Chapter 4
Laser Based Chemical Sensor Technology: Recent Advances and Applications

Frank K. Tittel, Yury A. Bakhirkin, Robert F. Curl, Anatoliy A. Kosterev, Matthew R. McCurdy, Stephen G. So, and Gerard Wysocki

Abstract There is an increasing need in many chemical sensing applications ranging from environmental science to industrial process control as well as medical diagnostics for fast, sensitive, and selective trace gas detection based on laser spectroscopy. The recent availability of continuous wave near infrared diode lasers-, mid-infrared quantum cascade and interband cascade distributed feedback (QC and IC DFB) lasers as mid-infrared spectroscopic sources addresses this need. A number of spectroscopic techniques have been demonstrated. For example, the authors have employed infrared DFB QC and IC lasers for the detection and quantification of trace gases and isotopic species in ambient air by means of direct absorption, cavity-enhanced, and photoacoustic spectroscopy. These spectroscopic techniques offer an alternative to non-spectroscopic techniques such as mass spectrometry (MS), gas chromatography (GC) and electrochemical sensors. The sensitivity and selectivity that can be achieved by both techniques (excluding electrochemical sensors) are similar, but the sensor response time, instrumentation size and cost of ownership for spectroscopic techniques can be advantageous as compared to MS-GC spectrometry.

Keywords: Laser absorption spectroscopy, cavity-enhanced and photoacoustic spectroscopy, near infrared diode lasers, mid infrared quantum cascade lasers, chemical sensing of trace gases

4.1 Introduction

Infrared laser absorption spectroscopy (LAS) is an extremely effective tool for the detection and quantification of molecular trace gases. The demonstrated detection sensitivity of LAS ranges from ppmv, ppbv to even sub-ppbv levels depending on the specific gas species and the detection method employed (Curl and Tittel 2002;

Rice University, Electrical and Computer Engineering Department, MS-366, 6100 Main St., Houston, TX 77005, USA

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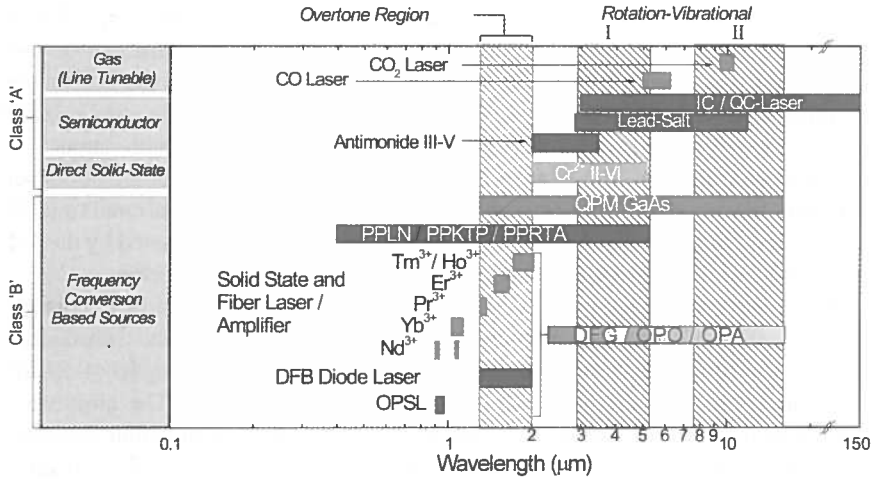

Fig. 4.1 Infrared laser sources and spectral coverage. PPLN, periodically poled lithium niobate; DFB, distributed feedback; OPSL, optically pumped solid state laser; DFG, difference frequency generation; OPO, optical parametrical oscillator; OPA, optical parametric amplifier; QPM, quasi phase matched; IC, interband cascade; QC, quantum cascade

Tittel et al. 2003). The spectral region of fundamental vibrational molecular absorption bands from 3 to 24 μm is the most suitable for high sensitivity trace gas detection. However, the usefulness of the laser spectroscopy in this region is limited by the availability of convenient tunable laser sources. Real-world applications require the laser source to be compact, efficient, reliable and operate at near room-temperatures. Existing options as shown in Fig. 4.1 include lead salt diode lasers, coherent sources based on difference frequency generation (DFG), optical parametric oscillators (OPOs), tunable solid state lasers, quantum and interband cascade lasers (QCLs and ICLs). Sensors based on lead salt diode lasers are typically large in size and require cryogenic cooling, since these lasers operate at temperatures <90 K. DFG sources (especially bulk and waveguide PPLN based) have been shown to be robust and compact (Yanagawa et al. 2005; Richter et al. 2006).

