

# Deuterium content of the Venus atmosphere

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**THERE is no liquid water on Venus. The water vapour in its atmosphere would, if condensed, form a layer only 20 cm deep which means, in contrast to the 3-km-deep oceans that cover its sister planet Earth, that Venus is very dry indeed. It is not known with certainty whether Venus has lacked water since its formation, or if water once present has been lost during its lifetime; the question is of special interest as water is generally thought to be a necessary ingredient for the development of life. The abundance of deuterium in the atmosphere of Venus is an important clue to the planet's history, because ordinary and deuterated water escape at different rates. Using the high-resolution mode of the International Ultraviolet Explorer (IUE), we measured hydrogen Lyman- $\alpha$ -emission but found only an upper limit on deuterium Lyman- $\alpha$ -emission, from which we inferred a D/H ratio of less than  $2\text{--}5 \times 10^{-3}$ . This is smaller by a factor of 3–8 than the D/H ratio derived from measurements by the Pioneer Venus Large Probe, and may indicate either a stratification of D/H ratio with altitude or a smaller overall ratio than previously thought.**

The Pioneer mass spectrometer detected a signal at mass 19 (HDO<sup>+</sup>), when the inlet became clogged by a droplet of sulphuric acid. The detection was taken<sup>1</sup> to imply a D/H ratio of  $1.6 \times 10^{-2}$ . If this modern ratio derives from an original D/H ratio similar to Earth's, that is,  $1.6 \times 10^{-4}$ , in sea water, but enriched by differential evaporation, Venus would have had enough water to form an ocean 20 m deep, although this is an extreme lower limit, because some deuterium would undoubtedly have escaped too.

The presence of HDO in the atmosphere of Venus will produce some D atoms by photodissociation and some consequent D Lyman- $\alpha$ -emission in the planet's ultraviolet airglow. In the upper atmosphere, the Lyman  $\alpha$  transition of H and D atoms can be excited by resonance scattering of solar photons, which can be observed by remote sensing from outside. The emission lines are separated by 0.33 Å (H emission is at 1,215.66 Å, and D at 1,215.33 Å), which is much more than the thermal width ( $\sim 10^{-2}$  Å) but less than the solar linewidth, so that both lines can be excited to an approximately equal extent.

The D Lyman- $\alpha$ -emission has been measured previously<sup>2</sup> in the upper atmosphere of the Earth with a dedicated Ly $\alpha$  spectrometer on board Spacelab 1, and was found to have an intensity of 300 rayleigh along a tangential line of sight at an altitude of 110 km, just above the O<sub>2</sub> absorption level. The corresponding D/H ratio was found to be  $\sim 3 \times 10^{-4}$ , indicating a twofold enrichment in D relative to sea water which results from the smaller exospheric escape for D atoms than for H atoms.

The International Ultraviolet Explorer (IUE), launched in 1978, has in principle the spectral resolution required to separate both D and H Ly $\alpha$  lines, and it was therefore proposed that it be used to detect deuterium in the upper atmosphere of Venus at the  $\sim 1\%$  level for D/H ratio following the Pioneer mass spectrometer measurement of HDO in the lower atmosphere.

A series of high-dispersion SWP (short-wavelength primary camera) spectra of the Venus dayside disk has been obtained with IUE, both in the course of this programme and in others. Measurements of the IUE echelle-grating scattered-light profile have shown that scattered H Ly emission 0.33 Å from the line centre—that is, where D Ly $\alpha$  emission should occur—is well below the level of  $10^{-2}$  expected for such emission<sup>3</sup>, so that the

detection of D Ly $\alpha$  becomes a problem of signal-to-noise ratio. In principle, the small aperture of IUE (circular, 3.2") would give the best separation of D Ly $\alpha$  and H Ly $\alpha$  spectral lines. However, the large aperture ( $23 \times 10''$ ) has a throughput on an extended source that is greater than that of the small aperture by a factor 30, and it was found that large-aperture SWP spectra of the longest duration (that is, with the H Ly $\alpha$  emission feature saturated) provided the best measurement of D Ly $\alpha$ , despite the slight overlap of the D and H features, because of the extended size of the aperture. D emission should be apparent as an asymmetric lineshape (specifically, as a short-wavelength shoulder; see Fig. 1).

