

VERIFICATION of H₂O lines from the HITRAN Database for remote sensing of the water vapour isotopic composition

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ABSTRACT

The quality of the spectroscopic line parameters from the HITRAN Database for remote sensing of the water vapour isotopic composition of the atmosphere is widely discussed. In this research we show that the HITRAN-2008 data for H₂O isotopologues in the near infrared spectral range (4000-6400 cm⁻¹) is reasonably good. The HITRAN data was tested with independent calculation (*ab initio* et al.). For the evaluation we've used two following criteria: a quality of the fitting of atmospheric spectra measured at the Ural Atmospheric Station (UAS, Kourovka) with the high-resolution Fourier-transform infrared spectrometer and an agreement between the retrieved HDO/H₂O relative concentration ratios in the atmospheric column and the results of the simulation of the isotopic general circulation model ECHAM5-wiso (validated for Kourovka region).

Key words: Water vapour isotopes, Remote sensing, Fourier-transform IR spectrometry, General circulation model, Kourovka, Contour of spectral line, Line width and shift coefficients, Semi-classical impact theory.

1. INTRODUCTION

Atmospheric measurements of water vapour isotopic composition can provide valuable information regarding atmospheric water cycle. Different water vapour isotopologues has different physical properties what leads to a depletion of a given air mass in the heavier isotopologue (HDO) on each condensation or evaporation event [1]. The target value of interest is a relative concentration of HDO/H₂O:

$$\delta D = \left(\frac{HDO / H_2^{16}O}{2 \frac{D}{H} VSMOW = 311.4 \cdot 10^6} \right) \cdot 1000\text{‰}, \quad (1)$$

where HDO and H₂¹⁶O are concentrations of these isotopologues respectively. Fig. 1. shows different isotopic signatures of different seasons measured at the UAS in Kourovka by a high-resolution in-situ isotopic analyzer. However precisions measurements of water vapour isotopic composition in atmospheric column remains a difficult task.

