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(54) **Title:** COUPLING-OPTIMIZED DOUBLE RESONANT PHOTOACOUSTIC SENSOR PLATFORM FOR THE DETECTION OF GASES AND THEIR CONCENTRATIONS

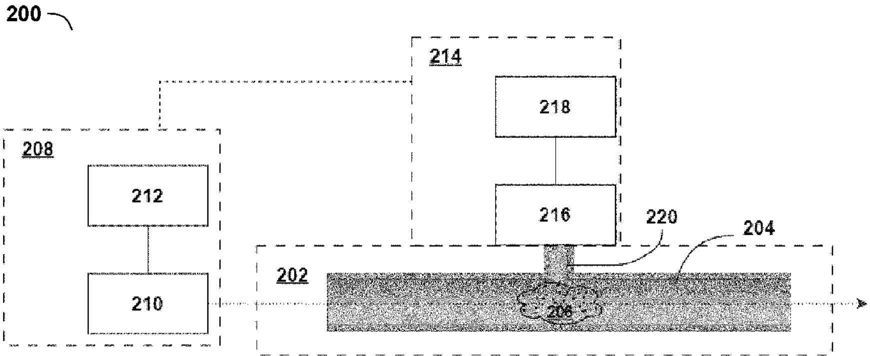

FIG. 2A

(57) **Abstract:** A photoacoustic spectroscopy system is provided including an acoustic cell, an electromagnetic radiation unit and a resonant transducer unit. The acoustic cell comprises a resonator cavity which supports a first resonance mode having a first resonant frequency, and is suppliable with a sample fluid. The resonant transducer supports a second resonance mode having a second resonant frequency, and is operatively connected to the resonator cavity. The first resonance mode and the second resonance mode are configured to be coupled in the significant coupling regime and the tuning between the first resonance mode and the second resonance mode is configured to yield an increase in signal strength or signal-to-noise ratio.

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Coupling-Optimized Double Resonant Photoacoustic Sensor Platform for the Detection of Gases and Their Concentrations

[0001] The present application claims priority from U.S. provisional patent application No. 63/509,211 filed on June 20, 2023, incorporated herein by reference, and U.S. provisional patent application No. 63/626,927, filed on January 30, 2024, incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to the field of photoacoustic spectroscopy.

BACKGROUND

[0003] Rapid and accurate detection of target analyte molecules contained within a sample fluid in environments with variable temperature, humidity and background analytes is useful in a variety of applications. For example, gas detection is now an integral part of industrial process monitoring, occupational risks mitigation, emission monitoring, military, and air quality assessments. The successful deployment of gas detection solutions in increasingly diverse applications relies on their continued improvement. These tight engineering constraints often translate to the need for a lower limit of detection as more and more applications require detection of gases at the parts-per-billion or even parts-per-trillion level. The gold-standard approach for trace gas detection is gas chromatography–mass spectrometry, which requires very expensive and large equipment, as well as expensive consumables. Some alternatives, such as semiconductor or resistive sensors are very compact and affordable, but they either lack sensitivity or specificity, and adapting them to different target molecules can require extensive redevelopment. A growing trend for low-concentration gas detection systems is the use of direct optical absorption spectroscopy (DAS), see for example Fathy et al., Direct Absorption and Photoacoustic Spectroscopy for Gas Sensing and Analysis: A Critical Review. Laser & Photonics Reviews 2022, 16, 2100556, wherein electromagnetic radiation is passed through the gas under analysis, and an electromagnetic radiation detector such as a photodiode, mercury cadmium telluride (MCT) detector, thermopile or other electromagnetic radiation sensing device is used to measure the quantity of electromagnetic radiation that has been absorbed by the gas under analysis. The reduction in measured electromagnetic radiation intensity can then be correlated to the concentration of the target gas. However, this approach is not background-free since the detector is exposed to a large intensity of electromagnetic radiation even in the absence of the target gas, which affects the system's dynamic range and requires a high-quality, low-noise detector. Furthermore, absorption spectroscopy for gases is often advantageous to operate using infrared electromagnetic radiation, which requires the use of compatible detectors which can be very costly and/or require power-intensive and bulky cooling solutions for some electromagnetic radiation wavelength ranges in the infrared. Another possible approach for trace gas detection is photoacoustic spectroscopy (PAS), a technique based on the detection of photogenerated acoustic waves, alleviating simultaneously the high-background signal issue and the noise restrictions, cost and size associated with the electromagnetic radiation detector. In this disclosure, systems and methods which utilize PAS to detect, measure and identify target analyte molecules within a sample fluid are detailed.

SUMMARY

[0004] One of the common approaches to meet modern engineering challenges for gas detection relies on the principle of photoacoustic spectroscopy. This approach offers an inherently background-free measurement and a fundamentally linear detection scheme. A typical photoacoustic spectroscopy system includes a source of electromagnetic radiation, which can be absorbed by a detection target, for example analyte gas molecules. Upon absorbing the electromagnetic radiation, the target heats up, and transfers heat energy to the surrounding medium (sample fluid), such as a gas matrix, which heats up that surrounding medium. The heating of the surrounding medium induces an increase in the pressure of that medium. When the interaction between the electromagnetic radiation and the target is modulated, the resulting pressure in the surrounding medium is also modulated, yielding an acoustic pressure wave. Under typical operating parameters, the amplitude of the acoustic pressure wave is proportional to the energy absorbed by the target, which is proportional to the electromagnetic radiation power, and to the target absorption. When the detection target is analyte gas molecules, the absorption is proportional to the concentration of the analyte gas molecules in the gas volume exposed to the electromagnetic radiation, as is the acoustic pressure wave amplitude. The acoustic pressure wave is typically measured by means of a mechanical transducer which transduces the acoustic pressure wave in the surrounding medium into a mechanical displacement of the transducer. Finally, a readout system converts this mechanical displacement into an electrical signal that can be read by a conventional electronic measurement device.

[0005] Ultimately, the limit of detection of a PAS system is limited by the noise floor of the entire apparatus which sets the signal-to-noise ratio for a given concentration of measured gas. The three main noise sources are (i) the acoustic thermal noise in the medium in which the target gas is to be detected, (ii) the thermal noise of the pressure (acoustical) to mechanical transducer and (iii) the noise in the readout system that translates the mechanical displacement of the transducer into an electrical signal of the desired final form, for instance a digital signal or an analog electrical signal. The magnitude of the acoustic thermal noise of the system is set by the acoustical configuration of the device. To increase the signal level, acoustic cells comprising a resonator cavity are often used in the implementation of the acoustical configuration. In this case, it is known that increasing the quality (Q)-factor of the resonator cavity leads to a lower acoustic thermal noise and is always desirable.

[0006] There are largely two approaches to minimize the noise floor in the output signal of a photoacoustic spectroscopy system with the concomitant increase in the signal-to-noise ratio. A first approach attempts to limit the noise of the acoustical to mechanical transducer and utilizes a low-noise readout system. If the combined noise of these two noise sources is brought significantly below the level of the acoustic thermal noise, then the resultant signal-to-noise ratio is limited only by the acoustical configuration, see for example US 7797983. This implementation of that approach requires a very stable laser light source and interferometer system, and increases the complexity of the readout system design, see for example US 9170397 and US 8497996. Another viable approach is to increase the signal measured from the acoustical domain, together with its intrinsic noise, beyond the combined noise of the acoustical to mechanical transducer and the readout system.

[0007] This second approach has been investigated in prior art in the form of double resonant photoacoustic spectroscopy, where the acoustic amplification provided by a resonator cavity is combined with the mechanical amplification provided by a resonant acoustical to mechanical transducer (resonant transducer) to increase the sensitivity of the photoacoustic system. These double resonant photoacoustic spectroscopy systems including a resonator cavity and a resonant transducer can be modeled as a coupled oscillator system, wherein the resonator cavity is a first oscillator and the resonant transducer is a second oscillator. Some examples of double resonant photoacoustic spectroscopy systems are discussed in the literature, for example on-beam quartz-enhanced photoacoustic spectroscopy (QEPAS) and off-beam QEPAS (see for example Kosterev et al., Applications of quartz tuning forks in spectroscopic gas sensing, Review of Scientific Instruments, 76(4):1–9 (2005), Liu et al., Off-beam quartz-enhanced photoacoustic spectroscopy, Opt. Lett. 34(10):1594–1596 (2009), and US 10908129). Typically, on-beam QEPAS utilizes a resonator cavity made of two tubes aligned with the gap between the tines of a quartz tuning fork (QTF), in order to increase the typically weak acoustic-mechanical coupling of QTFs. As a result, on-beam QEPAS is very sensitive to misalignment and vibration; a focused laser beam with high beam quality must pass through the typically sub-millimeter gap between the tines of the QTF without directly illuminating them, as this can increase noise significantly. Off-beam QEPAS utilizes a resonator cavity made of a single tube with a side slit. The QTF is placed near the side slit to maximize coupling of the acoustic-mechanical domains. While off-beam QEPAS does not require the same degree of alignment as on-beam QEPAS, the acoustic-mechanical coupling tends to be weaker. A double resonant photoacoustic spectroscopy system which is not sensitive to alignment or vibration, while still exhibiting high acoustic-mechanical coupling would be useful for many applications.

[0008] Additional examples of double resonant photoacoustic systems can be seen in Rück (2017) Development, characterization and miniaturization of a trace gas detection system for NO2 in air based on photoacoustic spectroscopy. Thesis. University of Regensburg. In this work, a two-sided open ended tube is used as a resonator cavity to provide acoustic amplification, and both a QTF and a resonant cantilever are investigated to serve as the resonant transducer. Rück notes the challenges of having high Q-factor QTFs in comparison to relatively low Q-factor resonant cavities, when such systems are exposed to variations in the speed of sound leading to photoacoustic signal attenuation. However, the work offers no clear approaches on tuning the coupling regime of the two oscillators to maximize the resonant transducer displacement (and thus readout system output signal amplitude), taking into account variations due to manufacturing tolerances of the resonator cavity, manufacturing tolerances of the resonant transducer, or environmental changes. For example, the detuning of the double-resonant photoacoustic system presented in Rück was not designed to be controlled. Also, the fluid handling system does not allow the temperature of the sample fluid, resonator cavity and resonant transducer to equilibrate, a critical step in tuning the coupling regime of the two oscillators. Some tunability may be possible via changing the gas composition, but this is not an optimal approach for trace gas sensing in a non-laboratory environment. This lack of tunability presents manufacturability concerns, as each resonator cavity would have to be individually tested and carefully matched with a suitable resonant transducer to achieve high acoustic-mechanical coupling. This is not feasible for high-volume production. Thus, it would be ideal if a tunable double resonant photoacoustic spectroscopy system could be provided, as well as methods for adjusting the detuning between the resonator cavity and resonant transducer of double resonant photoacoustic systems after assembly and/or during operation.

[0009] As previously described, quartz enhanced photoacoustic spectroscopy (QEPAS) utilizes a quartz tuning fork (QTF) as a resonant transducer to measure pressure variations amplified by a resonator cavity. Typically, QTFs have extremely high Q-factors, on the order of 10,000 in air and 100,000 in low vacuum. For very weakly-coupled systems, the Q-factor is proportional to the resonant amplification factor and inversely proportional to the losses in the system (which are related to the noise sources via the fluctuation-dissipation theorem). In the case of double resonant photoacoustic spectroscopy, maximizing the coupling of the resonant transducer to the acoustic domain is desired, with all other losses being undesirable. Thus, rather than utilizing a QTF or other transducer with an extremely high Q-factor in both air and vacuum, it may be desirable to utilize a resonant transducer which has (i) a Q-factor in the absence of coupling to the fluid domain as high as possible, (ii) a substantially lower Q-factor in a sample fluid (such as air), indicating a strong coupling with waves in the fluid domain and (iii) low coupling to dissipative vorticity waves and thermal waves in the fluid domain. When the resonant transducer is designed to display a much lower Q-factor in a sample fluid as compared to vacuum, its losses are dominated by those in the fluid domain. A high Q-factor in vacuum as compared to sample fluid thus indicates that the energy lost by the resonant transducer via interaction with a sample fluid vastly dominates any other losses inherent to the pure mechanical oscillations of the resonant transducer. Furthermore, low coupling to vorticity waves and thermal waves in the fluid domain ensures that most of the Q-factor losses observed when exposing the resonant transducer to the sample fluid as opposed to vacuum result from a high coupling with acoustic waves in the fluid domain. It may be desirable to design a double resonant photoacoustic system which utilizes this type of resonant transducer to maximize acoustic-mechanical coupling. Interestingly, commercially available double-resonant photoacoustic spectroscopy systems often operate in a very weakly coupled oscillator regime. The very weakly coupled regime is characterized by the displacement of the resonant transducer (which is proportional to the signal amplitude transduced by the resonant transducer) being proportional to the product of the quality Q-factors of the two oscillators. There may be advantages to operating in the significant coupling regime, which includes the strongly-coupled and the nearly-strongly-coupled regime, rather than the very weakly coupled regime.

[0010] The present disclosure demonstrates the significant gain in signal intensity, with concomitant increase in the signal-to-noise ratio of the output signal of a photoacoustic spectroscopy system, that can be obtained by (i) increasing the coupling between the resonator cavity and the acoustical to mechanical transducer and (ii) tuning the resonator cavity and resonant transducer closely to leverage the signal gains enabled by the increased coupling. This signal enhancement is independent and in addition to the signal increase as obtained by the use of high Q-factor resonators such as in QEPAS. To fully realize the possible signal gains, the coupling strength and the Q-factor of the resonant transducer should be increased until the signal-to-noise ratio of the resulting output signal is dominated by the intrinsic thermal noise contribution of the resonator cavity. This signal enhancement can also be realized without the use of complex or expensive low-noise readout systems by leveraging the large signal increase provided by the increased coupling between the resonator cavity and resonant transducer. The present disclosure also provides methods and approaches to design a photoacoustic apparatus with a signal-to-noise ratio that is limited only by the fundamental limit of the thermal acoustic noise associated to the acoustic configuration of the photoacoustic spectroscopy system using easily manufactured and low-cost readout systems that are not themselves state-of-the-art in terms of their intrinsic noise floor. Furthermore, in this disclosure, double resonant photoacoustic spectroscopy systems which are configured to operate in such a fashion that they can exploit the potential signal gains enabled by the significant coupling regime are provided. These systems overcome many of the disadvantages found in the prior art.

[0011] In one embodiment, a photoacoustic spectroscopy system is provided including: an acoustic cell comprising a resonator cavity, wherein the resonator cavity is configured to support a first resonance mode having a first resonant frequency, and wherein the acoustic cell is suppliable with a sample fluid; an electromagnetic radiation unit comprising an emitter and a control circuit, wherein the emitter is configured to transmit electromagnetic radiation through the resonator cavity; a resonant transducer unit comprising a resonant transducer and a readout system, wherein the resonant transducer is configured to support a second resonance mode having a second resonant frequency, and wherein the resonant transducer is operatively connected to the resonator cavity; and wherein the first resonance mode and the second resonance mode are configured to be coupled in a significant coupling regime.

