

## Measurement of the isotopic ratio distribution of HD<sup>16</sup>O and H<sub>2</sub><sup>16</sup>O in the 20 - 38 km altitude range from far-infrared spectra

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**Abstract.** The altitude distribution of the isotopic ratio between HD<sup>16</sup>O and H<sub>2</sub><sup>16</sup>O in the stratosphere is derived by retrieving the mixing ratio profiles (from 20 km to 38 km of altitude) of the two isotopic species from far-infrared emission spectra. The measurements were made with a balloon-borne Fourier Transform Spectrometer capable of 0.0025 cm<sup>-1</sup> spectral resolution during the IBEX 92 campaign. The retrievals were carried out using the global-fit procedure on a statistically significant number of spectra for each isotope, in the 40-75 cm<sup>-1</sup> spectral region. This measurement determines the D/H ratio in stratospheric water over an altitude range larger than that of previous measurements. The value of the HD<sup>16</sup>O/H<sub>2</sub><sup>16</sup>O ratio, normalized to the standard value, ranges from 0.4 to 0.5 (with a 10% random error) in the altitude range studied and is in good agreement with the values previously measured.

### 1. Introduction

In the last few years, interest in the isotopic composition of the stratosphere has increased due to the discovery of deviations from the natural isotopic abundance in some important isotopically substituted molecules such as ozone and water.

Production and loss processes of water in the stratosphere are thought to be well understood. Water vapor enters the stratosphere by means of the upward transport of gases through the tropopause. Additional water is formed by the oxidation of methane within the upper stratosphere and, to a smaller extent, by the oxidation of H<sub>2</sub>.

Water vapor diffused through the tropopause is depleted in its deuterium content by about 50–60 % with respect to the Standard Mean Ocean Water value

(SMOW), as is shown by numerous measurements of its isotopic composition in the troposphere (see [Kaye, 1987] and references therein). A linear correlation between altitude and the D depletion of tropospheric water exists, due to the vapor pressure isotopic effect [Taylor, 1972]. On the other hand, water formed in the stratosphere as a result of CH<sub>4</sub> and H<sub>2</sub> oxidation should show a smaller depletion in its D content [Kaye, 1990]. This is because, without condensation during upward movements, methane maintains its native isotopic composition which shows a D depletion of the order of 8% [Rinsland *et al.*, 1991]. Since the abundance of deuterium in stratospheric water is dependent on the equilibrium between these two processes, a measurement of the water isotopic composition can put a constraint to the models of the origin of water in the stratosphere.

Isotopic water species have been observed by several groups, both in the infrared and far infrared spectral regions [Baluteau *et al.*, 1977; Kendall and Clarke, 1981; Carli *et al.*, 1982; Carli *et al.*, 1985; Rinsland *et al.*, 1984, 1988, and 1991; Murcray *et al.*, 1988; Toon, 1996]. Vertical distributions of individual water isotopes have been retrieved from far infrared spectra by [Abbas *et al.*, 1987; Carli *et al.*, 1988; Guo *et al.*, 1989; Dinelli *et al.*, 1991; Camy-Peyret *et al.*, 1992]. A marked depletion in the D content of water in the stratosphere (about 50 %) is reported. In this paper we report the measurement of the isotopic ratio HD<sup>16</sup>O/H<sub>2</sub><sup>16</sup>O in the stratosphere for the 20-38 km altitude range. This ratio is obtained by the retrieval of the vertical mixing ratio distribution of the two isotopic species from the far-infrared spectra recorded in 1992 during a balloon measurement campaign.

### 2. Experiment

The far-infrared emission spectra of the stratosphere were recorded with a high-resolution Fourier Transform Spectrometer equipped with polarizing optics [Carli *et al.*, 1984], capable of 0.0025 cm<sup>-1</sup> unapodized resolution. Spectra were obtained during the 1992 Infrared Balloon EXperiment (IBEX 92) campaign of observation based at the National Scientific Balloon Facility in Fort Sumner, New Mexico [34.49° N; 104.22° W].

