



Determining the most suitable spectral range for TDLS – a quantitative approach



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ABSTRACT

We present a mathematical method which allows determination of an optimal spectral range for gas mixture analysis based on theoretical absorption spectra. The resulting center wavelength is particularly suited for tunable diode laser spectroscopy (TDLS). The procedure contains several steps of numerical calculations which can easily be implemented in almost any programming language. We apply our method to three exemplary mixtures of hydrocarbons and present and validate the individual results.

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1. Introduction

Optical spectroscopy is nowadays a well-established method for the analysis of gaseous mixtures. As soon as a high spectral resolution is required, spectrometers usually apply lasers as radiation sources [1–3]. In order to be able to probe different absorption features with a single laser, it is advantageous if its emission wavelength can be varied. Therefore, semiconductor lasers are predestined for this task, because they can be spectrally tuned via their operating temperature and current. The tuning range of distributed feedback interband cascade lasers is, for example, of the order of 10 nm at constant laser temperature with an emission linewidth in the single-digit megahertz range [4–7].

When designing a laser spectrometer, the definition of the laser's emission wavelength or, if tunable, its spectral range is crucial for its potential applications. As a matter of course, all the components of interest should exhibit absorption within the range. Furthermore, it is desirable that the absorption strengths of all components are high in order to achieve high detection sensitivity. Simultaneously, interferences of the absorbing compounds should be excluded to the greatest possible extent in pursuance of avoid-

ing metrological ambiguity and, thus, reach high detection selectivity [1,2].

The identification of the optimal spectral range for a certain application, i.e. for the analysis of a certain mixture of gases, is not trivial. In practice it is usually an educated guess based on the known spectra [2,8,9]. The spectra evaluation, i.e. the determination of the concentrations of the individual components, is then typically carried out using a multivariate calibration such as partial least squares regression. However, the quality of the results, especially the selectivity, strongly depends on the selected wavelength range and the selection becomes increasingly difficult if the single spectra strongly overlap, and even more so if the single components are very similar and their spectra differ only slightly.

In the following we present, to the best of our knowledge, the first quantitative method to determine a well suited spectral range for sensitive and selective gas analysis. The procedure is customized for lasers of a certain tuning range, such as semiconductor lasers, and delivers its optimal center wavelength. The following section describes the mathematical procedure. After that we present exemplary application results.

2. Mathematical procedure

For the application of the method, knowledge of the absorption spectra of all gaseous components in the mixture is required. The

