

Stand-off identification of aerosols using mid-infrared backscattering Fourier-transform spectroscopy

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We show that it is possible to identify the chemical composition of an aerosol by using Fourier transform spectroscopy of backscattered mid-infrared light at a range of 200 mm. An ultrafast mid-infrared optical parametric oscillator provides the illumination source for the measurement across a wavelength range from 3.2–3.55 μm containing characteristic optical absorption features for two different chemicals. A normalized detection sensitivity below 10 ppm $\text{m}^{-1} \text{Hz}^{-1/2}$ is obtained.

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Aerosols are small particles of solid or liquid material suspended in air, and typically with a size below 10 μm . Because of their implication in a variety of human health conditions, and their role as a dispersal mechanism for accidental and deliberate release of toxic chemicals, the identification of airborne aerosol particulates is of major interest. While direct particulate-matter sampling can play a role in assessing the size, type and presence of aerosol particles it is normally not a real-time monitoring procedure and can over-/under-estimate the concentration of aerosol species. Optical techniques based on recording the characteristic chemical-absorption or Mie-scattering spectral signature of aerosol particles offer an alternative and instantaneous means of identifying potentially hazardous airborne particulates. In this Letter we introduce a new approach for the detection and identification of liquid chemical aerosols based on mid-infrared backscattering Fourier-transform spectroscopy.

The detection of aerosolized airborne threats such as chemical warfare agents (CWAs) or toxic industrial chemicals is important in mitigating the damage they could cause. Optical solutions to this sensing problem work by detecting the total amount of energy lost by the optical radiation incident on an aerosol particle. This can be described by the extinction cross section—the sum of the scattering and absorption cross sections ($\sigma_{ext} = \sigma_{abs} + \sigma_{scat}$)—and Mie scattering theory can be

used to calculate these cross sections using the complex refractive index of the material in question. To date, several optical techniques have been reported in an attempt to develop systems to measure the optical cross sections for chemical or biological aerosols, but have been limited in their abilities to provide complete aerosol identification. Gurton, Ligon and Dahmani [1] used a Nernst glower source covering a wide spectral range (3–13 μm) transmitted through a chamber containing aerosol to measure the extinction with a Fourier transform spectrometer (FTIR). A range of materials were examined, with the measured extinction for some materials showing good agreement with their calculated values. The aerosol size distribution and mass density were measured simultaneously with the spectral extinction, because Mie theory calculations are strongly affected by these parameters.

By incorporating photo-acoustic spectroscopy with a CO₂ laser, simultaneous measurements of aerosol absorption were also made for aerosols of liquid CWA simulants [2]. Photo-acoustic spectroscopy uses a laser modulated at an acoustic frequency; the absorption of the laser induces a pressure difference, and the acoustic wave strength can be measured to determine the amount of absorption, making the signal insensitive to scattering. In the 9.2–10.7 μm laser wavelength range studied in [2] photo-acoustic absorption measurements were found to agree broadly with the Mie theory absorption predictions. The extinction was found to be either dominated by absorption, or to involve a significant contribution from both scattering and absorption, depending on the chemical. It was noted that there must be a considerable quantity of aerosol material present before changes in transmission could be observed.

The use of backscattered light for stand-off identification offers a reduced risk of harm from dangerous aerosols by avoiding the need to collect a sample for analysis, therefore eliminating the possibility of human contact with a toxic material. Surprisingly, despite the previously cited studies, there appear to have been no attempts to use the infrared scattering of aerosols for broadband identification. Lidar using a CO₂ laser has been used to reveal the scattering behavior for different particle sizes [3], but to our knowledge, beyond lidar experiments limited to the wavelength range of CO₂ lasers [4], no other results using infrared aerosol backscattering with active illumination have been reported. We note also that in separate work fluorescence emission or laser induced breakdown spectroscopy has been attempted for aerosol identification [5].

Aerosol spectroscopy experiments in which the optical detection sensitivity was quantified are limited to some recent lab based measurements. Raman scattering was used to identify small concentrations (12 pg cm^{-3}) of a powder aerosol of isovanillin [6,7]. In a separate study, dynamic photoacoustic spectroscopy (DPAS) was used to assess the absorption from silica spheres using a tunable CO_2 laser [8] with an estimated minimum detectable concentration of $500 \text{ particles ml}^{-1}$ due to their absorbance.

Previously we introduced an approach to implement stand-off spectroscopy of liquid chemicals deposited on non-compliant surfaces (e.g. concrete, painted metal) [9], and in this Letter we now discuss the extension of this technique to identify the chemical constituent of an aerosol by measuring the broadband spectrum of backscattered mid-infrared radiation.

