

Determination of vertical HDO/H₂O profile from high-resolution atmospheric transmission spectra

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Received September 12, 2006

We propose a method for determining vertical profiles of the ratio between HDO and H₂O content in the atmosphere from IR atmospheric transmission spectra, obtained with a ground-based high-resolution Fourier transform infrared (FTIR) spectrometer. We have used linear regression between the coefficients of series expansion of the HDO profiles in eigenvectors of the covariance matrix of *a priori* profiles and coefficients of expansion of the spectra in eigenvectors of the spectral covariance matrix used for determination of the HDO/H₂O vertical profile from the observed spectra of atmospheric transmission. The error of the method was estimated from closed model experiments with synthetic FTIR spectra, and its absolute value varies from 5 to 65‰ over the profile. For the relative content of heavy water in the entire atmospheric column the absolute error of the method did not exceed 8‰. For testing this method against the field measurements, we used data of FTIR spectrometer operated in Alaska. The values of the relative content of the heavy water in the atmosphere, taken from the samples of atmospheric transmission spectra in Alaska, observed in 2000–2004, have been compared with data on HDO/H₂O ratio, obtained using the atmospheric general circulation models.

Introduction

Measurements of HDO and H₂¹⁸O isotopes, contained both in precipitation and atmospheric water vapor, are required to improve the quantitative description of the processes of evaporation and condensation of moisture, determining the global water circulation between the ocean, the atmosphere, and the land.^{1–7}

Quantitatively the amount of deuterium in the atmospheric layer is expressed by the formula⁸:

$$\delta\text{HDO} = (\alpha_{\text{HDO}}/\alpha_{\text{HDO}}^0 - 1) \cdot 1000\text{‰}, \quad (1)$$

where α_{HDO} is the ratio of the number of the isotopomer HDO molecules to the number of the molecules of the main water isotopomer in the layer, $\alpha_{\text{HDO}}^0 = 3.1069 \cdot 10^{-4}$ is the average value of this ratio in ocean water (natural abundance). The relative atmospheric column deuterium content (‰) is expressed as:

$$\delta\text{HDO}^* = \frac{\int_0^H N_{\text{H}_2\text{O}}(h)\delta\text{HDO}(h)dh}{\int_0^H N_{\text{H}_2\text{O}}(h)dh}, \quad (2)$$

where H is the height of the upper atmospheric boundary and $N_{\text{H}_2\text{O}}(h)$ is the water vapor concentration. Taking into account the processes of fractionation of isotopes during evaporation and condensation of water, one can conclude that δHDO in the atmosphere ranges from –1000 to 0‰.

Our task was to develop a method of determination of the vertical δHDO profiles from high-resolution atmospheric transmission spectra and to test the method against the data obtained with a ground-based FTIR spectrometer.

The FTIR spectrometer, installed in Alaska (65.11° N; 147.42° W), measured the spectral brightness of solar radiation transmitted through the atmosphere in the spectral range from 750 to 4300 cm⁻¹ with the resolution about 0.002 cm⁻¹ (see Refs. 9–11). For analysis, we chose an interval from the spectral region 1204.5–1207.5 cm⁻¹, containing practically isolated absorption lines of the HDO isotopomer. The spectral step of FTIR measurements was ~0.003 cm⁻¹, and the interval of 3 cm⁻¹ contained ~1000 points. To reduce the measured and modeled spectra to one and the same instrumental function and a unified spectral grid, the initial spectra were additionally convolved with the instrumental Gauss functions having the half-width 0.01 cm⁻¹ and the grid interval 0.01 cm⁻¹.

The *a priori* information on the atmospheric parameters over the Alaskan region studied was taken to be:

1) set of data of atmospheric general circulation model (GCM), taking into account the isotopic fractionation of water (altitude profiles of pressure, temperature, and water vapor concentration and δHDO profiles)¹²;

2) radiosonde measurements over the region (corresponding to the location and time of the processed spectrum), including the altitude profiles of pressure, temperature, and humidity;

3) model profiles of the main isotopomers of the remaining gases (CO_2 , O_3 , N_2O , etc.).

The spectra were calculated, in the direct model, using radiosonde data (pressure, temperature, and humidity), model data on the main absorbing gases, and GCM data selected for the studied region and season (δHDO profiles including those for construction of the covariance matrices).

