

Modulation cancellation method for spectroscopy

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ABSTRACT

We report on a novel methods employing a modulation cancellation technique which result in a significantly increase in the sensitivity and accuracy of gas compounds detectors. These method can be applied for isotopomer abundance quantification, temperature measurements and large molecule detection.

Keywords: Laser sensors; Semiconductor lasers

1. INTRODUCTION

Several applications of analytical spectroscopy, such as isotope concentration ratios [1] or temperature measurements [2], require the determination of the deviation of the ratio R of intensities of two absorption peaks with respect to the ratio in the reference sample or for the reference conditions. Although much improved, current laser spectroscopic methods still possess some shortcomings. For example, in the context of a sample that contains two chemical species A and B having concentrations $[A]$ and $[B]$, respectively, concentrations are typically calculated from measurements of very small deviations of $R=[A]/[B]$ ratio from the same ratio R_{st} in the reference (standard) sample. The most common application where such measurements are required is isotopomer abundance quantification. In this case the deviation from standard is commonly expressed as

$$\delta[\%_{\text{v}}] = \frac{R - R_{st}}{R_{st}} \times 1000 \quad (1)$$

The existing spectroscopic approaches to measure δ require precise separate measurements of the absorption lines for A and B with the subsequent numerical calculation of (1). This approach requires an extremely high accuracy of measurement because practically important δ ranges are between $\sim 1\%$ to 0.1% . For example, in traditional approaches the required or desired measurement accuracy for $[B]$ may be 10^{-4} . In practice, making such precise measurements is extremely difficult due to small variations in temperature, pressure and other external factors.

Another problem with present laser spectroscopic techniques has been the detection of species with broad irresolvable absorption features, which is a characteristic of many polyatomic molecules. In such cases, a semiconductor laser usually can be wavelength modulated with a swing sufficient to cover the whole absorption feature. Thus, detection of such molecules would require amplitude modulation of the laser radiation. The scattered and subsequently absorbed light creates an incoherent background, making low-level concentration measurements difficult.

Accordingly, there is a need for a simple method of accurately measuring small deviations in concentration ratios or temperature using laser spectroscopy. It is further desired to provide a laser spectroscopic method to detect minute concentrations of complex molecules.

The proposed *modulation cancellation method (MOCAM)* is a variation of the modulation spectroscopy based on balancing and cancellation of modulated signals generated by two different excitation sources. The primary intended applications of the proposed approach are:

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- 1) Monitoring small deviations of the mixing ratio of two molecular species from the reference ratio (for example, to identify the isotopic signature of the gas sample by means of MIR absorption spectroscopy) or measurements of small temperature variation in a gas;
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- 3) Spectroscopic detection of broadband absorbers (complex molecules) in the presence of spectrally nonselective background absorption.

MOCAM relies on the *physical* cancellation of the measured sensor response under selected conditions. The idea is to adjust the powers and modulation phases of two lasers in such a way that under selected conditions the signal detected from a reference sample is zero [3]. MOCAM can be used in a variety of implementations, including $2f$ wavelength modulation (WM) absorption spectroscopy and amplitude modulation (AM) or WM (1f or 2f) using e.g. photodiodes as signal detectors or photoacoustic spectroscopy (PA) both standard and quartz enhanced (QEPAS). There are however some advantages in using PA detection:

- 1) Spectrophones feature much better linearity and wider dynamic range than photodiodes. This is essential for the sensor performance because it must detect a small difference of two high signals.
- 2) PAS is a physically background-free technique. In other words, the signal is not produced in the media if there is no optical absorption, even in the presence of the excitation source power fluctuations. On the contrary, photodiode-based WM absorption spectroscopy is sensitive to the source power fluctuations such as “interference fringes”. Such fluctuations may result in the higher signals than the difference to be measured.

This concept has been demonstrated using quartz enhanced photoacoustic spectroscopy (QEPAS) in a $2f$ wavelength modulation mode [4-5] as an absorption sensing technique and two different methodologies have been implemented.

1.1 isotope concentration ratios and temperature measurements

A schematic of the MOCAM-QEPAS setup for isotopic composition and temperature measurements is shown in Fig. 1. The two lasers are resonant with two selected absorption lines (in this case of temperature measurements the pair of optical transitions belongs to the same molecular species). Emission of each of the lasers 1, 2 is wavelength-modulated with the same frequency f . Then the combined emission of the two lasers is directed to the optical cells containing the reference gas sample (RGS) and the analyzed gas sample (AGS). The modulation phase and optical power are manually set in such a way that the QEPAS signals at $2f$ produced by the two lasers are identical and opposite in phase. The phase relations are maintained by a phase locked loop. In other words, the two QEPAS signals in the reference cell can be balanced in such a way that no generation of sound occurs and the transducer (the quartz tuning fork in QEPAS case) does not detect any signal. For this condition the *signal* from the analyzed sample will directly *proportional to the deviation* of the absorption line strength ratio *from the reference ratio* in selected optical configurations.

