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SPECTROSCOPY OF AMBIENT MEDIUM

Analysis of the Information Content and Vertical Resolution of Ground-Based IR Spectroscopy for Determining the Vertical Structure of CO_2

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Abstract—Determining the vertical structure of CO_2 content is important for studying the exchange of greenhouse gases between the troposphere, where anthropogenic factors determine their growth and content, and the stratosphere. In this work, we analyze the potential information content and vertical resolution of ground-based IR spectroscopy in determining CO_2 profiles from solar radiation measurements with a Bruker 125 HR Fourier spectrometer at the St. Petersburg site. Based on methodological studies of different spectral windows and regions, we show the possibility of determining 3–4 independent parameters of the CO_2 vertical structure. Measurements in strong and moderate absorption lines provide maximum information on the CO_2 content in the lower and middle troposphere with a vertical resolution of 3–5 km. Weak absorption lines provide information on the CO_2 content in the stratosphere with a vertical resolution of 10–25 km.

Keywords: infrared Fourier transform spectrometry, carbon dioxide remote sensing, information content, vertical resolution

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INTRODUCTION

Changes in the Earth's climate, largely due to an increase in the content of greenhouse gases and, above all, carbon dioxide, have promoted the creation of the global CO_2 monitoring system [1]. It consists of different ground-based local and remote measurement instruments, aircraft and satellite observation systems, observations from high masts, ships, etc. Ground-based spectroscopic international observation networks TCCON (Total Carbon Column Observing Network) [2] and NDACC (Network for the Detection of Atmospheric Composition Change) [3] play a significant role in receiving information. Most of the data in these networks is acquired in the form of total content or average gas mixing ratio for a dry atmosphere.

It is known (see [4, 5]) that high-resolution spectra of solar IR radiation carry some information about the vertical structure of certain atmospheric gases. Examples of deriving information about the profiles of O_3, H_2O, CH_4, CO, HCl, HF, and N_2O content are given in [5]. The information content of measurements is usually estimated by the degree of freedom for signal (dofs)—the number of independent parameters of vertical profiles; for the abovementioned gases, it is possible to determine two to four parameters [3].

Determination of the elements of the vertical structure of CO_2 content is of great importance for studies of the exchange of greenhouse gases between the troposphere, where anthropogenic factors determines how their content increases, and the stratosphere.

In this work, we analyze the potential information content and vertical resolution of the ground-based spectroscopic IR method for determining CO_2 profiles based on consideration of microwindows with individual spectral lines of different intensities and different degrees of absorption in the Earth's atmosphere, as well as combinations of these microwindows using the ground-based measurements of solar IR radiation by the Bruker 125HR Fourier spectrometer (FS) at St. Petersburg NDACC station as an example.

SPECTROSCOPIC MEASUREMENTS AND ESTIMATION OF THEIR INFORMATION CONTENT

Information about the vertical structure of gases can be extracted from high-resolution ground-based measurements of solar IR spectra due to two factors: the pressure dependence of the molecular absorption coefficients of spectral lines and the measurement of absorption spectra of solar radiation at different solar zenith angles [4, 5]. Since absorption line profiles in the real atmosphere are determined by two main effects, i.e., collisions (Lorentz) and the Doppler effect, and the contribution of the Doppler effect increases with the wavenumber, the longest wavelength absorption lines are to be chosen to increase the contribution of the Lorentz effect. However, other factors relating to the information content of solar spectra measurements for the vertical structure of the CO_2 content play the same important role. They are, primarily, the signal-to-noise ratio and the spectral resolution of measurements, the effect of other absorbing gases, the accuracy of specifying the air temperature which affects the line intensities, and the quality of the spectral information in the absorption lines used.

For a numerical analysis of the potential information content and vertical resolution of the method, we consider the matrix of averaging kernels (AK) [4, 5]:

$$\mathbf{A} = (\mathbf{S}_a^{-1} + \mathbf{K}^T\mathbf{S}_\varepsilon^{-1}\mathbf{K})^{-1}\mathbf{K}^T\mathbf{S}_\varepsilon^{-1}\mathbf{K}.$$

Here, $\mathbf{S}_a$ is the a priori matrix of variability of the atmospheric state vector sought; $\mathbf{K}$, the matrix of variational derivatives of radiation with respect to the atmospheric parameters; $\mathbf{S}_\varepsilon$, the matrix of uncorrelated radiation measurement errors. AKs are smoothing functions connecting variations in the true and retrieved profiles [4]. The AK half-width characterizes the vertical resolution of the method at different altitudes. We also analyzed dofs—the number of independent parameters of the vertical structure of CO_2 determined from spectroscopic measurements, which is the trace of the AK matrix.