Recent advances in QCLs and ICLs fabricated by band structure engineering offer an attractive new source option for mid-infrared absorption spectroscopy with ultra-high resolution and sensitivity (Kosterev et al. 2002a, b) (See Fig. 4.1). The most technologically developed mid-infrared QC laser source to date is based on type-I intersubband transitions in InGaAs/InAlAs heterostructures (Capasso et al. 2000; Faist et al. 2002; Beck et al. 2002; Mann et al. 2003; Evans et al. 2004; Troccoli et al. 2004; Diehl et al. 2006). More recently ICLs based on type-II interband transition have been reported in the 3–5 μm region (Yang et al. 2002; Yang et al. 2004; Bradshaw et al. 2004; Mansour et al. 2006).

The vast majority of chemical substances have vibrational fundamental bands in the 3–24 μm region, and the absorption of light by rotational–vibrational transitions

of these bands provides a nearly universal means for their sensitive and selective detection. Furthermore, near infrared spectroscopy from 1.3 to 3 μm can be used effectively in the quantification of numerous trace gas species. This application can use ultra-reliable, room temperature, single frequency distributed feedback (DFB) lasers that were primarily developed for optical telecommunications with output powers of tens of milliwatts. These lasers access molecular overtone or combination band transitions that are typically a factor of 30–300 weaker than the mid-infrared (mid-IR) fundamental transitions. However, in some cases this can be compensated by the judicious choice of the appropriate photoconductive or photovoltaic detector.

Pulsed and continuous wave (cw) DFB-QCLs allow the realization of compact, narrow linewidth sources combining single-frequency operation and substantially high powers (from tens to hundreds of milliwatts) at mid-IR wavelengths (4–24 μm) and temperatures that are attainable with thermoelectric cooling. The large wavelength coverage available with QCLs allows the detection, quantification and monitoring of numerous molecular trace gas species, especially those with resolved rotational–vibrational spectra. The high QCL output power permits the use of advanced detection techniques that significantly improve the detection sensitivity of trace gas species and decrease the complexity and size of the overall trace gas sensor architecture. This includes photoacoustic, laser absorption and cavity-enhanced spectroscopy. For example, in cavity ringdown spectroscopy (CRDS) (Berden et al. 2000) and integrated cavity output spectroscopy (ICOS), an effective absorption pathlength of hundreds of meters can be obtained in a compact device (Bakhirkin et al. 2004). In the following sections, a number of examples of laser-based analytical techniques based on absorption spectroscopy, laser photoacoustic spectroscopy and cavity-enhanced spectroscopy will be presented.

4.2 Chemical Sensing Based on Tunable Thermoelectrically Cooled CW Quantum Cascade Lasers

The development of laser spectroscopic techniques strongly relies on increasing the availability of new tunable laser sources. For applications in the mid-IR molecular fingerprint region, QCLs have proved to be convenient and reliable light sources for the spectroscopic detection of trace gases (Capasso et al. 2000). Spectroscopic applications usually require single-frequency operation. This is achieved by introducing a DFB structure into the QCL active region. Although DFB QCLs show high performance and reliability characteristics, the range of wavelength tuning of the emitted laser radiation is limited by the wavelength tuning range of the DFB structures. Typically the maximum thermal tuning range of DFB-QCLs is ~2 cm^{-1} achieved by laser current injection control or 10 cm^{-1} by varying the temperature of the QCL chip. The development of bound-to-continuum QC lasers (Faist et al. 2001) has addressed the issue of wide frequency tunability. Bound-to-continuum QC lasers have an intrinsically broader gain profile, because the lower state of the laser transition is a relatively broad continuum. A luminescence spectrum of

