The method of remote sensing of $^{13}CO_2/^{12}CO_2$ ratio in the atmosphere using high resolution transmittance IR spectra

V.I. Zakharov, M.S. Blagodareva, and K.G. Gribanov

Ural State University, Ekaterinburg

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Monitoring of the $^{13}CO_2/^{12}CO_2$ ratio in the atmosphere is one of the most important tasks of carbon cycle and global climate change control. The method of remote sensing of the column-averaged $^{13}CO_2/^{12}CO_2$ ratio in the atmosphere is proposed for the first time. It is based on measuring the ratio of atmospheric optical depths for a homologous couple of $^{13}CO_2$ and $^{12}CO_2$ lines in high resolution transmittance spectra of solar radiation within range 6100–6300 cm^{-1}, which depends only on the columnar ratio $^{13}CO_2/^{12}CO_2$ and does not depend on variations of temperature profile and solar zenith angle. A possibility of application of the method to atmospheric transmittance spectra measured with modern FTIR in the cloudless aerosol-free atmosphere is discussed.

Introduction

The carbon dioxide isotopomers in the atmosphere are indicators of global carbon cycle. In particular, the observed ratio of $N_{^{13}CO_2}/N_{^{12}CO_2}$ is an important characteristic of CO_2 emission sources. The ratio characterizes the reservoirs of CO_2 emission.[1] Due to the growing economical activity (production of the concrete, combustion of the organic fuel, agriculture, and so on) and climate warming the emission of CO_2 in the atmosphere from different reservoirs, such as the ocean, biota, earth crust carbonates, deposition of coal and hydrocarbons increases. Therefore, the problem of monitoring isotopomers in the atmosphere becomes more and more urgent.

At present, the methodology of determining the ratio of carbon dioxide isotope concentrations in the atmosphere is based on the air sampling with following laboratory analysis by mass-spectrometric, chromatographic, and optical methods.[2–4]

The purpose of this research work is to consider the possibility of application of optical methods to *in situ* determination of $N_{^{13}CO_2}/N_{^{12}CO_2}$ mean ratio in the whole atmospheric column using the ground-based Fourier spectrometers (FTIR), which measure the transmission function of the atmosphere.

Modern FTIR register atmospheric absorption (transmission) spectra of solar radiation with a high resolution (up to 0.0019 cm^{-1}) in the whole IR region and high noise-to-signal ratio, that gives a possibility of determination of vertical profiles of numerous atmospheric molecular components, such as CH_4, O_3, CO, N_xO_y, HNO_3, and so on, as well as full their content in the atmospheric column.[5,6]

In the present-day high resolution IR Fourier spectrometers used in field measurements[5,6] the width of the instrumental function is equal to ~0.002 cm^{-1} and, therefore, it can be neglected in contrast to the observed width of carbon dioxide lines at atmospheric pressure of ~0.1 cm^{-1}. Write the transmission function $T_r(\nu)$ for cloudless weakly aerosol atmosphere in the following way[7]:

$$T_r(\nu) = \exp\{-\tau(\nu)\}, \qquad (1)$$

where $\tau(\nu)$ is the optical depth of the atmosphere at the frequency ν. For a sufficiently isolated line of a molecule, for example, CO_2, being in local thermodynamic equilibrium, it can be represented as

$$\tau_{ij}(\nu) = \int_0^H \mathrm{d}h\,\sigma_{ij}(\nu) N(h) w_i\big[T(h)\big], \qquad (2)$$

where $N(h)$ is the concentration of given molecules at the altitude h (at zenith angle $\theta \neq 0$, h is substituted by $h/\cos\theta$); $w_i[T(h)] = \exp[-E_i/kT(h)]/Z[T(h)]$ is the Boltzmann population of a low absorbing level with the energy E_i at the temperature $T(h)$; $Z[T(h)]$ is a statistical sum; k is the Boltzmann constant.