Some of the archived spectra were taken with only part of the aperture imaging the disk of Venus, leading to a distorted Ly $\alpha$  lineshape. The photowrite images of all spectra were therefore examined so as to select only those images for which the aperture was filled. A customized reduction method was required to analyse these spectra, because the aperture width used to sum the emission region in the standard IUE reduction is designed to separate the orders of the echelle and is too narrow to include all of the emission entering the large aperture. The Venus spectra contain discrete Ly $\alpha$  emission with no adjacent continuum other than longer-wavelength light scattered by the cross-disperser grating across the region of Ly $\alpha$ . In the customized reduction we therefore (1) summed the entire emission region of the Ly $\alpha$  lines; (2) employed a more extended region of background measurement for an accurate removal of the scattered light; (3) re-processed all images with VAX floating-point accuracy in the intensity transfer functions using the SDPS processing routines at Goddard Space Flight Center; and (4) carefully aligned all spectra in wavelength to the observed centre of the H Ly $\alpha$  line before summing. Thermal drifts of the spectrum across the detector face with time are advantageous, as the fixed noise pattern of the SEC cameras is altered when the images are realigned in wavelength and the noise level is therefore reduced in the summed spectrum.

The longest archived exposures of Venus lasted for 60 min: exposures longer than this were precluded by extreme saturation of the camera at the long-wavelength end of the spectrum. Six spectra ranging in duration from 30 to 60 min were summed as described and the result is plotted in Fig. 1. These spectra were obtained near the Venus maximum elongation, on 12 and 13 April and 26 August 1980. The Ly $\alpha$  intensity, estimated from other shorter, unsaturated exposures, was found to be

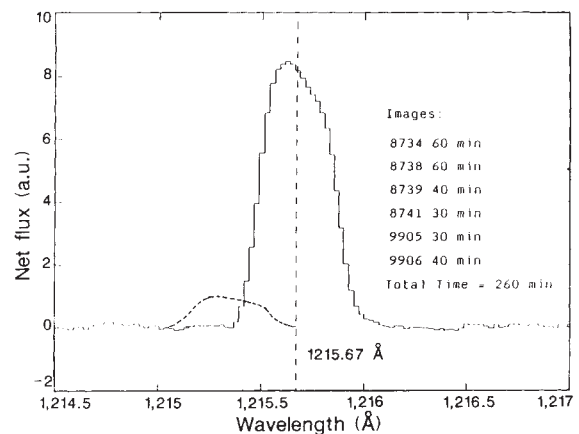


FIG. 1 Hydrogen Ly $\alpha$  spectra of bright-disk emission from Venus, obtained with the IUE large aperture and summing the six best images (solid line). The line intensity corresponds to  $21 \times 10^3$  rayleigh; the long-dashed line shows the line centre. The short-dashed line shows the profile calculated for deuterium Ly $\alpha$  emission of  $2.5 \times 10^3$  rayleigh (corresponding to a D/H ratio of  $1.6 \times 10^{-2}$ ). On the basis of the IUE observations, we can rule out such emission down to a factor of  $\sim 8$  times less than this. The numbers refer to spectra reference numbers and exposure times. a.u. denotes  $10^5$  IUE flux units.

$(21 \pm 5) \times 10^3$  rayleigh, which is consistent with the Pioneer Venus Orbiter ultraviolet spectrometer (PVO UVS) observations<sup>4,5</sup>. Although there is some saturation for the images summed in Fig. 1, the IUE procedure is able to account for this moderate saturation because intensity for the average spectrum is the same as that found for unsaturated exposures. The dashed line in Fig. 1 shows D Ly $\alpha$  emission of  $2.5 \times 10^3$  rayleigh modelled by scaling down the observed spectrum by a factor of 8 and displacing it by  $0.33 \text{ \AA}$ . As such a shoulder does not appear in the observed spectrum, there seems to be no significant D Ly $\alpha$  emission; an examination of the noise level in this region allows us to place an upper limit ( $2\sigma$ ) of 300 rayleigh for such an emission. Although this implies an upper limit of 1.5% on the ratio of intensities, we shall see below that it implies a substantially lower D/H density ratio.

