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Photo-vibrational spectroscopy using quantum cascade laser and laser Doppler vibrometer

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ABSTRACT

Photoacoustic/photothermal spectroscopy is an established technique for detection of chemicals and explosives. However, prior sample preparation is required and the analysis is conducted in a sealed space with a high-sensitivity sensor coupled with a lock-in amplifier, limiting the technique to applications in a controllable laboratory environment. Hence, this technique may not be suitable for defense and security applications where the detection of explosives or hazardous chemicals is required in an open environment at a safe standoff distance. In this study, chemicals in various forms were excited by an intensity-modulated quantum cascade laser (QCL), while a laser Doppler vibrometer (LDV) was applied to detect the vibration signal resulting from the photoacoustic/photothermal effect. The photo-vibrational spectrum obtained by scanning the QCL's wavelength in MIR range, coincides well with the corresponding spectrum obtained using typical FTIR equipment. The experiment in short and long standoff distances demonstrated that the LDV is a capable sensor for chemical detection in an open environment.

Keywords: Photoacoustic effects; laser interferometry; vibrometer; vibration analysis; spectroscopy.

1. INTRODUCTION

The photoacoustic (PA) effect was discovered by A. G. Bell in nineteenth century [1] and has become a conventional spectroscopic technology for different states of chemicals [2, 3]. A standard measurement is normally conducted in a sealed PA cell by a high-sensitivity microphone or other sensors in contact with or in proximity to the sample. However, the measurement limits the technique in a controllable laboratory environment. In addition, as the acoustic waves attenuate quickly in open environment, it is not suitable for explosives or hazardous chemicals tests, where a safe standoff distance is normally required. Recently research efforts were reported for standoff detection on explosives in open air [4] using high sensitivity microphone with large parabolic sound reflector array and a lock-in amplifier. The maximum standoff distance reported is 40 feet [5]. The detection distance was further increased to about 20 meters when a quartz tuning fork was applied [6]. In recent years, laser interferometry [7] became a non-contact detection technique of photoacoustic signal in open environment. Cho etc. reported an intensity-modulated quantum cascade laser (QCL) [8] as the excitation laser placed at 0.5m from the explosive targets, and a coherent detection system using a CW probe laser at 1550nm wavelength and realized a 5-meter detection of optical phase shifting due to photoacoustic/photothermal effects [9].

In this research, two QCLs were applied as the excitation light source in two tests with different standoff distances. An optical chopper was applied to modulate the intensity of illumination. A conventional laser interferometer, laser Doppler vibrometer (LDV) [10-12] is applied as the sensor to detect periodic optical path length (OPL) change caused by PA effect. The vibration intensity (displacement or velocity) obtained by LDV was normalized by QCL output power and photo-vibrational spectra [13,14] were obtained on two chemicals. One is a stretched Polytetrafluoroethylene (PTFE) tape with 0.075mm thickness; and the second one is trinitrotoluene (TNT), a typical explosive on aluminium plate with concentration of 10 μ g/mm². The comparison with FTIR absorbance spectrum database shows the sensitivity of LDV is high enough for photo-vibrational signal detection on surface-bound chemicals in open environment. The experiment demonstrates the potential of LDV on standoff detection of explosives or hazardous chemicals in national security applications.

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2. PHOTO-VIBRATIONAL SIGNAL ON CHEMICALS

In this study, an intensity-modulated QCL was applied to excite the photoacoustic effect on chemicals. A laser Doppler vibrometer was applied to measure the periodic change of OPL when the QCL is scanning at different wavenumbers. The change of OPL of the probing laser beam was then converted to vibration amplitude in displacement, or velocity whose frequency equals to the modulation frequency of excitation laser.

2.1 Photoacoustic spectroscopy and OPL variation

The theory behind the interpretation of photoacoustic signals detected in a photoacoustic cell was developed by McDonald and Westsel Jr. [2] for homogeneous bulk solid or liquid materials. It is a well-established analytical technique for solid and liquid chemicals. However, for other forms of material sample such as loose powders, thin film or even chemical residues, the conversion efficiency of laser power to signal intensity is simply too complicated to be simulated and expressed mathematically in one equation. It is also dependent upon many other factors related to the morphological, thermo-chemical, and transport properties of the chemicals, substrate and air mass [9]. The main factors contributed to change of OPL are:

- Localized surface (out-of-plane) displacement of chemicals and substrate due to thermo-elastic expansion;
- Heat conduction from the heated surface to the surrounding air layer producing a refractive index change in the air column.