Spectral transmission function

The atmospheric transmission function at a given frequency can be written¹³ in the following form:

$$T(\nu) = \exp[-\tau_{\text{HDO}}(\nu) - \tau_0(\nu)]. \quad (3)$$

Here, $\tau_{\text{HDO}}(\nu)$ is the optical depth due to absorption by the molecules of the HDO isotopomer, $\tau_0(\nu)$ is the optical depth due to absorption by the remaining gases and aerosol extinction. Given that in the chosen set of the spectral intervals the dependence of τ_0 on the wave number can be neglected, one can write:

$$\begin{aligned} \frac{T(\nu)}{T(\nu^*)} &= \frac{\exp[-\tau_{\text{HDO}}(\nu) - \tau_0]}{\exp[-\tau_{\text{HDO}}(\nu^*) - \tau_0]} = \\ &= \exp[-\tau_{\text{HDO}}(\nu) + \tau_{\text{HDO}}(\nu^*)], \end{aligned} \quad (4)$$

where ν^* is the reference chamber wave number. We have chosen as ν^* the point with the frequency 1206.7 cm^{-1} in the wing of the HDO line. Formula (4) makes the basis of the differential absorption spectroscopy.¹⁴ Thus, it is possible to obtain an expression for the difference of optical depth caused by the absorption of only HDO molecules in the measured spectral region:

$$\Delta\tau_{\text{HDO}}(\nu) = \tau_{\text{HDO}}(\nu) - \tau_{\text{HDO}}(\nu^*) = \ln(T(\nu^*)) - \ln(T(\nu)). \quad (5)$$

On the other hand, using the model of *line-by-line* calculation for the optical depth, one can write

$$\begin{aligned} \tau_{\text{HDO}}(\nu) &= \int_0^H N_{\text{HDO}}(h) \left(\sum_j S_j[t(h)] \Phi_j[\nu_j - \nu, t(h), p(h)] \right) \times \\ &\quad \times \sec(\theta(h)) dh, \end{aligned} \quad (6)$$

where $N_{\text{HDO}}(h)$ is the concentration of HDO molecules; $p(h)$, $t(h)$, and $\theta(h)$ are pressure, temperature, and local zenith angle of observations at the height h , S_j is the intensity, ν_j is wave number of the center, and Φ_j is the profile of the j th HDO line. Summation in Eq. (6) is over all HDO lines contributing to absorption at a given frequency.

The width of the spectral line depends on the temperature and atmospheric pressure at a given altitude. If the self-broadening of HDO line is neglected (in view of smallness of HDO partial pressure), using parameterization of the spectral database HITRAN¹⁵ for the Lorentzian half-width of the spectral line one can write:

$$\gamma(p, t) = \left(\frac{t_{\text{ref}}}{t} \right)^n \gamma(p_{\text{ref}}, t_{\text{ref}}) p, \quad (7)$$

where p is the pressure in bars, t is the temperature in K; $t_{\text{ref}} = 296 \text{ K}$, $p_{\text{ref}} = 1 \text{ atm}$; n is the coefficient of the dependence of broadening by air. In calculating the optical depth, we used the spectral parameters from HITRAN-2004 database¹⁶ and the direct model FIRE-ARMS.¹⁷ For the HDO spectral lines with the centers in the interval $1206\text{--}1207 \text{ cm}^{-1}$, $\gamma(p_{\text{ref}}, t_{\text{ref}})$ value is in the interval $0.06\text{--}0.08 \text{ cm}^{-1}/\text{atm}$, while the n value is in the interval $0.59\text{--}0.64$. Thus, the $\gamma(p, t)$ value in the troposphere for the subarctic summer model may vary in the range $0.02\text{--}0.08 \text{ cm}^{-1}$ and, hence, the ground-based FTIR instruments with the resolution 0.002 cm^{-1} (see Refs. 9, 18, and 19) offer potential possibility of retrieving the altitude HDO profiles from analysis of the atmospheric transmission spectra inferred with this spectral resolution.

The weighting functions (Fig. 1), determined in accordance with Ref. 20 for expression (4), characterize the sensitivity of the signal in HDO lines of the atmospheric transmission function in this spectral interval to the variations of HDO concentration at different altitudes.