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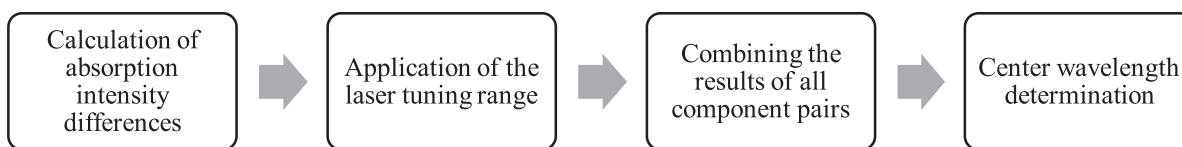
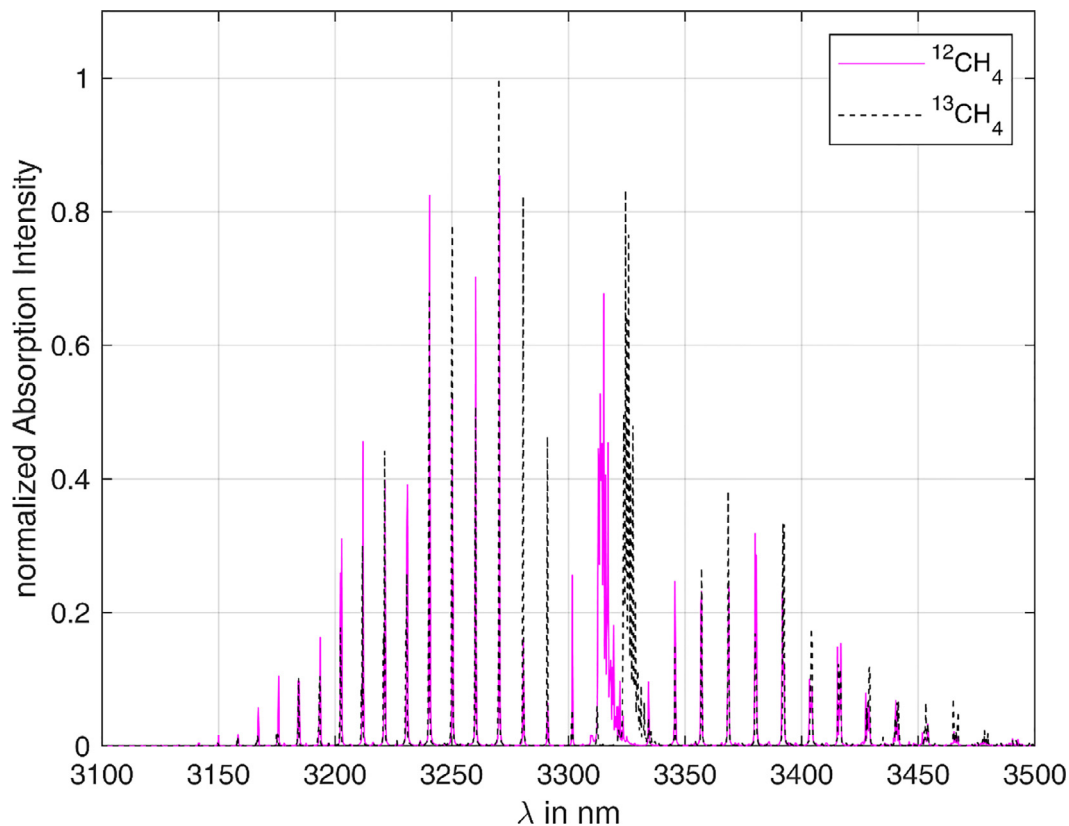


Fig. 1. Flowchart of the mathematical procedure.

Fig. 2. Absorption spectra of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ [20].

spectra can be measured beforehand, e.g. with a Fourier Interferometer, or extracted from databases such as HITRAN [10], GEISA [11], JPL [12] or NIST [13]. The flow chart of the method is shown in Fig. 1. The individual steps are explained in the following subsections.

2.1. Calculation of absorption intensity differences

In order to measure the individual gas components selectively or with least interference, it is necessary to identify the wavelengths at which the absorption spectra maximally differ from one another [14]. To find these spectral regions, all spectra are normalized to 1. A total number n of gases (spectra) results in:

$$\binom{n}{2} = \frac{n!}{2 \cdot (n-2)!} \quad (1)$$

dyads of spectra [15]. The individual absorption intensities of each gas $S(\lambda)$ are then used to calculate the intensity differences for each pair of gases (i and j) as function of the wavelength λ :

$$\Delta S_{ij}(\lambda) = S_i(\lambda) - S_j(\lambda). \quad (2)$$

2.2. Application of the laser tuning range

Semiconductor lasers exhibit a limited spectral tuning range. In the case of an interband cascade laser the tuning range $\Delta\lambda$ is typically of the order of 10 nm [4–7]. This has to be considered for the determination of best suited spectral range. The influence is represented by a sliding integral (Q -function) of the individual differences:

$$Q_{ij}(\lambda) = \int_{\lambda - \frac{\Delta\lambda}{2}}^{\lambda + \frac{\Delta\lambda}{2}} |\Delta S_{ij}(\lambda')| d\lambda'. \quad (3)$$

$Q_{ij}(\lambda)$ represents a measure of the spectral deviation of the species i and j in the wavelength range from $(\lambda - \frac{\Delta\lambda}{2})$ to $(\lambda + \frac{\Delta\lambda}{2})$. Due to the dependence of the integral limits on the wavelength, the integral acts like a window function. This window is sliding over the entire spectral range. Thus, the integral can also be described as a sliding integral.