[0012] In one embodiment, a method for performing photoacoustic spectroscopy is provided, the method including: providing a photoacoustic spectroscopy system as described above; operating the emitter in a modulated mode, such that the target analyte molecules in the sample fluid of the resonator cavity experience periodic absorption and heating at an operating frequency; configuring the acoustic cell such that the periodic heating induces an acoustic pressure wave with an amplitude proportional to a concentration of target analyte molecules in the sample fluid of the resonator cavity thus exciting the coupled resonator cavity and resonant transducer modes; detecting the excitation of the coupled resonator cavity and resonant transducer modes by measuring the displacement of the resonant transducer in a frequency-dependent basis with the readout system; and outputting via the readout system a signal representative of the concentration of target analyte molecules.

[0013] Another broad aspect is a photoacoustic spectroscopy system. The system includes an acoustic cell comprising a resonator cavity, wherein the resonator cavity is configured to support a first resonance mode having a first resonant frequency, and wherein the acoustic cell is suppliable with a sample fluid; an electromagnetic radiation unit comprising an emitter and a control circuit, wherein the emitter is configured to transmit electromagnetic radiation through the resonator cavity; a resonant transducer unit comprising a resonant transducer and a readout system, wherein the resonant transducer is configured to support a second resonance mode having a second resonant frequency, and wherein the resonant transducer is operatively connected to the resonator cavity; and wherein the first resonance mode and the second resonance mode are configured to be coupled in a significant coupling regime.

[0014] In some embodiments, first resonant frequency of the resonator cavity, the second resonant frequency of the resonant transducer or both resonant frequencies may be configured to be tunable such that the system can be tuned to attain at least one of (i) a closely-tuned configuration and (ii) an optimally-tuned configuration.

[0015] In some embodiments, the system may include control systems that are configured to at least stabilize one or a combination of (i) the temperature of the sample fluid, (ii) the pressure of the sample fluid, (iii) the humidity of the sample fluid, (iv) the mass flow of the sample fluid through the acoustic cell, (v) the temperature of the resonant transducer, and (vi) the temperature of the acoustic cell.

[0016] In some embodiments, the first resonant frequency of the resonator cavity may be configured to be less than the second resonant frequency of the resonant transducer at a first temperature (T1), wherein the first resonant frequency of the resonator cavity is configured to be greater than the second resonant frequency of the resonant transducer at a second temperature (T2), and wherein $T1 \neq T2$, and wherein the control systems may be configured to at least stabilize the temperature of the acoustic cell at any chosen temperature between T1 and T2.

[0017] In some embodiments, the resonant transducer may be selected from one or a combination of (i) an out-of-plane resonator, (ii) a tuning fork resonator, (iii) a cantilever resonator, and (iv) a diaphragm resonator.

[0018] In some embodiments, the acoustic cell further may include at least one acoustic frequency filter operatively connected to the resonator cavity.

[0019] In some embodiments, the acoustic cell may include at least one transducer enclosure, and wherein each of the at least one transducer enclosure is configured to encapsulate a volume of the sample fluid surrounding at least one active surface of the resonant transducer, separating the at least one active surface of the resonant transducer from an external environment.

[0020] In some embodiments, the readout system may be at least configured to sense the resonant transducer using a piezoelectric material.

[0021] In some embodiments, the readout system further may include a pre-amplifier proximal to the resonant transducer.

[0022] In some embodiments, the resonant transducer unit may include a printed circuit board (PCB), wherein the resonant transducer is mounted on the PCB, wherein the PCB is mounted to the acoustic cell such that the resonant transducer is operatively connected to the resonator cavity, and wherein at least some of the readout system may be located on the PCB.

[0023] In some embodiments, the acoustic cell may be constructed using a monolithic design and further comprises at least one acoustic frequency filter and an acoustic port which are machined from a single piece of material.

[0024] In some embodiments, the acoustic cell constructed using the monolithic design further may include a heat exchanger machined into the acoustic cell that allows the sample fluid to reach thermal equilibrium with the acoustic cell at least before entering the resonator cavity.

[0025] In some embodiments, a quality (Q-)factor of the second resonance mode of the resonant transducer in vacuum may be configured to be substantially larger than a free Q-factor of the second resonance mode of the resonant transducer in the sample fluid.

[0026] In some embodiments, the Q-factor of the resonant transducer in vacuum may be configured to be greater than 1000.

[0027] In some embodiments, the coupling strength (Ω) between the resonator cavity and the resonant transducer may be greater than or equal to the threshold value of $\sqrt{\frac{2}{\sqrt{Q_1 Q_2}}}\,\omega_0$.

[0028] In some embodiments, the resonant transducer may have a Q-factor, Q2, which is greater than or equal to the threshold value of $\frac{2{\omega_0}^3\beta^2\, m_2}{k_B T}$, wherein the readout system may have a noise amplitude spectral density of β, and wherein both the sample fluid in the resonator cavity and the resonant transducer may have a temperature, T.

[0029] In some embodiments, the acoustic cell further may include at least one acoustic port.

[0030] In some embodiments, the acoustic cell may include at least one optical window.

[0031] In some embodiments, the emitter may include one from a selection of (i) a quantum cascade laser (QCL), (ii) a continuous wave (CW) laser, (iii) a pulsed laser, (iv) an interband cascade laser (ICL), (v) a vertical-cavity surface-emitting laser (VCSEL), and (vi) a thermal emitter.

[0032] In some embodiments, the control circuit may be configured to at least modulate the output of the emitter, wherein modulating the output of the emitter comprises modulating one or a combination of (i) an emission wavelength of electromagnetic radiation (ii) an emission intensity of electromagnetic radiation (iii) a pulse repetition rate of electromagnetic radiation, and (iv) a patterned train of pulses of electromagnetic radiation.

[0033] In some embodiments, the readout system may include a pre-amplifier, wherein the pre-amplifier may include one of (i) a differential charge amplifier, (ii) a differential transimpedance amplifier, (iii) a single-ended voltage amplifier, (iv) a single-ended charge amplifier, (v) a single-ended transimpedance amplifier, and (vi) an instrumentation amplifier.

[0034] In some embodiments, the readout system may be configured to at least convert a displacement of the resonant transducer into one or more electrical signals and amplify and process the one or more electrical signals.

[0035] In some embodiments, the acoustic cell may be configured to be sealed with the sample fluid contained within.

[0036] In some embodiments, the acoustic cell further may include at least one port connected to a fluid handling system.

[0037] In some embodiments, the fluid handling system may be at least partly composed of low adsorption tubing.

[0038] Another broad aspect is a method for performing photoacoustic spectroscopy. The method includes providing a photoacoustic spectroscopy system as described herein; operating the emitter in a modulated mode, such that target analyte molecules in the sample fluid of the resonator cavity experience periodic absorption and heating at an operating frequency; configuring the acoustic cell such that the periodic heating induces an acoustic pressure wave with an amplitude proportional to a concentration of the target analyte molecules in the sample fluid of the resonator cavity, exciting the coupled resonator cavity and resonant transducer modes; detecting an excitation of the excited coupled resonator cavity and resonant transducer modes by measuring the displacement of the resonant transducer in a frequency-dependent basis with the readout system; and outputting via the readout system a signal representative of the concentration of target analyte molecules.

[0039] In some embodiments, configuring the control systems in such a way as to stabilize the temperature of the sample fluid, the resonant transducer unit and the resonator cavity such that the detuning between the first resonance mode and the second resonance mode may be actively stabilized and maintained in either the closely-tuned or the optimally-tuned configuration.

[0040] In some embodiments, the method may include increasing the amplitude of the signal transduced by the resonant transducer to improve the signal-to-noise ratio of the readout system by one or a combination of increasing the coupling strength by one or a combination of i) selecting a resonant transducer geometry with a large active surface area and ii) positioning the resonant transducer and the acoustic port at a pressure maximum in the resonator cavity; increasing the resonant transducer Q-factor via a reduction of the coupling to vorticity and thermal waves; and operating the photoacoustic spectroscopy system at the closely-tuned or optimally-tuned configuration.

[0041] In some embodiments, the readout system may possess an input-referred noise amplitude spectral density β and the sample fluid in the resonator cavity together with the resonant transducer are at a temperature of T, and wherein the method may include providing the photoacoustic spectroscopy system whereby the contribution of the intrinsic thermal acoustic noise of the resonator cavity to the total output noise of the resonant transducer unit is larger than the combination of the contribution of the intrinsic thermal mechanical noise of the resonant transducer and the contribution of the noise of the readout system to the total output noise of the resonant transducer unit, such that the noise of the electrical signal transduced by the resonant transducer unit is mostly comprised of the contribution of the intrinsic thermal acoustic noise of the resonator cavity by selecting the resonant transducer with a sufficiently high Q-factor which satisfies $Q_2 \geq \frac{64\omega_0{}^3\beta^2 m_2}{25\, k_B T}$; selecting the resonant transducer with a sufficiently high coupling strength which satisfies $\Omega^4 \geq 4\,\frac{\omega_0{}^4}{Q_1 Q_2}$; tuning the photoacoustic spectroscopy system at zero detuning; and operating the photoacoustic spectroscopy system at the operating frequency that corresponds to the uncoupled crossing frequency ω_0.

[0042] In some embodiments, the method my include operating the control circuit in such a way as to modulate a wavelength of the emitter at half the operating frequency of the resonator cavity and the resonant transducer, while using a signal band selection system to measure the signal output of the resonant transducer unit at the operating frequency such that the undesired background photoacoustic signal is reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0043] Embodiments of the disclosure will be described by way of example only with reference to the accompanying drawings, in which:

[0044] Figure 1A depicts a double-resonant photoacoustic spectroscopy system including a resonant transducer and a resonator cavity described as a coupled oscillator system.

[0045] Figure 1B depicts the theoretical MEMS displacement $|x_2|$ as a function of the normalized coupling strength Ω/Ω_0.

[0046] Figure 1C depicts the position of local maxima of the resonant transducer displacement as a function of the detuning δ between the resonant transducer and resonator cavity of the acoustic cell for a strongly-coupled system exhibiting frequency anti-crossing.

[0047] Figure 1D depicts experimentally-measured frequency anti-crossing behavior of two hybridized-coupled modes in a double-resonant photoacoustic system.

[0048] Figure 2A depicts a double-resonant photoacoustic spectroscopy system.

[0049] Figure 2B depicts a double-resonant photoacoustic spectroscopy system having a fluid handling system and a control system.

[0050] Figure 3 depicts an example acoustic cell.

[0051] Figure 4 depicts an example of using temperature as a tuning parameter.

[0052] Figure 5 depicts a flowchart of an exemplary method for performing photoacoustic spectroscopy.

DETAILED DESCRIPTION

I. Overview

[0053] It should be noted that there are multiple inventions described and illustrated herein. The following description is made for the purpose of illustrating the general principles of the present inventions and is not meant to limit the inventive concepts claimed herein. This disclosure provides systems and methods for detecting target analyte molecules within a sample fluid with PAS techniques.

[0054] The present disclosure references certain individual circuit components and elements such as capacitors, inductors, resistors, diodes, transformers, switches, etc.; combinations of these elements as networks, topologies, circuits, etc.; and objects that have inherent characteristics such as “resonant” objects. It will be understood by a person of ordinary skill in the art that adjusting and controlling variable components within a circuit or network may adjust the performance of that circuit or network and that those adjustments may be described generally as tuning, adjusting, matching, correcting, and so forth. A person of ordinary skill in the art will recognize that a particular topology discussed in this disclosure can be implemented in a variety of ways without departing from the present disclosure.

[0055] Terms “circuit” and “circuitry” may include either a single component or a plurality of components, which are active and/or passive and are connected or otherwise coupled together to provide the described function.

[0056] The various illustrative logics, logical blocks, modules, circuits and algorithms processes described in connection with the implementations disclosed herein may be implemented as electronic hardware, computer hardware, or a combination of both. The interchangeability of hardware and software has been described generally, in terms of functionality, and illustrated in the various illustrative components, blocks, modules, circuits and processes described throughout. Whether this functionality is implemented in hardware or software depends upon the particular application and design constraints imposed on the overall system.

[0057] One possible approach for trace gas detection is PAS, a technique based on the detection of photogenerated acoustic waves. Some of the main advantages of PAS-based systems are the small system size, the absence of consumables and the ability to generate real-time data. Thus, PAS-based systems are well suited for use in continuous monitoring applications, mobile applications, or large-scale applications which require high throughput of samples. Furthermore, laser-based PAS systems can be easily adapted to detect virtually any molecule while retaining a high specificity. Broadband tunable lasers or arrays of lasers can also allow simultaneous detection of a large number of different molecules, tailored to a specific application. Thus, PAS-based systems are easily customizable.

[0058] Typical PAS systems include an electromagnetic radiation source, an acoustic cell, which may include a resonator cavity, a means of modulating the electromagnetic radiation that reaches the acoustic cell, an acoustical to mechanical transducer operatively connected to the resonator cavity, and a readout system that measures the transducer displacement and converts it to a useable electronic signal. Herein and throughout this disclosure, it is assumed that the acoustical configuration of the acoustic cell and resonator cavity is designed in the state-of-the-art and is fixed.

[0059] In PAS, electromagnetic radiation of wavenumber υ [cm^{-1}] is absorbed by target analyte molecules in a sample fluid as it traverses at a rate proportional to the molar density ρ [mol cm^{-3}] of the target analyte molecules, the absorption cross-section σ(υ) [cm^2 mol^{-1}] at wavenumber υ, and the electromagnetic radiation source intensity I [W cm^{-2}] at wavenumber υ. The subsequent relaxation to the molecular ground state can occur through a number of processes: radiation (stimulated or spontaneous emission of a photon), chemical reactions, non-radiative relaxation, or a combination of these processes. Non-radiative relaxation can lead to an increase in the kinetic energy of the surrounding molecules, creating local heating and a corresponding local decrease in pressure. If the absorption process is periodically modulated either by the radiation source (intensity or wavelength), or by shifting the absorption lines, then the induced periodic heating will produce a pressure wave (synonymic for an acoustic wave) at the same frequency, or at a higher harmonic thereof. When the resulting pressure wave frequency, ω, coincides with a resonant frequency of a resonator cavity, it leads to an amplification of the acoustic wave generated within the resonator cavity. In this disclosure, the acoustic wave generated in the resonator cavity is not always driven to have the exact same frequency as the resonant frequency of the resonator cavity, and a different acoustic wave frequency can be chosen for a variety of reasons such as maximizing output signal amplitude or maximizing the signal-to-noise ratio. Herein and throughout this disclosure, the operating frequency is defined as the frequency of the pressure wave induced in the resonator cavity as a result of absorption of the modulated electromagnetic radiation by the target analyte molecules. . This periodic thermal excitation drives an acoustic resonance in the resonator cavity that is measured as pressure by a transducer. The pressure p [Pa] at the transducer location is proportional to the density, absorption cross-section and radiation source intensity, such that:

$$p \propto \rho \, \sigma(\upsilon) \, I$$

The transducer, and its associated readout system, must be able to convert the acoustic pressure signal p [Pa] into a suitable signal for the application, usually a digital or analog electrical signal.

