Chemical detection using broadband femtosecond optical parametric oscillators in the 6-12-micron spectral fingerprint region

D. T. Reid*, O. Karaa, M. Rutkauskasa and L. Maidmentb

a Scottish Universities Physics Alliance (SUPA), Institute of Photonics and Quantum Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK;
bChromacity Ltd., Livingstone House, 43C Discovery Terrace, Riccarton EH14 4AP.

ABSTRACT

The broad and slowly varying spectral features of liquids and solids require broadband sources in the mid- to long-wave infrared for their detection and identification. We present here a range of measurements made using uniquely tunable femtosecond optical parametric oscillators, which have enabled stand-off Fourier-transform spectroscopy to be implemented across a large part of the spectral fingerprint region. In this way we have achieved active stand-off detection of liquids on surfaces, of powders and of airborne liquid particles in aerosol form. We discuss the optical parametric oscillator technology, the spectroscopy implementations and the detection capabilities and limitations of the techniques.

Keywords: Chemical sensing; spectroscopy; mid-infrared; fingerprint region; long-wave infrared; stand-off spectroscopy.

1. INTRODUCTION

Standoff detection, identification of a sample at a distance without interfering with it, offers a reduced risk of harm from dangerous chemicals by avoiding the need to collect a sample for analysis, therefore eliminating the possibility of human contact with a toxic material. It has potential military applications in determining if a liquid deposition on a surface is dangerous, avoiding an unnecessary time consuming decontamination process. This is particularly important in the case of non-volatile chemical warfare agents (CWAs), as their presence persists for a long period. As an example, VX nerve agent is less volatile than water by a factor greater than 1000 [1]. A recent editorial in Optical Engineering [2] points out that, despite it being 100 years since the chemical weapons were first used on a large scale in the first world war, their use is presently an emerging threat. It argues that the easily accessible information on the internet and increased civil unrest fueling demand for improvised weapons could lead to wider use of CWAs. This scenario therefore motivates the development of standoff detection techniques for toxic chemicals based on molecular spectroscopy. There is a range of other possible applications for such technology, including security screening and sorting of different materials e.g. plastics in a recycling context.

While gas absorption spectroscopy is characterized by a rich spectral structure that permits species identification using carefully selected narrow absorption features, the identification liquid, aerosol and solid samples requires a fundamentally different approach. Here, no fine spectral structure is expected, but broadband coverage is important to distinguish chemicals by examining their gross spectral shapes, which may require measurements over a few 1000 cm⁻¹ to provide a confident diagnosis. Measurements in the mid-wave infrared (MWIR) region are useful for identifying certain hydrocarbon bonds, while other functional groups and their configurations can be revealed better at longer wavelengths. In particular, measurements in the long-wave infrared (LWIR) from 6 – 12 µm can not only identify functional groups, but show differences according to their relative positions on the molecule, enabling molecular isomers to be distinguished spectroscopically.

This article reviews our recent progress across a number of different approaches to stand-off chemical detection. We begin by introducing the basic concept of Fourier-transform spectroscopy with broadband active illumination, then describe how this has been applied to the spectroscopy and identification of liquids, aerosols and powder samples.
2. FOURIER-TRANSFORM SPECTROSCOPY WITH BROADBAND ACTIVE ILLUMINATION

Stand-off chemical detection using Fourier-transform spectroscopy (FTS) is well established as a passive technique (for example [3]), but as an active technique has been limited until recently by the availability of suitable sources. Femtosecond optical parametric oscillators (OPOs) satisfy the necessary requirements, namely they can provide broadband wavelength coverage in the appropriate region of the mid-IR needed to address diagnostically useful chemical absorption features, and their output is spatially coherent, meaning that the beam can be directed over a long distance with minimal broadening and distortion.

The approach proceeds by modulating the OPO output by passing it through a scanning Michelson interferometer, so that any subsequent detection of the modulated beam records a time-varying interferogram, from which the spectrum of the light can be extracted using a simple Fourier transform. As illustrated in Fig. 1, mid-infrared light from the OPO enters the scanning Michelson interferometer in parallel with a continuous-wave (cw) reference beam used to calibrate the interferometer path length difference (Fig. 1(a)). The interferometer design is reproduced in Fig. 1(b), and example data are shown in Fig. 1(c) and (d).