The measurements were made at a float altitude of about 38.5 km from a balloon-borne platform launched at sunrise on May 4, 1992. The flight lasted about

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**Table 1.** Frequencies (cm<sup>-1</sup>) of the analyzed transitions.

H <sub>2</sub> <sup>16</sup> O 1992	HD <sup>16</sup> O 1992
42.63838	43.29004
43.24340	54.99812
54.83520	60.65965
58.91410	65.05205
62.73511	65.56390
62.87309	—
65.68520	—

12 hours. The flight altitude was continuously derived from on-board pressure measurements, subsequently verified by ground-radar observations. The far infrared signals were detected by a composite germanium bolometer and were filtered to cover the 40-75 cm<sup>-1</sup> frequency interval. The atmosphere was observed in a limb-scanning mode at constant increments of about 3 km in tangent altitude, from 88° to 94° zenith angles, with an instantaneous field of view of 0.35° full aperture. The zenith angle was actively controlled by the Single Axis Platform (SAP), a pointing system with a theoretical error of 0.07° [Coyle *et al.*, 1986]. Unfortunately in this flight the azimuth control system failed, making also the operation of the SAP unreliable. Therefore, the limb-scanning zenith angle of each spectrum was determined from the observed spectra using the molecular oxygen lines at 50.873 and 60.455 cm<sup>-1</sup> as a reference (see [Carlotti *et al.*, 1989]).

The spectra were calibrated in intensity with an ambient temperature blackbody source which was periodically observed during the flight. The interferograms were phase corrected and Fourier transformed to obtain the correct spectral distribution. In order to exploit the best available resolution, no apodization was made. Spectra were also calibrated in frequency using HCl and O<sub>3</sub> lines.

### 3. Analysis

The global-fit procedure was used for the retrieval of the altitude profiles. A presentation of this analysis method is given by [Carlotti, 1988]. Here we briefly recall that global-fit uses a non-linear least squares procedure to fit simultaneously the whole concentration profile to an entire limb-scanning sequence of spectra. The retrieval of a profile is performed by determining the concentration values at a set of suitable altitudes and using an interpolation criterion in between. The separation between the altitudes where the values are retrieved determines the vertical resolution of the profile. Since each limb-scanning sequence has its own vertical resolution, equal to about 3 km, integer 1-km steps have been adopted in the interpolations to facilitate the subsequent averaging of the retrieved profiles. Thanks

to the automated computing procedure, this method makes possible the exploitation of a great number of lines and limb-scanning sequences. A statistical analysis of the results and of the errors becomes therefore possible as demonstrated in [Carlotti *et al.*, 1989].

Since these measurements were extended to low altitudes, a significant continuum emission level was present in the spectra. This continuum was modelled in the synthetic spectra calculation with an altitude dependent absorption coefficient fitted simultaneously to the concentration profiles.

All sequences were recorded during the day. Among the 14 sequences of IBEX 92, 13 of them were of satisfactory quality.

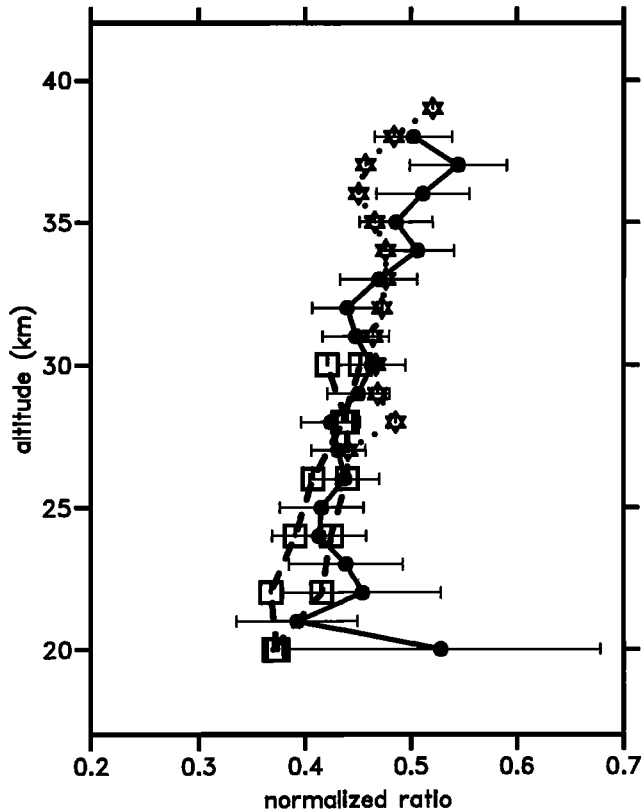
In the frequency interval covered by the detector a large number of lines of the two water isotopes was present. For the analysis, we selected the lines that met the following requirements:

