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Modulation-cancellation method for laser spectroscopy

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A novel technique that enables a significant increase in the sensitivity of gas sensors can be applied to isotope-abundance quantification, temperature measurements, and detection of large molecules.

Several applications of analytical spectroscopy, such as measurements of isotope-concentration ratios[1] or temperatures,[2] require determination of the deviation of the intensity ratio (R) of two absorption peaks with respect to that of a reference sample or for reference conditions. Existing spectroscopic approaches to determine R are based on precise measurements of two selected absorption lines, with subsequent numerical calculation of R. They require extremely accurate measurements because R values range from ~ 1 to $0.1^0/_{00}$.

Another problem with present laser-spectroscopic techniques is the difficulty of detecting species with broad and unresolved absorption features, a common property of many polyatomic molecules. In general, semiconductor lasers cannot be wavelength modulated over a sufficient spectral range to cover the entire absorption feature. Thus, detecting such broadband molecular-absorption troughs would require amplitude modulation of the laser radiation. Their scattered and subsequently absorbed light creates an incoherent background, rendering low-level concentration measurements difficult.

A simple laser-spectroscopic method for accurately measuring small deviations in concentration ratios or temperature is needed. It is also desirable to have access to a laser-spectroscopic method that is suitable for detecting minute concentrations of complex molecules. We propose a novel approach that relies on physical cancellation of the measured sensor response. The modulation-cancellation method (MOCAM) adjusts the powers and modulation phases of two lasers such that, for selected conditions, the signal detected from a reference sample is zero.[3] We have demonstrated this concept using quartz-enhanced photoacoustic spectroscopy (QEPAS) in double-frequency wavelength-modulation mode[4,5] as an absorption-sensing technique. We have implemented two different methodologies.

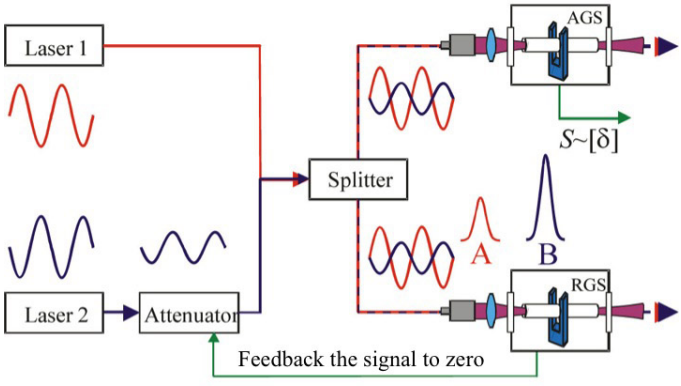

Figure 1. *Modulation-cancellation method (MOCAM) for isotope-concentration (A, B) ratios and temperature measurements. AGS, RGS: Analyzed, reference gas samples. S: Signal. δ: Deviation of absorption-line-strength from reference ratio.*

Figure 1 shows the principal architecture of our MOCAM-QEPAS setup. The two lasers are resonant with two selected absorption lines of species A. Emission of each of the lasers is wavelength modulated at the same frequency (f). Subsequently, the combined emission of the two lasers is directed at optical cells that contain the reference gas sample and that selected for analysis. The modulation phase is set manually such that the QEPAS signals at $2f$ produced by the two lasers are 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 so that no sound is generated and the transducer (the quartz tuning fork) does not detect a signal. For these conditions, the signal from the sample selected for analysis is directly proportional to the deviation of the absorption-line-strength ratio from the reference ratio in the selected optical configuration.

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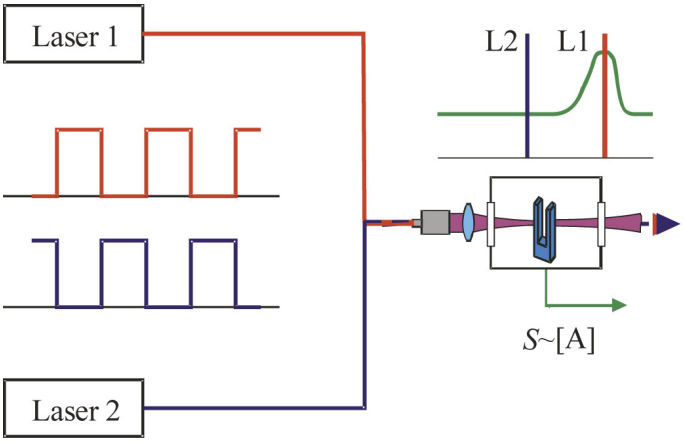

Figure 2. *MOCAM scheme for detecting broadband absorbers such as polyatomic molecules or aerosols. L1, L2: Laser 1, 2. [A]: Concentration of species A.*

To verify the operational setup of the MOCAM platform, we employed this particular scheme to spectroscopic measurements of small temperature differences in an acetylene (C_2H_2)/nitrogen (N_2) gas mixture with a 0.5% C_2H_2 concentration. Temperature measurements do not require expensive, isotopically pure gas samples, and this is, therefore, an easier approach to perform MOCAM feasibility experiments. Spectroscopic temperature measurements are based on the temperature (T) dependence of the absorption-line-strength ratio of a pair of optical transitions of the same chemical species with different lower-level energies. As a first approximation, the temperature difference between two samples can be calculated as

$$\Delta T = C\frac{S}{P_1 A_1} = C\frac{S}{S_1}$$

for small ΔT, where S is the signal detected from the sample being analyzed when the signal from the reference cell is zero, $S_1 = P_1 A_1$ is the signal detected when laser 2 is switched off (or its modulation is disabled), A_1 is the intensity of the weaker line in the pair, and P_1 is the power of laser 1. C is a constant that depends on the MOCAM configuration and is determined by an initial setup calibration. Using this approach, we recently demonstrated detection of temperature changes with a sensitivity of 30mK in 17s.[6]

Figure 2 shows a schematic overview of a MOCAM sensor for detecting species A with broad, unresolved absorption features. In this case, one of the lasers is centered on a target absorption band, while the second is tuned to the background region. When two lasers are amplitude modulated with a 180° phase shift, the modulation amplitudes can be adjusted so that there is no signal in the absence of A. If the concentration [A]≠0, the signal detected at the modulation frequency is proportional to the concentration.

To verify the possibility of using MOCAM for efficient large-molecule detection, we built a sensor platform for detecting hydrazine (N_2H_4). We used two Fabry-Perot diode lasers to detect the near-IR absorption signals from hydrazine vapor, with emission near the tail and the peak of the related absorption band. We modulated the laser injection currents from their thresholds to an adjustable maximum value using sinusoidal waveforms with a 180° phase shift. Initial experiments showed unwanted background suppression of 100–1000 times compared to unbalanced (single-laser) detection. We estimated an hydrazine-vapor detection limit of ∼1 part per million by volume.

In summary, we have demonstrated a novel spectroscopic technique that allows realization of efficient gas optical sensors. These 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 a reference ratio (for example, to identify isotopic signatures), and detecting broadband absorbers (complex molecules) in the presence of spectrally nonselective background absorption. We are continuing development of such applications.

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Vincenzo Spagnolo has been an assistant professor of physics since January 2004. His main scientific activity is related to thermal modeling of lasers and gas sensing. He holds two patents and is co-author of more than 70 refereed articles.

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