To verify this experimental method, we employ it for spectroscopic measurements of small temperature differences in a gas mixture. Temperature measurements do not require expensive isotopically pure gas samples, therefore it is an easier way to perform MOCAM feasibility experiments. Spectroscopic temperature measurements are based on the temperature T dependence of absorption line strength ratio for a pair of optical transitions of the same chemical species with different lower level energies.

The principle is selecting two spectroscopic transitions originating at lower states with different energy, in this case one obtains:

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where ΔE is the difference in lower state energy between the two absorption lines.

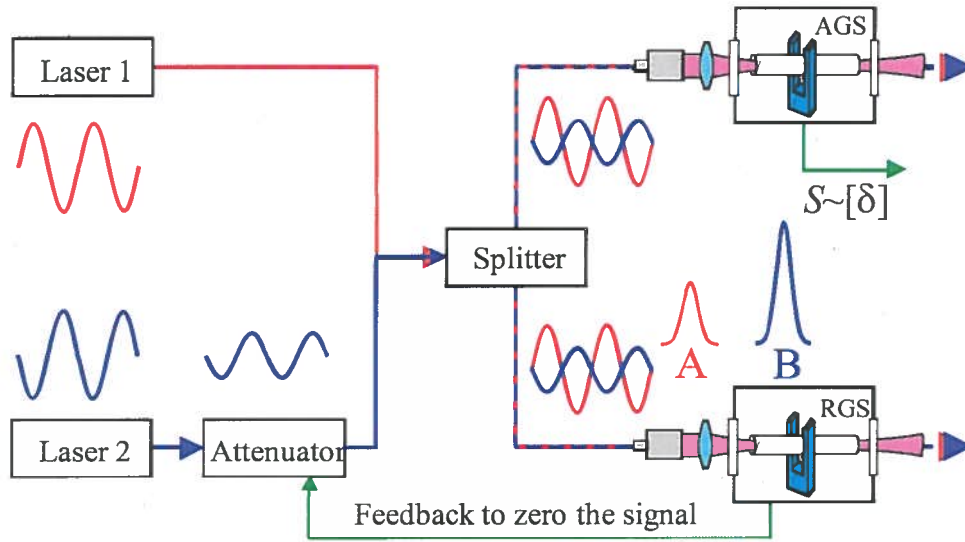


Figure 1. MOCAM applied for isotope concentration ratios and temperature measurements.

In the first approximation for small changes of temperature, ratio of intensities

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Here both E and T are expressed in energy units for simplicity. Thus

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T is approximately constant; hence, the error in dT (deviation of the analyzed sample temperature from the reference sample temperature) is determined by the error in measuring dR/R .

Temperature difference between two samples will be calculated using the equation (2). In practice, the term $T^2/\Delta E$ will be included in the coefficient obtained by means of calibration. Hence for small temperature variation we obtain,

$$\Delta T = C_1 \frac{S}{P_1 A_1} = C \frac{S}{S_1} \quad (5)$$

Here S is the signal detected from the AGS sample when the signal from the reference cell is zero, A_1 is the intensity of the weaker line in the pair and P_1 is power of laser 1. C is a constant which depends on the MOCAM configuration and is determined by an initial setup calibration.

The S_1 in (5) is the signal from one of the lines if laser 2 is switched off (or its modulation is disabled). This value is limited by (a) the sensor transfer function k , which is constant; (b) Maximum available laser power P_1 for the weaker line; and (c) strength of the weaker line A_1 .

Assuming that the spectrophones are similar and temperature difference is small compared to the absolute temperature, we get

$$\frac{\Delta R}{R} \approx \frac{1}{kP_1A_1} (S \pm \delta\sqrt{2}) \quad (6)$$

Based on equation (6) and using

$$\delta R = \frac{dR}{dT} \delta T \quad (7)$$

where δR is a change in R when temperature is changed, we can re-write (6) in the following form:

$$\delta T = \frac{R}{\frac{dR}{dT}} \frac{\delta S\sqrt{2}}{kP_1A_1} \quad (8)$$

Here δT is uncertainty in T measurements due to the noise in the photoacoustic signal δ . The factor $\frac{\delta}{kP_1A_1} = \frac{1}{SNR}$,

where SNR is signal to noise ratio when laser 2 is blocked.

A C_2H_2/N_2 gas mixture with a 0.5% C_2H_2 concentration was used as a test analyte. We demonstrated the detection of temperature changes with a sensitivity of 30 mK in 17s [6].

1.2 Large molecules detection

The schematic of the MOCAM scheme for large molecule detection is shown in Fig. 2. It refers to detection of the species A with broad unresolved absorption features such as a majority of polyatomic molecules have. In this case, one of the lasers is centered on a target absorption band while the second source is tuned to the background region. When two lasers are amplitude modulated with 180° phase shift, then the modulation amplitudes can be adjusted so that there is no signal in the absence of A . If the concentration $[A] \neq 0$, the signal detected at the modulation frequency is proportional to A concentration.

