OBSERVATIONS OF O₂, H₂O AND HD IN PLANETARY ATMOSPHERES

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Abstract. We have searched for molecular lines in planetary atmospheres using the PEPSIOS spectrometer with an instrumental width about equal to that of the expected absorption line, and in the case of Jupiter, with the additional feature of Doppler compensation over the planetary disc.

Following our earlier detection of O_2 (7635 Å) on Mars, where the mixing ratio is $O_2/CO_2 \simeq 1.3 \times 10^{-3}$, we attempted to observe the same lines on Venus. The observed spectra are shown in Figure 1, where the lowermost tracing is the sum of scans taken during one day. The strongly saturated absorption features are due to two lines of



Fig. 1. Observed spectra of Venus in the region of the 7635 Å line of O₂.

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terrestrial O_2 in the Fraunhofer A band. Also shown is a theoretical profile for these lines, which when divided into the data yields the spectra as they appear outside the Earth's atmosphere, except in the core of the lines where there is zero flux. Our three best summed scans are shown normalized at the top of the figure. The vertical line indicates the Doppler shifted position of the Venusian O_2 lines. From the sum of the two best spectra, we obtain an upper limit of 0.5% on the depth of a possible feature, which together with an expected line width of 26 mÅ, yields an equivalent width of less than 0.13 mÅ.

Using our radiative transfer computer program, which follows the method of calculation described by Grant and Hunt (1969), we have computed a corresponding abundance of O_2 . In this calculation, we used a cloud distribution with altitude which was developed to interpret our observations of CO_2 on Venus; it consists of a dense lower cloud at 300 mbar, along with a thin upper cloud at about 10 mbar, with optical depth 1.8. A forward peaked (Sobolev) scattering function was used. The computed equivalent width (EW) as a function of phase angle is shown in Figure 2 (upper curve). Scaling this curve down to the position of the O_2 observation, we see that the mixing ratio $O_2/CO_2 < 1 \times 10^{-6}$.

If this O_2 were solely due to dissociation of CO_2 into O and CO, with $O + O \rightarrow O_2$, we would then expect to have $CO/CO_2 < 2 \times 10^{-6}$, but in fact the value 45×10^{-6} has been observed. Clearly the O_2 is being tied up elsewhere, perhaps in water vapor.

We have also attempted to measure H₂O on Venus with these same techniques, using



Fig. 2. Computed equivalent width of O2 vs phase angle on Venus.



Fig. 3. Observed spectra of Venus near the 8197 Å H₂O line, for two different phase angles. The Doppler-shifted position and full-width at half-intensity of the expected Venusian feature are indicated.

the 8197 Å line. In Figure 3 we show the observed spectrum at two different phase angles, and also the curves which result from dividing out the telluric water vapor line profile. Again, we see no evidence for a line as deep as 0.4 and 1.0% for these respective curves. With an estimated width of 35 mÅ, the resulting EW values are 0.14 and 0.35 mÅ respectively. Referring to Figure 2 again, we see that this corresponds to a mixing ratio H₂O/CO₂ < 1×10^{-6} . Note that the upper curve refers to a condition of uniform mixing of H₂O with CO₂, which is not too likely, since the water will be frozen out at lower levels and will not extend above the upper cloud. The lower curve applies if H₂O is confined to the region between cloud layers. Since this H₂O line has been successfully detected at various times by Barker (to be reported at this symposium), it is clear that this is a variable entity, perhaps depending upon the extent of the upper cloud. Possibly there is a connection with the four-day variation in observed CO₂ equivalent width, reported by Young *et al.* (1973).

We have also searched for water vapor on Jupiter; the observed spectrum is shown in Figure 4. For this experiment we operated the Fabry-Perot etalons in an off-axis mode, in order to precisely cancel the rotational smearing from Jupiter. Also, since we were observing near opposition, it was necessary to utilize only the limb spectrum in order to produce a significant shift from the terrestrial water vapor line. A concomitant property of the off-axis PEPSIOS is that it also yields broadened, non-symmetrically distorted spectra of stationary sources, and in particular, the telluric H_2O line. Since we have not yet incorporated this asymmetry into our calculations, the divided spectrum will not be quite accurate. This is probably why the upper curve oscillates



Fig. 4. Observed 8197 Å line of H₂O on Jupiter.

near the line core. We expect that this line will be severely pressure broadened to about 102 mÅ, since the absorption will almost surely take place near the lower, warmer, cloud deck, where the gas pressure is of the order of 1 atm. For this width, we estimate an upper limit on the line depth to be 2%, so that EW < 2 mÅ. This is a factor of 5 smaller than the previously reported value due to Fink and Belton (1969). We intend to extend these observations by using the center of the disc at a time away from opposition, and by using a wider instrument function, in order to match the pressurebroadened line. Recently, Keay *et al.* (1973) have shown that 'hot spots' on the disc are correlated with blue and brown features; it is possible that H₂O will be more easily detected in these regions than in the colder surroundings.

