High-sensitivity detection of trace gases using dynamic photoacoustic spectroscopy

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1 Introduction

Chemical threats (in a variety of forms) are an area of pressing national security concern. Airborne threats of interest are gaseous or aerosol based. Additionally, certain solid hazardous materials emanate vapor signatures that potentially could be used to detect the solid. A detection system that is able to rapidly detect and/or identify a chemical threat is of great interest as it allows appropriate countermeasures to be taken. An ideal technique detects the threat rapidly and with high sensitivity. A wide-area coverage rate is also generally preferred. Numerous optical techniques have been investigated to perform these functions. Generally, an optical spectroscopy approach is taken whereby key absorption features are used to identify threats of interest. Differential optical absorption spectroscopy (DOAS) identifies absorption features in the ultraviolet and visible regions using a broadband optical source and a dispersive receiver (usually grating based). It has been used to detect NO$_3^-$ at concentration path lengths of 2 ppb-meter; however, to do so a remote retro-reflector was required. A similar technique known as differential infrared absorption lidar (DIAL) identifies infrared absorption features. It does not necessarily require a monostatic configuration, but there is a cost in sensitivity. It has been used to detect SF$_6$ at concentration path lengths of 2 ppb-meter; however, to do so a remote retro-reflector was required. Lidar systems measuring Raman shifts of a remote reflector. The theoretical analysis of this phenomenon was only partially successful at describing their acoustic waveform, which resembled that of a shock wave when the beam was swept at Mach 1. The dependence of the signal amplitude on source velocity fits a simple moving monopole model well. A related experiment utilized a sonically swept beam to generate pressure waveforms near an air/water interface. The theoretical analysis of this phenomenon was only partially successful at describing their results, implying the need for further analysis. In this work we quantify the sensitivity of the DPAS technique and discuss the factors limiting the sensitivity, i.e., receiver noise and ambient acoustic clutter. We extend the earlier work (which utilized a remote laser and local microphone) to a standoff configuration in which both laser and receiver are distant from the detected gas. Finally, we demonstrate the utility of the technique to detect the gas emanating from solid materials.
2 Detection Sensitivity
The experimental system has been described in detail elsewhere. For our detection sensitivity experiments, we used a CO2 laser to interrogate a target gas (SF6) contained within a loosely sealed anechoic chamber. The chamber walls were coated with anechoic foam to minimize reflections and simulate an open air environment. The gas concentrations were determined using an Online Technologies (now MKS Instruments, Andover, Massachusetts) Fourier transform infrared (FTIR) spectrometer that sampled the chamber gas. The laser was tuned to an absorption feature of interest (10.591 μm) of the target gas (SF6) within the long-wave infrared. The laser beam was rotated by a spinning mirror, and two omnidirectional microphone detectors (Earthworks M30; bandwidth ~50 kHz; sensitivity = 0.32 V/Pa when combined with our preamplifier) were placed at opposite sides on the far end of the chamber such that the laser beam rotated toward (approaching) one and away from (receding) the other.

Initially, the laser was chopped at 3.1 kHz, and the response of both microphones was measured for different laser sweep speeds. As expected based on the simple Doppler-shift physics of a moving source term, the measured signals are very different depending on whether the beam approaches or recedes from the given microphone. The measured spectral response of both microphones is shown in Fig. 1 for several different beam speeds. The dashed lines of the figure are the expected frequencies based on the Doppler shift of a source moving with the speed of the beam at the target range. They fit the measured responses quite well. As expected based on the physics of a moving source,10 the magnitude of the signal at the receding microphone decreases as the beam speed increases, becoming nearly negligible at Mach 1. In contrast, the signal magnitude at the approaching microphone increases as the beam speed approaches Mach 1. It also broadens spectrally. At Mach 1, the signal magnitude peaks; spectrally it spans roughly 30 kHz with a peak near 10 kHz. The corresponding temporal waveform at Mach 1 is a single pulse with width of ~0.1 ms.

Our measurements of detection sensitivity used the approaching microphone at the optimum beam speed of Mach 1 (mirror rotation rate of 20 Hz). The laser beam integrates over a gas path length of 0.43 m prior to reaching the microphone. Previous measurements indicate that the acoustic waveform is several inches in spatial extent. In order to capture all this energy we increase the collection area of our microphone by centering it within a 9-in diameter parabolic collector. We used a 3.5 W cw CO2 beam since previous measurements show the signal is maximized with no chopper. Internal fans were used to ensure homogenization of the gas. Signals were averaged over a 60-s data acquisition period (1200 scans through the sample). Note that the laser beam was inside the sample chamber only ~3% of the time it was rotating; so the active interrogation time was 1.8 s. The peak-to-peak microphone signals are displayed as a function of gas concentration (as measured via FTIR) in Fig. 2. Linearly extrapolating the detection sensitivity of the FTIR was only a few ppb, at which point the DPAS signal-to-noise ratio (SNR) was ~100. In order to estimate the DPAS system sensitivity, we recorded the ambient signal with no gas present. Since the experiment took place in a laboratory, a fume hood was the largest source of acoustic noise. The clutter level is shown in Fig. 2. Linearly extrapolating the SF6 data to the clutter level yields a detection limit of ~100 ppt. Given our 0.43 m path length and the absorption of SF6 (0.5 cm⁻¹ Torr⁻¹), this corresponds to a minimum measured absorbance of 1.7 × 10⁻⁶. An absorbance of 8.8 × 10⁻⁹ has been reported11 for PAS using resonant cells (5 s integration); however, these are inherently not standoff measurements. The receiver noise levels of the Earthworks microphone and a lower-noise microphone (Brul & Kjaer, Denmark) are also displayed in Fig. 2, indicating that the detection is clutter limited.

