Dr Kevin Smith and Damien Weidmann, Space Science and Technology Department,
Rutherford Appleton Laboratory

Spectroscopy in Space

Using Laser Heterodyne Radiometry to understand atmospheric chemistry

Increasing demands for energy and other resources pose threats to the Earth's climate and human health. Many climate models agree that rising anthropogenic green house gas emissions may lead to dangerous and irreversible climate change. Extreme weather, droughts, floods, famine, disease, migration of populations and threats to national security are just some of the predicted impacts of significant and rapid climate change. The quality of the air we breathe is strongly linked with human health. Various studies have shown links between episodes of poor air quality and increased hospital admissions and premature deaths. As worldwide industrialisation and urbanisation increases populations become increasingly exposed to polluted air.

Global observations of atmospheric composition from satellite instruments show that chemical species from industrial, agricultural or urban sources may be transported huge distances, leading to degraded air quality in other countries or even other continents. There is therefore an international research effort to understand the atmospheric chemistry and dynamics that determine the evolution of pollutants in the atmosphere. The foundations of international legislation regulating atmospheric emissions are based on the results of this type of research. It is widely recognised that international trading in emissions quotas may become increasingly economically important, but how will the international community ensure that regulations and quotas are being adhered to?

> "the only truly global observations are made from instruments on satellite platforms"

There are many techniques used to measure trace gases in the atmosphere, but the only truly global observations are made from instruments on satellite platforms. Indeed China's reluctance at the December 2009 Copenhagen Climate Change Summit to accept independent monitoring of its emissions would suggest that observations from space will perhaps, in some geographical regions, be the only possible method of verifying regulatory compliance.

During the last few decades remotely sensed atmospheric composition measurements have been made from space using a variety of spectroscopic and radiometric instruments. The majority of missions have been designed to answer key scientific questions about atmospheric chemistry and dynamics. These were often 'one-off' scientific studies lasting only a few years, and whilst data can be used to improve climate and air quality models they don't necessarily provide the basis for long-term operational monitoring. However, programmes such as the European Union's Global Monitoring for Environment and Security programme, the satellite-based component of which is managed by the European Space Agency (ESA), are specifically designed to provide a long-term monitoring capability.

> "for enforcement of international emissions regulations monitoring instruments on satellites will need to meet demanding requirements of detail, accuracy and traceability"

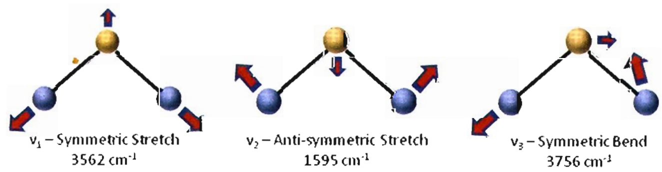
To become an effective part of the mechanism for enforcement of international emissions regulations and quotas, monitoring instruments deployed on satellites will need to have outstanding technical performance to meet demanding requirements of detail, accuracy and traceability. Observations at high spatial resolution will be required to unambiguously identify and accurately quantify sources and sinks of atmospheric pollution. However, for many types of instruments there is a trade off between sensitivity to trace gas concentrations and spatial resolution. Here we discuss the developing technique of laser heterodyne radiometry, and its potential to meet the technical challenges of detailed emissions monitoring on global, regional and city scales.

Infrared spectroscopy to probe the atmosphere

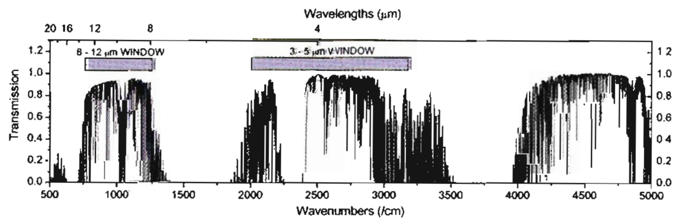
Before we can explore the advantages, in the context of emissions monitoring, of the laser heterodyne radiometer over more conventional remote sensing technologies, first it is necessary to review the spectroscopic methods used to study atmospheric composition.