Following the interferometer, light is directed onto a sample (for solids and liquids) or focused into an aerosol, where the spectroscopy concerns aerosol particles. The collection arrangements for the backscattered light differ according to the nature of the measurement. For aerosols, the scattering cross-section is very low, so the collection optics must be situated relatively close to the region where the aerosol is generated. For liquids and solids the light is back-scattered over a range of solid angles which is typically significantly less than 2\(\pi\) steradians and so provides a brighter return signal, allowing stand-off distances of up to several tens of metres.

3. STAND-OFF DETECTION OF LIQUIDS

Our original stand-off spectroscopy demonstration employed an Yb:fiber laser-pumped MgO:PPLN OPO, and is described in detail elsewhere [4]. The current embodiment of this system and its spectra coverage are shown in Fig. 2. The OPO is pumped by chirped few-ps pulses from an Yb:fiber master-oscillator power amplifier. Gain is provided by a 20-mm MgO:PPLN crystal with grating periods from 27.9 – 31.0 \(\mu\)m, giving tuning from 2.5 – 4.2 \(\mu\)m.
Using this system we have recorded spectra using light back-scattered from non-compliant materials such as concrete. Example data are shown in Fig. 3 for the detection of a drop of the liquid TDG on a concrete surface at a distance of 1 meter and of nitromethane vapor, where the return light is backscattered from a concrete target. Extensions to this approach are possible by using sensitive detectors and larger diameter collection optics. In this way we have extended the range of this system to tens of meters.

Fig. 2. MgO:PPLN OPO based on chirped-pulse pumping from an Yb:fibre laser. The OPO idler is used for stand-off chemical sensing and tunes from 2.5–4.2 µm.

Fig. 3. Left: Measured transmission spectrum of TDG on a concrete substrate (solid lines) and comparison with reference spectrum (dashed lines). Right: Measured (solid line) and simulated (dashed line) transmission spectrum of vaporized nitromethane obtained from a concrete substrate at a stand-off distance of 1 m.
4. STAND-OFF SPECTROSCOPY OF AEROSOLS

Understanding the infrared (IR) spectroscopy of aerosols is important for climate science, astronomy and industrial safety, but the spectral characteristics of light scattered from an aerosol are complicated by the dual contributions of the bulk chemical absorption and by particle-size effects (e.g. Mie scattering). At shorter IR wavelengths, aerosol spectra correspond well to the transmission profile of the equivalent bulk material, as our earlier work using wavelengths of 3.2 – 3.55 µm showed [4]; however, at longer IR wavelengths the behavior is quite different, with Mie-scattering strongly modulating the underlying chemical absorption signature. Infrared spectroscopy in the so-called spectral "fingerprint region" (ca. 6.5–20 µm) is routinely used to identify unknown vapor and condensed phase chemicals with high confidence, but extending this to aerosolized chemicals requires scattering effects to be taken into account. Here we show how this can be done, presenting a combination of novel theoretical calculations and broadband laser measurements for an aerosol of the chemical diethyl phthalate (DEP).

The illumination source used was an optical parametric oscillator (OPO) synchronously pumped by a passively modelocked Yb:fiber laser (Chromacity Spark) and amplifier, producing 100-MHz pulses with 2.7-W average power. The OPO used the quasi phase matched nonlinear material orientation patterned gallium phosphide (OP-GaP) to produce a collimated idler output with tuning between 5–12 µm (described in detail elsewhere [5]).

Broadband idler pulses from the OPO pass through a scanning Michelson interferometer, acting as a Fourier transform IR (FTIR) spectrometer. A weak reflection from a calcium fluoride (CaF$_2$) window is focused onto a liquid nitrogen cooled mercury cadmium telluride (MCT) detector, providing a reference spectrum measurement (see Fig. 1). The beam then passes through the output plume of a medical nebulizer, designed to produce respirable aerosols with a mass median aerodynamic diameter of 3.0 µm. A GRIMM laser aerosol spectrometer was used to measure the particle size distribution of aerosolized DEP, indicating a wide range of particle diameters were present, from 0.25 to 10 µm. Two 50-mm focal length CaF$_2$ lenses collected scattered light from the aerosol onto another MCT detector. Fig. 4 shows the optical arrangement.