In the upper atmosphere of Venus, D and H atoms are excited by the solar Lyman  $\alpha$  line at about the same rate. However, CO<sub>2</sub> absorbs Lyman  $\alpha$  at an altitude of 110 km, and only those atoms above this level contribute to the emerging intensity. The IUE upper limit ( $2\sigma$ ) of  $I_D = 300$  rayleigh implies an upper limit for the vertical column density,  $N_D$ , of D atoms above 110 km of  $N_D = I_D \times 10^6 / g_d$ , where  $g_d$  is the excitation rate of D atoms. The ratio  $g_d / g_h$  (with  $g_h$  defined in similar fashion for H atoms) can be estimated from the relative flux intensities at the solar line centre,  $F_s$  (H excitation), and at D resonance (displaced from line centre by  $0.33 \text{ \AA}$ ); these measurements have been made by OSO-5 (ref. 6) (Orbiting Solar Observatory), and indicate a ratio of 0.8. The value of  $g_h$  may be found from  $g_h = 0.544 \times 10^{-14} F_s s^{-1}$ , with  $F_s = 8 \times 10^{11}$  photon  $\text{cm}^{-2} \text{ s}^{-1} \text{ \AA}^{-1}$  at Venus (ref. 4). Variations in  $F_s$  over the 2-year period of IUE observations were smaller than  $\pm 10\%$  (ref. 5), this being confirmed by monitoring of the total solar Ly $\alpha$  flux from Earth's orbit by SME. Thus,  $g_h = 4.35 \times 10^{-3} \text{ s}^{-1}$ , so that  $g_d = 3.5 \times 10^{-3} \text{ s}^{-1}$  and, for  $I_D = 300$  rayleigh, we obtain  $N_D = 8.6 \times 10^{10} \text{ atom cm}^{-2}$ . The photometric uncertainty of IUE at the Ly $\alpha$  wavelength is estimated as  $< 25\%$ ; indeed, the H Ly $\alpha$  intensity of  $21 \times 10^3$  rayleigh measured by IUE agrees well with the nadir, subsolar value of  $20 \times 10^3$  rayleigh measured by PVO UVS at the same time<sup>4,5</sup>.

The ratio  $I_D / I_H$  from the disk of Venus is different from the D/H density ratio in the lower atmosphere, mainly because the atmosphere above 110 km is optically thin at Ly $\alpha$  for D atoms but is moderately thick for H atoms, so that here  $I_D / I_H$  is larger than the ratio of column densities  $N_D / N_H$ . Because of the nonlinear dependence of  $I_H$  on  $N_H$ , one cannot derive  $N_H$  directly from these IUE observations. Thus to estimate  $N_H$  we use instead the Pioneer observations analysed by Paxton *et al.*<sup>4,5</sup>; these were dayside observations, made not far from the subsolar point, and therefore are pertinent to the present IUE observations.

The PVO UVS was better situated than IUE to determine an absolute value of the H density in the Venus atmosphere, because the Pioneer measurements were performed both from outside and from inside the H atmosphere, and also because the spinning geometry of PVO UVS permits measurement of bright disk intensities as well as limb profiles. The H medium is optically moderately thick so that the shape of the Ly $\alpha$  variation over one spacecraft spin depends upon the absolute H concentration everywhere between 110 km and the outside exosphere. The H density vertical distribution can therefore be determined without knowledge of either the Ly $\alpha$  centre solar flux or the UVS calibration<sup>4</sup>, by comparing radiative transfer predictions, made on the basis of a wide range of models of H density distribution, with the observations.

