

High-resolution infrared spectroscopy for *in situ* industrial process monitoring

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Introduction

High-resolution, mid- and near infrared spectroscopy, where molecular rotational fine structure can be observed, has had limited applications to industrial process monitoring. Of course, for solid- and liquid-phase measurements little gain is to be had from measuring at high spectral resolution and low spectral resolution techniques showing the molecular vibrational structure are all that is required. However, for gas- and vapour-phase work several benefits arise from moving to higher resolution. One of the principal benefits is that the techniques become more species selective. Unambiguous identification of a spectral feature and its related molecular origin can be of great value. It may perhaps be argued that it is not necessary to understand the molecular origins of an absorption feature; it is just necessary to determine its magnitude and effect on other measurable properties, but parameters such as gas concentrations can be extracted with more confidence if the feature is understood and can then be simulated from first principles.

To achieve high spectral resolution there are two approaches: either Fourier transform infrared (FT-IR) spectroscopy, with a resolution of 0.5 cm^{-1} or better, or IR laser absorption spectroscopy. There are advantages of using lasers as light sources in process monitoring. Higher light intensities can give rise to higher detection sensitivities over broadband approaches and thus higher speed measurements. For example, near infrared (NIR) diode laser absorption spectroscopy¹ can achieve detection limits of 10^{-6} absorbance units and even 10^{-7} in some cases, whereas modern FT-

IR instruments attain nearer 10^{-3} . Often the laser linewidth is negligible so the absorption lineshapes become entirely due to molecular effects. From a more practical aspect, intense, collimated beams make optical alignment much easier than with classical sources.

Attached to these advantages are the inevitable disadvantages. The narrow wavelength tuning range of most lasers limits the number of chemical species that can be detected. Interpretation of the spectra can be more difficult due to the added complexity of rotational structure and some laser spectrometers require specialist operators and cannot be regarded as “turn-key” at present. They can also be expensive although this is not always the case for some NIR diode laser technology!

Measurement challenges

There are many challenges associated with *in situ* high-resolution infrared spectroscopic monitoring of industrial processes, amongst which are often high process temperatures, high dust loads, condensation of moisture, presence of hazardous or toxic gases, low concentrations of key species as well as high concentrations of interfering species. These are common to all optical techniques and optical integration of spectroscopic instrumentation to these processes is still the most challenging aspect. IR transmitting materials such as KBr are far from ideal. Figure 1(a) illustrates some of the spectroscopic difficulties. Here 10 ppmv HCl (in red) is to be measured in the presence of 15% H₂O at 600 K with a 1 m pathlength at atmospheric pressure. This is typical for an industrial

waste incinerator. At low spectral resolution it would not be possible to measure HCl due to the interferences but at high resolution, as shown here, one or two HCl lines can be seen to be clear of H₂O interference and can be used for monitoring purposes.

This brief review will explore some of the latest approaches to *in situ*, non-invasive industrial process monitoring with high-resolution infrared techniques such as IR diode laser and FT-IR spectroscopy. After a review of the information available from a high-resolution spectrum, we will review briefly current IR sources and techniques, followed by three examples illustrating NIR diode laser spectroscopy and FT-IR absorption spectroscopy for different application areas. Finally, future prospects and conclusions will be presented.

Information obtainable from high-resolution IR spectroscopy

A high-resolution infrared spectrum can provide an enormous amount of fundamental molecular information: the line positions and intensities give information on the geometric and electronic structure of the molecule and the line broadening gives information on molecular interactions. Figure 1(b) shows a section of the HCl spectrum in the NIR where the H³⁵Cl and H³⁷Cl lines are easily distinguished. The line positions are due to the vibrational and rotational motion of the molecule. The intensities of the lines are also temperature-dependent.