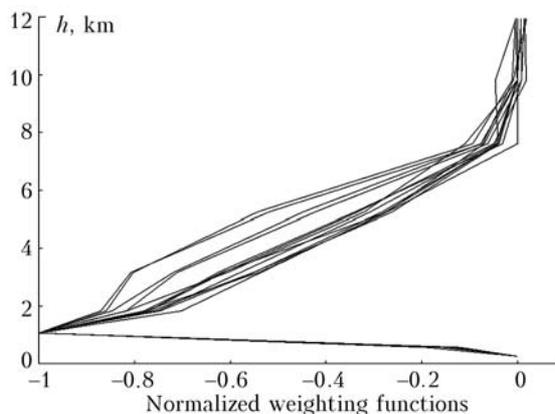


Fig. 1. Thinned set of the weighting functions for the direct model of transmission function on the variations of the profile of δHDO in the spectral interval $1205.8\text{--}1206.6 \text{ cm}^{-1}$.

Empirical orthogonal functions

For constructing the basis of empirical orthogonal functions (EOFs) in the space of the profiles,²¹ we have used the GCM data on the δHDO profiles¹² for the chosen region on the geographic network and time period, corresponding to the location of the FTIR spectrometer and time of the measurements of the spectra. Expansion of the vector of profile on a fixed grid of altitudes can be written as:

$$\delta\text{HDO} = \delta\text{HDO}_{\text{mean}} + \sum_{i=1}^N c_D^i \mathbf{u}_D^i, \quad (8)$$

where $\delta\text{HDO}_{\text{mean}}$ is the vector of the profile average over the set, N is the number of altitudes, c_D^i are the expansion coefficients, and \mathbf{u}_D^i is the set of eigenvectors of the covariance matrix of the δHDO profiles from the GCM.

In this paper, the δHDO profiles have been retrieved using data compression technique²² based on construction of EOF basis in the space of spectra. The basis is a set of eigenvectors of the covariance matrix of the measured spectra, normalized using the noise covariance matrix of measurements. Then, the expansion of the spectrum has the form

$$\Delta\tau_{\text{HDO}} = \Delta\tau_{\text{HDO}}^{\text{mean}} + \sum_{i=1}^M c_R^i \mathbf{u}_R^i, \quad (9)$$

where $\Delta\tau_{\text{HDO}}^{\text{mean}}$ is the vector of reference (average) spectrum on a specified wave number grid, M is the dimensionality of the basis (the number of spectral channels), c_R^i are the expansion coefficients, and \mathbf{u}_R^i is the set of basis vectors (EOFs).

The dimensionality of the basis can be restricted if the presentation of spectra is admissible at a given measurement error. Because only insufficient number of measured FTIR spectra are available, the EOF basis has been constructed on the model spectra according to the scheme:

1. We chose, from the GCM database, a set of δHDO profiles, covering a series of values in δHDO^* from -550 to -50% .

2. For each δHDO profile from the set, we have performed model calculation of the transmission function in the chosen spectral interval using FIRE-ARMS software. In this case, such atmospheric parameters as temperature and humidity profiles were taken from radiosonde measurements corresponding to the measured spectrum processed.

3. We have added, to each model spectrum, a normally distributed noise with the zero mean and 0.012 standard deviation, characteristic of the measured FTIR spectra of the atmospheric transmission. For that noisy set, we constructed the

covariance matrix, determined EOF of transmission, and selected the dimensionality of the basis.

Restricting the number of terms in expansion (9), one can calculate the discrepancy between the initial and obtained spectrum. The diagonal of the covariance matrix of discrepancies for the entire set of spectra evaluates the mean sum of residual terms in the series (9). Comparing this diagonal with the diagonal of covariance matrix of spectrometer measurement error, we can reduce the dimensionality of the EOF basis. It was found that, for the level of FTIR measurement error, three first basis vectors taken as principal components are sufficient for representation of the variations of the spectra, caused by the change of the δHDO profile.

Linear regression of the major components

The technique of processing an individual spectrum measured assumes that the profiles of temperature, pressure, and concentrations of the atmospheric gases (with the exception of the HDO isotopomer) are known (correspond to the coincident radiosonde measurements), also, the geometry and zenith angle of measurements of the spectrum are assumed to be known. Therefore, by varying δHDO profile, it is possible to match the measured and calculated spectra.

