Allan Deviation Plot as a Tool for Quartz Enhanced Photoacoustic Sensors Noise Analysis

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Abstract—We report here on the use of the Allan deviation plot to analyze the long-term stability of a quartz enhanced photoacoustic (QEPAS) gas sensor. The Allan deviation plot provides information about the optimum averaging time for the QEPAS signal and allows the prediction of its ultimate detection limit. The Allan deviation can also be used to determine the main sources of noise coming from the individual components of the sensor. Quartz tuning fork thermal noise dominates for integration times up to 275 s, whereas at longer averaging times, the main contribution to the sensor noise originates from laser power instabilities.

Index Terms—Noise measurement, Thermal noise, Laser noise, Optical sensors, Gas detectors.

I. INTRODUCTION

 Environmental monitoring, industrial process control analysis, breath diagnostics and security are just a few of the many fields of gas sensing applications requiring ever increasing improvements in sensitivity and selectivity [1]. Quartz-enhanced photoacoustic spectroscopy (QEPAS) is one of the most robust and sensitive trace-gas optical detection techniques. This method is based on photo-acoustic effect, i.e., heat conversion of light absorbed by a gas target via molecular collision-induced non-radiative relaxation of excited states [2]. This heating causes the gas to expand and, if the light is modulated, the periodic expansion produces pressure waves, i.e. sound, that can be detected. QEPAS is based on the use of a quartz tuning fork (QTF) resonator as an optoacoustic transducer and the frequency of light modulation has to match the QTF resonance frequency or one of its sub-harmonics. QEPAS is capable of extremely high detection sensitivities with a compact and relatively low-cost absorption detection module [3], [4]. Sensitivity represents a crucial figure of merit in any sensor system, and for QEPAS corresponds to the gas concentration providing a signal equivalent to the noise (signal-to-noise ratio SNR=1). Thus, the sensitivity of a QEPAS sensor can be improved by further averaging its signal. From a theoretical point of view, the signal from a perfectly stable system could be infinitely averaged, thus leading to extremely sensitive measurements. However, an optical sensor operating in the field is a limited stable system. There exists an optimum integration time at which the detection limit reaches a minimum value. At longer averaging time, drift effects emerge and the sensor performance deteriorates. The optimum integration time is both application– and installation– specific for a given sensor instrument. The Allan variance analysis allows the determination of how long optical sensor signals can be averaged in order to increase the detection sensitivity, and before noise sources like laser instability, temperature and mechanical drifts, as well as when moving fringes begin to dominate. This technique was initially developed by Allan in 1966 to study the frequency stability of precision oscillators [5]. In 1993, Werle applied the Allan variance to signal averaging in tunable laser absorption spectroscopy (TDLAS) instrumentation [6]. In this paper, we apply this approach to a QEPAS gas sensor in order to determine the main source of instabilities and the resulting optimum integration time.

II. EXPERIMENTAL SETUP

A schematic of the QEPAS experimental setup employed in this work is shown in Fig. 1. A tunable continuous wave (CW), DFB quantum cascade laser (QCL, from Alpes Lasers #sbcw1422DN) was used as an excitation light source, operating at a wavelength of 6.23 µm, fixed in an ILX mount (model LDM-4872) equipped with a water cooling system and a short focal lens for beam collimation. The QCL operation temperature was set to -7°C using a temperature controller (ILX Lightwave, LDT-5545B) and the laser was operated in CW mode by means of a current driver (ILX Lightwave, LDX-3232). At a current of 582.5 mA, we measured an output power of 10 mW. A CaF\textsubscript{2} focusing lens L\textsubscript{1} with a focal length of 50 mm was used to couple the QCL output beam into a hollow core waveguide (HCW) in order to improve the QCL beam quality. The employed HCW is a circular cross-section glass capillary tube with a core diameter of 200 µm and a length of 15 cm and provides single-mode propagation with a Gaussian-like output beam profile [7]-[10]. CaF\textsubscript{2} focusing optics L\textsubscript{2} is connected to the output of the fiber and provides a focusing distance of 38 mm [11], [12]. In the focal plane, an optical power of 1.2 mW was measured using a power meter, corresponding to HCW losses of ~7 dB. The QCL beam was coupled with the acoustic

