SPECTROSCOPIC MEASUREMENTS OF ATMOSPHERIC N_2O AT SYOWA STATION, ANTARCTICA: PRELIMINARY RESULTS

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Abstract: Spectroscopic measurement of atmospheric trace constituents at Syowa Station, Antarctica (69°00′S, 39°35′E) was started on 24 March 1983. Preliminary results of this measurement are presented. Total atmospheric nitrous oxide (N_2O) deduced from the transmittance of solar radiation at 2576 cm^{-1} (3.88 μm) indicated a seasonal variation with a maximum in spring. The deduced mixing ratios of N_2O were smaller than the value of 300 ppbv measured by a gas-chromatographic technique. The method of analysis was also examined in terms of the atmospheric models to be used and it was shown that a multi-layer model should be applied to the case of solar zenith angle larger than 85°.

1. Introduction

Nitrous oxide (N_2O) is chemically inactive in the troposphere and decomposed by photolysis and reaction with $O(^1D)$ in the stratosphere. The latter reaction is thought to be a major source of stratospheric NO_x and thus, the change of N_2O is an important factor in the ozone chemistry (CRUTZEN, 1971; MCELROY and MCCONNELL, 1971). This molecule also contributes to the atmospheric greenhouse effect by its infrared absorption bands (LACIS *et al.*, 1981). Knowledge of the behavior of atmospheric N_2O over Antarctica is necessary for understanding the global transport and distribution of sinks and sources. It is reported N_2O in Antarctica is increasing at a rate of 0.2–1% (WEISS, 1981; ROBINSON and BAMESBERGER, 1983). These data are concerned with the sampled air analyzed by the gas-chromatographic technique and do not indicate any distinct seasonal variation. On the other hand, a spectroscopic measurement of columnar amount of N_2O has been reported only for the limited period of the austral summer (GOLDMAN *et al.*, 1983).

As part of the Japanese Antarctic MAP (Middle Atmosphere Program) activity, ground-based spectroscopic observations of the atmospheric infrared transmittance were started at Syowa Station, Antarctica (69°00′S, 39°35′E) on 24 March 1983 and continued through the year, in order to elucidate the variation of the columnar density of atmospheric minor constituents such as N_2O, CH_4, $CFCl_3$, CF_2Cl_2 and HNO_3. In this paper, we report the preliminary results of the columnar density of N_2O deduced from the infrared solar spectra of the 2500 cm^{-1} region.

2. Experiments

Figure 1 shows a block diagram of the observation system. The details of the observation system will be reported elsewhere (MAKINO *et al.*, 1985). Therefore, only a brief description will be given here. The sunlight is introduced into a Fourier-transform infrared spectrometer (JEOL, JIR-40X) by a sun-follower and an optical connection system. The sun-follower, composed of a pair of gold-coated plane mirrors, was installed on the roof of the laboratory. The optical sensitibity of the spectrometer was calibrated with the reference radiation of a black body. The apodized resolution was set to be 0.7 cm^{-1} to save the data processing time. Fifty inter-

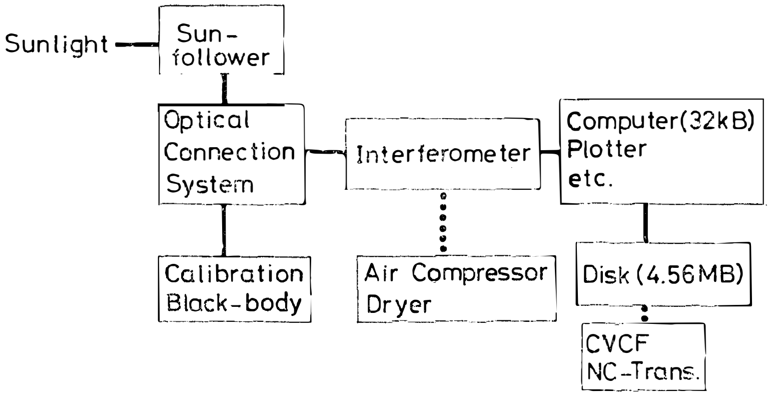

Fig. 1. A block diagram of the observation system. The sunlight and the reference radiation of a black body are introduced into a spectrometer by a sun-follower and an optical connection system. The Fourier-transform infrared spectrometer is composed of interferometer, computer, plotter and auxiliary disk unit.

