Resonant optothermoacoustic detection: technique for measuring weak optical absorption by gases and micro-objects

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We report a laser spectroscopy technique for detecting optical absorption in gases and micro-objects via linked thermal effects and by using a sharp mechanical resonance in a quartz crystal. The performance of this technique is studied using near-IR diode lasers and two gases, pure CO_2 and C_2H_2 diluted in nitrogen. A 7.3×10^{-8} cm^{-1} $W/(Hz)^{1/2}$ noise equivalent sensitivity to absorption in gases is demonstrated. Based on experimental results, it was estimated that 10^{-8} fractional absorption of optical radiation by a micro-object deposited on a thin transparent fiber can be detected. © 2010 Optical Society of America

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Techniques of analytical spectroscopy rely on different linear and nonlinear effects resulting from radiation–matter interaction, which include fluorescence, Raman scattering, radiation extinction, heating of the media, and acoustic waves accompanying such heating. Most spectroscopic chemical analyzers use optical absorption for quantifying chemical composition of the sample. The direct approach to absorption measurements is determining the ratio of optical power exiting the analyzed sample to the power of incident radiation. This method is experimentally challenging, because it involves measuring a small difference of two large values. There are a number of background-free techniques based on the effects that absorbed radiation induces in media. Probably the most widely used technique of this kind is photoacoustic spectroscopy (PAS), based on the detection of sound waves generated in a medium upon absorption of the modulated optical radiation. Other approaches include photothermal spectroscopy, where a change of refraction index of a medium is measured, and optothermal spectroscopy, where excited (hot) molecules are directly detected by means of a thermal sensor, such as a pyroelectric detector or bolometer.

Optothermal detection (OTD) was first proposed and theoretically analyzed by Rosengren in 1972 [1]. The author suggested the use of a pyroelectric material to detect temperature variations induced by the absorbed radiation and estimated the sensitivity to be "0.01 ppm for typical parameter values of available tunable lasers and pyroelectric materials and for typical molecular gases." The first experimental demonstration of OTD was performed by Hartung and Jurgeit in 1978 [2]. In that work, the authors noticed an important difference in OTD compared to PAS, namely its ability to detect absorbed optical energy at low gas pressures. OTD does not require thermalization of the absorbed optical energy. Instead, optically excited molecules can release their energy directly to the thermal detector in a collision with its surface. Because of this property, OTD was most often used to detect absorption by jet-cooled molecules [3,4]. OTD was also used to achieve sub-Doppler resolution in the linear absorption mode by detecting molecules with a mechanically filtered velocity distribution [5].

In this Letter, we describe a kind of optothermal detector where a mechanical (acoustic) resonance in the detector is used to amplify the signal. This technique will be called resonant optothermoacoustic detection (ROTADE). A ROTADE sensor functionally consists of three parts: (i) a *receiver* collecting the thermal energy and transforming it to mechanical motion, (ii) a *resonator* enhancing this motion, and (iii) a *transducer* converting the mechanical vibration of the resonator into an electrical signal.

Two practical implementations of the ROTADE sensor used in our experiments are shown in Fig. 1. For absorption spectroscopy of gases [Fig. 1(a)], the quartz tuning fork (QTF) performs all three functions listed above. The excited molecules diffusing from the laser beam area to the QTF surface produce a periodic local heating of the quartz crystal. A subsequent thermal expansion of the heated region forces a resonant vibration of the QTF, which, in turn, results in the charge separation on its electrodes due to the piezoelectric effect. A sensor for probing micro-objects [Fig. 1(b)] uses a thin transparent fiber