In order to realize this, the most practical approach is to use a pressure-to-mechanical displacement transducer, wherein the acoustic pressure exerts a force on one or more surfaces of the transducer, herein and throughout this disclosure referred to as an active surface, causing a mechanical displacement of one or more parts of the transducer. In a preferred embodiment, such a transducer includes a large active surface area, in order to increase the effective driving force applied by the acoustic pressure wave onto the transducer. In a preferred embodiment, the transducer is constructed in such a way as to minimize the force exerted by the acoustic pressure wave onto undesired surfaces other than the chosen active surface, wherein exerting force onto those undesired surfaces would reduce the total or effective transducer displacement amplitude. Examples of such resonant transducers can be found in US 63/480,069, which is incorporated by reference herein. This mechanical displacement shall then be converted into a suitable electrical signal by means of a readout system, which includes one of a piezoelectric element, a capacitive sensor, an optical interferometry system, a strain gauge or piezoresistive element, or other means of converting a mechanical displacement to an electrical signal now known or later developed. In many photoacoustic spectroscopy systems, the readout system further includes a signal band selection system, which is configured to select and extract a specific frequency band centered at or around the operating frequency from the signal that is generated from the mechanical displacement of the pressure-to-mechanical displacement transducer, in order to increase the signal-to-noise ratio. For example, the signal band selection system may operate by the use of a fast Fourier transform signal processing, by the use of lock-in amplification techniques, by the use of frequency filters, or by other means of isolating a signal frequency band now known or later developed. Herein and throughout this disclosure, it is understood that the readout system may include signal band selection systems.

II. Coupling Regimes in DoubleResonant Photoacoustic Spectroscopy Systems

[0060] Several types of transducers may be suitable for PAS, including both resonant transducers and non-resonant transducers. Suitable resonant transducers may include resonant microelectromechanical system (MEMS) transducers and quartz tuning forks (QTFs). Additionally, non-resonant transducers such as broadband MEMS microphones or electret microphones may be used. It may be beneficial to utilize a resonant transducer, because in addition to the acoustic amplification granted by the use of the resonator cavity, the photoacoustic signal can also be amplified through the use of a resonant transducer with a high Q-factor. This is known as a double-resonant system. A physical interpretation of the Q-factor of an oscillator is the ratio of the accumulated energy to the dissipated energy during one period of oscillation.

[0061] Figure 1A depicts a double-resonant photoacoustic spectroscopy system including a resonant transducer and a resonator cavity described as a coupled oscillator system **100** with a simple coupling arrangement. More complex coupling schemes exist and it is understood that the application of more complex coupling mechanisms are covered in the scope of this disclosure. Herein, the acoustic oscillation in the resonator cavity has an effective mass m_1, an effective spring constant k_1, an effective damping constant α_1 and an effective displacement x_1, while the resonant transducer has a sprung mass m_2, a spring constant k_2, a damping constant α_2 and a displacement x_2. The coupling is modeled with a spring of constant κ joining the two masses. The displacement is positive to the right for both masses. The equations of motion are given by:

$$m_1\ddot{x}_1 = -k_1x_1 - \kappa(x_1 - x_2) - \alpha_1\dot{x}_1 + F_1\,,$$

$$m_2\ddot{x}_2 = -k_2x_2 - \kappa(x_2 - x_1) - \alpha_2\dot{x}_2 + F_2\,,$$

where F_1 models an effective external force driving the acoustic oscillation in the resonator cavity and F_2 models an external force applied to the resonant transducer.

[0062] In the typical use case of the system for performing PAS, modulated electromagnetic radiation excites a sample fluid within a resonator cavity, and the resonant transducer is sensed. Thus, a skilled reader will understand that a transfer function may be obtained for the coupled oscillator system assuming $F_1 = F_i e^{i\omega t}$ and $F_2=0$. The transfer function H_{x2} describing the displacement of the resonant transducer x_2 upon excitation of the acoustic oscillation in the resonator cavity by the force F_1 is given by:

$$H_{x_2}(\omega) \equiv \frac{x_2(\omega)}{F_1(\omega)} = \frac{1}{\sqrt{m_1m_2}}\frac{\Omega^2}{(\omega_1^2 - \omega^2 + i\omega\gamma_1)(\omega_2^2 - \omega^2 + i\omega\gamma_2) - \Omega^4}$$

where $\omega_i = \sqrt{\frac{\kappa+k_i}{m_i}}$, $\gamma_i = \alpha_i/m_i = \omega_i/Q_i$, for $i = 1{,}2$ and $\Omega^2 = \frac{\kappa}{\sqrt{m_1m_2}}$. Herein and throughout this disclosure Ω is referred to as the coupling strength, the physical quantities pertaining to the acoustic oscillation in the resonator cavity are identified with the subscript 1 and the physical quantities pertaining to the mechanical oscillation of the resonant transducer are identified with the subscript 2. Herein and throughout this disclosure, ‘uncoupled’ refers to the behavior of oscillators that do not exchange energy between themselves. This behavior is derived by modeling the evolution of the physical parameters of each oscillator as a function of the tuning parameter.

[0063] The analytical modeling of a double-resonant system such as coupled oscillator system **100** is most simply understood with one oscillator considered of fixed resonant frequency, while the other oscillator has a variable resonant frequency that can be tuned via a variety of parameters. In one non-limiting example, the skilled reader may consider a scenario where temperature is the tuning parameter, the resonant frequency of the resonant transducer has a moderate temperature dependency while the resonant frequency of the resonator cavity strongly depends on the temperature. This enables temperature to act as a tuning parameter that controls the detuning between the two oscillators. As such, for a simple model, one can consider ω_2 to be fixed and equal to ω_0, while $\omega_1(\delta) = \omega_0 + \delta$ is a function of the detuning δ, which itself depends on temperature, without losing the mathematical generality of the model. A skilled reader will understand that a variety of other tuning parameters exist, including pressure, humidity, composition of sample fluid, geometry, etc.

[0064] Figure 1B depicts the behavior of the coupled oscillator system **100** in plot **104**. Coupled oscillator systems exchange energy between oscillators and dissipate energy to the surrounding environment; qualitatively distinct behavior emerges when energy exchange or energy dissipation dominates. These distinct behaviors are referred to as the strong coupling regime, indicated by bracket **504** of plot **104**, and the weak coupling regime, indicated by bracket **505** of plot **104**, respectively. In the weak coupling regime, the transfer function H_{x_2} of the coupled oscillator system **100** has only one maximum at the point where the two oscillator frequencies are the same ($\delta = 0$). When $\omega = \omega_1 = \omega_2 = \omega_0$, the transfer function H_{x_2} can be simplified to:

$$H_{x_2}(\omega_0) = \frac{-1}{\sqrt{m_1 m_2}} \frac{\Omega^2}{\frac{\omega_0^4}{Q_1 Q_2} + \Omega^4}$$

[0065] In the weak coupling regime, the global transducer displacement maximum is found where the two oscillator frequencies are the same. The solid curve **500** of plot **104** depicts the normalized theoretical transducer displacement $|x_2|$ at zero detuning ($\delta = 0$) as a function of the normalized coupling strength Ω/Ω_0 for $\omega_0 = \omega_1 = \omega_2$, where Ω_0 is the threshold value of the coupling strength for strong coupling. The maximum value $max_\Omega |H_{x_2}(\omega_0)| = \frac{\sqrt{Q_1 Q_2}}{2\omega_0^2 \sqrt{m_1 m_2}}$ is attained when $\Omega^2 = \omega_0 \sqrt{\gamma_1 \gamma_2} = \frac{\omega_0^2}{\sqrt{Q_1 Q_2}} = {\Omega_p}^2$, as indicated by the vertical dashed line **502** of plot **104**.

[0066] Frequency anti-crossing behavior is a phenomenon observed in the response of a symmetrical coupled oscillator system, wherein two distinct local resonance maxima can be observed even when the detuning between both of the coupled oscillators is zero. In non-symmetrical coupled oscillator systems, such as in the presence of differential or common-mode loss mechanisms or when both oscillators display differing Q-factors, this notion is naturally extended by considering the splitting of the maxima of fitted Lorentzian curves, as is explained further, instead of the local maxima. As this phenomenon arises, the significantly-coupled modes take on a hybridized nature when the resonance frequency of the first oscillator is sufficiently close to the second oscillator. Both of the hybridized-coupled modes will exhibit a component from both oscillators. In other words, in a system with a strongly coupled resonant transducer and resonator cavity, the hybridized-coupled modes will exhibit both a substantial resonant transducer displacement and a substantial pressure-wave displacement, when the resonance frequency of the resonant transducer is sufficiently close to the resonance frequency of the resonator cavity (or vice versa).

[0067] As mentioned, in the presence of frequency anti-crossing behavior, the frequency response of the coupled harmonic oscillators, even at low detuning when both oscillator uncoupled resonant frequencies are close to being equal, splits into two Lorentzian peaks, the sum of which may or may not display two local maxima. This implies that the global maximum of the transfer function H_{x_2} is no longer at the point where $\omega_1 = \omega_2$ as was the case in the weak coupling regime. Thus, in the literature, one of the definitions for the strong coupling regime is defined as: $\Omega^2 > \omega_0 \frac{\gamma_1+\gamma_2}{2} = \omega_0^2 \frac{Q_1+Q_2}{2Q_1Q_2} = \Omega_0^2$, where ω_0 is the frequency at which the uncoupled resonant frequencies would meet with $\omega_0 = \omega_2 = \omega_1|_{\delta=0}$, see for example Rodriguez "Classical and quantum distinctions between weak and strong coupling" Eur. J. Phys., 31 (2), 025802. In the case of symmetrical coupled oscillator systems, this definition ensures that the strong coupling regime begins precisely when the zero detuning point is no longer the global maximum. Herein and throughout this disclosure, the strong coupling regime is understood to mean a coupling regime where the coupling strength Ω if greater than $\Omega_0 = \sqrt{\omega_0 \frac{\gamma_1+\gamma_2}{2}}$. Knowing that the geometric mean of positive numbers is upper bounded by their arithmetic mean, one can determine that $\Omega^2 = \omega_0 \frac{\gamma_1+\gamma_2}{2} \geq \omega_0 \sqrt{\gamma_1\gamma_2}$, such that the strong coupling regime threshold is greater or equal than the coupling strength yielding the maximum transfer function for the weak coupling regime. As the maximal value as plotted in curve **500** of plot **104** is the global maximum until $\Omega \geq \Omega_p$ throughout most of the weak coupling regime, it follows, by continuity, that the maxima entering the strong coupling regime are similar. An analytical expression is not as manageable in this case as it requires solving quartic equations. Nevertheless, not only is the maxima comparatively continuous, but it stays at substantially the same value when the coupling is increased beyond the strong coupling threshold. This is shown by the dashed curve **501** of plot **104** where the transducer displacement maxima have been numerically determined.

[0068] The location of the two Lorentzian peaks for varying detuning in the strong coupling regime can be found by finding the resonance frequencies of the coupled oscillator system **100**. This is achieved by solving the characteristic equation of the system given by:

$$(\omega_1^2 + i\omega\gamma_1 - \omega^2)(\omega_2^2 + i\omega\gamma_2 - \omega^2) - \Omega^4 = 0.$$

While an analytical solution can be obtained as this is a quartic equation, the result is complex as this quartic equation is generic. A good approximation is obtained by first solving the equation with no damping and adding it to the solution afterwards. Assuming that $\gamma_i \ll \omega_i$ corresponding to high Q-factors for both oscillators, the solution to the damping-free equation is readily obtained and the damping can be subsequently added as $\omega_i \rightarrow \omega_i + i\frac{\gamma_i}{2}$, retaining the first order in γ_i.

[0069] Referring to plot **106** in Figure 1C, the behavior of the resulting expressions describing strongly-coupled oscillators is shown as the continuous lines that map the resonance frequencies as a function of the detuning δ, exhibiting frequency anti-crossing behavior. Conversely, the dashed lines indicate the resonant frequencies of both oscillators as a function of detuning for a system that does not exhibit anti-crossing behavior. At the zero detuning point, such that $\omega_0 = \omega_1 = \omega_2$, one obtains the following expressions for the resonant frequencies:

$$\omega_\pm = \sqrt{\omega_0^2 + i\omega_0\frac{\gamma_1+\gamma_2}{2} \pm \frac{1}{2}\sqrt{4\Omega^4 - \omega_0^2(\gamma_1-\gamma_2)^2}}.$$

An expression for the separation Γ of the resonance frequencies, or peak splitting, at zero detuning is readily obtained by taking $\gamma_i \ll \omega_i$ and $\Omega \ll \omega_i$ and yields:

$$\Gamma = \sqrt{\frac{\Omega^4}{{\omega_0}^2} - \frac{(\gamma_1-\gamma_2)^2}{4}}.$$

[0070] In the limit of very low coupling strength, a series development around $\Omega = 0$ yields the following, $H_{x_2}|_{\omega_0} \approx \frac{Q_1 Q_2 \Omega^2}{\omega_0^4} + O(\Omega^6)$ which indicates that the signal amplitude is proportional to the product of the Q-factors of the two oscillators. Herein and throughout this disclosure the ‘very weak coupling regime’ refers to the region where coupling strength is low enough to yield the proportionality between the displacement amplitude and the product of the oscillator Q-factors. The very weak coupling regime is indicated as bracket **506** in plot **104**. This proportionality is no longer true for higher couplings.

[0071] Herein and throughout this disclosure, the ‘significant coupling regime’ refers to a regime which includes the strong coupling regime and the upper portion of the weak coupling regime, where the coupling strength Ω between the two coupled oscillators is considered to be a significant fraction of the coupling strength threshold for the strong coupling regime (Ω_0). In some embodiments, this significant fraction may be at least 10%, or at least 20%, or at least 30%, or at least 40%, or at least 50%, or at least 60%, or at least 70%, or at least 80% of the coupling strength threshold for the strong coupling regime (Ω_0). Bracket **503** on Figure 1B indicates the significant coupling regime for a significant coupling threshold corresponding to 10% of Ω_0. In the significant coupling regime, the amplitude of the displacement of one oscillator that is part of a system of two coupled oscillators departs from the Q-factor product proportionality characteristic of the very weak coupling regime.

[0072] It must be noted here that any potential signal gain granted by the use of a photoacoustic spectroscopy system operating in the significant coupling regime cannot be realized if the detuning δ between the resonator cavity and the resonant transducer is too large, as the resonant transfer of energy between two oscillators can only occur when their frequencies are closely matched, or in other words the system is optimally-tuned. Herein and throughout this disclosure, an optimally-tuned configuration is understood to be a system where the detuning between both oscillator uncoupled frequencies (here the resonator cavity and resonant transducer) is adjusted so that the resulting resonant transducer displacement, and thus signal strength, is at its global maximum. This optimal detuning value δ_0 is close to zero, but in some highly-coupled systems, or in the presence of additional phenomena that are not taken into account in the model presented herein, the value of δ_0 may be nonzero, but is typically bounded by $|\delta_0| \leq \sqrt{-\frac{(\gamma_1-\gamma_2)^2}{4}+\frac{\Omega^4}{{\omega_0}^2}}$. Herein and throughout this disclosure, a closely-tuned configuration is understood to be a system with a detuning value δ which is within the range $-\Omega \leq \delta \leq \Omega$.