Since the vertical δHDO profile and the corresponding optical depth (6) are linearly related, there obviously must exist a linear relation between the major components (MC) of the expansion of the δHDO profile and MC of the optical depth series expansion. Using a set of model "noisy" spectra, calculated from GCM δHDO profiles, it is possible to construct a linear dependence between MC of δHDO profiles and MC of the spectra:

$$\mathbf{c}_D = \mathbf{B}\mathbf{c}_R. \quad (10)$$

Here \mathbf{c}_D is the vector of expansion coefficients of the profile in the basis of the profiles, \mathbf{c}_R is the vector of expansion coefficients in the basis of the optical depth spectra, \mathbf{B} is the 3×3 matrix of regression coefficients. The regression coefficients are determined from the formula²²:

$$\mathbf{B}^T = (\mathbf{C}_R^T \cdot \mathbf{C}_R)^{-1} \cdot \mathbf{C}_R^T \cdot \mathbf{C}_D, \quad (11)$$

where \mathbf{C}_D is the matrix whose rows contain transposed vectors of expansion coefficients of the profiles from the set, for which the transmission spectra are calculated, and \mathbf{C}_R is an analogous matrix of the corresponding expansion coefficients in the basis of spectra. The matrix in parentheses in formula (11) is diagonal because MC do not correlate. The solution for the profile sought is

calculated by use of formula (10) by substituting MC of the measured spectrum.

Accuracy of the method was estimated by reconstructing the model transmission spectra, calculated for the test set of δHDO profiles, which was compiled also from the GCM data. The diagonal of the covariance matrix of discrepancy between the initial and reconstructed profiles serves as an estimate of δHDO profile retrieval error (Fig. 2), found to vary over the profile from 5 to 65% in absolute value.

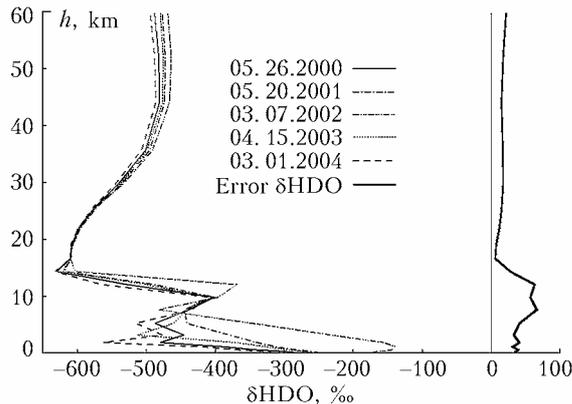


Fig. 2. The δHDO profiles reconstructed from FTIR spectra for five measurements; and root-mean-square retrieval error of δHDO profiles, that is obtained in closed model experiments with model FTIR spectra.

It is worthy to note that when the number of terms in expansion (8) of the model δHDO profiles is restricted to just three MCs (which are determined in the method), the error of such an expansion is no more than 10% relative to the initial profiles.

By analogy to expression (10), one can also construct a linear regression for the relative column deuterium content:

$$\delta\text{HDO}^* - \delta\text{HDO}_{\text{mean}}^* = \tilde{\mathbf{B}}\mathbf{c}_R, \quad (12)$$

where $\delta\text{HDO}_{\text{mean}}^*$ is the average value over the set of the profiles. This relation can be used to infer δHDO^* directly from the spectral data instead of calculating it from reconstructed profile according to Eq. (2). The error in the retrieved column density of deuterium δHDO^* was $< 8\%$ for the spectra processed.

Results

To test the method, we used five FTIR measurements of atmospheric transmission function in Alaska under clear-sky conditions and the corresponding radiosonde measurement data on the vertical profiles of temperature and humidity. The measurements were conducted on May 26, 2000; May 20, 2001; March 07, 2002; April 15, 2003; and March 01, 2004. For all measurements of the spectra, we

compiled the sets of the model δHDO profiles, calculated model spectra, and retrieved δHDO profiles and relative column density of δHDO^* .

The δHDO profiles reconstructed from the five FTIR spectra measured are presented in Fig. 2. Figure 3 presents an example of spectra fitting: shown are the spectrum measured with the FTIR spectrometer, spectrum modeled in the direct FIREARMS model for a reconstructed deuterium profile, and the difference between them. The mean error of the model fit to measured spectra was 1.2%.

