

# INFRARED MEASUREMENTS OF TOTAL NITROUS OXIDE AT TSUKUBA

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**Abstract:** From measurements of transmittance in the  $3.9\ \mu\text{m}$  band ( $2525\text{--}2600\ \text{cm}^{-1}$ ) of  $\text{N}_2\text{O}$  to solar radiation, the equivalent width is obtained. Combining these measurements with calculations using a one-layer model, the total amount of  $\text{N}_2\text{O}$  in a vertical column is estimated to be  $6.48 \times 10^{18}$  molec.  $\text{cm}^{-2}$ . A simpler method using the transmittances at  $2554.6$  and  $2575.0\ \text{cm}^{-1}$  gives practically the same result for the total amount of  $\text{N}_2\text{O}$ .

## 1. Introduction

Nitrous oxide ( $\text{N}_2\text{O}$ ) is a permanent constituent of the earth's atmosphere. This gas is transported into the stratosphere, where it is decomposed by photolysis and reaction with  $\text{O}(^1\text{D})$ . This process is thought to be the dominant source of stratospheric nitric oxide (NO). Nitric oxide acts as a catalyst for recombination of odd oxygen. Thus a change of the amount of  $\text{N}_2\text{O}$  has a significant influence on the chemistry of the ozone layer (CRUTZEN, 1971; MCELROY and MCCONNELL, 1971). Nitrous oxide has an effect on the earth's radiative balance through the absorption of infrared radiation (WANG *et al.*, 1976; DONNER and RAMANATHAN, 1980).

There is uncertainty concerning the source and sink strengths, lifetime and anthropogenic effect of atmospheric  $\text{N}_2\text{O}$ . The only currently established sink is photolysis in the stratosphere with additional loss due to reaction with  $\text{O}(^1\text{D})$  (MCELROY, 1980). The magnitude of the global source is uncertain. It has become apparent that  $\text{N}_2\text{O}$  is produced primarily by nitrifying bacteria in soils (BREITENBECK *et al.*, 1980; LIPSCHULTZ *et al.*, 1981). The role of the ocean as a source or sink is not clear.

There is evidence for a steady increase and seasonal variation of  $\text{N}_2\text{O}$  in surface air (WEISS, 1981; KHALIL and RASMUSSEN, 1983). It is important to know if these variations can be seen for the total amount of  $\text{N}_2\text{O}$  in a vertical column. GOODY (1969) obtained the seasonal variation of total  $\text{N}_2\text{O}$  in a vertical column from the ground-based infrared solar spectra, but SCHÜTZ *et al.* (1970) suggested a global increase rather than a seasonal variation from their measurements by a gas chromatographic method and GOODY's (1969) results.

In this report we describe a method to measure the total amount of  $\text{N}_2\text{O}$  from ground-based infrared solar spectra and the results obtained at Tsukuba.

## 2. Instrumentation

The infrared solar spectrum is obtained using the Fourier transform technique. The system consists of a solar tracker used to keep solar radiation on the entrance window and a Michelson interferometer (IF-3) equipped with a Hg-Cd-Te detector cooled by liquid nitrogen. The instrument covers the spectral range from 2 to 15  $\mu\text{m}$  and has a spectral resolution of  $0.5\text{ cm}^{-1}$  at best (restricted by the maximum scan length of 1.0 cm). Typically 30 to 50 scans are collected at one time and are coadded onto a single interferogram, and a spectrum is calculated by minicomputer (MAKINO *et al.*, 1982).

## 3. Method of Analysis

### 3.1. Equivalent width method

The (2 0 0) band of  $\text{N}_2\text{O}$  at  $3.9\ \mu\text{m}$  (band center is  $2563.3\text{ cm}^{-1}$ ) was selected. An example of the observed spectrum is shown in Fig. 1. The equivalent width (or absorption area) for the spectral range  $2525\text{--}2600\text{ cm}^{-1}$  is obtained from this spectrum. As the absorption of water vapor and carbon dioxide overlaps in this spectral range, the observed equivalent width  $EW^{\text{obs}}$  is given by,

$$EW^{\text{obs}} = \int_{\nu_1}^{\nu_2} (1 - \tau_{\text{N}_2\text{O}} \cdot \tau_{\text{H}_2\text{O}} \cdot \tau_{\text{CO}_2}) d\nu, \quad (1)$$

where,  $\tau_{\text{N}_2\text{O}}$ ,  $\tau_{\text{H}_2\text{O}}$  and  $\tau_{\text{CO}_2}$  are the transmittances of  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , respectively,  $\nu$  is wave number ( $\text{cm}^{-1}$ ),  $\nu_1 = 2525.0\text{ cm}^{-1}$  and  $\nu_2 = 2600.0\text{ cm}^{-1}$ . Equivalent widths of  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are given by,

