Column density of atmospheric water vapour over Ahmedabad

D K Chakrabarty
Centre for Environment Survey, Vidyagan Society, 29/251, Ahmedabad 380 015

and

S Patel & P Vala
Physics Department, St. Xavier's College, Ahmedabad 380 009

and

K N Iyer
Physics Department, Saurashtra University, Rajkot 360 002

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Water vapour spectrum has a strong absorption feature around 442.7 nm. Using this property column density of water vapour has been determined at Ahmedabad, a low latitude station. Measurements have been made from 1996 to 2000. Slant column density has been found to be $10^{24}$ cm$^{-2}$. The period stretches from a minimum to maximum solar activity. A decreasing trend of water vapour content with an increase of solar activity level is also seen.

Keywords: Water vapour, Column density

1 Introduction

Water vapour is a minor greenhouse gas in the earth's atmosphere. It plays a significant role in climate, atmospheric chemistry and hydrology. Traditional water vapour observing system includes radiosondes, surface-based humidity sensors, surface and satellite-based radiometers and research aircrafts. No single instrument is capable of measuring water vapour at all altitudes. In the low altitude region (up to about 8 km), water vapour concentrations are regularly being measured by the standard meteorological balloon soundings all over the world. For upper troposphere, stratosphere and mesosphere also several observations exist$^{1-10}$. Satellite data, though have wide global coverage for a long period of time, are not yet found to be very reliable in terms of their accuracy and long-term homogeneity. The latest water vapour measurement technique is the retrieval of total column water vapour based on Global Positioning System (GPS) data$^{14}$. A good review of water vapour observations taken by various techniques has been made by SPARC Water Vapour Working Group (SPARC Rep. No. 2, 2000). Recently Michelsen et al.$^{12}$ have compared a new version of atmospheric trace molecule spectroscopy experiment (ATMOS) retrievals (version 3) of stratospheric and mesospheric water vapour with observations from shuttle-borne, satellite-borne, balloon-borne and aircraft-borne instruments. Though advances have been made in the water vapour climatology, some essential aspects of the distribution and variability of atmospheric water vapour are still poorly documented$^{13}$. The present work makes an effort to find out the column density of water vapour and its variability at a low latitude station, Ahmedabad (23°N, 72°E).

2 Experiment and justification

A ground-based visible absorption spectroscopy technique has been used for the present study. Harder and Brault$^6$ have demonstrated that this technique can be successfully used to determine the column density of water vapour. In the wave number range 22200-22700 cm$^{-1}$, water vapour absorption occurs due to vibration-rotation lines in the 4n$+$3n3 and 5n$+$2n3 overtones band. These transitions are very weak. There are 229 lines of widths varying from 0.151 to 0.183 cm$^{-1}$ in this band. Harder and Brault$^6$ measured this spectrum at high resolution (0.001 nm) on the Fourier transform spectrometer which has got almost all the lines. Then they synthesized the spectrum for use in low resolution instrument for the measurement of stratospheric concentrations (Fig. 2 of Ref. 6). The absorption cross-section changes with change of
resolution. At high resolution of 0.001 nm, the cross-section is \(\sim 60 \times 10^{-26} \text{ cm}^2\) and at low resolution of 0.5 nm the cross-section is \(\sim 3 \times 10^{-26} \text{ cm}^2\). At high resolution the degree of absorption will be more (since cross-section is more), but the noise will also be more as can be seen in Fig. 1 of Ref. 6. At low resolution the amount of absorption will be less (since cross-section is less), and the noise will be considerably reduced. This spectrum has been further smoothed by Harder and Brault\(^6\). It has been shown by Noxon's group at Boulder in 1970s that this experimental set-up (i.e. visible absorption spectroscopy with photomultiplier tube as a detector) can measure absorption up to about 3%. This technique has been used by many groups and at many places in the world to measure minor neutral species. Now, with the sophistication, this technique can measure absorption up to 0.5%. We have done the measurements at a resolution of 0.4 nm which gives a spectrum encompassing 11 lines. Harder and Brault\(^6\) have given the absorption cross-section values at this resolution. These cross-section values have been used in the present work. At this resolution, the half-width is about 0.5 nm [Fig. 2(d) and Fig. 2(e) of Ref. 6]. These cross-section values are shown in Fig. 1. From Fig. 1 one can see that the absorption cross-section of water vapour, \(\sigma_{\text{H}_2\text{O}}\), at 442.7 nm is \(\sim 3 \times 10^{-26} \text{ cm}^2\), and the column density of water vapour \([\text{H}_2\text{O}]\) is \(\sim 10^{21} \text{ cm}^{-2}\). Thus, the product of \(\sigma_{\text{H}_2\text{O}} \times [\text{H}_2\text{O}] = 0.03\). This is about 3% absorption and is easily measurable. Harder and Brault\(^6\) have used the sun as source. In this study, the scattered radiation coming from zenith has been used as the source.