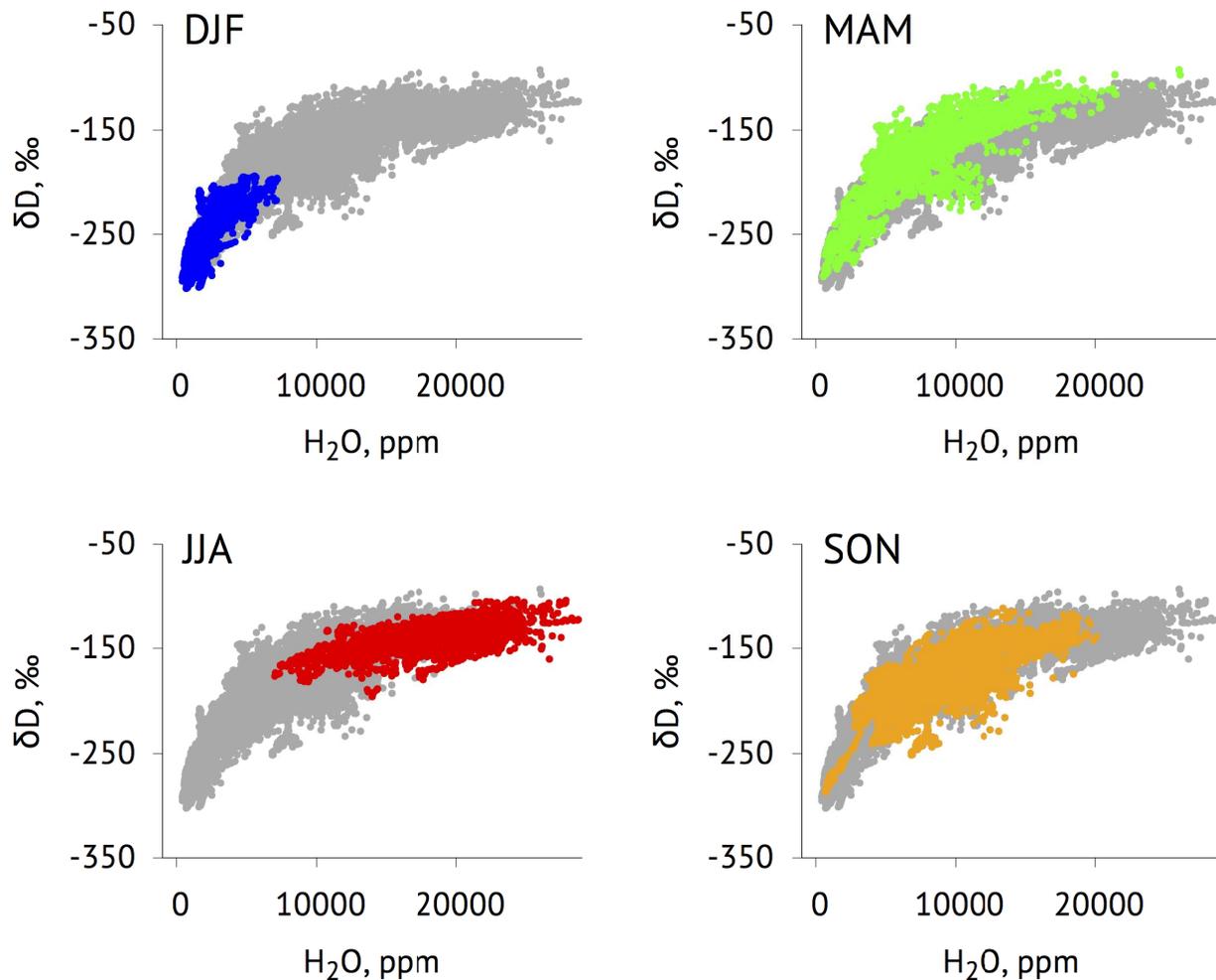


Fig.1. Isotopic signatures of different seasons measured at the UAS in Kourovka by in-situ Picarro analyzer

Ground-based Fourier-transform (FTIR) and satellite remote sensing measurements are actively used to get an access to the total content and the vertical distribution of atmospheric species [2,3,4,5,6,7]. Retrieval algorithms in such techniques rely on the information from spectroscopic databases like HITRAN [8]. Accuracy and precision of retrieval is highly sensitive to the spectroscopic data especially when dealing with isotopic content [9]. We analyzer the HITRAN 2008 instead of the HITRAN 2012 line list because the latter introduced some dramatic changes to water vapour spectral data [10]. And these changes didn't show an improvement in terms of atmospheric spectroscopy [9]

2. SPECTROSCOPY

This section describes the selection of spectroscopic parameters for the verification of the HITRAN 2008 Database.

Calculations of $H_2^{16}O$ rotation-vibration line broadening, shifting and temperature exponents due to air pressure effects are performed using a semi-empirical approach developed by using anharmonic wavefunctions in the estimates of the line profiles. Calculations are based on impact theory modified by introducing additional parameters to extend the use of empirical data. It includes correction factors whose parameters can be determined by fitting the calculated broadening or shifting coefficients to experimental data. The semi-empirical method distinguished by the relative simplicity of calculations is effective in description of line broadening processes for molecules characterized by so-called strong interactions, when the distance of closest approach is less than the interruption parameter in the cut-procedure.

The semi-empirical method remains the main of the cut-off method: clear physical meaning and the possibility to calculate separately the contributions of different types of intermolecular interactions and different scattering channels to the contour parameters. The last aspect allows us to analyse the vibration-rotational dependence of line broadening and shifting coefficients. The semi-empirical approach gives the possibility to make numerous calculations of the line contour parameters without a noticeable loss of precision. Earlier, the above semi-empirical method and the method of effective Hamiltonians were applied for the calculation of line profile parameters and coefficients of their temperature dependence in the case of colliding molecules H₂O–N₂, H₂O–O₂. [11-13].

