

Determination of atmospheric carbon dioxide concentration using Raman spectroscopy

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ABSTRACT

The paper demonstrates the possibility of measuring the carbon dioxide (CO₂) concentration in atmospheric air using Raman spectroscopy. Three methods have been studied for deriving the CO₂ concentration from the Raman spectra (the peak intensity ratio, the integrated intensity ratio, the contour fit method). The best results were obtained when the contour fit method is applied for Raman spectra processing. In this case the deviations from reference mixtures of known concentration were below 3 ppm. Methods for improving the sensitivity of the Raman gas analysis method are proposed and the possibility for using this technique for the simultaneous determination of the concentrations of significant amount of greenhouse gases in air with single device is discussed.

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1. Introduction

Carbon dioxide (CO₂) is an important greenhouse gas in the Earth's atmosphere, which has a great impact on the radiative exchange between the planet and the surrounding space. Despite the fact that its concentration in the atmosphere has daily and seasonal variations, its average annual concentration over the past two centuries is steadily increasing [1], which is associated with both natural and anthropogenic factors. In this regard, information on the atmospheric CO₂ concentration is of great importance for both environmental protection and development of models used in climate change predictions.

To date, there are various methods for measuring CO₂ concentration in atmospheric air. These are electrochemical [2,3], gas chromatography [4,5], mass spectrometry [6], Fourier transform infrared (FT-IR) spectroscopy [7,8], cavity ring-down spectroscopy (CRDS) [9], and nondispersive infrared spectroscopy (NDIR) [10]. Sensors based on NDIR are the most frequently used due to their simplicity and relatively low cost. However, this method requires frequent calibrations that do not permit users to take full advantage of autonomous operation [9].

Gas analysis based on Raman spectroscopy is developing rapidly owing to the fact that high-sensitivity detectors and powerful compact-size lasers are available. The potential of this

method has been demonstrated for diagnostics of natural gas composition [11–14], biogas [15], exhaled air [16,17] and environmental research [18,19]. The main advantage of Raman spectroscopy is the possibility of simultaneous detection of all molecular components of the gaseous medium (including homonuclear diatomic molecules such as N₂, O₂, H₂, etc.) for which the concentration exceeds the sensitivity threshold of the equipment. In addition, this method has high selectivity, and Raman signals, unlike signals in absorption spectroscopy, are linearly dependent on the concentration of the target gas.

This work is devoted to studying of the possibility of using Raman spectroscopy for measuring CO₂ concentration in atmospheric air.

2. Experimental details

To achieve the measurements, a Raman gas analyzer based on a 90°-geometry of the scattered light collection was used [11]. To excite Raman spectra, a DPSS continuous wave Nd:YAG laser with an output power of 2 W at a wavelength of 532 nm was used. The scattered radiation was collected and focused onto the spectrometer input slit employing two f/1.8 lens objectives (f = 50 mm). For simultaneous registration of Raman spectra in the range 200–3800 cm⁻¹, a no-moving-parts f/1.8-spectrometer MKR-2 with a Hamamatsu S10141 CCD matrix (2048 × 256 pixels) was used. The matrix was operated as a linear CCD since charges were summed in columns (vertical binning was performed). In addition, in order to increase the Raman signal intensity, the

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samples of atmospheric air were compressed to a pressure of 25 bar using a compact oil-free pneumatic pump.

Experimental studies were conducted at the Institute of Monitoring of Climatic and Ecological Systems (Tomsk, Russia) located at 56.47°N, 85.05°E for 5 days in June 2017. Sampling of atmospheric air was carried out at a significant distance from traffic at a height of 5 m above the surface. The measurements were performed twice a day at 6 am and 6 pm, because approximately at this time the concentration of CO₂ in the atmospheric air reached its maximum and minimum values. The exposure time of each Raman spectrum was 2000 s (the sum of 2000 spectra within a 1 s integration time). Simultaneously, the concentration of CO₂ was measured using a certified gas analyzer LGR 907-0010, based on cavity ring-down spectroscopy [20], by averaging the measurements over 10 min.