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III. EXPERIMENTAL MEASUREMENTS

In the QEPAS technique, it is critical that the laser beam entering the MR tubes does not illuminate the tubes walls and the QTF prongs in order to avoid photo-thermal effects and, consequently, a fringe-like non-zero background strongly limiting the QEPAS detection sensitivity [14], [15]. The 3D laser beam profile in the focusing plane of the collimator, acquired by a pyrocamera (Spiricon Pyrocam III) with pixel sizes of 0.085 mm x 0.085 mm is shown in Fig. 2a.

A one-dimensional Gaussian-profile fit (Fig. 2b) yields an estimate of the average beam-waist diameter of 200 µm, well below the QTF prongs spacing (300 µm) and the MR internal diameter. As a result, > 97% of the laser beam was transmitted through the ADM leading to a negligible photo thermal-induced background signal.

For a QEPAS based sensor signal analysis, we selected a water vapor absorption line at λ=6.2371 µm with a line-strength $S=4.481 \times 10^{-21}$ cm/mol, according to the HITRAN database [16]. In Fig. 3 is shown the QEPAS signal obtained by setting the lock-in time constant at 100 ms. The associated bandwidth is 1.6675 Hz with a 12 dB/oct filter slope. At a QCL current of 582.5 mA, the laser wavelength is resonant with the selected water absorption peak. For these conditions, we measured a QEPAS peak signal of 102.6 mV with a 1-σ noise of 95 µV, corresponding to a signal-to-noise ratio of 1080. Thus, starting from a 3.1% water concentration, the minimum detection limit (MDL) was determined to be $\approx 30$ part-per-million (ppm). A useful parameter to estimate the sensor performance is the noise equivalent absorption normalized to the laser power and the acquisition time (NNEA). We obtained a NNEA = $9.2 \times 10^{-9}$.
W·cm⁻¹·Hz⁻¹/₂, which is a typical value for a QEPAS gas-sensing system [4].

![Graph](image.png)

Fig. 3. Second-harmonic high-resolution QEPAS scans of standard air with a 3.1% water vapor content. The QEPAS cell pressure was set to 60 mbar. The inset depicts the noise oscillations measured far from the QEPAS peak signal.

IV. QEPAS SENSOR ALLAN VARIANCE ANALYSIS

To determine the long-term stability of a sensor system an Allan variance analysis is mandatory. This analysis allows investigating drifts and establishing the sensor signal averaging limits. Given a set of \( M \) time-series data acquired with an integration time \( \tau \), its Allan variance \( \sigma_y^2(\tau) \) is defined as:

\[
\sigma_y^2(\tau) = \frac{1}{M} \sum_{k=1}^{M} \frac{1}{2} (y_{k+1} - y_k)^2 \tag{1}
\]

where \( y_k \) is the \( k \)-th data averaged over an integration time \( \tau \), \( y_{k+1} \) is the difference between adjacent values of \( y_k \), and \( M \) is the total number of data, usually of the order of \( 10^3\text{-}10^4 \). To estimate how \( \sigma_y^2(\tau) \) changes with the integration time; we implemented a LabView-based code. Starting from the set of \( M \) data acquired at an integration time \( \tau_0 \) and assuming that there is no dead time between adjacent measurements, the software averages the values for \( y_1 \) and \( y_2 \) and obtains a new \( y_2 \) value averaged over \( 2\tau_0 \). Subsequently, this routine averages values for \( y_3 \) and \( y_4 \) and changes them as a new value \( y_2 \) averaged over \( 2\tau_0 \) and finally applies Eq. (1) to determine \( \sigma_y^2(2\tau_0) \). The software repeats this process for other integer multiples \( m \tau_0 \) and at the end of the processing, it generates values for \( \sigma_y^2(m\tau_0) \) as a function of \( m\tau_0 \). Thus, to perform an Allan variance \( \sigma_y^2 \) analysis, all the data subsets have to be stacked together and treated as a single uninterrupted time sequence. Usually the Allan deviation \( \sigma_y \) is shown instead of the variance and expressed in terms of absorption coefficient or absorbing gas concentration, thus determining the minimum detectable concentration as a function of the integration time.

