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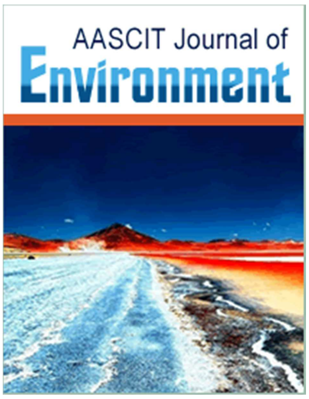

Quantum Cascade Laser in Atmospheric Trace Gas Analysis

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Abstract
A key issue in ecosystem research and atmospheric studies is to detect and quantify low and ultra low concentrations of toxic trace gases. There has been an increasing concern about pollution of our living environment. Emission of a gas into the atmosphere usually dilutes rapidly and even at low levels of concentration, adverse effects can be noticed. The exact measurement of such low concentrations of atmosphere species poses a challenge to science and technology. When we take a 'sample' of the gas emission, the gas is extracted from a particular point and it is preconditioned. The method usually adopted is the 'wet chemistry' method. There are other methods in use, such as, gas chromatography, mass spectrometry, elemental analysis, etc. These methods require that the gas samples be preconditioned before using it for analysis. Also, these methods are slow. Optical spectroscopic techniques work without the need for preconditioning of the gas sample. They can be used for real-time measurement and 'in-situ' analysis. In industrial applications, monitoring gases like oxygen/ozone, carbon monoxide, ammonium hydrochloride and hydrogen fluoride are routinely carried out. A laser based gas monitor provides continuous measurement with a fast response and high sensitivity of the order of a few seconds.

1. Methodology

The basic principle of operation is that the gas molecules absorb laser photons at wavelengths specific to the energy-level structure of the given species under investigation. It uses the Beer-Lambert extinction law and at a wavelength slightly different from these absorption lines, there is no absorption. Thus by scanning the wavelength, in the 2μm to 15μm range in the infrared region, across the absorption lines of the target gas and by measuring the magnitude of absorption, one can deduce the concentration of gas molecules integrated over the interaction path. The measurement is expressed in terms of ppm times meters or (ppm. m).Trace gases like the CH_4 and Nitrogen Oxides are the most abundant organic gases besides the green house gases CO_2 and O_3 which destroy the chlorofluorocarbons (CFC's).Nitrogen dioxide (NO_2) is an important reactive nitrogen species, and its photolysis is the primary source of O_3 in the troposphere. Nitrogen oxides play an important role in the photochemistry of the troposphere and it controls O_3 formation affecting the concentration of hydroxyl radical and contributes to acid precipitation.

The timeline expected for each step, (for a total of three steps) is about six month's duration each, subject to all instrumentation facility being available for measurement.

2. Experimentally New or Unusual Techniques

An ideal gas monitor should have the following properties:

1.) It should measure the analyte correctly without influence from other gases or dust or aerosols;

2.) It should be fully automatic and should compensate for temperature and pressure effects;

3.) It should use components that operate at room temperature and without any cryogenic cooling;

4.) It should measure continuously with a short response time and it should be insensitive to mechanical instabilities;

5.) It should produce reliable results and it should require very little maintenance with few consumable components.

A tunable quantum cascade laser is an ideal choice, which will not only understand but also monitor the chemical processes that affect our atmosphere. Absorption spectroscopy exploits wavelengths in the mid-IR region for many scientific and technical applications. All organic components and many inorganic compounds exhibit strong absorption in the mid-IR region of 2µm to 15µm, due to resonance with the rotation-vibrational modes of the molecules. Quantum cascade laser used in absorption spectroscopy provides continuous measuring and monitoring of extremely small concentrations of selected gases due to the progress in laser technology.