Differences $\Delta S_{ij}(\lambda)$ of components with weak absorption can lead to inaccurate results in the following steps and, therefore, need to be suppressed. In order to do this, an auxiliary value D_{ij} is defined:

$$D_{ij} = \int_{\lambda_0}^{\lambda_1} |\Delta S_{ij}(\lambda)| d\lambda. \quad (4)$$

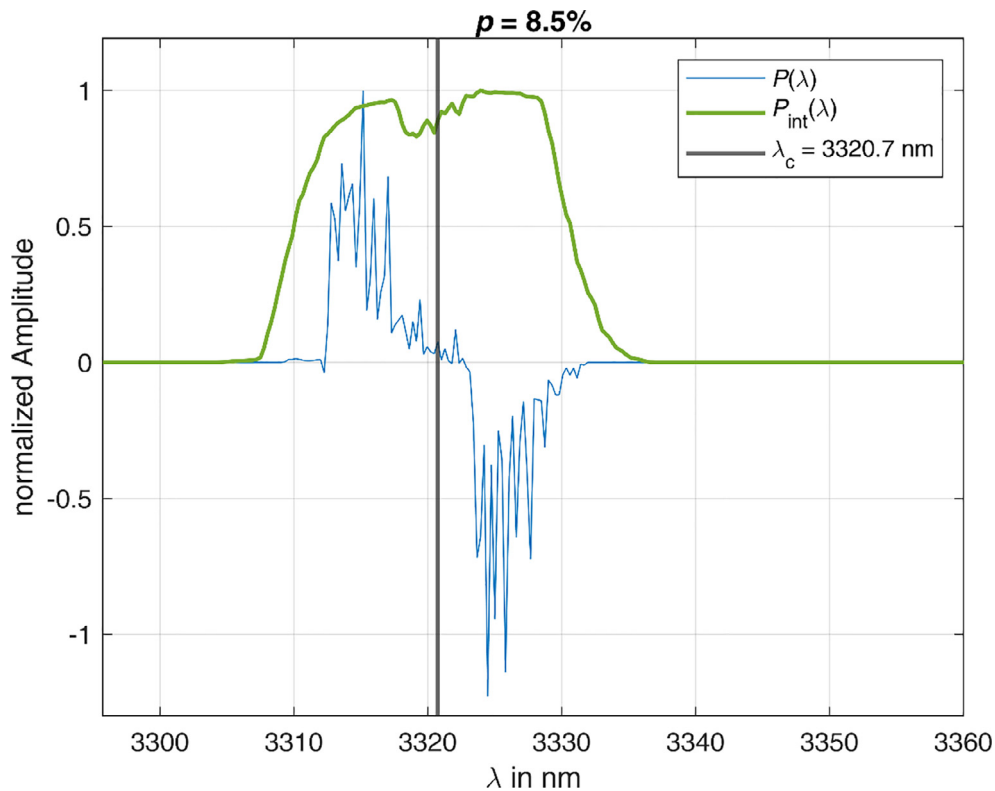


Fig. 3. Evaluation of the mixture $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$, all quantities are normalized to “one”.

Here, λ_0 and λ_1 are the lower and the upper boundary of the wavelength range under evaluation. Subsequently, a parameter $0 < p \ll 1$ has to be determined empirically, which is related to the threshold values of the individual Q -functions:

$$Q_{ij,th} = p \cdot D_{ij}. \quad (5)$$

The threshold values are needed to obtain an unambiguous result for the optimal laser wavelength. The parameter p is chosen optimally if Eq. (9) provides only a single range – the absolute maximum. $Q_{ij,th}$ is applied to $Q_{ij}(\lambda)$ according to:

$$\tilde{Q}_{ij}(\lambda) = \begin{cases} Q_{ij}(\lambda), & \text{if } Q_{ij}(\lambda) > Q_{ij,th} \\ 0, & \text{else} \end{cases}. \quad (6)$$

In a next step the Q -functions are multiplied by the difference spectra:

$$\Delta S_{ij,Q}(\lambda) = \Delta S_{ij}(\lambda) \cdot \tilde{Q}_{ij}(\lambda). \quad (7)$$

$\Delta S_{ij,Q}(\lambda)$ can be considered to be the difference spectrum for the gas pair i and j filtered by the Q -functions.