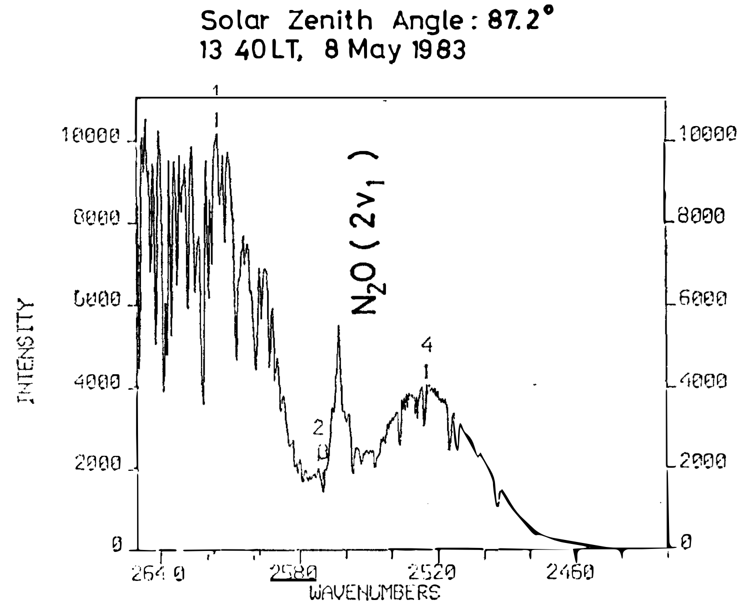

Fig. 2. An example of observed solar spectrum in the 2420–2650 cm^{-1} region at 1340 LT of May 8, 1983 at Syowa Station, Antarctica. Solar zenith angle is 87.2°.

ferograms obtained for 5 min were coherently added and transformed into a spectrum by a computer with 4.56 MW auxiliary disk memory. The 408 spectra were obtained for 72 days in ten months from 24 March 1983 to 23 January 1984 and were recorded on removable disks. An example of observed spectrum is shown in Fig. 2.

3. Method of Analysis

As a preliminary estimate of total column N_2O abundance, a graphical method is applied. MURAMATSU *et al.* (1984) have shown that transmittance as well as equivalent width of the absorption band can be used to deduce the N_2O abundance. In this work, the relation between the transmittance and the total amount of N_2O in the ray path of sunlight is calculated with the standard N_2O altitude profile (see Fig. 3).

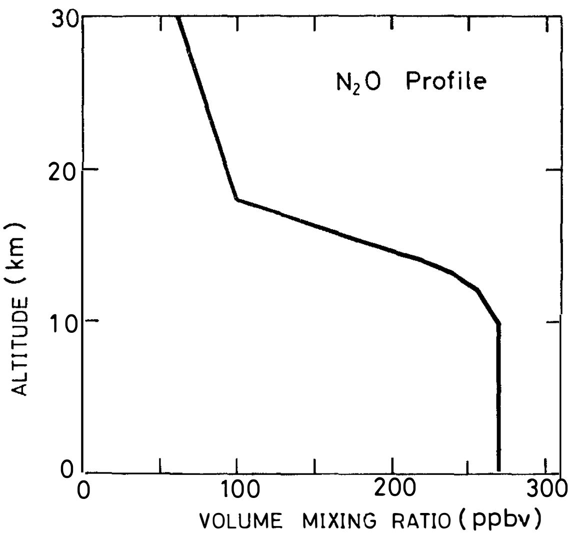

Fig. 3. *The N_2O profile used in the calculation. The N_2O mixing ratio is assumed to be constant below an altitude of 10 km and decrease with altitude above 10 km. Figure shows the case for the tropospheric mixing ratio of 270 ppbv.*

The tropopause height is assumed to be 10 km as in the U.S. Standard Atmosphere, 1976 (U. S. COMMITTEE ON EXTENSION TO THE STANDARD ATMOSPHERE, 1976). Since the one-layer calculation is more economical of time but less precise than the multilayer calculation, both models are applied. The N_2O profile is assumed to have a constant volume mixing ratio in the troposphere below 10 km and decrease with altitude in the stratosphere as shown in Fig. 3. The curve of growth for the N_2O absorption is used to estimate the total N_2O abundance along the solar ray path.

Because pressure broadening is more effective than Doppler broadening in the altitude range considered here, synthetic transmittance spectra are obtained from the line-by-line calculation assuming Lorentzian line shape given as

$$k(\nu)=\frac{S\alpha}{\pi\{(\nu-\nu_0)^2+\alpha^2\}}, \tag{1}$$

where $k(\nu)$ is absorption coefficient (molecule^{-1} cm^2) at wavenumber ν (cm^{-1}), ν_0 is resonant wavenumber, α is Lorentzian line width (cm^{-1}) and S is line intensity (cm molecule^{-1}).