The optical phase shift of LDV due to these two factors can be expressed as [9]

$$\Delta\phi \approx \frac{4\pi}{\lambda_{LDV}} (\Delta n_a \mu_a - n_a \Delta L) \approx \frac{4\pi \cdot \Delta T}{\lambda_{LDV}} \left[\left(\frac{dn}{dT} \right)_a \mu_a - n_a \mu_s \beta_s \right], \quad (1)$$

where ΔT is the temperature rise associated with periodic heating of the illuminated region by the excitation laser, and ΔL is the thermo-elastic expansion of the chemical. λ_{LDV} is the wavelength of probe laser in LDV. n_a is the refractive index of air; μ_a and μ_s are the air and chemical thermal diffusion lengths, respectively, and β_s is the linear thermal expansion coefficient of the chemical. Other factors include the generation of outward propagating surface acoustic Rayleigh wave; transient surface reflectance change; and thermal expansion of air gap between particles, when the powder sample is thick.

2.2 Excitation light sources

Two QCLs were used in this study. The first QCL is a widely tunable MID-IR OEM laser module (Model No. MINI-QCL) from Block Engineering. It is an air-cooled pulsed laser with tunable range from wave number of 940cm^{-1} to 1375cm^{-1} . A compact-size control electronics, mini-QCL-200 was used to communicate with a laptop through a wireless router. Figure 1(a) shows its output CW power at different wavelengths. The second QCL used in this research is MIRcat-1200-1824 from Daylight Solutions. It includes two QCL modules and a co-axial red aiming laser for easy alignment. The tunable wavelength range is narrower than the first QCL but the output CW power is much higher. The maximum output CW power being $>200\text{mW}$. Hence, its size is larger and requires water cooling during operation. Figure 1(b) shows its power distribution at various wave numbers. The laser is suitable for chemicals in liquid or in powder form where high excitation power is needed for a detectable photo-vibrational signal.

Figure 1. (a) OEM QCL module from Block engineering and (b) MIRcat QCL from Daylight Solutions

2.3 Home-developed LDVs

Two home-developed LDVs were applied in the tests. The first one is a near-field single-point LDV using 633nm He-Ne laser. The second one is a long-distance single-point LDV using 1550nm narrow-linewidth laser. Both designs are based on a Mach-Zehnder interferometer. In both designs, a 40MHz acousto-optic modulator was applied in the reference beam to introduce a carrier frequency. The output laser beams were focused on target at different standoff distance. The reflected object beam interferes with the frequency-shifted reference beam and the output signal from the photodetector is a frequency-modulated (FM) signal with a central carrier frequency of 40MHz. The advantage of LDV is that the amplitude and frequency of vibration signal retrieved is only relevant to the frequency shift of the received laser beam. Hence, when the interferometric signal is acceptable by the demodulation system, for example >40dB, the vibration signal obtained is standoff-distance-independent. A home-developed demodulation system based on FPGA was used to demodulate the FM signal in order to retrieve the OPL change. The output signal can either be displacement or velocity, up to user selection. Generally, displacement is directly proportional to the phase change and velocity is proportional to the frequency shift of the probe laser beam. When the SNR of the interferometric signal output from detector is more than 45dB, the noise floor of the displacement measurement is <5pm when integration time of one second is selected. Figs.2(a) and 2(b) show the near field and long-distance LDV used in the experiments.