3. Expected Results and Their Significance and Application (Estimated)

Table I. *Trace Gases detection sensitivity of QCL.*

Species	Semiconductor IR lasers(µm)	Sensitivity(ppm v m)	Quantum cascade laser (QCL)(µm)	Sensitivity (ppb v m)
CH_4	1.68	0.2		
CO	1.59	7	4.9	<12
CO_2	2.04	0.7		
HCl	1.73	0.04		
HCN	1.57	0.03		
H_2O	1.43	3		
NH_3	1.59	0.25		
N_2O	1.57	2		
NO	1.86	5	5.45	<84
NO_2	0.69	0.03		
O_2	0.78	14		
SO_2			7.56	1-4

4. Mid-Infrared Region Benefits

Since most chemical compounds have their fundamental vibrational modes in the mid-infrared, spanning approximately the wavelength region from 2 to15µm, this part of the electromagnetic spectrum is very important for gas sensing and spectroscopy applications. Even more important are the two so-called atmospheric windows at approximately 2-5µm and 8-12µm. The high transparency of the atmosphere in these two windows allows remote sensing and detection. As an example, here are the relative strengths of CO_2 absorption lines as a function of frequency:

Table II. *Relative absorption strength for various wavelengths.*

Wavelength (µm)	Relative absorption strength
1.432	1
1.602	3.7
2.004	243
2.779	6800
4.255	69000

Approximate relative line strengths for various bands of the CO_2 gas. Moreover, because of the long wavelength, Rayleigh scattering from dust and rain drops will be much less severe than in the visible, allowing applications such as radars, ranging, anti-collision systems, covert telecommunications and so on. As an example, Rayleigh scattering decreases by a factor 104 between wavelengths of 1µm and 10µm.

5. QCL Principles of Operation

QCLs are unipolar semiconductor devices consisting of complex layered structures of two or more semiconductor alloys.The light is generated in the active region by an inter-sub band transition of the single charge carriers (i.e., the electrons) between two quantized levels in the conduction band.Since the energy difference between the two quantized levels is determined by the specific structure design (i.e., the quantum well [QW] and barrier widths),the wavelength emitted can be tailored by band engineering to be any value within a broad spectral range. This range is limited only by the conduction-band offset available between the two materials of choice and the Reststrahlen region.

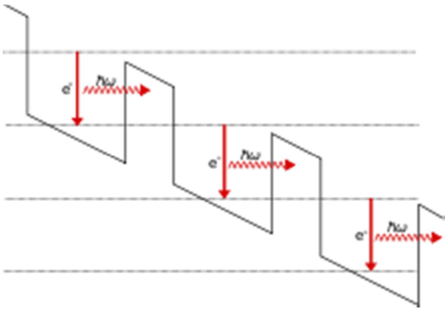

Figure 1. *Inter sub-band transition of a QCL (Courtesy: Wikipedia)*

The operating range of QCLs makes them ideal for chemical and biological sensing applications. Most of the chemical compounds of interest for environmental or defense applications have absorption features in the mid-infrared. Strong absorption peaks have been identified for trace gases, such as NO, NH3, CH4, and CO. Several spectroscopic techniques have been used to detect these gases. The simplest method is direct absorption. In this set up, the change in intensity of a laser beam passing through a cell containing the target chemical is measured. The most commonly used optical method for trace-gas sensing is tunable infrared laser diode absorption spectroscopy (TILDAS).