The illumination source was based on a passively mode-locked Yb: fiber laser, which was amplified in an Yb: fiber amplifier to produce chirped pulses ($\sim 2.5 \text{ ps}$) at a 100 MHz repetition rate with 2.7 W average power. This was used to synchronously pump a signal-resonant optical parametric oscillator (OPO) incorporating a 20-mm MgO-doped periodically poled lithium niobate (PPLN) crystal with nine grating periods and producing a collimated idler output tunable from $2.6\text{--}4.2 \mu\text{m}$. A similar OPO is described in detail in [10]. The OPO idler pulses entered a Michelson interferometer scanning at 2 Hz , which acted as a Fourier-transform spectrometer providing a measurement resolution of 3 cm^{-1} . After the interferometer the idler power was 70 mW , lower than the 250 mW OPO output due to the 50% loss from the interferometer and additional losses from the metal mirrors and Ge filter used. A weak reflection from a calcium fluoride (CaF_2) window was used to sample the idler spectrum to provide a reference measurement, with the remaining power being directed into the aerosol.

The aerosol was produced by using a medical nebulizer, designed for creating aerosols of medicine for inhalation with a mass median aerodynamic diameter of $3.0 \mu\text{m}$. The p-polarized idler beam after the CaF_2 filter had a 3.2-mm diameter and passed 10 mm above the top of the aerosol nebulizer. Idler radiation scattered by the aerosol was collected by a 50-mm diameter, 100-mm focal length CaF_2 lens which imaged the scattering point onto an uncooled PbSe detector, identical to that used for the reference measurement. This arrangement is shown in Fig. 1, with the inset showing a HeNe laser beam, co-aligned with the mid-IR beam, scattering as it passed through the aerosol.

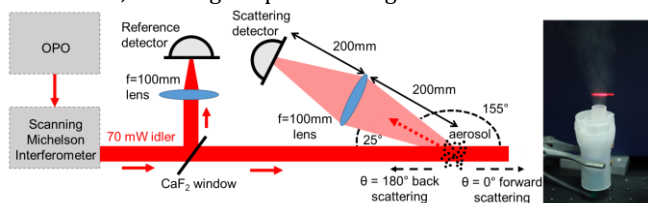


Fig. 1. Optical arrangement for recording the reference and scattered spectra. Inset: He-Ne laser beam scattering from the aerosol.

Our detection approach employed Fourier transform spectroscopy, which offers a number of important advantages. Firstly, the acquisition of the reference and backscattered spectra simply entails the synchronous collection of the respective mid-IR light on two separate photodetectors, so a spectral measurement can be made anywhere with a point detector. Fig. 2(a) shows typical interferograms recorded on the reference detector (in orange) and on the scattering detector (blue). The signal from the scattered light experiences low frequency noise due to the turbulent and inhomogeneous aerosol flow. As the Fourier-transform spectrum is encoded on a high-frequency carrier this low-frequency noise has no influence on the measurement and is automatically filtered out by the Fourier transform. We can contrast this

with a grating-scanned approach operating at the same acquisition rate (2 Hz): such a scheme would be unable to distinguish between turbulent intensity variations and those caused by wavelength dependent absorption features. In effect the Fourier-transform method acts like a lock-in detector, shifting the measurement to a higher frequency (the fringe period) at which $1/f$ noise is much lower.

Fig. 2(b) shows a typical idler reference spectrum (solid line), and compares it with a scattered-light spectrum (dotted line) recorded simultaneously. The scattering signal is much weaker than the reference, so here and in later results the scattered-light spectrum is normalized to the reference spectrum for clarity. A further advantage of FTIR is the measurement of the entire spectrum in one scan, useful considering the relatively broad spectra of the idler pulses.

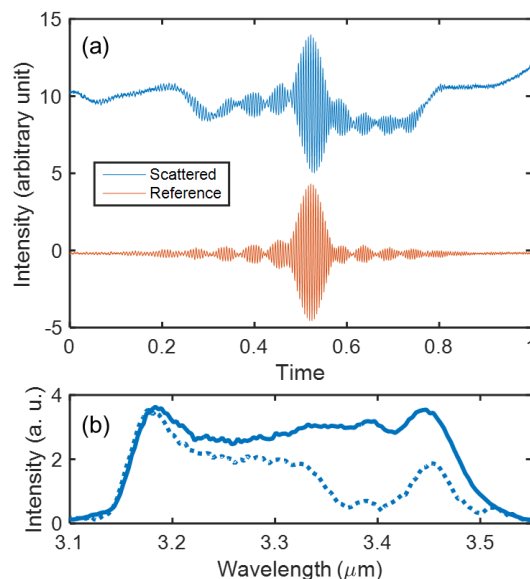


Fig. 2. (a) Example interferograms measured by the scattered-light (blue) and reference (orange) detectors. (b) Example reference (solid) and scattered-light (dotted) spectra.