Figure 2. Home-developed (a) near-field LDV and (b) long-distance LDV

3. EXPERIMENTAL SETUP

Two tests were conducted in this study. The first one is a near-field test in laboratory environment. Figure 3(a) shows the experiment setup. The laser beam output from QCL module passes through an optical chopper and is focused onto material samples by a parabolic mirror. The excitation QCL beam is superimposed with the probe laser beam on the samples. The detection distance of LDV in these experiments is about 1m. The tested sample is a PTFE tape with 0.075mm thickness fixed at both ends and suspended in the middle as shown in Fig. 3(b). The output power of QCL was measured before the experiments. The fluctuations of output power between two measurements were less than 5%. The frequency of the optical chopper was selected to avoid other vibration frequencies detected from the environment, typically at a frequency range between 100Hz to 3kHz. In the second experiment, the excitation laser source used to test trace TNT sample on aluminium plate [Fig.3(c)] was the high power QCL from Daylight Solutions. The excitation distance is around 0.5m and the detection distance is about 100m in open environment. The environment temperature is around 32°C, humidity is >90%. The environment sound level is around 60 decibel, mainly from the air blower in cooling tower of the buildings and the water chiller of the QCL.

4. RESULTS AND DISCUSSION

The wavenumber of QCLs was scanned at a 5cm^{-1} step, and the vibration amplitude was recorded at each step. The velocity was then normalized by QCL output CW power and plotted against wavenumber. Figure 4 shows the comparison of the normalized vibration amplitude and the corresponding IR absorbance spectrum of PTFE from NICODOM IR libraries. Due to the membrane structure of PTFE sample and the boundary condition in the experiment, the vibration amplitude value detected was quite large. The half maximum displacement was around 48nm when chopper frequency was set as 340Hz. The reading from LDV was observed to be very stable based on one-second integration

time. Two absorbance peaks at 1165cm^{-1} and 1205cm^{-1} of the measured photo-vibrational spectra were observed to coincide very well the FTIR spectra.

Figure 3. (a) Schematic layout of experimental setup; (b) Sample 1: PTFE tape (0.075mm in thickness); (c) Sample 2: TNT on an aluminum plate with concentration of $10\mu\text{g}/\text{mm}^2$.

Figure 4. (a) IR absorbance spectrum of PTFE from NICODOM IR libraries; (b) Normalized vibration amplitude obtained by LDV at different wave numbers.

In the second experiment, trace TNT deposited on an aluminum plate was tested. In order to verify that the vibration detected was from the photoacoustic/photothermal effect of tested chemical, the aluminum plate was also measured beforehand. No obvious vibrations were detected for the aluminum substrate within the scanning frequency range. The QCL from Daylight Solutions was applied, and the chopper frequency was set as 1300Hz. The vibration amplitude value was observed to be about 10 times lower than that of the PTFE tape. Hence, the readings were not as stable due to the influence of noise floor. Two-second integration time was selected on LDV at each wave number instead to compensate for the noise. Figure 5 shows the comparison of the obtained photo-vibrational spectra of TNT against the FTIR spectra

from NICODOM IR libraries. The LDV can still detect stable vibration amplitude at the absorbance peak and the result still coincides well with the standard FTIR spectra.

Figure 5. (a) IR absorbance spectrum of TNT from NICODOM IR libraries; (b) Normalized vibration amplitude obtained by long-distance LDV at different wave numbers.

In the photo-vibrational spectroscopy, it is always assumed that the detected vibration amplitude by LDV is proportional to the power density of excitation laser and the absorbance efficiency of chemicals. Besides the absorbance efficiency of chemicals at certain wavelength, other factors were also observed to affect the vibration amplitude detected by LDV. Ref. [14] listed several of them. Unfortunately the effect of these factors may not be always linear. Hence the nonlinearity may slightly affect the qualitative value of the photoacoustic spectra of the analyte which was based on the relative signal intensity at different wavelengths.

5. CONCLUDING REMARKS

In this study, two types of home-developed LDV was applied as sensors to detect the photo-vibrational signal of chemicals at different standoff distances. QCL was adopted as the excitation light source due to its high power, broadly tunable wavelength in mid-IR range and compact size over other light sources. The intensity of QCL beam was modulated by an optical chopper, while the LDV was used to detect the vibration signals due to photoacoustic effect in the illuminated area. The photo-vibrational spectra obtained by plotting the normalized vibration amplitude against the QCL output wavenumber range were compared with standard FTIR spectra. The results demonstrate that the LDV is a good non-contact sensor for photo-vibrational signal detection in open environment. It is a necessary demonstration in a series of developments to realize the standoff detection of hazardous materials in defense and security screening applications.

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