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Study of acoustic resonator electro-thermal properties for photoacoustic gas spectroscopy

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Abstract

During my three-year PhD scholarship, I will work on the realization of novel quartz tuning forks to be used as acoustic transducers in Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) setup for trace gas detection. The geometry of tuning fork, as well as prongs sizes, will be optimized to enhance the performance of QEPAS operation for detection of both slow- and fast-relaxing gas species. A study will be dedicated for the realization of a QTF capable to efficiently vibrate both at the fundamental and first overtone mode, for simultaneous detection of two different gas species.

Introduction

The detection and measurement of trace gas concentrations is important for a wide variety of applications, including environmental monitoring, industrial process control analysis, biomedicine, combustion processes and the detection of toxic and hazardous gases. For example, trace gas sensors capable of high detection sensitivity and selectivity are required in atmospheric science for the monitoring of different trace gas species including greenhouse gases and ozone, while in breath diagnostics gas species like nitric oxide, ethane, ammonia and numerous others are used as biomarkers.

Techniques based on laser absorption spectroscopy (LAS) for trace gas sensing, compared to other techniques, are considerably faster, highly sensitive and selective. The Photoacoustic Spectroscopy (PAS) technique is based on an optical absorption process but

differs in the physical phenomenon used for the detection of the absorption signal. The PAS effect in gases can be divided into three main steps:

- localized heat release in the sample gas due to relaxation of absorbed light energy through molecular collisions;
- acoustic and thermal wave generation due to localized transient heating and expansion;
- detection of the acoustic signal in the PA cell with a microphone.

Molecular absorption of photons results in the excitation of molecular energy levels (rotational, roto-vibrational or electronic levels). The absorbed energy is almost completely released as heat, and since the absorbed radiation is intensity-modulated, the internal heating of the sample is periodic. Thus, since the volume is fixed, a pressure wave is generated, i.e. sound. The key advantage of PAS is that no optical detector is required, and sound waves can be detected by a commercial hearing aid microphone. The laser light is intensity-modulated at one of the resonance frequency of the acoustic cell containing the gas target. The photoacoustic signal S can be expressed by the relation:

$$S=CP\alpha$$

where Q is the quality factor of the acoustic resonator, P is the laser power, and α is the gas absorption coefficient. It follows that there is linear relationship between the sample concentration and the photoacoustic signal.

The research team of A. Kosterev and F.K. Tittel at Rice University reported in 2002 the first demonstration of a novel technique based on PAS and named quartz-enhanced photoacoustic spectroscopy (QEPAS) [1]. The basic idea of QEPAS is to accumulate the acoustic energy in a sharply resonant acoustic transducer, a quartz tuning fork (QTF), avoiding the use of acoustic gas cells, thereby removing restrictions imposed on the gas cell design by the acoustic resonance conditions. The QTF is positioned in the acoustic near-field zone of the focused laser beam and the gas cell only serves to separate the target sample from the surrounding environment and fix and control its pressure. QTFs are perfect candidates to detect weak photoacoustic excitation, since they are characterized from a high quality factor, therefore by a sharp resonant acoustic profile. The sound wave generated between the two prongs causes a symmetric vibration of the prong in the QTF plane. In addition, the gas sensor with tuning fork requires small optical paths and, due to the geometry of the electrode pattern, is immune to external noise which causes antisymmetric movements of the prongs.

Since its introduction, standard low-cost QTFs with resonance frequencies at 32.7 kHz are typically employed in QEPAS sensors. With respect to the standard PAS, QEPAS operates at higher resonance frequencies. Operating at high frequencies, the QEPAS performance can be affected to. The gas must have enough time to relax the accumulated excess of energy before the absorption of next excitation pulse. This feature depends both on the gas species and the QTF resonance frequency. For this reason, we can distinguish two categories: slow- and fast-relaxing gas species. For slow relaxing gases, such as CO, CO₂ and NO a QEPAS

