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Resolving the $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ lines of Raman spectrum

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Abstract: We demonstrate a method to determine the volume fraction of gaseous isotopologues of methane $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in a mixture from a Raman spectrum under spectral overlap and limited resolution.

1. Introduction

Resolving densely spaced spectral lines is a common spectroscopic problem. For example, methane isotopologues $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ Raman scattering lines are at a distance of less than 4 cm^{-1} from each other [1], making it a problem to distinguish between them in a gas mixture. There is also a demand for a high-dynamic range, versatile, and precise tool for isotopic analysis, e.g., to confirm the origin of biomethane, and Raman spectroscopy is a right candidate for that [2-3]. This paper presents a method to define the isotopologue volume fraction using a nonlinear regression model complemented by a two-peak Lorentz approximation of the scattering spectrum.

2. Theory

At the preparation step, Raman spectra of pure gases mixed with nitrogen are measured under the varied setup parameters, i.e., laser power, camera exposure time, the pressure of the gas in the cuvette. Then they are fitted with a single-peak Lorentz function:

$$S_k(\nu) = f_L(\nu, A_k^S, \mu_k^S, \sigma_k^S) + \beta_k^S, \quad (1)$$

where k – index (1 for $^{12}\text{CH}_4$, 2 for $^{13}\text{CH}_4$); ν – Raman frequency in wavenumbers; A_k^S – amplitude of the Raman scattering signal peak; μ_k^S – central wavenumber of the Raman scattering signal peak; σ_k^S – width of the Raman scattering signal peak measured at the half of the amplitude; β_k^S – baseline parameter; f_L – the Lorentz function:

$$f_L(\nu, A, \mu, \sigma) = A / [1 + 4(\nu - \mu)^2 / \sigma^2]. \quad (2)$$

The Lorentz profile is used due to the good characterization of the Raman spectrum of gases [4]. The approximation by eq. (1) involves evaluation of A_k^S , μ_k^S , σ_k^S , β_k^S parameters employing the least-squares fitting method. After the approximation, the nonlinear regression model is build based on extracted values A_k^S , and the experimental parameters. The following equation describes the model:

$$A_k^S(P, W, \tau, X_{\text{vol.}\%}) = p_{1,k} PW \tau X_{\text{vol.}\%,k} + p_{2,k}, \quad (3)$$

where P – pressure in the cuvette (in atmospheres); W – laser power; τ – exposure time of camera; $X_{\text{vol.}\%,k}$ – volume fraction of the component; $p_{1,k}$, $p_{2,k}$ – parameters determined by the regression. The parameter $p_{1,k}$ describes fixed unspecified experimental parameters. Parameter $p_{2,k}$ describes the camera noise. The volume fraction can be determined from (3) using an equation:

$$X_{\text{vol.}\%,k}(P, W, \tau, A) = (A_k^S - p_{2,k}) / (p_{1,k} PW \tau), \quad (4)$$

In order to determine each component's portion in the gas mixture, its Raman scattered signal is approximated by the sum of two Lorentz functions. The two-peak model of the signal can be written as the equation:

$$M(\nu) = \sum_{k=1}^2 f_L(\nu, A_k, \bar{\mu}_k, \bar{\sigma}_k) + \beta, \quad (5)$$

where values with upper dashes are fixed and defined from a single-peak approximation by eq. (1). Extracting the peak intensities of the corresponding gas component and putting it and the experimental parameters into eq. (4). we can calculate its volume fraction.

3. Experimental results

To verify our method, we conducted a series of experiments measuring the volume fraction of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in gaseous mixtures. The experimental setup is described in our previous work [3]. Figure 1 demonstrates both measured and fitted Raman scattering signals (green lines are for measured spectra; red lines are for $^{12}\text{CH}_4$ Lorenz profile; blue lines are for $^{13}\text{CH}_4$ Lorenz profile; black lines are their sum as given by eq. (5)).

Fig. 1. Approximation of different gaseous mixtures: (a) $^{12}\text{CH}_4$ – 50,8%, N_2 – res.; (b) $^{13}\text{CH}_4$ – 92,8%, N_2 – res.; (c) $^{12}\text{CH}_4$ – 0,01028%, $^{13}\text{CH}_4$ – 0,01057%, N_2 – res.; (d) $^{12}\text{CH}_4$ – 4,84%, $^{13}\text{CH}_4$ – 4,98%, N_2 – res.

The results, presenting measured volume fraction values and relative errors for a gaseous mixture containing 4.84% of $^{12}\text{CH}_4$ and 4.98% of $^{13}\text{CH}_4$, are shown in table 1. The error value depends on the volume fraction and accuracy of measuring the experimental parameters and does not exceed 11% (for the 100 ppm gaseous mixtures).

Table 1. Experimental results

Component	Measured value, %	Real value, %	Relative error, %
$^{12}\text{CH}_4$	4.88	4.84	0.8
$^{13}\text{CH}_4$	4.99	4.98	0.2

4. Conclusion

We demonstrate a method that can determine the volume fraction of gaseous components in densely spaced lines. The relative error depends on volume fraction and accuracy of measuring the experimental parameters but does not exceed 11%.

5. Acknowledgement

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