The mid-infrared scattering of light was modelled using Mie theory [6], which sums all the possible oscillating electric field dipoles in a particle. Resonances in these oscillations mean the scattered signal can differ significantly for different particle sizes. Our model includes the complex refractive index of the particle material, so also accounts for absorption. The model integrated the differential scattering cross section over a solid angle (determined by the aperture and position of the collection lens) for a particular particle size distribution (chosen to match the measured range) to calculate the scattered power as a function of wavelength.

Figure 5(a) shows the liquid transmission of DEP over the wavelength range of 3-12 µm, calculated from the imaginary refractive index (measured at 2 cm$^{-1}$ resolution using a standard FTIR spectrometer). Also shown is the simulated scattering spectrum, modelled using the DEP complex refractive index, measured particle size distribution, polarization of incident light, and solid angle defined by the size and position of the collection lens. The result is normalized for comparison with the liquid transmission. The simulated scattering generally shows similar features to the liquid transmission spectrum, but with some significant baseline intensity differences and wavelength shifts in absorption features, especially at wavelengths above 7 µm.

Scattering from an aerosol of DEP was measured at a forward scattering angle of 25 degrees, using the p-polarized mid-IR photons from two OP-GaP gratings. The illumination spectrum of one grating (an average of 8 spectrum measurements) covering 7.1-8 µm is shown in Fig. 5(b), along with the scattered light spectrum from the DEP aerosol. To find the spectral content of the scattered light, the scattered spectrum was divided by the reference spectrum, resulting

![Fig. 4. Layout of the OPO, spectrometer, and aerosol scattering measurement system.](image-url)
in the aerosol spectrum. The aerosol spectrum for these wavelengths is shown in Fig. 5(c), with the liquid transmission and simulated aerosol scattering spectra. The data are normalized again to allow a clearer comparison. The liquid transmission shows a large absorption feature at 7.85 µm, while the simulated scatter signal shows this shifted to around 7.65 µm. The experimentally measured aerosol spectrum agrees much more closely with the simulated scatter signal, showing the main absorption feature just above 7.60 µm. The second OP-GaP grating covered 8–8.85 µm, and the aerosol spectrum is shown in Fig. 5(d). The signal was weaker due to lower output power from the OPO and absorption in CaF₂, but still the aerosol spectrum more closely mimics the simulated scatter signal than the liquid transmission spectrum, although there are no large absorption features in this range.

These results are an experimental verification of this aerosol scattering model, which predicts that the scattered light spectrum of aerosol particles is heavily dependent on particle size distribution, as well as measurement angle and polarization. Scattered light spectra will sometimes closely follow the infrared absorption of a particular chemical, but can also significantly differ.

Scattering results from a range of different chemicals, as well as a range of particle size distributions will help to further validate the model. The system will be improved in the future by replacing the CaF₂ optics with zinc selenide, allowing measurements up to 12.5 µm (the full spectral range of the OPO).

5. IDENTIFICATION AND DISCRIMINATION OF WHITE POWDER SAMPLES USING STANDOFF SPECTROSCOPY

As already discussed, obtaining diagnostically useful information does not demand high resolution—liquids and solids exhibit broad absorption features, so cm⁻¹-level resolution is sufficient—but unique identification makes it important to capture information over a broad bandwidth, making femtosecond sources ideally suited to this problem.

Our preferred source was an OP-GaP femtosecond OPO, described elsewhere in detail already [5]. For powder spectroscopy the beam was directed through a scanning Michelson interferometer (acting as a Fourier transform

Fig. 5. (a) Infrared transmission of liquid DEP (light orange), and simulated scattering spectrum at an angle of 25° (dark orange). (b) Spectrum from OPO used to illuminate the aerosol (light blue), and scattered light spectrum (green). (c) Aerosol spectrum between 7.1-8 µm (blue), along with liquid transmission and simulated scattering spectra. (d) Aerosol spectrum between 8-8.85 µm (blue), along with liquid transmission and simulated scattering spectra.
spectrometer) before being directed vertically onto a white powder sample (~10 g) on a card. The illumination was normal to the card, with diffuse light scattered over the full range of solid angles. To avoid spectroscopic contributions from the substrate we chose to collect light scattered at nearly 90° to the incident beam and focused this onto a mercury cadmium telluride detector [Fig. 6(a)]. The spectrum of the light scattered from caffeine powder was measured by Fourier transforming the interference fringes detected, using three different OPO gratings (Λ = 29, 31 and 32.5 µm) to generate broadband incident radiation from 8–11 µm. The illumination and scattered spectra are shown in Fig. 6(b), each one based on an average of 7 measurements recorded in 250 ms at 2 cm⁻¹ resolution. The scattered spectrum in each case is divided by the illumination spectrum to find the spectral response of the powder, shown in Fig. 6(c–e), revealing clear absorption features.