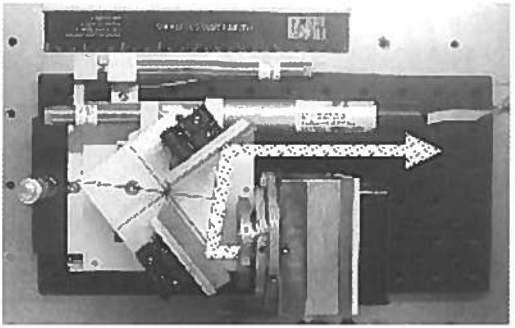

Fig. 4.2 Compact tunable external grating cavity quantum cascade laser

297 cm^{-1} FWHM (full width at half maximum) at room temperature was observed for $\lambda \approx 10\,\mu m$ QCL devices employing bound-to-continuum transitions (Maulini et al. 2004). To take advantage of the broadband gain of such QCLs, an external cavity (EC) configuration can be used for wavelength selection (Wysocki et al. 2005; Peng et al. 2003). Recently, even broader gain profiles with FWHM of ~350 cm^{-1} were achieved by using a heterogeneous quantum cascade structure based on two bound-to-continuum designs emitting at 8.4 and 9.6 μm (Maulini et al. 2006). The development of a QC laser spectrometer for high resolution spectroscopic applications and multi species trace gas detection in the mid-IR through the design and implementation of a novel EC-QCL architecture is described by Wysocki et al. 2005. The instrument depicted in Fig. 4.2 employs a piezo-activated cavity mode tracking system for mode-hop free operation. The mode-tracking system provides independent control of the EC length, diffraction grating angle and laser current. The system performance and spectroscopic application capability was demonstrated by studying nitric oxide (NO) absorption features at ~1945 cm^{-1} with a gain medium operating at ~5.2 μm. The EC-QCL exhibited a coarse tuning range of ~35 cm^{-1} and a continuous mode-hop free fine tuning range of 1.2 cm^{-1} as shown in Fig. 4.3. Wide wavelength tunability and a narrow laser linewidth of <30 MHz, which allowed resolving spectral features separated by less than 0.006 cm^{-1} (see inset of Fig. 4.3) makes such an EC-QCL an excellent light source suitable for high resolution spectroscopic applications and multiple species trace gas detection. The flexibility of this arrangement makes it possible to use it with other QC lasers at other wavelengths without changing the EC configuration.

4.3 Trace Gas Detection Based on Laser Photoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS), based on the photoacoustic effect, in which acoustic waves result from the absorption of laser radiation by a selected target compound in a specially designed cell, is an effective method for sensitive trace

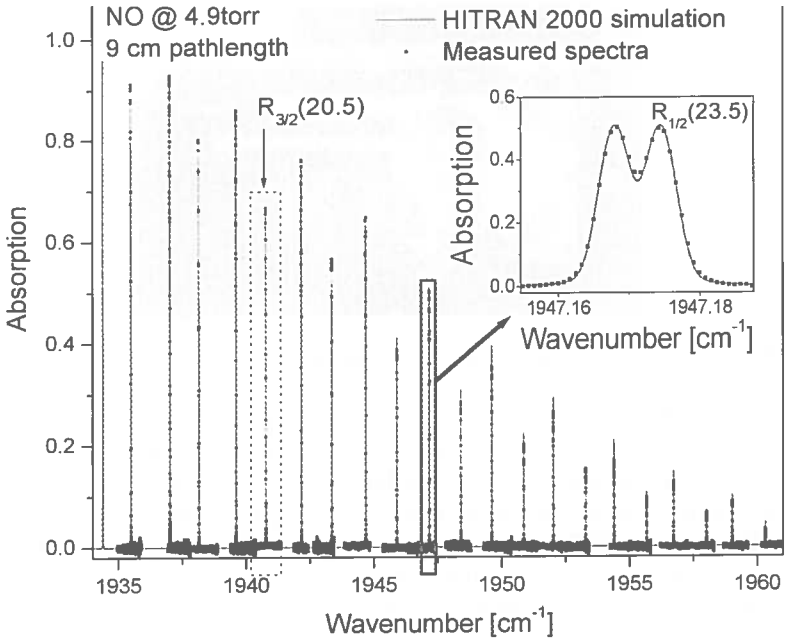

Fig. 4.3 Nitric oxide absorption spectra measured at different EC-QCL grating angles. The narrow laser linewidth allows a spectral selectivity of <0.006 cm^{-1}

