

OBSERVATION OF ATMOSPHERIC MINOR CONSTITUENTS  
IN THE ANTARCTIC REGION  
BY GROUND-BASED ABSORPTION SPECTROSCOPY  
(EXTENDED ABSTRACT)

Kazuo SHIBASAKI and Toshihiro OGAWA

*Geophysics Research Laboratory, Faculty of Science, University of Tokyo,  
3-1, Hongo 7-chome, Bunkyo-ku, Tokyo 113*

### 1. Introduction

The upper atmosphere in high latitudes is quite different from that in low- and mid-latitudes from various aspects. Auroral particle precipitation associated with magnetospheric storms is peculiar to polar regions and may affect chemical and dynamical processes in the polar upper atmosphere. In polar regions the seasonal variation of solar radiation flux which is a basic quantity in considering the energy balance in the atmosphere is also much different. Measurements of atmospheric minor constituents in high latitude regions will give us useful information to elucidate transport and photochemical processes in the atmosphere. They are also important in testing the validity of many atmospheric models which have been developed on the basis of low- and mid-latitude observations. With respect to monitoring the influence of man's activities on the atmospheric environment, Antarctica seems to be the best place.

In the 24th Japanese Antarctic Research Expedition, it is planned to carry out ground-based measurements of atmospheric minor constituents. Visible and infrared absorption spectrometry will be used in these observations. A detailed description of infrared spectrometry using a Fourier transform interferometer is given elsewhere in this issue (MAKINO *et al.*, 1982). In this abstract, the visible absorption spectroscopy is mainly mentioned; objects of this observation are NO<sub>2</sub> and NO<sub>3</sub> which play key roles in ozone chemistry in the atmosphere. Examples of data analysis will also be presented.

### 2. Principle of Measurement

Our observational method is based on differential absorption spectroscopy. In this section the principle of measurement will be simply described. A detailed description of our method is given in OGAWA *et al.* (1981).

Differential absorption spectroscopy using the sun or moon as a light source is one of the most common and useful techniques when measuring total content of atmospheric minor constituents, because a long atmospheric path can be obtained. One example is the Dobson method, which has been adopted all over the world

as the standard to derive total atmospheric ozone content. Note that only the column density integrated along the ray path is determined from this type of observation. Although it is mathematically possible to derive a vertical distribution from ground-based observations, it is practically difficult.

Spectral intensities at a pair of wavelengths which correspond to the peak and bottom of an absorption band are simultaneously measured in application of differential absorption spectroscopy. However, a spectrum in the appropriate wavelength region including several absorption bands is taken in our method, and the data analysis is done statistically using all of the spectral data. This procedure improves the accuracy of measurement, especially in case of observations in which the object substances have weak absorption bands or are of very small content in the atmosphere.  $\text{NO}_2$  has strong absorption bands in the 420–460 nm region, and  $\text{NO}_3$  in the 610–670 nm region. The wavelength regions of 430–450 nm and 650–680 nm will be employed for measurements of  $\text{NO}_2$  and  $\text{NO}_3$  respectively in our observations in Antarctica.

A reference spectrum which is free from absorptions due to objective species is essential in estimating absorption. A solar spectrum outside the atmosphere is best; however, a spectrum obtained at high solar zenith angle can be used. In the observation of  $\text{NO}_2$  a spectrum which will be obtained during a balloon experiment will be used as a reference spectrum.

### 3. Instrumentation

The main instruments employed are a monochromator and a Fourier transform interferometer. The former is used to take visible absorption spectra for the atmospheric  $\text{NO}_2$  and  $\text{NO}_3$ . The latter is used to take infrared absorption spectra for the atmospheric  $\text{N}_2\text{O}$  and other minor constituents.

A sun (moon) tracking system must be installed to use the spectrophotometers. To track the sun is rather easy, because the solar intensity is strong enough. On the other hand, moon sensors must be specially designed for the purpose of continual observations for full moon to half moon, since the intensity at full moon is about  $10^{-6}$  of that of the sun. In order to improve signal to noise ratio, a condenser lense in front of the entrance slit of the monochromator and a cooler for a photomultiplier are also needed.

A spectral resolution of about 2 Å is enough in visible absorption spectroscopy, while a high resolution of about  $0.1 \text{ cm}^{-1}$  is required in infrared spectrometry to separate one absorption line from others.

### 4. Example of Data Analysis

Figure 1 shows absorption spectra taken at Kakioka along with synthetic spectra best fitted by using the least square method. The band structure due to absorption by  $\text{NO}_2$  can be clearly recognized. The derived column densities and the solar zenith angles are given in the figure. Since it took about four minutes to obtain one spectrum, the derived density represented the average value during the observation. This spectrum acquisition time will be shortened to about one minute. The

Fig. 1. Absorption spectra observed at Kakioka in the morning and evening of February 1, 1980. Dotted curves are from observations, and solid curves from calculation with  $\text{NO}_2$  column densities given in the figure; e.g.  $8.67(16) = 8.67 \times 10^{16} \text{ cm}^{-2}$ .

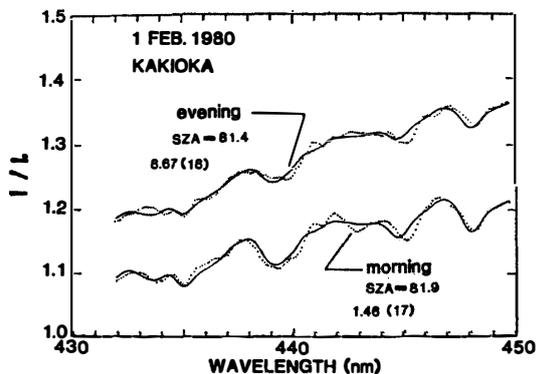


Fig. 2. Absorption cross section of  $\text{NO}_3$  (after GRAHAM and JOHNSTON, 1978).