High-resolution infrared molecular spectroscopy is a powerful technique that may be applied to the measurement and monitoring of trace gas species in the atmosphere. In particular the mid-infrared part of the spectrum between 3 and 20 microns (μm) is useful for the qualitative and quantitative measurement of a large number of molecular species. Spectroscopy undertaken with a variety of measurement techniques can be used to determine atmospheric gas concentrations remotely, or in situ. In all these techniques high spectral resolution enables discrimination between multiple gas species.

Gas molecules are not rigid structures of atoms, they are flexible and able to rotate, bend and stretch as the electronic inter-atomic bonds deform. The frequencies at which these vibrations and rotations occur are discrete, corresponding to resonances that are determined by the species of atoms present in the molecule and their arrangement. When a molecule is exposed to broadband radiation it will absorb discrete frequencies corresponding to excitation of the vibrational and rotational resonances of the inter-atomic bonds. The fundamental and therefore strongest, molecular rotational-vibrational absorption frequencies occur in the mid-infrared spectral region, with vibrational overtones extending to the near-infrared.

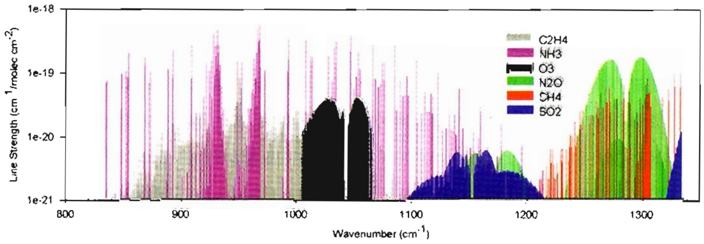


Above: The three independant vibrational modes of the water molecule (H2O), and their corresponding fundamental resonant frequencies.



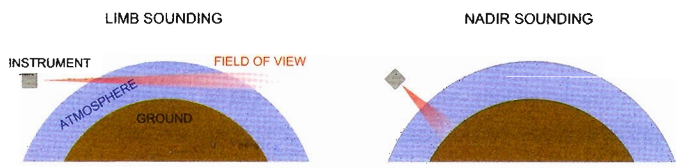
Above. Zenith sky atmospheric transmission showing strong absorption features, principally from water vapour, carbon dioxide and ozone. Spectral regions of high atmospheric transmission between 8 and 12 μm and 3 and 5 μm are used to measure the concentration of other atmospheric trace gas species. Note that the regions corresponding to the fundamental vibrational modes of water vapour are opaque.

The specific resonant frequencies that are absorbed by a particular molecular species provide a unique spectroscopic fingerprint, often consisting of a series of relatively narrow line-like spectral features, commonly referred to as the molecule's 'spectrum.' When excited rotation-vibration states relax molecules emit thermal infrared radiation at wavelengths corresponding to the absorption frequencies. The strength of infrared absorption or emission is related to the concentration of molecules, and therefore spectral analysis enables both qualitative and quantitative measurements to be made. There are many ways of achieving this practically, and all require some kind of spectro-radiometric system to record radiation intensity as a function of wavelength. Provided that measurements are made at sufficiently high spectral resolution to fully resolve the observed spectral lines, additional information relating to the thermo-physical properties of the gas may be obtained from the shape, width and relative intensities of absorption or emission lines. Line shape information can be used to retrieve information on local pressure and temperature, or if the gas is non-uniformly mixed and spatial thermo-physical properties are known by other means, the spatial distribution of the gas may be retrieved.



Above: Example molecular spectral signatures lying within the 8 to 12 μm atmospheric window. Data taken from the HITRAN spectroscopic database [1].