gas detection. In contrast to other infrared absorption techniques, PAS is an indirect technique in which the effect on the absorbing medium and not the direct light absorption is detected. Light absorption results in a transient temperature effect, which then translates into kinetic energy or pressure variations in the absorbing medium that can be detected with a sensitive microphone. PAS is ideally a background-free technique, since the signal is generated only by the absorbing gas. However, background signals can originate from nonselective absorption of the gas cell windows (coherent noise) and external acoustic (incoherent) noise. PAS signals are proportional to the pump laser intensity and therefore, PAS is most effective with high power laser excitation. A sensitivity of 8 ppmv was demonstrated with only 2 mW of modulated diode laser power in the CH_4 overtone region (Liang et al. 2000; Gomes et al. 2006). The implementation of high power cw DFB-QCL excitation in the fundamental absorption region leads to considerably improved trace gas detection sensitivity.

A recently introduced novel approach to photoacoustic detection of trace gases utilizing a quartz tuning fork (QTF) as a sharply resonant acoustic transducer was first reported in 2002 (Kosterev et al. 2002c; Kosterev et al. 2005a). The basic idea of quartz-enhanced photoacoustic spectroscopy (QEPAS) is to invert the common PAS approach and accumulate the acoustic energy not in a gas-filled cell but in a

sharply resonant acoustic transducer. A natural candidate for such an transducer is crystalline quartz, because it is a low-loss piezoelectric material. A variety of packaged quartz crystals for use in timing applications is commercially available. Readily available low-frequency quartz elements are quartz tuning forks (QTF) intended for use in electronic clocks as frequency standards. These QTFs resonate at 32 768 (2^{15}) Hz in vacuum. A typical QEPAS absorption detection module (ADM) consisting of a QTF equipped with an accoustic micro-resonator is shown in Fig. 4.4. Only the symmetric vibration of a QTF (i.e. when the two QTF prongs bend in opposite directions) is piezo-electrically active. The laser beam is focused between the prongs of the QTF and its wavelength is modulated at $f_m = f_0/2$ frequency, where f_0 is the QTF resonant frequency. A lock-in amplifier is used to demodulate the QTF response at f_0. Spectral data can be acquired if the laser wavelength is scanned. To increase the effective interaction length between the radiation-induced sound and the QTF, an acoustic gas-filled micro-resonator can be added similarly as in the traditional PAS approach. Acoustically, a QTF is a quadrupole, which results in excellent environmental noise immunity. Sound waves from distant acoustic sources tend to move the QTF prongs in the same direction, thus resulting in no photoacoustic response. Advantages of QEPAS compared to conventional resonant photoacoustic spectroscopy include QEPAS sensor immunity to environmental acoustic noise, a simple absorption detection module design, no spectrally selective element is required, applicable over a wide range of pressures, including atmospheric pressure and its capability to analyze small gas samples, down to 1 mm^3 in