We studied the AK matrix based on the data of field measurements of the Bruker 125HR FS at the St. Petersburg NDACC station in Peterhof [6]. These measurements have been carried out regularly since 2009 using three filters in the spectral regions 650–1400 cm^{-1} (MST detector, F1 filter), 1700–3400 cm^{-1} (InSb detector, F3 filter), and 2350–5400 cm^{-1} (InSb detector, F5 filter). Taking into account the wide spectral range of the device and the large number of absorption bands and lines of different atmospheric gases which affect the solar radiation recorded by the device, we preliminarily analyzed the absorption spectra based on HITRAN data bank and identified a number of spectral ranges with CO_2 lines, where the radiation absorption by other gases is weak. At this stage, to select the CO_2 spectral lines directly, the transmission functions of the atmosphere were calculated taking into account the line interference by the technique in [7].

To analyze the information content of spectroscopic measurements at St. Petersburg, we chose two days (September 16, 2018, and May 18, 2019) with different temperature profiles, humidity, CO_2 content, solar zenith angles, etc. We analyzed the spectra measured those days and selected microwindows 0.6 cm^{-1} wide centered at the following wavenumbers: 951.19 cm^{-1} (F1), 2626.63 cm^{-1} (F3), 3315.79 cm^{-1} (F5), 3344.81 cm^{-1} (F5), 4864.83 cm^{-1} (F5), and 4883.14 cm^{-1} (F5). The spectral lines were chosen so that the weak, moderate, and strong absorption modes in the atmosphere were implemented for different lines. The absorption is moderate at the 951 cm^{-1} line, weak at the 2627 cm^{-1} line, moderate and weak at the 3316 cm^{-1} and 3345 cm^{-1} lines, and very strong and strong at the 4865 cm^{-1} and 4883 cm^{-1} lines. Figure 1 shows unapodized solar radiation absorption spectra of the CO_2 lines under study measured by the Bruker 125HR FS with a spectral resolution of 0.005 cm^{-1} on May 18, 2019.

We analyzed spectra measured in the six microwindows shown in Fig. 1 using the PROFFIT software package [8]. For more accurate determination of the CO_2 profiles when interpreting the spectra, we applied the first-order Tikhonov–Phillips regularization [9], where the variability of the first derivative of the desired profile is restricted at each step of the solution of the iterative inverse problem. In this case, for each microwindow considered, its own real signal-to-noise ratios, determined during the primary processing, were used.

RESULTS AND DISCUSSION

The AK matrices were studied for both days in order to analyze the potential information content and vertical resolution of spectral measurements of solar IR radiation relative to the CO_2 profile. Figure 2 shows the AK values at several altitudes from 0 to 50 km in six microwindows for September 16, 2018.

The absorption in the CO_2 spectral lines evidently strongly determines the altitude range of remote measurements of CO_2 content and the AK halfwidth. The maximal altitude range 0–50 km is characteristic of the absorption line at 951 cm^{-1}; 0–40 km, of the line 2627 cm^{-1}; 0–30 km, of the lines 3316 and 3345 cm^{-1}; and 0–25 km, of the 4883 cm^{-1} line. All AK have maxima near the surface (up to 5–8 km) for the very strong line at 4865 cm^{-1}.

This behavior of the AK is because the 951 cm^{-1} line is characterized by moderate absorption, and the information about the CO_2 content at different altitudes is derived from different parts of the spectral line. The strong absorption lines 4865 and 4883 cm^{-1} carry information about the CO_2 content in the lower troposphere in their wings. The line 2627 cm^{-1} is characterized by relatively weak absorption (the transmission function is close to 0.8 at the line center); therefore, the measurements at the line center are of the highest information content and, hence, the maximal AK in this line are located in the middle stratosphere. The 3345 cm^{-1} line is weaker than the 3316 cm^{-1} line; therefore, the AK maxima of this line are higher, and