To measure the composition of the atmosphere spectroscopically we can employ any one of a number of methods. In situ techniques sample the local atmosphere, for example by drawing air into a gas cell for analysis. The advantages of this approach are that one can easily measure the physical conditions of the sample to calculate concentration, and high sensitivity can be obtained from multi-pass or resonant cavity optical systems. Clearly this type of measurement is unsuitable for truly global observations because it is not practical to cover the surface of the Earth with sensors, but it is well suited to local monitoring, for example in city centres, and for validation of alternate measurement techniques. Remote sensing techniques, of which there are many, measure along an open atmospheric path. Depending on the configuration of the system, there is the potential to scan spatially and build up a more complete picture of trace gas distribution over larger areas than are possible with in situ sensing alone. A number of spectroscopic remote sensing techniques are suitable for measurements from satellite platfoms and some are considered here.



Above: Schematic showing two commonly used satellite instrument viewing geometries

Spectroscopic observations from space may be divided into two camps: passive, where an instrument collects and measures naturally occurring radiation, and active, where the scene is illuminated by an artificial radiation source. To date passive instruments are by far the most common, and these may be further classified by viewing geometry. First we will consider satellites in low Earth orbit, at an altitude of around 1000 km. Atmospheric limb sounding uses either direct solar radiation (solar occultation) of thermal atmospheric >

emission to make measurements through the atmosphere along paths that are tangential to the Earth's surface. Complex tomographical approaches are required to derive vertical and horizontal distributions of trace gases from limb data, and measurements in the troposphere are virtually impossible due to the presence of opaque water vapour clouds. In contrast nadir observations view in a direction perpendicular to the Earth's surface and measure either scattered solar radiation or emitted thermal infrared radiation. The advantage of nadir measurements compared to limb viewing is the relatively high horizontal spatial resolution. However, retrieving vertical distributions is challenging, requiring high spectral resolution and, depending on the trace gas species, measurements from more than one spectral region. Cloud cover is problematic for infrared and visible nadir measurements in the troposphere, however clear sky observational frequencies are strongly inversely related to an instrument's field of view (commonly referred to in the context of satellite observations as pixel size). Therefore instruments with the smallest pixel sizes provide the best spatial resolution and the highest incidence of cloud-free observations.

Single satellites in low Earth orbit provide poor temporal resolution, since their revisit time is measured on a timescale of days. This may be improved by deploying several identical instruments on different satellite platforms, increasing the overpass frequency, and also the cost. Improved temporal resolution is possible from geostationary orbit, at an altitude of approximately thirty six thousands of kilometres. However, as the name suggests the instrument is permanently positioned above a single position on the Earth. Whilst a single instrument can in theory view half of the Earth's surface, spatial resolution is significantly degraded towards the limbs, so global coverage requires instruments on several satellites. Also, due to the greater distance from the Earth, it is technically much more challenging to achieve high spatial resolution at the surface.

Active techniques may employ a laser source to illuminate the atmosphere, with the instrument measuring backscattered radiation. Unlike passive methods one is not reliant on the intrinsic infrared emission of the atmosphere or on scattered sunlight. Therefore, in theory, active infrared measurements may be more sensitive compared to passive techniques, and visible spectra could be recorded during night time. Clearly active systems have some disadvantages compared to passive instruments, for example, instrument complexity, mass and power consumption are likely to be considerably higher, and these are important considerations for space flight.

A revolution in mid-infrared spectroscopy

Earlier we determined that for high spatial resolution monitoring of surface emissions technology is required that can deliver high sensitivity and high spectral resolution with a narrow nadir field of view. High spectral resolution is required for a) spectral selectivity necessary to distinguish multiple trace gas species, and b) the retrieval of vertical distribution along the nadir path.