2.3. Combining the results of all component pairs

The “filtered” difference $\Delta S_{ij,Q}(\lambda)$ is large for wavelength regions, in which the spectra of a certain gas pair differs and, at the same time, absorption is strong. In order to consider the contribution of all possible gas pairs, all filtered differences are multiplied:

$$P(\lambda) = \prod_{i,j=1}^n \Delta S_{ij,Q}(\lambda), \text{ where } i < j. \quad (8)$$

The product $P(\lambda)$ is large if the previous conditions are satisfied for all gas component dyads. For absorption-weak wavelengths or wavelengths at which the spectra of the species do not differ significantly, the product $P(\lambda)$ is small. Thus, wavelength ranges with

large values of $P(\lambda)$ mark the regions preferable for a sensitive and selective measurement. In order to consider the limited tuning range of semiconductor lasers an integral parameter equivalent to Eq. (3) is introduced:

$$P_{int}(\lambda) = \int_{\lambda - \frac{\Delta\lambda}{2}}^{\lambda + \frac{\Delta\lambda}{2}} |P(\lambda')| d\lambda'. \quad (9)$$

2.4. Center wavelength determination

The wavelength region around the maximum of $P_{int}(\lambda)$ indicates the spectral range in which the center wavelength of the semiconductor laser should ideally be located. We chose the median of P_{int} as center wavelength since it considers all values of P_{int} and is therefore “well-balanced”.

In general, the median m of a function $f(x)$ is defined as [16]:

$$\int_{-\infty}^m f(x) dx = \frac{1}{2} \int_{-\infty}^{+\infty} f(x) dx. \quad (10)$$

The application of this definition leads to the optimal center wavelength λ_c of the laser:

$$\int_{\lambda_0}^{\lambda_c} P_{int}(\lambda) d\lambda = \frac{1}{2} \int_{\lambda_0}^{\lambda_1} P_{int}(\lambda) d\lambda. \quad (11)$$

With the aid of software like MATLAB [17] it is easy to extract λ_c from this equation.

3. Exemplary results

The mathematical procedure described above was programmed in MATLAB and applied to assumptive gas mixtures. The absorption spectra of the single components were measured beforehand or extracted from the HITRAN database, respectively [18–20].

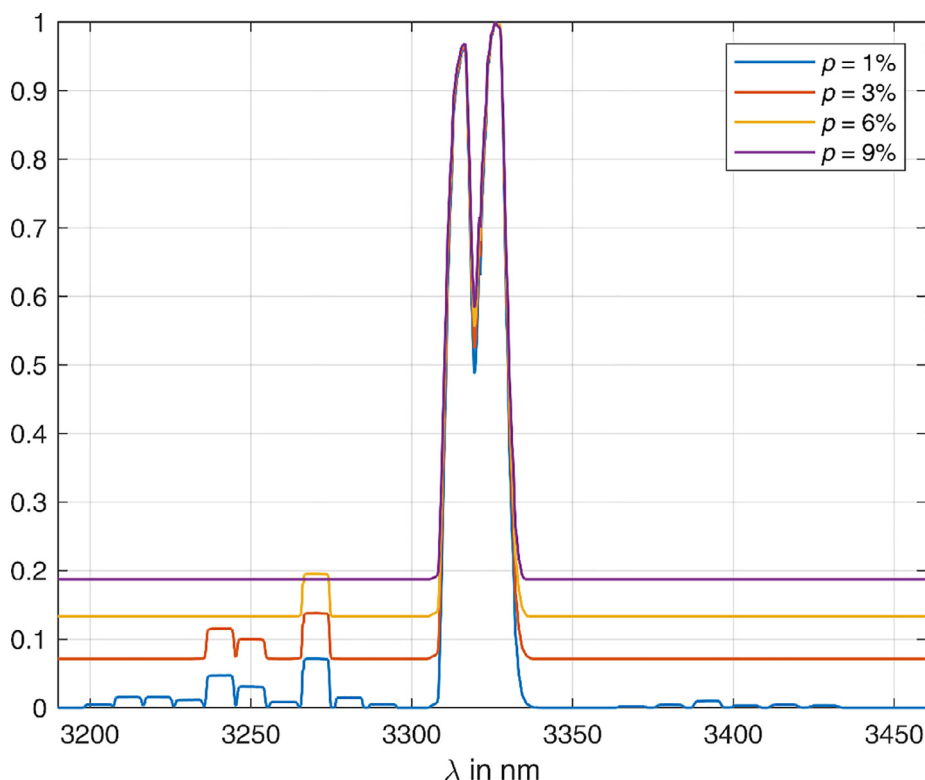


Fig. 4. Normalized $P_{int}(\lambda)$ of the mixture $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ for different values of p .