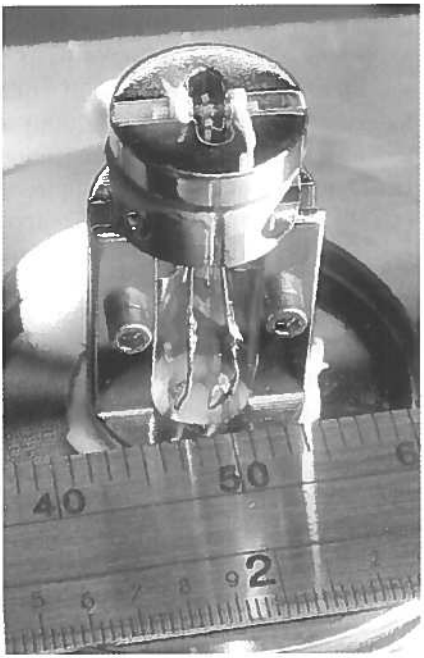

Fig. 4.4 QEPAS absorption detection module with micro-resonator

volume. QEPAS has already been demonstrated in trace gas measurements of NH_3 (Kosterev et al. 2004a), CO_2 (Weidmann et al. 2004; Wysocki et al. 2006), N_2O (Kosterev et al. 2005b), HCN (Kosterev et al. 2006), CO in propylene (Kosterev et al. 2004b) and CH_2O (Horstjann et al. 2004; Angelmahr et al. 2006).The measured normalized noise equivalent absorption coefficient for H_2O is 1.9×10^{-9} cm^{-1} $W/Hz^{-1/2}$ in the overtone region at 7306.75 cm^{-1} is the best among the tested trace gas species to date using QEPAS and is indicative of fast vibrational–translational relaxation of the initially excited states. An experimental study of the long-term stability of a QEPAS-based NH_3 sensor (Kosterev et al. 2005a) showed that the sensor exhibits very low drift, which allowed data averaging over >3 h of continuous concentration measurements.

Formaldehyde (H_2CO) is widely used in the manufacture of building materials and numerous household products. Outgassing of formaldehyde from these materials may lead to elevated indoor levels, particularly for poorly ventilated structures. It is also an important intermediate species in the oxidation of hydrocarbons in both combustion systems and in the troposphere. Thus, H_2CO may be present in substantial concentrations in both indoor and outdoor air samples. Tropospheric H_2CO concentration measurements provide a means of validating photochemical model predictions that play a key role in our understanding of tropospheric ozone formation chemistry (Wert et al. 2003).

Formaldehyde is a pungent-smelling, colorless gas that causes a variety of effects (including watery and/or burning eyes, nausea, and difficulty in breathing) in some humans exposed to H_2CO levels of only 100 ppbv. Known to cause cancer in animals, it is also a suspected human carcinogen. Formaldehyde is detectable by scent in humans in concentrations of 0.07–1.2 ppmv in air. The US Occupational Safety and Health Administration (OSHA) has established permissible exposure limit (PEL) of 0.75 ppmv averaged for an 8 h work day and short-term exposure limit (STEL) of 2 ppmv averaged over 15 min (Occupational Safety and Health Standards, 2006). At levels ten times the PEL, respiratory protection is required. Other organizations have taken a more aggressive approach to H_2CO management. For example, the threshold limit value (TLV) for H_2CO established by the American Conference of Governmental Industrial Hygienists is 0.3 ppmv as a "ceiling limit" not to be exceeded at any time, and has classified it as a "suspected human carcinogen". A committee of the National Academy of Sciences, working on behalf of NASA, has extensively reviewed the toxicity of H_2CO and has established spacecraft maximum allowable concentrations for various times of exposure (Crossgrove 1994–2000). Their recommended upper limits range from 0.4 ppmv for short-term (1 h) exposure down to 0.04 ppmv for 7–180 day space missions.

A novel continuous-wave mid-IR DFB ICL was utilized to detect and quantify H_2CO using quartz-enhanced photoacoustic spectroscopy (Horstjann et al. 2004). The sensor architecture is depicted in Fig. 4.5. Unlike the Fabry–Perot gain chip, which is used in the widely tunable EC-QCL configuration described in Section 4.2 it is possible to use an ICL or QCL chip with an embedded

