Influence of error in spectroscopic data on methane concentration retrieval

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Received August 29, 2007

The influence of errors in spectroscopic data on the accuracy of the inverse problem of the concentration analysis is considered by the example of methane. The error of spectroscopy parameters in a range 900–7000 cm^{-1} is considered for three isotope methane modifications. Calculations for methane absorption bands from the visible to IR spectral range are presented, for which characteristics of typical and new laser emitters are known.

Introduction

Methane (CH_4) is a trace atmospheric gas, participating in many atmospheric processes. It is produced near the Earth's surface and progressively lifted to the altitudes, where it oxidizes transforming into carbon oxide (CO) and formaldehyde (H_2CO).[1] The mean life time of CH_4 in the atmosphere is 4–10 years. Methane is the second in order of importance greenhouse gas due to the presence of a strong IR absorption band near 7.66 μm. Therefore, methane concentration measurement throughout the atmosphere is an issue of the day.

Among all gas concentration measurement methods, optical methods are the most technologically and methodically developed. Recent achievements in measurement and emitting (semiconductor lasers) technologies require the estimate of the promise of their use in gas analysis.

Absorption techniques are basic in optical methods for gas concentration measurements. Specialized database contain the data on spectroscopic parameters of methane absorption lines (for example, HITRAN).[2] The data on CH_4 absorption bands from this database are given in the next part of the work.

The signal measured with an open-path differential absorption gas analyzer and the concentration x_0 of the gas under study are correlated by the known equation[3–5]

$$\tilde{y}(\lambda) = y_{\text{inp}}(\lambda)\eta(\lambda)\exp\{-L[K_0(\lambda)x_0 + \beta(\lambda)]\}, \quad (1)$$

where $\tilde{y}$ and y_{inp} are the radiation powers after passing though the atmosphere and emitting, respectively; $\eta(\lambda)$ is the instrumental function of the measurement system (obtained from calibration results) including the photodetector efficiency, transceiving optics transmittance, degree of beam interception, target reflectivity, and other losses; $K_0(\lambda)$ is the absorption coefficient of analyzed gas at λ; L is the total path length; $\beta(\lambda)$ is the so-called optical thickness of the background, i.e., "interfering" (all except for the gas under study) gases, absorbing in the given spectral range:

$$\beta(\lambda) = \beta_a(\lambda) + \beta_k(\lambda) + \sum_{j\neq 0}^{N_g} K_j(\lambda)x_j.$$

Here $\beta_a(\lambda)$ is the aerosol component of attenuation, $\beta_k(\lambda)$ is the continual absorption of water vapor; N_g is the number of gases of the analyzed mixture except for the gas under study (index 0); $K_j(\lambda)$, x_j are the absorption coefficient and concentration of the jth gas in the mixture.

As is known,[3–6] the concentration of analyzed gas (0-th) is determined from comparison of signals (1), recorded at two wavelengths: on the absorption line of the gas under study (λ_{on}) and beyond it (λ_{off}):

$$x_0 = \frac{1}{L\Delta K}\left(\ln\left\{\frac{\tilde{y}(\lambda_{\text{off}})}{\tilde{y}(\lambda_{\text{on}})}\right\} + \Psi\right), \quad (2)$$

$$x = \breve{K}z, \quad (3)$$

where

$$\Psi = \ln\left\{\frac{y_{\text{inp}}(\lambda_{\text{on}})\eta_{\text{on}}}{y_{\text{inp}}(\lambda_{\text{off}})\eta_{\text{off}}}\right\} - \Delta\beta;$$

$$\Delta\beta = L\sum_{j\neq o}\Delta K_j x_j + \Delta\beta_a + \Delta\beta_k.$$

Here $\breve{K}$ is the matrix constructed of the elements $\Delta K = K_0(\lambda_{\text{on}}) - K_0(\lambda_{\text{off}})$ (so-called differential absorption); z is the measurement vector; $\Delta\beta$ is the differential background, defined as follows:

$$\Delta\beta_a = \beta_a(\lambda_{on}) - \beta_a(\lambda_{off}),\ \Delta\beta_k = \beta_k(\lambda_{on}) - \beta_k(\lambda_{off}).$$

It is evident from Eq. (2), that the differential absorption ΔK is one of the variables which, on the one hand, are the measuring technique basis, and, on the other hand, determine the gas concentration retrieval error by the differential absorption lidar (DIAL) method. The absorption coefficient can be obtained experimentally or calculated on the base of spectroscopic data. For calculation, two key spectroscopic parameters are required to be known: the intensity and the half-width of the absorption line. As is shown in Ref. 6, the relative error of the retrieved gas concentration can be estimated from the equation

$$\delta x_0 \approx cond(K)\{\delta K + \delta y\}, \quad (4)$$

where $cond(K)$, δK, δy are the condition number of the absorption coefficients matrix, the relative accuracy of the set absorption coefficient, and the measurement error of the signal y.