The algorithm was tested on combinations of gaseous, i.e. short-chained, hydrocarbons. Their strongest absorption is associated with the fundamental vibrations and occurs in the mid-infrared wavelength region, typically between 3 and 4 μm [21]. The lower and the upper boundary of the wavelength range under evaluation (λ_0 and λ_1) are 3000 nm and 3600 nm, respectively. Since the absorption spectra strongly overlap, it is often not possible to visually identify the optimal spectral range for the analysis.

3.1. Mixture of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$

In a first test, we investigated a mixture of the two main isotopologues of methane, $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$. Fig. 2 shows both absorption spectra normalized to one. The graph of the $^{12}\text{CH}_4$ isotopologue does not reach intensity “one” because downsampling had to be performed after normalization so that the described computational operations can be applied to both isotopologues.

The two gases were selected because the spectral positions of the single rotational lines in the respective P- and R-branch are almost identical, but the positions of the Q-branches clearly differ. The $^{12}\text{CH}_4$ Q-branch is approximately located between 3310 and 3320 nm; the $^{13}\text{CH}_4$ one between 3320 and 3330 nm. Since the Q-branches additionally exhibit relatively high absorption strength, it would be expected that the laser of a perfectly suited spectrometer (tunability: 10 nm) covers a large part of these regions.

Because this mixture contains only two gases, the measure of the spectral deviation filtered with the Q-function, $\Delta S_{ij,Q}(\lambda)$, equals the product parameter $P(\lambda)$ according to Eq. (8) which is displayed in Fig. 3. $P_{int}(\lambda)$, the integral of $P(\lambda)$ over the 10 nm laser tuning range according to Eq. (9), is shown as well.

Fig. 3 shows $P_{int}(\lambda)$ for $p = 8.5\%$ on the larger scale whereas the dark grey vertical line represents its median which corresponds to the optimal center wavelength of the laser according to Eq. (11).

The laser exhibits a center wavelength of 3320.7 nm and reaches from 3315.7 to 3325.7 nm. Since this covers a large part of the Q-branches of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ as it would have been expected, the test represents an evidentiary confirmation of the mathematical procedure.

The parameter p according to Eq. (8) determines the quality of the result to a large extent. Fig. 4 shows $P_{int}(\lambda)$ around its absolute maxima at 3315 and 3326 nm for values of p between 1 and 9%. The individual curves are shifted by 0.5 relative to each other in vertical direction so that the progress can be clearly seen. With increasing p the secondary maxima between 3200 and 3300 nm and between 3350 and 3450 nm successively disappear whereas the main maximum remains almost unaffected. From 8.5% on only the absolute maximum remains, and for that reason this value was chosen in the previous paragraph.

3.2. Mixture of $^{12}\text{CH}_4$, $^{12}\text{C}_2\text{H}_6$ and $^{12}\text{C}_2\text{H}_4$

The second test of the algorithm was performed on a (simulative) mixture of methane, ethane and ethylene (all carbon atoms with the mass number 12). Fig. 5 displays the three absorption spectra normalized to one. This combination was chosen, because it is apparently not possible to visually identify the most suited wavelength range for a spectroscopic analysis with a single laser (tunability 10 nm).

Fig. 6 displays the evaluation results. It shows:

- The $\Delta S_{ij,Q}(\lambda)$ according to Eq. (7) for the three possible gas dyads $^{12}\text{CH}_4 - ^{12}\text{C}_2\text{H}_6$, $^{12}\text{CH}_4 - ^{12}\text{C}_2\text{H}_4$ and $^{12}\text{C}_2\text{H}_6 - ^{12}\text{C}_2\text{H}_4$.
- $P(\lambda)$ (the product of all filtered differences according to Eq. (8)) and
- $P_{int}(\lambda)$ (the integral of $P(\lambda)$ over the 10 nm laser tuning range according to Eq. (9)).