Aerosols of two chemicals were examined, diethyl phthalate (DEP) and bis(2-ethylhexyl) sebacate (BES). Both chemicals exhibit infrared absorption in the $3.20\text{--}3.55 \mu\text{m}$ wavelength band. To examine this range two MgO:PPLN grating periods were used, $\Lambda = 29.98 \mu\text{m}$ and $29.52 \mu\text{m}$. For aerosolized DEP, Fig. 3(a) shows the spectra for both grating periods, with a cut off at $3.4 \mu\text{m}$ where the spectra overlap. Eight spectra were averaged to construct each plot. The averaged scattered-light spectrum was divided by the reference spectrum to find the spectral content of the scattered aerosol light, referred to from hereon as the aerosol spectrum. The blue line in Fig. 3(b) shows the DEP aerosol spectrum, co-plotted with the NIST library absorption spectrum for liquid DEP [11]. Fig. 4 presents the same information for BES. The two aerosols are clearly distinguished by their different aerosol spectra, with their measured absorption behavior corresponding well with the principal features of the library spectrum.

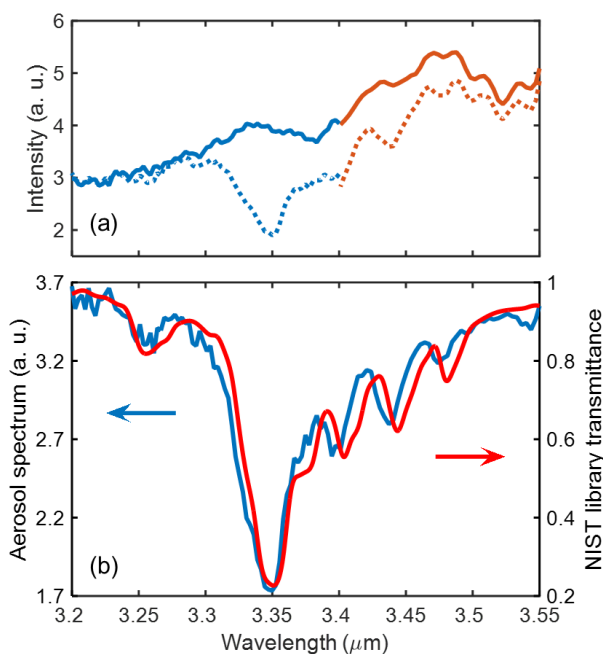


Fig. 3. (a) Reference (solid) and DEP scattered-light (dotted) spectra. Two OPO gratings were used, identified by orange ($\lambda = 29.52 \mu\text{m}$) and blue ($\lambda = 29.98 \mu\text{m}$) lines. (b) Aerosol spectrum (see text for definition) for DEP co-plotted with the library transmission spectrum [11].

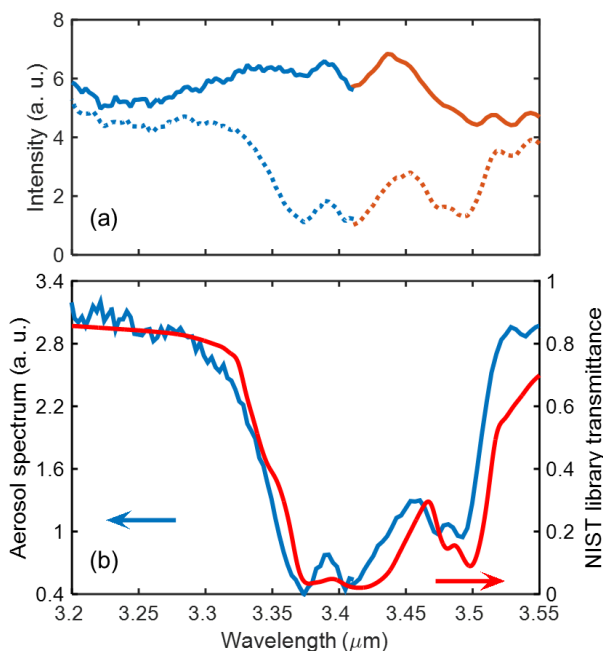


Fig. 4. (a) Reference (solid) and BES scattered-light (dotted) spectra. Two OPO gratings were used, identified by orange ($\lambda = 29.52 \mu\text{m}$) and blue ($\lambda = 29.98 \mu\text{m}$) lines. (b) Aerosol spectrum for BES co-plotted with the library transmission spectrum [11].

We consider now the sensitivity provided by aerosol backscattering Fourier-transform spectroscopy. The signal-to-noise ratio (SNR) can be defined as the ratio of the maximum value of the signal to the standard deviation of the noise. Constructing a measurement by averaging eight

scattered-light interferograms resulted in a SNR greater than 100, and even using a single scattered spectrum resulted in a SNR of 40 for both chemicals. However, some caution is needed since a considerably higher SNR than unity would be required to accurately characterize the absorption behavior of a chemical under examination. We estimate that $\text{SNR} = 10$ would be the minimum required, so with a single scattered spectrum it would be possible to detect and identify aerosol absorption features with a signal four times weaker than we used in our experiments.