The temperature dependence of the line intensity is represented as

$$S(T)=\frac{S(T_s)Q_v(T_s)Q_r(T_s)}{Q_v(T)Q_r(T)}\exp\left\{\frac{1.439E''(T-T_s)}{TT_s}\right\}, \tag{2}$$

where E'' is the energy of the lower state of the transition (in cm^{-1}) and Q_v and Q_r are the vibrational and rotational partition functions, respectively.

The temperature and pressure dependence of Lorentzian line width is represented as

$$\alpha(T,P)=\alpha_0(T_s,P_0)\ (P/P_0)(T/T_s)^{-n}, \tag{3}$$

where $\alpha_0(T_s,P_0)$ (cm^{-1}) is that at the pressure $P_0=1$ atm and the temperature $T_s=$ 296 K.

The four essential line parameters for each line, ν_0, S, α and E'' were taken from AFGL atmospheric absorption line parameters compilation, 1982 (Rothman *et al.*, 1983). Q_v and Q_r were referred to McClatchey *et al.* (1973) and n was taken to be 0.5.

3.1. One-layer analysis

Assuming the constant pressure of 500 mb and temperature of 260 K along the optical path in the atmosphere, which is for the case of the U. S. Standard Atmosphere, 1976 and the solar zenith angle smaller than 85°, we can calculate the synthetic spectrum. Since the zero-absorption baseline cannot be known inherently in the observed chart of solar spectra, we define the apparent transmittance $\tau_a(\nu)$ from synthetic spectrum (see Fig. 4a) as,

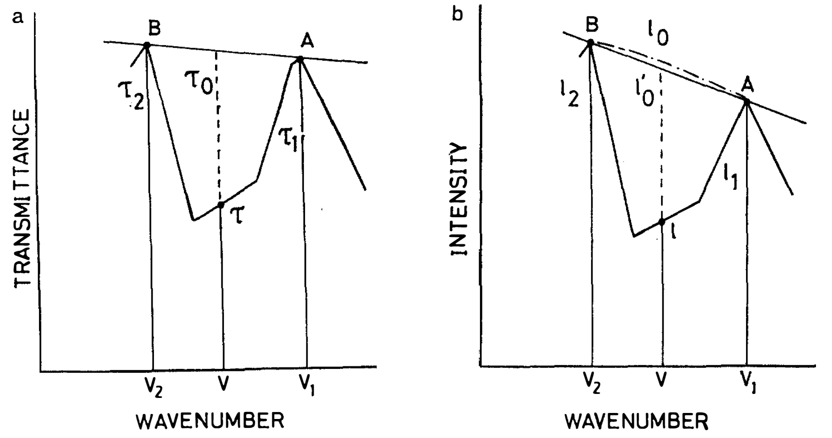

Fig. 4. A schematic sketch of (a) synthetic and (b) observed spectra. The straight lines between A and B represent eqs. (5) and (7), respectively. The dash-dotted curve between A and B in Fig. 4b represents eq. (6).

$$\tau_a(\nu)=\tau(\nu)/\tau_0(\nu), \tag{4}$$

where $\tau(\nu)$ is the calculated transmittance at wavenumber $\nu(cm^{-1})$ in the absorption band of N_2O, and

$$\tau_0(\nu)=a\nu+b, \tag{5}$$

representing the straight line between A and B in Fig. 4a. The two constants a and