The mid-infrared spectral range generally provides information on fundamental vibrations whereas the weaker vibrational

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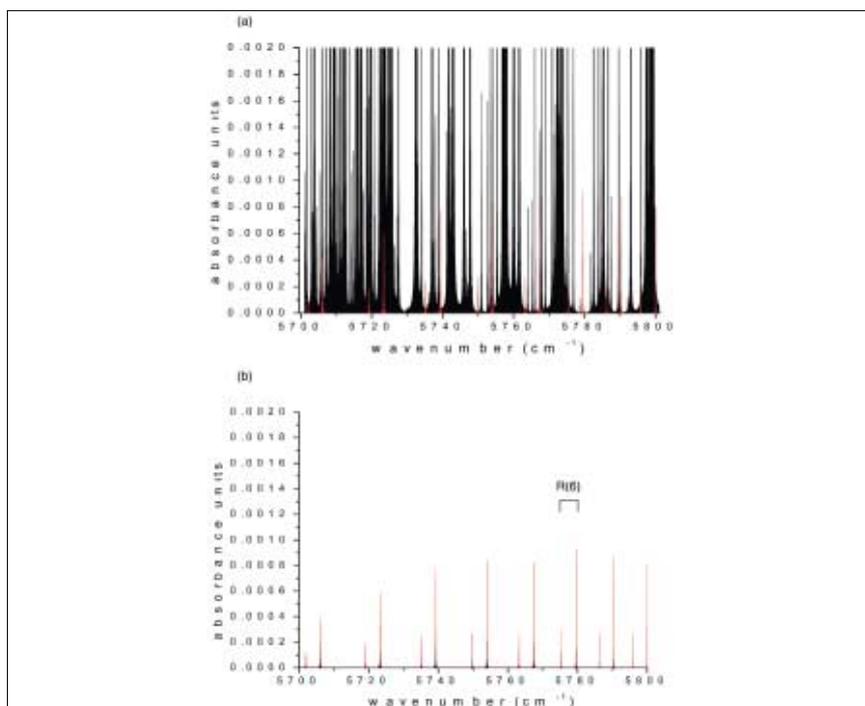


Figure 1. Upper (a) a simulated NIR spectrum between 5700 and 5800 cm^{-1} (1724–1754 nm) showing typical absorption lines arising from 15% H_2O (black) and 10 ppm HCl (red) at 600 K and atmospheric pressure with a 1 m absorption pathlength as might be observed from a waste incinerator. Only high-resolution spectroscopic techniques can easily detect HCl under such conditions such as by a narrow wavelength scan across the HCl line at 5780 cm^{-1} . Lower (b) the same conditions as above but without the H_2O . Each line arises due to the rotation of the molecule and pairs occur due to the isotopic abundance of Cl: H^{37}Cl is the weaker and H^{35}Cl is the stronger line of each pair.

overtone and combination bands are usually found in the NIR range with the boundary often considered to be around 4000 cm^{-1} or 2500 nm. Part of the first overtone of HCl is shown in Figure 1(b) and this is approximately 40 times weaker than the fundamental in the mid-infrared. Of more interest to process monitoring and analysis are gas concentration, temperature and pressure. How can these be extracted from the spectrum?

Gas concentration can be determined from the integrated absorbance of a single vibration–rotational line using the Beer–Lambert law. The linestrength at the measurement temperature and the absorption pathlength are required. The linestrength is related to the absorption coefficient and is dependent on fundamental quantum mechanical properties of the molecule such as the transition moment and the distribution of energy levels within the molecule (partition functions).

From the ratio of the intensities of two integrated absorbance lines of the same

species arising from different lower state energies, the **temperature** can be determined. This is called *two-line thermometry* and the sensitivity of the ratio to temperature depends on the relative energy separation of the lower state energy levels of the two transitions. So the wider the spacing, the higher the temperature range that can be explored.

The **gas pressure** can be extracted from the line broadening in principle. At atmospheric pressure and above, the lineshapes are generally due to collisional or pressure broadening giving rise to a Lorentzian lineshape. For low gas pressures below, say, 10 mbar the lineshapes are determined by Doppler broadening and gives rise to a Gaussian lineshape. At intermediate pressures a convolution of the two is observed which is called a Voigt lineshape. In the higher pressure regimes and if the collisional gases are known then the pressure can be extracted from the absorption lineshape. Different collisional or background gases broaden lines to a greater or lesser extent.