sensor operational frequency as high as 32.7 kHz can limit the sound wave generation efficiency [2,3]: in the case of a slow V-T relaxation rate with respect to the modulation frequency, the translational gas temperature cannot follow fast changes of the laser induced molecular excitation rate, so that the QEPAS signal is weaker than in the case of an instantaneous V-T energy transfer (fast-relaxing gas species) and is given

$$S = \frac{Q \cdot P_L \cdot \alpha}{\sqrt{1 + (2\pi f_0 \tau_{V-T})^2}}$$

where f_0 is the QTF resonance frequency and τ_{V-T} is the relaxation time of the investigated molecule in the gaseous matrix in which it is immersed. For this formula, it follows that the straightforward approach to design QTFs optimized for QEPAS sensing is to reduce the resonance frequency while keeping high the quality factor. The dependence of the resonance frequency and related quality factor on the QTF relevant dimensions has been investigated with a set of custom QTFs (named as 2nd generation), designed with the aim of determining the dependence of the QTF parameters (f , Q) and performance on their relevant dimensions. This study [4] showed that resonance frequencies of in-plane flexural modes can be well predicted by using the Euler-Bernoulli equation. Considerations about the quality factor are more challenging. The Q-factor depends on all the energy dissipation mechanisms occurring in a vibrating prong of a QTF. The main contributions are due to damping by the surrounding fluid, the interaction of the prong with its support and thermo-elastic damping. All these loss mechanisms strongly depend on the QTF prongs size. Although several theoretical models have been proposed to describe the dependence of each loss mechanism on the prongs geometry, there is no theoretical model capable to take into account all the dissipation mechanisms in one, consistent formulation. An experimental investigation [4] on the QTF fundamental flexural mode resonance at atmospheric pressure demonstrates that the overall quality factor is proportional to the ratio T/L, where T and L are the prong thickness and length, respectively.

In my thesis work, I realized a MATLAB-based software to relate the quality factor and the resonance frequency at different prong geometries. For each fixed prong geometry (T and L), the software calculates the resonance frequency and the related Q-factor, and plots ordered points on the x- (frequencies, f) and y- (Q-factors) axis of the coordinate plane. The calculated ordered points (Q , f) shows that for a selected resonance frequency, different prong sizes can be chosen, providing quality factors values spanning in a certain range. Moving to low resonance frequencies, this range of possible quality factor values, as well as the Q-factor values itself, is reduced. In particular, QTFs with a resonance frequency lower than 10 kHz cannot ensure a Q-factor higher than 15,000, at atmospheric pressure. For a novel generation of QTFs optimized for QEPAS operation we selected a resonance frequency of ~16 kHz (a half of the standard 32.7 kHz). At $f = 16$ kHz, L and T values (with fixed prong width) maximizing the quality factor (18,000) are 9.4 mm and 2.0 mm, respectively. The first tuning fork designed and built in my thesis work, called QTF-S08, shares almost the same Q-factor value (15,710), about 12% different from the predicted value. This means that the

combination between the Euler-Bernoulli model and the empiric dependence of the quality factor with prong width/length ratio is an efficient tool for the prediction of the quality factor values. Even if the resonance frequency of QTF-S08 is almost a half of the standard 32.7 kHz-QTF, a high quality factor was measured. Subsequently, commercial finite element software COMSOL Multiphysics was used to simulate the QTF geometry and estimate the stress field distribution along the prongs. The simulation shows that the T-shape causes a better distribution of the stress field associated with the vibration along the internal prong surface, where the generated charges are collected in QEPAS experiments. A decrease of the resonance frequency of the fundamental mode was also predicted. Starting from these considerations, a modified geometry for QTF prongs was proposed, in which the prong thickness T is not constant along the prong axis. For the T-shaped QTF, called QTF-T1, a lower resonance frequency has been measured with respect to QTF-S08, as predicted by COMSOL simulations and it is due to the non-uniformity of the moments of inertia along the prong section. Moreover, a quality factor of 15,260 was measured, as well. Despite the prong T-geometry led to a decrease of the prong width far from prong top, the quality factor was not affected.