Previous measurements8 indicate that the strength of the DPAS response scales linearly with gas absorbance and
integration path length; thus we can extrapolate the DPAS
response to other materials using known absorptivities.
Using the absorptivity\(^\text{12}\) of NH\(_3\) at 10.33 \(\mu\text{m}\) (0.03 cm\(^{-1}\) Torr\(^{-1}\)), we estimate the DPAS response to NH\(_3\) over a 1 m path (see Fig. 2). Extrapolating to the clutter level indicates an NH\(_3\) sensitivity of \(\sim 1\) ppb. In Sec. 4, we test these conclusions via direct measurements of NH\(_3\).

3 Remote Measurements

The performance of the DPAS technique in an ambient environment at ranges exceeding 5 m was investigated using two different sensors: a parabolic microphone and a laser vibrometer. A laser vibrometer\(^\text{13}\) could be quite useful when coupled with the DPAS concept because it detects the acoustic signal near the source itself, rather than relying on a back-propagating acoustic signal as would be the case when using a remote parabolic microphone. Laser vibrometers function as interferometers, sending out a (typically) eyesafe beam of light and examining the phase shifts of the backscattered return. Pressure disturbances along the path of the beam induce changes in the local index of refraction, which are detectable as phase shifts by the vibrometer. We used a Polytec OFV 5000 with VD06 decoder yielding a bandwidth of 20 kHz and a sensitivity of 1 mm/s/V, where 1 mm/s is the gas particle speed. Assuming standard atmospheric conditions, this yields a sensitivity of 2.5 V/Pa. For these measurements, we removed the top from our sample chamber and aimed the vibrometer above the chamber, scattering it off a surface at the far end of the chamber (Fig. 3). The vibrometer beam was aimed 6 in. above the CO\(_2\) beam. Note that the vibrometer beam is thus in a direction off-axis from the acoustic wave propagation direction. We released a quick (~seconds) burst of SF\(_6\) gas, with a concentration we estimate (based on the local microphone response) to be in the single-digit ppm. The responses of both the vibrometer and the local microphone (no parabolic collector) are displayed in Fig. 4. Also displayed are their responses in the absence of SF\(_6\) gas. The local microphone records a sharp peak 1.7 ms after the beam enters the chamber, consistent with a signal (and laser beam) moving at the speed of sound toward the local receiver. The vibrometer records a somewhat broader signal occurring 0.25 ms later than the microphone signal. The delay is consistent with an acoustic signal propagating upward several inches. The fact that the vibrometer signal is broader than that of the microphone is likely the result of the fact that the vibrometer responds to acoustic signals along its entire path length,
whereas the microphone responds to acoustic disturbances only at its range.

In a setup similar to that of the vibrometer, a parabolic collector (52 cm diameter; \(\sim 30 \text{ dB} \) gain at 20 kHz) with an Earthworks M30 microphone was placed 5.1 m from the far wall. The parabolic microphone (unlike the vibrometer) relies on the detection of a back-propagating signal to the detector, which results in a signal that is delayed relative to the local microphone (Fig. 5). The observed delay of 14 ms is consistent with speed of sound travel to the remote parabolic microphone.

As noted in the Introduction, traditional PAS requires direct sampling of a gas within a closed resonant cell and is not amenable to standoff detection. A direct comparison of our DPAS results to PAS performance is thus not possible. We can, however, use our data collected using a stationary, chopped beam (see Fig. 1) as a surrogate for a PAS response. Note that our surrogate PAS response does not have the advantage of a closed resonant cell. Table 1 compares the DPAS response at a distance (both via vibrometer (Fig. 4) and parabolic microphone (Fig. 5)) to the surrogate PAS response. The different measurement conditions are listed. For the DPAS data, the SNR was calculated as the mean signal over the standard deviation of the background. For the PAS data, the SNR was calculated as the ratio of the power spectral densities at 3.1 kHz. The final row displays SNR normalized to 6 m (assuming an inverse-squared range dependence), 10 ppm, and 100 scan averages; it indicates many orders of magnitude advantage for the DPAS technique. While the PAS technique could be improved via the use of a parabolic collector, the collection area would have to be exceedingly large to increase the SNR to a level comparable to the demonstrated DPAS performance.

