Raman gas analyzer for detecting carbon isotopologues

V V Vitkin, I K Chubchenko, A V Polischuk, A V Kovalev and E E Popov

Saint Petersburg National Research University of Information Technologies, Mechanics and Optics ITMO University, Saint-Petersburg, Russia

E-mail: popov_st@rambler.ru

Abstract. A Raman gas analyzer for detecting carbon isotopologues with an excitation laser with a power of 5 W, generating at a wavelength of 532 nm, focusable in a waist of 7 μm using a lens with compensation for spherical aberration is presented. The signal is detected by a high-resolution spectrometer with a matrix cooled to -40° C. The program optimization of the system parameters is presented: focusing lens, cuvette windows.

1. Introduction
Raman spectroscopy allows the analysis of gaseous media, including the determination of atomic isotopes in compounds, including carbon isotopes in carbon oxides, methane, as shown in [1, 2]. The prevalence of some isotopes differs significantly, which implies a low concentration of such compounds in the samples under study, which causes difficulties in their detection. To detect such compounds, it is necessary to increase the intensity of the Raman scattered signal. The increase in the intensity of the Raman signal can be increased by: increasing the intensity of the laser signal, measuring the signal at high pressure.

The Raman natural gas analyzer, presented in [3] is of interest. The analyzer has a signal accumulation time of 100 s, which makes it possible to detect natural gas components with concentrations from 0.01%. The scheme of this gas analyzer can be taken as a basis for creating a multifunctional Raman gas analyzer for detecting carbon isotopologues.

2. The design of the multifunctional Raman gas analyzer
A multifunctional Raman gas analyzer consists of: a radiation source, a focusing system, a cuvette containing the sample to be studied, a system that collects a scattered signal, a system that ensures human interaction with the device.

MSL-R-532 single-frequency solid-state laser model is used as a probe radiation source. Laser power is 5 W, central wavelength is 532 nm. This laser has M² quality parameter close to unity ~ 1.1. The output diameter of the laser beam at a level of 1/e² is 1.5 mm. Laser radiation has a degree of polarization of 100:1.

The width of the spectral line of such a laser allows exciting only a narrow band of the Raman signal. High power allows getting a greater signal to noise ratio with less signal accumulation time. The Stokes components induced by a wavelength of 532 nm in CO₂ and CH₄ gases are located in the region where the quantum efficiency of the receiver is more than 90%. A diagram of a Raman gas analyzer is shown in figure 1.
2.1. Focusing system

The radiation at the exit from the laser is incident on a tenfold beam expander of BE10-532-10X UVFS model, manufactured by Thorlabs. The beam expander, being a lens telescope of the Kepler scheme, increases the diameter of the radiation beam, decreasing the angular field, which allows reducing the divergence of laser radiation from 1.5 to 0.15 milliradians. This reduction in divergence can significantly reduce the diameter of the waist.

To select the focusing optics, the power distribution in the constriction of the focusing probe radiation of the system was simulated. Several options were considered as a focusing system: a standard single-lens lens; standard achromatic doublet. Modeling was carried out in the Zemax program. Based on the design features of the cell, the focal length for the system could not be less than 50 mm. The diameter of the focusing lens must be at least 15 mm. LA1119 model manufactured by Thorlabs was considered as a standard single-lens lens. Lens had a diameter of 18 mm, focal length was 50 mm. The optical scheme of the focusing system is shown in figure 2.

The spot diameter at the focus of a single-lens lens at a level of 80% was 347.8 μm, with an Airy diameter of 4.2 μm. Such a high value is explained by significant spherical aberration. The next step was considered a TF4 single lens, with a relative aperture of 3.2, a focal length of 48.5 mm. The lens parameters are obtained as a result of software optimization to achieve a minimum spot diameter in focus. The glass brand is chosen so as to reduce spherical aberration. The dependence of the power distribution on the cross section in the waist is shown in figure 3.
It can be seen from the figure that the presented single-lens lens has a diameter in the waist at the level of 80% - 42 microns. Despite a significant reduction in diameter, single-lens lenses have significant spherical aberration. To compensate for aberration, adhesion from two lenses is standardly used. As two compared options, an individually designed lens was considered, and AC127-050 standard lens, manufactured by Thorlabs, an individually designed two-lens lens with a relative aperture of 3.1, with a focal length of 45.4 mm. The lens parameters are obtained as a result of software optimization to achieve the minimum diameter of the scattering spot in focus. Glass brands are selected to compensate for spherical aberration. The dependence of the radiation intensity on the cross-section for the standard and the lens of an individual project is shown in figures 4 and 5.