A library of powder scattering spectra was compiled by collecting 14 interferograms of 11 white powder samples including caffeine (the samples are listed in Table 1) using the 29 and 31 µm gratings. The powders were chosen as they are readily available and require minimal safety precautions when handling. Examples of the library spectra between wavelengths of 8.2–8.9 µm, recorded using the 29 µm grating are shown in Fig. 7. To compare a spectrum with the library, Pearson’s correlation coefficient was used (in a similar approach to [7]), which is particularly suitable as it is insensitive to differences in magnitude between compared signals, since it only recognizes the shape and position of features, and returns a maximum value of 1 for perfect correlation. To classify a spectrum, its correlation coefficient with respect to every library spectrum was found, and the correlation values for each particular chemical were averaged, giving a single correlation value for each powder. The library match was then considered to be the chemical with the highest coefficient. This approach worked perfectly to classify any individual spectrum recorded at the same time as the library data was recorded.

To test the robustness of the library classification scheme, new data were recorded at a later time, after reconstructing the scattering setup and using new samples of the same powders. The signal strengths of these data were weaker than the library data. Table 1 presents representative results, displaying the mean correlation coefficient of three tests with each
library chemical. As indicated by colored cells, taurine and l-glutamine were matched correctly, while creatine was not and matched equally with the taurine and creatine library data.

Table 1. Mean correlation coefficient of three test powders with each library powder.

<table>
<thead>
<tr>
<th>Library</th>
<th>Test powders</th>
<th>caffeine</th>
<th>aspirin</th>
<th>paracetamol</th>
<th>n acetyl L cysteine</th>
<th>l-glutamine</th>
<th>inositol</th>
<th>taurine</th>
<th>leucine</th>
<th>creatine</th>
<th>beta alanine</th>
<th>dextrose</th>
</tr>
</thead>
<tbody>
<tr>
<td>taurine</td>
<td>-0.96</td>
<td>-0.70</td>
<td>-0.89</td>
<td>-0.72</td>
<td>-0.44</td>
<td>-0.48</td>
<td>0.95</td>
<td>0.34</td>
<td>-0.06</td>
<td>-0.52</td>
<td>-0.72</td>
<td></td>
</tr>
<tr>
<td>l-glutamine</td>
<td>0.53</td>
<td>0.51</td>
<td>0.52</td>
<td>0.69</td>
<td>0.89</td>
<td>0.47</td>
<td>-0.36</td>
<td>-0.21</td>
<td>-0.26</td>
<td>0.61</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>creatine</td>
<td>-0.57</td>
<td>-0.63</td>
<td>-0.40</td>
<td>-0.70</td>
<td>-0.45</td>
<td>-0.20</td>
<td>0.53</td>
<td>0.36</td>
<td>0.53</td>
<td>-0.22</td>
<td>-0.09</td>
<td></td>
</tr>
</tbody>
</table>

The library classification scheme definitively identified spectra from powders with distinctive spectral features between 8.2 – 8.9 µm, even when measurements were made again with weaker signals. Fig. 7(a) and (b) show the distinctive spectra of taurine and l-glutamine which were easily matched. (c) shows the library spectra for creatine, which is weaker and noisier, with less distinctive features. This is the reason that creatine scattering measured later was not clearly identified by the library.

By extending the library across a greater wavelength range, it would be possible to correctly identify a wider range of powders with greater confidence.

6. CONCLUSIONS

We have described here an approach to active and broadband standoff chemical spectroscopy using coherent illumination provided by femtosecond optical parametric oscillators based on MgO:PPLN and OPGaP. Results presented for the detection of a variety of liquid, aerosolised and powdered samples show the potential of the technique to identify these chemicals from the infrared absorption features between 3–12 µm. The techniques presented here use mechanically scanned Fourier-transform spectroscopy but would be equally well suited to an OPO-based implementation of dual-comb spectroscopy [8,9,10] with no moving parts.

REFERENCES