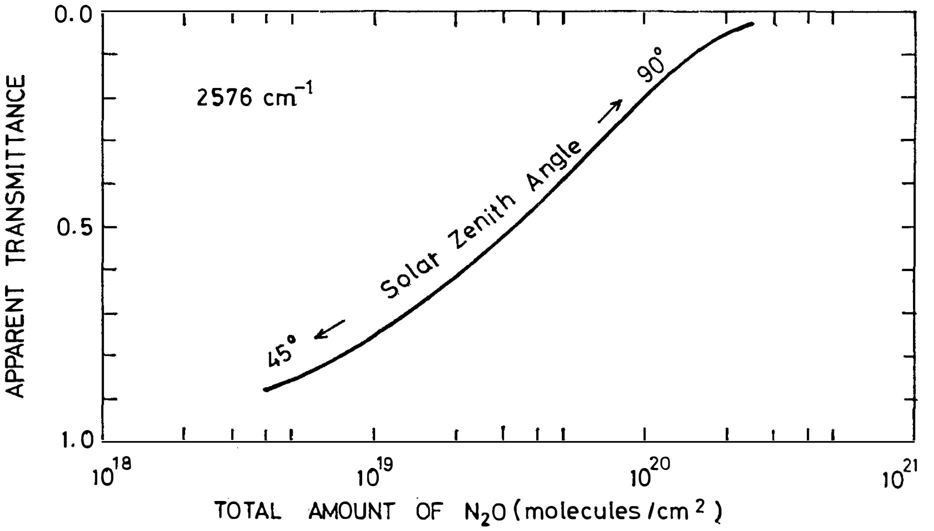

Fig. 5. The curve of growth for the N_2O absorption. The calculated apparent transmittance versus N_2O amount in the ray path of sunlight. The calculation is made with the effective pressure and temperature of 8 May 1983 (see Fig. 8).

b can be given by two transmittances τ_1 and τ_2 at wavenumbers ν_1 and ν_2, respectively. The wavenumber, where the $\tau_a(\nu)$ is calculated, is chosen to be 2576 cm^{-1}. ν_1 and ν_2 are chosen to be 2521 and 2611 cm^{-1}, respectively. An example of the curve of growth is shown in Fig. 5, which includes the effect of the change of solar zenith angle.

Generally, eq. (5) does not correspond to the straight line in the observed spectrum of Fig. 4b. The straight line defined by eq. (5) is transformed into

$$I_0(\nu)=f(\nu)\tau_0(\nu)\,, \tag{6}$$

on the measured spectrum, where $f(\nu)$ is a function proportional to the intensity of solar radiation and modified with the spectral response of the instrument and the effect of the continuum absorption. Equation (6) is shown as the dash-dotted curve in Fig. 4b. For a preliminary analysis, we assume

$$I_0(\nu)\cong I_0'(\nu)=c\nu+d\,, \tag{7}$$

and $I_0'(\nu)$ represents the straight line between A and B in Fig. 4b. The two constants c and d can be given by two intensities I_1 and I_2 at wavenumbers ν_1 and ν_2.

The apparent transmittance is calculated as

$$\tau_a'(\nu)=I(\nu)/I_0'(\nu)\,, \tag{8}$$

where $I(\nu)$ is the observed intensity at wavenumber ν(cm^{-1}).

Comparing $\tau_a'(\nu)$ with $\tau_a(\nu)$ in the curve of growth, we can deduce the total amount of N_2O in the ray path of sunlight. The average N_2O mixing ratio was calculated in terms of the ratio of total amount of N_2O to total air molecules in the ray path of sunlight. Figure 6 shows the average N_2O mixing ratios deduced from the data from April to August in 1983.

The deduced values largely depend on the solar zenith angle (SZA) in particular for SZA>85°. This may originate from a wrong set of constant pressure and temperature. To improve this, we calculate the effective pressure and temperature from the radiosonde data (see Fig. 7, JAPAN METEOROLOGICAL AGENCY, 1985) as weighted by the N_2O abundance along the solar ray path considering atmospheric refraction. The upper part of the model atmosphere, where no data of radiosonde are available,

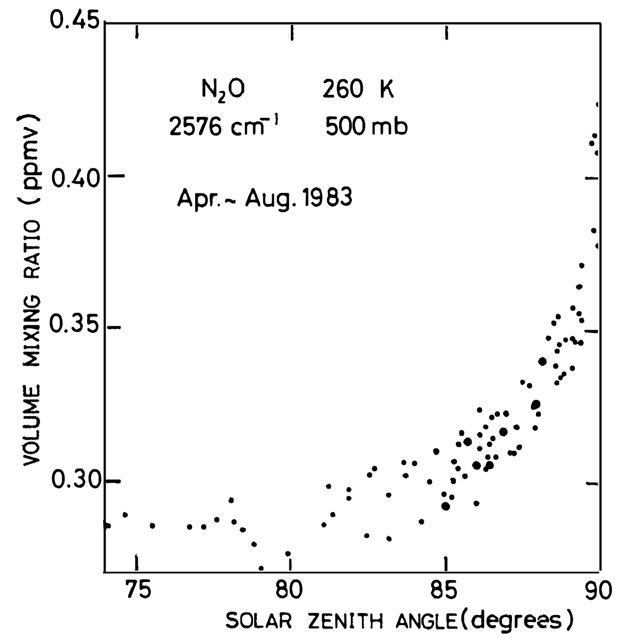

Fig. 6. The N_2O volume mixing ratio averaged over the ray path deduced from the application of a uniform atmosphere of constant 500 mb and 260 K. SZA<90° and the data were obtained from 2 April to 23 August 1983. The double points are shown as large circle.