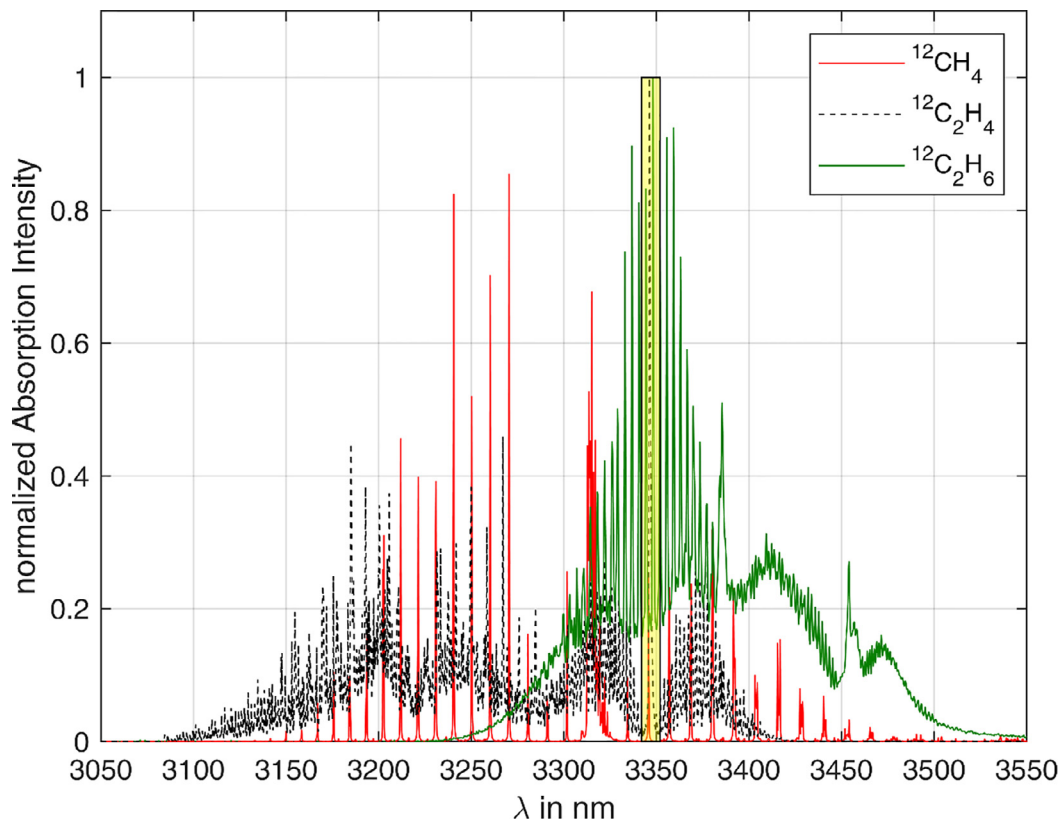


Fig. 5. Absorption spectra of $^{12}\text{CH}_4$, $^{12}\text{C}_2\text{H}_6$ and $^{12}\text{C}_2\text{H}_4$ [18–20].

