

Recent Advances in Resonant Optothermalacoustic Detection

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ABSTRACT

Optothermal detection is a spectroscopic technique where the energy input into a gas or other media caused by absorption of optical radiation is measured directly by means of a thermal detector.¹⁻³ A fraction of the absorbed energy is transported to the thermal detector by heat conduction or molecular diffusion. In this work a conventional thermal sensor was replaced by a quartz tuning fork (QTF), and the optical power input into the gas was modulated at the QTF resonant frequency. We call this approach “resonant optothermoacoustic detection”, or ROTADE. The same experimental setup can be used to conduct a closely related technique, quartz enhanced photoacoustic spectroscopy (QEPAS).⁴ QEPAS relies on energy transfer from the initially excited molecular vibrational state to the translational degrees of freedom. In some cases this process is too slow to follow the modulation required for QEPAS. In other cases, the resonant energy transfer can result in vibrational excitation of nitrogen, which relaxes very slowly. ROTADE, on the other hand, detects the energy delivered by molecules even if this energy is still in the form of vibrational excitation. The molecules will then release their energy to the QTF upon collision with its surface. Experimental investigations of ROTADE and its comparison with QEPAS were performed in pure CO₂ and 0.5% acetylene in N₂ using near-infrared diode lasers. A fiber collimator and a refocusing lens were used to focus the laser to a $\approx 15 \mu\text{m}$ diameter waist. Its position was scanned in the QTF plane using a 3D translation stage with computer-controlled actuators. Different QTFs were used to compare the effect of modulation frequency on the ROTADE signal.

1. INTRODUCTION

Spectroscopic instruments allow access to information about atoms and molecules. For example, wavelength measurements determine a system’s energy levels, line intensity measurements yield the transition probabilities, and Zeeman and Stark splittings help extract information about the magnetic and electric moments as well as the momentum couplings in atoms or molecules. Often selecting a particular phenomena can also allow for the abundance of a particular species to be determined. In most applications the attenuation of light due to absorption is used to determine the concentration of the analyte. When the absorption coefficient $\alpha(\omega)$ and path length L are small, such that $\alpha L \ll 1$, then detectable concentration is

$$N_i \geq \frac{\Delta I}{I_0 L \sigma_{ik}}, \quad (1)$$

where σ_{ik} is the absorption cross section and $\Delta I/I_0$ is the smallest measurable difference in the intensity of the transmitted light. Measuring precisely the small difference ΔI between large values is difficult. Thus measurements techniques that only generate a signal in the presence of the analyte are attractive. Notable examples of background free detection include Faraday Rotation Spectroscopy⁵ (FRS), Photoacoustic Spectroscopy⁶ (PAS), and Optothermal Detection¹ (OTD).

In PAS the laser source excites the ro-vibrational states, and through collisions with other molecules and the walls of the gas cell, the energy is transferred to translational motion. The resulting pressure wave is then detected by a sensitive microphone. The signal can be enhanced by using a gas cell which acts as an acoustic resonator. Another technique uses a quartz tuning fork as resonant transducer instead of the resonant cavity.⁷ The quartz tuning fork (QTF) has a resonant frequency $f \approx 32 \text{ kHz}$ which has several advantages including reducing pick up of mechanical vibrations and $1/f$ noise, while the high Q factor means that only frequency components in a narrow spectral band produce significant excitations of the transducer.⁷ However, if the mean

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relaxation time of the ro-vibrational to translational state (V-T relaxation rate) is long compared to $1/f$ then the acoustic wave becomes severely attenuated.

OTD does not require the thermalization of the absorbed optical energy. The molecules transfer their energy directly into the transducer through collisions with its surface. Recently it was shown that the same transducer that was used in QEPAS could be used as a mechanically resonant optothermal detector.⁸ Resonant optothermal acoustic detection (ROTADE) occurs when the optically excited gas molecules impact the wall of the QTF and cause localized heating. The QTF deforms due to the localized heating and the piezo-electric quartz converts the deformation into an electrical signal. ROTADE out performs QEPAS for gases with slow V-T relaxation rates, and when the pressure is low and collision between molecules are less frequent.⁸

2. THERMAL WAVE

It is informative to consider a simple model that describes the thermal wave. First recall that the laser beam is frequency modulated at the resonant frequency of the tuning fork $f = \omega/2\pi$ [s⁻¹]. Thus when the frequency of the laser coincides with the maximum absorption, molecules are excited to higher ro-vibrational states and diffuse from where they were excited. So, consider the classical diffusion equation, which is the same as the conductive heat equation in a isotropic medium, with the addition of a harmonic driving term.