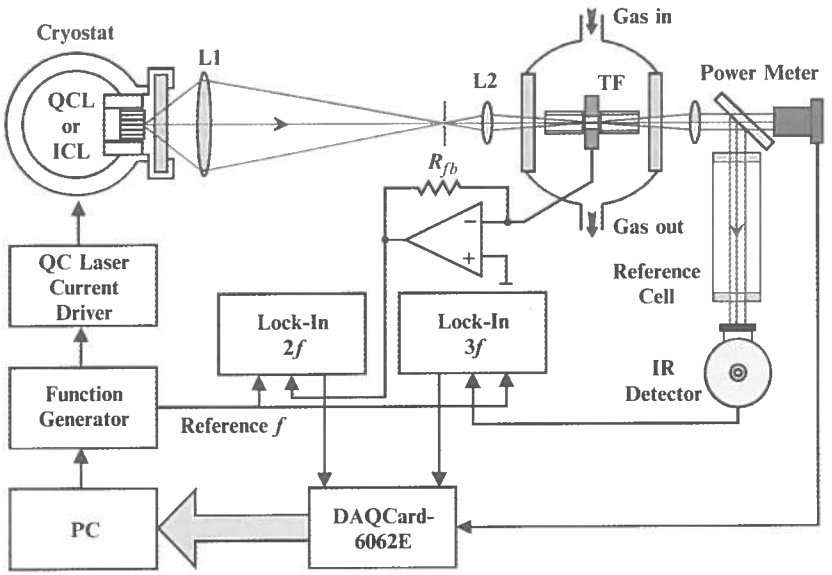

Fig. 4.5 Schematic diagram of a QCL- or ICL-based QEPAS sensor platform

DFB structure that provides a single-frequency output. This allows the ICL or QCL to be matched to a specific target analyte with a limited tuning range of ~1 cm^{-1} with current control and a few cm^{-1} with temperature control. The ICL was operated at liquid-nitrogen temperatures and provided a single-mode output power of up to 12 mW at 3.53 μm (2832.5 cm^{-1}). The noise equivalent (1 σ) detection sensitivity of the sensor was measured to be 1.1×10^{-8} cm^{-1} $W/Hz^{-1/2}$ for H_2CO in ambient air with 75% relative humidity, which corresponds to a detection limit of 0.20 ppmv for a 1 s sensor time constant and 4.6 mW laser power delivered to the QEPAS absorption detection module.

Recently, Wojcik et al., 2006 demonstrated the performance of a novel infrared photoacoustic laser absorbance sensor for gas-phase species using an amplitude-modulated (AM) QCL and a quartz tuning fork microphone. A photoacoustic signal is generated by focusing 5.3 mW of a Fabry–Perot QC laser operating at 8.41 μm between the tines of a quartz tuning fork which served as a transducer for the transient acoustic pressure wave. The sensitivity of this sensor was calibrated using the infrared absorber Freon-134 a by performing a simultaneous absorption measurement using a 31 cm absorption cell. The power and bandwidth normalized noise equivalent absorption sensitivity (NEAS) of this sensor was determined to be 2.0×10^{-8} cm^{-1} $W/Hz^{-1/2}$, which translates into noise equivalent concentration of 40 ppbv for the available QCL laser power and a data acquisition time of 1 s.

4.4 Trace Gas Sensors using a High-Finesse Optical Cavity

Sensitive laser absorption spectroscopy often requires a long effective optical pathlength of the probing laser beam in media that are to be analyzed. Traditionally, this requirement is satisfied using an optical multipass cell. Such an approach can be difficult to implement in certain field applications, requiring compact gas sensor configurations. For example, a typical commercial 100 m long multipass cell has a volume of 3.5 L. An alternative way to obtain a long optical path is to make the light bounce along the same path between two parallel ultralow-loss dielectric mirrors. An effective optical pathlength of several kilometers can be obtained in a very small volume. The light leaking out of such an optical cavity can be used to characterize the absorption of the intracavity medium. Presently a variety of techniques exists to perform high sensitivity absorption spectroscopy in a high-finesse optical cavity (Berden et al. 2000). Two methods are cavity ringdown spectroscopy (CRDS) (Kosterev et al. 2001) and integrated cavity output spectroscopy (ICOS) (Bakhirkin et al. 2004).

