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Ultrasonic Standoff Photoacoustic Sensor for the Detection of Explosive and Hazardous Molecules

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ABSTRACT

Standoff photoacoustic spectroscopic technique has been studied for the detection of hazardous molecules adsorbed on surfaces and in vapour/aerosols form in open air. Detection and identification of components in explosive mixtures in trace amounts is very challenging by any point or standoff spectroscopic detection technique. Discusses detection and identification of such components using standoff laser photoacoustic spectroscopic technique. Laser photoacoustic spectra of various trace molecules in the mid-infrared spectral band 7 µm - 9 µm have been recorded in vapor, aerosol, liquid forms as well as samples adsorbed on surfaces such as plastic and cloth. Pulsed quantum cascade laser is modulated at a frequency of 42 kHz resonant with that of microphone. Hazardous chemicals/explosives adsorbed on plastic and cloths surfaces were detected from a standoff distance up to 1.5 m. The sensitivities were found to be 20 µg/cm^2, 20 µl liquid and 1.0 ppm corresponding to solid, liquid and vapour phases respectively. The chemicals/explosives used in the study were PETN, DNT, Acetone, and DMMP. Our study suggests that the photoacoustic technique has high selectivity and sensitivity for the trace detection and be used for screening of suspicious objects for security applications as a handy product.

Keywords: Photoacoustic sensor; Ultrasonic photoacoustic spectroscopy; Quantum cascade laser; Standoff detection

1. INTRODUCTION

The standoff quartz-enhance photoacoustic spectroscopy (QEPAS) has been used by many researchers as a tool for detection purposes[1-3]. In the QEPAS technique, the diffused reflection of incident laser light from the target is collected by optical receiver to focus on to the detector. The reflected light suffers absorption by the materials adsorbed on the target surface and thus gives the absorption signatures characteristic to the adsorbed materials when the spectra are recorded by tuning the laser wavelength in the entire wavelength range of interest. Standoff detection of various explosives using QEPAS from distances of up to 25 m has been reported[3]. Though the detection can be done from such an appreciable standoff distance, the success of the technique depends heavily on the target reflection as well as the alignment of the target. In real scenario, possibility of finding such a cooperative target is remote. Therefore, the QEPAS technique is suitable in retro reflector configuration. The system as well as the retro reflector can be fixed with workable distance between them and kept aligned permanently. It will detect the hazardous material/toxic gases coming in between the two. On the other hand, microphone based standoff sensor does not depend on the target reflection. It depends on generated non-radative transitions occurring in sample which in turn depend on the optical intensity of the incident light, absorption coefficient of the sample and number of incident photons interacting with the sample material. Microphone based indirect standoff detection of liquid contamination on surface using CO_2 laser Photoacoustic spectroscopy has been reported[4]. Standoff detection of hazardous chemicals/explosive materials using quantum cascade laser have been demonstrated. In these studies, acoustic receivers of aperture sizes up to 60 cm coupled with microphones have been used[4-6]. Further, Microphone based Standoff laser photoacoustic spectroscopy technique is much sensitive than other technique such as Raman Spectroscopy due to higher infrared absorption cross section than Raman scattering cross section. In addition, the technique offers an economic solution for sensing of trace amount of analytes in comparison to the optical sensing techniques as the receiving optics associated with the optical sensing are very costly as compared to the acoustic reflector associated with the present scheme.

The objective of the present study is to develop a standoff photoacoustic spectroscopy based sensor, employing a 12 cm parabolic acoustic reflector coupled to a microphone detector. A microphone having resonant frequency in ultrasonic region was selected for the purpose as the ambient noise in this region is lower than that in audio range. Using the developed setup, we have carried out experiments for detection and identification of hazardous chemicals and explosive materials in the forms of liquids, aerosols/vapours and samples on adsorbed on surfaces. The experiments have also been performed for detection and identification of components of the mixture of hazardous materials. The work will be very useful in the development of

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system for safety screening and other defence applications.