Research plan for 3-year PhD

As discussed in the previous section, PAS typically operates typically at a modulation frequency much smaller than molecular relaxation time of the target species $f \ll 1/\tau_r$ (typically < 1 kHz). Conversely, QEPAS operates at ~ 32 kHz and at such a high frequency the sensor response as well as the ultimate detection limit strongly depends on the gas specie. We can distinguish two categories for gas species classification: the molecules with slow relaxation rates (such as NO, CO, CO₂), and those with fast relaxation times, such as H₂O and SF₆. Moreover, it has been shown that the presence of a promoter in the analysed mixture can efficiently increase the V-T relaxation rate resulting in a stronger QEPAS signal. However, different promoter concentrations lead to different sensitivities.

The main objective of my work in the three years of PhD will be the investigation of dependence of the QTF resonance frequency on the QEPAS response, both for slow- and fast-relaxing gases. The aim is to realize a QTF with a resonance frequency as low as making the sensor response independent from the gas specie, without affecting the QEPAS performance. Moreover, the realization of QTFs with different geometries and the study of their performances will allow to study the non-radiative relaxation rates occurring in gas when it is optically excited. In addition, the dependence of the gas relaxation time as a function of the gas matrix will be also analysed. Although absorption spectra of many molecules are well known and listed in the HITRAN database, non-radiative relaxation times are still object of study, lacking of a theoretical analysis and experimental investigation.

The strong dependence of the QEPAS signal from the gas relaxation promoter as well as on the matrix composition opens the way to investigation of QEPAS technique for simultaneous detection of multi-gas species. Anyhow, multi-gas on-line detection is a topic

of considerable interest in recent years because of its important applications in environmental monitoring, medical diagnosis, industrial process control, agriculture and food industries and pollution monitoring. In several cases, like isotope concentration ratios, to retrieve the actual ratio value the concentration measurements of two isotopes must be performed simultaneously. This is also the case when the control and monitoring of relative concentration of two different gas target in a matrix that rapidly changes with time, as in agricultural applications or from sample to sample, as in breath analysis (e.g. NO and H₂O) is required. With a standard QEPAS approach, simultaneous gas detection is not feasible since the force sensing based QTF cannot recognize the molecular source of a photo-induced acoustic wave. Even when a single laser source is able to separate two absorption features referred to two different gas species, there is a delay in time in the measurements of two different target gas concentrations, since the laser source has to be tuned from one absorption line to the other absorption line. However, due to the reduction in the fundamental resonance frequency achieved with custom QTFs, the 1st overtone flexural mode became available for QEPAS operation, allowing the simultaneous excitation of the QTF both on the fundamental and 1st overtone modes, using the same or two different laser sources. The capability of the QEPAS sensor to perform simultaneous dual-gas spectral detection was demonstrated by implementing a DFB laser source targeting an acetylene (C₂H₂) absorption line and a diode laser targeting a H₂O absorption line [7]. The QEPAS spectra of both H₂O and C₂H₂ were acquired continuously without signal cross-talking. The resonance frequency difference between two flexural modes ensures that the correlated photoacoustic signals generated by different target gases do not interfere with each other. The dual-gas QEPAS methodology realizes a continuous real-time monitoring with a simple setup and small sensor size compared with previous multi-gas QEPAS sensors. Furthermore, the lower f_0 values of the custom QTFs are not only beneficial to detect gases with slow V-T relaxation rates but also allow the implementation of their 1st overtone flexural modes for QEPAS trace-gas detection. The proposed dual-gas sensing approach can be implemented when detecting gas with slow energy relaxation rates (such as NO, CO, and CH₄). Typically, to enhance the QEPAS signals, relaxation promoters (H₂O or SF₆) are added to the gas mixture, and thereby, it is also crucial to control their concentrations. The detection sensitivities of the two independent detection channels (at the fundamental and first overtone mode) can be adjusted by means of an appropriate design of the QTF prongs. Further improvements of the detection sensitivity can be achieved by acoustically coupling dual-tube acoustic micro-resonator to the QTF, in order to enhance the acoustic wave intensity. A stainless-steel resonator tube will be cut into two pieces and a QTF is inserted between them. The two half-tubes, positioned on the two sides of the QTF, will confine the acoustic waves and drive the QTF prongs to vibrate. Two pairs of tubes will be located at the first antinode point of the fundamental mode and the second antinode point of the first overtone mode of the QTF. The influence of tube geometrical parameters (namely the internal diameter, the external diameter and the tube length) on the sensor performance will be investigated in order to enhance the response both at the fundamental and first