Note, that almost all the information on gas composition is determined from measurement data in the optical range,[4,5,7–9] obtained with the help of laser gas analyzers, as well as satellite and airborne spectrometers of different types.

In addition to the problems of atmospheric gases concentrations retrieval, there arise simulation problems (atmospheric transmittance, radiation transfer equation), the search for optimal measurement channels, and so on. The accuracy of spectroscopic data is very important and generally determines solutions of all these problems. In the majority of references, the influence of spectroscopic data accuracy on gas concentration retrieval from measurements is considered for such gases as H_2O, CO_2, O_3, and CH_4. However, these works consider the influence of differences between HITRAN versions on calculations of atmospheric path radiation propagation rather than the influence of accuracy of the spectroscopic information itself.

As is seen from Eq. (4), the calculation errors of atmospheric transmittance, weight functions, and gas concentration retrieval are determined by the accuracy of absorption coefficients of the matter under study. This work estimates the influence of spectroscopic data error on the accuracy of methane concentration retrieval within the range of different laser emitters.

Accuracy of spectroscopic data

Figure 1 shows the main absorption bands of the methane according to the HITRAN-2004 database.[2,10] Eighteen bands from 3–8.5 μm (1000–9000 cm^{-1}) range are included into the atlas, among which nine bands of the main isotopic modification $^{12}CH_4$, six bands of $^{13}CH_4$, and three bands of $^{12}CH_3D$. The total number of absorption bands is 24439; 1060 bands between 2430 and 3195 cm^{-1} are not identified (they are presented without rovibrational transition indication).

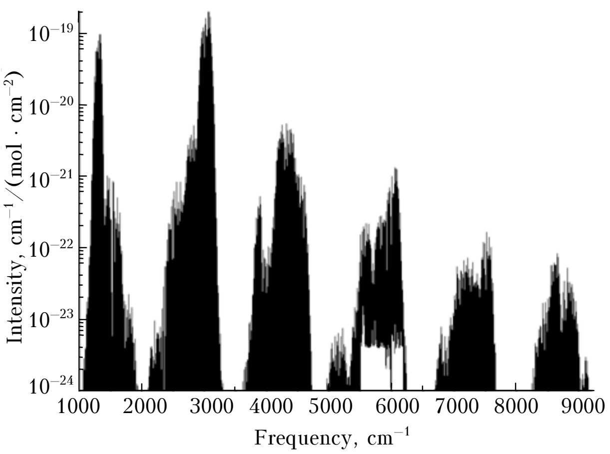

Fig. 1. Main IR methane absorption bands according to the HITRAN-2004 database.

IR methane spectra can be conventionally divided into five ranges: dyad (1100–1700 cm^{-1}), pentad (2200–3200 cm^{-1}), octad (3500–4800 cm^{-1}), tetradecade (4900–6200 cm^{-1}), and higher 6500 cm^{-1}. Such division is caused by the characteristic polyadic structure of the methane spectrum.[11]

The dyad and pentad ranges are studied most extensively. In these ranges, both absorption band position (average error does not exceed $2\cdot10^{-3}$ cm^{-1}) and intensity (typical error is 3–4%) are sufficiently well simulated with half-widths for three basic isotopic modifications $^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$.[7–9] Besides, hot bands are well predicted in these ranges.[10,11]

In the octad range (3500–4800 cm^{-1}), the simulation accuracy of $^{12}CH_4$ bands positions is insufficient. The mean square calculation error for band centers is 0.041 cm^{-1} [Ref. 12].

At the same time, band intensities are calculated quite accurate: the mean square error does not exceed 15%. Broadening parameters and self-pressure shifts have been measured in Ref. 13 for $^{12}CH_4$ bands in the 4100–4635 cm^{-1} range. The octad has been simulated in Refs. 14 and 15 in more detail. However, hot transitions in this range, e.g., from dyad to tetradecade, have not been simulated; band positions and intensities for the $^{13}CH_4$ molecule in the octad have not been simulated as well.