Absorption cross section for $i \to j$ transfer is equal to $\sigma_{ij}(\nu) = \sigma f(\nu - \nu_{ij})$, where $f(\nu - \nu_{ij})$ is the spectral line profile. In case of troposphere, it is quite accurately approximated by the Lorenz profile[7]:

$$f(\nu - \nu_{ij}) = \frac{1}{\pi}\frac{\alpha_{ij}(h)}{\alpha_{ij}(h)^2 + \big[\nu - \nu_{ij} - \beta_{ij}(h)\big]^2},$$

where $\alpha_{ij}(h)$ and $\beta_{ij}(h)$ are coefficients of line broadening and shift due to the pressure at the altitude h.

The analysis of data on vertical profiles of $\delta^{13}C$ obtained from aircraft measurements in the troposphere[3]

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$$\delta^{13}\mathrm{C} = \left\{ \frac{\dfrac{N_{^{13}\mathrm{CO}_2}}{N_{^{12}\mathrm{CO}_2}}}{\left(\dfrac{N_{^{13}\mathrm{CO}_2}}{N_{^{12}\mathrm{CO}_2}}\right)_0} - 1 \right\} \cdot 1000‰, \qquad (3)$$

where $N_{^{13}\mathrm{CO}_2}/N_{^{12}\mathrm{CO}_2}$ is the measured ratio of a given CO_2 isotope concentration in the atmosphere and $(N_{^{13}\mathrm{CO}_2}/N_{^{12}\mathrm{CO}_2})_0$ is its standard ratio,[2,3] shows that the observed variations of $\delta^{13}\mathrm{C}$ with the altitude are low (do not exceed 1.8%). The mean value of $\delta^{13}\mathrm{C}$ in the atmospheric profile can vary near 15% and higher, depending on the place and time of the conducted measurements. When this weak altitude dependence of $N_{^{13}\mathrm{CO}_2}/N_{^{12}\mathrm{CO}_2}$ concentration ratio is neglected, the atmospheric optical depth $\tau_{ij}^{^{13}\mathrm{CO}_2}$ in $i \to j$ absorption line of $^{13}\mathrm{CO}_2$ is proportional to the optical depth in the homologous line of $^{12}\mathrm{CO}_2$ isotope absorption (vibrational-rotational transition at the same quantum numbers)

$$\tau_{ij}^{^{12}\mathrm{CO}_2}(\nu) = \frac{N_{^{13}\mathrm{CO}_2}}{N_{^{12}\mathrm{CO}_2}} A\tau_{ij}^{^{12}\mathrm{CO}_2}(\nu);$$

$$A\tau_{ij}^{^{12}\mathrm{CO}_2}(\nu) = \int_0^H \mathrm{d}h\,\sigma_{ij}^{^{13}\mathrm{CO}_2}(\nu) N_{^{12}\mathrm{CO}_2}(h) w_i^{^{13}\mathrm{CO}_2}[T(h)]. \qquad (4)$$

Spectroscopic parameters σ, α, β for homologous pair of $^{13}\mathrm{CO}_2$ and $^{12}\mathrm{CO}_2$ isotopes lines with the energy E of low levels are close,[8] and the temperature dependences of their population $w_i[T(h)] = \exp[-E_i/kT(h)]/Z[T(h)]$ coincide accurate to the constant factor (due to the virtually linear temperature dependence of the statistical sum in the region of tropospheric temperatures[9]). The absorption line profiles are close as well. This means that A = const can be expected with a high accuracy; and the ratio of the atmospheric optical depths for such pair of homologous lines is defined as

$$\frac{\tau^{^{13}\mathrm{CO}_2}}{\tau^{^{12}\mathrm{CO}_2}} = A\frac{N_{^{13}\mathrm{CO}_2}}{N_{^{12}\mathrm{CO}_2}}. \qquad (5)$$