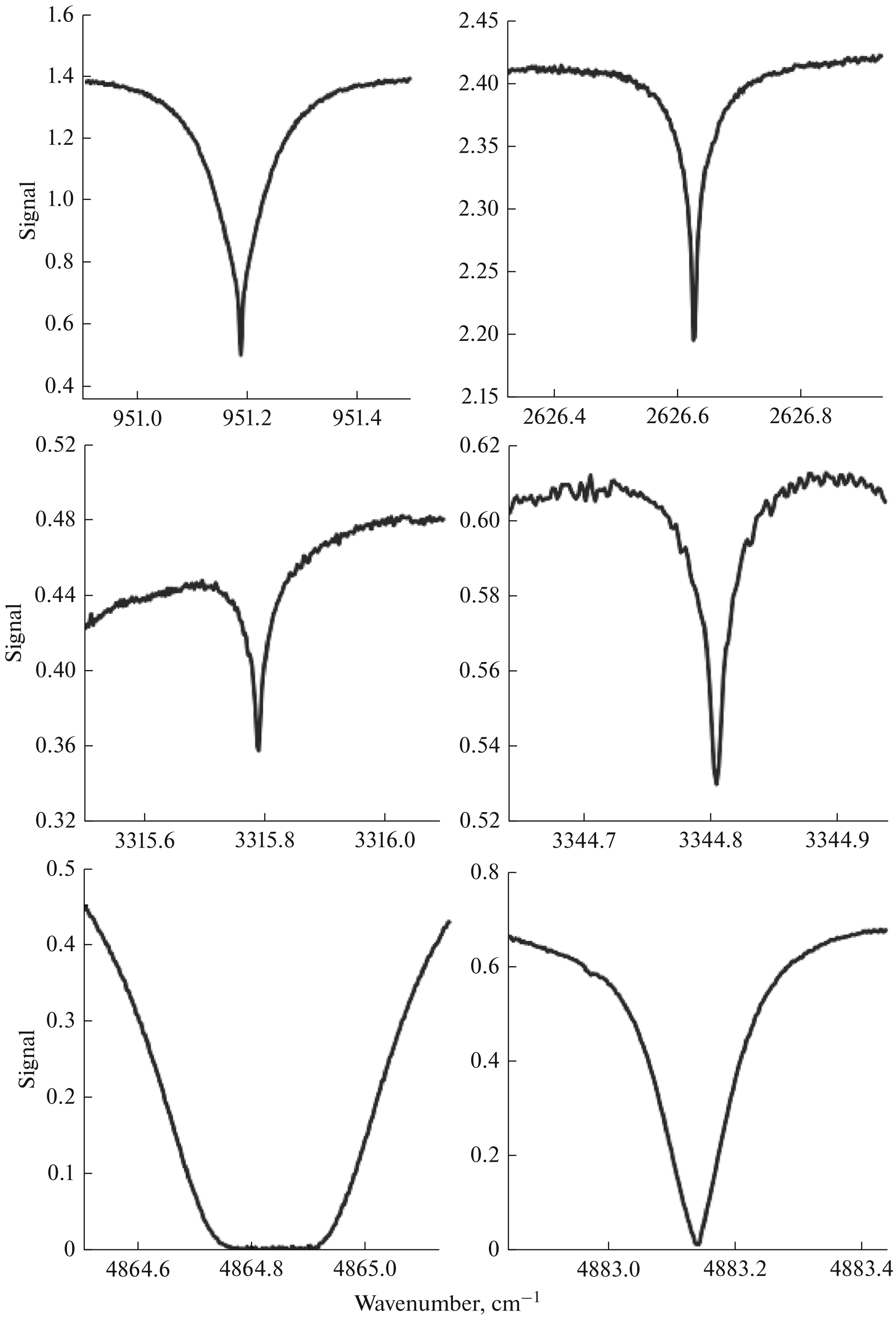

Fig. 1. Spectra of solar radiation absorption of the lines under study of different intensities in different absorption modes in the Earth's atmosphere (May 18, 2019, SZA ~ 40°).

more information can be derived from measurements at the line center.

The vertical resolution of the ground-based remote sounding technique, most often characterized by the AK halfwidth, strongly varies: it is 3–5 km in the lower troposphere for the 951 and 4883 cm^{-1} lines and 10–20 km in the stratosphere for the 951, 2627, and 3345 cm^{-1} lines.