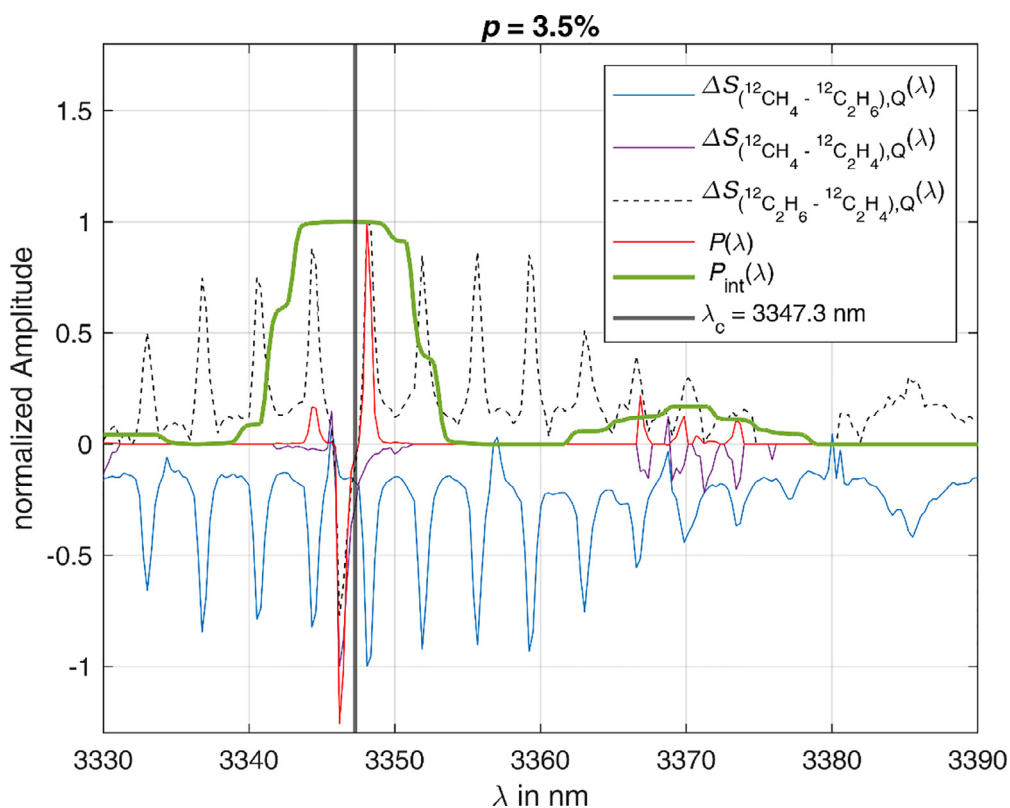


Fig. 6. Evaluation of the mixture $^{12}\text{CH}_4$, $^{12}\text{C}_2\text{H}_6$, and $^{12}\text{C}_2\text{H}_4$ all quantities are normalized to "one".

The resulting optimal center wavelength of the laser according to Eq. (11) equals 3347.3 nm. It is marked in Fig. 6 with a dark grey vertical line. The laser allows spectral tuning from 3342.3 to 3352.3 nm. It covers the characteristically high $^{12}\text{C}_2\text{H}_4$ line at ca. 3346 nm as well as the two strongest rotational lines of $^{12}\text{C}_2\text{H}_6$ and one relatively strong and discrete line of $^{12}\text{CH}_4$. The range is marked in Fig. 5 (yellow box). The result of this evaluation is very plausible and represents another confirmation for the applicability of the mathematical procedure.

4. Conclusion

We presented, to our knowledge, the first quantitative method to determine the optimal spectral range for a sensitive and selective analysis of a gaseous mixture. The method is particularly suitable for spectrometers based on tunable diode lasers. A prerequisite for its application is that absorption spectra of all gases in the mixture are known. The mathematical procedure identifies wavelength regions, in which the spectra of the single gases significantly differ and, at the same time, the absorption is strong. The definition of a threshold ensures that the best suited spectral region is found. The median of the optimal spectral range is selected as the laser's center wavelength.

The procedure was tried on two simulative gas mixtures. A first test was carried out on a mixture that allowed it to identify the perfect region through educated guessing. That the algorithm yielded the expected region is a convincing confirmation of the method. The second test of the algorithm was performed on a mixture where it was obviously not possible to visually identify the most suited wavelength range. The result of this evaluation is very plausible and represents another confirmation for the method.

Finally, it should be mentioned that the applicability depends primarily on the available spectra and that the number of components in the mixture is theoretically limited only by the available computing power. In practice, a spectrometer based on a single diode laser will probably never be applied to mixtures of more than 10 gases.

A limitation of the practical applicability is the fact that the algorithm is based on perfect spectra. Noise and other aspects of metrological reality are not taken into account. Only under these conditions are the results independent of the concentration of the individual components and their ratios.

CRediT authorship contribution statement

Marc-Simon Bahr: Conceptualization, Validation, Resources, Writing original draft, Visualization, Term. **Bernd Baumann:** Conceptualization, Validation, Writing review & editing, Term. **Marcus Wolff:** Conceptualization, Validation, Resources, Writing review & editing, Supervision, Project administration, Funding acquisition, Term.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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