A gas analyzer based on a continuous-wave mid-infrared quantum cascade laser operating at ~5.2 μm and off-axis integrated cavity output spectroscopy (OA-ICOS) has been developed to measure NO concentrations in human breath (Bakhirkin et al. 2004). A compact sample cell, 5.3 cm in length and with a volume of ~80 cm^3, which is suitable for online and off-line measurements during a single breath cycle, was designed and tested. A noise-equivalent (signal-to-noise ratio of 1) sensitivity of 10 ppbv of NO was achieved. The combination of ICOS with wavelength modulation resulted in a 2 ppbv noise-equivalent sensitivity. The total data acquisition and averaging time was 15 s in both cases. In 2005, a pulsed, non-cryogenic cavity-enhanced spectrometer that operates at 5.2 μm was developed (Silva et al. 2005).

Subsequently, a nitric oxide sensor based on a thermoelectrically cooled, cw DFB QCL laser operating at 5.45 μm (1835 cm^{-1}) and off-axis ICOS combined with a wavelength-modulation technique was developed to determine NO concentrations at the sub-ppbv levels that are essential for a number of applications, such as medical diagnostics (specifically in detecting NO in exhaled human breath) and environmental monitoring (Bakhirkin et al. 2006; McCurdy et al. 2006). Exhaled nitric oxide (eNO) is an important biomarker in many respiratory diseases (Namjou et al. 2006). Exhaled NO levels have been extensively studied in asthma. These measurements may be clinically useful in other chronic respiratory conditions, such as chronic obstructive pulmonary disease, particularly if the NO contributions are partitioned into alveolar and conducting airway regions. eNO levels are generally in the range of 4–15 ppbv in healthy human subjects and 10–160 ppbv in subjects with untreated asthma when breath is collected at the standard 3 L min^{-1}, in accordance with the American Thoracic Society recommendations.

The sensor as shown in Fig. 4.6 employs a 50 cm-long high-finesse optical cavity that provides an effective path length of 700 m. A noise equivalent minimum detection limit of 0.7 ppbv with a 1 s observation time was achieved (Bakhirkin et al. 2006). A wavelength modulated signal for a calibrated NO concentration of 23.7 ppbv was fitted using a general linear fit procedure (Kosterev et al. 2002d) (see Fig. 4.7).

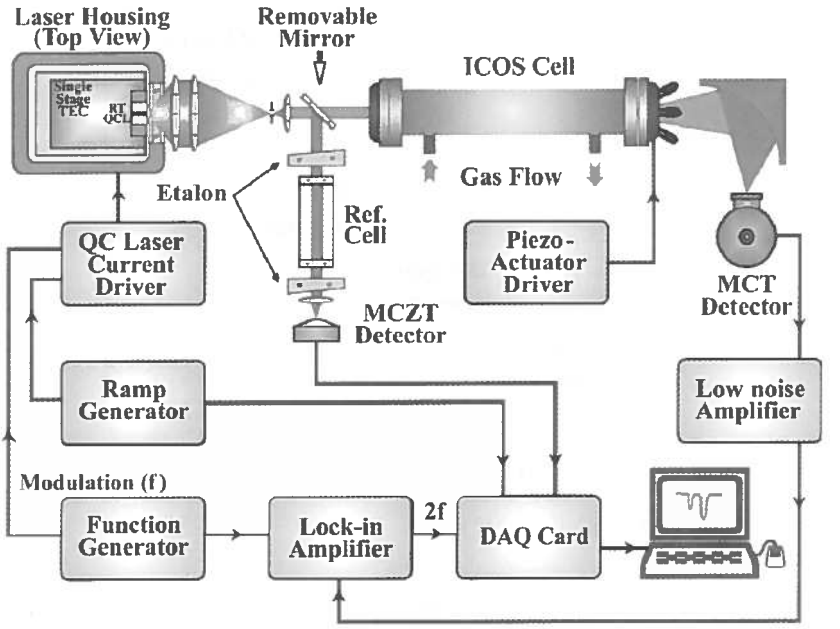

Fig. 4.6 Schematic diagram of a CW-TEC-DFB QC laser-based nitric oxide off-axis integrated cavity output spectrometer

