

A-1.3 Spectroscopic Study on the Ozone-layer with an Airborne Fourier-transform Infrared Spectrometer

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Abstract A Fourier-transform infrared spectrometer (FTIR) with resolution of 0.02 cm^{-1} was used for measuring solar spectra during the aircraft experiments of February and December in 1992. Measurements were made between 25N-45N over Japan. The preliminary results show that the total HCl or equivalent width measured in December, 1992 was larger at the higher latitudes and smaller at the lower latitudes. Total ozone, measured at the same period in Japan, shows same latitudinal tendency, indicating the measured HCl gradient is thought as one of the typical distribution of stratospheric HCl during the chemically non-disturbed condition. In the case of measurement in February, 1992, it is shown that the total HCl in lower latitudes was still similar to the results for December, 1992. However, the total HCl in higher latitudes was much smaller than that in December, 1992, indicating any chemical or dynamical disturbance from the average occurred in February, 1992.

Key Words Ozone-Layer, Hydrogen Chloride, Infrared Spectrometer, Aircraft Observation

1. Introduction

In recent years, the emission of the man-made chemical product such as chlorofluorocarbons is thought to cause the global change of the ozone layer in the stratosphere through the chemical processes. It is also thought to cause the global warming in the lower atmosphere through the greenhouse effects. The aim of this study is to develop a technique of infrared remote-sensing and to measure the behaviour of key minor constituents related to the ozone chemistry.

2. Research Objective

Estimation of two-dimensional numerical model with photochemical processes shows the major part of chlorine species of the stratosphere exists in the form of hydrogen-chloride (HCl) in mid-latitudes. It also shows that in the normal condition the amount of HCl is about few times larger than that of ClO_x, which is directly connected to the catalytic cycle of ozone destruction. Recent theory of the Antarctic ozone hole has been established on a basis of heterogeneous chemical reaction between HCl and ClONO₂ in cold stratosphere, where the polar stratospheric clouds (PSCs) are formed. Reactants of the heterogeneous reaction (HNO₃ and Cl₂) on the surface of PSCs have the role to remove NO_x and supply ClO_x in the stratosphere, which catalytically destructs the stratospheric ozone. In these years, the total ozone in the northern hemisphere shows large depletion during winter to spring, especially at higher latitudes (WMO, 1992)¹). It is pointed out that the heterogeneous chemistry has possibly some role in the Arctic stratosphere and any influence spreads to the lower latitudes. Also, stratospheric aerosol, brought by large volcanic eruption such as Pinatubo, plays

some role in the mid-latitude stratospheric chemistry. As well, because of the large gradient of total ozone from north to south in Japan, the dynamical processes play an important role, i.e., if air-mass from lower latitudes covers over the north part of Japan it makes the total ozone abnormally small. Both of chemical and dynamical roles should be estimated for any ozone variation.

To understand the role of chemical or dynamical processes, it is necessary to make clear the spatial distribution and the change of chemical species such as HCl, HF, HNO₃ or ClONO₂, as well as ozone itself. These species have their maximum concentration in the stratosphere with less concentration in the troposphere. The possibility of detecting the real change in the stratosphere is highly expected with a technique of the infrared spectroscopy.

3. Research Method

Infrared solar spectra measured at ground or on board aircraft show a lot of absorption lines which can be attributed to the atmospheric minor constituents. Large absorption due to carbon dioxide or water vapour covers almost all the wavenumber (or wavelength) in mid-infrared solar spectra. In atmospheric window regions, for example, around 8-13 μm or 3-4 μm , we can find absorption due to HNO₃, ClONO₂, HCl, HF, etc., which are thought as important species related to the chemistry of stratospheric ozone layer. To measure these species accurately it is required to use high-performance infrared spectrometer. A high-resolution Fourier-transform infrared spectrometer (FTIR), which is designed especially for airborne experiment, has been prepared. Unapodized maximum resolution of the spectrometer is 0.02 cm^{-1} , and the absorption line of HCl can be easily identified at the wavenumber of 2925.86 cm^{-1} (3.418 μm in wavelength) over the wing of CH₄ absorption bands.

Because the large portions of H₂O and CO₂ contents in the atmosphere are contained in the lower atmosphere it is advantageous to make measurement at higher altitude in the atmosphere. It is also required for the detection of stratospheric minor constituents to make measurement at the small solar elevation angle, i.e., with long optical path during sunrise or sunset.

4. Result

In 1990, an airborne-type FTIR, basically same as the model DA2 made by BOMEM Inc., was prepared and the operational examinations on ground were continued. In 1992, after some flight tests the measurements of solar infrared spectra were made successfully with the highest resolution of 0.02 cm^{-1} .

(1) Experiment of the stratospheric HCl remote sensing in 1991.