[0073] In order to verify experimentally the coupling strength of a double-resonant photoacoustic spectroscopy system, it is necessary to first measure the uncoupled oscillator dissipation factors for the resonator cavity γ_1 and for the resonant transducer γ_2, and then determine the peak splitting Γ of the tuned and coupled oscillators. This can be achieved by measuring the excitation response power of the system for multiple detuning values and fitting Lorentzian functions $L(\omega) = \frac{A}{\pi}\frac{\gamma/2}{(\omega-\omega_c)^2+(\gamma/2)^2}$ on the response power peaks from the resonator cavity and resonant transducer, where ω_c is the central frequency of the peak, γ is the dissipation factor, and corresponds to the peak full width at half maximum (FWHM) and A is the peak area. Note that it is necessary to measure a quantity which corresponds to signal power, which can be for example the square of the signal amplitude.

[0074] Figure 1D depicts an example of such a measurement in plot **107**, where the central frequencies $\omega_{c_{1,2}}$ of both measured peaks are shown as a function of the temperature, which acts as a detuning control parameter. Note that the peak frequencies follow two curves that do not cross, and the fitted peaks near zero detuning are not representative of the uncoupled resonator cavity and uncoupled resonant transducer behavior shown in dashed lines. In order to obtain valid approximations for the uncoupled dissipation factors of each of the oscillators, corresponding to $\gamma_{1,2} = FWHM_{1,2}$, data to be fitted must be selected for detuned system conditions such that the frequency separation between both peak central frequencies is between the sum of both their FWHMs and twice that sum. This limited range ensures that the fitted data closely approximates the actual uncoupled behavior in the region surrounding the frequency crossing, by selecting weakly-hybridized modes not too far from the crossing point. The second parameter that needs to be extracted from this data is the peak splitting $\Gamma = |\omega_{c_1} - \omega_{c_2}|$ taken at zero detuning, which corresponds to the minimum peak splitting observed on the graph. The value of the uncoupled crossing frequency ω_0 can be estimated as the mean of both peak central frequencies at zero detuning $\omega_0 = \frac{1}{2}(\omega_{c_1} + \omega_{c_2})$. Finally, the coupling strength between the resonator cavity and resonant transducer can then be estimated as $\Omega^2 = \sqrt{\omega_0{}^2(\Gamma^2 + \frac{1}{4}(\gamma_1 - \gamma_2)^2)}$ to determine the coupling regime of the system. For the data measured on plot **107** in Figure 1D, the calculated coupling strength is $\Omega = 1593$ Hz, which corresponds to the significant coupling regime, being 82% of the coupling strength Ω_0 required to attain a strong coupling.

III. Thermal Noise in Double-Resonant Photoacoustic Systems

[0075] In double-resonant PAS systems, it may be desirable to utilize a resonant transducer which exhibits (i) a high Q-factor in vacuum and (ii) a lower free Q-factor in a sample fluid (for example, air) as compared to vacuum, where the free Q-factor is the Q-factor measured when the resonant transducer is not coupled to a resonator cavity. This indicates that the energy dissipation (losses) are dominated by those in the fluid domain as compared to mechanical etc. In other words, the Q-factor of the resonant transducer in vacuum is configured to be substantially larger than the free Q-factor of the resonant transducer in a sample fluid. In this case, ‘substantially larger’ includes a ratio between the Q-factor of the resonant transducer in vacuum compared to the free Q-factor of the resonant transducer in a sample fluid that is larger than 2, or larger than 5 or larger than 20. For example, in one example, it may be desirable to utilize a MEMS-based resonant transducer with a Q-factor on the order of 4500 in vacuum, and a free Q-factor on the order of 150 in air (sample fluid). Elsewhere in this disclosure, ‘substantially larger’ includes a ratio between a first Q-factor and a second Q-factor that is larger than 2, or larger than 5 or larger than 20.

[0076] As the Q-factor of a resonant transducer is reduced by any energy loss or dissipation mechanisms that affect the resonant transducer, a high Q-factor in vacuum vs a sample fluid such as air thus indicates that the energy lost by the resonant transducer via interaction in the sample fluid vastly dominates any other losses inherent to the pure mechanical oscillation of the resonant transducer. Furthermore, the energy lost by the resonant transducer via its coupling to the fluid domain can be dissipated in the surrounding sample fluid in many different forms. Acoustic waves, vorticity waves and thermal waves are the only three possible types of linear waves in a gaseous fluid (see for example Chu et al. “Non-linear interactions in a viscous heat-conducting compressible gas” J. Fluid Mech., 3, p. 494–514), and so together they make up the total energy losses by linear phenomena of the resonant transducer into the air or gas medium. Therefore, for small amplitudes, the loss of resonant transducer Q-factor between a vacuum environment and a sample fluid environment (such as an ambient air environment) is caused by the introduction of these three additional energy loss pathways. Since coupling to acoustic waves is essential to the use of a resonant transducer in photoacoustic systems, this coupling can be considered not as a loss pathway, but rather as a signal pathway, between the acoustic wave in the resonator cavity and the resonant transducer itself. Note that this effect is taken into account when the Q-factor is measured when coupled to the acoustic resonator as explained above. Conversely, vorticity waves and thermal waves are strongly dissipative, and coupling to those two types of waves should be minimized as much as possible. Coupling to those three types of waves can be estimated using finite element analysis (FEA) with thermoviscous acoustic models or other suitable methods now known or later developed. Using such analysis the geometry and design of the resonant transducer can be optimized to increase the Q-factor in the sample fluid by i) increasing the Q-factor in vacuum by designing the support structure so that it minimizes coupling to the environment, ii) limiting the tangential component over all surfaces of the fluid velocity field that results from the resonant transducer mechanical oscillation in a sample fluid, iii) lowering the thermal conductivity and the thermal capacity of the resonant transducer by a careful choice of construction material and geometry and iv) avoiding the use of capacitive readout systems that require small gaps between moving surfaces with concomitant squeeze film damping.

[0077] In any measurement apparatus, the readout system will display a noise floor that depends on the principle of its operation, the quality of its construction, its temperature, etc. In order for the noise floor not to affect the signal-to-noise ratio of a PAS system, the maximization of the resonant transducer displacement resulting from a pressure signal from the acoustic cell as described in the present disclosure can be applied. This amplification of the resonant transducer displacement resulting from a pressure signal from the acoustic cell is concomitantly applied to the noise from the coupled system. The efficient energy transfer between the significantly-coupled and closely-tuned, or ideally optimally-tuned, resonator cavity and resonant transducer through resonant coupling can allow for a much higher displacement amplitude of the one or more active surface of the resonant transducer, compared to a very-weakly coupled system for a given excitation of the resonator cavity. In such a configuration, if the coupling strength Ω is sufficiently high, so that it satisfies $\Omega^2 \geq \frac{{\omega_0}^2}{\sqrt{Q_1 Q_2}}$, such that the resonant transducer displacement amplitude is maximal, one can derive that if the Q-factor of the resonant transducer Q_2 is sufficiently high, so that it satisfies

$$Q_2 \geq \frac{2{\omega_0}^3 \beta^2 m_2}{k_B T_{\square}},$$

with $T_{\square}$ being the temperature of both the sample fluid in the resonator cavity and the resonant transducer. If these conditions are satisfied then the input-referred noise amplitude spectral density β, associated with the readout system, contributes less than 12% to the total output noise of the resonant transducer unit consisting of the noise from the readout system and the thermal noise, such that the total output noise is mostly comprised of the noise contribution from the coupled system, even for moderately noisy and potentially less expensive readout systems, such as those employing piezoelectric transduction, as opposed to ultra-low-noise readout systems. In order to obtain numerical values for this inequality, one must use a value for m_2 which is simply the sprung mass of the resonant transducer, which can be calculated from the geometry and the densities of the materials from which the resonant transducer is fabricated.

[0078] By the fluctuation-dissipation theorem, the sources of thermal noise in a system are in correspondence with the losses. Referring to the coupled oscillator system **100** in Figure 1A, the noise in Newtons attributable to all dissipation mechanism is given by $F_i^{\square} = \sqrt{4 k_B T \alpha_i}$, with k_B being the Boltzmann constant and T being the temperature of both the sample fluid in the acoustic resonator and the resonant transducer. Using the transfer functions of the system to refer all noise sources to the resonant transducer displacement and summing all the non correlated noise in a root-mean-square manner, a skilled reader can derive an expression for the signal-to-noise ratio of the PAS system. It is straightforward to derive that the signal-to-noise ratio is maximal when the operating frequency of the PAS system coincides with the resonator cavity resonance frequency. Assuming that the PAS system operates at that frequency, that the detuning is set to zero such that $\omega_1 = \omega_2 = \omega_0$ and that $Q_1 \gg 1$, it can be shown that the thermal noise arising from the losses in the resonant transducer will contribute less than 12% to the total resonant transducer displacement due to thermal noise in the coupled oscillator system **100** if

$$\Omega^4 \geq 4\,\frac{{\omega_0}^4}{Q_1 Q_2}\,.$$

A PAS system that satisfies the above inequality will have that the displacement noise of the resonant transducer is mostly due to the contribution of the intrinsic thermal acoustic noise of the resonator cavity.

[0079] A PAS system that is limited in signal-to-noise ratio only by the acoustical thermal noise of the acoustic cell can be designed via the maximization of the resonant transducer displacement resulting from a pressure signal from the acoustic cell and the minimization of the noise contribution of the resonant transducer as described in the present disclosure. In some embodiments, selecting the operating frequency to be that of the resonator cavity with a detuning of zero, it can be derived that selecting the resonant transducer such that the following inequalities are satisfied

$$\Omega^4 \geq 4\,\frac{{\omega_0}^4}{Q_1 Q_2} \text{ and } Q_2 \geq \frac{64{\omega_0}^3\beta^2 m_2}{25\,k_B T_{\square\square}}\,,$$

with $T_{\square}$ being the temperature of both the sample fluid in the acoustic cell and the resonant transducer, allows one to obtain an acoustic thermal noise limited signal-to-noise ratio without demanding that the readout system be inherently low-noise which allows simpler and cheaper readout system transduction mechanisms such as piezoelectric transducers to be applied.

IV. Double-resonant Photoacoustic Spectroscopy System Implementation

[0080] Figure 2A depicts one embodiment of a double-resonant photoacoustic spectroscopy system **200**. The photoacoustic spectroscopy system **200** includes: an acoustic cell **202** including a resonator cavity **204**, wherein the resonator cavity **204** supports a first resonance mode having a first resonant frequency, and wherein the acoustic cell **202** is suppliable with a sample fluid **206**; an electromagnetic radiation unit **208** comprising an emitter **210** and a control circuit **212**, wherein the emitter **210** transmits electromagnetic radiation through the resonator cavity **204**; and a resonant transducer unit **214** comprising a resonant transducer **216** and a readout system **218**, wherein the resonant transducer **216** supports a second resonance mode having a second resonant frequency, wherein the resonant transducer **216** is operatively connected to the resonator cavity **204**, and ; wherein the first resonance mode and the second resonance mode are configured to be coupled in the significant coupling regime.

[0081] The acoustic cell **202** is configured to support a resonant acoustic wave within the resonator cavity **204**. The electromagnetic radiation unit **208** is configured to control the transmission of electromagnetic radiation through the resonator cavity **204**. In particular, the control circuit **212** is configured to controllably operate the emitter **210**. The resonant transducer unit **214** is configured to transduce a pressure signal into a mechanical displacement, and convert that mechanical displacement into an electrical signal. In particular, the readout system **218** is configured to output a signal corresponding to the signal transduced by the resonant transducer **216** (i.e. by converting the mechanical displacement of the resonant transducer into an electrical signal).

[0082] A skilled reader will understand that herein and throughout this disclosure, the first resonance mode of the resonator cavity **204** is not necessarily referring to the first normal mode of the resonator cavity **204**, rather a particular resonance mode of many possible resonant normal modes. Similarly, the second resonance mode of the resonant transducer **216** is not necessarily referring to the second normal mode of the resonant transducer **216**, rather a particular resonance mode of many possible resonant normal modes.

[0083] Figure 2B depicts a further embodiment of a double-resonant photoacoustic spectroscopy system **250**. The system **250** further includes a fluid handling system **302** and control systems **232**. The fluid handling system **302** is configured to supply the acoustic cell **202** with sample fluid **206**. The fluid handling system further includes at least a heat exchanger **230** configured to allow the supplied sample fluid **206** to reach thermal equilibrium with the acoustic cell **202** before entering the resonator cavity **204**. In some embodiments, the heat exchanger **230** is operatively connected to an inlet port **112a**.

[0084] Control systems **232**may monitor and/or control one or a combination of (i) the temperature of the sample fluid **206**, (ii) the pressure of the sample fluid **206**, (iii) the humidity of the sample fluid **206**, (iv) the mass flow of the sample fluid **206** through the acoustic cell **202**, (v) the temperature of the resonant transducer **216**, and (vi) the temperature of the acoustic cell **202**. In some embodiments, one of a combination of (i) the temperature of the sample fluid **206**, (ii) the pressure of the sample fluid **206**, (iii) the humidity of the sample fluid **206**, (iv) the mass flow of the sample fluid **206** through the acoustic cell **202** are measured at an outlet port **112b** of the acoustic cell **202**. In some further embodiments, the control systems **232** control at least a heating device **234** which can heat the acoustic cell **202**, and the control systems **232** at least measure the temperature of the resonator cavity **204** by measuring the temperature of the acoustic cell **202** at one or more points **238** positioned near the resonator cavity **204** which have good thermal contact with the resonator cavity **204**.

[0085] Figure 3 depicts an example interface between the acoustic cell **202** and the resonant transducer unit **214**. The acoustic cell **202** includes a resonator cavity **204**. The acoustic cell **202** is suppliable with a sample fluid **206**. In this example, the acoustic cell **202** further includes: at least one acoustic port **220**, at least one transducer enclosure **222**, at least one acoustic frequency filter **226**, at least one optical window **224** and at least one port **112** for supplying the sample fluid **206**.

