# Modulation cancellation method for measurements of small temperature differences in a gas

Vincenzo Spagnolo,[1,2,*] Lei Dong,[1] Anatoliy A. Kosterev,[1] David Thomazy,[1]
James H. Doty, III,[1] and Frank K. Tittel[1]

[1]*Department of Electrical and Computer Engineering, Rice University, 6100 South Main Street, Houston, Texas, USA*

[2]*Dipartimento Interateneo di Fisica, Università e Politecnico di Bari, CNR—IFN UOS BARI, Via Amendola 173, Bari, Italy*

*Corresponding author: spagnolo@fisica.uniba.it*

An innovative spectroscopic technique based on balancing and cancellation of modulated signals induced by two excitation sources is reported. For its practical implementation, we used quartz-enhanced photoacoustic spectroscopy as an absorption-sensing technique and applied the new approach to measure small temperature differences between two gas samples. The achieved sensitivity was 30 mK in 17 s. A theoretical sensitivity analysis is presented, and the applicability of this method to isotopic measurements is discussed.    © 2011 Optical Society of America

*OCIS codes:*    280.3420, 140.5960.

Several applications of analytical spectroscopy require the determination of the absorption line strengths ratio, $r$, of two optical transitions relative to the corresponding ratio, $r_0$, in a reference sample or for reference conditions. Examples of such applications are the quantification of isotopic composition [1] and temperature measurements in gases [2]. Existing spectroscopic approaches to measuring $r$ are based on precise separate measurements of selected absorption lines followed by a calculation of $r$ [1–4]. This method requires an extremely high accuracy of measurement, because practically important $(r - r_0)/r_0$ values range from ~1‰ to 0.1‰.

We propose here an approach that relies on the *physical* cancellation of the sensor response at the selected reference conditions. The basic concept of the modulation cancellation method (MOCAM) requires that the respective powers and modulation phases of the two lasers resonant with two selected absorption lines are adjusted in such a way that the signal detected from the reference sample is zero. For this condition the *signal* from the analyzed sample is directly *proportional to the deviation* of the absorption line strength ratio *from the reference ratio* in the selected optical configuration [5]. In this work we utilized this concept using quartz-enhanced photoacoustic spectroscopy (QEPAS) in a $2f$ wavelength modulation mode [6] as an absorption-sensing technique and employed the MOCAM approach for spectroscopic measurements of small temperature differences. A $C_2H_2/N_2$ gas mixture with a 0.5% $C_2H_2$ concentration was used as a test analyte.

The simplified architecture of the MOCAM-QEPAS ratiometer and an illustration of its operating principle are shown in Fig. 1. Two diode lasers, DL1 and DL2, are wavelength-modulated and locked respectively to absorption lines at $\lambda_1$ and $\lambda_2$ with line strengths $S_1$ and $S_2$. Line locking is achieved using 99 : 1 fiber beam couplers and reference cells as described in [6]; line-locking feedback loops are not shown in Fig. 1.

The wavelength of each laser is modulated via a sinusoidal current dither at the frequency $f \approx (f_R + f_A)/4$, where $f_R$ and $f_A$ are resonant frequencies of the two spectrophones [7], labeled "Reference" ($R$) and "Analyzer" ($A$); ideally, $f_R = f_A$. DL1 is mounted inside the control electronics unit (CEU) [7], which generates the modulation wave internally.