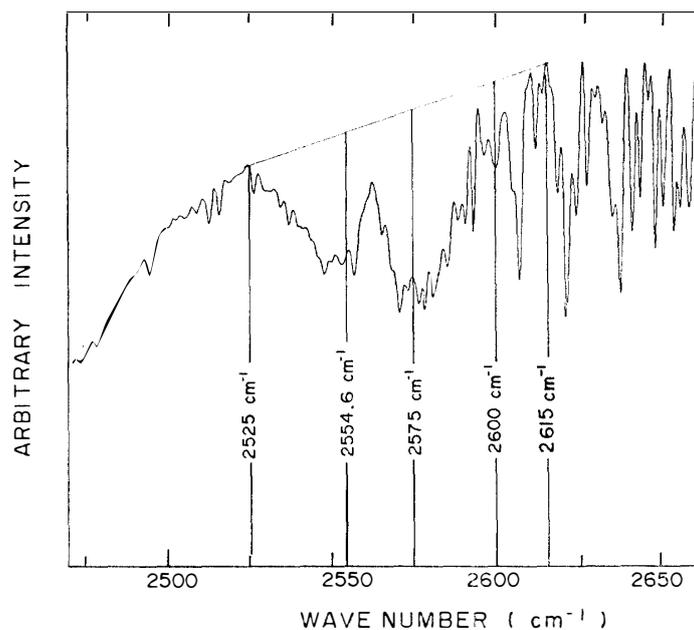


Fig. 1. Spectral transmittance for  $3.90\ \mu\text{m}$  band of  $\text{N}_2\text{O}$  observed on 5 April 1983 at Tsukuba.

$$\left. \begin{aligned} EW(\text{N}_2\text{O}) &= \int_{\nu_1}^{\nu_2} (1 - \tau_{\text{N}_2\text{O}}) d\nu, \\ EW(\text{H}_2\text{O}) &= \int_{\nu_1}^{\nu_2} (1 - \tau_{\text{H}_2\text{O}}) d\nu, \\ EW(\text{CO}_2) &= \int_{\nu_1}^{\nu_2} (1 - \tau_{\text{CO}_2}) d\nu. \end{aligned} \right\} \quad (2)$$

Using these relations eq. (1) is written as (abbreviating wave number limits  $\nu_1$  and  $\nu_2$ ),

$$\begin{aligned} EW^{\text{obs}} &= \int (1 - \tau_{\text{N}_2\text{O}}) d\nu + \int \tau_{\text{N}_2\text{O}}(1 - \tau_{\text{H}_2\text{O}} \cdot \tau_{\text{CO}_2}) d\nu \\ &= EW(\text{N}_2\text{O}) + \bar{\tau}_{\text{N}_2\text{O}} \int (1 - \tau_{\text{H}_2\text{O}} \cdot \tau_{\text{CO}_2}) d\nu \\ &= EW(\text{N}_2\text{O}) + \bar{\tau}_{\text{N}_2\text{O}} \left\{ \int (1 - \tau_{\text{H}_2\text{O}}) d\nu + \bar{\tau}_{\text{H}_2\text{O}} \int (1 - \tau_{\text{CO}_2}) d\nu \right\} \\ &= EW(\text{N}_2\text{O}) + \bar{\tau}_{\text{N}_2\text{O}} \cdot EW(\text{H}_2\text{O}) + \bar{\tau}_{\text{N}_2\text{O}} \cdot \bar{\tau}_{\text{H}_2\text{O}} \cdot EW(\text{CO}_2). \end{aligned} \quad (3)$$