To date all research and monitoring satellite instruments operating in the mid-infrared have been passive devices. Until very recently spectrometers capable of measuring at high spectral resolution across the entire mid-infrared spectral region have been physically large, rather complex and not particularly well suited to operation in environments outside of the laboratory. Ruggedized Fourier transform spectrometers (FTSs) are routinely used for mid-infrared measurements in the field. However, there are a number of factors that limit the performance of FTS instruments in the context of global emissions monitoring from space:

- *For instruments based on Michelson interferometers there is a compromise between the spectral resolving power and the physical size and mass of the instrument*
- *Measurement integration time increases non-linearly with spectral resolution*
- *Restricting the field of view of the FTS, to increase spatial resolution, decreases the sensitivity of the instrument*
- *A large volume of data is generated, particularly if the instrument is equipped with a detector array, resulting in high demands on data links to ground stations*
- *FTS instruments are generally rather complex with moving parts and a high degree of sensitivity to mechanical shocks and vibration*

Despite these limitations FTS instruments have been successfully deployed in space for research purposes. The flexibility offered by the inherent broadband measurement capability of FTS instruments is particularly well suited to research applications, and consequently these types of instrument have provided much new information about atmospheric composition, transport and chemistry.

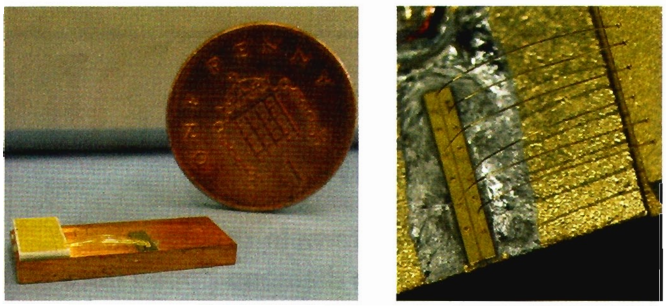
In theory the inherent narrow line width of continuously frequency-tunable lasers may be used to perform absorption spectroscopy at high resolution without the need for physically large optical arrangements. This is certainly the case in the near-infrared spectral region where there are many successful in situ instruments based on telecoms diode lasers. However, until relatively recently, mid-infrared spectrometers based on lasers have had a number of limitations:

- *Diode laser systems have been based on lead salt devices which operated at cryogenic temperatures with very low power and were notoriously unreliable, suffering from degradation due to temperature cycling. These devices were suitable for research but were less than ideal for routine monitoring*
- *Gas lasers, such as carbon dioxide, operate at discrete wavelengths and are not continuously tuneable. Measurements can only be made if a laser emission line coincides in wavelength with absorption* >

from a target gas

- *The use of optical parametric oscillators, or sources based on difference frequency generation, require complex optical systems and high power laser sources*

The world of mid-infrared laser spectroscopy changed markedly with the introduction and subsequent maturation of quantum cascade laser (QCL) technology. These revolutionary solid state devices are robust, compact (a few millimetres in size), high power (milliwatts), operate at close to room temperature and can be tuned over quite large wavelength ranges. Unlike other semiconductor lasers that rely on the energy band-gaps of specific materials, the operating wavelength of a QCL is determined solely by the architecture of nanometric layers within the laser cavity. Therefore the operating wavelength may be manufactured to order, to suit specific applications. QCLs have enabled the commercial development of compact and lightweight in situ gas sensors, and triggered worldwide instrument research and development activities. But how would one use of this revolutionary type of laser to make measurements from outside the atmosphere in space?

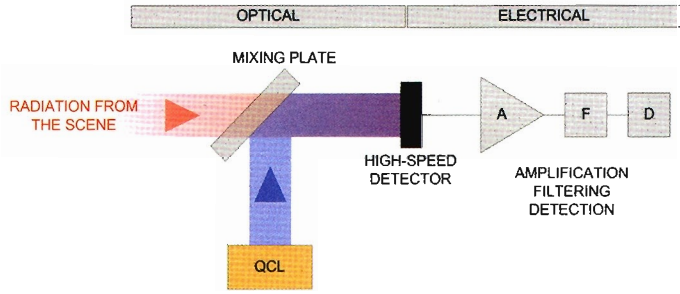


Above: Photographs of a quantum cascade laser. The left hand image shows a QCL mounted on a copper sub-mount. The right hand image shows the semiconductor crystal in detail, constituting the laser itself and gold electrical contact wires. Crystal size is 3 mm by 0.5 mm.