3. Results and discussion

3.1. Raman spectrum of atmospheric air

Fig. 1 shows one of the obtained Raman spectra of atmospheric air, including its unscaled pattern (Fig. 1a), as well as some large zooms in specific spectral ranges (Fig. 1b–d). The main part of the spectrum is occupied by fundamental vibrational bands (1–0) of molecular nitrogen (¹⁴N₂) and molecular oxygen (¹⁶O₂) having maxima at 2329 cm⁻¹ and 1555 cm⁻¹, respectively. It should be noted that at the exposure time used, the signal of the Q-branch of nitrogen slightly exceeded the limit of the dynamic range of

the photodetector, therefore its intensity was “cut off”. The Raman spectrum of carbon dioxide (¹²C¹⁶O₂) is a Fermi doublet with maxima at 1285 cm⁻¹ and 1388 cm⁻¹ resulting from the interaction of the ν_1 fundamental band and the $2\nu_2$ overtone. In this paper we will identify these bands according to Ref. [21], i.e., the band with a lower Raman shift (1285 cm⁻¹) is called ν_1 , and the band with the higher Raman shift (1388 cm⁻¹) is called $2\nu_2$, although the Ref. [22] is using the opposite convention (which could change by isotopic substitution). Also, the fundamental vibrational bands ν_1 of water vapor (H₂¹⁶O) and methane (¹²CH₄), as well as the overtone (2–0) of ¹⁶O₂ with maxima at 3652 cm⁻¹, 2917 cm⁻¹, 3087 cm⁻¹, respectively, are clearly visible in the recorded spectra (Fig. 1d). In addition we can observe in the spectra the bands corresponding to isotopic modifications of some molecules. For example, in the O-branch of ¹⁴N₂, the Q-branch of the fundamental vibrational band (1–0) of the ¹⁴N¹⁵N with a Raman shift of 2291 cm⁻¹ [23] (Fig. 1b), and a Q-branch of the ν_1 band of the ¹³C¹⁶O₂ molecule between Q-branches of ¹²C¹⁶O₂ are observed (Fig. 1c).

3.2. Determination of CO₂ concentration

During the study, we tested three methods for deriving CO₂ concentration from the Raman spectra obtained. Let us consider them below.

It is known that the Raman intensity I_R of an individual rovibrational band ν_j from the volume V to the solid angle $\Delta\Omega$ for molecules of one kind is given by Eq. (1)

