

Determination of HDO/H₂O ratio in the atmosphere from the data of the ground-based sensor TIIS

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In this study we have identified the signals from the HDO isotope of water molecule in the emission spectra of the atmosphere recorded with a TIIS sensor along the zenith direction under clear sky conditions in December 1997 near Tokyo. Based on the algorithms available in the FIRE-ARMS software package we have developed a technique to determine the concentration ratio HDO/H₂O in the troposphere from the TIIS spectra recorded in the range from 700 to 1500 cm⁻¹ with the resolution of 0.15 cm⁻¹. Thus obtained HDO/H₂O concentration ratios agree with the characteristic values of this ratio that are being observed at these latitudes under similar conditions.

The advent of ground-based IR Fourier-spectrometers, enabled observations of the atmospheric self-radiation in the range 600–3000 cm⁻¹, with a sufficiently high spectral resolution,^{1–4} at different zenith angles has given a motivation for the development of methods of reconstructing some atmospheric parameters from thus obtained spectra. At present, a series of methods for retrieving the temperature profiles and concentration of greenhouse gases is available.⁵ Thus, the method of estimating the HDO/H₂O ratio from the data on outgoing thermal radiation of the Earth's atmosphere, acquired with an IMG sensor from the ADEOS satellite, is described in Ref. 6. In this work we propose the method for reconstructing the HDO/H₂O ratio based on the results of passive sensing of the atmosphere along zenith in the spectral range 700–1500 cm⁻¹ by use of a TIIS Fourier spectrometer. Specifications of this instrument are as follows:

Spectral range, μm 3.3 – 16
Spectral resolution, cm⁻¹ 0.06 (without apodization)
Accuracy of the wave number referencing, cm⁻¹ 0.005
Range of measured brightness temperature, K 255 – 320
Radiometric accuracy, K < 1
Radiometric stability, K < 0.5

Measuring spectra of the black body radiation at the temperatures of 300 and 77 K made the radiometric calibration of the spectrometer. The calibration procedure for TIIS was described in Ref. 4.

The spectrum of radiation of a cloudless atmosphere for the case of observation along the zenith is determined by the following formula:

$$W(\nu) = \int_0^H (K_{\text{gas}} + K_{\text{abs}}) B(\nu, T) \times \exp \left(- \int_0^h (K_{\text{gas}} + K_{\text{abs}} + K_{\text{sca}}) dh' \right) dh, \quad (1)$$

where $W(\nu)$ is the spectral brightness of the atmospheric radiation, W/(m²·cm⁻¹·sr), at the frequency ν ; $B(\nu, T)$ is the Planck's radiation at the temperature T ; h is the current altitude; H is the altitude of the upper atmosphere taken into account; K_{gas} , K_{abs} , and K_{sca} are the coefficient of absorption by atmospheric gases, aerosols, and the aerosol scattering coefficient, respectively. K_{gas} can be expressed through

$$K_{\text{gas}}(\nu, h) = K_{\text{cont}}(\nu, h) + N_0(h) \sum_{i=1}^{N_g} n_i(h) \sum_{j=1}^{N_i} \alpha_{ij} \sigma_{ij}[\nu, T(h)], \quad (2)$$

where $K_{\text{cont}}(\nu, h)$ is the coefficient of continuum absorption by water vapor; $N_0(h)$ is the number density of the molecular atmosphere at the altitude h ; $T(h)$ is the altitude profile of temperature; $n_i(h)$ is the relative concentration of all isotopic modifications for the i th gas; α_{ij} is the natural abundance of the j th isotopic modification of the i th gas; σ_{ij} is the absorption cross section calculated by line-by-line method using the parameters from the HITRAN-96 (Ref. 7); N_g is the number of gases under consideration; N_i is the number of isotopic modifications of the i th gas taken into account.

In this work, we use the algorithms for solving the inverse problem in the form (1), available in the FIRE-ARMS^{8,9} software package, intended for minimization of the following goal function:

$$F = \sum_{i=1}^M \left[\frac{W_i^{\text{obs}}}{W_i^{\text{calc}}} - \frac{W_i^{\text{calc}}}{W_i^{\text{obs}}} \right]^2, \quad (3)$$

where W_i^{obs} and W_i^{calc} are the observed and calculated spectral densities of the atmospheric radiance at the i th frequency; M is the number of points on the frequency scale. This algorithm minimizes function (3) by the

Fletcher–Reeves method, which can be presented as a series of the following steps¹⁰:

a) stage 0: X_0 is the initial state, and the direction of the first displacement is determined as

$$D_0 = -\nabla F(X_0); \quad (4)$$

b) stage k : choosing the number λ_k that minimizes the function

$$g(\lambda) = F(X_k + \lambda D_k), \quad (5)$$

setting

$$X_{k+1} = X_k + \lambda D_k, \quad (6)$$

$$D_{k+1} = -\nabla F(X_{k+1}) + \beta_k D_k, \quad (7)$$

$$\beta_k = \frac{\|\nabla F(X_{k+1})\|^2}{\|\nabla F(X_k)\|^2}; \quad (8)$$

c) end test: if performed, then stop else put $k \leftarrow k + 1$ and go to step b).