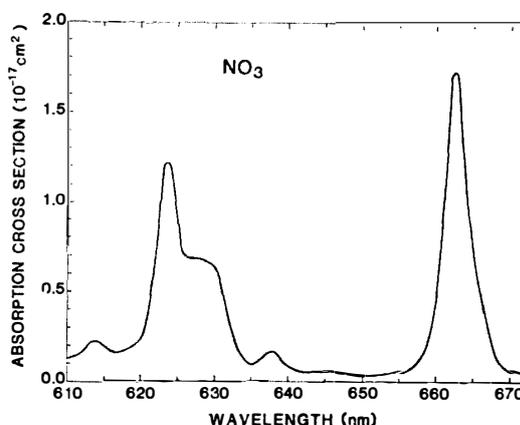
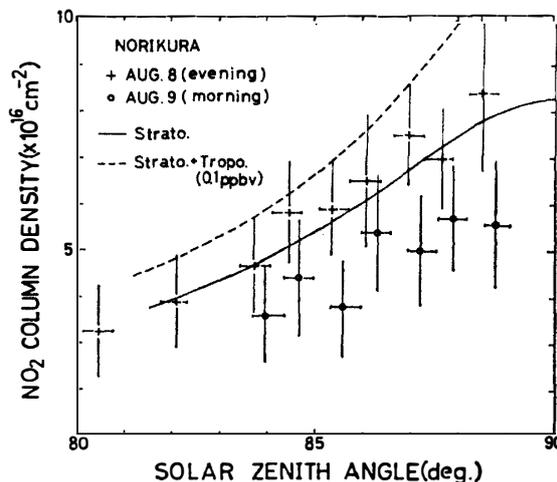


Fig. 3. Apparent variation of the  $\text{NO}_2$  column density with solar zenith angle as observed at Mt. Norikura on August 8/9, 1979. The solid curve is for a model  $\text{NO}_2$  distribution only in the stratosphere, and dashed curve for a model with a tropospheric mixing ratio of 0.1 ppbv together with the stratosphere (after SHIBASAKI and OGAWA, 1981).



difference between the observed and calculated curves shown in Fig. 1 is due to a fluctuation of solar intensity due to Mie scattering, mismatching of wavelengths between the reference and observed spectra, absorption by  $\text{H}_2\text{O}$  and  $\text{O}_3$ , and so on.

Figure 2 illustrates the absorption cross section of  $\text{NO}_3$ . Although the absorption by  $\text{NO}_3$  may be small because of its very small concentration in the atmosphere, this band structure is expected to be observed. The measurement of  $\text{NO}_3$  will be made only at night.

In Fig. 3 the apparent variation of the  $\text{NO}_2$  column density, as observed at Mt. Norikura, is demonstrated. Each horizontal bar indicates the time of obtaining one spectrum, and each vertical bar does the variance of data points as converted to the uncertainty of the  $\text{NO}_2$  column density. As can be seen in Fig. 3, the main part of the atmospheric  $\text{NO}_2$  content exists in the stratosphere. NOXON (1979) reported the seasonal variation of total stratospheric  $\text{NO}_2$  content from ground-based measurements using almost the same method as ours. The total stratospheric  $\text{NO}_2$  (or  $\text{NO}_3$ ) content can then be monitored by ground-based observations in Antarctica which is considered to be free from air pollution. In cooperation with experiments using a balloon and aircraft as platforms, the reliability of the data analysis can be checked.

### 5. Concluding Remarks

Atmospheric minor constituents such as nitrogen oxides play a great role in ozone chemistry and, therefore, in global climate. It is important to observe minor constituents in the polar region for ascertaining the detailed photochemical processes in the atmosphere and for monitoring the influence of man's activities on the stratospheric ozone.

Continuous observations of atmospheric  $\text{NO}_2$  and  $\text{NO}_3$  have never been made in the polar regions. Our present plan to measure the atmospheric  $\text{NO}_2$  and  $\text{NO}_3$  both at night and day throughout a year at Syowa Station is expected to provide valuable data about the nitrogen distribution in the polar atmosphere.

### References

- GRAHAM, R. A. and JOHNSTON, H. S. (1978): The photochemistry of  $\text{NO}_3$  and the kinetics of the  $\text{N}_2\text{O}_5\text{-O}_3$  system. *J. Phys. Chem.*, **82**, 254–268.
- MAKINO, Y., MURAMATSU, H., HIROTA, M. and SASAKI, T. (1982): Observation of atmospheric trace constituents by FTIR. *Mem. Natl Inst. Polar Res., Spec. Issue*, **24**, 303–306.
- NOXON, J. F. (1979): Stratospheric  $\text{NO}_2$ . 2. Global behavior. *J. Geophys. Res.*, **84**, 5067–5076.
- OGAWA, T., SHIBASAKI, K. and SUZUKI, K. (1981): Balloon observation of the stratospheric  $\text{NO}_2$  profile by visible absorption spectroscopy. *J. Meteorol. Soc. Jpn.*, **59**, 410–416.
- SHIBASAKI, K. and OGAWA, T. (1981): Observational implication for the tropospheric  $\text{NO}_2$  burden. *J. Meteorol. Soc. Jpn.*, **59**, 429–430.

*(Received April 30, 1982)*