The calculation of detection sensitivity relies on knowing the exact quantity of aerosol with which the OPO idler radiation interacts. Based on the nebulizer specifications of a 41 min^{-1} air output with a nebulization rate of $0.06 \text{ cm}^3 \text{ min}^{-1}$, we calculated that the beam interacted with 730 ppm of BES and 1700 ppm of DEP. Assuming a minimum SNR of 10, and using detection sensitivity units normalized for path length and integration time, a sensitivity in the range of 3 – 6 $\text{ppm m}^{-1} \text{ Hz}^{-1/2}$ was calculated for BES and DEP respectively. This calculation relies on nebulizer specifications quoted by the manufacturer which we have not independently verified, nevertheless we consider a sensitivity of $< 10 \text{ ppm m}^{-1} \text{ Hz}^{-1/2}$ to be indicative of the technique's capability in its current embodiment. This value is comparable to the sensitivities reported in other standoff gas detection techniques [13, 14]. While the Raman and DPAS aerosol point detection techniques detailed earlier [9, 10] are not directly comparable, the Raman system appears to be considerably more sensitive.

In the 3–4- μm wavelength band applying to this investigation, our results show that the scattered-light absorption spectrum broadly reflects the absorption characteristic of the chemical constituent of the aerosol. This makes intuitive sense, as during the interaction with the liquid particles it can be expected that some light will be absorbed where the wavelength corresponds with a chemical absorption feature. Unlike gas-phase spectroscopy, the aerosol spectrum can also be influenced by Mie scattering resonances, implying that the particle size distribution of an aerosol could have a significant influence on the aerosol spectrum. An angular dependence of the scattered light intensity is also expected; modelling by Niu, Philbrick and Hallen [13] studied scattering angles from 0–90°, finding that the aerosol spectrum was almost particle-size invariant at small scattering angles. Modelling the scattering process, as well as measuring the particle size distribution is therefore the next step to understand these results more fully. In both Fig. 3(b) and Fig. 4(b) the aerosol spectrum appears to have its absorption features shifted slightly to the left of the library spectrum. Calibration of the FTIR spectrometer using a HeNe reference laser makes it unlikely that this wavelength shift is due to a calibration problem (attributed to the Connes advantage of FTIR [14]). The NIST spectra were recorded on dispersive instruments (with a comparable resolution of 4 cm^{-1} and 2 cm^{-1} for DEP and BES respectively), and it is mentioned that these may differ in details from FTIR measurements. It is possible that the wavelength shift we observed could be due to a Mie scattering effect that needs further investigation before its contribution to the spectrum can be properly understood. Nevertheless, our results using BES and DEP show that the aerosol scattering spectrum tends to follow the liquid behavior, and in an experiment with a water aerosol not presented here we also found its absorption in the 2.8–3.4- μm range followed the absorption behavior of liquid water.

As well as chemical threats, monitoring of atmospheric aerosols is an area of interest especially in terms of pollution monitoring and climate change. Stand-off aerosol detection may allow greater flexibility compared to point aerosol detectors, so it is surprising how little published work exists on the subject. Modern spatially coherent infrared sources such as OPOs and quantum cascade lasers have the potential to deliver greater performance than CO_2 lasers, because of

their continuous and broad tuning ranges. Chemical detection could also be combined with range gating. Boudreau [15] used dual comb spectroscopy around 1.56 μm to measure the narrow absorption lines of gaseous hydrogen cyanide. By dispersing water droplets in the gas chamber, this study used the backscattering from the droplets, as well as the reflection from a diffuse scattering surface at the back of the chamber, to measure the gas absorption. Incorporating lidar, it was also possible to distinguish between the light scattered by the aerosol and the light scattered by the back surface. Our system operates in a stand-off configuration, with a short stand-off distance of 200 mm, however using heterodyne detection would significantly improve the detection sensitivity, as well as allowing range gating. Our current sensitivity appears to be significantly less than the Raman system detailed earlier [6,7], and there are no similar mid-IR techniques reported which provide a quantitative sensitivity against which our results can be compared. Only one aerosol is examined using Raman scattering though, with the sensitivity defined by a single Raman shift. Further investigation would be required to determine how well different chemical aerosols could be distinguished. It also may not be practical to use Raman scattering for stand-off detection due to the weak Raman signal.

In summary, we have shown that chemical aerosols can be distinguished or even identified, based only on the backscattered mid-IR radiation from the aerosol itself. Active illumination using two grating periods in an ultrafast OPO allowed measurement of the aerosols' scattered spectra in the 3.20–3.55- μm wavelength range, producing data which correlated well with the library absorption spectra for the liquid phase of the chemicals DEP and BES.

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