The phase-lock-loop (PLL) function generator is triggered by a rectangular synchronization wave from the CEU and produces the phase-shifted sinusoidal modulation signal for DL2. A 50 : 50 fiber coupler (FC1) combines the radiation from DL1 and DL2, and a similar coupler (FC2) splits the combined radiation into two channels. The ratio of the optical power at $\lambda_1$ to the power at $\lambda_2$ is presumably the same in the $R$ and $A$ channels. The modulation phase, $\varphi$, is manually set in such a way that the QEPAS signals at $2f$ produced by DL1 and DL2 are opposite in phase. The phase relations are maintained by a PLL. The detected signal $U_R$ from the $R$ spectrophone is used as an error signal in a
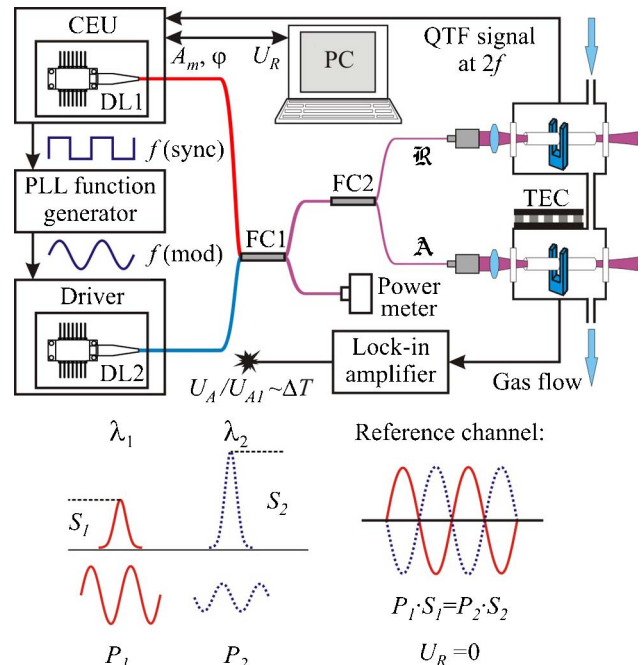


Fig. 1. (Color online) Schematic of QEPAS-MOCAM ratiometer: QTF, quartz tuning fork; FC1, FC2, 50 : 50 optical fiber couplers; CEU, control electronics unit; $f$ (sync), synchronization signal from CEU; $f$ (mod), modulation signal for the DL2 driver.

computer-controlled feedback loop adjusting the modulation index $A_m$ of DL1.

The signal produced by each of the two spectrophones will be

$$U_j = k_j(P_1 S_1^j - P_2 S_2^j) \pm \delta_j, \qquad (1)$$

with $j = R; A$. $\delta_j$ is the quartz tuning fork (QTF) thermal noise in the channel, and $k_j$ describes the responsivity of the spectrophone. The effective optical excitation power, $P_1$ [8], depends on $A_m$, which allows balancing out the signal from the reference cell by adjusting the modulation index:

$$U_R = k_R(P_1 S_1^R - P_2 S_2^R) = 0 \pm \delta_R. \qquad (2)$$

Therefore, the balancing is achieved when the optical excitation power of DL2 is

$$P_2 = P_1 \frac{S_1^R}{S_2^R} \pm \frac{\delta_R}{k_R S_2^R}. \qquad (3)$$

Substituting this expression for $P_2$, we obtain the signal detected from the analyzed sample:

$$U_A = k_A P_1 S_2^A \left( \frac{S_1^A}{S_2^A} - \frac{S_1^R}{S_2^R} \right) \pm \frac{k_A}{k_R} \frac{S_2^A}{S_2^R} \delta_R \pm \delta_A. \qquad (4)$$

The expression in brackets is $\Delta r$, the difference between $r_A$ and $r_R$. Assuming that the QEPAS spectrophones are similar ($k_R \approx k_A = k$ and $\delta_R \approx \delta_A = \delta$) and that $S_2^A \approx S_2^R = S_2$, we obtain

$$\frac{\Delta r}{r} \approx \frac{1}{U_{A1}} \left( U_A \pm \delta\sqrt{2} \right), \qquad (5)$$

where $U_{A1} = k_A P_1 S_1^A$ is the signal generated in the analyzer cell by DL1 when DL2 is inactive (for example, when its modulation is disabled) and the $2^{1/2}$ coefficient reflects the fact that the noise of the two spectrophones is uncorrelated and therefore adds up in quadrature. Hence, the value of interest is directly proportional to the ratiometer signal and the measurement error is determined by the ratio of the combined detector noise to the lower of the signals from the two absorption lines.

Spectroscopic temperature measurements are based on the temperature dependence of $r$ for a pair of optical transitions with different lower level energies. This ratio and its temperature dependence can be calculated for acetylene ($C_2H_2$) using the HITRAN spectral database. Substituting $\delta r = (dr/dT) \cdot \delta T$ in Eq. (5) and considering the term describing the measurement error, we can obtain

$$\delta T = \frac{1}{dr/dT^{S_2}} \frac{\delta\sqrt{2}}{kP_1}. \qquad (6)$$

Thus, the most accurate temperature measurements can be performed when $K = (dr/dT) \cdot S_2$ is largest, $S_2$ referring to the weaker line.