2. EXPERIMENTAL

The block diagram of the experimental arrangement is depicted in Fig. 1. Figure 2 shows the hardware of the experimental setup. Most of the equipment used in the present work were utilised in our previous work where a cylindrical resonant cavity was used to enhance the photoacoustic signal[13]. In the experimentations done for the present study, the microphone was placed at the focal point of a 12 cm diameter parabolic acoustic reflector. A quantum cascade laser (model number Uber Tuner UT-8, make: M/s. Daylight Solutions) was used in the experiment. The laser is tunable in the wavenumber range 1420 cm^{-1} to 1130 cm^{-1} with resolution of 1 cm^{-1} and line width of ~ 0.5 cm^{-1}. The output of the quantum cascade laser was modulated at 42 kHz. A function generator was used for modulating the laser. The maximum average power of the laser is 10 mW at 42 kHz. A reference signal at the same frequency (42 kHz) is fed to lock-in-amplifier. The modulated laser is allowed to interact with target sample (explosive/hazardous species adsorbed on surfaces or in vapour/aerosol form). The sample absorbs the laser radiation at wavelengths governed by their absorption cross section. After the absorption, a pressure wave is generated due to the non radiative transitions which are collected by an acoustic reflector and focused on to a sensitive microphone placed at the focal point of the same as shown in Fig. 1. The frequency of the generated pressure wave is same as the modulation frequency.

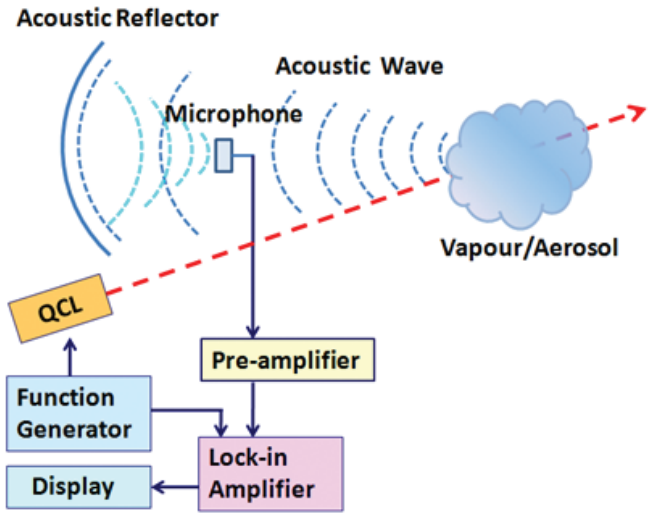


Figure 1. Schematic of experimental setup.

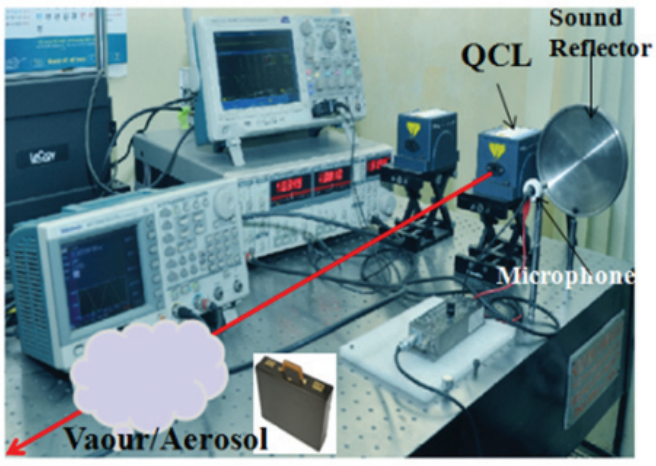


Figure 2. Hardware of the experimental setup.