Finally, for high gas velocities the Doppler shift of the peak absorption wavelength can be used to determine gas velocities. Combined with gas concentration measurements, **mass flow** can thus be extracted.²

IR sources

For standard IR spectroscopy with FT-IR instruments, global sources are used which have relatively weak intensity; the high spectral resolution is then obtained by the distance the mirror moves in the Michelson interferometer part. For IR laser sources, the laser itself generally has an emission linewidth much smaller than the absorption lines being measured. An ideal infrared source for high-resolution spectroscopy would perhaps be a widely tunable laser (tunable over several thousand cm^{-1}), with a single frequency output (single mode), with high spectral power density, small size, turn-key operation and built in wavelength calibration. Unfortunately, such a laser light source does not exist.

For many years now the tunable semiconductor diode laser has been the only suitable IR laser source. In the NIR, the growth in telecommunications technology has pushed the development of diode lasers based on gallium arsenide, indium phosphide and antimonide substrates. Each device only has a narrow tuning range (limited by the band-gap of the semiconductor). Various semiconductor structures have been made to limit the laser emission to a single wavelength (single mode) rather than several, which are emitted in simple devices. Some of these are: distributed feedback lasers (DFB), vertical cavity surface emitting lasers (VCSEL) and external cavity diode lasers (ECDL) with wider tuning ranges.

In the mid-infrared diode lasers are based on lead–salt structures and operate only at cryogenic temperatures with low output powers, but are available over a wide spectral range. Quantum cascade lasers have been developed more recently which can operate at room temperature with higher output powers. They are, however, limited to a very narrow tuning range but have been demonstrated in several research applications for detecting small molecules such as NH_3 , NO and CO. Alternative

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approaches to producing tunable IR laser light have been mixing laser light at two shorter wavelengths on non-linear crystals such as lithium niobate, LiNbO₃. These are called difference frequency lasers. Optical parametric oscillators are also based on non-linear optical effects in crystals between two different wavelengths and are capable of producing all solid-state IR laser light. Table 1 summarises the available IR sources.

IR techniques

Tunable IR laser absorption spectroscopy on one level is a simple technique. The laser beam is passed through the cell or process to a detector and the spectrum is obtained by tuning the laser wavelength (by changing current through the device or the temperature in the case of diode lasers) and measuring the changes in transmission as a function of wavelength. It has intrinsically high spectral resolution as the laser linewidth is usually insignificant compared to molecular linewidths (at atmospheric pressure). Uncertainties in the instrument lineshape function are generally of no concern, unlike FT-IR spectroscopy. Detection sensitivity can be enhanced by employing such techniques as balanced detection and wavelength modulation spectroscopy with harmonic detection.¹

NIR diode laser absorption spectroscopy is already becoming accepted in environmental and process monitoring due to the quality of the telecommuni-

cations lasers, the ease of optical integration compared to mid-infrared systems and the low maintenance of instruments. The following examples illustrate the use of NIR diode lasers and FT-IR in industrial process applications.

Example 1. *In situ* process analysis of tin oxide APCVD

Atmospheric pressure chemical vapour deposition (APCVD) is used for the production of coatings and thin films on substrates for a wide variety of applications, such as tin oxide onto glass substrates. These transparent conducting oxide coatings are used for low emissivity glass, for gas sensors and also for solar cells. Heat drives the chemical reactions starting with the breakdown of a precursor molecule. The often complex reactions can be predominantly in the gas phase with the subsequent deposition of the target species directly on the surface of the substrate. Identification of the key reacting species is fundamental to the understanding of the process and its subsequent control. Mass spectrometry and gas chromatography are proven techniques for this, but are inherently invasive and can affect the gas flow and heat transfer in the reactor. Non-invasive optical techniques are thus preferred.

Various organotin compounds are used as precursors and in this example,³ dimethyltin dichloride (DMT) was used combined with oxygen and water vapour.

The laboratory scale reactor made of quartz glass was of a cold-walled, horizontal flow design with a glass substrate of area 22.2 × 9 cm², maintained at 645°C and a top glass plate 10 mm above the substrate to maintain laminar flow. A test reactor employed side-arms with KBr infrared windows so that FT-IR absorption spectroscopy could be used to determine the species present before using a NIR diode laser spectrometer for specific species monitoring. The main species present were HCl and CH₄, with smaller amounts of CO, CO₂, CH₃OH, CH₂O, C₂H₂, C₂H₄, C₂H₆. Problems with the FT-IR approach were related to the long acquisition time and the difficulty of alignment through the 10 mm gap above the substrate.

