is well known to determine the severity of springtime ozone depletion in Polar Regions. In the winter 1996/1997, the Improved Limb Atmospheric Spectrometer (ILAS) on board the Advanced Earth Observing Satellite (ADEOS) detected denitrification in both hemispheres. Here, the Match technique and a Lagrangian model are used to analyze nitric acid variation between a pair of measurements belonging to the same air parcel. Eleven cases are studied in Antarctica and seventeen cases are studied in the Arctic, allowing to test the laboratory-measured homogeneous freezing rate of liquid ternary aerosol into nitric acid hydrates, thought to be the determining step of the denitrification process. Over the Antarctica, height cases over eleven lead to result in agreement with the measurements, taking into account uncertainties of the measurement and possible acceptable bias in the temperature field used for the modeling study. Over the Arctic, more cases remain unexplained even taking into account the possible scavenging of nitric acid

by big NAT particles falling from the layers above. Those disagreements are mainly due to very warm temperatures along the trajectories that do not lead to significant NAT or NAD freezing. Then it appears that some additional mechanisms are required to explain the denitrification in the Arctic winter. Also, the occurrence of denitrification due to the NAT particles with very large (few mm) but few numbers, so-called "NAT rocks[4]", over the Antarctic winter in 1997 was suggested.

4. References

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