$$\nabla^2 \Psi(\vec{r}, t) - \frac{1}{D_t} \frac{\partial}{\partial t} \Psi(\vec{r}, t) = -\frac{1}{k} q(\vec{r}, t) e^{i\omega t}, \quad (2)$$

where D_t is the thermal diffusivity [m²s⁻¹], k is the thermal conductivity [Wm⁻¹K⁻¹], and q is the thermal source's volumetric density [Wm⁻³]. Due to the periodic nature of the driving force, we can assume oscillatory solutions of the form $\Phi(\vec{r}, \omega) e^{i\omega t}$. It is possible to neglect the ambient temperature (Ψ_{amb}) and any small DC offset ($\Psi_{\text{DC}}(\vec{r})$) to the temperature of the gas, because the QTF will not generate a signal in response to these factors. Taking a Fourier transform of Equ. 2 results in a quasi-Helmholtz type problem.

$$\nabla^2 \Phi(\vec{r}, \omega) - \sigma(\omega)^2 \Phi(\vec{r}, \omega) = -\frac{1}{k} Q(\vec{r}, \omega), \quad (3)$$

where $\sigma(\omega) = (1 + i) \sqrt{\omega/2D_t}$ [m⁻¹] is the dispersive complex wave number.⁹ From Equ. 3 a simple plane wave solution of the form $\Phi(x, \omega) = A e^{-\sigma x}$ can be assumed, where $A \propto 1/\sqrt{\omega}$.¹⁰ This result would suggest that all things being equal, that a lower frequency thermal wave would more efficiently transfer the excited molecular energy to the transducer. In these experiments a standard 32 kHz QTF was compared against an 8 kHz QTF, and a signal enhancement factor of about ≈ 2 was expected.

3. EXPERIMENTAL SETUP

The same experimental set can be used to investigate both QEPAS and ROTADE.⁸ Radiation from a near-IR diode laser is coupled to a single mode fiber, and then focused between the prongs of the QTF with a waist size of $\approx 15 \mu\text{m}$. The position of the beam was controlled by moving the focusing optics with a computer controlled 3D translation stage (Newport ESP300 Motion Controller w/3D stage). The laser was wavelength modulated at half the resonant frequency ($f_0/2$) of the QTF, and detection was performed at f_0 ($2f$ wavelength spectroscopy) with a lock-in amplifier. A schematic can be seen in Fig. 1. Two gases were used in this study. 0.5% C₂H₂ in N₂ was used because it has a fast V-T relaxation time as compared with the pure CO₂ used. The CO₂ was excited at 6361.25 cm⁻¹ in its $3\nu_1 + \nu_3$ band with 30.7 mW of laser power, and the absorption coefficient for the selected line at 1 atm is $1.37 \times 10^{-3} \text{cm}^{-1}$, according to HITRAN data. C₂H₂ was excited at 6523.879 cm⁻¹ with 37.5 mW of laser power, and the absorption coefficient at 1 atm for 0.5% C₂H₂ in N₂ is $5.3 \times 10^{-3} \text{cm}^{-1}$. These absorption coefficients are sufficiently low enough to neglect the laser attenuation for $\approx 1 \text{cm}$ optical path across the gas cell.

The same setup can detect both thermal and acoustic waves, and so the position of the laser beam determines which type of signal dominates. While the waist is positioned a few tenths of a cm above the bottom of the QTF, the localized deformation due to heating is the primary cause of recorded signal. Moving the beam closer to the end of the QTF results in signal that comes primarily from the acoustic wave, which pushes on the tines, and

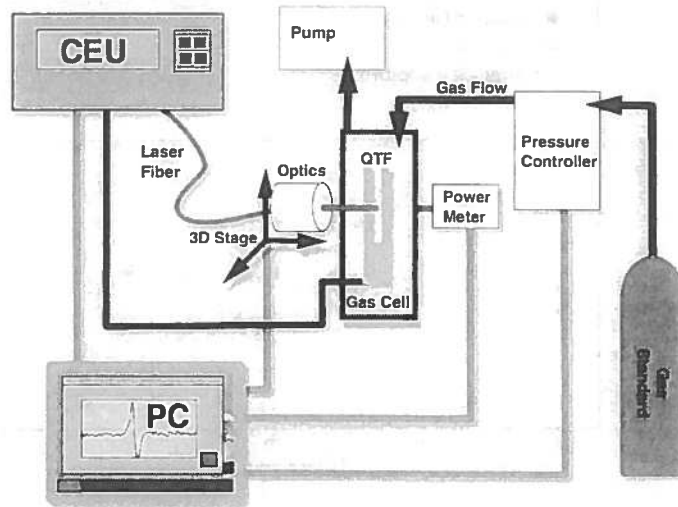


Figure 1. Experimental Setup. The DFB fiber-coupled diode laser was modulated at $f_0/2$ of the QTF, the computer controlled 3D stage had a resolution of $1\mu\text{m}$, and the beam had a waist size of approx. $15\mu\text{m}$.

thus benefits from having a longer lever arm. All of the ROTADE signal measurements were thus taken with the beam center $\approx 10\mu\text{m}$ above the bottom of the QTF. Two QTF's were used, and their resonant frequency as a function of pressure is shown in Fig. 2.