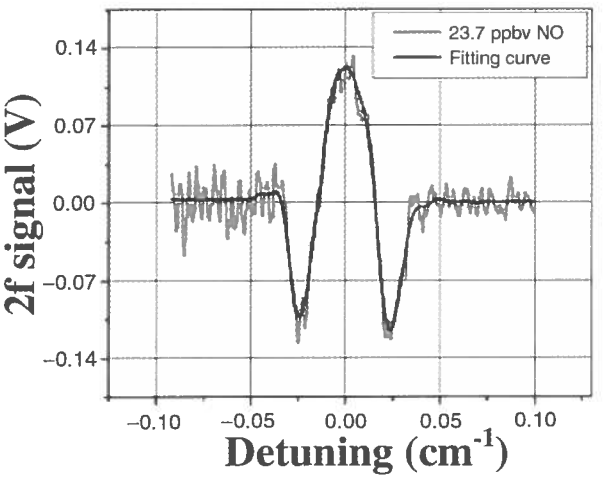

Fig. 4.7 2f OA-ICOS based NO absorption spectrum

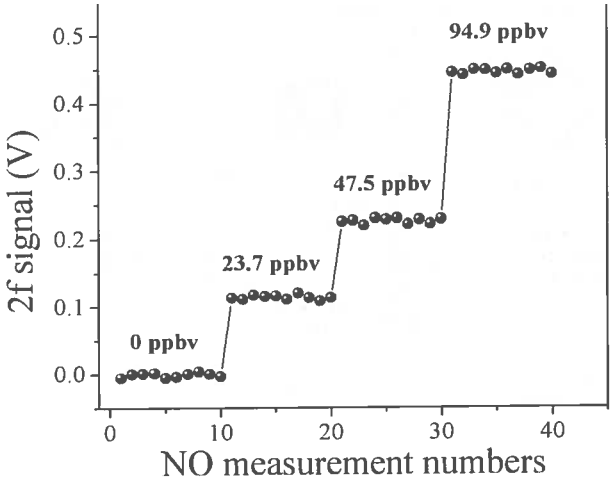

Fig. 4.8 Calibration of an OA-ICOS NO sensor

A 1 σ deviation of the amplitude obtained as a fit result corresponds to 0.7 ppbv. Step concentration measurements of NO are depicted in Fig. 4.8. Each measurement was repeated ten times and the amplitude of the wavelength-modulated spectroscopic signal was retrieved and plotted in Fig. 4.8. More recently (Nelson et al. 2006), a detection sensitivity of 0.03 ppbv was achieved with 30 s averaging time with a path length of 210 m, corresponding to an absorption coefficient of 1.5×10^{-10} cm^{-1}.

Detection of formaldehyde using off-axis ICOS with a 12 mW ICL was recently demonstrated (Miller et al. 2006). A 3.53 µm continuous-wave, mid-infrared, distributed feedback ICL was used to quantify H_2CO in gas mixtures containing ≈1–25 ppmv of H_2CO. Analysis of the spectral measurements indicates that a H_2CO concentration of 150 ppbv would produce a spectrum with a signal to noise ratio of 3 for a data acquisition time of 3 s. This is a relevant sensitivity level for formaldehyde monitoring of indoor air, occupational settings, and on board spacecraft in long duration missions in particular as the detection sensitivity improves with the square root of the data acquisition time.

4.5 Summary

Compact, sensitive, and selective gas sensors based on near infrared and mid-infrared semiconductor lasers have been demonstrated to be effective in numerous real-world applications. These applications include such diverse fields as environmental monitoring (e.g. CO, CO_2, CH_4 and H_2CO are important carbon gases in global warming and ozone depletion studies), industrial emission

measurements (e.g. fence line perimeter monitoring in the petrochemical industry, combustion sites, waste incinerators, down gas well monitoring, gas pipeline and compressor station safety), urban (e.g. automobile traffic, power generation) and rural emissions (e.g. horticultural greenhouses, fruit storage and rice agroecosystems), chemical analysis and process control for manufacturing processes (e.g. semiconductor, pharmaceutical, food), detection of medically important molecules (e.g. NO, CO, CO_2, NH_3, C_2H_6 and CS_2), toxic gases, drugs, and explosives relevant to law enforcement and public safety, and spacecraft habitat air-quality and planetary atmospheric science (e.g. such planetary gases as H_2O, CH_4, CO, CO_2 and C_2H_2).

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