Lasers in space

There are numerous proposals to fly high power lasers on satellites. Used in a lidar configuration these active instruments would probe the atmosphere with laser radiation and measure the fraction that is backscattered to the satellite. There are many technical challenges associated with flying this type of instrument in space. Not least is the requirement for large amounts of power. Secondly, optical components if contaminated can be prone to sudden and catastrophic failure. But there is an alternative, more subtle approach.

The passive technique of heterodyne detection is routinely employed in communications technologies for receiving radio signals and in remote sounding from space in the microwave spectral range. The same basic principles can be used in the optical wavelength domain. A passive instrument called the laser heterodyne radiometer (LHR) works in an analogous way to a radio receiver. However, the radiation the



Above: Schematic showing the basic arrangement of an optical heterodyne receiver where the radiation coming from the scene is mixed with that from a laser and directed onto a high-speed photodiode. The radio-frequency power produced by the photodiode is then amplified filtered and measured.

instrument is sensitive to has wavelengths lying in the mid-infrared part of the electromagnetic spectrum, the local oscillator is a continuously tunable mid-infrared laser and the resulting intermediate frequency signal is down-converted to radio wavelengths.

The LHR and instruments of its type can be operated by mixing radiation transmitted through, or emitted from, the atmosphere with that from the local oscillator. Because the laser is not transmitted outside of the instrument power requirements are minimal. By scanning the local oscillator frequency and filtering the heterodyne signal with a fixed narrow-band radio frequency filter, a high-resolution radio frequency version of the infrared atmospheric spectrum may be recorded. There is nothing new about optical heterodyne detection of trace gases in the atmosphere: it was first performed with gas lasers and later with lead salt diode lasers. What is new is the use of QCL local oscillators, which for the first time offer the prospect of producing optical heterodyne instruments in low power, robust and compact packages well suited for routine atmospheric monitoring.

The LHR has the following key features, which make the instrument suitable for atmospheric trace gas monitoring with high spatial resolution:

- *The spectral purity of the laser coupled with the use of narrow-band radio frequency filters allows excellent spectral selectivity for discrimination between trace gas species and efficient atmospheric vertical profiling*
- *The coherent nature of the detection system has an intrinsically narrow field of view, enabling observations with a high degree of spatial selectivity*
- *Heterodyne detection offers high sensitivity, with the potential for shot noise limited measurement*

At Rutherford Appleton Laboratory (RAL) we have been working to develop a LHR for atmospheric trace gas monitoring, with the long-term aim of deploying an instrument in space [2,3]. As with any new technology there is a considerable amount of work to be done before it can be considered for space flight. Prototype instruments have already successfully demonstrated aspects of the technology through laboratory studies and ground-based atmospheric measurements.

Identification of industrial emission source

Earlier we saw that high spectral resolution is the key to unambiguous measurement of individual trace gas species concentrations in the atmosphere. Fully resolved spectral lines can also be used to retrieve physical properties of the gas, i.e. temperature and pressure, which are directly related to spectral line widths and shapes. In nadir measurements this information may provide a handle on the vertical distribution of trace gases along the optical path.

Ground-based LHR measurements on atmospheric ozone made at RAL have demonstrated that vertical profiling is possible with a vertical resolution up to 2 km. By combining vertical profiling with a detector array or scanning mechanism, three dimensional tomography of trace gas concentrations may be possible using a nadir viewing geometry.