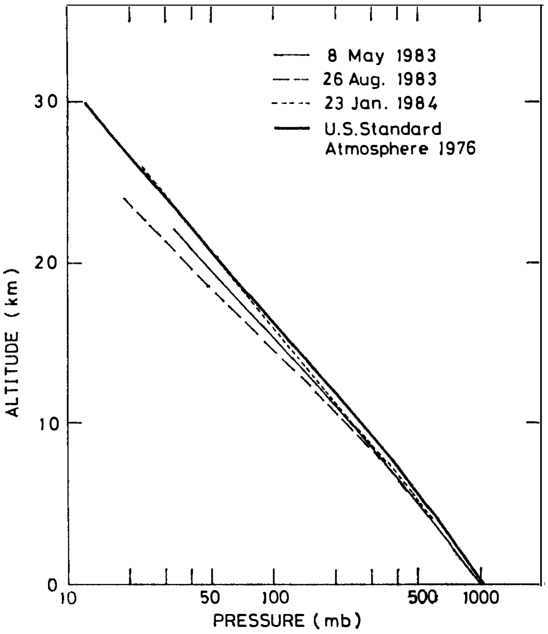

Fig. 7a.

Fig. 7. Four radiosonde data and the U. S. Standard Atmosphere, 1976. (a) Pressure profiles and (b) temperature profiles.

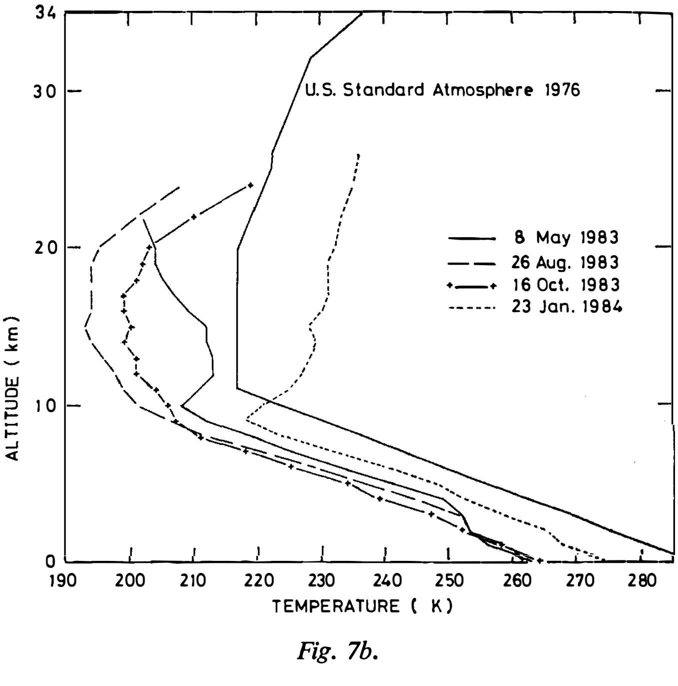

Fig. 7b.