For line parameters calculations using any method one needs to know accurate wave functions, energy levels, and collision-induced transition probabilities. It should be noted that previous works used wave functions, determined by the method of effective rotational Hamiltonians. This method disregarded the strong intramolecular perturbations caused by high vibration excitation and don't describe accurately spectra in high frequency region. In [14,15] we have shown the necessity to use more accurate wave functions than those arising from simple effective Hamiltonians. It was proposed approach where the accurate wave functions, calculated using DVR3D nuclear method [16] were used. Wave functions were obtained with a high accuracy potential energy surface based on high quality *ab initio* calculations augmented by relativistic and diagonal non-Born-Oppenheimer corrections. These wave functions have been used to calculate dipole transition probabilities with the *ab initio* dipole moment surface of Partridge and Schwenke [17]. This approach explicitly takes into account all scattering channels induced by collisions. In principle, the use of the accurate wave functions, obtained from global variational calculations, extends the applicability of the method up to dissociation energy of molecule.

Transition probabilities required for application of the semi-empirical approach were derived from the Einstein A coefficients in BT2 list, which are used for the line intensity calculation. We have selected the required Einstein A coefficients from the values presented in the full BT2 list. The BT2 line list contains all the transitions between the vibration-rotation states of water up to 30 000 cm⁻¹ (22 1000 states, 5.08 · 10⁸ transitions), for which the rotation quantum numbers reach *J* = 50. First of all we estimated the contributions of corresponding scattering channels to the line contour parameters and then sorted the Einstein A coefficients. We took account of all the scattering channels induced by collisions and allowed by symmetry.

The main feature of the present calculation is the use of a complete set of high accuracy vibration-rotation dipole transition moments calculated for all possible transitions using wavefunctions determined from variational nuclear motion calculations and an *ab initio* dipole moment surface. This approach explicitly takes into account all scattering channels induced by collisions.

Comparison between theoretical calculations and high-resolution measurements [15] of pressure broadening for near-infrared water spectra are present on the Fig.2, it is seen a really good agreement. Obtained using the frequency-stabilized cavity ring-down spectroscopy method the relative uncertainties for the broadening parameters is in the range 0.40 % to 2.13 %, and the agreement with calculated data is in the same range.

Temperature exponents are determined, by the usual least-squares method, the temperature exponents *N* from the standard relation

$$\gamma_{if}(T) = \gamma_{if}(T_{ref}) \left(\frac{T}{T_{ref}} \right)^{-N}, \quad (2)$$

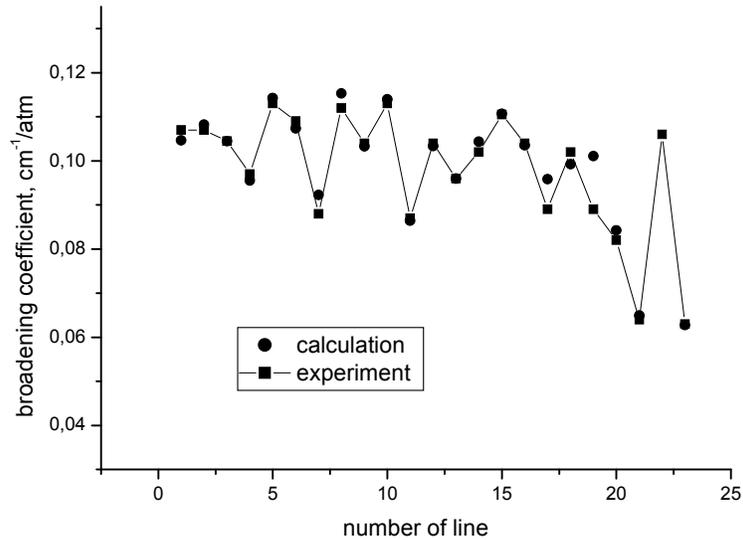


Fig.2. Comparison between theoretical calculations and high-resolution measurements [15] of pressure broadening for band.

with the reference temperature $T_{ref} = 296$ K. We note that the deduced N values are very sensitive to the precision of self-broadening coefficients, especially for narrow lines: even small errors in the determination of γ induce large uncertainties in N .

Calculations of HDO rotation-vibration line broadening due to air pressure effects are performed using the averaged energy difference method. The influence of the buffer gas on the internal state of the absorbing molecule is emphasized in this method. Some version of this approach in applying to HDO line width calculations are presented in [18].