A computer program was developed that calculates this value for all pairs of absorption lines in the spectral range from 6396 to 6541 cm$^{-1}$. The best pair of lines is 6544.442 and 6523.879 cm$^{-1}$. Based on our inventory of near-IR diode lasers, we selected the pair $(\nu_1, \nu_2) = (6539.454, 6529.172)$ cm$^{-1}$, which is the fifth-best choice with a $K$ value of 0.6 of the best pair of lines.

A similar substitution into Eq. (5) and considering the signal term yield the temperature difference between the $R$ and $A$ channels for balanced $R$ conditions as

$$\Delta T = \frac{r}{dr/dT} \frac{U_A}{U_{A1}} = C \frac{U_A}{U_{A1}}. \qquad (7)$$

The optical powers of DL1 and DL2 passing through the two spectrophones were 16 mW and 14 mW, respectively. Measurements were carried out at atmospheric pressure, with the gas flow set at a constant rate of 100 SCCM (SCCM denotes cubic centimeters per minute at standard temperature and pressure.). The volume of each QEPAS cell was ~1.3 cm$^3$. The temperature of both cells was monitored using thermistors, which are attached to the walls of the cells. Four additional thermistors were placed at the entrance and the exit points of each cell to verify that thermal equilibrium would be reached. These measurements confirmed our assumption that due to the small specific heat, the gas mixture rapidly reaches thermal equilibrium with solid walls. We varied the temperature of the gas inside the $A$ cell by using a thermoelectric cooler (TEC), while the $R$ cell was kept at room temperature. Initially, both $R$ and $A$ spectrophones were at room temperature, and the signal from $R$ was balanced out via a $\varphi$ and $A_m$ adjustment. However, it was observed that the signal from $A$ was not zero for these conditions, because of the wavelength selectivity of FC2. The unbalance was ~3% of the full DL1-induced signal. Therefore, we readjusted $A_m$ to make the signal in the $A$ channel zero when $\Delta T = 0$. This procedure resulted in a nonzero $U_R$ signal, and a computer-controlled feedback loop was set to keep this signal at a constant level. This way the output signal of the ratiometer is proportional to $\Delta T$, as initially intended. Next, the $A$ temperature was varied by means of the TEC and measured using a thermistor to verify Eq. (6) and obtain the calibration constant $C$. The results, shown in Fig. 2, confirm that the ratio of the $U_A$ and $U_{A1}$ signals is proportional to $\Delta T$.

To determine the best achievable sensitivity of this MOCAM-QEPAS temperature sensor, we performed an Allan variance analysis [9], measuring and averaging its response at $\Delta T = 0$. The Allan plot is shown in Fig. 3. A minimum error is achieved with 17 s averaging (i.e., a 0.046 Hz bandwidth) and corresponds to 30 mK or 140 mK/Hz$^{1/2}$. To compare this value with the theoretically expected value, Eq. (6) can be rewritten as

$$\delta T = \frac{r}{dr/dT} \frac{\delta\sqrt{2}}{U_{A1}}. \qquad (8)$$

For the selected pair of lines, $r/(dr/dT) = -690$ K, and the right coefficient, $\delta\sqrt{2}/U_{A1}$, is an inverse signal-to-noise ratio (SNR).