The intensity of scattered sunlight from the zenith sky in the 436-448 nm range has been measured. For that purpose, a plane mirror with front surface coated with aluminium and mounted at 45° to the horizontal axis of the optical system is used. The block diagram of the experimental set-up is shown in Fig. 2. A McPherson 270 model scanning monochromator fixed with a rotating diffraction grating has been used in this study. The grating has 1200 lines/mm with a dimension 48×48 mm. At a particular angle it allows only one wavelength to pass through, depending upon the resolution of the instrument. A R732 Hamamatsu photomultiplier tube has been used as a detector. The tube is operated at 1000 V (DC). A laboratory mode converter was used in DC mode with a variable gain. The current DC mode has been converted into voltage DC mode. A lock-in-amplifier (Stanford Research System Model SR530) was used for enhancing the signal-to-noise ratio. A chopper had been used with 6/5 slots and frequency 330 Hz. The sensitivity of the lock-in-amplifier was at 500 mV throughout the observation with time constant 0.3 s. A preamplifier (Model SR550) was used to amplify the signal. The
output of the amplifier was fed to a computer through an A/D (PCL-205) card. This PCB was able to record in 5 V range. The analog signal voltage was digitized with 12 bit accuracy. The stepper motor of the monochromator was controlled by computer. The digitized pulses were given from computer to the controller of the monochromator to stop, start and reverse the direction of scanning. The scanning speed was 360 Å/min. The entrance and exit slit-width of the monochromator was 0.04 mm.

3 Observation

Observations were taken during the evening twilight for solar zenith angle of about 90°. At that time the radiation coming from the sun travels a longer path through the atmosphere; thus the signature of the absorption will be large. The measured signal includes contribution from Fraunhofer absorption lines also. To remove the Fraunhofer component, observations were also taken during noontime. By taking the ratio of the morning to noon spectra or evening to noon spectra, the ratio spectrum was made free, to a large extent, from the contribution due to Fraunhofer lines. Both the forward and backward scannings were done. Twelve scannings were done in 3 minutes. Then the average of these 12 spectra was taken. This process nullifies the scintillating effect of the earth’s atmosphere.

4 Theory

The measured flux, \( I(\lambda) \), at wavelength, \( \lambda \), is given by Beer-Lambert’s law:

\[
I(\lambda) = I_0(\lambda) \exp[-a(\lambda) m x] \quad \text{... (1)}
\]

where, \( I_0(\lambda) \) is the flux incident at the top of the atmosphere, \( a(\lambda) \) the absorption cross-section of the absorbing species, \( m \) the number density of the absorbing species and \( x \) the path length over which the absorption takes place. Equation (1) can be written as:

\[
I(\lambda) = I_0(\lambda) \exp[-a(\lambda) \int m dx] \quad \text{... (2)}
\]

where, \( \int m dx \) shows that integration is taken over the total thickness of the atmosphere. Observations are taken during noontime and during twilight time. If \( I_0(\lambda) \) and \( I(\lambda) \) are the observed intensities during noontime and during twilight time conditions, then from Eq. (2), we can write:

\[
\log_{10}[I(\lambda)/I_0(\lambda)] = -a(\lambda)[\int m dx] = a(\lambda) M \quad \text{... (3)}
\]

or, \( R(\lambda) = -a(\lambda) M \quad \text{... (3)} \)

where, \( R(\lambda) = \log_{10}[I(\lambda)/I_0(\lambda)] \) and \( M = \int (m \delta x) \), called the slant column density. This procedure also removes the necessity of knowing \( I_0(\lambda) \). In the region 436-448 nm, the absorption is mainly due to NO\(_2\) and O\(_3\); besides H\(_2\)O and air (Rayleigh) and aerosol scattering. The values of \( R(\lambda) \) will, therefore, depend on the densities of NO\(_2\), O\(_3\) and H\(_2\)O present in the atmosphere and Rayleigh and aerosol scatterings. Equation (3) then becomes

\[
R(\lambda) = -a_1(\lambda)[M_1] - a_2(\lambda)[M_2] - a_3(\lambda)[M_3] - A\lambda^4 - B\lambda \quad \text{... (4)}
\]

where, \( a_1(\lambda), a_2(\lambda) \) and \( a_3(\lambda) \) are absorption cross-sections of H\(_2\)O, O\(_3\) and NO\(_2\), respectively, at wavelength \( \lambda; A \) and \( B \) are constants associated with Rayleigh scattering and aerosol scattering and \([M_1],[M_2],[M_3]\) are slant column densities of H\(_2\)O, O\(_3\) and NO\(_2\), respectively. In Eq. (4), \( R(\lambda) \) is the measured quantity; \( a_1(\lambda), a_2(\lambda) \) and \( a_3(\lambda) \) are known from laboratory measurements and \([M_1],[M_2],[M_3]\), \( A \) and \( B \) are five unknowns. The values of \( a_1(\lambda) \) and \( a_2(\lambda) \) are taken from Harrison\(^{14}\) and those of \( a_3(\lambda) \) are taken from Harder and Braulit\(^{16}\). We have 512 values of \( R(\lambda) \) which will form 512 linear equations. In actual calculations there are 487 linear equations, because observed spectra are smoothed by 25 points running average. These equations are transformed into a 5x5 matrix by least square method. Then by matrix inversion method the values of five unknowns are calculated.