$$I_R = I_L V N \sigma_j \Delta\Omega C(\lambda), \quad (1)$$

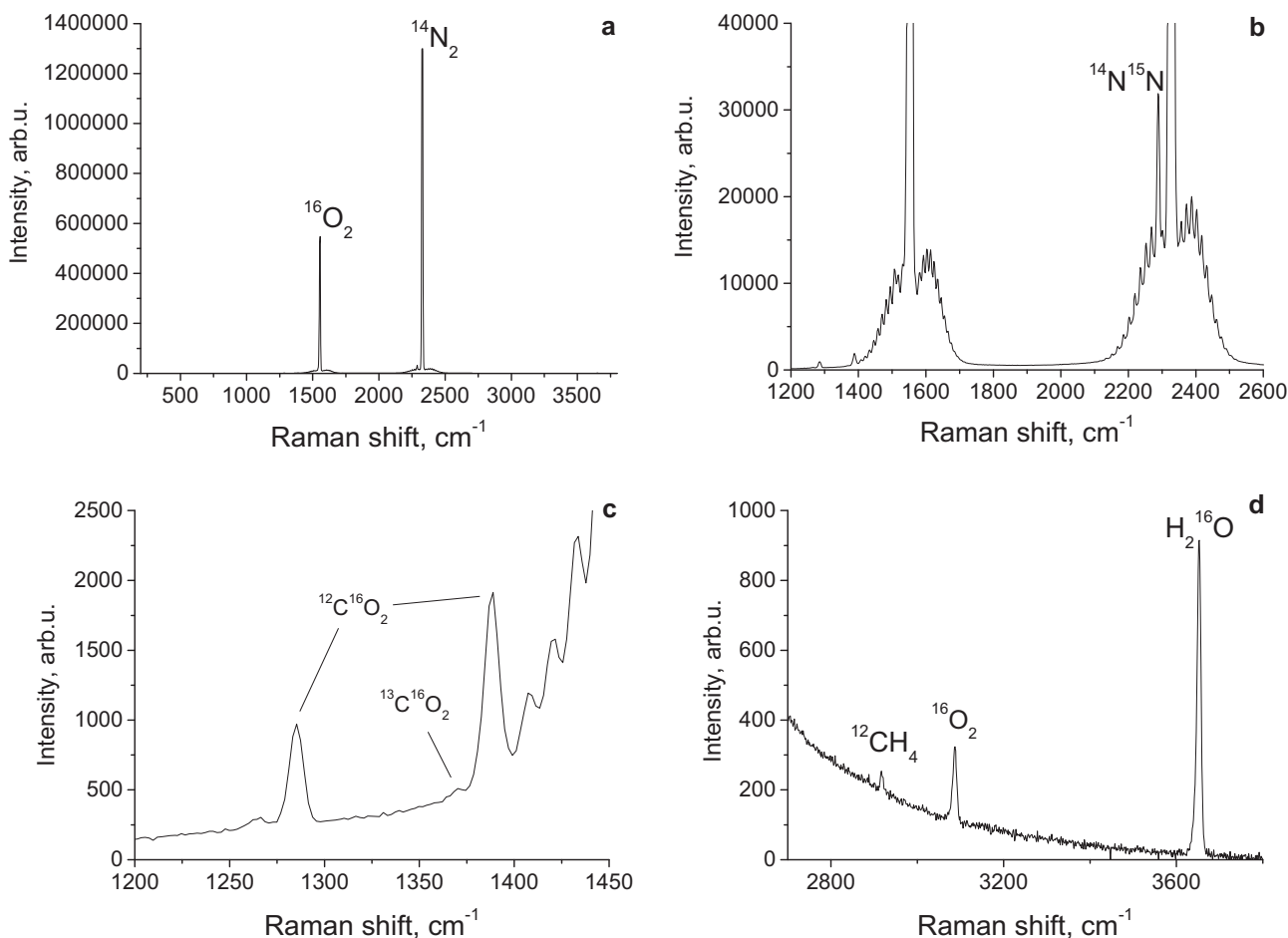


Fig. 1. Raman spectrum of atmospheric air in ranges of 200–3800 cm⁻¹ (a), 1200–2600 cm⁻¹ (b), 1200–1450 cm⁻¹ (c), and 2700–3800 cm⁻¹ (d).

where I_L is the intensity of the exciting laser radiation, σ_j is the differential scattering cross section (for an observation angle of the scattered radiation fixed relative to the direction of polarization and to the direction of propagation of the exciting radiation), N is the absolute concentration of specific molecules in the gas medium, $C(\lambda)$ is the spectral sensitivity of the spectrometer at a wavelength corresponding to the location of the band ν_j .

It is seen from Eq. (1) that it is difficult to determine the CO_2 concentration from the intensity of its Raman bands, since the laser power, the configuration of the collection optics and the density of molecules (due to different pressures) can vary from one measurement to other, which will lead to a corresponding change in the parameters I_L , $\Delta\Omega$ and N . To eliminate these effects, we can use relative measurements (Eq. (2)). It is reasonable to use the nitrogen signal as a reference one, because it has a weak chemical activity and consequently its relative concentration in dry atmospheric air is quite stable.

$$\frac{I_{\text{CO}_2}}{I_{\text{N}_2}} = \frac{N_{\text{CO}_2} \sigma_{\text{CO}_2} C(\lambda_{\text{CO}_2})}{N_{\text{N}_2} \sigma_{\text{N}_2} C(\lambda_{\text{N}_2})}. \quad (2)$$

Note that in order to determine CO_2 variations at the ppm level, the corresponding values of the scattering cross sections and spectral sensitivity should be known with very high accuracy. Consequently, in order to avoid the need to use these values, it is sufficient to use a calibration mixture with a well-known ratio of carbon dioxide and nitrogen concentrations (Eq. (3)).

