

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 N_2O to solar radiation, the equivalent width is obtained. Combining these measurements with calculations using a one-layer model, the total amount of N_2O in a vertical column is estimated to be $6.48 \times 10^{18} \text{ molec. cm}^{-2}$. A simpler method using the transmittances at 2554.6 and 2575.0cm^{-1} gives practically the same result for the total amount of N_2O .

1. Introduction

Nitrous oxide (N_2O) 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 N_2O 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 N_2O . 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 N_2O 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 N_2O 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 N_2O in a vertical column. GOODY (1969) obtained the seasonal variation of total N_2O 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 N_2O 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 μm and has a spectral resolution of 0.5 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 N_2O at $3.9\text{ }\mu\text{m}$ (band center is 2563.3 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^{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 τ_{CO_2} are the transmittances of N_2O , H_2O and CO_2 , respectively, ν is wave number (cm^{-1}), $\nu_1 = 2525.0\text{ cm}^{-1}$ and $\nu_2 = 2600.0\text{ cm}^{-1}$. Equivalent widths of N_2O , H_2O and CO_2 are given by,

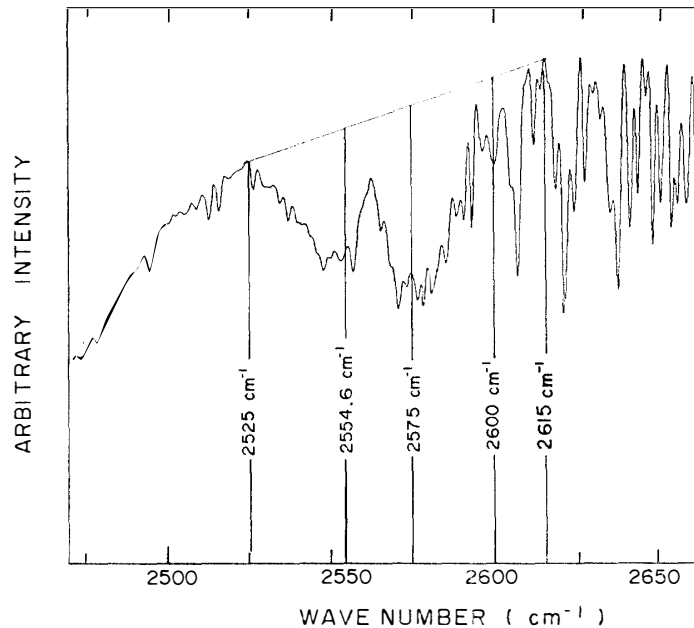


Fig. 1. Spectral transmittance for $3.90\text{ }\mu\text{m}$ band of N_2O observed on 5 April 1983 at Tsukuba.

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

Using these relations eq. (1) is written as (abbreviating wave number limits ν_1 and ν_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 N_2O $EW(\text{N}_2\text{O})$ is estimated and then the corresponding column density of N_2O is derived assuming a one-layer atmospheric model with the effective pressure and the temperature.

Constant mixing profiles are assumed for N_2O and 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 N_2O and CO_2 and at 800 mb for H_2O obtained from radiosonde data.

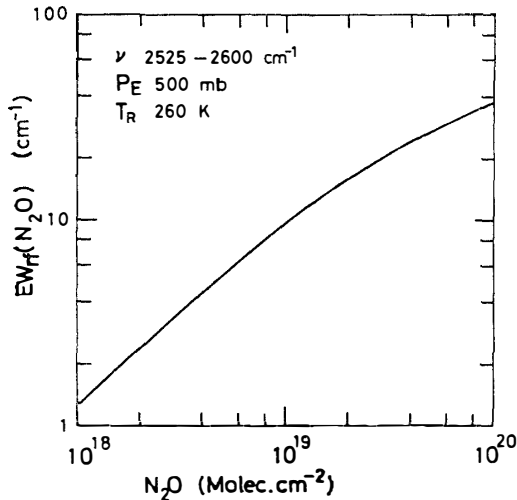


Fig. 2. Equivalent width $EW_{\text{rf}}(\text{N}_2\text{O})$ for $3.90 \mu\text{m}$ band of N_2O , calculated by one-layer model with effective pressure $P_E=500 \text{ mb}$ and reference temperature $T_R=260 \text{ K}$.