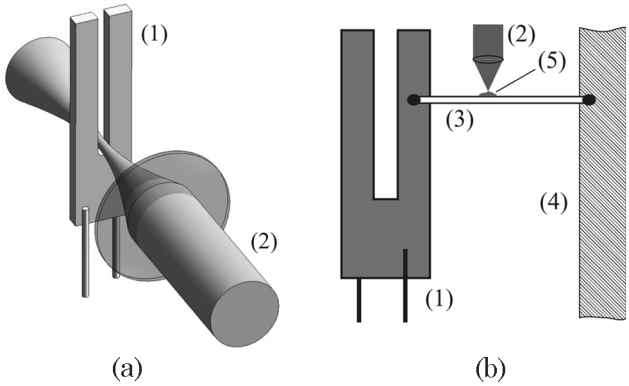

Fig. 1. (Color online) (a) QTF used as a ROTADE sensor to detect optical absorption in gases. (b) ROTADE sensor for detecting optical absorption by micro-objects: (1), QTF; (2), excitation radiation; (3), thin transparent fiber; (4), substantial wall; (5), micro-object.

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as a receiver, stretched between a QTF and a rigid wall, while the QTF acts as a resonator and a transducer. This configuration can be used for detecting optical absorption in gases as well, if the excitation radiation avoids contact with the fiber or the QTF.

Experiments on gas sensing using the ROTADE technique were performed in a similar manner to QEPAS [6,7], because the ROTADE sensor in Fig. 1(a) uses QTF as its key element. Radiation of a near-IR diode laser was delivered to a gas cell enclosing QTF by means of a single-mode fiber and a focuser coupled to it to form a beam waist of $\sim$15 μm diameter. The focuser was mounted on a computer-controlled 3D translation stage with a 1 μm resolution. The laser wavelength was modulated at half the resonant frequency f_0 of the QTF, and detection was performed at f_0 ($2f$ wavelength modulation spectroscopy). We used two kinds of gases for this study: pure CO_2 and 0.5% C_2H_2 in N_2. The CO_2 was excited at 6361.25 cm^{-1} in its $3\nu_1 + \nu_3$ band. The laser power delivered to the sensor was measured to be 30.7 mW, and the absorption coefficient for the selected line at 1 atm is 1.37×10^{-3} cm^{-1}, according to HITRAN data. Acetylene was excited at 6523.879 cm^{-1} with 37.5 mW laser power; the absorption coefficient at 1 atm for 0.5% in N_2 is 5.3×10^{-3} cm^{-1}. These high absorption coefficients ensured a high signal-to-noise ratio of the ROTADE signal for detailed characterization of the sensor; at the same time, they are sufficiently low to neglect the laser attenuation for $\sim$1 cm optical path across the gas cell.

Both acoustic and thermal waves are generated following the optical excitation of the gas molecules. Therefore, whether the QTF acts mostly as QEPAS or ROTADE sensor is determined by the vibrational-to-translational (V-T) relaxation and the position of the laser beam. Figure 2 shows two examples of the observed signal as a function of such conditions. At 300 Torr, V-T relaxation of excited CO_2 molecules is sufficiently fast to produce a strong photoacoustic signal, distributed in agreement with theoretical predictions [8]. The thermal wave decays too fast at this pressure to result in an observable ROTADE signal. At low (20 Torr) pressure, CO_2 produces a strong ROTADE signal, which can be readily recognized by the distribution with a maximum near the QTF base, where the strain corresponding to the natural oscillation of the QTF is highest and hence the impact of the local heating on the QTF motion is the strongest. The photoacoustic signal is weak (V-T relaxation time exceeds the modulation period), and there are areas of destructive interference between the optothermal and photoacoustic actions. These observations emphasize the short-range nature of the thermal waves [9]. A flat thermal wave decays e times at a distance $L(\omega) = \sqrt{2D_t/\omega}$, where D_t is the thermal diffusivity. For gases, D_t is equal to the diffusion coefficient. For CO_2 at 20 Torr and a QTF resonant frequency, $f_0 = 32.8$ kHz, $L(2\pi f_0) \approx 67$ μm. The thermal wavelength is $\lambda_{th} = 2\pi\, L(\omega)$.