In our experiments this factor was $2.5 \times 10^{-5}$ 1/Hz$^{1/2}$. Thus, we can expect a sensitivity of 17 mK/Hz$^{1/2}$. The
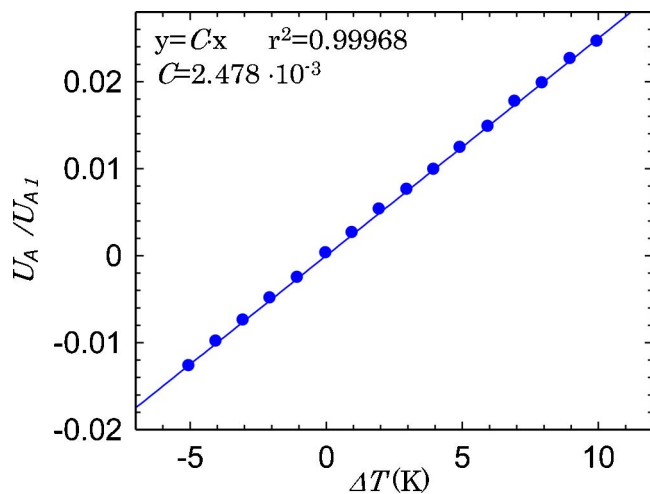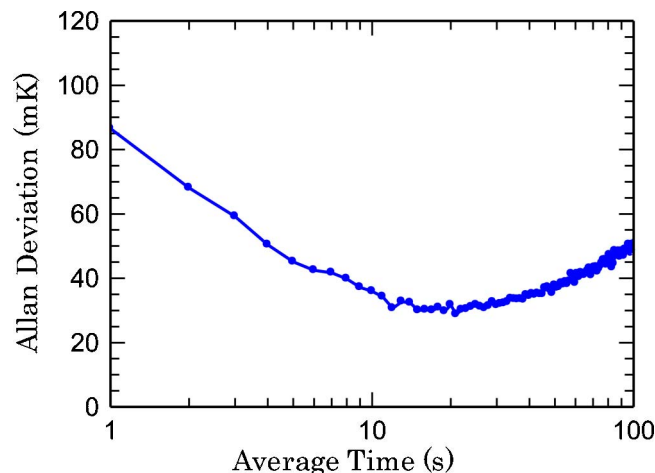
Fig. 2.    (Color online) Ratiometer validation and calibration.



Fig. 3. (Color online) Allan deviation of the gas-mixing temperature as a function of the integration time.

observed excess noise is most likely due to the non-optimal configuration when the signal in channel $R$ is not zero but exceeds the thermal noise $\sim 8$ times in 0.0785 Hz bandwidth.

This makes the ratiometer sensitive to fluctuations of laser power and gas pressure. Hence, exact balancing is required to achieve a practically useful sensitivity for isotopic measurements. Such balancing would zero out the ratiometer sensitivity to the target species concentration, gas pressure, and temperature, as well as laser power. Possible ways to minimize the observed unbalance are (1) use of a thin-film beam splitter instead of the fused coupler FC2; (2) insertion of additional couplers and adjustable attenuators to restore the balance; or (3) use of polarization control for the same purpose. The theoretically achievable sensitivity of isotopic measurements is given by Eq. (4) and is determined by a lower SNR for one of the two one-laser signals, $k_1 P_1 S_1$ and $k_2 P_2 S_2$. The technical limit of $SNR/2^{1/2}$ for the currently used CEU is $\sim 10^4$ $1/Hz^{1/2}$, which leads to an error in $\Delta r/r = 0.1‰$ for a 1 Hz bandwidth. This limit can be improved by modifying the electronics, while other sources of errors must be studied experimentally.

### References

1. A. Castrillo, G. Casa, E. Kerstel, and L. Gianfrani, Appl. Phys. B **81**, 863 (2005).
2. J. A. Silver and D. J. Kane, Meas. Sci. Technol. **10**, 845 (1999).
3. M. Erdélyi, D. Richter, and F. K. Tittel, Appl. Phys. B **75**, 289 (2002).
4. J. B. McManus, D. D. Nelson, J. H. Shorter, R. Jimenez, S. Herndon, S. Saleska, and M. Zahniser, J. Mod. Opt. **52**, 2309 (2005).
5. A. A. Kosterev and R. F. Curl, "Modulation cancellation method in laser spectroscopy," International Patent WO/2007/056772 A2 (2007).
6. A. A. Kosterev, F. K. Tittel, D. V. Serebryakov, A. L. Malinovsky, and I. V. Morozov, Rev. Sci. Instrum. **76**, 043105 (2005).
7. L. Dong, A. A. Kosterev, D. Thomazy, and F. K. Tittel, Appl. Phys. B **100**, 627 (2010).
8. N. Petra, J. Zweck, Anatoliy A. Kosterev, S. E. Minkoff, and D. Thomazy, Appl. Phys. B **94**, 673 (2009).
9. P. Werle, "Accuracy and precision of laser spectrometers for trace gas sensing in the presence of optical fringes and atmospheric turbulence," Appl. Phys. B, doi: 10.1007/s00340-010-4165-9.