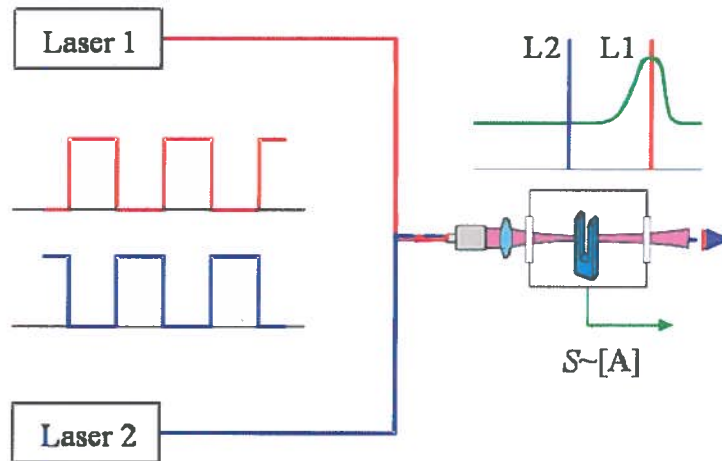


Figure 2. MOCAM applied for detection of broadband absorbers such as polyatomic molecules or aerosols.

To verify the possibility of use MOCAM for efficient large molecule detection, we realized a setup aimed at the detection of Hydrazine (N_2H_4), an highly toxic, dangerously unstable, strongly corrosive substance, used in polymers production, pharmaceutical industry, and as a rocket fuel. Two independent wide stripe Fabry Perot diode lasers were used to detect near-IR absorption of hydrazine (N_2H_4) vapor, with emission on the tail and on the peak of the related absorption band. Fig. 3 shows the schematic of the setup. We use a Glann prism and a $\lambda/2$ in order to obtain two laser beams propagating in the same optical axis. The two beams are then focused between the prongs of a tuning fork.

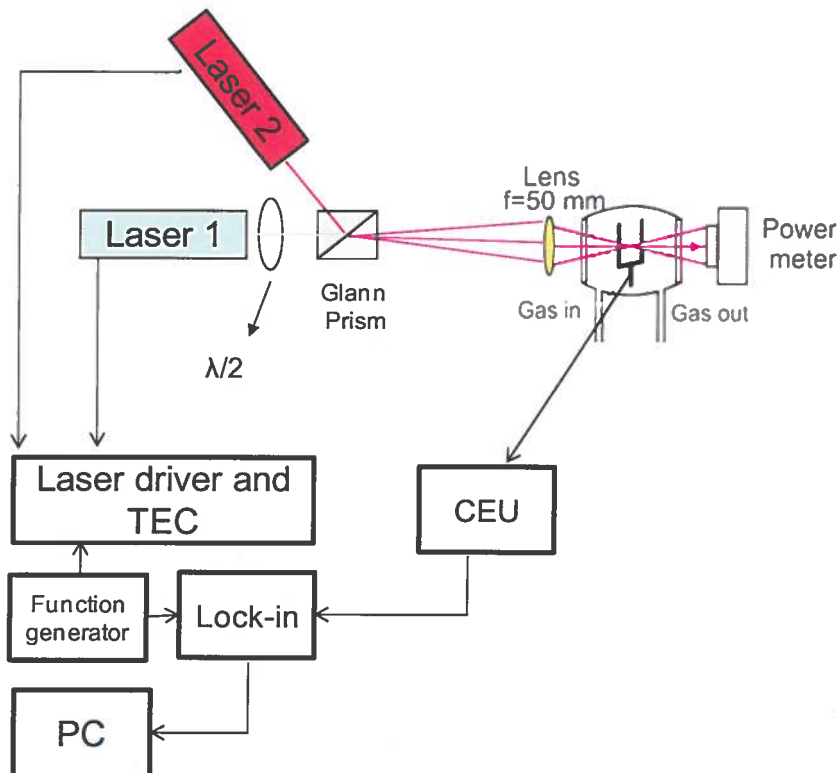


Figure 3. Schematic of the MOCAM setup for detection of Hydrazine

Injection currents of the lasers were modulated from threshold to an adjustable maximum value using sinusoidal waveforms with a 180° phase shift. Measurements were carried out at atmospheric pressure. Initial experiments showed an unwanted background suppression of 100 to 1000 times compared to unbalanced (one laser) detection. The hydrazine vapor detection limit was estimated to be ~ 1 part per million in volume in 1 sec.

Conclusion

In summary, we demonstrated a novel spectroscopic technique named the modulation cancellation method (MOCAM) allowing the realization of efficient gas optical sensors, which can be used for a number of applications, such as small temperature variation measurements, monitoring small deviations of the mixing ratio of two molecular species from the reference ratio (for example, to identify the isotopic signature) and broadband absorbers (complex molecules) detection in the presence of spectrally nonselective background absorption.

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