Evolved methane was selected as a target species for NIR diode laser spectroscopy through the 2ν₃ overtone transition around 1665 nm. The diode laser beam could be passed through the walls of the quartz glass reactor without the necessity of specialised IR windows allowing the concentration of methane at different heights above the substrate and at different distances along the reactor to be determined as can be seen in Figure 2. The higher sensitivity resulted in a time resolution of less than a second. It was shown that there was a correlation of methane concentration with tin oxide film thickness thus allowing the possibility of process control.

Table 1. Summary of infrared devices for high-resolution spectroscopy.

	Range (nm)	Individual device range	Comments
Distributed feedback (DFB) diode laser	700–5,000	~3 cm ⁻¹ with current ~30 cm ⁻¹ with temperature	Single mode, mW, commercially available systems
Vertical cavity surface emitting diode laser (VCSEL)	700–2,000	~6 cm ⁻¹ with current ~30 cm ⁻¹ with temperature	Wide tuning range for each mode. Low currents, easier coupling to fibres, lower costs
External cavity diode laser (ECDL)	700–2,000	~300–400 cm ⁻¹	More expensive, moving parts, wider tuning range, single mode
Lead-salt diode laser	3,000–30,000	~1 cm ⁻¹ with current ~100 cm ⁻¹ with temperature	Requires cryogenic cooling, can be difficult to operate, low output power
Quantum cascade laser	4,000–100,000	~0.5 cm ⁻¹ with current ~20 cm ⁻¹ with temperature	Room temperature in pulsed mode only, high output power, only selected wavelengths available
Difference frequency laser	700–5,000	Several 100 cm ⁻¹	More expensive as two lasers required, low output power
Optical Parametric Oscillator (OPO)	700–5,000	Several 100 cm ⁻¹	Commercial sources available, more expensive as two lasers required, larger laser linewidth

This example demonstrates the complementary nature of FT-IR and NIR diode laser spectroscopy with the FT-IR useful for preliminary survey work and the NIR diode laser useful for spatial monitoring of individual components.

Example 2. Quantitative SiO measurement by FT-IR absorption and emission spectroscopy

Another example from atmospheric pressure chemical vapour deposition is the use of high-resolution FT-IR spectroscopy to measure *in situ* SiO, a key intermediate species in the production of amorphous silicon oxynitride fibres at 1450°C.⁴ These fibres have the properties of excellent chemical stability at high temperature, coupled to a very high tensile stress. Determination of the SiO concentration would allow verification of the proposed reaction mechanism and enable process enhancements via control mechanisms.

Access to SiO transitions were not possible in the NIR because of the low fundamental vibrational frequency of the Si–O bond around 1241 cm⁻¹. FT-IR spectroscopy, with an apodised spectral resolution of 0.5 cm⁻¹, was used in both transmission and emission modes. A complicated rotationally-resolved structure is clearly seen in the spectrum (Figure 3) which is due to the three primary isotopic species ²⁸SiO, ²⁹SiO, ³⁰SiO and the population of high vibrational levels up to 7 and rotational levels up to 120.

Calibration was achieved by simulations of the spectra. The line positions were well-known from literature values but the temperature-dependent line strengths, which are required for the intensities, were unknown so were determined from *ab initio* calculation of the electric dipole moment function to give the transition moment. Figure 3 shows

the close agreement between the experimental and the calculated spectrum. During ideal growth conditions it was shown that the SiO concentration was 1.0×10^{17} molecules cm⁻³ ($\pm 5\%$). This can thus lead to correlation of gas-phase species with fibre properties and subsequently to real-time process control. The rapid determination of accurate synthetic calibration datasets reduces the need for extensive experimental calibration libraries and is especially true for unstable species.