$\bar{\tau}_{\text{N}_2\text{O}}$  and  $\bar{\tau}_{\text{H}_2\text{O}}$  are defined by,

$$\bar{\tau}_{\text{N}_2\text{O}} = \frac{\int \tau_{\text{N}_2\text{O}}(1 - \tau_{\text{H}_2\text{O}} \cdot \tau_{\text{CO}_2}) d\nu}{\int (1 - \tau_{\text{H}_2\text{O}} \cdot \tau_{\text{CO}_2}) d\nu}, \quad \bar{\tau}_{\text{H}_2\text{O}} = \frac{\int \tau_{\text{H}_2\text{O}}(1 - \tau_{\text{CO}_2}) d\nu}{\int (1 - \tau_{\text{CO}_2}) d\nu}. \quad (4)$$

From eq. (3) the equivalent width of  $\text{N}_2\text{O}$   $EW(\text{N}_2\text{O})$  is estimated and then the corresponding column density of  $\text{N}_2\text{O}$  is derived assuming a one-layer atmospheric model with the effective pressure and the temperature.

Constant mixing profiles are assumed for  $\text{N}_2\text{O}$  and  $\text{CO}_2$ , and the effective pressure  $P_E$  over the observed optical path is assumed to be 500 mb from the Curtis-Godson approximation (GOODY, 1964). The effective pressure of water vapor is assumed to be 800 mb from the 5-year average vertical profile obtained by radiosonde data at Tateno. For the effective temperature for the path we adopt the temperature at 500 mb for  $\text{N}_2\text{O}$  and  $\text{CO}_2$  and at 800 mb for  $\text{H}_2\text{O}$  obtained from radiosonde data.

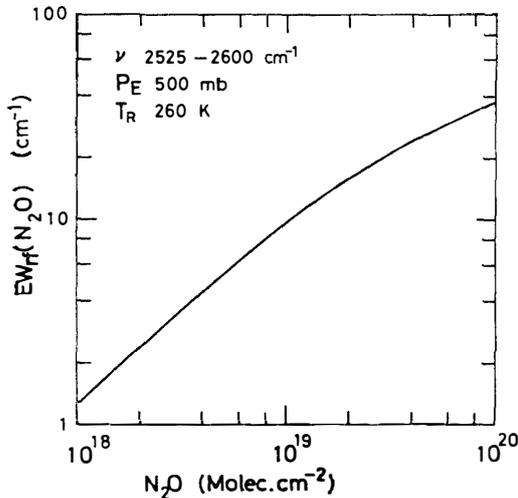


Fig. 2. Equivalent width  $EW_{\text{rf}}(\text{N}_2\text{O})$  for  $3.90 \mu\text{m}$  band of  $\text{N}_2\text{O}$ , calculated by one-layer model with effective pressure  $P_E=500 \text{ mb}$  and reference temperature  $T_R=260 \text{ K}$ .

Transmittances for  $N_2O$ ,  $H_2O$  and  $CO_2$  are estimated by line-by-line calculations using the line parameters compiled by MCCLATCHEY *et al.* (1973) for a layer with the effective pressure and reference temperature. Corresponding values for effective