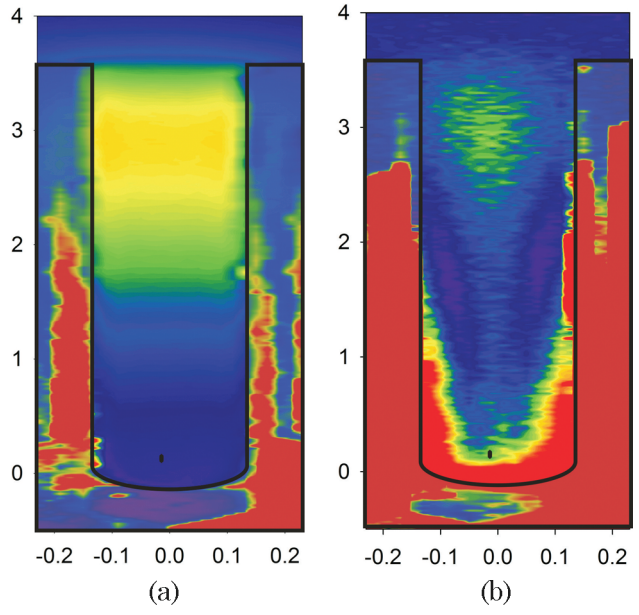

Fig. 2. Maps of the detected signal from the QTF as a function of the laser beam position, scale in millimeters, with pure CO_2. The QTF area is shaded. (a) 300 Torr pressure and QEPAS dominates; (b) 20 Torr, ROTADE dominates, and the regions of destructive interference between optothermal and photoacoustic signals are visible.

Figure 3 shows the observed signal in the acetylene mixture at 5 Torr when the incident laser beam is on the symmetry plane of the QTF. Three areas are distinguishable here:

1. From 0 to 0.3 mm, the signal is mostly caused by the thermal wave acting on the center of the QTF saddle. A plane-wave approximation works well in this region, explaining the exponential decay accompanied by the linear phase change.
2. From 0.3 to 2.0 mm, the signal is mostly caused by the thermal wave acting on the prongs of the QTF. The distance from the prongs does not change, and therefore the phase stays almost constant. The signal decreases linearly, because in the static approximation a prong is bent to a certain angle at the point of the heat application and the deviation of its tip is proportional to the distance from that point to the tip.

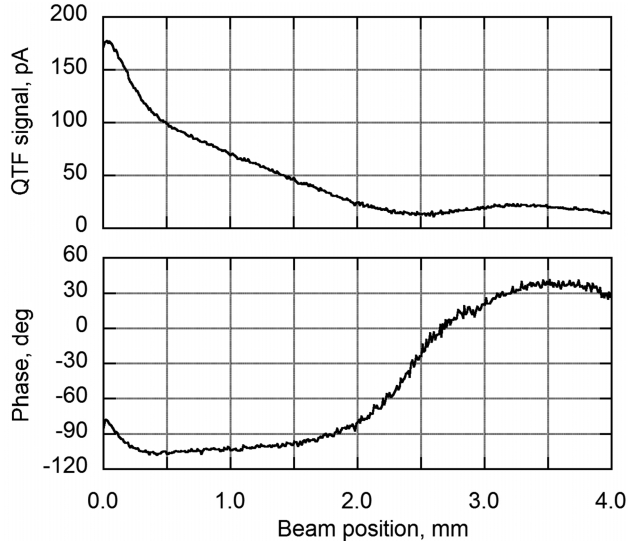

Fig. 3. Detected QTF signal as a function of the beam distance from the QTF saddle when the beam is on the symmetry plane of the QTF; 0.5% C_2H_2 in N_2, 5 Torr total pressure.

3. From 2.5 mm on, the photoacoustic effect dominates, and the phase of the resulting signal is almost constant but different from the phase of the thermal effect.