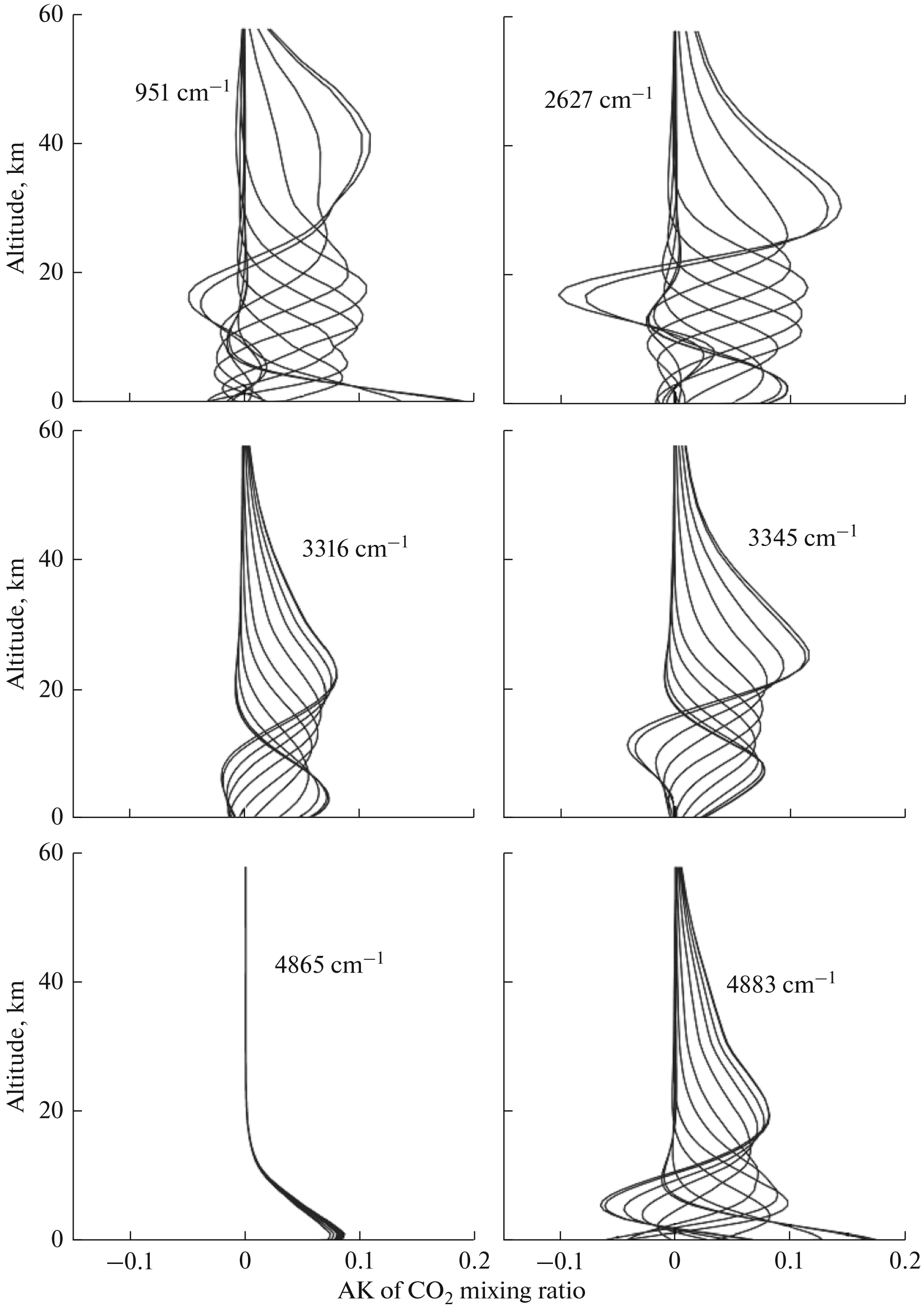

Fig. 2. AK of the CO_2 mixing ratio (solid curves) from 0 to 60 km for different lines (microwindows) (September 16, 2018, SZA ~ 60°).

Table 1 shows dofs, i.e., the number of independent parameters of the CO_2 vertical profile, potentially determined during the solution of the inverse problem with the use of microwindows with individual lines or their combinations (schemes A–D).