overtone mode. The analysis of the concentration of two gases simultaneously will allow the evaluation of the isotopic concentration ratio, which is of interest, for example, for oil and gas companies (for the detection of isotopes 12 and 13 of the methane) and for human breath sensing (for the detection of CO and NO in a human breath having substantial different water concentrations).

First year goals

During the first year of my PhD I will design and realize of a set of custom quartz tuning forks optimized for QEPAS sensing. The guideline is to reduce the resonance frequency while keeping high the quality factor. A QTF design will be optimized for efficiently vibrate both at the fundamental and first overtone mode, with to be implemented in a simultaneous dual-gas sensor setup. An experimental setup will be realized in order to measure the fundamental parameters (Q , f , R) of the tuning forks, at different operating conditions.

Following years goals

A QEPAS setup equipped with QTFs tested during the first year will be realized for the detection of different gaseous species, by means of different laser sources operating in the near- and mid-infrared range. The sensor performance will be studied and analysed as a function of the target molecule (fast- and slow-relaxing gases), the matrix composition and the frequency of the tuning forks. The acoustic coupling between QTF and dual-tube resonator system will be studied as a function of main tube geometrical parameters, with the aim to enhance the signal-to-noise ratio. The final step will be the realization of a QEPAS sensor for simultaneous dual-gas detection.

References

- [1] A.A. Kosterev, Y.A. Bakhirkin, R.F. Curl, F.K.Tittel, Quartz-enhanced photoacoustic spectroscopy, *Opt. Lett.* 27 (2002) 1902–1904.
- [2] P. Patimisco, G. Scamarcio, F.K. Tittel, V. Spagnolo, Quartz-Enhanced Photoacoustic Spectroscopy: A Review, *Sensors* 14 (2014) 6165-6206.
- [3] G. Wysocki, A. A. Kosterev, F. K. Tittel, Influence of molecular relaxation dynamics on quartz-enhanced photoacoustic detection of CO₂ at $\lambda = 2 \mu\text{m}$. *Appl. Phys. B* 85 (2006) 301-306.
- [4] P. Patimisco, A. Sampaolo, H. Zheng, L. Dong, F.K. Tittel, V. Spagnolo, Quartz-enhanced photoacoustic spectrophones exploiting custom tuning forks: a review, *Advances in Physics X* 2 (2016) 169-187.
- [5] V. Spagnolo, A.A. Kosterev, L. Dong, R. Lewicki, F.K. Tittel, NO trace gas sensor based on quartz-enhanced photoacoustic spectroscopy and external cavity quantum cascade laser, *Appl. Phys. B* 100 (2010) 125–130.

[6] L. Dong, V. Spagnolo, R. Lewicki, F.K. Tittel, Ppb-level detection of nitric oxide using an external cavity quantum cascade laser based QEPAS sensor, *Optics Express* 19 (2011) 24037-24045.

[7] H. Wu, X. Yin, L. Dong, K. Pei, A. Sampaolo, P. Patimisco, H. Zheng, W. Ma, L. Zhang, W. Yin, L. Xiao, V. Spagnolo, S. Jia, F.K. Tittel, Simultaneous dual-gas QEPAS detection based on a fundamental and overtone combined vibration of quartz tuning fork, *Appl. Phys. Lett.* 110 (2017) 121104.