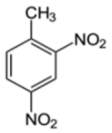
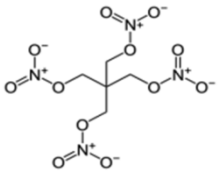
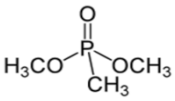
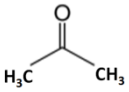
Figure 2 shows the hardware of the experimental setup. In our experiments, commercially available microphone (Murata MA40B5R) was used as the detector for sensing photoacoustic signals. The detector is having a narrow frequency response centered at 42 kHz. The experiments were performed with varied distance (between sample and transmitter receiver setup) of up to 1.5 m. For the pre-amplification of photoacoustic signal, 50 kHz bandwidth current amplifier (Femto de, DLPCA-200) having input noise 43 femto ampere/√Hz is used at bandwidth 50 kHz settings. The photoacoustic signal amplified by the pre-amplifier is fed to a lock-in-amplifier (SR 830). During all the measurements, the sensitivity of Lock-in-amplifier was kept at 2 mV scale. The output of the lock-in amplifier is analog. This analog signal is converted in to digital form by utilising a multifunction data acquisition card (USB 4716 Advantech) and then fed to the computer for recording. Photoacoustic spectra were recorded using a Labview based graphical user interface. The laser was operated in forward scanning mode. In this mode, the wavelength accuracy is ±2 cm^{-1}. The thin layers of the analytes to be investigated were prepared by dissolving the materials in Acetone/alcohol and left to dry for long hours to get rid of residues of Acetone. The quantity of materials deposited was estimated to be around of 40-50 $\mu g/cm^2$. Separate target plates were used for different materials. We used plastics and cloths as target materials on which analytes were deposited. The names analytes used in the experiments with their abbreviations, chemical formulae and structures are tabulated in Table 1.

Standoff photo-acoustic spectra of DMMP and acetone in vapour/aerosol form in open air were recorded from 1.5 m distance.

3. RESULTS AND DISCUSSION

The spectra recorded by the present scheme from the standoff distance of 1.5 m are shown in Figs. 3 to 5. For comparing the signal strength of the spectra taken by present scheme with those taken by point detection scheme, we have included the spectra recorded in our previous work[7]. In our previous work, we had used a resonant photoacoustic cell coupled to the microphone for point detection of the similar kind of analytes. In the point detection scheme using resonant photoacoustic cell, a modulated laser beam from tunable quantum cascade laser radiations are allowed to interact with the sample kept at the bottom of the cell. Absorption of laser radiation is followed by the non-radiative relaxation accompanied by emission of heat. Subsequently a pressure wave is generated which propagates to the boundary layer of the samples. Then the acoustic wave travels to the microphone detector through the atmospheric air present inside the cell. This pressure wave is converted in the electrical signal by the piezo microphone detector. Photoacoustic spectra are then recorded as voltage versus wavenumber of the tunable quantum cascade laser. In all set of spectra (shown in Figs. 3-5), (a) correspond

Table 1. Analytes used in the experiment

Name of the analyte	Abbreviation	Chemical formula	Structure
2,4-Dinitrotoluene	DNT	$C_7H_6N_2O_4$	
Pentaerythritol tetranitrate	PETN	$C_5H_8N_4O_{12}$	
Dimethyl methylphosphonate	DMMP	$(CH_3)CH_3$-PO_3	
Acetone		CH_3COCH_3	

