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DERIVATION OF WATER VAPOUR ABSORPTION CROSS-SECTIONS
IN THE RED REGION

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Absorption spectrum in 436 to 448 nm wavelength region gives NO_2 and O_3 column densities (Noxon 1975). This spectrum can also give H_2O column density (Noxon 1975, Syed and Harrison, 1979). The spectrum in the range of 655 to 667 nm contains absorption due to NO_3 and H_2O . Combining the absorption spectra in the wavelength ranges of 436 to 448 and 655 to 667 nm, water vapour absorption cross-sections in the range of 655 to 667 nm have been derived. The average value of absorption cross-sections in this range comes out to be of the order of $2.0 \times 10^{-24} \text{ cm}^2$.

Introduction

Water vapour is one of the most important trace gases in the biosphere whose uptake and release determines the chemical composition of the atmosphere. This species is a strong absorber over a great span of the electromagnetic spectrum. The visible and near-infrared attenuation spectrum of solar radiation in the atmosphere presents identifiable lines from a large number of water vapour absorption bands related to ground state transitions. Those in the visible are relatively weak, whereas those in the near infrared are all rather strong, to such an extent as to cause regions of complete absorption. Other less intense bands are due to polyatomic gases such as NO_2 , NO_3 , O_3 , OCIO , BrO etc.. Attenuation of solar radiation is mainly because of molecular scattering, absorption due to polyatomic gases, in which water vapour has less attenuation but it has significant contribution in the visible region. Hence to calculate the distribution of any minor species by absorption spectroscopy where spectrum contains water vapour absorption, the absorption cross-section of the spectrum must be accurately known. The absolute values of water vapour absorption cross-sections in the range of 655 to 667 nm are not yet known. In the red region, i.e., 645 to 680 nm region, differential absorption cross sections of water vapour have been measured at NASA, Ames Research Center, using multiple pass path lengths as large as 5 km. In that experiment,

water vapour was introduced directly into the cell and the absorption spectrum was recorded. These values are, however, not in absolute unit. Atmospheric water vapour has been used by Solomon et al. (1989) to determine differential absorption cross-section of water vapour. In the present work, absolute values of atmospheric water vapour cross section have been derived.

Experimental technique

We used a McPherson Monochromator of Model 270 (f/6.4, resolution 0.5 nm at 500 nm) with a grating so chosen that appropriate colour filter provided first order light in the wavelength ranges 436 to 448 nm and 655 to 667 nm. R955 Hamamatsu photo-multiplier tube has been used as a detector which has sufficient signal to noise ratio in these regions. All observations had been taken at constant supply voltage 1200 volt. At this voltage, possibility of thermal noise can not be ignored, which has been taken into account by cooling the PMT system upto -20°C . The structure of the PMT housing is such that the wires connected through the PMT are fully isolated from the window system through insulator, by which possibility of spurious modulation of the electrical noise with signal is minimized. Current to voltage converter was used for the output signal of the photo-multiplier. A lock-in amplifier of model SR-530 (Stanford Research System) was used for enhancing the signal to noise ratio. The output of the photo-multiplier was given to a HCL-AT computer through an A/D converter. Monochromator operation was controlled by a computer. All the observations were taken at 0.5 nm resolution. A software has been developed in such a way that a scan of 12 nm range takes 14 seconds. 9 such scans were taken and stored in floppy.

Methodology

This work has two experimental parts. First part corresponds to the scanning of solar spectrum in the blue region and the second part to the red region. Water vapour has absorption at 442.6 nm. The water vapour absorption cross section at 442.6 nm is known and its value is $(3.1 \pm 0.3) \times 10^{-26} \text{ cm}^2$ (Johnston and McKenzie, 1984) at 0.5 nm resolution. We scan the zenith solar spectrum in wavelength

region 436 to 448 nm at about 88° solar zenith angle. Another solar spectrum has been taken during noontime, which has been assumed as a background spectrum. In the blue region, Fraunhofer contribution is very large. Therefore the observed spectrum during the morning time has been divided by noontime spectrum. The resultant ratio spectrum contains the contribution of water vapor, because in this case, water vapor contribution is very large due to the longer optical path length. Using the Lambert-Beer's law, number density of water vapour has been calculated as follows :

$$I = I_0 \exp(-\sigma \cdot N \cdot m(\chi))$$

where, I = intensity of light at 442.6 nm, I_0 = intensity of light, where the absorption is minimum; σ = water vapour absorption cross section at 442.6 nm, N = column density, $m(\chi)$ = a mass factor. The values of $m(\chi)$ have been taken from (Smith and Smith 1972). Using the above formula, we have calculated the value of water vapour column density. This comes out to be of the order of 10^{20} molecules cm^{-2} .