$$\frac{I_{\text{CO}_2}}{I_{\text{N}_2}} \cdot \left(\frac{N_{\text{CO}_2}}{N_{\text{N}_2}}\right)^{\text{ref}} = \left(\frac{I_{\text{CO}_2}}{I_{\text{N}_2}}\right)^{\text{ref}} \cdot \frac{N_{\text{CO}_2}}{N_{\text{N}_2}}. \quad (3)$$

Assuming the stability of the nitrogen concentration in dry atmospheric air, we obtain the following equation

$$N_{\text{CO}_2} = \frac{I_{\text{CO}_2}}{I_{\text{N}_2}} \cdot \left(\frac{I_{\text{N}_2}}{I_{\text{CO}_2}}\right)^{\text{ref}} \cdot N_{\text{CO}_2}^{\text{ref}} = \frac{I_{\text{CO}_2}}{I_{\text{N}_2}} \cdot K, \quad (4)$$

where K is the calibration coefficient.

Note that in this case it is possible to use both peak and integrated intensities.

Within the first approach for estimating CO_2 concentrations, we used Eq. (4) and peak intensities. Since the Q-branch of $^{14}\text{N}_2$ is reaching saturation, we used the intensity at the peak of the Q-branch of $^{14}\text{N}_2^{15}\text{N}$. The peak intensity of the ν_1 band (1285 cm^{-1}) was used as the CO_2 signal. The choice of this band, rather than the more intense $2\nu_2$ (1388 cm^{-1}), is justified by the fact that the rovibrational lines of the O-branch of molecular oxygen with rotational quantum numbers $N = 12, 13, 14$ contribute to the intensity of the $2\nu_2$ band of CO_2 and as a result, it is quite difficult to determine the intensity of this latter feature in a reliable manner. The values of the peak intensities of the Q-branches were taken directly from the experimental data taking into account the baseline level. Our study has shown that any other proxy for the intensity of these Q-branches (for example, using a Gauss function) is not granted, since the resulting values differ by a negligible amount (see Fig. 2).

Within the second approach, we used Eq. (4) and integrated intensities. For the CO_2 signal, the Q branch of ν_1 is also used, and the integration is carried out in the range of $1274.9\text{--}1295.7 \text{ cm}^{-1}$. In turn, for molecular nitrogen the signal is integrated in the range $2144.9\text{--}2307.0 \text{ cm}^{-1}$, where the rovibrational lines of the O-branch of $^{14}\text{N}_2$ as well as the Q-branch of $^{14}\text{N}_2^{15}\text{N}$ are located.

Within the third approach, the method of decomposing the recorded Raman spectra of atmospheric air into the spectra of nitrogen, oxygen, and carbon dioxide was used. This method is also called «contour fit method» and in essence can be described as follows.

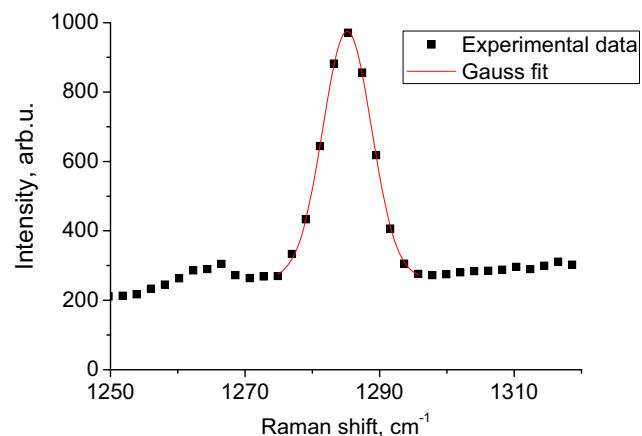


Fig. 2. Example of Gauss function fit used to extract the peak intensity of the $\text{CO}_2 \nu_1$ band.