[0086] The at least one acoustic port **220** extends from the resonator cavity **204** and is operatively connected to at least one active surface of the resonant transducer **216.** The at least one acoustic port **220** may take various forms including i) a hollow tube which extends from the resonator cavity 204, as depicted in Figure 3, ii) a hole in the wall of the resonator cavity 204 or iii) any other form which allows the active surface of the resonant transducer 216 to be operatively connected to an acoustic wave in the resonator cavity **204**. The at least one transducer enclosure **222** may serve several purposes including; i) sealing at least one encapsulation volume which covers at least one active surface of the resonant transducer 216 and isolates it from the external environment, ii) shielding the resonant transducer unit **214** from electromagnetic noise, iii) minimize vulnerability to ambient acoustical noise through mechanical shielding of the resonant transducer **216** from external pressure waves, iv) protecting the resonant transducer **216** from contamination and damage, and v) minimizing the steady gas flow around or through the structure of the resonant transducer **216** which would otherwise occur due to the possible pressure differential between the acoustic cell **202** and the ambient fluid. The at least one acoustic frequency filter **226** in this example includes two buffer volumes. Buffer volumes reduce the background noise generated by laser absorption in the at least one optical window **224**. The at least one optical window **224** may be made of quartz, zinc selenide (ZnSe), UV-fused silica, sapphire, silicon, germanium or other materials which reduce the adsorption of energy from the electromagnetic radiation source, and may be coated in an anti-reflection optical coating. The at least one optical window **224** serves to isolate the acoustic environment inside the acoustic cell **202** from that of the external environment. Where necessary, the acoustic cell **202** and specifically the transducer enclosure **222** may be made gas tight with the use of sealing gaskets. The at least one port **112** includes the inlet port **112a** and the outlet port **112b**.

[0087] Still referring to Figure 3, in this example the resonant transducer unit **214** includes resonant transducer **216** mounted on a printed circuit board (PCB) **228**. The PCB **228** may be mounted to the acoustic cell **202** such that the resonant transducer **216** is positioned correctly to be operatively connected to the resonator cavity **204**. At least some of the readout system **218** may be located on the PCB **228**.

V. Gas Handling System

[0088] Operating the double-resonant photoacoustic spectroscopy system **200** and **250** at a constant temperature may be optimal for several reasons. First, resonant MEMS transducers are typically formed from silicon, which has a significantly higher temperature-induced frequency drift than other materials commonly used to manufacture resonators, such as AT-quartz (3750 ppm for silicon vs 20 ppm for AT-quartz over a temperature range of -40°C to 85°C). In addition, the resonance frequency of the resonator cavity **204** will drift significantly due to the change in sound velocity in the sample fluid **206** contained within. Thus, heating and maintaining the acoustic cell **202** and resonant transducer **216** at a precise temperature is necessary to enable reliable performance. The temperature-induced frequency drifts of the resonator cavity's 204 resonance frequency and of the resonant transducer's 216 resonance frequency can also be exploited to correct for any frequency variations that may be introduced by manufacturing tolerances of those components, ensuring operation close to the optimal detuning δ_0. Heating the acoustic cell **202** also has the added benefit of reducing the adsorption of analytes on the acoustic cell **202** and resonator cavity **204** inner walls. In order to maintain a stable and controlled temperature of the resonator cavity **204**, the resonant transducer 216 and the sample fluid 206, a heat exchanger **230** may be machined into the external structure of the acoustic cell **202**.

[0089] Plot **400** in Figure 4 depicts an example of using temperature as a tuning parameter, plotting the effect of the acoustic cell **202**, resonant transducer **216** and sample fluid **206** temperature (which are assumed to be equal in this example) on the measured photoacoustic system response as a function of frequency. The curves shown correspond to increasing temperatures from the bottom to the top and are offset vertically for visibility. The frequency of both the resonator cavity **204** and the silicon-based resonant transducer **216** shifts with temperature, although the resonant transducer **216** frequency shift is not only due to changes in the temperature-dependent elastic constants of silicon. The resonant transducer **216** (in this example, a piezoelectric MEMS pressure transducer) is only expected to shift approximately -30 ppm/°C, whereas the observed shift is approximately -540 ppm/°C. This shift is mostly due to the change in acoustic properties of the volume of sample fluid 206 located behind the resonant transducer **216** in the encapsulation volume **222**.

[0090] In some embodiments, either the first resonant frequency of the resonator cavity **204**, the second resonant frequency of the resonant transducer **216** or both resonant frequencies are configured to be tunable such that the system can be tuned to at least one of (i) the closely-tuned configuration and (ii) the optimally-tuned configuration.

[0091] Herein and throughout the disclosure, 'tunable' refers to a parameter which is deliberately controlled to produce a desired output. While the material properties of the sample fluid **206**, acoustic cell **202**, resonator cavity **204,** and resonant transducer **216** may vary with environmentally-induced changes such as temperature, pressure or humidity, these parameters must be externally controlled in some way to be considered tunable.

[0092] In some embodiments, the system further includes the control systems **232** that are configured to at least stabilize one or a combination of (i) the temperature of the sample fluid **206**, (ii) the pressure of the sample fluid **206**, (iii) the humidity of the sample fluid **206**, (iv) the mass flow of the sample fluid **206** through the acoustic cell **202**, (v) the temperature of the resonant transducer **216**, and (vi) the temperature of the acoustic cell **202**.

[0093] In some further embodiments, the first resonant frequency of the resonator cavity **204** is configured to be less than the second resonant frequency of the resonant transducer **216** at a first temperature (T1), wherein the first resonant frequency of the resonator cavity **204** is configured to be greater than the second resonant frequency of the resonant transducer **216** at a second temperature (T2), wherein T1 ≠ T2and wherein the control systems **232** are configured to at least stabilize the temperature of the acoustic cell **202** at any chosen temperature between T1 and T2. Herein and throughout the disclosure, 'stabilizing the temperature of the acoustic cell **202'** may be understood to mean stabilizing the temperature of one or a combination of i) the resonant transducer **216**, ii) the resonator cavity **204**, iii) the sample fluid **206** within the resonator cavity **204** and iv) the entirety of the acoustic cell **202**.

[0094] In some embodiments, the resonant transducer **216** is selected from one or a combination of (i) an out-of-plane resonator, (ii) a tuning fork resonator, (iii) a cantilever resonator, and (iv) a diaphragm resonator.

[0095] In a preferred embodiment, the resonant transducer **216** is a MEMS device.

[0096] In some embodiments, the acoustic cell **202** further includes at least one acoustic frequency filter **226** operatively connected to the resonator cavity **204**. Herein and throughout this disclosure, an 'acoustic frequency filter' is any type of filter configured to reduce the transmission of noise to the resonator cavity **204**. The at least one acoustic frequency filter **226** is selected from i) a band-stop filter, ii) a low-pass filter or iii) an attenuation filter, which could be implemented as one or a combination of quarter-wave tubes, buffer volumes or acoustical attenuators. The at least one acoustic frequency filter **226** may be connected to the at least one port **112** and/or the resonator cavity **204**.

[0097] In some embodiments, the acoustic cell **202** further includes at least one transducer enclosure **222**, and wherein each of the at least one transducer enclosure **222** encapsulates a volume of sample fluid **206** surrounding at least one active surface of the resonant transducer **216**, separating the at least one active surface of the resonant transducer 216from an external environment.

[0098] In some embodiments, the readout system **218** is configured to sense the resonant transducer **216** using a piezoelectric material.

[0099] In some embodiments, the readout system **218** may be configured to sense the resonant transducer 216 using a piezoelectric material.

[0100] In some embodiments, the readout system 218 further includes a pre-amplifier proximal to the resonant transducer **216**.

[0101] In some embodiments, the resonant transducer **216** is mounted on a printed circuit board (PCB) **228,** wherein the PCB **228** is mounted to the acoustic cell 202 such that the resonant transducer **216** is operatively connected to the resonator cavity **204**, and wherein at least some of the readout system **218** is located on the PCB **228**.

[0102] In some embodiments, the acoustic cell **202** is constructed using a monolithic design including a resonator cavity **204**, at least one acoustic frequency filter **226**, and an acoustic port **220** which are machined from a single piece of material. A monolithic design may be desirable for reducing assembly steps and ensuring fixed positioning and good thermal contact between components, as well as with the portion of the resonant transducer unit **214** comprising the resonant transducer **216** that is mounted on this monolithic acoustic cell.

[0103] In some further embodiments, the acoustic cell **202** constructed using the monolithic design further includes a heat exchanger **230** machined into the acoustic cell **202** that allows the sample fluid **206** to reach thermal equilibrium with the acoustic cell **202** at least before entering the resonator cavity **204**.

[0104] In some embodiments, the Q-factor of the resonant transducer **216** in vacuum is configured to be substantially larger than the Q-factor of the resonant transducer **216** in the sample fluid **206**.

[0105] In some further embodiments, the Q-factor of the resonant transducer **216** in vacuum is configured to be greater than 1000.

[0106] In some embodiments, the coupling strength Ω between the resonator cavity **204** and the resonant transducer **216** is greater than or equal to the threshold value of $\sqrt{\frac{2}{\sqrt{Q_1 Q_2}}}\,\omega_0$.

[0107] In some embodiments, the readout system **218** has an input-referred noise amplitude spectral density of β, the sample fluid **206** in the resonator cavity **204** and the resonant transducer **216** have a temperature of T and the Q-factor Q_2 of the resonant transducer **216** is greater than or equal to the threshold value of $\frac{2{\omega_0}^3\beta^2 m_2}{k_B T}$.

[0108] In some further embodiments, the coupling strength Ω is greater than or equal to the threshold value of $\sqrt{\frac{{\omega_0}^2}{\sqrt{Q_1 Q_2}}}$ such that the noise from the readout system **218** contributes less than 12% to the total output noise of the resonant transducer unit **214** consisting of the noise from the readout system **218** and the thermal noise of the resonator cavity **204** and of the resonant transducer **216**.

[0109] In some embodiments, both the sample fluid **206** in the resonator cavity **204** and the resonant transducer **216** are at a temperature T, the operating frequency is configured to be the first resonant frequency of the resonator cavity **204**, the detuning is configured to be zero, the coupling strength satisfies $\Omega^4 \geq 4\frac{{\omega_0}^4}{Q_1 Q_2}$, and the Q-factor of the resonant transducer **216** is configured to be greater than or equal to the threshold value of $\frac{64{\omega_0}^3\beta^2 m_2}{25\,k_B T_{\square\square}}$ such that the noise in the electrical signal transduced by the resonant transducer unit **214** is mostly due to the contribution of the intrinsic thermal acoustic noise of the resonator cavity **204**.

[0110] In some embodiments, the acoustic cell **202** further includes at least one acoustic port **220**.

[0111] In some embodiments, the acoustic cell **202** further includes at least one optical window **224**.

[0112] In some embodiments, the emitter **210** includes one from a selection of (i) a quantum cascade laser (QCL), (ii) a continuous wave (CW) laser, (iii) a pulsed laser, (iv) an interband cascade laser (ICL), (v) a vertical-cavity surface-emitting laser (VCSEL), and (vi) a thermal emitter.

[0113] In some embodiments, the control circuit **212** is configured to at least modulate the output of the emitter **210**, wherein modulating the output of the emitter **210** includes modulating one or a combination of (i) an emission wavelength of electromagnetic radiation (ii) an emission intensity of electromagnetic radiation (iii) a pulse repetition rate of electromagnetic radiation (iv) a patterned train of pulses of electromagnetic radiation.

[0114] In some embodiments, the readout system **218** further includes a pre-amplifier, wherein the pre-amplifier consists of one from a group of (i) a differential charge amplifier, (ii) a differential transimpedance amplifier, (iii) a single-ended voltage amplifier, (iv) a single-ended charge amplifier or (v) a single-ended transimpedance amplifier, (vi) an instrumentation amplifier or (vii) another pre-amplifier architecture now known or later developed.

[0115] In some embodiments, the readout system **218** is configured to at least convert the displacement of the resonant transducer **216** into one or more electrical signals and amplify and process these one or more electrical signals.

[0116] In some embodiments, the acoustic cell **202** is configured to be sealed with the sample fluid **206** contained within.

[0117] In some embodiments, the acoustic cell **202** further includes at least one port **112** connected to a fluid handling system **302**.

[0118] In some embodiments, the fluid handling system **302** is at least partly composed of low adsorption materials, such as glass, ceramic, aluminum, stainless steel, fluoro-polymers (PTFE, PFA, etc.). In some embodiments, at least part of these components are coated with a passivation layer. In a preferred embodiment, the fluid handling system **302** is at least partly composed of metal components coated with a silicon-based passivation layer.

[0119] In some embodiments, the resonator cavity **204** has an absolute rate of change of the first resonant frequency as a function of temperature ($\left|\frac{\partial \omega_1}{\partial T}\right|$), wherein the resonant transducer **216** has an absolute rate of change of the second resonant frequency as a function of temperature ($\left|\frac{\partial \omega_2}{\partial T}\right|$), and wherein $\left|\frac{\partial \omega_1}{\partial T}\right| \neq \left|\frac{\partial \omega_2}{\partial T}\right|$.

[0120] In some embodiments, one or both of the first resonant frequency of the resonator cavity **204** and the second resonant frequency of the resonant transducer **216** are configured to be tunable with pressure.

[0121] In some embodiments, one or both of the first resonant frequency of the resonator cavity **204** and the second resonant frequency of the resonant transducer **216** are configured to be tunable with humidity.

[0122] In some embodiments, the Q-factor of the uncoupled resonant transducer **216** in the sample fluid **206** is configured to be substantially larger than the Q-factor of the resonator cavity **204**.

[0123] In some embodiments, the method further includes operating the system in an optimally tuned configuration.

[0124] In some embodiments: the resonator cavity supporting a first resonance mode having a first resonant frequency further includes a plurality of resonator cavities supporting a first resonance mode having a first resonant frequency; the resonant transducer supporting a second resonance mode having a second resonant frequency further includes a plurality of resonant transducers supporting a second resonance mode having a second resonant frequency; the coupling of the first resonance mode of the plurality of resonator cavities and the second resonance mode of the plurality of resonant transducers is configured to be in the significant coupling regime and closely tuned; wherein the emitter transmits electromagnetic radiation through the plurality of resonator cavities and wherein the gas handling system is configured to circulate the sample fluid throughout the plurality of resonant cavities.

[0125] In some embodiments: the resonator cavity supporting a first resonance mode having a first resonant frequency further includes a plurality of resonator cavities supporting a first resonance mode having a first resonant frequency; the resonant transducer supporting a second resonance mode having a second resonant frequency further includes a plurality of resonant transducers supporting a second resonance mode having a second resonant frequency; the electromagnetic radiation unit comprising an emitter and a control circuit further includes a plurality of emitters; the coupling of the first resonance mode of the plurality of resonator cavities and the second resonance mode of the plurality of resonant transducers is configured to be in the significant coupling regime and closely tuned; wherein each emitter from the plurality of emitters transmits electromagnetic radiation through one resonator cavity from the plurality of resonator cavities and wherein the gas handling system is configured to circulate the sample fluid throughout the plurality of resonant cavities.

[0126] Figure 5 depicts a method for performing photoacoustic spectroscopy. Step **512** includes providing a photoacoustic spectroscopy system **200** or **250** as described above. Step **514** includes operating the emitter **210** in a modulated mode, such that the target analyte molecules in the sample fluid 206 of the resonator cavity 204 experience periodic absorption and heating at an operating frequency. Step **516** includes configuring the acoustic cell 202 such that the periodic heating induces an acoustic pressure wave with an amplitude proportional to a concentration of target analyte molecules in the sample fluid 206 of the resonator cavity 204 thus exciting the coupled resonator cavity and resonant transducer modes (in other words exciting the coupled first resonance mode and second resonance mode).. Step **518** includes detecting the excitation of the coupled resonator cavity and resonant transducer modes by measuring the displacement of the resonant transducer 216 in a frequency-dependent basis with the readout system 218..Step **520** includes outputting via the readout system 218 a signal representative of the concentration of target analyte molecules.