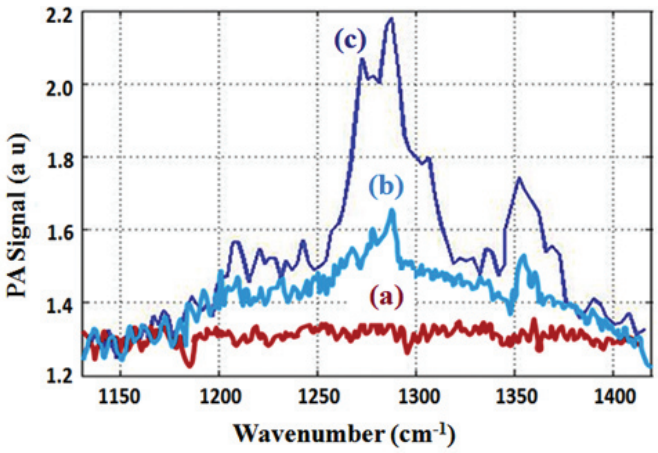


Figure 3. Photoacoustic spectra of mixture of DNT and PETN (adsorbed on plastic surface) taken from (b) standoff distance of 1.5 m with sample quantity 40 µg/cm² and (c) point distance with sample quantity 20 µg/cm²; (a) shows the base line.

to the base line i.e. spectra taken from the standoff distance without sample, (b) correspond to the spectra taken by the present scheme, and (c) correspond to the spectra taken using point detection setup used in our previous work. The reason behind comparing the spectra taken by the two schemes is to have a feel of decrease in the signal strength when we switch over to the standoff measurement in order to develop compact hand held standoff sensor for defense applications. Figure 3 shows photoacoustic spectra of mixture of DNT and PETN.

There are three clearly resolved peaks at 1272 cm^{-1}, 1284 cm^{-1}, and 1352 cm^{-1}, in both the spectra (b) and (c). The first two peaks are due to the presence of PETN in the mixture and the last peak is attributed to the presence of DNT molecules. DNT which is basically a precursor of TNT shows a very strong peak at 1352 cm^{-1} due to $–NO_2$ symmetric stretching and matches well with Fourier transform infrared (FTIR) spectra[7,8]. Strong overlapping peaks at 1272 cm^{-1} (- NO_2 Stretching) and 1284 cm^{-1} (- CH_2 bending) are clearly resolved and belong to PETN[9, 10]. With these peak assignments, PETN and DNT can be identified in the mixture. By comparing spectra (b) and (c), we observe that the signal strength goes down and becomes noisy as well when we use acoustic reflector based standoff technique in comparison to the photoacoustic cell based point detection technique but signal to noise ratio remains sufficient enough. Here, it is worth mentioning that the quantity of analyte under examination in the standoff case was double (~ 40 µg/cm²) in comparison to that used in the point detection (~ 20 µg/cm²). The spectrum (c) as shown in Fig. 3 is base line recorded without any sample adsorbed on plastic surface.

The present technique is also successful in detecting chemical warfare agents such as nerve agent Sarin. We have successfully recorded the photoacoustic spectra of DMMP, a stimulant of Sarin. Figure 4 shows the recorded spectra. As earlier, the spectra (b) and (c) correspond to the recording by present technique and point detection technique respectively. The spectrum (a) is recorded with the target surface i.e. without any sample. The sample was used in liquid form. One drop of DMMP (~ 50 µl) was used on the cloth surface for the detection using standoff laser photoacoustic spectroscopy. In the case of spectrum recorded using point detection technique, the quantity of sample was ~ 10 µl. The strongest peak is observed at 1276 cm^{-1} and is attributed to overlapping stretching H_3C–P=O and –C-H bending as reported by Zhang [12], *et al.* Standoff Laser photoacoustic spectrum of DMMP was recorded using experimental set shown in Fig. 2. Standoff photoacoustic spectrum was recorded as depicted in Fig. 4(b). In this case only one peak (at 1276 cm^{-1}) was resolved. It is in very good agreement with point detection photoacoustic spectrum (Fig. 4 (c)). Standoff spectrum was also recorded in aerosol form.