The presence of at least one pair of closely spaced, distinctly observed, and sufficiently isolated $^{13}\mathrm{CO}_2$ and $^{12}\mathrm{CO}_2$ lines in atmospheric natural transmission spectra can give us a possibility to measure the mean $N_{^{13}\mathrm{CO}_2}/N_{^{12}\mathrm{CO}_2}$ concentration ratio and, correspondingly, $\delta^{13}\mathrm{C}$ all along the observation path. At a relatively high spectral resolution, the accuracy of $\delta^{13}\mathrm{C}$ determination can be limited only by the noise-to-signal ratio in calculation of the ratio of optical depths $\tau_{ij}^{^{13}\mathrm{CO}_2}/\tau_{ij}^{^{12}\mathrm{CO}_2}$ from atmospheric transmittance spectra. The analysis of spectroscopic data on carbon dioxide isotopes received from HITRAN [Ref. 8] and LSD [Ref. 9] databases, as well as the analysis of model atmospheric transmittance spectra in the region 6100–6300 cm^{-1}, calculated with the help of FIRE-ARMS [Ref.10] allowed us to choose 4 pairs from the absorption band (00001–30013): $^{13}\mathrm{CO}_2$ (6127.86 cm^{-1}) and $^{12}\mathrm{CO}_2$ (6219.80 cm $^{-1}$), $^{12}\mathrm{CO}_2$ (6236.04 cm $^{-1}$), as well as $^{13}\mathrm{CO}_2$ (6104.76 cm $^{-1}$) and $^{12}\mathrm{CO}_2$ (6212.79 cm $^{-1}$), $^{12}\mathrm{CO}_2$ (6241.40 cm $^{-1}$), with similar low energy levels equal to 42.96 and 13344 cm^{-1}, respectively. The conducted calculation experiment shows that all the chosen homologous pairs have the ratios of atmospheric optical depths, which do not depend (with an accuracy of ~0.1%) on the variation of temperature profiles in the range ±10 K and zenith angle in the range ±10° (see Eq. (5)).

However, it is seen from the analysis of model and natural spectra, measured by FTIR in the region 6100–6300 cm^{-1}, only one sufficiently isolated (from other lines observed in the spectrum of atmospheric lines) pair $^{13}\mathrm{CO}_2$ (6127.86 cm^{-1}) and $^{12}\mathrm{CO}_2$ (6236.04 cm^{-1}) can be chosen. Figure 1 presents the fragments of the synthetic spectrum of FTIR, where the given lines are situated.

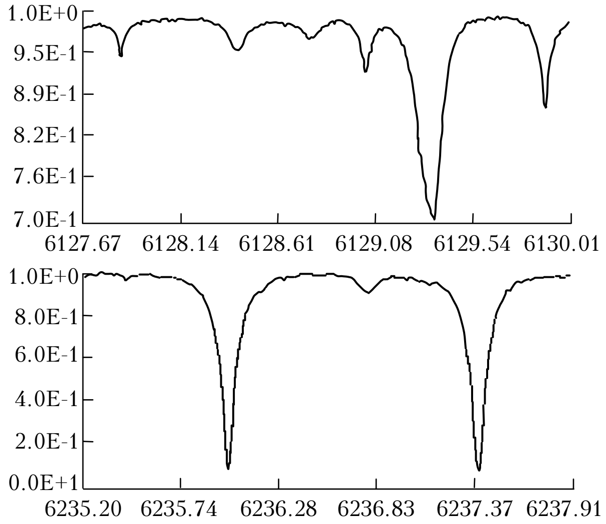

Fig. 1. Samples of atmospheric synthetic transmittance spectra measured by ground-based high-resolution Fourier spectrometers (modelling with the help of FIRE-ARMS, http://remotesensing.ru) in the region of IR-bands of carbon dioxide isotopomers absorption. Isolated lines of $^{13}\mathrm{CO}_2$ (6127.86 cm^{-1}) (top) and $^{12}\mathrm{CO}_2$ (6236.04 cm^{-1}) (bottom) are very promising for the method of $^{13}\mathrm{CO}_2/^{12}\mathrm{CO}_2$ determination in the atmospheric column.

Figure 2 shows a sufficient isolation of the chosen lines of carbon dioxide isotopes. The contribution of the lines belonging to other atmospheric gases in the vicinity of $^{13}\mathrm{CO}_2$ (6127.86 cm^{-1}) and $^{12}\mathrm{CO}_2$ (6236.04 cm^{-1}) is less than 0.1%.

The proposed method of $N_{^{13}\mathrm{CO}_2}/N_{^{12}\mathrm{CO}_2}$ ratio determination, based on Eq. (5) and the conception of differential absorption,[11] is aiming at exclusion of different nonselective spectral contributions to the transmission function (1) connected with the radiation attenuation by scattering, continual absorption by water vapor, wings of strong neighboring lines, and other contributions with a weak spectral dependence.