[0127] In some embodiments, the method further includes configuring the control systems **232** in such a way as to stabilize the temperature of the sample fluid **206**, the resonant transducer unit **214** and the resonator cavity **204** such that the detuning between the first resonance mode and the second resonance mode is actively stabilized and maintained in either the closely-tuned or the optimally-tuned configuration.

[0128] In some embodiments, the method further includes increasing the amplitude of the signal transduced by the resonant transducer **216** to improve the signal-to-noise ratio of the readout system **218** by one or a combination of: increasing the coupling strength by one or a combination of i) selecting a resonant transducer **216** geometry with a large active surface area and ii) positioning the resonant transducer **216** and the associated acoustic port **220** at a pressure maximum in the resonator cavity **204**, and iii) increasing the resonant transducer **216** Q-factor via a reduction of the coupling to vorticity and thermal waves and operating the photoacoustic spectroscopy system at the closely-tuned or the optimally-tuned configuration.

[0129] In some further embodiments, the readout system **218** possesses an input-referred noise amplitude spectral density β, wherein the method is further applied so that the coupling strength satisfies $\Omega^2 \geq \frac{{\omega_0}^2}{\sqrt{Q_1 Q_2}}$ and the Q-factor of the resonant transducer **216** is at least equal or greater than the threshold value of $Q_2 \geq \frac{2{\omega_0}^3\beta^2 m_2}{k_B T}$, such that the noise from the readout system **218** contributes less than 12% to the total output noise of the resonant transducer unit **214** consisting of the noise from the readout system **218** and the combination of the thermal noise of the resonator cavity **204** and of the resonant transducer **216**.

[0130] In some embodiments, the readout system **218** possesses an input-referred noise amplitude spectral density β and the sample fluid **206** in the resonator cavity **204** together with the resonant transducer **216** are at a temperature of T, and wherein the method further includes providing the photoacoustic spectroscopy system whereby the contribution of the intrinsic thermal acoustic noise of the resonator cavity **204** to the total output noise of the resonant transducer unit **214** is larger than the combination of the contribution of the intrinsic thermal mechanical noise of the resonant transducer **216** and the contribution of the noise of the readout system **218** to the total output noise of the resonant transducer unit **214**, such that the noise of the electrical signal transduced by the resonant transducer unit **214** is mostly due to the contribution of the intrinsic thermal acoustic noise of the resonator cavity **204** by: selecting the resonant transducer **216** with a sufficiently high Q-factor which satisfies $Q_2 \geq \frac{64{\omega_0}^3\beta^2 m_2}{25\, k_B T}$, selecting the resonant transducer **216** with a sufficiently high coupling strength which satisfies $\Omega^4 \geq 4 \frac{{\omega_0}^4}{Q_1 Q_2}$, tuning the photoacoustic spectroscopy system at zero detuning, and operating the photoacoustic spectroscopy system at the operating frequency that corresponds to the uncoupled crossing frequency ω_0.

[0131] In some embodiments, the method further includes operating the control circuit **212** in such a way as to modulate a wavelength of the emitter **210** at half the operating frequency of the resonator cavity **204** and the resonant transducer **216**, while using a signal band selection system to measure the signal output of the resonant transducer unit **214** at the operating frequency such that the undesired background photoacoustic signal is reduced.

[0132] It is to be understood that the disclosure describes a few embodiments and that many variations of the invention can easily be devised by those skilled in the art after reading this disclosure and that the scope of the present invention is to be determined by the following claims.

[0133] Although the invention has been described with reference to preferred embodiments, it is to be understood that modifications may be resorted to as will be apparent to those skilled in the art. Such modifications and variations are to be considered within the purview and scope of the present invention.

[0134] Representative, non-limiting examples of the present invention were described above in detail with reference to the attached drawing. This detailed description is merely intended to teach a person of skill in the art further details for practicing preferred aspects of the present teachings and is not intended to limit the scope of the invention. Furthermore, each of the additional features and teachings disclosed above and below may be utilized separately or in conjunction with other features and teachings.

[0135] Moreover, combinations of features and steps disclosed in the above detailed description, as well as in the experimental examples, may not be necessary to practice the invention in the broadest sense, and are instead taught merely to particularly describe representative examples of the invention. Furthermore, various features of the above-described representative examples, as well as the various independent and dependent claims below, may be combined in ways that are not specifically and explicitly enumerated in order to provide additional useful embodiments of the present teachings.

WHAT IS CLAIMED IS:

1. A photoacoustic spectroscopy system, the system comprising:

an acoustic cell comprising a resonator cavity, wherein the resonator cavity is configured to support a first resonance mode having a first resonant frequency, and wherein the acoustic cell is suppliable with a sample fluid;

an electromagnetic radiation unit comprising an emitter and a control circuit, wherein the emitter is configured to transmit electromagnetic radiation through the resonator cavity;

a resonant transducer unit comprising a resonant transducer and a readout system, wherein the resonant transducer is configured to support a second resonance mode having a second resonant frequency, and wherein the resonant transducer is operatively connected to the resonator cavity; and

wherein the first resonance mode and the second resonance mode are configured to be coupled in a significant coupling regime.

2. The system according to claim 1, wherein either the first resonant frequency of the resonator cavity, the second resonant frequency of the resonant transducer or both resonant frequencies are configured to be tunable such that the system can be tuned to attain at least one of (i) a closely-tuned configuration and (ii) an optimally-tuned configuration.

3. The system according to any one of claims 1 to 2, further comprising control systems that are configured to at least stabilize one or a combination of (i) the temperature of the sample fluid, (ii) the pressure of the sample fluid, (iii) the humidity of the sample fluid, (iv) the mass flow of the sample fluid through the acoustic cell, (v) the temperature of the resonant transducer, and (vi) the temperature of the acoustic cell.

4. The system according to claim 3, wherein the first resonant frequency of the resonator cavity is configured to be less than the second resonant frequency of the resonant transducer at a first temperature (T1), wherein the first resonant frequency of the resonator cavity is configured to be greater than the second resonant frequency of the resonant transducer at a second temperature (T2), and wherein $T1 \neq T2$, and wherein the control systems are configured to at

least stabilize the temperature of the acoustic cell at any chosen temperature between T1 and T2.

5. The system according to any one of claims 1 to 4, wherein the resonant transducer is selected from one or a combination of (i) an out-of-plane resonator, (ii) a tuning fork resonator, (iii) a cantilever resonator, and (iv) a diaphragm resonator.

6. The system according to any one of claims 1 to 5, wherein the acoustic cell further comprises at least one acoustic frequency filter operatively connected to the resonator cavity.

7. The system according to any one of claims 1 to 6, wherein the acoustic cell further comprises at least one transducer enclosure, and wherein each of the at least one transducer enclosure is configured to encapsulate a volume of the sample fluid surrounding at least one active surface of the resonant transducer, separating the at least one active surface of the resonant transducer from an external environment.

8. The system according to any one of claims 1 to 7, wherein the readout system is at least configured to sense the resonant transducer using a piezoelectric material.

9. The system according to claim 8, wherein the readout system further includes a pre-amplifier proximal to the resonant transducer.

10. The system according to any one of claims 1 to 9, wherein the resonant transducer unit further comprises a printed circuit board (PCB), wherein the resonant transducer is mounted on the PCB, wherein the PCB is mounted to the acoustic cell such that the resonant transducer is operatively connected to the resonator cavity, and wherein at least some of the readout system is located on the PCB.

11. The system according to any one of claims 1 to 10, wherein the acoustic cell is constructed using a monolithic design and further comprises at least one acoustic frequency filter and an acoustic port which are machined from a single piece of material.

12. The system according to claim 11, wherein the acoustic cell constructed using the monolithic design further comprises a heat exchanger machined into the acoustic cell that allows the sample fluid to reach thermal equilibrium with the acoustic cell at least before entering the resonator cavity.

13. The system according to any one of claims 1 to 12, wherein a quality (Q-)factor of the second resonance mode of the resonant transducer in vacuum is configured to be substantially larger than a free Q-factor of the second resonance mode of the resonant transducer in the sample fluid.

14. The system according to any one of claims 1 to 13, wherein the Q-factor of the resonant transducer in vacuum is configured to be greater than 1000.

15. The system according to any one of claims 1 to 14, wherein the coupling strength (Ω) between the resonator cavity and the resonant transducer is greater than or equal to the threshold value of $\sqrt{\frac{2}{\sqrt{Q_1 Q_2}}}\,\omega_0$.

16. The system according to any one of claims 1 to 15, wherein the resonant transducer has a Q-factor, Q_2, which is greater than or equal to the threshold value of $\frac{2{\omega_0}^3\beta^2 m_2}{k_B T}$, wherein the readout system has a noise amplitude spectral density of β, and wherein both the sample fluid in the resonator cavity and the resonant transducer have a temperature, T.

17. The system according to any one of claims 1 to 16, wherein the acoustic cell further comprises at least one acoustic port.

18. The system according to any one of claims 1 to 17, wherein the acoustic cell further comprises at least one optical window.

19. The system according to any one of claims 1 to 18, wherein the emitter comprises one from a selection of (i) a quantum cascade laser (QCL), (ii) a continuous wave (CW) laser, (iii) a pulsed laser, (iv) an interband cascade laser (ICL), (v) a vertical-cavity surface-emitting laser (VCSEL), and (vi) a thermal emitter.

20. The system according to any one of claims 1 to 19, wherein the control circuit is configured to at least modulate the output of the emitter, wherein modulating the output of the emitter comprises modulating one or a combination of (i) an emission wavelength of electromagnetic radiation (ii) an emission intensity of electromagnetic radiation (iii) a pulse repetition rate of electromagnetic radiation, and (iv) a patterned train of pulses of electromagnetic radiation.

21. The system according to any one of claims 1 to 20, wherein the readout system further

comprises a pre-amplifier, wherein the pre-amplifier comprises one of (i) a differential charge amplifier, (ii) a differential transimpedance amplifier, (iii) a single-ended voltage amplifier, (iv) a single-ended charge amplifier, (v) a single-ended transimpedance amplifier, and (vi) an instrumentation amplifier.

22. The system according to any one of claims 1 to 21, wherein the readout system is configured to at least convert a displacement of the resonant transducer into one or more electrical signals and amplify and process the one or more electrical signals.

23. The system according to any one of claims 1 to 22, wherein the acoustic cell is configured to be sealed with the sample fluid contained within.

24. The system according to any one of claims 1 to 23, wherein the acoustic cell further comprises at least one port connected to a fluid handling system.

25. The system according to claim 24, wherein the fluid handling system is at least partly composed of low adsorption tubing.

26. A method for performing photoacoustic spectroscopy, the method comprising:

providing a photoacoustic spectroscopy system as described in any one of claims 1 to 25;

operating the emitter in a modulated mode, such that target analyte molecules in the sample fluid of the resonator cavity experience periodic absorption and heating at an operating frequency;

configuring the acoustic cell such that the periodic heating induces an acoustic pressure wave with an amplitude proportional to a concentration of the target analyte molecules in the sample fluid of the resonator cavity, exciting the coupled resonator cavity and resonant transducer modes;

detecting an excitation of the excited coupled resonator cavity and resonant transducer modes by measuring the displacement of the resonant transducer in a frequency-dependent basis with the readout system; and

outputting via the readout system a signal representative of the concentration of target analyte molecules.