In the above procedure $X_k = \{t_i, \dots, t_N, n_{ii}, \dots, n_{iN}\}_k$ is the vector that includes, in our case, the profiles of temperature and water vapor.

The choice of the Fletcher–Reeves method is conditioned by two reasons. First, this method needs for storing only small bulk of information (three n -dimensional vectors, where n is the dimension of the vector X_k); second, this method turns to be the best among the gradient methods applicable to the problem of retrieving the profiles. Apart from that, the method, initially intended for the limit-free optimization, was then modified to take into account physical limitations imposed on the atmospheric parameters. In this work we use the limitations of the form

$$ax_i^{\text{ref}} \leq x_i \leq bx_i^{\text{ref}}, \quad (9)$$

where x_i and x_i^{ref} are the varied and reference atmospheric parameters (the temperature or concentration of absorbing gases) at the i th altitude, and the parameters a and b obey the conditions $0 < a < 1$ and $b > 1$, being the same at all nodes of the altitude grid, while varying for different atmospheric parameters. The modification of the Fletcher–Reeves method is in the following:

1) before making the minimization (5), maximum possible parameter $\lambda = \lambda_{\text{max}}$ is determined leading to saturation of at least one of the limitations (9);

2) the one-dimensional minimum (5) is searched in the interval $\lambda \in [0, \lambda_{\text{max}}]$;

3) if the minimum (5) falls onto $\lambda = \lambda_{\text{max}}$, then the projection of the vector $-\nabla F(X_k)$ on the range determined by the inequality (9) is taken as the next direction D_k ; at this iteration $\beta_k = 0$.

Besides, the programmed realization of this method includes a possibility at the stage a) to take the vector of the initial state or opposite to it ($D_0 = X_0$ or $D_0 = -X_0$) as the initial direction. This is equivalent to varying the multiplier, by which the initial state is multiplied at the first iteration. Owing to this fact, in

many cases just the first iteration gives a good agreement between the measured and calculated spectra. The next iterations of the gradient method only make the solution more accurate and improve the agreement between the spectra.

Contrary to statistical methods for solving the inverse problem based on linearization of Eq. (1) (Refs. 11–13), the above procedure does not require *a priori* information on the statistical properties of the solution sought.

The procedure of HDO/H₂O determination in the atmosphere

The lines observed with a TIIS near 1206 cm⁻¹ we have identified as a signal from HDO. A fragment of a spectrum recorded with the TIIS that contains the HDO signal is presented in Fig. 1. Under clear sky conditions in the atmosphere the signal observed in the range 1205–1207 cm⁻¹ is determined by three components: HDO molecule, continuum absorption by water vapor, and the background aerosol. Figure 2 presents two calculated spectra: one with the account for HDO and the other one without it.

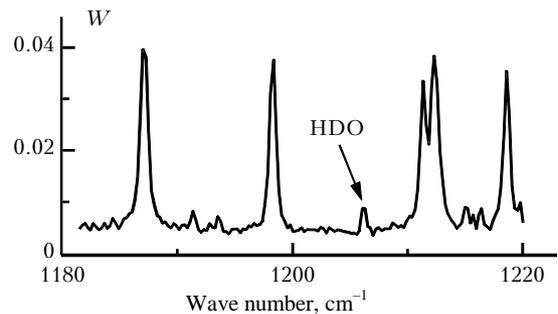


Fig. 1. A fragment of the TIIS spectrum with HDO signal detected during observations under clear sky conditions in the atmosphere along the zenith on December 10, 1997, at 13:55 (local time) near Tokyo (35.6347°N, 139.5869°E).

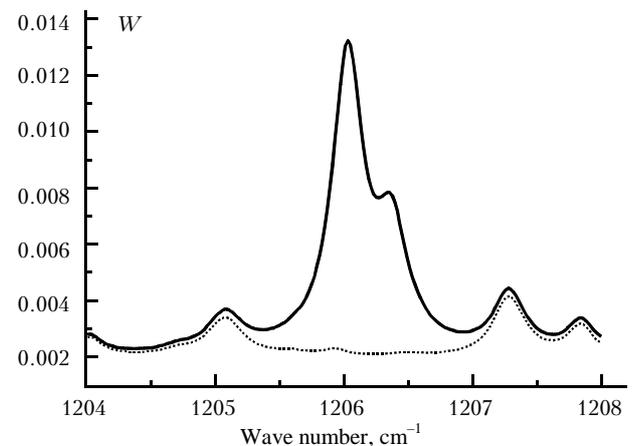


Fig. 2. Identification of the HDO line. Solid curve presents the spectrum calculated with the account of the HDO molecule, dotted curve – the spectrum calculated ignoring the HDO molecule.