Using the same Doppler compensation technique, we have recently measured the HD (7467 Å) 4–0 P(1) absorption line on Jupiter (Trauger *et al.*, 1973). In Figure 5 we see this line, along with a nearby Jovian line which is probably due to CH₄. The identification of this line as HD follows from both the wavelength coincidence (within 7 mÅ of the laboratory line) as well as its width, which is comparable to the pressurenarrowed H₂ lines. We also searched for the 4–0 R(0) and R(1) lines, but found these regions to have a number of stronger, interfering lines which completely obscured the HD. For comparison, we also measured the H₂ 4–0 S(1) line during the same period, finding an EW = 8.1±0.2 mÅ. Note that both of these observations are for the full, integrated disc.

To derive the number ratio HD/H_2 , we assume that the atmosphere is homogeneous and has an effective rotational temperature of 150K. We also assume that mixing



Fig. 5. Spectrum of Jupiter in the region of the 7467 Å line of HD.

occurs down to a level where the temperature is sufficiently great to establish a 3:1 ortho-to-para-H₂ ratio. For this case then, calculated absorption coefficients are available for the H₂ line; in addition, we apply a saturation correction of 1.10. For HD, we can combine recent theoretical work on the 1–0 through 4–0 bands (Ford and Browne, 1973), with laboratory observations of the 4–0 R(0) line (McKellar, 1973). We then have D/H=(HD/H₂)/2, neglecting the isotope fractionation effects of minor species such as CH₃D. The result is D/H=(2.1 ± 0.4) × 10⁻⁵, where the uncertainty is one standard deviation and includes both observational and laboratory error estimates.

Recently Beer and Taylor (1973) analyzed the Jovian CH_3D spectrum and found $D/H = (5.1 \pm 2.2) \times 10^{-5}$, using a model dependent calculation of radiative transfer and deuterium fractionation. Since our result is nearly model independent, this suggests that the CH_3D observations can be used instead to determine that the deuterium enrichment of methane is between 1.3 and 5.6 times the stochiometric ratio. For such strong fractionation to have occurred, the effective temperature must lie in the range of about 240 to 520 K. However, in this range, the thermal equilibration time is about 10^7 yr or more. Therefore, there must exist a catalytic agent in the main cloud deck of Jupiter which drastically increases the rate of fractionation of deuterium.

Identifying the Jovian D/H ratio with that of the primitive solar nebula, we can compare our direct determination with independent estimates of this quantity. From analysis of meteoritic gases, Black (1973) has estimated a protosolar D/H=1.5 $(+1.5, -0.7) \times 10^{-5}$, and from consideration of helium isotopes in the Sun and solar wind, Geiss and Reeves (1972) have suggested D/H=2.5 $(\pm 0.5) \times 10^{-5}$. Both values are in good agreement with our determination.

If the observed D/H ratio can be taken to be directly representative of the production in a Big Bang (Wagoner, 1973), then the present density of the Universe is about $(4.3\pm0.3)\times10^{-31}$ g cm⁻³. If, on the other hand, there is significant D production in supernovae shock waves (Colgate, 1973), then the present density of the Universe can be greater than indicated, and the possibility is raised that the density may be high enough to allow the Universe to be gravitationally closed.

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DISCUSSION

Beer: Do you have direct laboratory measurements of the 4-0 P(1) line of HD to compare to the astronomical data?

Traub: We used the very recent laboratory work on HD by McKellar, who has measured lines in the 1-0 through 4-0 bands. Also there exist calculations of these lines by Ford and Browne (1973). However the calculations are quite sensitive to cancellation effects, and it is therefore not surprising that it is found that the observations and calculations are different by an approximately constant factor, for all bands. Therefore, since in fact the 4-0 P(1) line was not observed in the laboratory, we have scaled the calculated 4-0 P(1) intensity by the empirical constant just mentioned. Details of this appear in Astrophys. J. 184, L137, 1973.

Trafton: What is the basis for your estimate that the Jovian H₂O line has a half width of 0.1 Å at 1 atm pressure? Did you use room temperature results?

Traub: I took as a basis the results for H_2O published by Farmer. Room temperature results have been used.

Fox: Recent calculations by Tejwani of broadening of CH_3D lines by H_2 , as a function of temperature, indicate significant differences from the values used by Beer *et al.* in deriving a Jovian D/H ratio from CH_3D/CH_4 .

Beer: This would not affect our D/H ratio significantly because our most serious source of error lies in the model atmospheres employed, not in the data themselves.

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