5 Results

The observed raw spectra are first smoothed by 25 point running average and then normalized. Figure 3 shows the evening twilight and noontime spectra for 6 Jan. 1999. Both the spectra appear to be similar owing to the presence of strong Fraunhofer structures in the incoming solar radiation. These spectra are the averages of 12 spectra taken in one day.

Figure 4 shows the ratio of the twilight time to the noontime spectra of Fig. 3. In this spectrum Fraunhofer component is minimized. But due to the difference in geometry of the scattering at the twilight time and noontime conditions, the Fraunhofer component is not fully removed (Ring effect). In Fig. 4 absorption signature of H\(_2\)O is clearly seen (point B). Also seen are signatures of NO\(_2\) and O\(_3\) (points A and C, respectively). Using the ratio
1.50
1.35
1.20
1.05
0.90
0.70
0.50
0.25
0.00

WAVELENGTH, Å

1.00E+26 1.00E+25 1.00E+24 1.00E+23 1.00E+22 1.00E+21

YEAR

Fig. 5—Plots of water vapour slant column density from January 1996 to May 2000

Fig. 4—Plots of ratio of two spectra of Fig. 3. [Here absorption signature due to water vapour is at point B. At points A and C, the signatures are due to NO₂ and O₃, respectively.]

Fig. 3—Spectra obtained in the range 436-448 nm during noontime (at 1237 hrs IST, dotted line) and evening time (at 1700 hrs IST, continuous line) for 6 Jan. 1999

spectrum shown in Fig. 4 and the proper values of absorption cross-sections, the slant column densities of NO₂, O₃ and H₂O have been calculated in the manner described earlier.

Figure 5 shows the slant column density values of water vapour from January 1996 to May 2000. Here, the averaged value and the maximum and minimum values are shown for each month. There are about 20 observations in a month. The graph shows that the slant column density of water vapour is approximately of the order of \(10^{24}\) cm\(^{-2}\). A large scatter is noticed in the values of water vapour slant column density. This could be due to the fact that, during one day, several observations were taken from 80° to 90° solar zenith angles. Also the possibility of day-to-day variation of water vapour value exists\(^7\). The present result agrees with those of Ghosh \textit{et al.}\(^5\) who using infrared absorption technique found that the vertical column density of water vapour at Delhi varies from \(6.5\times10^{22}\) to \(2\times10^{23}\) cm\(^{-2}\). They also reported day-to-day and seasonal variation of water vapour column density. The present values are, however, somewhat lower than those reported by Harder and Braault\(^6\) taken at Kitt Peak, a mid-latitude station. They\(^7\) found the vertical column density to be \(\sim10^{24}\) cm\(^{-2}\).

The present water vapour data cover a period from solar minimum to solar maximum conditions. In Fig. 6 we have plotted 10.7 cm solar flux as an index of solar activity (lower panel) and the water vapour content (top panel) from 1996 to 2000. It can be seen from Fig. 6(a) that water vapour content decreases with time. Regression analysis shows that the decrease is about 1% per month. It is also to be seen from Fig. 6(a) that during the period of study while the value of water vapour content decreases, the value
of 10.7 cm flux increases, indicating thereby an anti-correlation between the two parameters. However, Ghosh et al.\textsuperscript{15} have not found any correlation between water vapour content and 10.7 cm solar flux. There could be several reasons for this disagreement. They\textsuperscript{15} have correlated data of 9 months, from September 1992 to May 1993, with the corresponding data of 10.7 cm solar flux [see Figs 7 and 8(d) of Ref. 15], whereas we have considered data of five years. Ghosh et al.\textsuperscript{15} have not considered the seasonal variation of water vapour (which is quite significant), whereas in the present study, data of one season, i.e. winter only, have been considered. It could be desirable to correlate water vapour content with UV flux. Ghosh et al.\textsuperscript{15} have found a good correlation between UV flux and water vapour content. But we cannot undertake this kind of study, because we do not have simultaneous measurements of UV flux and water vapour. A regression analysis between 10.7 cm solar flux and water vapour content has also been made. The correlation coefficient comes out to be about $-0.5$.

In the stratosphere-troposphere, water vapour is controlled by the following reactions:

\[
\text{O}_3 + hv \rightarrow \text{O}_2 + \text{O}^\text{(D)}
\]

\[
\text{O}^\text{(D)} + \text{H}_2\text{O} \rightarrow 2\text{OH}
\]

It is now known that solar UV increases by a factor of about 1.5 from low to high solar activity period\textsuperscript{16}. In that case, production of O$^\text{(D)}$ will increase with increase of solar activity level, resulting in decrease of H$_2$O during high solar activity period, though the actual situation could be more complex.

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**References**