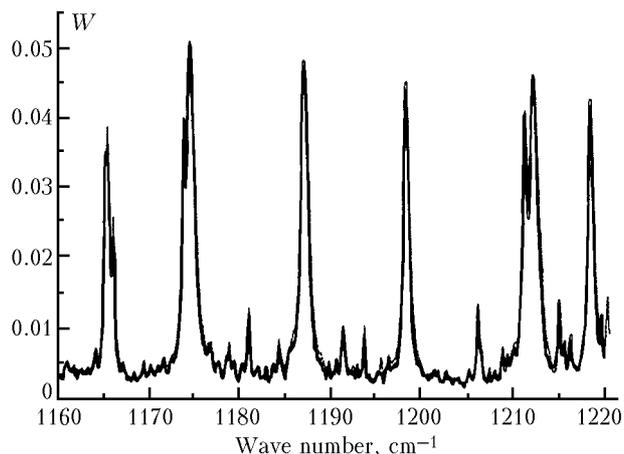


Fig. 3. Fitting of the calculated and measured spectra after reconstruction of the water vapor profile. Solid curve presents the measured spectrum, the dotted line – the calculated one.

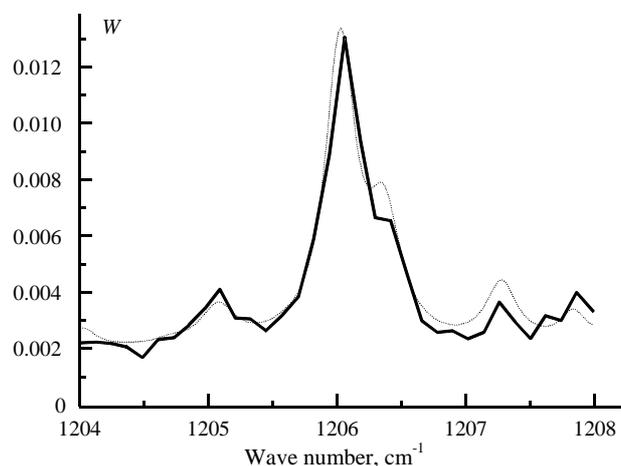


Fig. 4. Fitting of HDO lines in the calculated and measured spectra after reconstruction of the HDO/H₂O ratio.

Our approach to determination the ratio HDO/H₂O from TIIS spectra obtained at observation of the atmosphere along the zenith consists of a certain sequence of steps.

The first step is in determination of the atmospheric temperature profile. Contribution of the background urban aerosol was considered in the framework of the corresponding model from Ref. 14; the continuum absorption by water vapor – by the model from the FASCOD 3P software.

The second step is the retrieval of water vapor profile and total content in the atmospheric column of 1×1 m² area using data from the spectral range 1160–1200 cm⁻¹. The results of fitting the observed and model spectra obtained after this step are shown in Fig. 3.

The third step is similar to the second one, but the HDO retrieval is made using data from the range 1205–1207 cm⁻¹. Fitting of the spectra after this step is presented in Fig. 4.

Calculation of the HDO/H₂O ratio in the atmospheric column by use of data from the range used in the observations is made at the fourth step by the following formula:

$$\delta\text{HDO} = \left[\frac{(\text{HDO}/\text{H}_2\text{O})}{(\text{HDO}/\text{H}_2\text{O})_{\text{SMOW}}} - 1 \right] \times 1000,$$

where SMOW is the standard ratio of these isotopes for the ocean conditions.

The value of HDO/H₂O obtained on December 10, 1997, at 13:55 of the local time from the TIIS spectrum recorded near Tokyo agrees with the data from Ref. 15 and equals to (0.0279 ± 0.0006)%, (δHDO = -103 ± 20).

In estimating the confidence interval for the obtained value of HDO/H₂O, the following sources of error may be considered:

- errors in the temperature profile retrieval;
- errors in the moisture content profile retrieval, which, in turn, depend on the errors in the temperature profile;
- inadequate account for the background aerosol;
- errors in direct model (1) connected with the possible errors in the parameters taken from the spectroscopic databases.

The direct radiosonde measurements of the temperature and moisture profiles up to 5.2 km, conducted simultaneously with the TIIS ones, allowed estimating the errors of retrieving the corresponding parameters from the TIIS spectra and the relevant errors in determination of the HDO/H₂O ratio. The latter was made by substitution of the radiosonde profiles at the third step of the above-cited calculation algorithm.

Conclusion

Since the comparison between the TIIS and direct radiosonde measurements of the temperature and water vapor profiles has been used in our study to estimate the errors in reconstruction of these parameters, inadequate account for the background aerosol can be treated as the basic source of uncertainty in the above schemes of the HDO/H₂O ratio calculation. However, simultaneous determination of the extinction coefficient with a lidar and of the atmospheric emission spectrum with a Fourier spectrometer can eliminate this source of uncertainty. Consequently, the proposed method of determination of HDO/H₂O ratio in the atmosphere from the data of ground-based IR Fourier spectrometers, such as TIIS,⁴ EISAR,⁵ and others, complemented with lidar data, can be applicable to monitoring of the deuterium in the atmosphere and verification of the climatic models.

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