The first trial to measure solar spectrum was operated at the fall in 1991 over Kii Channel from Osaka Bay to Muroto Peninsula. An aircraft of the Fairchild Swearingen SA226-AT (Merlin IV) owned by Showa Avi. Co. was used for experiment with unpressurized condition. Sunlight was introduced by a sun-follower through a hole of window. The interferometer of FTIR was installed on a base, which was mechanically isolated from high-frequency vibration. Scanning for 16 times with highest resolution of 0.02 cm^{-1} required about 16 minutes. In that case, there may possibly occur fatal shocks during scanning for interferograms to be transformed into the spectra. However, spectrum of lower resolution of 1.0 cm^{-1} has good results because of the shorter scanning time.

(2) Experiment of the stratospheric HCl remote sensing in 1992.

The second trial of measuring solar spectra was operated on 9 to 14 February in 1992 over Seto Inner Sea and along 140E from Iwo-jima Is. to Hokkaido. An improvement for the mechanical isolation and the optical alignment allowed us to measure solar spectra of good S/N ratio during one scan with the highest resolution.

The third aircraft experiment was operated on 16 to 22 December in 1992 over Japan Is. from Asahikawa/Hokkaido to Ishigaki-jima Is. The flight path for the campaign is shown as in Figure 1. The aircraft used was same as before and which flew at the fixed altitude of about 5 km. The experimental condition was almost same as previous one except coaddition of five interferograms to get a spectrum. The spectra which show good S/N ratio were selected and the equivalent widths of the HCl R1 line in the (0-1) vibrational-rotational band were calculated. Figure 2 shows the result of latitudinal distribution of equivalent widths, which are proportional to the vertical column density of HCl molecules above observation platform. It is clear from Fig.2 that the HCl column density shows higher value in higher latitudes over Japan in the December 1992 campaign.

5. Discussion

Total amount of hydrogen-chloride in the vertical column of the atmosphere, which is proportional to the equivalent width in the case of weak absorption, increased at the higher latitudes over Japan in December 1992 (Fig.2). This is thought as general characteristic for most of reservoirs such as HNO_3 , ClONO_2 and HF. This latitudinal change agrees with those measured over the North America (Mankin and Coffey, 1983)²⁾. Total ozone observed in December, 1992 over Japan shows normal or average distribution, i.e., the higher value of total ozone was observed in higher latitude and the observed total ozone falls within the standard deviation of long-term average of monthly mean (JMA, 1992)³⁾. This latitudinal tendency may be related to that of total HCl.

On the contrary, the result obtained in February, 1992 shows rather disturbed latitudinal distribution as shown in Figure 3. In the case of February, 1992, it is shown that the total HCl at the lower latitudes was similar to the results of December, 1992. However, the total HCl at the higher latitudes was much lower than those of December, 1992, indicating chemical or dynamical disturbance occurred in February, 1992. Total ozone observed in February, 1992 shows also lower values than the average in higher latitudes.

It may be concluded that the total HCl and the total ozone show good positive correlation over Japan in winter or early spring when recent measurements of total ozone show the larger depletion in the northern mid- and high-latitudes (WMO, 1992)¹⁾.

To get more precise information concerning the stratospheric ozone processes, it is necessary to develop the measurement of various species such as HF, HNO_3 or ClONO_2 as well as HCl and to make clear the behaviour of these species over wide range of latitude.

Reference;

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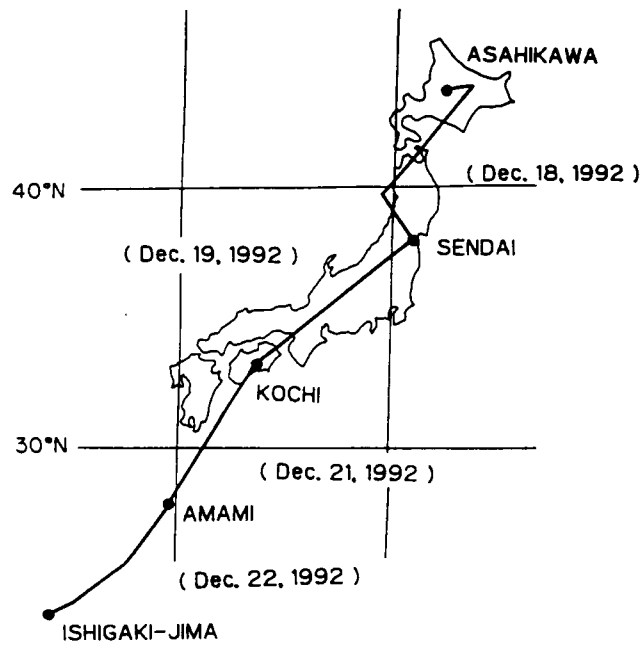


Figure 1. Flight path for the airborne experiment in December, 1992.