The high sensitivity and specificity of this technique is achieved by modulating the frequency of the laser so that it periodically scans through the absorption peak of the chemical of interest. The absorbing material converts the frequency modulation into an amplitude modulation that is detected by a lock-in technique. NO detection is important for a number of applications, such as atmospheric pollution and toxic process monitoring, vehicle exhaust control, and non-invasive medical diagnostics. NO in exhaled breath is a possible biomarker for various lung diseases. Similarly, carbonyl sulfide (COS) in human breath has been related to liver and lung diseases. A detection sensitivity of 30 parts in 10^9of COS and the selectivity of two stable isotopes has been demonstrated .Other QCL spectroscopy studies include ammonia, methane, CO2, and ethylene. Recently, a trace gas sensor based on quartz-enhanced photo acoustic spectroscopy with a QCL operating at 4.55µm was developed for the detectionof N2O and CO and was found to have a sensitivity of 4ppb for N2O.In addition to their use in in-situ trace-gas sensing, QCLs could have an impact on remote sensing with LIDAR. Gittins et al. have used a multimode Fabry-Perot QCL operating at 8µm for backscatter absorption measurements on isopropanol vapor. They explored the use of QCLs for differential-absorption LIDAR (DIAL) and found that even a simple configuration resulted in a detection limit of 12 ppm.Another class of applications for which QCLs have strong potential to be of use is free-space optical communications. Because of lower Rayleigh and Mie scattering, the attenuation of mid-infrared light through open atmosphere is much lower than it is for visible or near-infrared light. Losses nearly one hundred time slower than those for shortwave infrared transmission can be expected in the second atmospheric window (i.e., 8 mm to 13 mm) in clear weather conditions. For lower visibility conditions, the advantage is even greater. An optical link based on QCL technology has been demonstrated to transmit audio, video, and data signals over 200 m at speeds up to 2.5 Gbit/s. A unique feature of QCLs is their ultrafast carrier relaxation lifetime (1ps), which is dominated by electron-optical phonon scattering. This property makes QCLs ideally suited for high-speed modulation.Active and passive mode-locking hasbeen achieved with QCLs and sub-picosecond pulses have been produced with a repetition rate of 100 MHz to 10 GHz.

6. Detection Methods

6.1. Direct Absorption

In a direct absorption measurement, the change in intensity of a beam is recorded as the latter crosses a sampling cell where the chemical to be detected is contained. This measurement technique has the advantage of simplicity. In a version of this technique, the light interacts with the chemical through the evanescent field of a waveguide or an optical fiber.

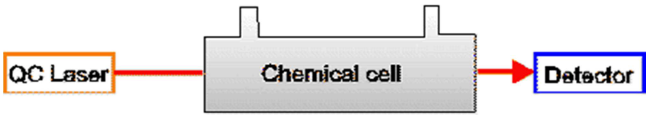

Figure 2. *Direct absorption technique using a QCL.*

One example is the use in a direct absorption technique:

6.2. Frequency Modulation Technique (TILDAS)

In this technique, the frequency of the laser is modulated sinusoidally so as to be periodically in and out of the absorption peak of the chemical to be detected. The absorption in the cell will convert this FM modulation into an AM modulation which is then detected usually by a lock-in technique.

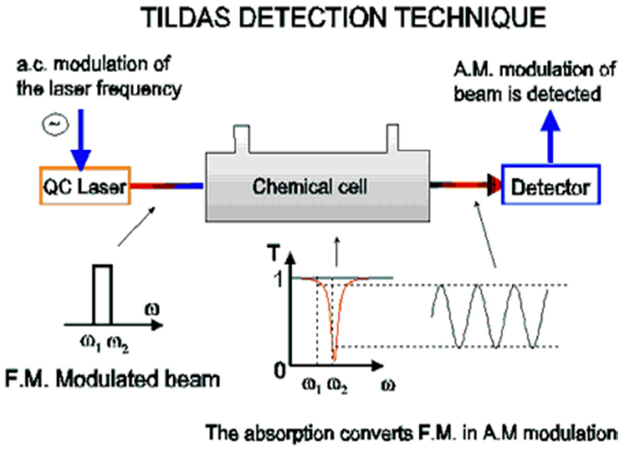

Figure 3. *TILDAS absorption technique.*

The advantage of the TILDAS technique is mainly its sensitivity. First of all, under good modulation condition, an a.c. signal on the detector is only present when there is absorption in the chemical cell. Secondly, this signal discriminates efficiently against slowly varying absorption backgrounds. For this reason, this technique will usually work well for narrow absorption lines, requiring also a mono mode emission from the laser itself.

7. Conclusion

Quantum Cascade Lasers are ideal detection units for analyzing trace gas samples and to detect chemical compounds in the mid-infrared region of the electromagnetic spectrum between 2µm -15µm wavelength ranges.

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