1. For each limb-scanning sequence, the line was visible in the spectrum with the highest tangent altitude and was not too broad in the spectrum with the lowest tangent altitude.
2. The line was not too close (within 0.2 cm<sup>-1</sup>) to other strong lines (line strength at 296 K  $\geq 1.0 \times 10^{-25} \text{cm}^{-1}/\text{molec} \times \text{cm}^{-2}$ ) of the different water isotopes.

The spectroscopic data used in the simulations are from the HITRAN line compilation, 1992 edition, [Rothman *et al.*, 1992], integrated with data from the Jet Propulsion Laboratory (JPL) 1985 line compilation [Poynter

**Table 2.** Retrieved H<sub>2</sub><sup>16</sup>O, HD<sup>16</sup>O mixing ratios and HD<sup>16</sup>O/H<sub>2</sub><sup>16</sup>O with its errors. The mixing ratios have been normalized to their isotopic composition, and the ratio to the standard value of 0.00031069 as given in the HITRAN 92 line list [Rothman *et al.*, 1992].

Alt. (km)	H <sub>2</sub> <sup>16</sup> O (ppmv)	HD <sup>16</sup> O (ppmv)	Norm. Ratio	rand. err. (%)	tot. err. (%)
20	5.53	3.02	0.528	28.4	33.1
21	5.90	2.39	0.392	14.5	22.3
22	5.84	2.75	0.454	16.4	23.6
23	5.36	2.43	0.439	12.2	20.9
24	5.41	2.31	0.414	10.7	20.1
25	5.05	2.17	0.416	9.5	19.5
26	4.77	2.16	0.438	7.5	18.6
27	4.71	2.10	0.425	5.9	18.0
28	4.77	2.09	0.425	6.5	18.2
29	4.49	2.09	0.451	6.5	18.2
30	4.57	2.18	0.463	6.9	18.3
31	4.67	2.16	0.448	7.0	18.4
32	4.84	2.20	0.439	7.5	18.6
33	4.77	2.31	0.470	7.8	18.7
34	4.72	2.47	0.506	6.9	18.3
35	4.96	2.49	0.486	7.2	18.4
36	5.07	2.68	0.511	8.6	19.0
37	4.72	2.65	0.545	8.4	18.9
38	4.99	2.59	0.502	7.3	18.5



**Figure 1.** Comparison of the reported normalized isotopic HD<sup>16</sup>O/H<sub>2</sub><sup>16</sup>O ratio in the stratosphere. The error reported for this measurement (full circles joined by a solid line) is the random error (see text). The other measurements are from *Dinelli et al.*, [1991] (stars joined by a dotted line) and from *Rinsland et al.*, [1992] (open boxes joined by a dashed line).

and *Pickett*, 1985] for the missing data of hot bands and isotopes of ozone. Unfortunately, the line positions of several water transitions were not accurate enough for our purposes. Therefore, when available, we used the line frequencies measured by [*Johns*, 1985]; otherwise, we used the positions estimated from the stratospheric spectra themselves. The line strengths of all isotopic species were corrected for the natural isotopic abundances given by the HITRAN 1992 compilation [*Rothman et al.*, 1992].