The maximum information content (approximately four independent parameters) corresponds to the microwindow centered at the 951 cm^{-1} line (F1 filter). Similar information content (more than three independent parameters) was also found for a set of microwindows C, which includes strong lines in the short wavelength range (4800 cm^{-1}) and middle and weak lines in the region 3100–3300 cm^{-1} (F5 filter). For these spectral schemes (corresponding microwindows), the problem of determining the CO_2 in four atmospheric layers, e.g., the lower, middle, and upper

Table 1. Dofs for different microwindows and their combinations for two days of measurements (SZA is the solar zenith angle)

Centers of microwindows and their combinations, cm^{-1}	dofs	
	Sept. 16, 2018 (SZA = 60°)	May 18, 2019 (SZA = 40°)
951	3.85	3.62
2627	3.63	3.08
3316	2.22	2.50
3345	2.37	2.25
4865	1.00	1.41
4883	2.74	3.02
A: 2627 + 3316 + 4883	2.77	3.07
B: 4854 + 4883 + 4885	3.44	3.86
C: 3316 + 3345 + 4865 + 4883 + 4885	3.57	4.00
D: 2627 + 3316 + 3345 + 4865 + 4883 + 4885	3.27	3.67

Table 2. Parameters of solution of the inverse problem (channels and gases taken into account) and dofs for different schemes for two days of measurements

Scheme	Channels, cm^{-1}	Filter	TAG	dofs	
				Sept. 16, 2018 (SZA = 60°)	May 18, 2019 (SZA = 40°)
I	950.5–953.8	F1	H_2O, CO_2, O_3, N_2O	4.18	3.94
II	2620.55–2621.1 2626.4–2626.85 2627.1–2627.6 2629.275–2629.95	F3	H_2O, CO_2, N_2O, CH_4	3.86	3.44
III	3160.14–3160.3 3161.6–3161.8 3315.5–3316.05 3316.87–3318.0 3344.68–3344.94	F5	H_2O, CO_2, O_3, N_2O, CH_4, C_2H_2	2.88	2.92

troposphere and the stratosphere, can be stated. Note also that dofs increase with the solar angle for most schemes with strong shortwave lines and most often decreases for longwave lines.

In addition to individual spectral lines in microwindows 0.3–0.6 cm^{-1} wide, we also considered schemes for measuring solar radiation spectra using other combinations of different microwindows in different spectral regions.

After preliminary consideration and selection of versions for two test days of measurements, we settled on three spectral schemes (Table 2). Microwindows for scheme II were taken from [10], for scheme III, from [11], and for scheme I they were selected during the analysis of the absorption spectra of atmospheric gases and preliminary estimation of the AK. Table 2 also gives trace atmospheric gases (TAGs) taken into account when calculating the transmission functions, filters used in the measurements, and dofs values.

The information content is maximal (3.94–4.18) for scheme I. When comparing it with the dofs values from Table 1, where the microwindow width is 0.6 cm^{-1}, we can see that the expansion of the spectral channel made it possible to increase the number of potentially determined parameters of the CO_2 profile. The same is true for scheme II: a combination of four microwindows in the 2620–2630 cm^{-1} range increased the information content of spectroscopic measurements with respect to the CO_2 profile as compared to only one window 0.6 cm^{-1} wide (see Table 1). For scheme III, with five channels in the 3100–3300 cm^{-1} range, the information content is also higher than for individual microwindows. Scheme I provides uniform coverage of AK in the wide altitude range 0–50 km. In this case, the vertical resolution is ~3–5 km in the lower troposphere and it drops to 20–25 km in the stratosphere. The other two schemes have a more limited altitude range: 0–40 km in scheme II, with a more uniform vertical resolution (10–20 km), and 0–30 km in scheme III, with a vertical resolution of 15–20 km.

CONCLUSIONS

The features of the formation of averaging kernels of the remote IR technique and the information content of measurements of solar IR spectra are analyzed on the basis of methodological numerical studies. The following results have been obtained during the analysis.

(1) The information content of spectral measurements in different CO_2 lines from different spectral regions has been estimated in terms of dofs—the number of independent parameters determined; it attains 3–4 for Bruker 125HR FS measurements.

(2) The behavior of AK has been analyzed when determining the CO_2 profiles in different spectral lines and spectral ranges of the IR region. It is shown that the top boundary of high-altitude ground-based sounding and the altitude resolution of remote measurements change versus the character of the solar radiation absorption in the Earth's atmosphere (weak, moderate, or strong). Measurements at strong absorption lines provide maximum information on the CO_2 content in the lower and middle troposphere with a vertical resolution of 3–5 km. Weak absorption lines provide information on CO_2 content in the stratosphere with a vertical resolution of 10–25 km.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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