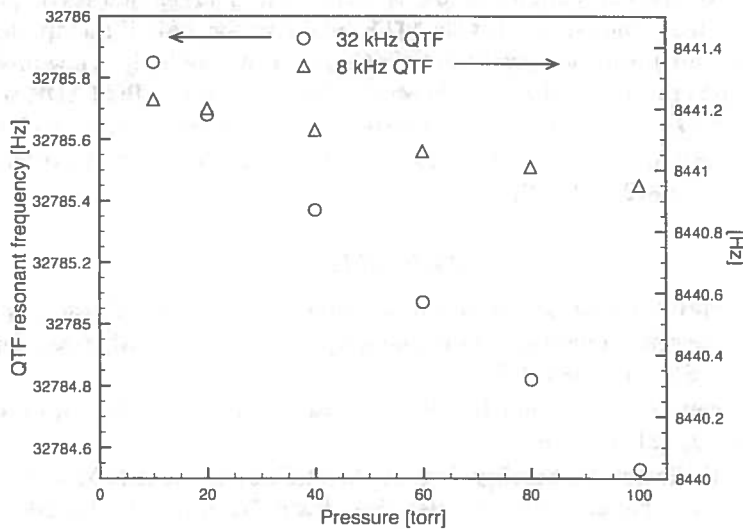


Figure 2. QTF resonant frequency at various pressures.

4. CONCLUSION

The 8 kHz QTF had similar background noise and DC offset as compared to the 32 kHz QTF. In Fig. 3 it can be seen that for certain pressures the 8 kHz QTF does in fact deliver a factor of 2 improvement in the signal. However, the simple solution posited above does not seem to be sufficient to explain the pressure dependence of the improvement. The simple diffusion model does not include intermolecular interactions, and it may be that the plane wave solution neglects the fact that the radius of the beam waist is comparable to the distance from the center of the waist to the bottom of the QTF. While more advanced mathematical modeling may prove difficult,

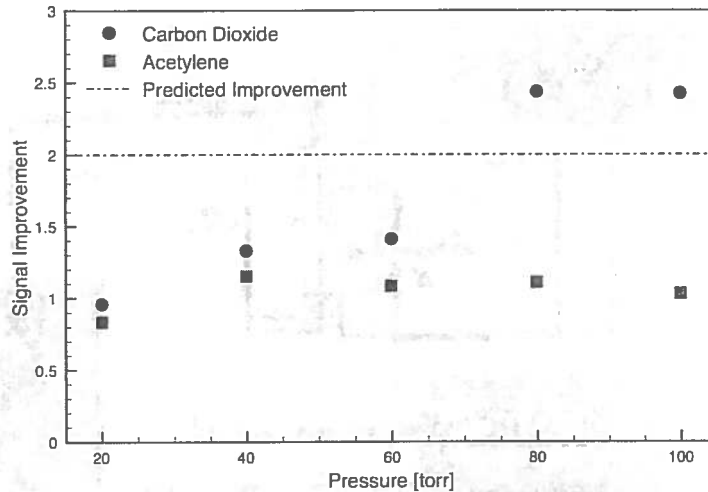


Figure 3. Signal improvement was calculated by comparing the maximum ROTADE signal for each gas at various pressures.

it seems plausible that more information from the thermal wave can be extracted by looking at the QTF signal as a function of beam distance from the bottom of the QTF.¹¹

Practically it may not be feasible to use the 8 kHz QTF in production spectrometers, due to the fact that the 8 kHz transducer is not commercially available and is several times larger than its 32 kHz counterpart. With size and cost being one of the major advantages of the QTF based sensor, only if the application warrants measuring a slowly relaxing gas with an absorption coefficient that stays relatively high at low pressure would the system be configured to measure the opto-thermal signal. However, another use of the ROTADE sensor is the determination of the diffusion coefficient (D_t) of a gas. Since the dispersive wave number $\sigma(\omega) = (1 + i)\sqrt{\omega/2D_t}$. This implies that the thermal wavelength $\lambda_{\text{thermal}}(\omega) = 2\pi\sqrt{(2D_t/\omega)}$. For example with CO_2 at 20 Torr and a QTF resonant frequency of 32.8 kHz, $\lambda_{\text{thermal}}(2\pi f_0) = 67\mu\text{m}$.

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