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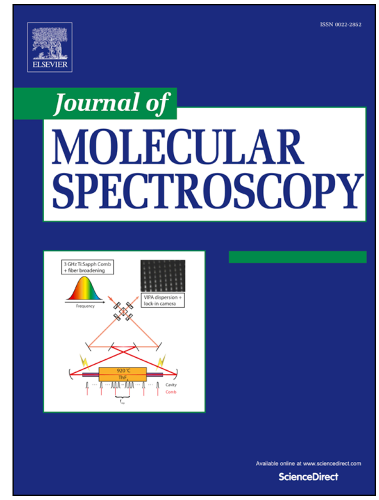

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Determination of atmospheric carbon dioxide concentration using Raman spectroscopy

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The paper demonstrates the possibility of measuring the carbon dioxide (CO_2) concentration in atmospheric air using Raman spectroscopy. Three methods have been studied for deriving the CO_2 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.

Keywords: Carbon dioxide, atmospheric air, gas analysis, Raman spectroscopy.

1. Introduction

Carbon dioxide (CO_2) 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 CO_2 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 CO_2 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 N_2, O_2, H_2, etc.) for which the concentration exceeds the sensitivity threshold of the equipment. In addition, this method has