### 4 Detection of Ammonia in an Ambient Environment

We used a solid source of ammonia vapor to demonstrate the utility of the DPAS technique to detect important vapors in an open, ambient environment. The solid-state source relied on an acid-base reaction using an ammonium salt to produce \(\text{NH}_3\). Solid samples were placed in open trays extending over a 4 in. \(\times\) 36 in. line (Fig. 6). A local microphone with 9 in. collector (same as Sec. 2) was placed at the end of the array. The \(\text{CO}_2\) laser was tuned to an \(\text{NH}_3\) absorption line at 10.33 \(\mu\text{m}\) and scanned 0.5 in. above the sample at Mach

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**Table 1** Comparison of DPAS to open cell PAS at a range of 6 m.

<table>
<thead>
<tr>
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<th>DPAS (parabolic mic)</th>
<th>DPAS (vibrometer)</th>
<th>PAS</th>
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<tr>
<td>(\text{SF}_6) concentration</td>
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<td>(~7 \text{ ppm})</td>
<td>15 ppm</td>
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<td>Integration time</td>
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<td>100 scans</td>
<td>100 scans</td>
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<td>Range</td>
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<td>6 m</td>
<td>(~1 \text{ cm})</td>
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<tr>
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<td>200</td>
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<tr>
<td>Normalized SNR ((6 \text{ m}; 10 \text{ ppm}; 100 \text{ scans}))</td>
<td>(4.7 \times 10^2)</td>
<td>(2.4 \times 10^1)</td>
<td>(3.7 \times 10^{-4})</td>
</tr>
</tbody>
</table>

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**Fig. 4** Response of (a) laser vibrometer at 6 m standoff (upper; red) and (b) local microphone (lower; blue) to a release of \(\text{SF}_6\) gas. Black curves are responses with no gas present.

**Fig. 5** Response of (a) remote parabolic microphone at 5.1 m standoff (upper; red) and (b) local microphone (lower; blue) to a release of \(\text{SF}_6\) gas.

**Fig. 6** Test setup used to detect \(\text{NH}_3\) vapors emanating from a solid source of ammonia in an ambient environment.
1 (12 Hz rotation). An Online Technologies FTIR spectrometer sampled the local head space, recording varying concentrations of NH3 as high as 300 ppb. The microphone response averaged over 12 scans (1 s data acquisition; 0.042 s on target gas) is displayed in Fig. 7. The ~20 mV peak at 3.5 ms is due to the NH3 absorption (verified via background measurements for which no peak was observed). The SNR is estimated at ~20 based on the ~1 mV background signal (no material present). Our limiting sensitivity for NH3 detection based on these ambient measurements (SNR = 1) is thus ~15 ppb. We can compare this ambient result to our estimates of Fig. 2 by assuming SNR scales as the square root of integration time. If the ambient data were scaled to the 1.8 s integration (45× longer) of Fig. 2, then the detection sensitivity is ~2 ppb, which is in fairly reasonable agreement with the 1 ppb estimate of Fig. 2.

5 Conclusions

Laboratory measurements indicate that the DPAS technique may be useful for the standoff detection of trace vapors. Our anechoic chamber measurements indicate clutter-limited sensitivities of ~100 ppb (SF6; 0.43 m integration) and ~1 ppb (NH3; 1 m integration). Additionally, we demonstrate in an ambient laboratory environment that DPAS can be useful at standoff ranges of at least several meters. Of the two sensing modalities tested, the vibrometer is more amenable to monostatic standoff detection. In order to ascertain the technique’s field utility, outdoor measurements are planned in which realistic clutter levels will be assessed.

Acknowledgments

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References


Charles M. Wynn is currently leading several efforts at Lincoln Laboratory (LL), Massachusetts Institute of Technology (MIT) focused on laser-based trace detection. He has two patents (and one pending) related to trace explosives’ detection techniques he developed. Prior to joining MIT in 2000, he was at XonTech Inc, and The Ohio State University, where he studied designer organic magnets. He earned a BS, MS, and PhD all in physics from the University of Connecticut, Carnegie Mellon University and Clark University, respectively. He has over 30 scientific publications spanning a diverse range of topics.

Stephen Palmacci was an assistant staff member in the Submicrometer Technology Group at MITLL. He worked for more than 35 years on laser-based research at Spectra Physics Laser Analytics division and Lincoln Laboratory. He retired in 2013.

Michelle L. Clark is currently a staff member at MIT Lincoln Laboratory. She received her PhD in chemistry from MIT and ScB from Brown University. Prior to joining MIT, she worked as a senior systems engineer at Raytheon and as a principal scientist at Physical Sciences Inc. She was also a National Research Council of Canada postdoctoral researcher at National Institute of Standards and Technology. The majority of her research has focused on the development of novel laser-based ultrasensitive spectroscopic detection techniques spanning the UV to far-infrared region. Her current work focuses on phenomenology measurements of homemade explosives using a variety of standard analytical methods as well as development of optical measurements for trace detection of explosives, and chemical and biological agents.

Roderick R. Kunz is an assistant group leader in the Chemical Sensing and Synthetic Materials Group at MITLL. His current focus is on the analysis and implementation of sensors for chemical and explosives defense and threat signature phenomenology. He received his bachelor’s degree in chemistry from Rensselaer Polytechnic Institute and his doctoral degree in chemistry from the University of North Carolina at Chapel Hill.