3. FITTING OF GROUND-BASED NIR ATMOSPHERIC SPECTRA

For the assessment of the quality of the HITRAN 2008 H₂O spectral data we selected about 3300 ground-based atmospheric spectra from the Ural Atmospheric Station (UAS, Kourovka, [6]). These selection covers a wide range of atmospheric conditions. We then retrieved concentration of HDO and H₂O in atmospheric column using the two line lists: HITRAN 2008 and HIT* (HIT* is HITRAN with changes of γ_{air}). The retrieval has been done using the GGG/GFIT software package of the Total Carbon Column Observing Network (TCCON, [19]) using an extended HDO spectral window set proposed in [9]. The retrieval workflow followed a traditional TCCON approach with a one difference. To generate HDO a priori data from H₂¹⁶O NCEP profile the following relationship has been used:

$$x_{HDO}^{apr}(h) = 0.0825 \cdot x_{H_2^{16}O}^{apr}(h) \cdot \left(15.2 + \log\left(x_{H_2^{16}O}^{apr}(h)\right)\right), \quad (3)$$

where $x_{apr}^{HDO}(h)$ and $x_{apr}^{H_2^{16}O}(h)$ are the vertical profiles of HDO and H₂¹⁶O volume mixing ratios respectively, h is the altitude. This relationship better describes lower tropospheric δD values than the one built-in in GFIT. ([9] and TCCON meeting talk).

A priori vertical profiles of temperature, pressure and humidity were derived from the National Centers for Environmental Prediction and the National Center for Atmospheric Research (NCEP/NCAR) data [20].

We've averaged spectral residuals over the whole spectral set to see how good the HITRAN 2008 parameters fit the spectra set at average. The same analysis was also performed separately for low temperature measurements (with atmospheric temperatures below -10°C) and for normal temperature measurements (with atmospheric temperatures close to the HITRAN reference temperature of 296K) but didn't show any significant differences. The average quality of the spectral fitting is presented in Table 1 (lower is better).

Gas	Window	St.Dev. (Meas - Fit) • 10 ³	
		HITRAN08	HIT*
HDO	4037.00 – 4039.00 cm ⁻¹	1.81	2.26
HDO	4052.96 – 4056.25 cm ⁻¹	3.54	4.57
HDO	4099.91 – 4100.81 cm ⁻¹	0.62	0.61
HDO	4112.11 – 4120.10 cm ⁻¹	5.97	13.27
HDO	4144.11 – 4144.90 cm ⁻¹	1.08	1.59
HDO	4157.10 – 4158.30 cm ⁻¹	1.54	2.22
HDO	4211.51 – 4213.40 cm ⁻¹	4.76	5.73
HDO	4227.00 – 4238.00 cm ⁻¹	8.66	6.68
HDO	5058.66 – 5059.25 cm ⁻¹	1.69	2.02
HDO	6307.31 – 6352.80 cm ⁻¹	2.46	2.57
HDO	6352.30 – 6402.49 cm ⁻¹	2.24	2.25

Table 1. Quality of the spectral fitting in the HDO spectral windows

4. COMPARISON TO A GCM

To assess the quality of the retrievals we performed a comparison of retrieved XδD quantity (the X prefix means that we're dealing with the columnar values calculated a posteriori from the retrieved HDO and H₂¹⁶O columnar concentrations) with simulations of the full physics isotopic general circulation model (GCM) ECHAM5-wiso [21]. The model has been validated against high-precision in-situ measurements of δD by Piccaro analyzer for the Kourouka region [7].

Since the remote sensing products are affected by different vertical sensitivity the model profiles have to be 'corrected' before the comparison. Such correction is usually obtained by a convolution of an original model vertical profile with a column averaging kernel of the retrieval (see [9], for more details). The column averaging kernels are presented at Fig. 3 and show how different is the vertical sensitivity of the method for H₂¹⁶O and HDO concentration retrievals.