Paxton *et al.*<sup>5</sup> use two parameters to describe the H vertical profile: the exobase density  $n_c$  at 200 km, and the escape flux  $\phi_c$  (also at 200 km), which, for a given  $n_c$ , influences the density at the homopause level. The PVO UVS results indicate that, over the two-year period of observations (May 1979 to May 1981), the H profile near the subsolar point is remarkably con-

stant and can be described by  $n_c = (6 \pm 1.5) \times 10^4 \text{ cm}^{-3}$  and  $\phi_c = 7.5 \pm 1.5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ . The corresponding column density  $N_H$  above 110 km was determined to be  $(2.4 \pm 0.8) \times 10^{13} \text{ cm}^{-2}$  (ref. 5).

Combining the various uncertainties quadratically gives an upper limit ( $2\sigma$ ) to the ratio  $N_D / N_H$  of  $(3.6 \pm 1.5) \times 10^{-3}$ . The ratio of densities  $n_D / n_H$  at some reference level (say, 100 km) will be slightly different from the value of  $N_D / N_H$ , because the D and H vertical profiles are not identical. Integrating the equation of diffusion<sup>7</sup> for D atoms using the VIRA atmospheric profile<sup>8</sup> we obtain the relation  $n_D / n_H (100 \text{ km}) = \alpha (N_D / N_H)$ . If the escape flux of D atoms is zero then  $\alpha = 0.55$ ; if it is equal to the H escape flux (relative to the exobase density at 200 km) then  $\alpha \approx 1$ , and if it is 0.32 to make a rough allowance for the mass fractionation effect, then  $\alpha \approx 0.97$ .

Therefore, regardless of the value assumed for the D escape rate,  $N_D / N_H$  above 110 km is not very much different from the D/H ratio below the homopause. This is to be expected, as the homopause occurs at around 130 km well above the penetration level of Ly $\alpha$  in CO<sub>2</sub>. The upper limit of D/H at 100 km of  $\sim (3.6 \pm 1.5) \times 10^{-3}$  is lower by a factor of 4.4 than the value previously reported for the lower atmosphere<sup>1</sup>, and in fact is probably closer to  $2 \times 10^{-3}$  if present-day deuterium escape is negligible, which is entirely possible.

This low value can be compared with another set of measurements made by the Pioneer Venus Orbiter ion-mass spectrometer. Ions of mass 2 were originally identified as H<sub>2</sub><sup>+</sup> ions,<sup>9</sup> but were later assigned to D<sup>+</sup> (refs 10, 11). A detailed ionospheric model<sup>12</sup> of the pre-dawn bulge ionosphere supported this assignment to D<sup>+</sup> but showed that it required D/H neutral-atom ratios at the homopause of 1.4 and 2.5% respectively for the two orbits during which measurements were made. Clearly, the non-detection of D Ly $\alpha$  emission in the IUE data argues against such a quantity of deuterium at the homopause, suggesting that the mass-2 ions may indeed have been H<sub>2</sub><sup>+</sup> ions. To obtain an H<sub>2</sub><sup>+</sup> signal of the magnitude observed would require an H<sub>2</sub> abundance of 10 p.p.m. on Venus<sup>13</sup>, which is consistent with previous gas-chromatograph data from Venera 13–14 (ref. 14).

Despite the apparently small content of deuterium in the upper atmosphere of Venus, it is possible that more substantial amounts exist in the lower atmosphere—as suggested by the identification of a mass-19 signal, measured by the Neutral Mass Spectrometer, with HDO<sup>+</sup>—as a result of some atmospheric fractionation process. On the other hand, Spacelab-1 results have shown clearly that such processes do not operate on the Earth, and given that the aeronomy of H<sub>2</sub>O, H<sub>2</sub> and H does not seem to differ greatly for the two planets, they would not be expected to occur on Venus either. It seems possible, therefore, that the D/H ratio measured in the upper atmosphere of Venus does indeed represent the bulk atmospheric ratio. The Hubble Space Telescope will provide the means to test these results, as its High Resolution Spectrometer will be capable of resolving a D/H ratio of  $1.6 \times 10^{-4}$  (the value on the Earth) on Venus. □

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