Example 3. Non-invasive furnace temperature measurement by NIR diode laser absorption spectroscopy

An 8 m wide furnace provided a challenging environment in which to measure temperature non-invasively by two-line thermometry. Thermocouples are traditionally employed but can only be placed easily close to the side of the furnace and

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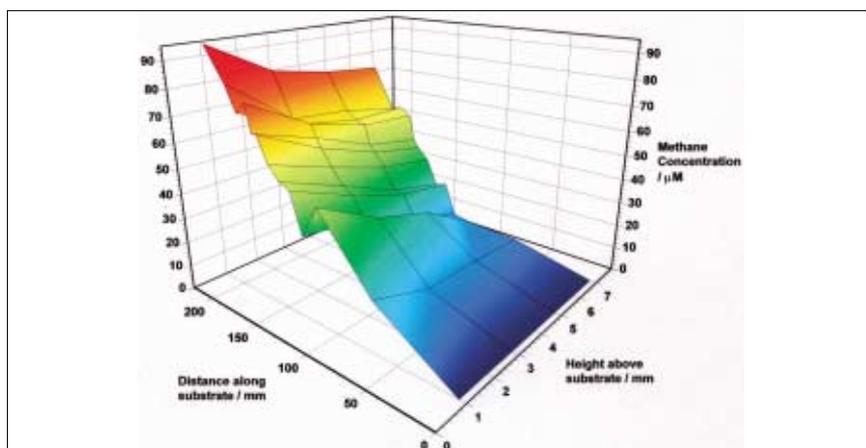


Figure 2. Distribution of evolved methane above the glass substrate and distance along the APCVD reactor measured from the point of entry of the precursor species.

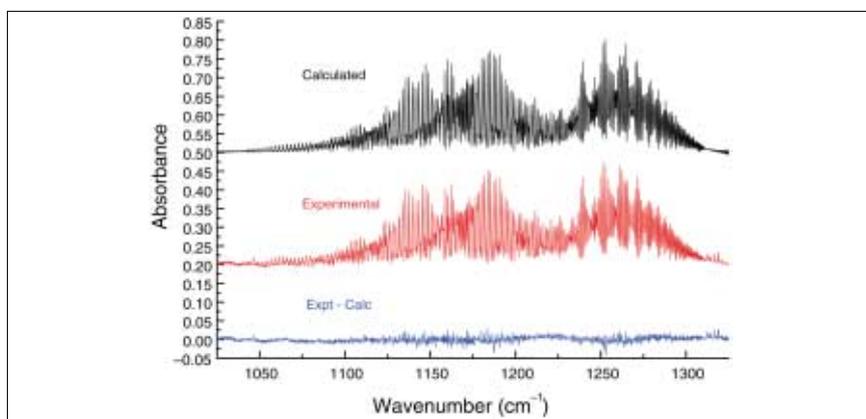


Figure 3. Experimental FT-IR absorption spectrum of SiO with the simulated spectrum showing the close match between theory and experimental intensities.

they have relatively short lifetimes. Previous attempts to use FT-IR spectroscopy had failed due to alignment difficulties over the long pathlength. A NIR diode laser spectrometer provided a solution.⁵ The requirement to temperature stabilise the laser to $\pm 0.005^\circ\text{C}$ at 25°C suggested a fibre-coupled laser mount placed several metres away from the furnace. The NIR beam was then launched from a cooled transmitter unit through a wedged sapphire window across the furnace to another cooled mount housing an InGaAs photodiode detector (see Figure 4). IR emission from the furnace on the detector was minimised with optical narrow bandpass filters optimised for the laser wavelength. A NIR DFB diode laser at around 1393 nm was rapidly swept across several vibrational-rotational absorption features of water. These absorption features could be simulated at specific temperatures using

parameters from the HITRAN/HITEMP database and a ratio determined for selected line-pairs and compared to experimental values. In such a manner, a line-of-sight temperature of between 1005 and 1020 K was determined. These values could then be used to extract chemical species concentrations; H_2O in this case. In Figure 5 a time series can be seen of furnace measurements. When a window on the furnace was briefly opened the H_2O mole fraction increases as the temperature decreases, as would be expected. In conclusion, NIR diode laser spectroscopy can extract important process information such as temperature even though it is only a line-of-sight value.