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

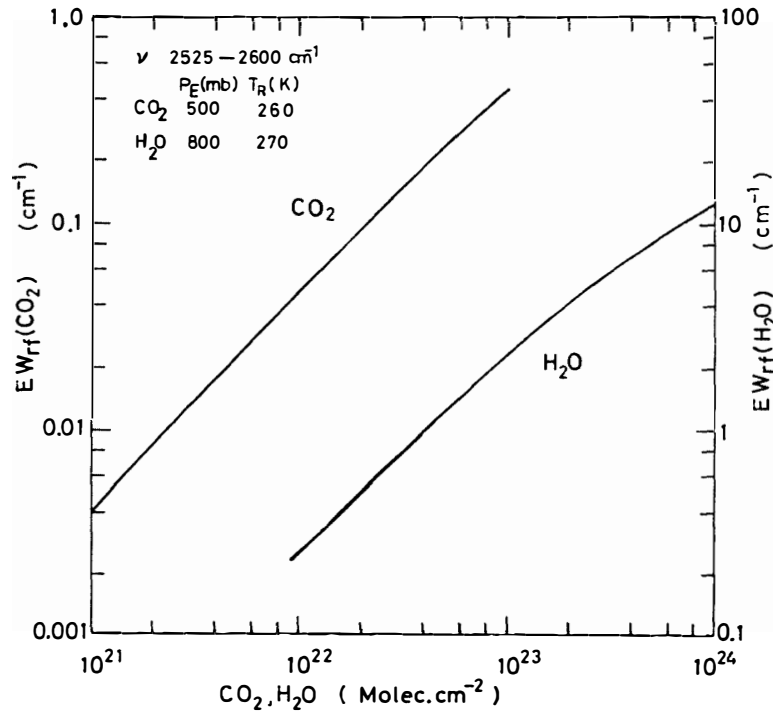


Fig. 3. Equivalent widths of CO_2 $EW_{rf}(CO_2)$ and water vapor $EW_{rf}(H_2O)$ for $3.90 \mu m$ band of N_2O . Effective pressure P_E and reference temperature T_R are 500 mb and 260 K, respectively for CO_2 ; 800 mb and 270 K, respectively for water vapor.

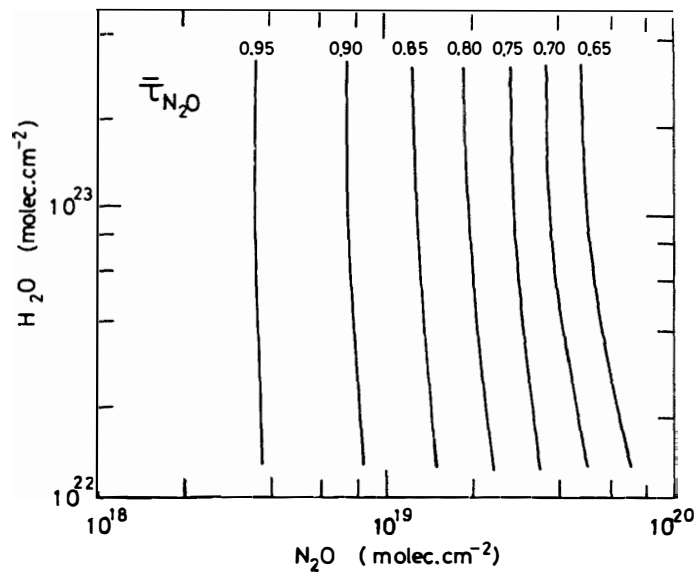


Fig. 4. τ_{N_2O} is determined from the amount of N_2O and H_2O . The effect of temperature is negligible.

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 260 K and for H_2O to be 270 K. These are close to the average temperature observed at 500 and 800 mb, respectively.