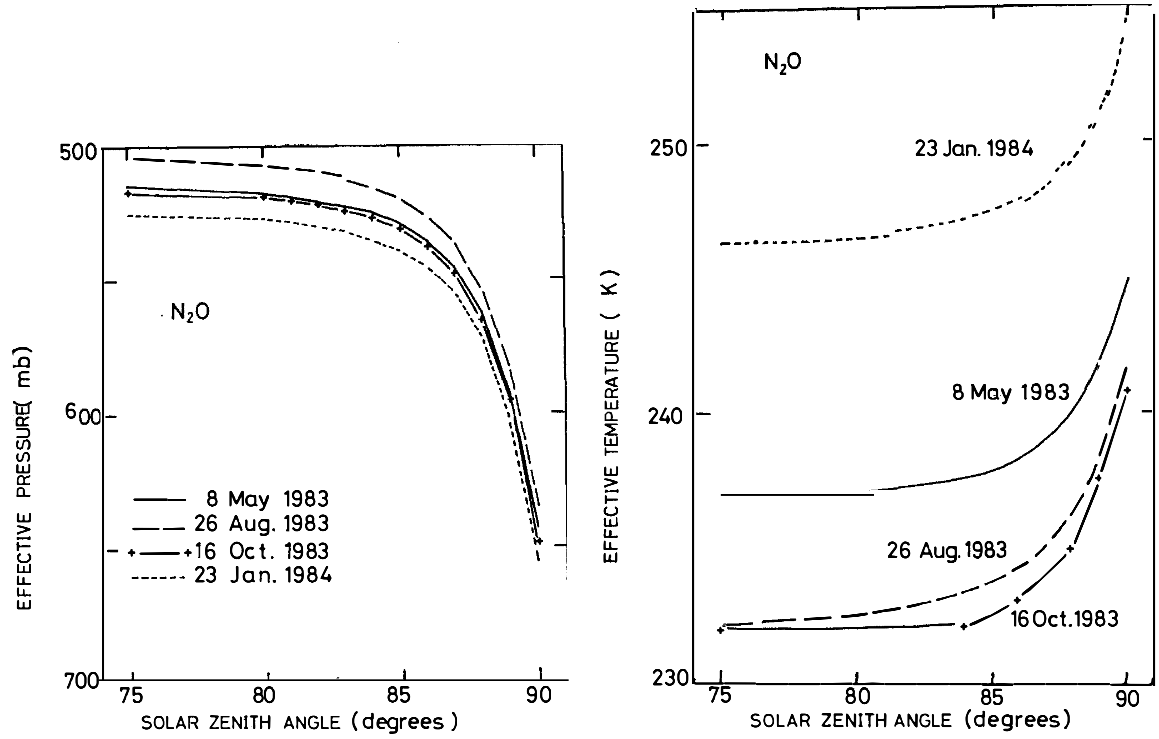

Fig. 8. Effective pressure and temperature versus solar zenith angle calculated from the radiosonde data at Syowa Station.

was taken from the U. S. Standard Atmosphere, 1976. In Fig. 8 is shown how the effective pressure and temperature vary with SZA.

The synthetic spectra were calculated again using the effective pressure and temperature. The volume mixing ratios averaged along the ray path are deduced and shown in Fig. 9. Comparing Figs. 6 and 9, the situation is improved and the points at SZA $<85°$ imply an average mixing ratio of 270 ppbv; yet there is a systematic deviation of the mixing ratio on SZA, especially in the case of SZA$>85°$.

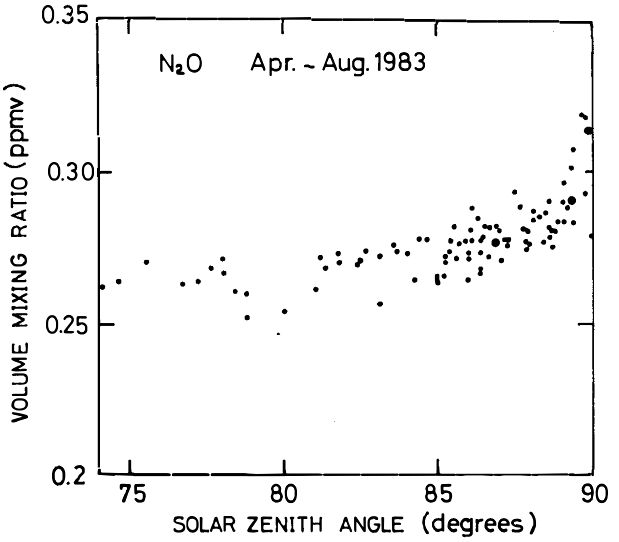

Fig. 9. Same as Fig. 6 except for the case with the effective pressure and temperature calculated from the radiosonde data on 8 May 1983 (see Fig. 8).

3.2. *Multi-layer analysis*

Multi-layer analysis was made with the model atmospheres which have 40 uniform layers of 1 km thickness below a height of 40 km and three uniform layers with a larger thickness above a height of 40 km. In the altitude region, where meteorological radiosonde data can be available, four radiosonde data were selected as the typical cases in the year (see Fig. 7). The U. S. Standard Atmosphere, 1976 was adopted to the upper part of the model atmosphere where no radiosonde data can be available. The pressure profile was shifted so as to agree with the radiosonde data. Interpolated values were adopted to the temperature profile in the altitude range below the height of 35 km and above the height where the radiosonde reached.