Intensities, halfwidths, and band positions for $^{12}CH_3D$ are sufficiently well simulated in the 3250–3600 cm^{-1} range,[16] while higher 3600 cm^{-1} the bands have not been identified. The 3250–3600 см$^{-1}$ range is attractive for $^{12}CH_3D$ concentration search, because bands of the main isotopic modification $^{12}CH_4$ are weak here.

The tetradecade (4900–6200 cm^{-1}) is studied much worse. In HITRAN-2004, only a small number of $2\nu_3$-band lines are identified. Somewhat more number of lines have been identified in Ref. 11, but their reliability is not always adopted.[17,18] Identification, performed in HITRAN-2004, does not correspond to Ref. 14 even for the strongest band $2\nu_3(F_2)$. The tetradecade can be conventionally divided into three ranges: 4900–5200, 5200–5900, and 5900–6200 cm^{-1}.

The tetradecade (4900–6200 cm^{-1}) range includes mainly well-simulated $4\nu_4$ bands.[11] The 5200–5900 cm^{-1} range is the most difficult for analysis, where only $\nu_3 + 2\nu_4$-band identification can be considered as universally adopted. The strongest tetradecade band $2\nu_3(F_2)$ is within the 5900–6200 cm^{-1} range. As was mentioned above, this band is differently identified in different works. Identification of sufficiently strong bands from this range $2\nu_2 + \nu_3(2F_2 + F_1)$ and $2\nu_3(E)$ [Ref. 11] is beyond doubt. Spectral line half-widths were not systematically studied in the tetradecade range. A half-width value of 0.08 cm^{-1}/atm is given in HITRAN-2004 for all lines. At the same time, the study of half-width in the lower octad range (3500–4800 cm^{-1}) has shown quite large half-width variations[19]: from 0.085 cm^{-1}/atm for small J to 0.060 cm^{-1}/atm for large J. Several lines are given in HITRAN-2004 for the $^{13}CH_4$ molecule in the tetradecade range for the $2\nu_3(F_2)$ band. The tetradecade line parameters are evidently needed in refining, especially because the Q-branch of the $2\nu_3(F_2)$ band is quite attractive for methane concentration retrieval.

Spectroscopic parameters (line positions, intensities, and half-width) errors are partly systematized and presented as additional information in HITRAN-2004. The peculiarity of the intensity error representation is in its correspondence to some particular error range (e.g., 15–20, 10–15%, etc.) but not to an individual absorption line. CH_4 intensity errors from HITRAN-2004 are shown in Fig. 2.

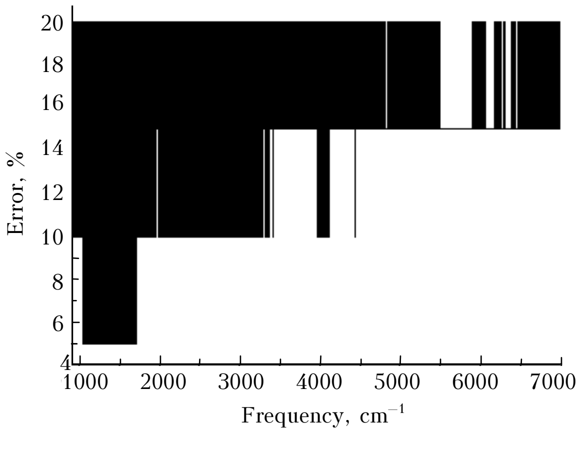

Fig. 2. Intensity errors of CH_4 molecule bands from HITRAN-2004.

It is evident that the standard intensity error is between 15 and 20-%, and it is within 5% only in the 7–12 μm region.

Spectroscopic parameters of absorption bands are the basis for absorption coefficient calculation. The most common is the *line-by-line* technique.[20] We have calculated the absorption coefficients for three main atmospheric gases (H_2O, CO_2, and CH_4), which are required for further calculations (Fig. 3).