The Raman signal from the gaseous mixture registered by the k th column of the CCD matrix of the gas analyzer can be written by Eq. (5).

$$\begin{cases} I^{(1)} = a_1 I_1^{(1)} + a_2 I_2^{(1)} + \dots + a_i I_i^{(1)} \\ I^{(2)} = a_1 I_1^{(2)} + a_2 I_2^{(2)} + \dots + a_i I_i^{(2)} \\ \dots \\ I^{(k)} = a_1 I_1^{(k)} + a_2 I_2^{(k)} + \dots + a_i I_i^{(k)} \end{cases} \quad (5)$$

where a_i describes the contribution of the i th component of the gaseous medium to the signal $I^{(k)}$ and $I_i^{(k)}$ is the Raman signal of the same molecular species measured for a pure reference by the k th column of the CCD matrix. Since the number of equations k considerably exceeds the number of unknown species, this system of equations is overdetermined and is solved by the least squares method. The relative concentrations N_i are determined by normalization of the derived a_i values by 100% taking into account the calibration coefficients K_i which included design parameters of the gas analyzer, laser power and concentration of molecules in the reference gas (Eq. (6)).

$$N_i = \frac{K_i a_i}{\sum_{i=1}^m K_i a_i} \cdot 100\%. \quad (6)$$

It should be noted that in our case the decomposition, according to Eq. (5), was performed in the $1200\text{--}2307 \text{ cm}^{-1}$ range. This is because there is no useful information below 1200 cm^{-1} , and because the saturated Q-branch of $^{14}\text{N}_2$, as well as the water vapor bands (for simulation of dry air analysis) were excluded from consideration.

The main advantage of this method is the proper extraction of the intensity of one species against the background possibly perturbed by the other species, and the possibility to use more points for fitting the spectrum.

The results obtained are shown in Table 1. Note that before the series of measurements, the required calibration coefficients for the three methods described above were obtained by recording the Raman spectrum of a reference gas mixture with a CO_2 concentration (in dry synthetic air) equal to $400 \pm 1 \text{ ppm}$.

According to the data given in Table 1, the calculated values of the concentrations are fairly close to the values obtained by the reference CRDS gas analyzer, however the differences (Δ) of the three investigated methods from the reference data are different. According to the results obtained, the greatest deviations are observed when using the peak intensities ratio, they are slightly less when using the integrated intensities ratio and they are the

Table 1
Results of determination of the CO₂ concentration using the Raman gas analysis and the CRDS gas analysis. Delta is the difference between the CO₂ mixing ration from the reference CRDS measurement and that retrieved from the Raman measurements.

No.	CRDS analysis		Raman gas analysis					
	N_{CO_2} , ppm	N_{CO_2} , ppm	Peak intensity ratio method		Integrated intensity ratio method		Contour fit method	
			N_{CO_2} , ppm	Δ , ppm	N_{CO_2} , ppm	Δ , ppm	N_{CO_2} , ppm	Δ , ppm
1	422	429.0	7.0	426.7	4.7	425.0	3.0	
2	405	414.9	9.9	407.0	2.0	407.9	2.9	
3	460	463.4	3.4	461.8	1.8	458.1	-1.9	
4	401	404.6	3.6	404.3	3.3	403.2	2.2	
5	480	479.8	-0.2	491.3	11.3	480.7	0.7	
6	393	388.4	-4.6	392.9	-0.1	394.9	1.9	
7	418	410.5	-7.5	411.9	-6.1	415.0	-3.0	
8	400	399.1	-0.9	400.9	0.9	402.7	2.7	
9	422	418.2	-3.8	421.5	-0.5	421.8	-0.2	
10	401	393.9	-7.1	395.5	-5.5	398.1	-2.9	

smallest when using the contour fit method. Primarily, this is resulting from the different number of points of the spectra used in the calculations.