The equivalent width of N_2O $EW_{\text{rf}}(\text{N}_2\text{O})$ 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 $EW_{\text{rf}}(\text{CO}_2)$ and water vapor $EW_{\text{rf}}(\text{H}_2\text{O})$ 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).

$\bar{\tau}_{\text{N}_2\text{O}}$ 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. $\bar{\tau}_{\text{N}_2\text{O}}$ changes less than 1% for a temperature change of 10 K, so $\bar{\tau}_{\text{N}_2\text{O}}$ is approximated by the amounts of N_2O and H_2O as shown in Fig. 4. It is seen that the variation of $\bar{\tau}_{\text{N}_2\text{O}}$ with the amount of H_2O is very small. The effects of CO_2 amount and temperature on $\bar{\tau}_{\text{H}_2\text{O}}$ are very small, so $\bar{\tau}_{\text{H}_2\text{O}}$ is approximated by the amount of H_2O as shown in Fig. 5.

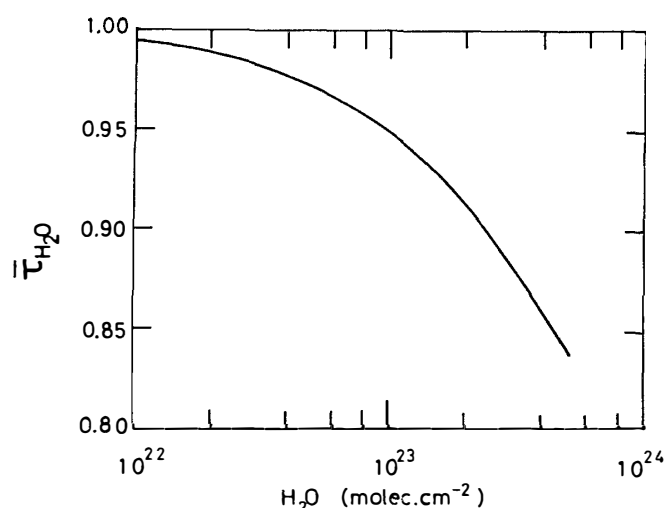


Fig. 5. $\bar{\tau}_{\text{H}_2\text{O}}$ is determined from the amount of H_2O . The effect of temperature is negligible.

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} , $EW(\text{CO}_2)$, $EW(\text{H}_2\text{O})$, $\bar{\tau}_{\text{N}_2\text{O}}$ and $\bar{\tau}_{\text{H}_2\text{O}}$.

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 CO_2 is assumed to be 3.22×10^{-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 cm^{-1} with the transmittance calculated from the line parameters compiled by McCLATCHY *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_{obs} is the observed temperature at 800 mb and $T_{\text{R}} = 270 \text{ K}$. C_1 is given by,

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

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

The equivalent width of N_2O for the reference temperature $EW_{\text{rf}}(\text{N}_2\text{O})$ is estimated from eq. (3). The total amount of N_2O 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 $\bar{\epsilon}_{\text{N}_2\text{O}}$ depends on the amount of N_2O , $W_{\text{rf}}(\text{N}_2\text{O})$ is obtained by an iterative method. Then the total amount of N_2O 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_{obs} is the observed temperature at 500 mb. C_2 is given by,

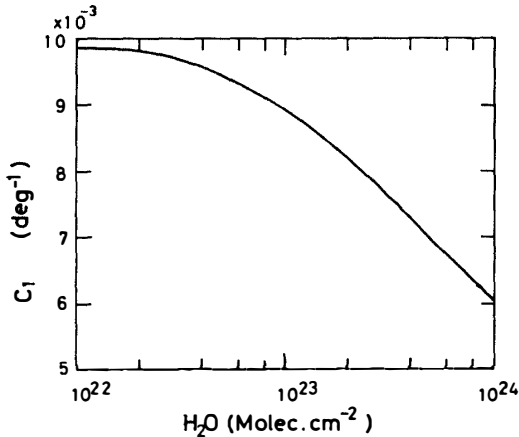


Fig. 6. Change of C_1 with the amount of H_2O .