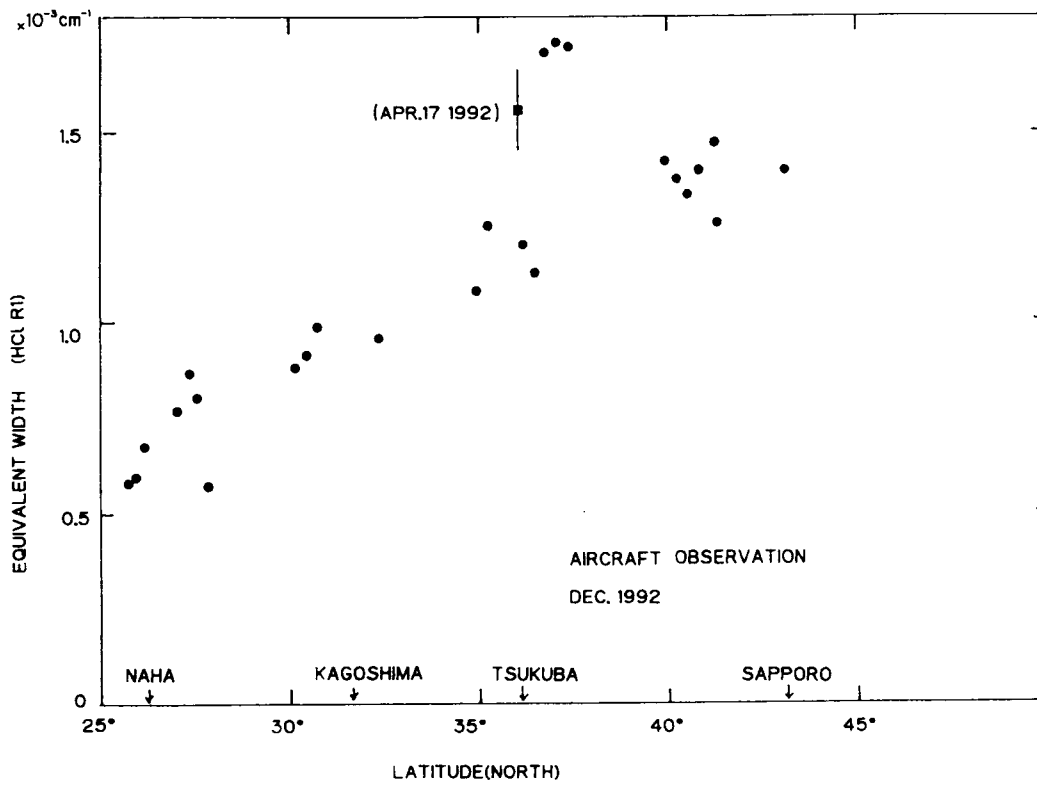


Figure 2. Latitudinal distribution of the equivalent width for HCl R1 line of (0-1) vibration-rotation band, proportional to the HCl column density, obtained during the airborne experiment in December, 1992.

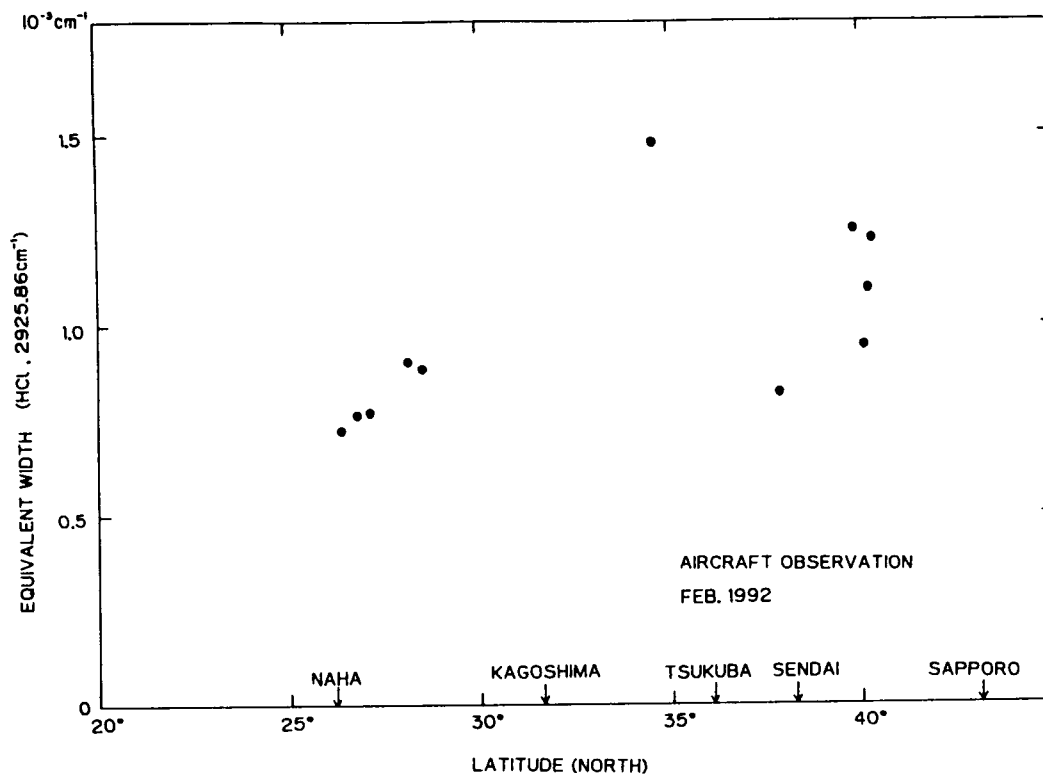


Figure 3. Same as Fig.2 except during the experiment in February,1992.