The same instrument has been used for the second part of the experiment. In that, we have scanned direct solar spectrum at maximum possible solar zenith angle between 655 and 667 nm region. Like blue region, this region does not contain significant amount of Fraunhofer component. This wavelength region contains absorption due to water vapour and NO_3 . Since NO_3 content during day time is about 1000 times less than that at night time, in this solar spectrum NO_3 will have negligible contribution. Only water vapour and Fraunhofer contributions will remain in the solar spectrum. A background spectrum has been taken at about 80° zenith angle. After dividing the spectrum obtained at 88° by the spectrum obtained at 80° solar zenith angle a ratio spectrum has been obtained. This ratio spectrum contains the contribution due to the water vapour, scattering due to aerosols and molecules. Since aerosol scattering varies with wavelength as λ^{-1} and molecular scattering varies with wavelength as λ^{-4} ,

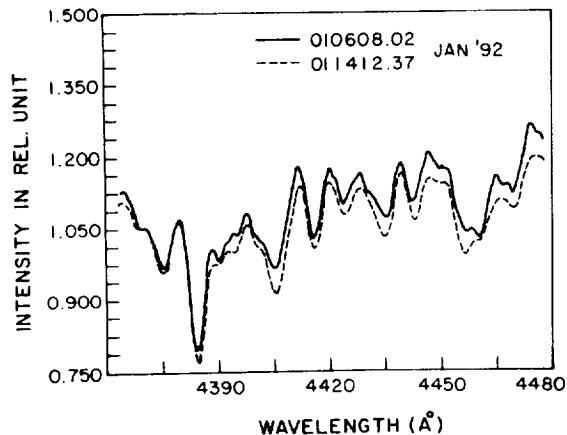


Figure 1. Zenith sky spectra at 0802 and 1237 hrs IST in the month of January 1991 for blue region.

scattering due to aerosols and molecules had been removed by subtracting the ratio spectrum from a straight line parallel to the ratio spectrum. The residual spectrum now contains contribution of only water vapour. This spectrum is equivalent to the product $\sigma \cdot N$ where σ is the absorption cross-section of water vapour in the range 655 to 667 nm. By substituting the column density of H_2O obtained from the first part of the experiment in this product, the absolute values of absorption cross section of water vapour can be calculated.

Results and discussion

Fig. 1 shows the direct solar spectrum obtained during morning time at 88° solar zenith angle (solid line) in the 436 to 448 nm region. In this figure, mostly Fraunhofer structure is seen. A pronounced dip occurring at 438.6 nm has been used for positioning the spectra. This corresponds to the Fe II line of the sun. Similar structure has

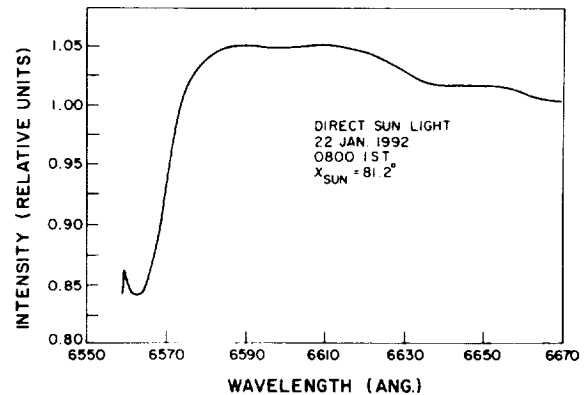


Figure 3. Direct sunlight spectrum for 22 January 1992 for large zenith angles in the red region.

also been seen in the noontime spectrum when solar zenith angle is minimum, which has been used as a background spectrum. During noon time, atmospheric mass factor for direct sunlight and for zenith sky sunlight do not differ much. Even though we have used direct sun as a light source during the noontime (shown by dotted line), the morning and noontime spectra do not show much difference owing to the maximum contribution of Fraunhofer components present in the raw spectrum.

After dividing the morning spectrum by the noon time spectrum, ratio spectrum is obtained. This ratio spectrum has lot of structures owing to the not complete removal of Fraunhofer structure. We have taken a 50 point (distance between two points is 0.01 nm) running average of the ratio spectrum for smoothing. An example of smoothed ratio spectrum thus obtained is shown in Fig. 2. Since this corresponds to the direct solar spectrum, the tropospheric path length covered by the solar radiation is large compared to the zenith sky spectrum. Most of the water vapour is lying below the boundary layer. Therefore the water vapour absorption signature can easily be seen in the ratio spectrum. This ratio spectrum shows the

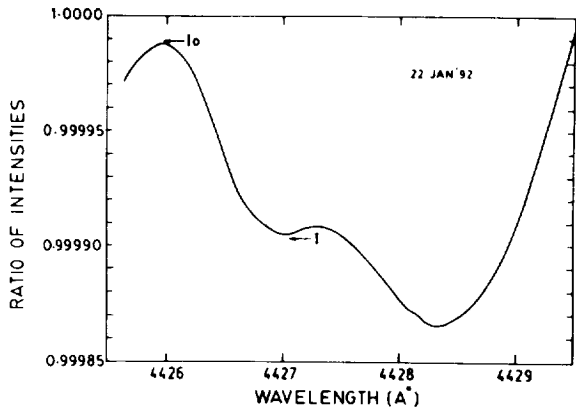


Figure 2. Ratio of twilight spectrum to background spectrum in the blue region.

absorption of water vapour at 442.7 nm. Besides, another dip is also seen around 442.85 nm, which may also be due to water vapour. Therefore, for the calculation of water vapour amount, we have used the average of 442.7 nm and 442.85 nm values.