Multispecies and multipoint

In general, each NIR diode laser can only measure one chemical species due to the narrow wavelength tuning range. A

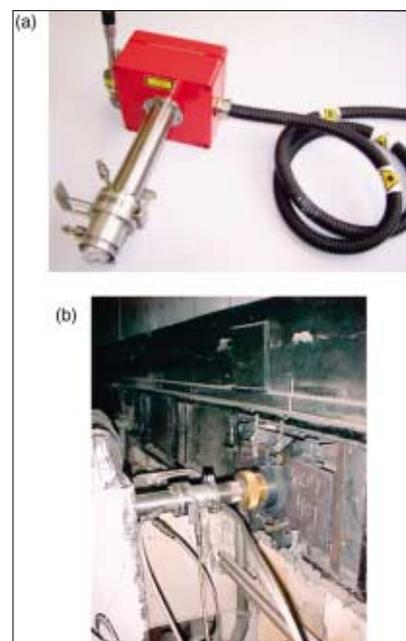


Figure 4. Upper (a) photo of the NIR diode laser transmitter unit used for trials at an industrial furnace. The cable on the right houses the fibre optic bringing the laser light to the launch unit. Lower (b) photo of the transmitter integrated with the furnace with cooling system and wedged sapphire windows.

solution is to multiplex the lasers using fused-coupled fibres so that several laser wavelengths propagate down a single fibre and onto a single detector. Time-multiplexing then allows separation of each laser signal. This goes some way towards bridging the gap between single species diode laser measurements and multispecies FT-IR spectroscopy.

Multipoint measurement for several species is attained by splitting the resulting fibre into any number of components with individual detectors at each measurement point. This approach then lends itself to tomographic reconstruction methods to determine spatial distribution of both chemical species and temperature.

Future prospects and conclusions

Further advances in high-resolution infrared spectroscopy for industrial process monitoring are likely to come from the development of room temperature mid-IR lasers such as quantum cascade lasers and fibre optics capable

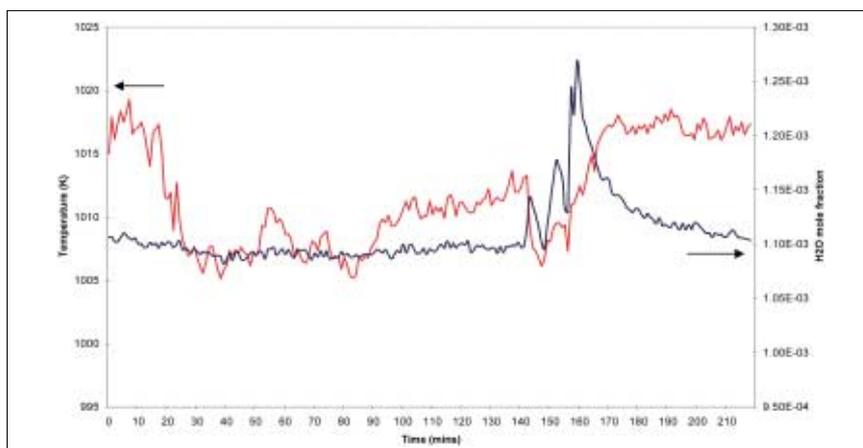


Figure 5. Time series of non-invasive line-of-sight temperature (red) and water concentration measurements (blue) by NIR diode laser spectroscopy in a furnace.

of mid-IR transmission. Miniaturisation of components is also being developed especially with micro electro mechanical systems (MEMS) technology and systems are starting to become commercially available.

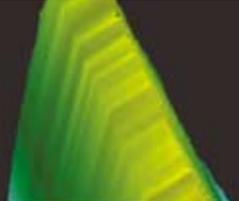
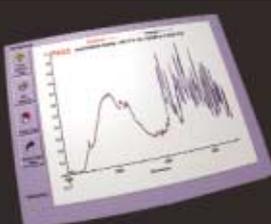
In conclusion, high-resolution IR spectroscopy, both laser absorption and FT-IR spectroscopy can meet many of the measurement challenges offered by *in situ* process analysis and at the same time provide enhanced process information.

Acknowledgements

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