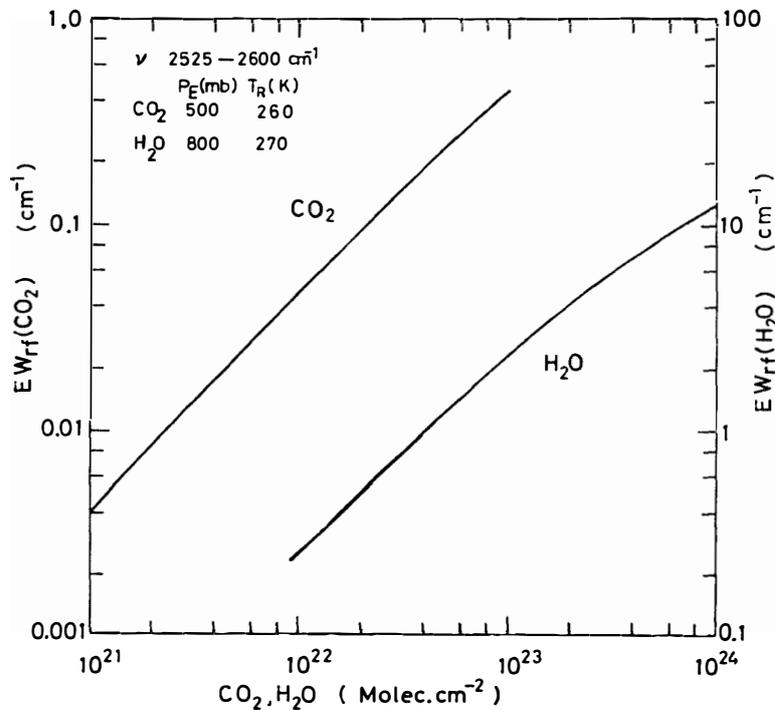


Fig. 3. Equivalent widths of  $CO_2$   $EW_{rf}(CO_2)$  and water vapor  $EW_{rf}(H_2O)$  for  $3.90 \mu m$  band of  $N_2O$ . Effective pressure  $P_E$  and reference temperature  $T_R$  are 500 mb and 260 K, respectively for  $CO_2$ ; 800 mb and 270 K, respectively for water vapor.

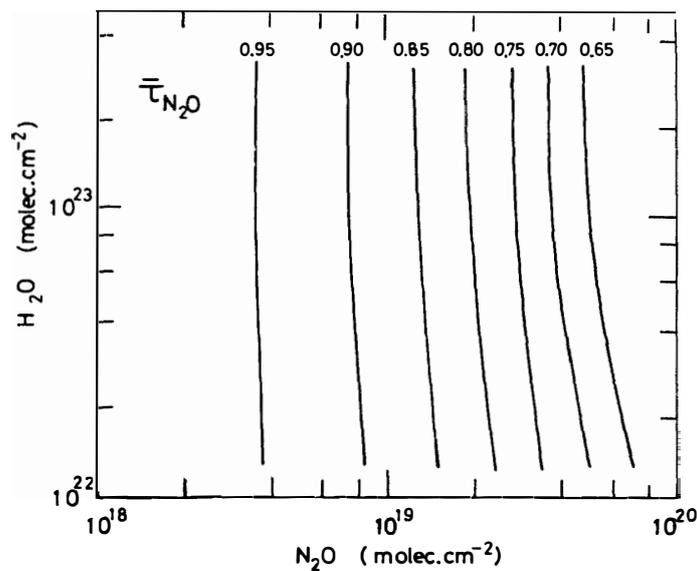


Fig. 4.  $\tau_{N_2O}$  is determined from the amount of  $N_2O$  and  $H_2O$ . The effect of temperature is negligible.

temperature (the observed temperature for individual case) are estimated from the reference temperature. For  $N_2O$  and  $CO_2$  the reference temperature is taken to be 260K and for  $H_2O$  to be 270K. These are close to the average temperature observed at 500 and 800 mb, respectively.

The equivalent width of  $N_2O$   $EW_{rf}(N_2O)$  which is estimated from eq. (2) with the effective pressure  $P_E=500$  mb and reference temperature  $T_R=260$  K is shown in Fig. 2. Equivalent widths of  $CO_2$   $EW_{rf}(CO_2)$  and water vapor  $EW_{rf}(H_2O)$  for the reference temperatures are shown in Fig. 3. It is seen that the equivalent width of  $H_2O$  is one order and that of  $CO_2$  is two orders smaller than that of  $N_2O$  in most cases (the total column densities of  $N_2O$ ,  $H_2O$  and  $CO_2$  are  $\sim 10^{19}$ ,  $\sim 10^{23}$  and  $\sim 10^{22}$  molec.  $cm^{-2}$ , respectively).

$\bar{\tau}_{N_2O}$  is a function of the amounts of  $N_2O$  and  $H_2O$ , and the reference temperatures of  $N_2O$  and  $H_2O$ . The effect of temperature is small.  $\bar{\tau}_{N_2O}$  changes less than 1% for a temperature change of 10K, so  $\bar{\tau}_{N_2O}$  is approximated by the amounts of  $N_2O$  and  $H_2O$  as shown in Fig. 4. It is seen that the variation of  $\bar{\tau}_{N_2O}$  with the amount of  $H_2O$  is very small. The effects of  $CO_2$  amount and temperature on  $\bar{\tau}_{H_2O}$  are very small, so  $\bar{\tau}_{H_2O}$  is approximated by the amount of  $H_2O$  as shown in Fig. 5.