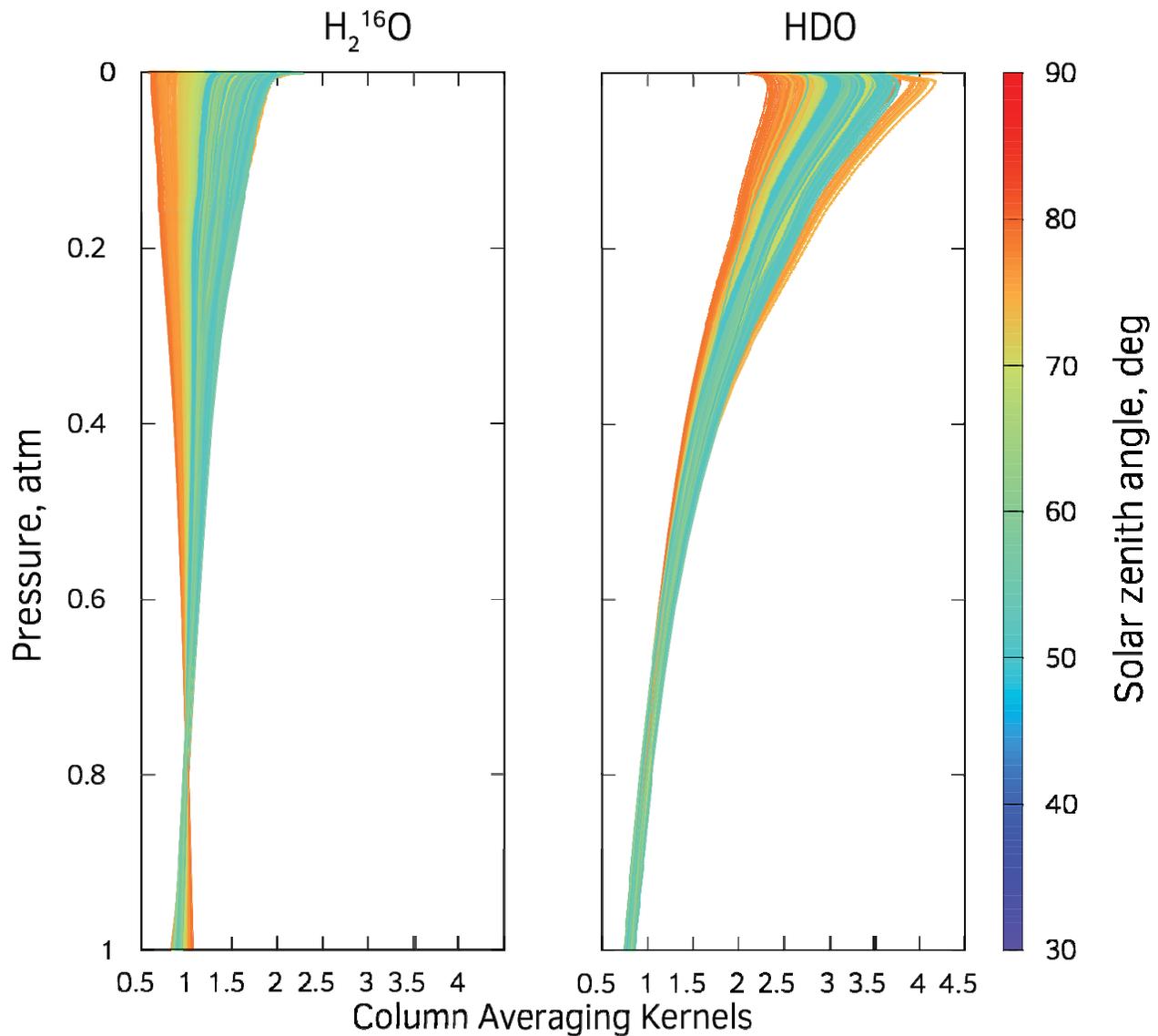


Fig.3. H_2^{16}O and HDO Column averaging kernels of the retrieval show different vertical sensitivity

Time series of the X δ D over Kourouva retrieved from the selected measurements along ECHAM5-wiso simulations are presented at Fig. 4. While Fig. 5. shows a scatterplot of the retrieved vs. simulated values. One can see that HITRAN 2008 performs pretty well and shows a good agreement with the ECHAM5-wiso GCM: $r^2 = 0.93$ with a slope of 1.25.