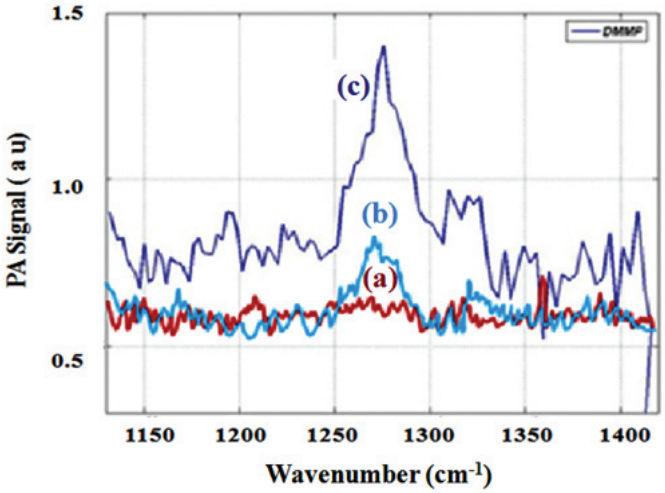


Figure 4. Photoacoustic spectra of DMMP (adsorbed on cloth surface) taken from (b) standoff distance of 1.5 m and (c) point distance; (a) shows the base line.

Figure 5 depicts spectra of Acetone in aerosol form taken from standoff distance of 1.5 m (spectrum b) and by point detection using photoacoustic cell (spectrum c); spectrum (a) shows the base line. The aerosol sample was prepared using small amount of Acetone in water and spraying it in the path of the laser beam. In the point detection case, three peaks (1218 cm^{-1}, 1230cm^{-1}, and 1376 cm^{-1}) are clearly resolved where as in the case of standoff detection; only two peaks (1218 cm^{-1}, 1230$cm^{-1)}$ are resolved. The two stronger peaks which are visible in both (b) and (c) are attributed to vibration of -C=O and C-C stretching[3].

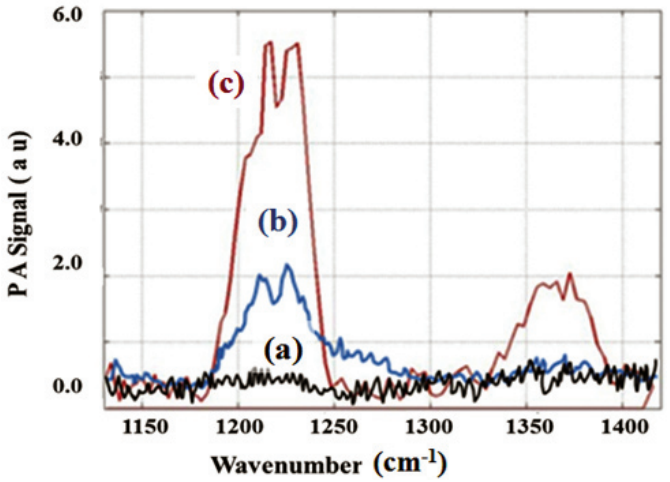


Figure 5. Photoacoustic spectra Acetone (in aerosol form) taken from (b) standoff distance of 1.5 m and (c) point distance; (a) shows the base line.

4. CONCLUSIONS

The standoff detection of hazardous materials using ultrasonic photoacoustic spectroscopy has been demonstrated successfully and photoacoustic spectra have been recorded from a distance of 1.5 meter. The results are compared with those recorded with photoacoustic cell based point detection mechanism. The recorded spectra from both the mechanisms are in good agreement with each other as well as with standard IR spectra. Of course, the signal strengths as well as signal to noise ratios are lower in case of standoff measurement technique but it has advantage of standoff detection. The technique is non-invasive and fast as the molecular species are detected in 6 sec (duration of laser scanning). This methodology is capable of detecting explosive agents, chemical warfare agents from a distance of ~ 1.5 m. The standoff range can be enhanced further by increasing laser energy and with better design of acoustic reflector. The technique can be used to detect materials in powder, liquid, and vapour/aerosol forms. It is also useful in detection of samples adsorbed on surfaces such as plastics and cloths. The technology has the potential of getting converted in to a compact standoff sensor useful for defense and homeland security. In future, we also intend to carryout experiments with biological warfare agents and drugs.

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