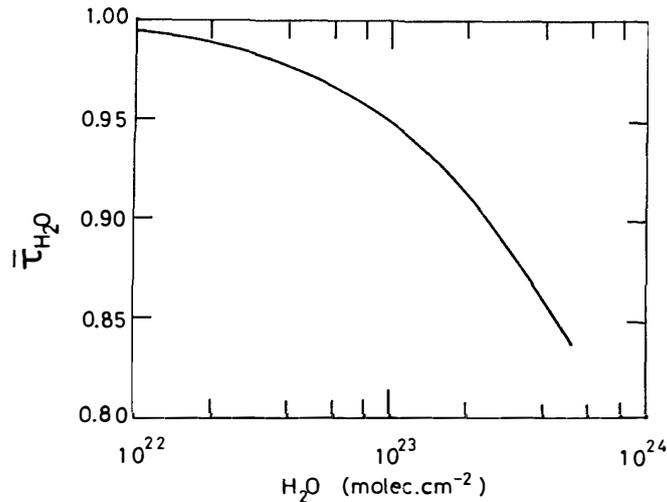


Fig. 5.  $\bar{\tau}_{H_2O}$  is determined from the amount of  $H_2O$ . The effect of temperature is negligible.

### 3.2. Estimation of total amount of $N_2O$

To estimate the total column density of  $N_2O$  along the optical path from eq. (3) it is necessary to know  $EW^{obs}$ ,  $EW(CO_2)$ ,  $EW(H_2O)$ ,  $\bar{\tau}_{N_2O}$  and  $\bar{\tau}_{H_2O}$ .

To estimate  $EW^{obs}$  from the observed spectrum as shown in Fig. 1, the transmittance of 100% is approximated by a straight line connecting the peak transmittances at 2525.0 and 2615.0  $cm^{-1}$ , allowing for the absorption by  $N_2O$ ,  $H_2O$  and  $CO_2$ . At 2615.0  $cm^{-1}$  the transmittance is larger than 0.996 for the observed maximum amounts of  $N_2O$ ,  $H_2O$  and  $CO_2$ , so no corrections are made at this wave number. At 2525.0  $cm^{-1}$  the effect of  $H_2O$  and  $CO_2$  is negligible, as their effect is less than 1%. The effect of  $N_2O$  cannot be neglected, and the transmittance line of 100% is corrected (less than 8%) by estimating the transmittance of  $N_2O$ .

The volume mixing ratio of  $\text{CO}_2$  is assumed to be  $3.22 \times 10^{-4}$ , so the total amount along the optical path is estimated as a function of solar zenith angle. As the temperature change of  $EW_{\text{rf}}(\text{CO}_2)$  is very small  $EW(\text{CO}_2)$  is approximated by  $EW_{\text{rf}}(\text{CO}_2)$ .

The total amount of water vapor along the optical path is estimated by comparing the observed transmittance at  $5809.6 \text{ cm}^{-1}$  with the transmittance calculated from the line parameters compiled by McCLATCHEY *et al.* (1973) assuming a one-layer model as adopted before. The equivalent width  $EW(\text{H}_2\text{O})$  for the observed temperature is estimated from  $EW_{\text{rf}}(\text{H}_2\text{O})$  and the temperature difference as,

$$EW(\text{H}_2\text{O}) = EW_{\text{rf}}(\text{H}_2\text{O})\{1 + C_1 \cdot \Delta T_1\},$$

where  $\Delta T_1 = T_{\text{obs}} - T_{\text{R}}$ .  $T_{\text{obs}}$  is the observed temperature at 800 mb and  $T_{\text{R}} = 270 \text{ K}$ .  $C_1$  is given by,

$$C_1 = \frac{\partial EW_{\text{rf}}(\text{H}_2\text{O})}{\partial T} \cdot \frac{1}{EW_{\text{rf}}(\text{H}_2\text{O})} \Big|_{T=T_{\text{R}}},$$

where  $T$  is the temperature.  $C_1$  is evaluated at  $T = T_{\text{R}}$  and given in Fig. 6.