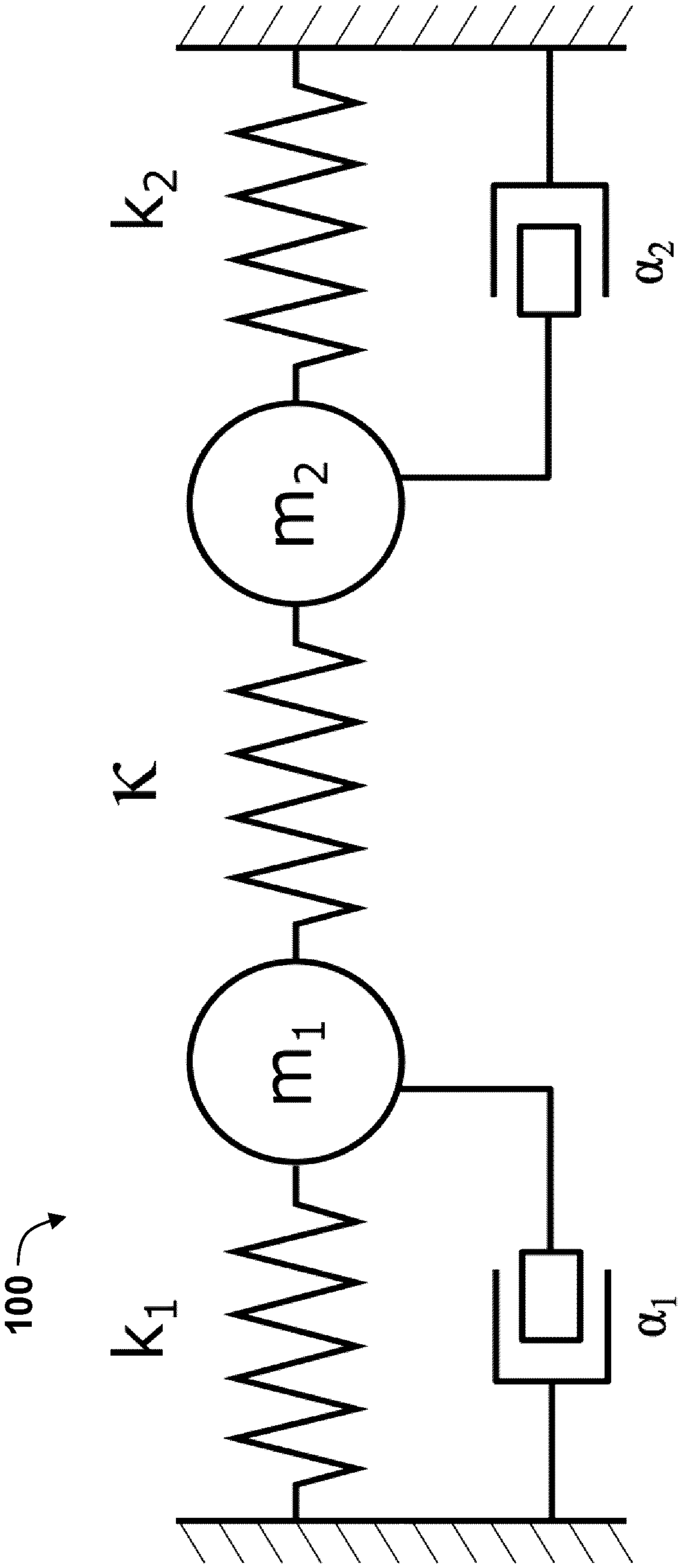


FIG. 1A

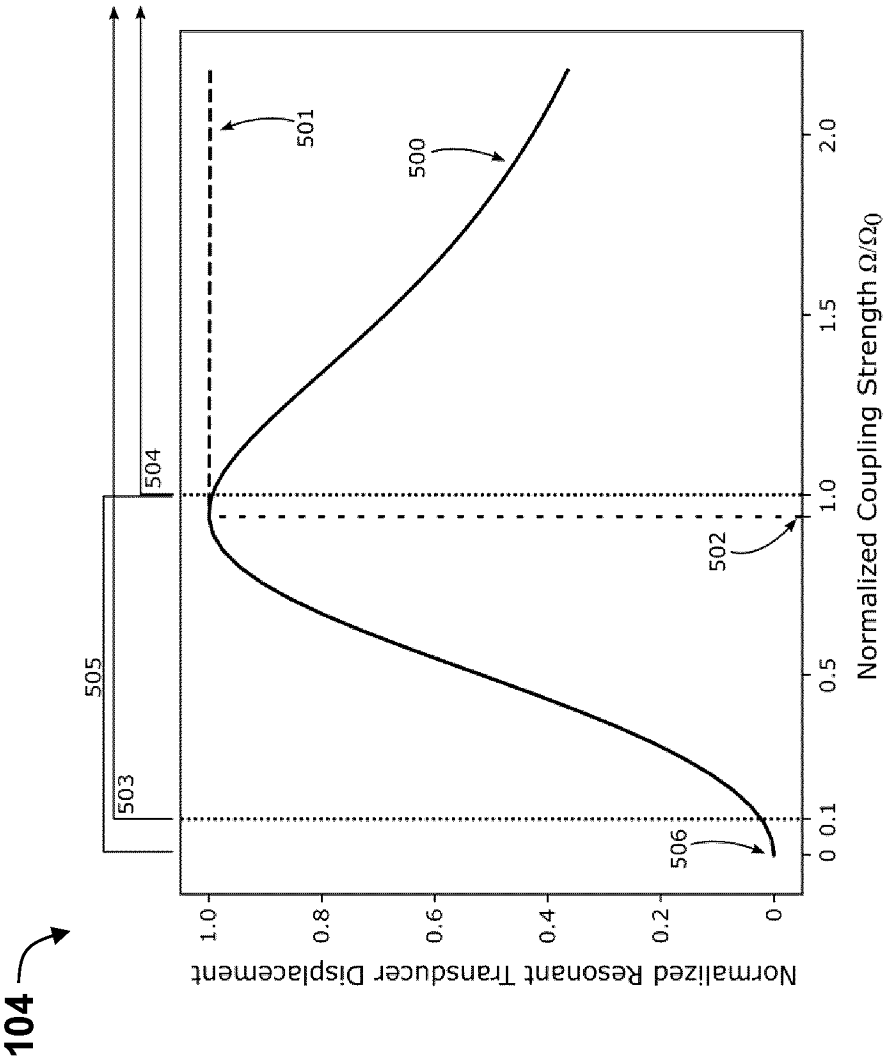
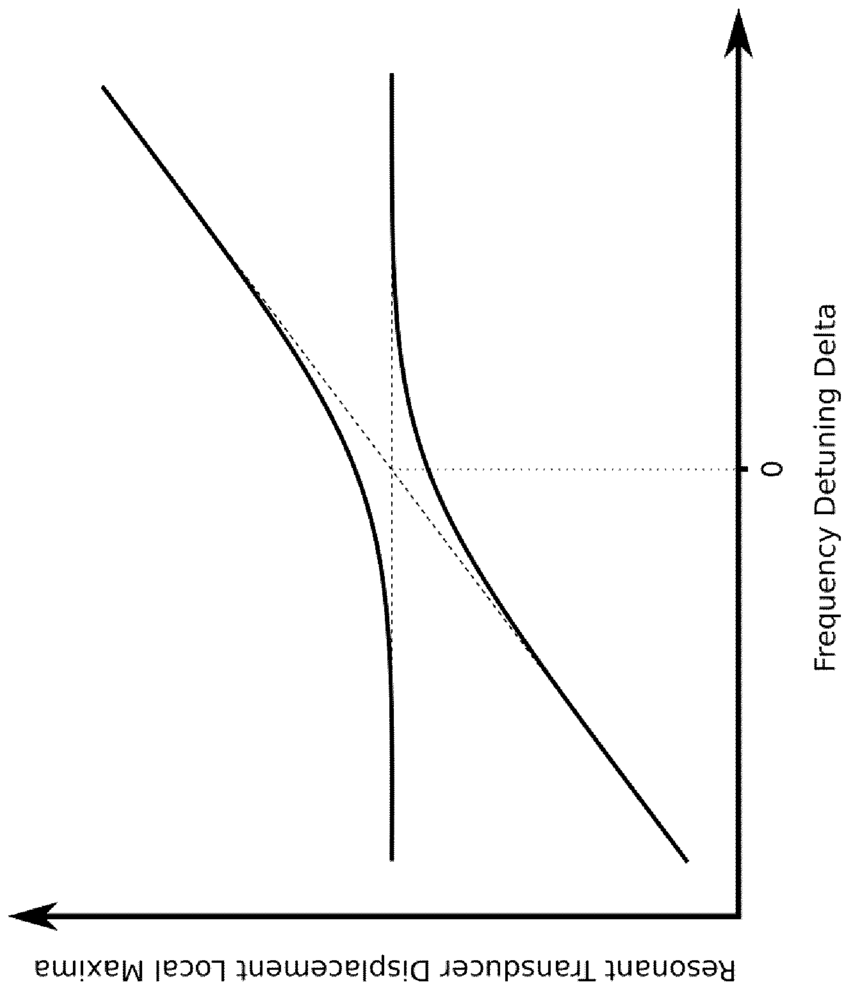
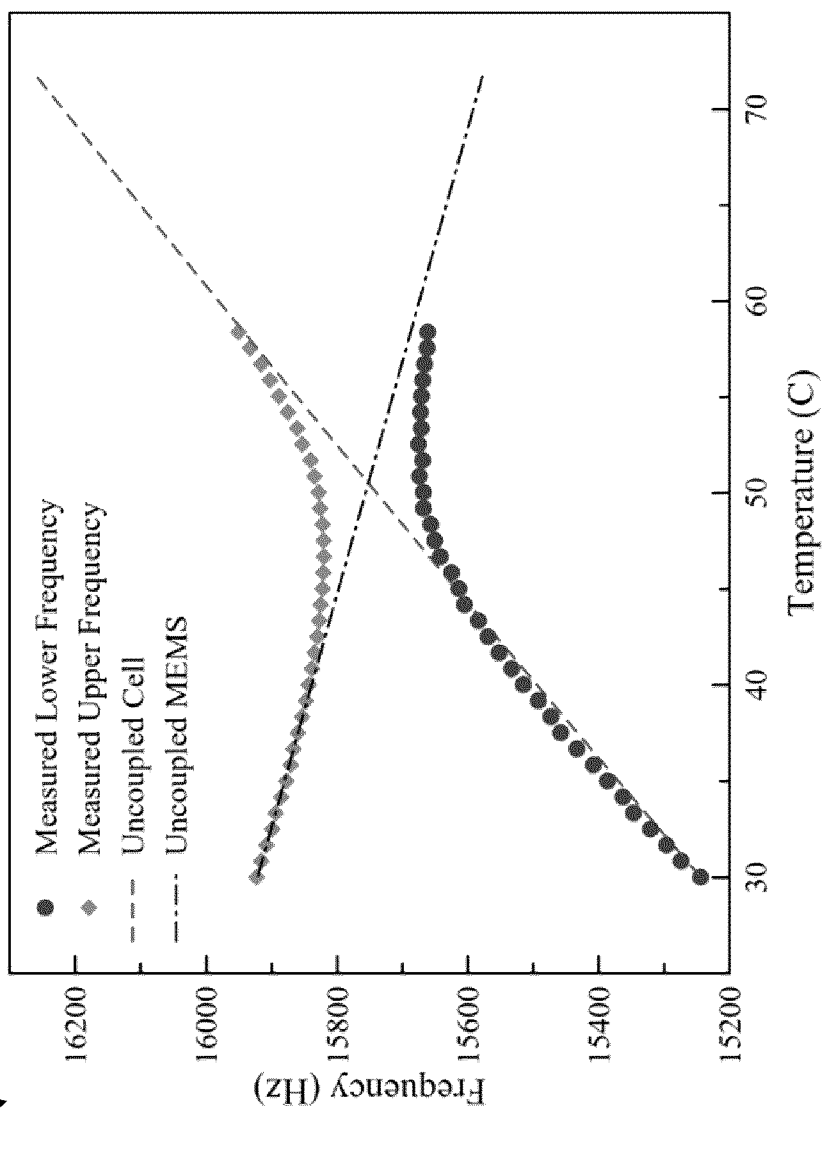

104
Normalized Resonant Transducer Displacement
1.0
0.8
0.6
0.4
0.2
0
0
0.1
0.5
1.0
1.5
2.0
Normalized Coupling Strength Ω/Ω0
500
501
502
503
504
505
506

FIG. 1B


Resonant Transducer Displacement Local Maxima
Frequency Detuning Delta
0

106

FIG. 1C


Measured Lower Frequency
Measured Upper Frequency
Uncoupled Cell
Uncoupled MEMS
Frequency (Hz)
16200
16000
15800
15600
15400
15200
Temperature (C)
30
40
50
60
70