Let us estimate the minimum concentration, which can be detected using the developed Raman gas analyzer. It is obvious that this value is different for the different molecules. When the Raman signal has a very small intensity without overlap by the bands of other species, the minimum concentration $N_{\min}^{x(\text{band})}$ for gas x will depend on the cross section of the band used for quantification $\sigma^{x(\text{band})}$ and of the standard deviation of the noise δ . Thus, using the measured intensity value I^{ref} for a Raman band with a scattering cross section σ^{ref} of a target species with a known concentration of N^{ref} , $N_{\min}^{x(\text{band})}$ can be estimated as

$$N_{\min}^{x(\text{band})} \approx \frac{N^{\text{ref}} \delta \sigma^{\text{ref}}}{I^{\text{ref}} \sigma^{x(\text{band})}} \quad (7)$$

In our case, for the Raman spectrum of a gas medium with a CO₂ concentration of $N^{\text{ref}} = 400$ ppm, the peak intensity of its ν_1 band, having a cross section $\sigma^{\text{ref}} = \sigma^{\text{CO}_2(\nu_1)} = 0.7$ [24], was $I^{\text{ref}} \approx 600$ (in arbitrary unit), and the standard deviation of the noise signal was $\delta \approx 5.3$ (in arbitrary unit). Thus, when we use the ν_1 band to determine the CO₂ concentration, we get $N_{\min}^{\text{CO}_2(\nu_1)} \approx 3.5$ ppm, while when using the more intense $2\nu_2$ band with $\sigma^{\text{CO}_2(2\nu_2)} = 1.1$ [24], Eq. (7) gives $N_{\min}^{\text{CO}_2(2\nu_2)} \approx 2.2$ ppm. Note, that these values are close to the Δ values obtained by various Raman spectra processing methods. In turn, due to the fact that for the ν_1 band of ¹²CH₄ the scattering cross section $\sigma^{\text{CH}_4(\nu_1)} \approx 9$ [24], its detection limit would be $N_{\min}^{\text{CH}_4(\nu_1)} \approx 0.28$ ppm. This means that variations of the methane concentration in the atmospheric air higher than this value could also be detected with the Raman gas analyzer. However, during the measurement period these variations did not exceed 0.2 ppm, therefore we could not derive useful CH₄ value.

3.3. Methods for improving the sensitivity

Let us consider the possibilities for increasing the sensitivity of Raman gas analysis. On one side, this could be achieved through the use of a detector with a lower noise level, which can be obtained by thermoelectric cooling down to -70 °C. On the other side, according to the Eq. (1), the Raman signal intensity can be increased by increasing the intensity of the exciting radiation in the scattering volume. This can be achieved by using a laser with a higher output power, or by using special multipass optical systems. An example of such a system was demonstrated in Ref. [25], where a 20-fold increase in the Raman signal intensity was obtained. Obviously, these approaches can be used simultaneously

and as a result their impact will have a multiplicative effect. For example, in comparison with the Raman gas analyzer used in the present study, an increase of the laser power up to 10 W and the use of a multipass optical system, providing a 20-fold increase in laser intensity, could provide a ~ 100 -fold increase in intensity of the Raman signals. This means that for many gas species with scattering cross sections comparable to ¹²CH₄ (or higher), the limit of detection will reach the ppb level, and the CO₂ measurement error will be a fraction of ppm. This increased sensitivity opens the possibility of using Raman gas analysis to control atmospheric air composition at the background concentrations for many pollutants. In addition, depending on the application, such sensitivity will allow either to avoid the preliminary compression of the analyzed gas medium, or to substantially reduce the time for one analysis.

4. Conclusion

This work has demonstrated the possibility of measuring the concentration of carbon dioxide in atmospheric air using Raman spectroscopy. As compared to the methods of peak intensity ratio and of integrated intensity ratio, the contour fit method provided the best results for deriving concentrations from the Raman spectra. The latter fitting method results in deviations from the reference CRDS measurements that are below 3 ppm. This is explained by the fact that the fitting uses a larger number of spectral points, and that the spectral features of one target species can be better distinguished from the background and from the contributions of the other species.

Obviously, since Raman spectroscopy offers the possibility to monitor simultaneously big amount of gaseous species with improved sensitivity, this technique can be employed to control other pollutants or greenhouse gases, including their isotopologues. We believe that, in the near future and with the proposed improvements, this method could become a powerful analytical tool in the field of atmospheric air pollution monitoring.

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