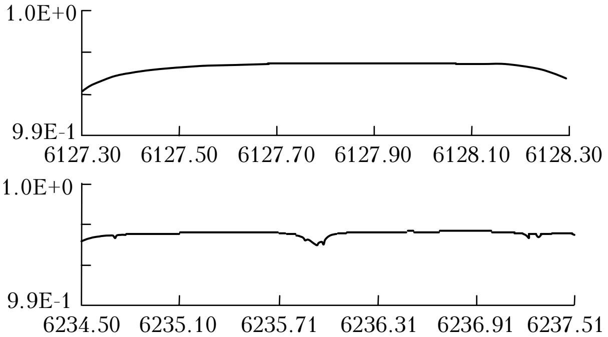

Fig. 2. Transmission function of the standard atmosphere (US standard) in spectral intervals of $^{13}CO_2$ (top) and $^{12}CO_2$ (bottom) isotopes lines position, modeled with accounting for all the gases included in HITRAN-2000, excluding the CO_2 molecule.

In general case, 2 reference points are defined in each of the chosen lines of carbon dioxide isotopes: $^{13}\nu_1$, $^{13}\nu_2$ for $^{13}CO_2$ line (6127.86 cm^{-1}) and $^{12}\nu_1$, $^{12}\nu_2$ for $^{12}CO_2$ line (6236.04 cm^{-1}), satisfying conditions $^{13}\nu_2 - {}^{13}\nu_1 = {}^{12}\nu_2 - {}^{12}\nu_1$ and $^{13}\nu_1 - {}^{13}\nu_0 = {}^{12}\nu_1 - {}^{12}\nu_0$, where $^{13}\nu_0$, $^{12}\nu_0$ are the frequencies of line centers of the corresponding isotopes. Then, from data of the measured atmospheric transmittance spectra, the sought ratio of $N_{^{13}CO_2}/N_{^{12}CO_2}$ is calculated, equal to the ratio of differences of optical depths in reference points of each isotope line profile:

$$A\frac{N_{^{13}CO_2}}{N_{^{12}CO_2}} = \frac{\tau^{^{13}CO_2}(^{13}\nu_2) - \tau^{^{13}CO_2}(^{13}\nu_1)}{\tau^{^{13}CO_2}(^{12}\nu_2) - \tau^{^{12}CO_2}(^{12}\nu_1)}. \qquad (6)$$

It is evident that it is not necessarily to know the value of A constant for the monitoring of a relative change with time of $N_{^{13}CO_2}/N_{^{12}CO_2}$ ratio in the atmosphere (in the region of ground-based FTIR location), because this constant is reduced. When it is necessary to determine the absolute values of a given ratio, the numerical value of A constant can be obtained from Eq. (6) for the $N_{^{13}CO_2}/N_{^{12}CO_2}$ ratio in the atmospheric column, known from independent measurements conducted with the help of sampling method, synchronized with atmospheric transmittance spectra measurements with FTIR. Theoretical estimations based on spectroscopic information from the database[9] for the pair of $^{13}CO_2$ (6127.86 cm^{-1}) and $^{12}CO_2$ (6236.04 cm^{-1}) lines yield $A \approx 0.557$.

From the theoretical point of view, it is most convenient to choose in Eq. (6) point 1 in the center of the line and point 2 at its wings. However, in natural spectra, measured by ground-based FTIR, the atmospheric transmission is often equal to zero (saturated absorption) in the line center of the CO_2 main isotope. The analysis of natural transmission l spectra shows that for practical application it is appropriate to choose the following reference points: point 1 approximately at 0.02 cm^{-1} and point 2 approximately at 0.2 cm^{-1} to the direction of higher frequencies from the line centre, because the signal saturation is less probable in these points. This method can be efficient also for weakly aerosol atmosphere in the case when the multiple IR radiation scattering at 6100–6300 cm^{-1} and its contribution to the observed spectrum of the atmosphere can be neglected.

Note in conclusion that with the increase of spectral resolution and noise-to-signal ratio in future FTIR systems this methodology can become a tool of routine remote monitoring of $^{13}CO_2/^{12}CO_2$ ratio in the atmosphere.

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