In our experiments, each measurement lasted 4 hours using a 2f-wavelength modulation approach. However, prior to analyzing the stability of our sensor system, its fundamental noise limit must be determined. It is known that a QTF can be modeled as a RLC circuit [4]. The electrical response of the QTF is measured by means of a trans-impedance amplifier with a gain resistor \( R_g = 10 \text{ M}\Omega \). The root mean square of the QTF thermal (Johnson) noise, is expressed as:

\[
\sigma_{\text{thermal}} = R_g \sqrt{\frac{2k_B T}{\pi \tau}} \tag{2}
\]

where \( k_B \) is the Boltzmann constant, \( T = 298 \text{ K} \) is the QTF temperature and \( \tau \) is the integration time. \( R_g \) also introduces noise, which is several times lower than the thermal QTF noise and can be neglected for typical values of \( R \) in the range 10-100 K\( \Omega \), as in our case. Thermal noise determines the minimum detection limit of the QEPAS sensor. If the QTF thermal noise is the dominant noise source, the Allan deviation closely follows a \( 1/\sqrt{t} \) dependence (see Eq. (2)), for the entire duration of the concentration measurements. To verify this assumption, a long time acquisition of the QTF signal was performed in the absence of laser illumination (dark-noise). The acquired Allan deviation plot in mV is shown in Fig. 4, together with the expected thermal noise trend evaluated from Eq. (2). For comparison, the experimental data was rescaled by a factor 30 in order to take into account the transimpedance pre-amplifier gain.

The experimentally measured dark-noise dependence on the integration time matches the theoretically thermal one, thus confirming that for laser-off conditions only the Johnson noise influences the QEPAS sensor. The small hump between 2 and 10 s can be attributed to slow mechanical oscillations of the sensor system. The constant decrease of the Allan deviation over long integration times demonstrates that, in these conditions, the QEPAS sensor allows unlimited data averaging without base line or sensitivity drift. The next step was to investigate the sensor stability when the QCL is switched-on. The QCL was electrically driven with a DC current plus a sinusoidal dither at \( f_0/2 \) and the QEPAS signal was acquired at \( f_0 \) by the Lock-in amplifier 1 (see Fig. 1). To determine the contribution of optical noise, for both off- and on-resonance conditions, we operated with the laser wavelength locked far from the water absorption line (at a DC current of 565 mA) or on its peak, respectively. The corresponding Allan deviations (in mV) of the QEPAS signal acquired under these two operating conditions, together with the previously measured
dark noise, are shown in Fig. 5.

Fig. 5. Allan deviation plot in mV of the QEPAS sensor signal with laser-off (black curve), with the laser-on and wavelength-locked far from the absorption line (off-resonance, blue curve), and with the laser-on and locked on the water absorption wavelength peak (on-resonance, red curve), all as a function of integration time. The dashed lines mark the QEPAS-sensor optimum integration time of $\tau=275$ s and the corresponding MDL of $\sim1.2$ ppm.