Fig. 3 shows the direct solar spectrum obtained on 18 January 1992 at 0800 hours IST for $\chi_{\text{sun}} = 81.2^\circ$. This solar spectrum has been used as a background spectrum. Similarly direct solar spectrum has been observed on the same day at about 88° solar zenith angle, which corresponds to the larger air mass factor compared to the background spectrum. Both the spectra have been obtained with the same instrumental field of view. The region 655 to 667 nm contains absorption due to NO_3 and water vapour. The NO_3 content during daytime being about three orders of magnitude less than that during nighttime, the contribution of NO_3 in the direct solar spectrum will be negligible. The structure will be, therefore, due to the water

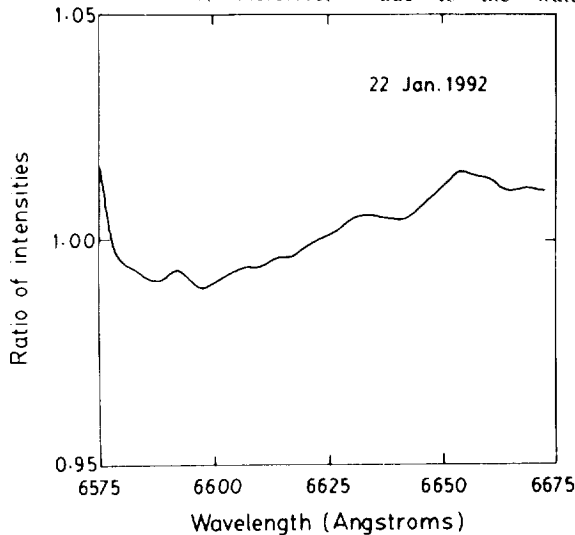


Figure 4. Ratio of two consecutive spectra in the red region for large zenith angle. Y-axis of this figure gives the product $\sigma \cdot N$.

vapour absorption and Fraunhofer component. Unlike the blue region, in this region the Fraunhofer component is insignificant. Hence, this spectral region is ideal for calculating the water vapour contribution during daytime. This spectral region also contains absorption due to Balmer alpha (H_α) at 656.3 nm, which has been used for positioning the spectra as explained earlier.

After dividing the two solar spectra, as explained above, the ratio spectrum has been obtained. We have taken the running average of the ratio spectrum for removing the Fraunhofer structure. After this is done, the contribution due to scattering of aerosols and Rayleigh still remains, which can be seen as a tilt in the ratio spectrum. The aerosols scattering and absorption cross-sections linearly vary with wavelength in the region of our concern, even at the time when Pinatubo aerosols are present. Therefore, for removing this contribution, the observed ratio spectrum has been subtracted from the straight line parallel to the slope. The spectrum thus obtained is shown in Fig. 4. This spectrum shows good agreement with the corresponding spectra obtained by Solomon et al. (1989) and by NASA Ames Research Center. In Fig. 4, Y-axis gives the product $\sigma \cdot N$. Substituting the value of water vapour column density obtained from the first experiment in this product, the absolute value of water vapour

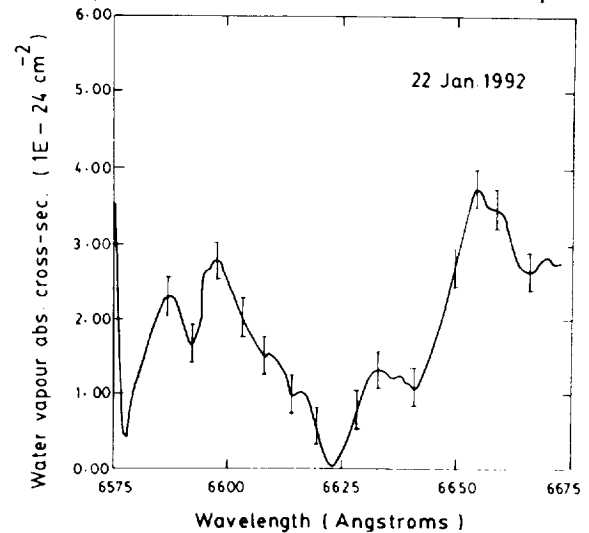


Figure 5. Water vapour absorption cross-section in the spectra range 657.5 to 667.5 nm.

absorption cross section have been derived in 655 to 667 nm region. This has been shown in Fig.5. The absolute value of water vapour absorption cross section shows maximum absorption at 659.0 nm and then a decrease with increase of wavelength up to about 662 nm. It shows an increasing tendency after 663 nm. Since no laboratory measurements of absorption cross section in absolute unit are available in 655 to 667 nm range, a direct comparison of our results is not possible.

Conclusion

(1) The value of water vapour column density was found to be about 1.12×10^{20} molecules cm^{-2} .

(2) The water vapour absorption cross section in the spectral range 667.2 nm to 657.5 nm was found to vary from 4.02×10^{-24} cm^2 to 2.04×10^{-26} cm^2 . These values of water vapour absorption cross section need to be verified by direct laboratory experiments.

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