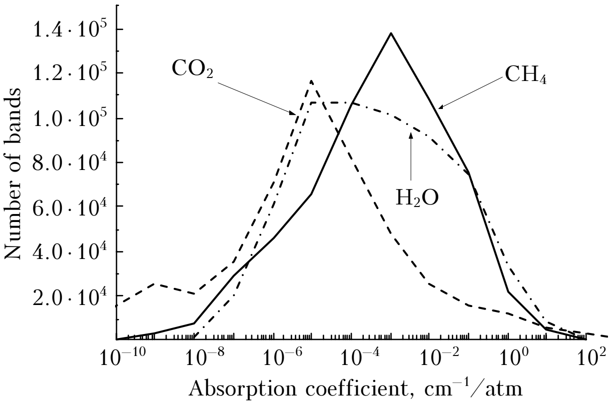

Fig. 3. Distribution of the line numbers of H_2O, CO_2, and CH_4 molecules as a function of their intensities (absorption coefficients).

As is seen, the maximal number of methane lines falls to the 10^{-4}–10^{-2} cm^{-1}/atm absorption coefficient range. In contrast to CO_2 and CH_4, distribution maximum for water molecule is not so clearly pronounced and is extended from 10^{-6} to 10^{-1} cm^{-1}/atm. These values will be used for further calculations.

Estimation of the transmittance calculation error

Atmospheric transmittance calculation is connected with calculation of the absorption coefficient K, which, in its turn, is determined by spectroscopic parameters, namely, the line intensity S and half-width γ. The influence of their errors (see Fig. 2) on the error of gas concentration retrieval should be estimated. Note, that S and γ are functionally connected in the equation of the absorption line profile and subject to maximal experimental errors.

Assume that intensity and half-width determination errors are defined as

$$\frac{\Delta S_i}{S_i} = \text{const} = \delta_S \text{ and } \frac{\Delta\gamma_i}{\gamma_i} = \text{const} = \delta_\gamma, \tag{5}$$

where ΔS and $\Delta\gamma$ are errors of the intensity and half-width measurement; δ_S and Δ_γ are the fractional errors of setting the intensity and half-width. Usually for calculations just fractional errors are set rather than measurement errors, which depend on numerous experimental conditions, as well as the type and parameters of the radiation source.

To estimate the atmospheric transmittance calculation error caused by the influence of spectroscopic parameters errors, consider the conditions of ground measurements, in which profile shape is determined by the Lorentz form.[6] The atmospheric transmittance calculation error due to intensity and half-width errors is maximal for the line center and defined by the following equation:

$$\Delta K_{\max} = (\delta_S + \delta_\gamma)K. \quad (6)$$

Accounting for Eq. (6), the error in determining optical depth is

$$\Delta\tau = (\delta_S + \delta_\gamma)\tau \quad (7)$$

and transmittance

$$\Delta T = \Delta\tau T = (\delta_S + \delta_\gamma)\tau T. \quad (8)$$

As is seen from Eqs. (6)–(8), the transmittance calculation error caused by spectroscopic data errors is determined by the summarized error in setting the intensity and half-width.

Numerical experiment

Spectral regions, most prospective for analyzing methane concentration in air, have been selected for numerical computations. These regions are concerned, first of all, with known sources of laser radiation (Fig. 4).

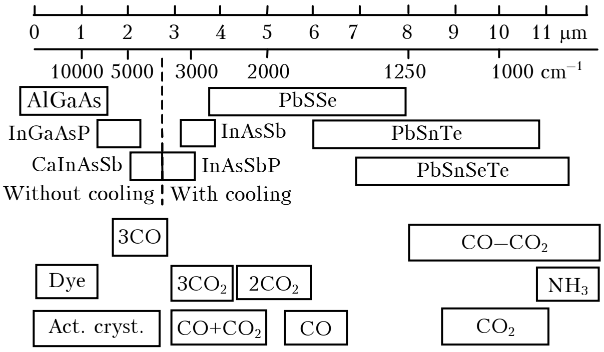

Fig. 4. Spectral ranges of radiation wavelengths of different types of lasers (gas, semiconductor, activated crystals, and dye lasers).

Wavelength ranges for different laser types are shown in Fig. 4: dye and activated crystal lasers, gas (CO, CO_2, and NH_3) lasers – molecular media lasers; $CO-CO_2$ and $CO+CO_2$ lasers with difference and summary harmonic generators; $2CO_2$, 3CO, and $3CO_2$ lasers with 2nd and 3rd harmonic generators, as well as diode lasers with different ways of cooling. It is evident that radiation ranges of different laser sources cover almost whole optical spectral range: from the Visible to IR.