The equivalent width of  $\text{N}_2\text{O}$  for the reference temperature  $EW_{\text{rf}}(\text{N}_2\text{O})$  is estimated from eq. (3). The total amount of  $\text{N}_2\text{O}$  in the optical path for the reference temperature  $W_{\text{rf}}(\text{N}_2\text{O})$  is estimated from  $EW_{\text{rf}}(\text{N}_2\text{O})$ . As  $\bar{\tau}_{\text{N}_2\text{O}}$  depends on the amount of  $\text{N}_2\text{O}$ ,  $W_{\text{rf}}(\text{N}_2\text{O})$  is obtained by an iterative method. Then the total amount of  $\text{N}_2\text{O}$  for the effective temperature (or observed temperature at 500 mb)  $W(\text{N}_2\text{O})$  is obtained from,

$$W(\text{N}_2\text{O}) = W_{\text{rf}}(\text{N}_2\text{O})\{1 + C_2 \cdot \Delta T_2\},$$

where  $\Delta T_2 = T_{\text{obs}} - T_{\text{R}}$ .  $T_{\text{obs}}$  is the observed temperature at 500 mb.  $C_2$  is given by,

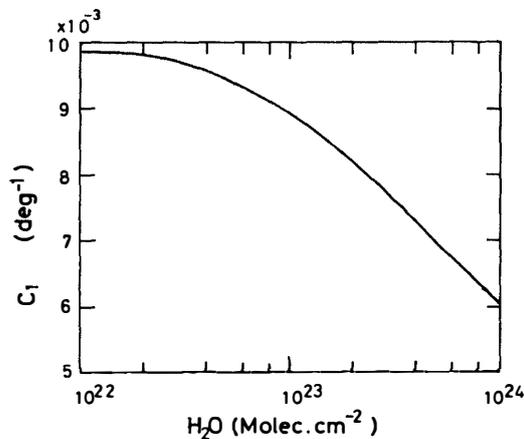


Fig. 6. Change of  $C_1$  with the amount of  $\text{H}_2\text{O}$ .

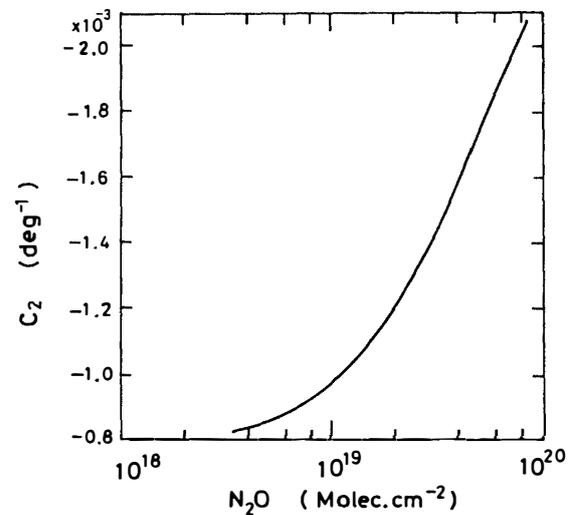


Fig. 7. Change of  $C_2$  with the amount of  $\text{N}_2\text{O}$ .

$$C_2 = \frac{\partial W_{rf}(N_2O)}{\partial T} \cdot \frac{1}{W_{rf}(N_2O)} \Big|_{T=T_R}$$

$C_2$  is evaluated at  $T=T_R$  and shown in Fig. 7.

#### 4. Results and Discussion

The results of our measurements during spring 1983 at Tsukuba are shown in Fig. 8 as a function of the day of the year. The average total amount of  $N_2O$  in a vertical column is  $6.48 \times 10^{18}$  molec.  $cm^{-2}$  with a standard deviation of  $0.46 \times 10^{18}$  molec.  $cm^{-2}$ . The mean tropospheric volume mixing ratio is estimated to be 0.326 ppm from the assumption that the mixing ratio is uniform below 150 mb, above which the mixing ratio decreases exponentially with scale height 4.00 km. This value is close to the tropospheric mixing ratio measured by GC-EC technique, *e.g.*, 0.300 ppm (WEISS, 1981), 0.305 ppm (KHALIL and RASMUSSEN, 1983) and 0.306 ppm (HIROTA *et al.*, 1984).