The diameter of the spot in the waist at a level of 80% for the AC127-050 lens is 6.4 microns, for an individually designed lens it is 3.4 microns. It is seen that the lens of individual development allows getting a spot close to the diffraction limit. Due to the high cost of manufacturing a single sample, it was decided to use standard AC127-050 doublet as an objective.

2.2. Cuvette for an experimental sample
The cuvette for the experimental sample is designed to work with high-pressure gases. The volume of the working area of the cell is limited to a cubic centimeter, which is convenient for processing measurement results. The high cost of gas isotopologists also imposes a limitation on the volume of the working area of the cell. The Raman signal is detected at an angle of 90 ° to the optical axis of the probe radiation.

An important element of the cuvette is leucosapphire windows, through which probe radiation is directed to the sample under study, and through which scattered radiation is collected. Since the thickness of the glass limits the solid angle from which radiation can be collected, the thickness of the optical window should be minimally acceptable.
The thickness of the optical window was determined using software optimization. The safety factor is 10. The ultimate stress for leucosapphire is taken to be equal to the elastic limit of 275 MPa [4]. The design pressure is 100 atmospheres. Under these conditions, the minimum window thickness is 6 mm. The maximum window diameter is determined from the design features and is 15 mm for the passage of laser radiation, 20 mm for collecting the scattered signal. The results of modeling the load on the windows are presented by stress and displacement diagrams shown in figures 6, 7. With a stress limit of 275 MPa [4], the maximum stress in the window, as a result of the simulation, was 26 MPa.

![Figure 6. Stress diagram.](image1)

![Figure 7. Movement plot.](image2)

2.3. Signal registration
To detect signals with a narrow spectral width, it is planned to use the Czerny-Turner interferometer, manufactured by SOL Instruments. A 70 × 70 × 10 mm diffraction grating is installed in the interferometer, with a light wavelength of 500 nm and a line density of 1800 lines per millimeter. The receiving matrix is 2048 × 128 pixels. The design of the interferometer allows the receiver to record a radiation range with a spectral contour width of 80 nm. Thus, the resolution of the spectral instrument is about 40 pm. The matrix planned for use is cooled to a temperature of -40° C, which can significantly reduce noise. The matrix accumulates a signal with a period of 2 μs.

The scattered radiation is collected by a lens with a relative aperture of f/1.4. The parameters of the receiving lens are determined by the design features of the cuvette. Passing through the first lens, the radiation is filtered by a notch filter in order to lower the radiation intensity at the laser wavelength by 6 orders of magnitude. Then the signal is focused on the entrance slit of the spectrometer, 20 μm wide.

To analyze the possibility of detecting a signal scattered by gas molecules of carbon isotopologues, an estimated analysis of the received signal is carried out. For the calculation, the accumulation time was taken as 75 s. The calculation was made for 12CO2. The absolute value of the Raman scattering cross section for this isotopolog according to [5] is \(53 \times 10^{-30}\) cm\(^2\)/sr. The detected radiation was taken as an example of a peak with a Raman shift of 1388 cm\(^{-1}\) and a width of 0.4 nm, according to [6]. The calculation method is taken from [7]. The pressure at which it is planned to measure is 30 atm. The diameter of the spot in the constriction is 7 μm. The signal-to-noise ratio for such conditions was 10 for a pure sample with losses on the receiving optics of no more than 40%. A decrease in concentration leads to a decrease in signal-to-noise ratio. Increasing the accumulation time allows resolving less intense components. The dependence of the detected concentration on the accumulation time, at different signal-to-noise ratios, is shown in figure 8.
Figure 8 shows that the detection of the $^{12}$CO$_2$ isotope, with a concentration of 0.01%, with a signal-to-noise ratio of 5 is possible with an accumulation time of 520 s.

3. Conclusion
As a result of the work, a Raman gas analyzer capable of detecting a $^{12}$CO$_2$ carbon isotopologue with a concentration of 0.01% at an accumulation time of 520 s, with a signal to noise ratio of 5, is presented. The Raman signal is excited by radiation with a wavelength of 532 nm, a power of 5 W, a focused spot with a diameter of 7 μm.

Acknowledgements
This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation, grant RFMEFI57518X0180.

References
[1] Keiner R, Frosch T, Massad T, et al. 2014 The Analyst 139 3879
[2] Finsterholzl H 1982 Phys. Chem. 86 797-805
[3] Petrov D V and Matrosov I I 2019 Applied spectroscopy 70 1770-6
[4] Weber M J 2003 Handbook of optical materials (New York: CRC Press)
[5] Penney C M et al. 1974 Journal of the Optical Society of America 64 712
[6] Petrov D V et al. 2018 Journal of Molecular Spectroscopy 348 137–41
[7] Richard L 2000 McCreery Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications (John Wiley & Sons)