The coherent nature of the heterodyne detection technique means that the LHR has an inherently narrow field of view. In fact calculations show that an antenna of modest size (10 cm diameter) would allow an instrument in low Earth orbit to view an area on the ground tens of metres in diameter. This compares favourably with many existing satellite instruments that have pixel sizes measured in kilometres. Provided that signal integration times can be kept short, identification and monitoring of individual industrial emission sources should be possible. One might imagine that known industrial facilities could be targeted by the instruments antenna as the satellite passes overhead. Combined with vertical profiling, tomography and knowledge of local wind velocities emission fluxes could be calculated. The intrinsically narrow field of view of the LHR deployed in geostationary orbit would potentially allow monitoring with kilometre-sized pixels at the surface. In this configuration, and equipped with a steerable antenna, the instrument would be able to provide real-time monitoring of specific locations within most of the Eurasian continent.

LHR: The global emissions monitor of the future?

The LHR itself is not without technical challenges. This is an emerging technology and many performance limitations need to be overcome. However, enabling technologies are advancing rapidly, and RAL are working with partners in several key development areas.

Funded by the Centre for Earth Observation Instrumentation we are working with QinetiQ to develop an optically integrated version of the instrument using hollow waveguides. Besides increasing robustness and compactness whilst reducing manufacturing costs, early studies show that the performance of the instrument may be significantly enhanced by the properties of the waveguide itself. As part of this work the first heterodyne spectroscopic measurements of incoherent radiation using a high-speed room-temperature detector have been made, removing completely the requirement for cryogenic operation.

Following on from the initial prototype instrument, a new development project in partnership with Princeton University will see the first ground-based multi-species atmospheric heterodyne measurements using an external cavity QCL. As part of the Mid-Infrared Technologies for Health and the Environment (MIRTHE) centre activity led by Princeton, external cavity systems with tuning ranges of more than 20% of the laser's central wavelength have been developed. For the first time QCL spectrometers are beginning to challenge the broadband measurement supremacy of FTS instruments.

Current trends are towards smaller, lighter and cheaper satellite platforms. Our vision of a shoebox sized LHR, capable of meeting all the requirements for global emissions monitoring, is consistent with this trend. Whether or not all of the technical challenges associated with the LHR are met, it is likely that a combination of instrument types, viewing geometries and measurement techniques will be required to address future monitoring needs.

During February 2010 the Space Innovation and Growth Team, a joint UK government and industry initiative, announced a twenty year vision and strategy for development of the UK space industry. Hopefully this announcement will mark the beginning of a new commitment to the development of space technology in the UK, and emerging technologies such as the LHR will reach their full potential. ■

References

1. The HITRAN 2004 molecular spectroscopic database, L.S. Rothman, et al., Journal of Quantitative Spectroscopy and Radiative Transfer, 96, 139–204, 2005
2. Retrieval of atmospheric ozone vertical profiles from an infrared quantum cascade laser heterodyne radiometer: results and analysis, D. Weidmann, W.J. Reburn and K.M. Smith, Applied Optics, 46 (29), 7162-7171, 2007
3. A ground-based prototype quantum cascade laser heterodyne radiometer for atmospheric studies, D. Weidmann, W.J. Reburn and K.M. Smith, Review of Scientific Instruments, 78, 073107, 2007

Author

Kevin Smith heads the Spectroscopy Group (www.sstd.rl.ac.uk/sg) within the Space Science and Technology Department at Rutherford Appleton Laboratory. Besides instrument development the Group operates the Molecular Spectroscopy Facility (MSF, www.msf.rl.ac.uk) for use by academic and industrial researchers. The MSF is equipped with high resolution Fourier transform spectrometers and diode laser systems. Most projects supported by the Facility are related to atmospheric science and Earth observation, funded by the UK Natural Environment Research Council. Particular research interests include water vapour and aerosol spectroscopy.

Damien Weidmann leads the laser spectroscopy research and development activity within the Spectroscopy Group. He has more than ten years experience in laser spectroscopy techniques and instrument development applied to in-situ and remote trace gas detection, primarily using quantum cascade lasers.