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Ultrasonic photoacoustic spectroscopy of trace hazardous chemicals using quantum cascade laser

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ABSTRACT

We report an ultrasonic sensor based on open-cell photoacoustic spectroscopy method for the detection of explosive agents in traces. Experimentally, we recorded photoacoustic spectra of traces of hazardous explosives and molecules. Tunable mid-infrared quantum cascade lasers in the wavelength range 7.0–8.8 μm lying in the molecular fingerprint region are used as optical source. Samples of Pentaerylthirol Tetranitrate (PETN), Tetranitro-triazacyclohexane (RDX), Dinitrotoluene, p-Nitrobenzoic acid and other chemicals like Ibuprofen having quantity ~1.0 mg were detected using a custom made photoacoustic cells in both open and closed configurations. The explosive traces were swiped using paper from contaminated surface and detected. Finite element mesh based simulation of photoacoustic cell is carried out for optimization of geometry at ultrasonic frequency (40 kHz). A point sensor based on above approach will be very effective for forensic applications and suspicious material screening.

1. Introduction

Photoacoustic effect was invented by Alexander Graham Bell in 1880 while doing experiments on the transmission of sound via a beam of collimated sunlight [1]. The effect is basically an indirect effect of light, relying on thermally generated acoustic waves in a sample due to periodic irradiation of light. Photoacoustic Spectroscopy (PAS) is essentially a spectral study of photoacoustic effect on a sample. A thermal/acoustic signal generated due to light absorbed at different wavelengths give qualitative and quantitative information about a sample. The temperature rise in any sample is primarily governed by its non-radiative relaxation transitions. PAS is a highly sensitive method that can be used to detect trace levels of samples. It is an excellent spectroscopic tool for the study of materials in all three phases (solid, liquid and gas). PAS technique offers several advantages such as wide dynamic range, non-destructive detection, simplicity and compactness of experimental hardware. PAS has been widely used in diverse fields such as atmospheric sciences, combustion process, medical diagnosis, homeland security, food industry and atmospheric pollution monitoring. The invention of quantum cascade lasers (QCL) has boosted the research in the field of Photoacoustic Spectroscopy. Availability of room temperature operation of QCL and broad tunability in the molecular vibrational fingerprinting band, typically 500–1500 cm^{-1} has enhanced selectivity and opened new avenues for PAS based sensors [2–4]. Applicability of photoacoustic spectroscopy to various spectroscopic measurements is discussed by Gary A. West et al., applications like linear absorption spectroscopy (vibrational and electronic), vibrational overtone spectroscopy, trace analysis, reaction kinetics and nonlinear spectroscopy (multiphoton as well stimulated Raman scattering) and photoacoustic Raman spectroscopy (PARS) and myriad applications to gaseous trace component analysis has been reviewed and discussed [5]. In year 2008, pulsed external-cavity quantum-cascade laser (EC-QCL) tunable in 9.3–0.10 μm band was used for the acquisition of mid-IR photoacoustic (PA) spectra of solids [6]. Researchers have demonstrated detection of solid traces of RDX, PETN, TNT, and TBP adsorbed on surfaces with a limit of detection of 100 ng/cm^2 and a standoff distance of 20 m using a reverse photoacoustic spectroscopy employing EC-QCL [7]. Pietro Patimisco, et al. has reviewed the Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) for gaseous species concentration monitoring. Quartz enhanced photoacoustic spectroscopy employs a resonant quartz crystal tuning fork as the detector. The technique has shown best gaseous species detection sensitivity in the mid-IR fingerprint range where powerful QCLs are available, sensitivity of QEPAS has reached record detectable trace gas concentration levels in part-per-trillion range [8].

Xing Chen et al. reported standoff detections of TNT powder from a range of 240 cm of quantity 1 mg, using 7.35 μm quantum cascade lasers (QCLs) based photoacoustic (PA) experiments [9].

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Photothermal cantilever deflection spectroscopy (PCDS) based quantification of picogram levels of ternary mixtures of similar explosives (trinitrotoluene (TNT), cyclotrimethylene trinitramine (RDX), and pentaerythritol tetranitrate (PETN)) using nanomechanical IR spectroscopy has been reported [10]. Highly resolved IR bands of RDX and TNT sample and their soil mixtures were recorded in the 9.6 and 10.6 mm regions of the CO_2 laser [11]. Acoustically open ultrasonic photoacoustic detector having optically multipass arrangement has been reported for trace gas and atmospheric pollution studies using CO_2 laser source [12]. Photoacoustic (PA) signals were detected by Gianfranco Giubileo and Adriana Puiuin in the entire frequency 9–11 µm band of CO_2 laser by their home-made photoacoustic apparatus. The Laser PAS spectral absorptions recorded with a CO_2 laser source were reported for 2, 4-DNT; 2, 6-DNT; HMX; TATP; PETN; TNT and RDX having concentrations ~100 µg [13]. PAS measurements of solid explosive material /energetic material covering the wavelength region of 400–1600 nm were reported using xenon and halogen lamps as a source [14].

The aim of the present work is to carry out the mid-infrared photoacoustic spectroscopy of microgram level quantity of energetic materials and other chemicals in ultrasonic regime (40 kHz) using open acoustic resonator cell geometry. The aim is also to develop an Open-Cell Laser Photoacoustic Spectroscopy (OC-LPAS) Sensor for rapid detection of suspicious traces.