The transmittance $\tau(\nu)$ was calculated as

$$\tau(\nu)=\exp\{-\sum_{i=1}^{43} k_i(\nu)\rho_i l_i\} * \text{(slit function)}, \tag{9}$$

where the suffix i means the number of layer, and $k_i(\nu)$ (molecule^{-1} cm^2), ρ_i (molecule/cm^3) and l_i (cm) are the absorption coefficient, the number density of N_2O and the sunlight path length in the i-th layer, respectively. The apparent transmittance, represented by eq. (4) was calculated in terms of eq. (9), assuming the standard N_2O profile as shown in Fig. 3 with its magnitude proportional to the tropospheric N_2O mixing ratios of 216, 270 and 324 ppbv, respectively. Figure 10 shows the calculated curves of the apparent transmittance versus SZA for the period of April, May, September and October in 1983, along with the observed ones by the solid dots.

Throughout the year, the typical N_2O mixing ratio fitted to the observation is

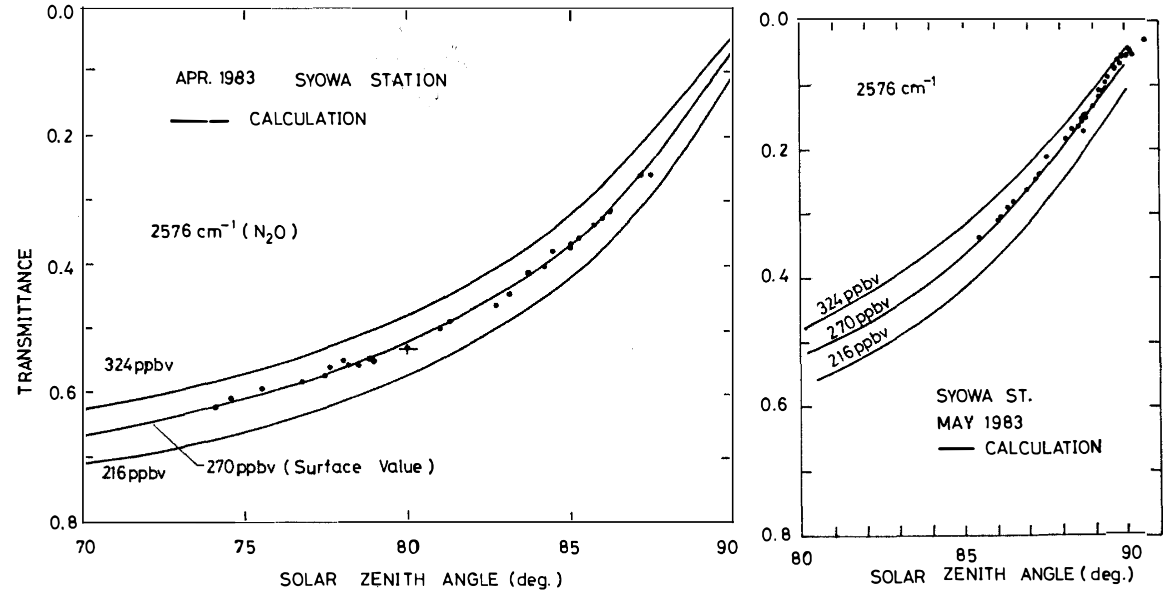

Fig. 10a. *Fig. 10b.*

Fig. 10. Transmittance at 2576 cm^{-1} observed (shown by the solid dots) and calculated (shown by the curves) as a function of solar zenith angle, in (a) April 1983, (b) May 1983, (c) September 1983 and (d) October 1983. The typical accuracy is shown as the cross in Fig. 10a for the case of April, May and October in 1983 and as that in Fig. 10c for the case of September 1983.

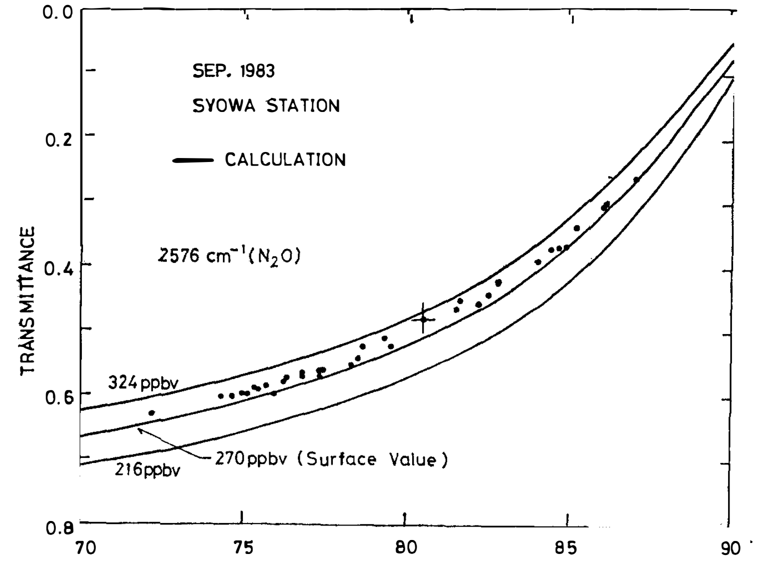

Fig. 10c.