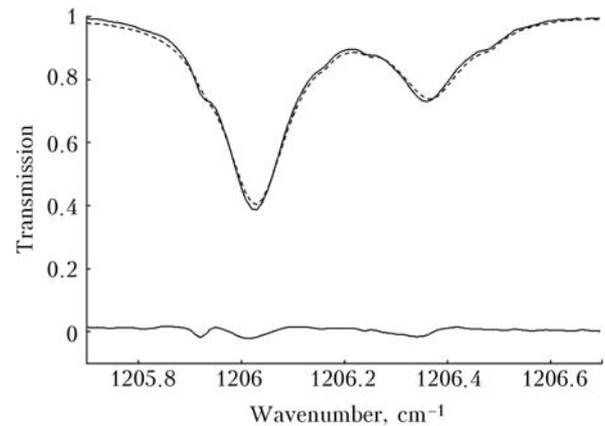


Fig. 3. Fit of the spectrum measured with the ground-based FTIR in Alaska on March 1, 2004 (viewing zenith angle 72.73° , solid line) to the calculated spectrum using the deuterium profile reconstructed (dashed line), and their difference (bottom curve).

Figure 4 shows δHDO^* values, obtained from processing the available FTIR measurements, and annual δHDO^* behavior, calculated from GCM for this Alaskan region. Also shown are δHDO values near the surface (at ~ 1000 hPa level).

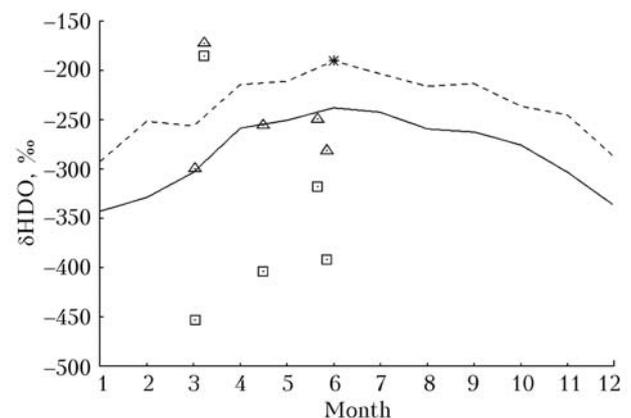


Fig. 4. Variations of the relative δHDO content in the near-ground layer (dashed line shows GCM data,¹² and triangles the reconstructed values) and in the atmospheric column, δHDO^* (solid line shows GCM data, and squares the reconstructed values). Asterisk shows annually mean δHDO content in the near-ground layer according to the data of the ECHAM4 model (see Ref. 3) for 65° N.

Conclusion

We have developed a method for reconstructing vertical δHDO profiles in the atmosphere with the use of the compression of atmospheric transmission spectra and *a priori* information in the form of vertical δHDO profiles from atmospheric general circulation model taking into account the isotopic water partition. By constructing the linear regression between major components of δHDO profiles and atmospheric transmission spectra, it is possible to rapidly obtain both the profile and total atmospheric column of the $\text{HDO}/\text{H}_2\text{O}$ ratio from high-resolution spectra measured with a ground-based FTIR. Error analysis made using closed calculations has demonstrated satisfactory accuracy of the linear regression method developed in retrieving the δHDO profile and good accuracy of the δHDO^* retrievals. However, this is the lower error estimate, because it is calculated for error arising in the regression scheme itself, without the account of uncertainties associated with the errors in spectroscopic data from HITRAN database.

The proposed method was tested using the atmospheric transmission spectra measured with FTIR under clear-sky conditions and supported by simultaneous radiosonde measurements of temperature and humidity profiles. The results, obtained for the retrieved profiles of relative column δHDO density, are compared with the GCM data for the geographic region under study (see Fig. 4).

There are systematic deviations of δHDO and δHDO^* values obtained from FTIR spectra from those used in the models. One of the possible reasons for this discrepancy is the inaccuracy of the coefficients of broadening of HDO lines in the spectral interval $1205\text{--}1207\text{ cm}^{-1}$, taken from HITRAN data base. More accurate data on the coefficients of HDO line broadening are required to improve the accuracy of the method proposed for determination of the vertical $\text{HDO}/\text{H}_2\text{O}$ profiles from high-resolution atmospheric transmission spectra.

With this method, it would be possible to obtain representative time series of δHDO variations at different altitudes in the atmosphere based on the data of quasi-global FTIR network, covering latitudes from 77.81° S to 78.91° N .¹⁹

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