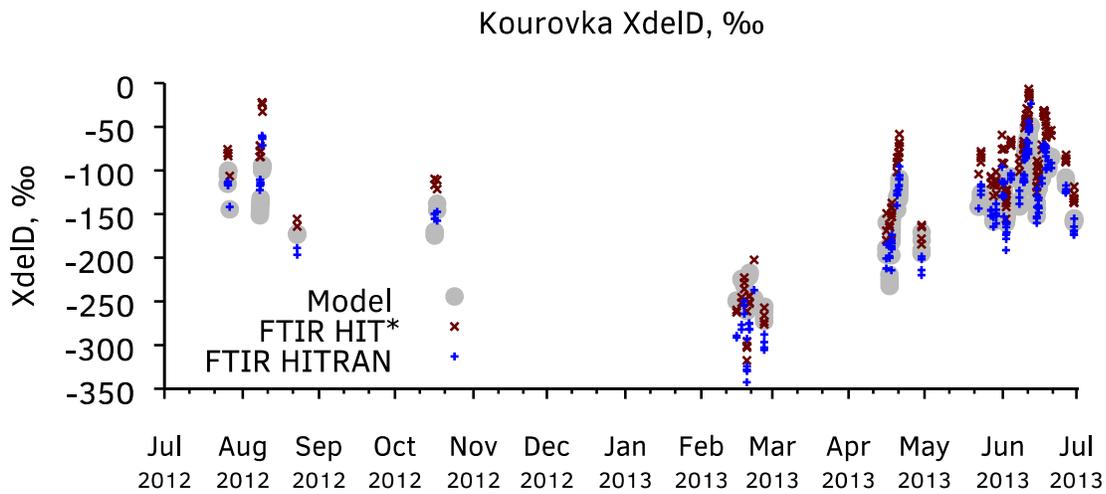


Fig.4. Time series of the X δ D simulated by a GCM and obtained from the FTIR measurements at the UAS in Kourovka

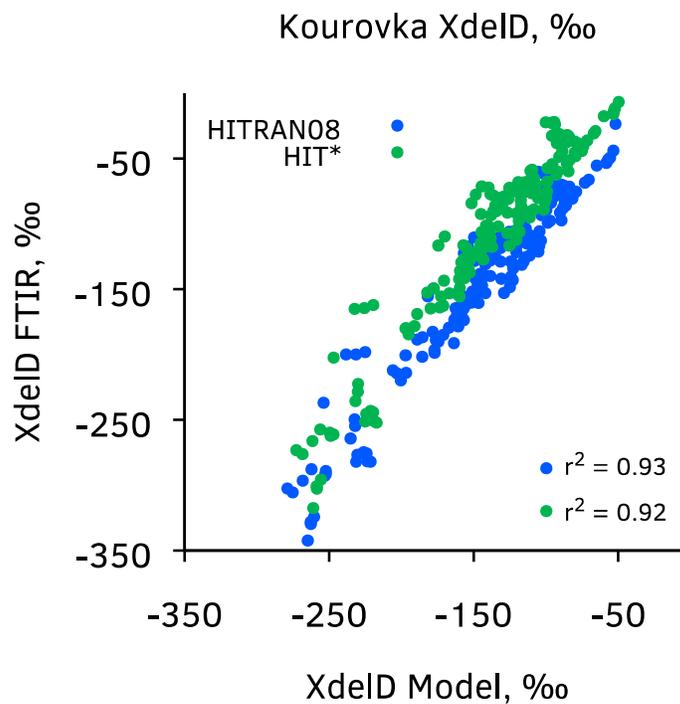


Fig.5. Scatterplot of the retrieved X δ D vs. simulated X δ D

5. CONCLUSIONS

We've showed that the HITRAN 2008 Database is a reasonably good source of spectroscopic parameters for atmospheric applications related to remote sensing of water vapour isotopologues.

An existing slope between the model and the remote sensing data is most likely to be related to the uncertainties in the coefficient of temperature dependence of the air-broadened half-width and probably to the deficiencies of the Voigt line shape [22]. Correction of the temperature dependence seems to be a difficult but an important task for the improvement of atmospheric δD measurements from ground-based and satellite spectrometers. It would enable a possibility for critical evaluation of the GCMs for improvement of future climate change predictions.

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