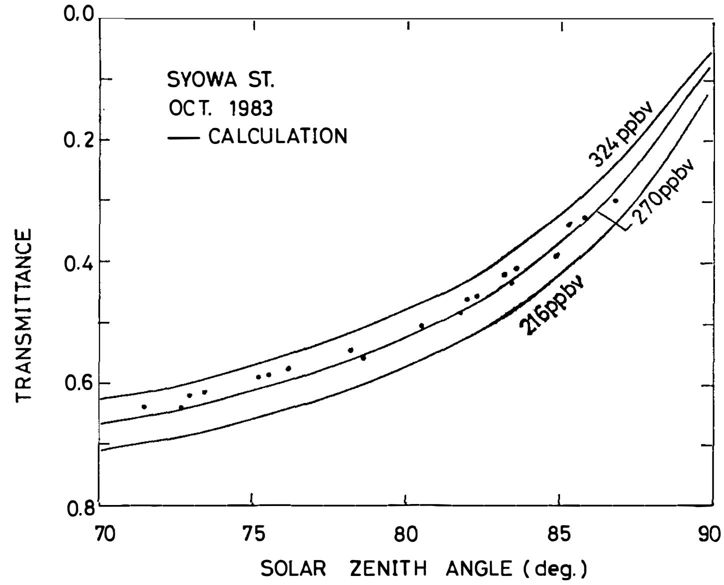

Fig. 10d.

270 ppbv, but in spring of the southern hemisphere, *i.e.*, in September and October, the N_2O mixing ratio appears to be dispersive with its average being higher than 270 ppbv. This seasonal change is similar to that observed by GOODY (1969) with the spectrographic technique in the northern hemisphere.

4. Discussion

The gas-chromatographic technique has exhibited the N_2O mixing ratio being close to 300 ppbv. WEISS (1981) obtained 299.2±0.2 ppbv at the South Pole in 1978, ROBINSON and BAMESBERGER (1983) did 300.3–301.2 ppbv at Palmer Station in 1982, and HIROTA *et al.* (1985) did the average of 302 ppbv at Syowa Station from October 1982 to February 1983. On the other hand, GOLDMAN *et al.* (1983) made the spectrosocopic measurements of the N_2O absorption line at 1248.697 cm^{-1} with a high resolution and to get the tropospheric N_2O mixing ratio of 283–310 ppbv depending on their model distribution of N_2O and best-fitted value of 302 ppbv. All of these values are larger than 270 ppbv of our preliminary result and several explanations are possible. Since the spectroscopic technique uses the sunlight as a radiation source, it measures the total effect of the molecular absorption, including the local effect, in the whole ray path of sunlight, and the deduced mixing ratio is sensitive to the model N_2O distribution. Therefore, we should make a more careful analysis based on the radiosonde data. The altitude of tropopause is an important factor because it seems to be a boundary of airs which contain different amounts of N_2O. Another source of error in the deduced N_2O content is the assumed baseline of zero absorption. SUSSKIND and SEARL (1978) found the continuum absorption in the far wings of 4.3 μm CO_2 absorption lines and the (1,0) fundamental band of N_2 on the synthetic atmospheric transmittance spectra near 4.0 μm. The continuum absorption makes the assumption of linearity of eq. (7) difficult and causes an error in the deduced N_2O content.

The multi-layer analysis seems to give a N_2O volume mixing ratio independent of the zenith angle, and yet it gives a systematic increase around SZA$\sim$90° in the case of May 1983 just before the polar night (Fig. 10b). There are two possible explanations for this increase in May. One is due to a real increase of the total N_2O in late autumn, although there was no indication of increase from the gas-chromatographic measurement in the surface air (HIROTA *et al.*, 1985; ROBINSON and BAMESBERGER, 1983). Another is due to the influence of the continuum absorption in the 4 μm region, which is thought to be effective when SZA is close to 90°.

We will make the more detailed analysis including these effects in the near future.

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