#### 4. Results

Among the numerous H<sub>2</sub><sup>16</sup>O lines present in the spectra of IBEX 92, we found 7 that best satisfied the stated requirements. They are listed in column 1 of Table 1. These lines, grouped in 6 spectral intervals and analyzed over the 13 limb-scanning sequences, gave rise to 78 retrieved concentration profiles. We discarded 3 of them because their estimated standard deviation (*esd*) was very large and didn't include the lowest altitude section of 8 of them in the average because the concentration was undetermined in this region (*esd* ≥ 100%).

In the case of HD<sup>16</sup>O, we found five lines suitable for the analysis, listed in column 2 of Table 1. These

lines, grouped in 5 intervals, two of which were simultaneously fitted, generated 52 profiles but 1 of them was eliminated because of large errors and for 7 of them the lowest altitude portion was not used because was undetermined in the fit.

The resulting HD<sup>16</sup>O and H<sub>2</sub><sup>16</sup>O mixing ratios profiles are reported in Table 2.

The isotopic ratios HD<sup>16</sup>O / H<sub>2</sub><sup>16</sup>O, computed at 1 km steps, are given in Table 2 and plotted in Figure 1. These ratios have been normalized to the standard value of 0.00031069 reported by the HITRAN 92 catalogue [*Rothman et al.*, 1992].

Table 2 also reports the random errors and the total error budget associated with the isotopic ratio at each km of altitude, while in the figure only the random errors are reported. The total error budget for the isotopic ratios was calculated taking into account that some of the systematic errors quoted in [*Carlotti et al.*, 1989] affect the two profiles in the same way and so cancel out when the ratio is taken. This is the case for the error arising from the pointing calibration, and is important because of the large pointing error present. The residual systematic errors were due to the following sources:

- Errors on the pressure broadening coefficients and line strength values used in the synthetic spectra calculation (≈ 11 % for H<sub>2</sub><sup>16</sup>O and ≈ 13 % for HD<sup>16</sup>O).
- The finite-length subdivision of the line of sight and the finite steps in the frequency domain (2.5%)

A quadratic summation was used to combine, at each integer km of altitude, the random and the systematic components of the error.

#### 5. Discussion

The new measurements provide the vertical distribution of the D/H ratio in the stratospheric water vapor from 20 to 38 km with a vertical resolution of 1 km and a random error of about 10%. The overall error budget is dominated by spectroscopic uncertainties which lead to an accuracy of about 20%.

Figure 1 shows a comparison between this work and the isotopic ratio profiles already published. The new result is in good agreement with the results obtained ten years before with the same instruments (stars) and a slightly different analysis method [*Dinelli et al.*, 1991], and with the measures of [*Rinsland et al.*, 1991] in the middle infrared (open boxes). Our result is also in good agreement with the normalized column-averaged D/H ratio of 0.44±0.06 measured above Mauna Loa, Hawaii by [*Rinsland et al.*, 1988]. The good agreement between the profiles obtained with far infrared and middle infrared measurements suggests that our estimate of spectroscopic uncertainties may be too conservative. Improvement in the quality of spectroscopic data can be

used to refine this result. Our result is in good agreement with the HD<sup>16</sup>O / H<sub>2</sub><sup>16</sup>O isotopic ratio profile recently reported by [Moyer et al., 1996].

The new measurement determines the D/H ratio over an altitude range larger than that of previous individual measurements with improved accuracy and vertical resolution. The measurement precision, as measured by the random error, is sufficiently small to measure a constant trend in the altitude distribution. As can be seen in Figure 1, the D content of water increases with altitude. This suggests that at low altitudes the source of water vapor in the stratosphere is mainly the upward transport of tropospheric water, while at higher altitudes the amount of water formed by oxidation of methane (less depleted in its D content) increases, reducing in this way the total D depletion.

This measurement gives information about the origin of water vapor in the stratosphere at midlatitude regions of the Northern hemisphere. The extension of these measurements to either polar or tropical regions could provide important information on the origin of the different air masses and therefore on the dynamics of both the polar vortex and the tropical tropospheric-stratospheric exchange.

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