As is follows from the comparison of Figs. 1 and 4, almost all methane absorption bands are used in gas analysis of atmospheric air. However, its own conditions correspond to each absorption band (optimal wavelengths, path length, etc.), which is concerned, on the one hand, with the value of absorption coefficient, and, on the other hand, with the laser radiation energy.

The error of gas concentration retrieval was modeled on the base of the equation

$$x_0 = \frac{1}{KL}\ln\left(\frac{1}{T}\right),$$

where K, L, and T are the absorption coefficient, optical path length, and transmittance. Though this equation approximates Eq. (2), it allows considering just the influence of absorption coefficient on the error of gas concentration retrieval.

Hence, taking Eq. (8) into account, this error can be obtained from the equation

$$\sigma_x^2 = \left(\frac{\partial x}{\partial K}\right)^2 \sigma_K^2 + \left(\frac{\partial x}{\partial T}\right)^2 \sigma_T^2 \approx \left(\frac{\ln(1/T)}{KL}\right)^2 (\delta S^2 + \delta\gamma^2). \quad (9)$$

Here σ_K^2 and σ_T^2 are the dispersions of absorption coefficient and transmittance measurements.

On the base of the equation for transmittance determination error, computations were carried out for all transmittance values from 0 to 1 with the step 0.1 and characteristic absorption coefficients 10^{-6}–10^{-1} cm^{-1}/atm (Fig. 3). The computation results are shown in Fig. 5 (the distance was taken equal to 1 km).

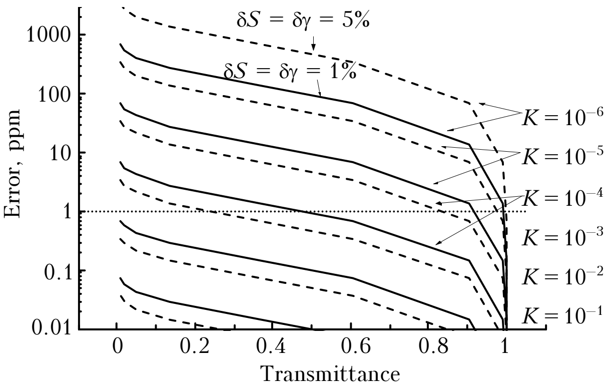

Fig. 5. Errors of CH_4 concentration retrieval as functions of absorption coefficient and spectroscopic errors.

It is evident, that the error of concentration retrieval decreases with the increase of absorption coefficient. Naturally, this fact is limiting owing to our assumption about the absence of transmittance measurement errors, but sufficient to estimate the influence of spectroscopic data error. Nevertheless, it can be concluded that the absorption coefficient should not be less than 10^{-3}–10^{-2} cm^{-1}/atm (the majority of CH_4 lines has such a value, see Fig. 3) to attain the error of methane concentration retrieval at a level of 0.01 ppm. In this case, the optimal transmittance is to be at the 0.5–0.8 level, which agrees with the measurement data[4,5] and corresponds to spectrometric practice (see also Ref. 21). It also follows from Fig. 5, that absorption coefficient uncertainties (1 or 5%) can result in essential errors in gas concentration retrieval.

Conclusion

The influence of spectroscopic data accuracy on the error of gas concentration retrieval from an optical experiment has been considered in this work. The quality of data from the HITRAN-2004 database has been analyzed, as well as from recent works, results of which have not been yet included in the modern versions of spectroscopic database. The equation has been obtained allowing estimation of the error of gas concentration retrieval depending on errors of available spectroscopic data (line intensity and half-width), used in the DIAL method.

Note, that according to computation results (see Fig. 5), the accuracy of spectroscopic data in HITRAN-2004 is usually insufficient for the gas analysis. To attain the 1-ppm level of the methane concentration determination error, lines with the absorption coefficient up to 10^{-4} cm^{-1}/atm can be used. But errors in the intensity determination for these lines should not exceed 1% (see Fig. 5). Individual spectral regions, containing stronger lines, e.g., the 1000–1700 cm^{-1} range can be used in measurements (line intensity and half-width errors are not more than 5%, see Fig. 2). However, parameters of spectral lines (intensity error attains 15–20%), containing in HITRAN-2004, need in refinement in majority of cases, especially in the near-IR range. Qualitative data improvement in the pentad (2200–3200 cm^{-1}) and octad (3500–4800 cm^{-1}) ranges is expected in the nearest future.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Grant No. 06-05-65010-a).

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