2. Theory

The primary source of acoustic signal in a photoacoustic cell arises from the periodic heat flow from the solid to the surrounding gas as the solid is cyclically heated by the chopped/modulated light. Only a relatively thin layer of air adjacent to the surface of the solid responds thermally to the periodic heat flow from the solid to the surrounding air via piston effect. This boundary layer of air can then be regarded as a vibratory piston, resulting in generation of acoustic signals in the cell. Since the magnitude of the periodic pressure fluctuations in the cell is proportional to the amount of heat emanating from the solid absorber, there is a close connection between the strength of the acoustic signal and the amount of light absorbed by the solid [15,16]. Theory of photoacoustic effect in solids was formulated by Rosencwaig and Gersho. With regard to solid samples there are three important parameters which are as listed below: 1. Sample thickness 'l', 2. Optical absorption length '$\mu_\beta = 1/\beta$', where β is the optical absorption coefficient in cm^{-1} and 3. Thermal diffusion length 'μ_t', which determine how far a periodic wave can travel into a solid without dissipation.

$\mu_t = \sqrt{\frac{2.\alpha}{\omega}}$, where '$\alpha$' is thermal diffusivity of medium ($\alpha = \frac{k}{\rho.C}$); k is thermal conductivity, ρ is the density of medium and C is the specific heat capacity of medium and 'ω' is the frequency of heat waves (radians/s) or the chopping frequency of laser. It is clear that the thermal diffusion length is inversely proportional to the chopping frequency and hence at higher frequency in ultrasonic band the thermal diffusion length is very small as compare to audio frequencies. Under the condition of thermal diffusion length 'μ_t' being smaller than optical absorption length 'μ_β', photoacoustic spectrum will be a true representation of the optical absorption spectrum, otherwise the property of backing material would also come into the measurement. In Photoacoustic measurements of solid samples, the acoustic response of the air above the sample is measured and related to the thermal properties of the sample. The time dependent component of the temperature of solid in the surrounding gas/air attenuates rapidly with increasing distance from the surface of the solid. The boundary of air, which respond thermally to the periodic temperature at solid gas interface is $2.\pi/a_{gas}$, where a_{gas} is known as the thermal diffusion coefficient of surrounding gas. The typical value of air boundary is $2.\pi/a_{gas}$ ~0.2 cm for a chopping rate of 100 Hz. In the study presented in this paper the air boundary length decreases to 0.008 cm at chopping frequency 40,000 Hz.

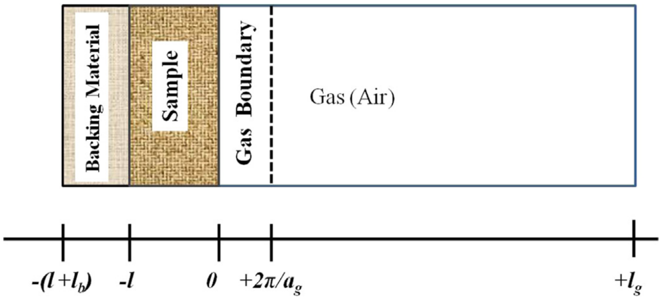

Fig. 1. Cross-sectional view of a simple photoacoustic cell.

2.1. Simulation and theoretical analysis

Fig. 1 shows a typical cross section of photoacoustic cell, showing the positions of a solid sample, backing material and gas column. According the Rosencwaig and Gersho (RG) one dimensional thermal diffusion model the photo-acoustic signal intensity δp (physical pressure variation due to modulated light source) is given as

$$\delta p = \frac{(1-j)\beta.\, l.\, \mu_b.\, Y}{2.\, a_g.\, k_b} \tag{1}$$

where a_g, μ_b, k_b, l and β are the thermal diffusion coefficient of air (cm^{-1}); the thermal diffusion length of the backing material (cm), the thermal conductivity of the backing material (W/m K), the film thickness and the optical absorption coefficient of the film (cm^{-1}) for the wavelength λ, respectively; and Y as a constant factor. The acoustic signal is thus proportional to $\beta.l$ which means that the whole sample length contributes to photoacoustic signal. For the thermally thin case in which thermal diffusion length $\mu_t \gg l$, the thermal properties of the backing material come into play in the expression for photoacoustic signal intensity (Pascal). The factor 'Y' appearing in the above equation is $Y = \frac{\gamma.P_0.I_0}{2\sqrt{2}.l_g.T_0}$, where γ is the ratio of specific heats at constant pressure and volume, I_0 is the incident, monochromatic light flux (W/cm^2), P_0 and T_0 are is ambient pressure and temperature respectively and l_g is length of gas column above the sample.

Fig. 2 shows a variation of the thermal diffusion length of RDX powder with chopping frequency and its comparison with the optical penetration length. As an estimation, a 10 µg weight of RXD with a uniform thickness having a diameter of 4 mm on paper

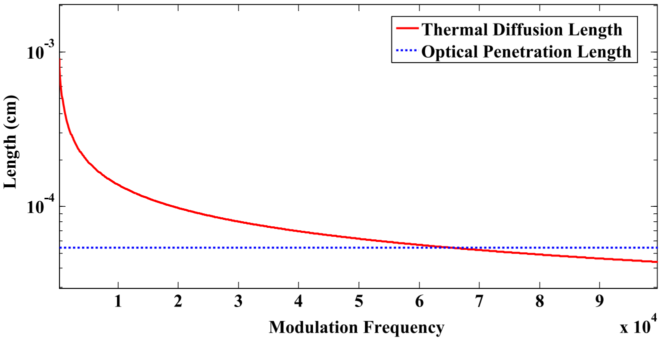

Fig. 2. Comparison of optical and thermal diffusion length for RDX powder.

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