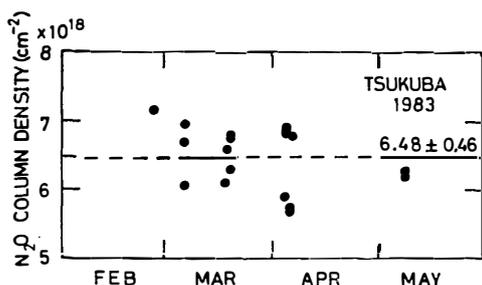


Fig. 8. Total amount of  $N_2O$  in a vertical column over Tsukuba obtained by the equivalent width method plotted as a function of the day of the year. Dashed line shows the average.

Total amounts of  $N_2O$  are plotted as a function of the column amount of water vapor in Fig. 9. It is seen that the total amount of  $N_2O$  is independent of the amount of water vapor, which means that the effect of water vapor is correctly evaluated. The variation of the total amount of  $N_2O$  with air mass is shown in Fig. 10, which shows no discernible relation between them.

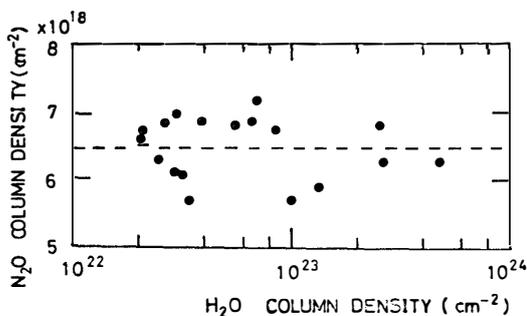


Fig. 9. Similar to Fig. 8, but plotted as a function of the total amount of water vapor in a vertical column.

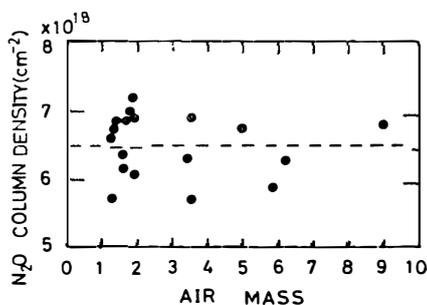


Fig. 10. Similar to Fig. 8, but plotted as a function of air mass.

GOODY (1969) has measured the total amount of  $N_2O$  by selective spectrographic technique in the  $3.9 \mu m$  band. His result shows that the mean total amount in a vertical column is close to  $0.250 \text{ atm-cm}$  ( $6.7 \times 10^{18} \text{ molec. cm}^{-2}$ ), and from the middle of January to the end of March the amount is significantly higher, rising to  $0.30 \text{ atm-cm}$  ( $8.1 \times 10^{18} \text{ molec. cm}^{-2}$ ). GOODY's mean value is higher than ours by about 3%.

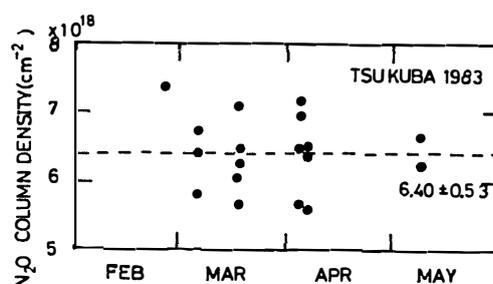


Fig. 11. Similar to Fig. 8, but obtained from the transmittances at  $2554.6$  and  $2575.0 \text{ cm}^{-1}$ .

Another simple method to estimate the total amount of  $N_2O$  from the transmittances at  $2554.6$  and  $2575.0 \text{ cm}^{-1}$  was examined. At these wave numbers the deviation of the transmittance due to instrument resolution (within the range  $0.5$  to  $1.0 \text{ cm}^{-1}$ ) and water vapor is small. Observed transmittances are compared with calculated transmittances from the one-layer model as adopted in the equivalent width method. The vertical amounts of  $N_2O$  are in good agreement with those obtained from the equivalent width method as shown in Fig. 11. The average value is  $6.40 \pm 0.53 \times 10^{18} \text{ molec. cm}^{-2}$ , which is in good agreement with the value obtained from the equivalent width method but with a slightly larger standard deviation.

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