107

FIG. 1D

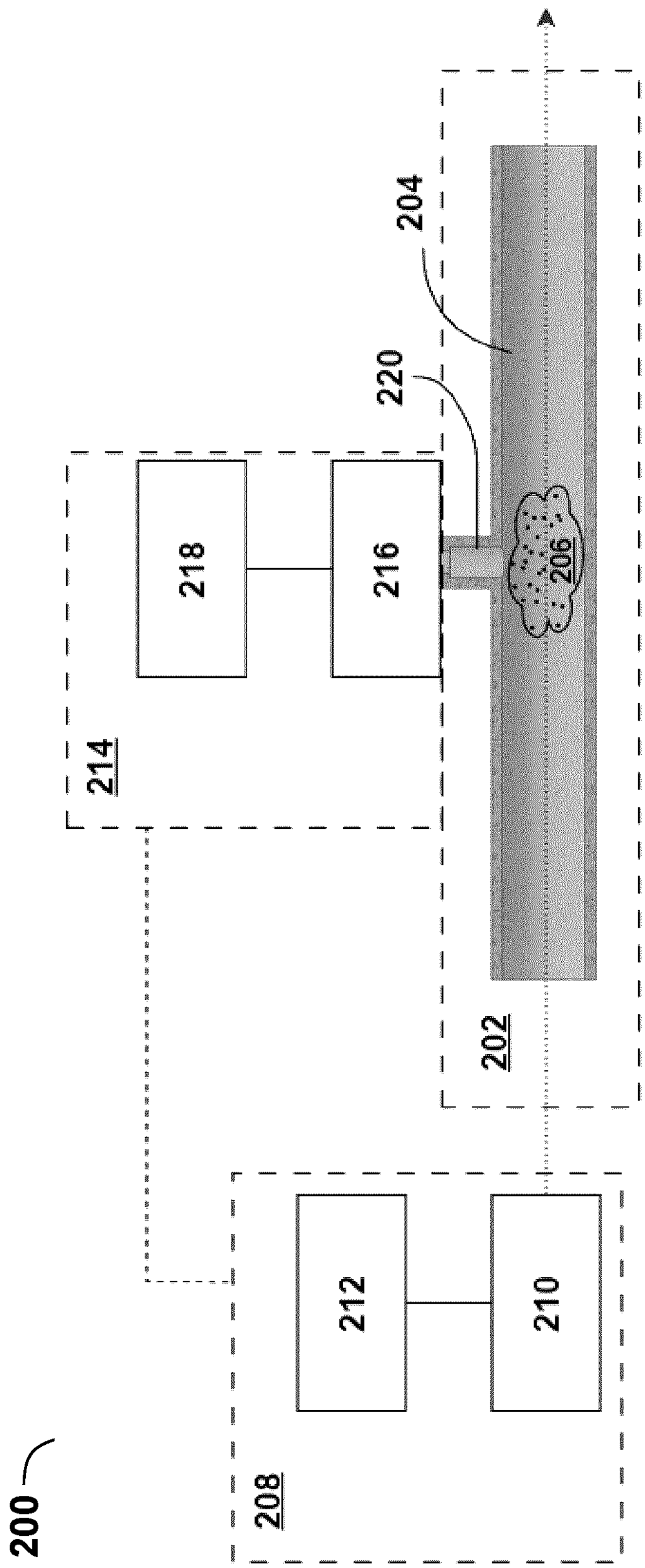


FIG. 2A

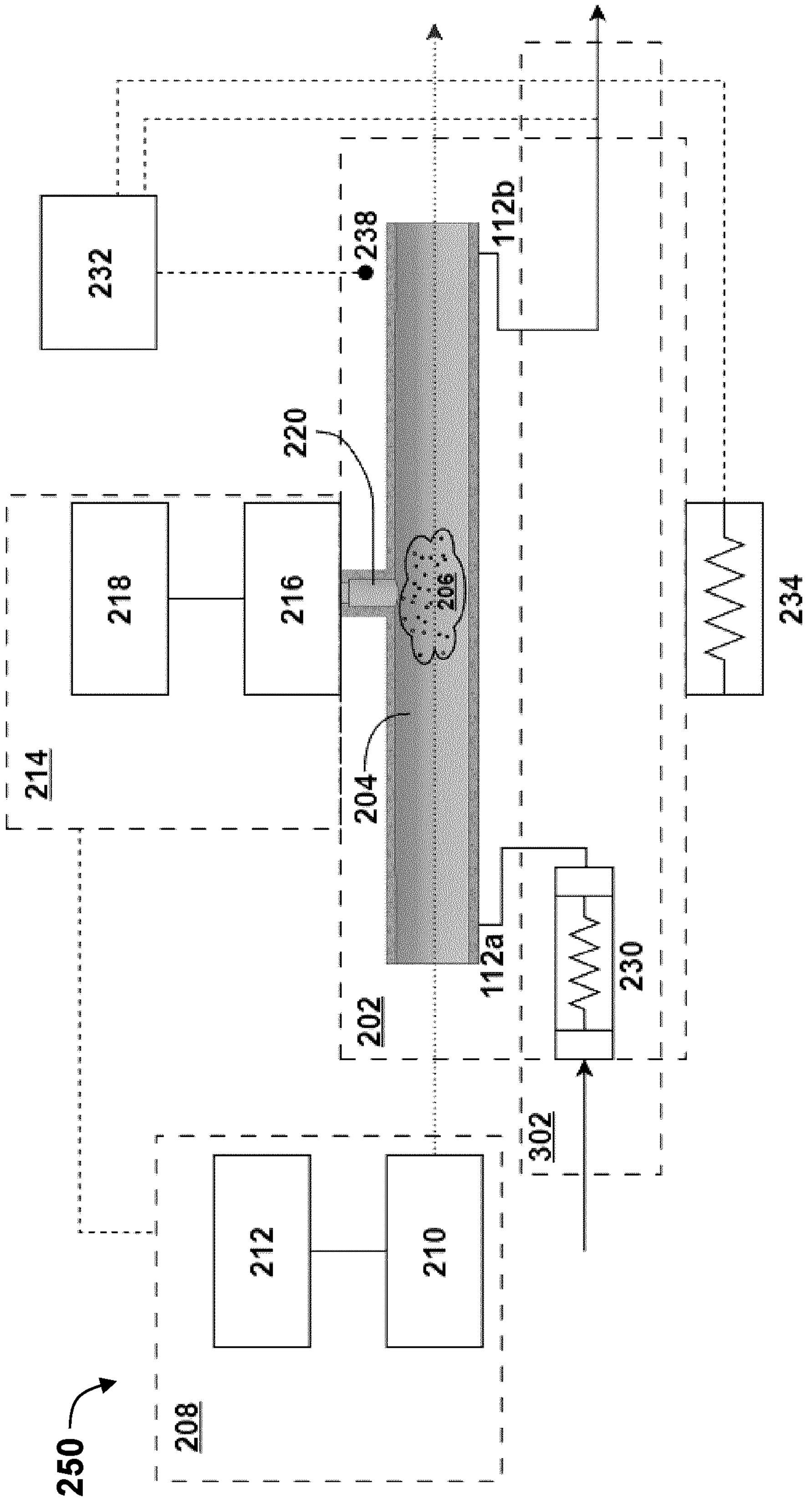

232
238
112b
220
218
216
206
214
204
234
202
112a
230
302
212
210
208
250

FIG. 2B

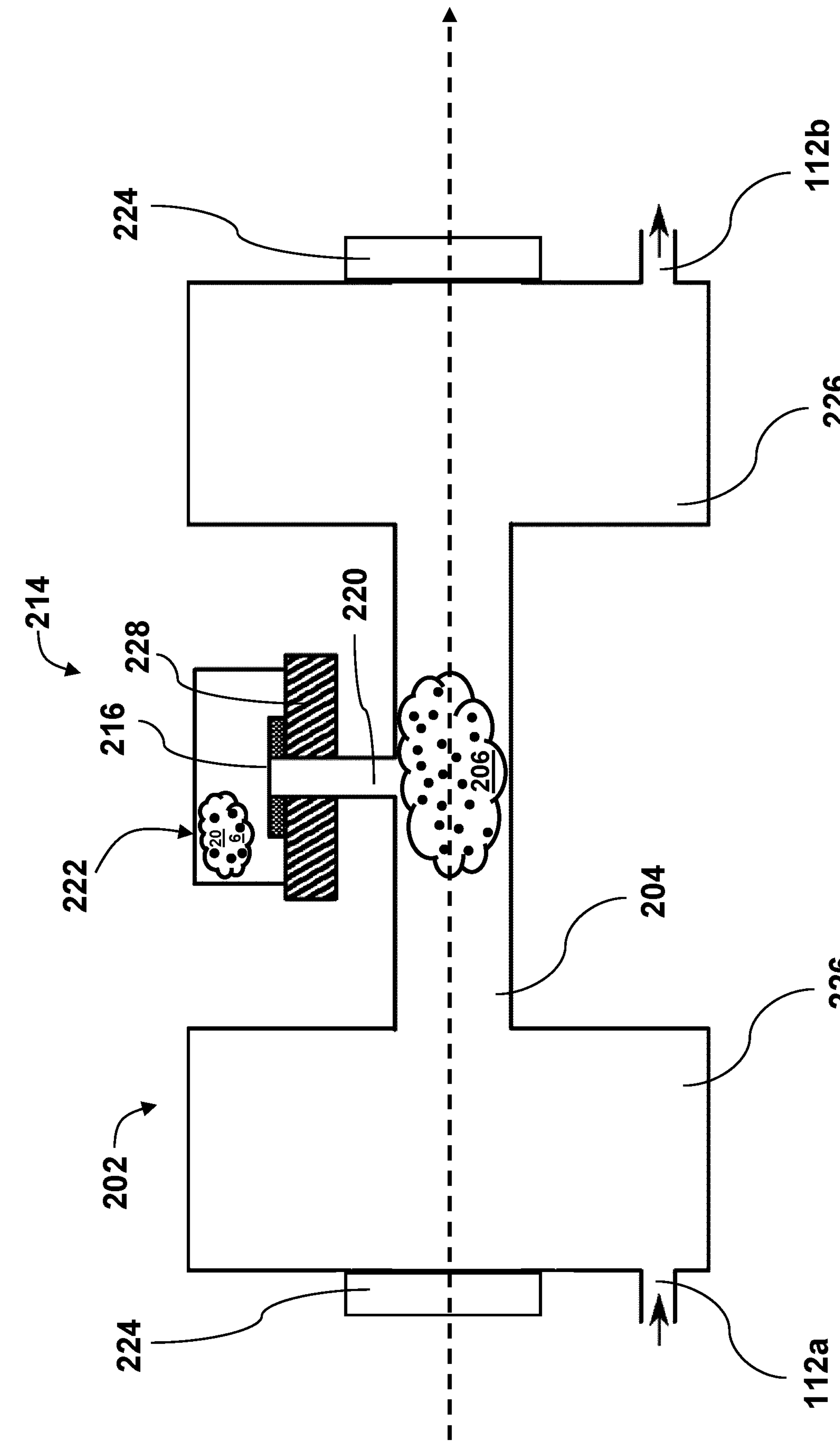


FIG. 3

400

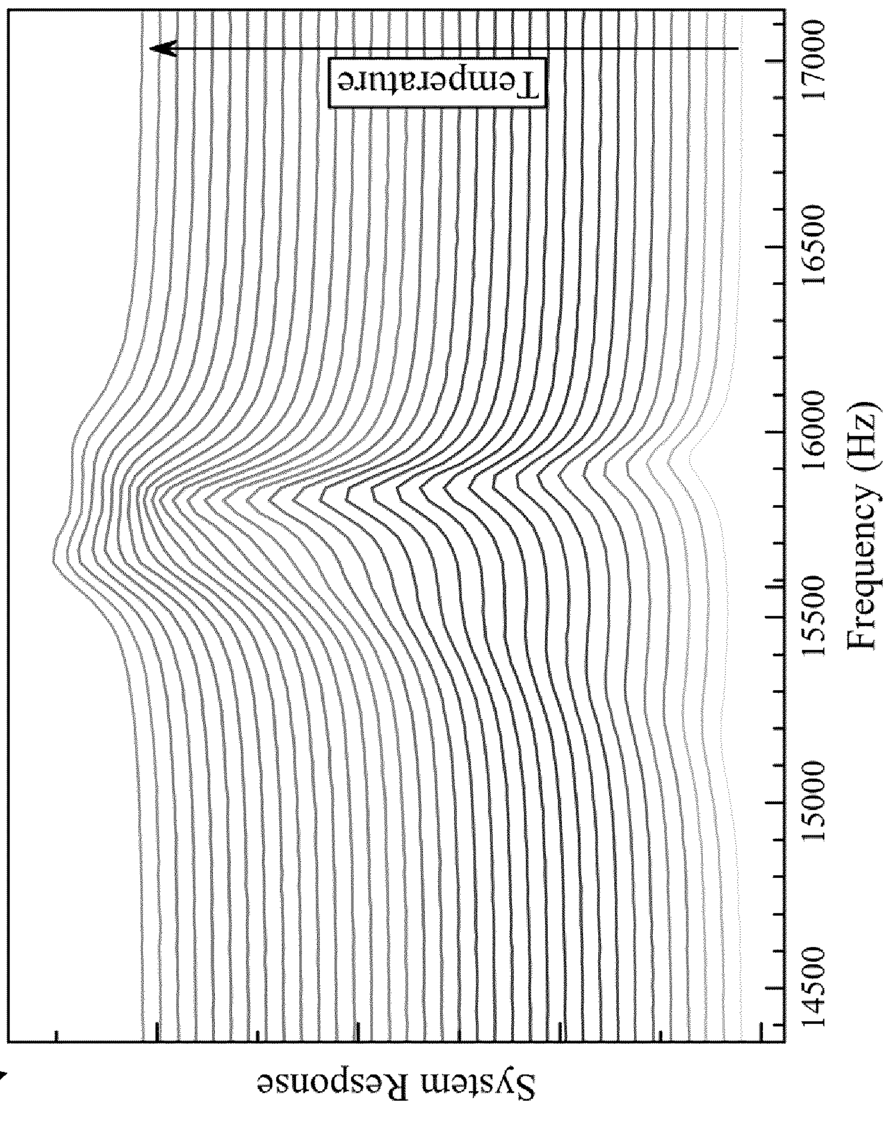

System Response
Frequency (Hz)
14500
15000
15500
16000
16500
17000
Temperature

FIG. 4

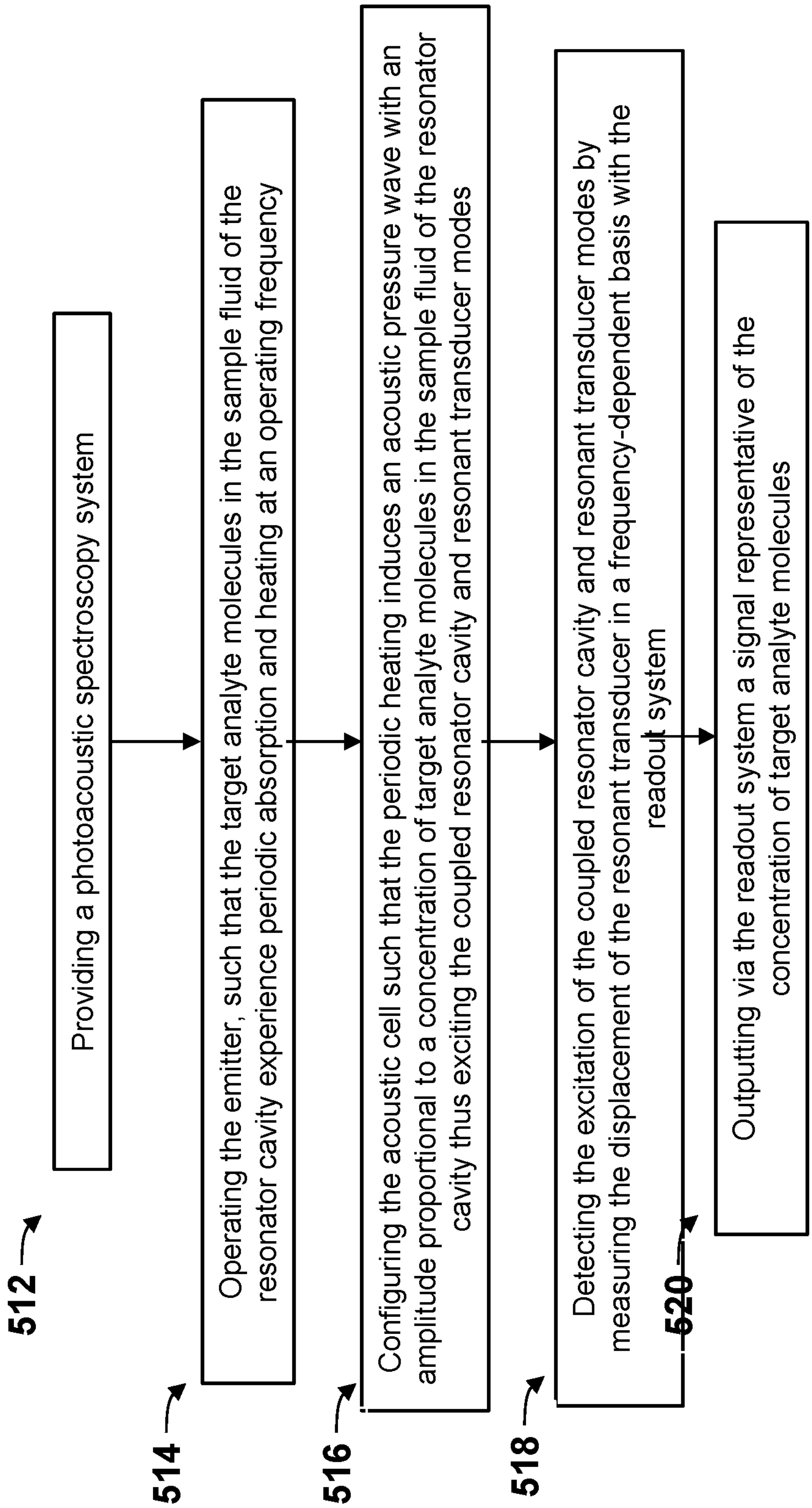

512
Providing a photoacoustic spectroscopy system
514
Operating the emitter, such that the target analyte molecules in the sample fluid of the resonator cavity experience periodic absorption and heating at an operating frequency
516
Configuring the acoustic cell such that the periodic heating induces an acoustic pressure wave with an amplitude proportional to a concentration of target analyte molecules in the sample fluid of the resonator cavity thus exciting the coupled resonator cavity and resonant transducer modes
518
Detecting the excitation of the coupled resonator cavity and resonant transducer modes by measuring the displacement of the resonant transducer in a frequency-dependent basis with the readout system
520
Outputting via the readout system a signal representative of the concentration of target analyte molecules

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2024/050827

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***G01N 29/14*** (2006.01)

CPC: G01N 29/14 (2013.01), G01N 2291/014 (2013.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Keywords applied across all IPCs and CPCs

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Questel-Orbit, Scopus, IEEE Xplore, Google Scholar: photoacoustic, spectroscopy, coupl*, coupling regime, reson*, electromagnetic, EM, emit*, oscillator, double resonant, dual resonant, freq*, Double Resonant Photoacoustic Sensor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 10,908,129 B2 (BLANCHARD et al.) 2 February 2021 (02-02-2021) *the entire document, particularly the abstract, column 2 line 26-column 3 line17, column 3 lines 52-57, column 8 lines 27-65, column 19 line 47-column 20 line 41, fig. 1A*	1-26
A	LEE et al., "*Coupled acoustic resonance for wave control and sensing*". Frontiers in Physics, 12 October 2022 (12-10-2022),pp. 01-18, DOI: 10.3389/fphy.2022.998253 *the entire document, particularly the Abstract, 3.3 Exceptional point and rabi splitting, 3.4 Fano resonance in weakly coupling regime, 4 Conclusions and outlook, fig. 2, 4-6*	1-26
A	RÜCK, "*Development, characterization and miniaturization of a trace gas detection system for NO2 in air based on photoacoustic spectroscopy*". University of Regensburg, 2017,pp. 57-60 * the entire document, particularly 1.3.3 Double-resonant systems"	1-26

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"D"	document cited by the applicant in the international application	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"E"	earlier application or patent but published on or after the international filing date	"&"	document member of the same patent family
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
10 September 2024 (10-09-2024)

Date of mailing of the international search report
22 October 2024 (22-10-2024)

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Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US10908129B2	02 February 2021 (02-02-2021)	US2018196012A1	12 July 2018 (12-07-2018)
		US2021208108A1	08 July 2021 (08-07-2021)
		US2023358709A1	09 November 2023 (09-11-2023)