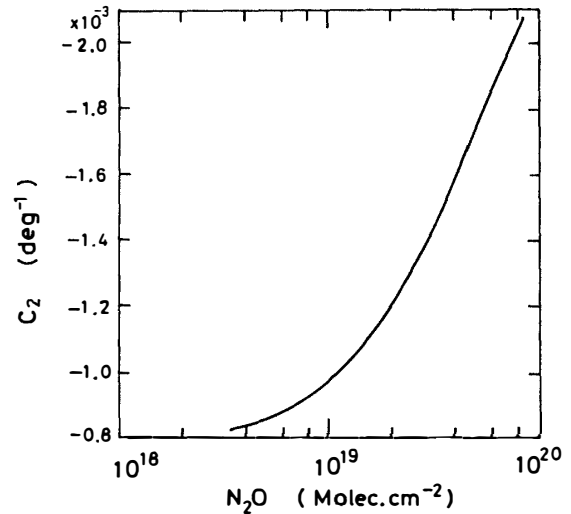


Fig. 7. Change of C_2 with the amount of N_2O .

$$C_2 = \frac{\partial W_{\text{rf}}(\text{N}_2\text{O})}{\partial T} \cdot \frac{1}{W_{\text{rf}}(\text{N}_2\text{O})} \Big|_{T=T_R}.$$

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 $6.48 \times 10^{18} \text{ molec. cm}^{-2}$ with a standard deviation of $0.46 \times 10^{18} \text{ molec. cm}^{-2}$. 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).

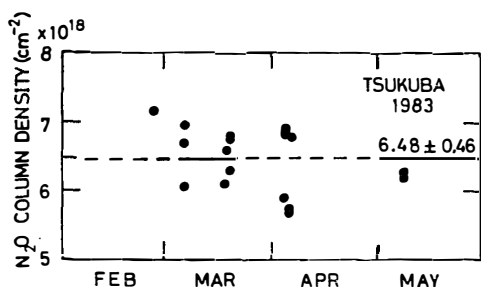


Fig. 8. Total amount of N_2O in a vertical column over Tsukuba obtained by the equivalent width method plotted as a function of the day of the year. Dashed line shows the average.

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.

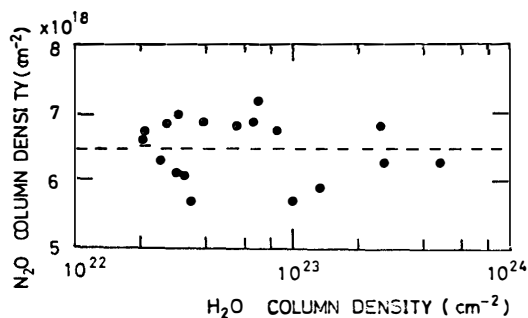


Fig. 9. Similar to Fig. 8, but plotted as a function of the total amount of water vapor in a vertical column.

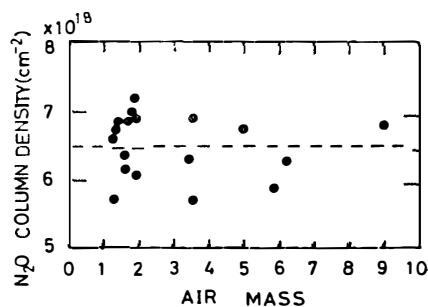


Fig. 10. Similar to Fig. 8, but plotted as a function of air mass.

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

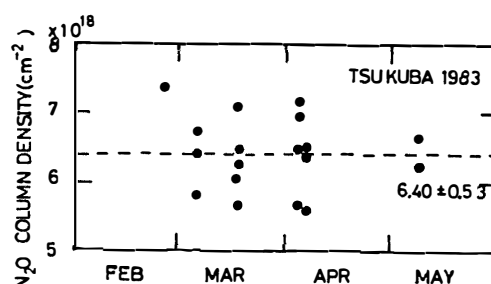


Fig. 11. Similar to Fig. 8, but obtained from the transmittances at 2554.6 and $2575.0\ \text{cm}^{-1}$.

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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