The Allan deviation measured for the off-resonance condition follows the Johnson noise trend and is almost identical to the QEPAS dark-noise, for an integration time of $\tau=1000$ s. For longer integration times, a slight deviation is visible, implying that photothermal induced noise can play a role only at very long $\tau$, which are unrealistic for QEPAS operation. This result confirms the achievement of very good alignment and focusing conditions, due to the high quality of the HCW fiber-output laser beam. The Allan plot of the QTF signal for the on-resonance condition also follows the dark-noise trend, for an integration time of $\sim275$ s, where it reaches a minimum value of 3.7 $\mu$V. The conversion factor between the QEPAS signal in $\mu$V and ppm of water vapor concentration was $\sim3.17$ $\mu$V/ppm. The minimum detection value corresponds to the turnover point of the Allan deviation plot; at longer $\tau$ values, the QEPAS sensitivity starts to deteriorate. The data of Fig. 5 suggest that this behavior may be related to laser intensity fluctuations when operating on-resonance condition. To verify this assumption, we performed an Allan deviation analysis of the laser power signal measured by the pyroelectric detector. The PD signal was acquired at $f_0$ by the lock-in amplifier 2, for both laser-off (dark-noise) and laser-on on-resonance operating conditions. The results are shown in Fig. 6.

For the QCL-off condition, the PD Allan deviation shows a Johnson noise ($1/\sqrt{\tau}$) trend for $\sim1000$ s integration times. For the QCL-on condition, the noise level increased by at least one order of magnitude. A nearly flat-noise behavior is visible up to an integration time of 20 s, followed by a steady noise level increase with $\tau$. The small hump between 2 and 10 s can be attributed to slow mechanical oscillations of the system.

The Allan deviation analysis demonstrates that QCL-related power fluctuations dominate the PD noise signal, especially at long integration times.

Fig. 6. Allan plot in mV of the PD noise when the QCL is off (black), and when the QCL is on and the sensor is locked on the H$_2$O absorption line peak (on-resonance, blue).

To investigate how laser fluctuations affect the QEPAS noise, we converted the PD noise into laser power fluctuations and subsequently extracted the related equivalent-QEPAS noise contribution. The conversion factor between the PD signal and the laser optical power was 70 $\mu$W/V. To convert laser power into a QEPAS signal, we used a conversion factor of 85.5 mV/mW (for an optical power of 1.2 mW, we measured a QEPAS peak signal of 102.6 mV, see Fig. 3). In Fig. 7, we compared the PD equivalent-QEPAS noise Allan deviation with the measured QEPAS sensor on-resonance.

The results show that, for $\tau < 275$ s the contribution to the QEPAS noise due to the laser power fluctuations is negligible and QTF thermal noise dominates. However, for longer integration times, laser power instabilities contribute with the photothermal induced noise to the increase of the QEPAS noise level, compromising the system stability and hence decreasing the minimum detection limit of the reported sensor system.

V. CONCLUSIONS

In summary, we demonstrated the merits of employing the Allan variance analysis to investigate the long-time stability of
a QEPAS based sensor system and particularly in providing information about the optimum averaging time and predicting the achievable minimum detection limits.

It was shown that, the sensor noise is dominated by the QTF thermal noise up to t=275 s. For longer integration times, laser power instabilities become the main noise source and a steady noise level increase is observed. Therefore, one has to reduce the laser power fluctuations in order to improve the sensor sensitivity. This will require the implementation of more stable laser current driver and temperature controller technologies.

REFERENCES

In the period 1994-1996, in 2000 and 2001 he was a visiting scientist of Bell Laboratories, Lucent Technologies (formerly AT&T), Murray Hill, NJ (U. S. A.). In 2006, he was an invited professor at the University of Paris 7. His research interests include the development and applications of quantum cascade lasers, optical, vibrational and transport properties of semiconductor structures at the nanoscale, spectroscopic techniques for real-time monitoring of optoelectronic devices, optoelectronic sensors for mechatronics. Gaetano Scamarcio was the recipient of the Award of the Italian Physical Society in 1989, the Firestone Prize for young laureates in 1985 and a NATO-CNR Advanced Fellowship in 1995.

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