Similar to QEPAS, the noise in ROTADE is fundamentally determined by the random thermal motion of the QTF [7]. The signal grows when the optically excited gas region approaches the crystal; the minimum distance is determined by the beam waist size and the condition that the QTF heating by stray radiation is weaker than its heating by gas molecules. For a ROTADE sensitivity estimate, we selected a beam position closest to the QTF saddle without direct illumination of the crystal. Using HITRAN data for the 6361.25 cm^{-1} absorption peak of CO_2, we estimated the best sensitivity to absorption observed in our experiments in pure CO_2 to be 16.4×10^{-8} cm^{-1} $W/(Hz)^{1/2}$ at 5 Torr total gas pressure, the lowest pressure tested. For a 0.5% C_2H_2:N_2 mixture, this number is 7.3×10^{-8} cm^{-1} $W/(Hz)^{1/2}$, also achieved at 5 Torr. In terms of concentration, the best sensitivity of 0.26 ppm $W/(Hz)^{1/2}$ was observed at 40 Torr because of a higher peak absorption coefficient at higher pressures. The detection sensitivity in terms of concentration is expected to be better in the mid-IR spectral region, where Doppler broadening is less. For instance, ROTADE may appear superior to QEPAS for NO sensing at 1900 cm^{-1} in dry gases, where V-T relaxation is slow but the peak absorption coefficient at 40 Torr is only 20% less than at atmospheric pressure.

For evaluation of the sensor sketched in Fig. 1(b), a 25 μm diameter, 5-mm-long glass fiber (normally used in fiber illumination bundles) was stretched between a QTF and a rigid metal frame. The calculated force constant of this fiber piece was 5800 N/m, much lower than the effective QTF force constant of 26800 N/m referred to its tip. Measurements were performed in ambient air. After assembly of this sensor, the QTF resonant frequency changed from 32,760 to 33,550 Hz, and its Q factor from 13,000 to 6400. A pigtailed diode laser with $\lambda =$ 1570 nm was used. The incident optical power was sine wave modulated from 0 to 40 mW at the QTF resonant frequency. The laser beam was shaped to have a 200 μm diameter ($1/e^2$ FWHM power density level, Gaussian distribution) when crossing the fiber, resulting in a 0.18 fraction of the laser power to be obstructed by the fiber.

While scanning the laser beam along the fiber, it was noticed that the lowest signal appearing at different parts of the fiber is consistently at the same level and having the same phase. We attribute this signal to optical absorption of the fiber proper, while higher signals come from accidental contamination of the fiber surface. Signals from contaminated portions of the fiber showed a phase delay up to 1.4 μs, indicating heat propagation from the fiber surface to its core before it expands. Based on the glass data from the manufacturer and geometric overlap of radiation and fiber, we estimated the fraction of radiation absorbed by the clean fiber as 1.8×10^{-6}. This absorption resulted in 3.3×10^{-10} A amplitude current generated by the QTF, compared to 2.2×10^{-13} $A/(Hz)^{1/2}$ rms observed when the laser was turned off, in agreement with the calculated QTF thermal noise. Thus, the sensitivity to absorption by an object attached to the fiber will be limited by the fundamental QTF thermal noise if the laser power stability is $<10^{-3}$, or if the signal is normalized to the optical power measured to such an accuracy. Assuming that the thermal noise limit is achieved in a bandwidth of 1 Hz, and a 20 mW average power laser beam is focused to a 100% overlap with the fiber, the minimum fractional absorption by an attached micro-object that can be achieved with ROTADE is estimated to be 10^{-8}. It is feasible that the geometry of a ROTADE sensor can be optimized for improved performance.

The sensor shown in Fig. 1(b) can be used for probing absorption in gases as well, if the laser radiation does not overlap with the fiber but propagates in close proximity. In this case, a material with an optimum combination of nonoptical properties can be selected. We derived that better performance is achieved for a higher value of a dimensionless property $A = \frac{E\beta}{c\rho}$, where E is the Young modulus, β is a thermal expansion coefficient, c is specific heat, and ρ is the material density. From a number of common materials, gold has the highest $A = 0.445$, compared to a glass fiber with $A = 0.254$. A thinner fiber or film can be stretched directly across the tips.

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