Chapter I

TUNABLE DIODE LASER SPECTROSCOPY AND HIGH-RESOLUTION SPECTROSCOPY – A REVIEW

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1.1 Introduction

Spectroscopy is an analytic technique concerned with the measurement of the interaction of light with matter usually in the form of absorption or emission of radiant energy. The instruments necessary to make such measurements at the fundamental level and for practical analysis deals with the spectroscopic instrumentation. The interpretation of the interaction of light with matter describes the spectroscopic analysis. A display of the intensity of the emitted or transmitted radiant energy (or some function of the intensity) versus the energy of that light is called a spectrum. Spectra due to the emission of radiant energy are produced as radiation emitted from matter after some form of excitation. The emitted light is collimated by passing through a slit and then separated into components of different energy. Either the transmission through a prism (refraction) or reflection from a ruled grating or a crystalline solid (diffraction) is used for separation of different wavelengths and finally detected by a photodetector. Spectra due to the absorption of radiant energy are produced when radiant energy from a stable source, collimated and separated into its components by a monochromator, passes through the sample whose absorption spectrum is to be measured, and is detected. Instruments, which produce spectra, are commonly known as spectrosopes, spectrometers, spectrographs and spectrophotometers [1].

Interpretation of spectra provides fundamental information on atomic and molecular energy levels, the distribution of species within those levels, the nature of process involving change from one level to another, molecular geometries, chemical bonding and interaction of molecules in solution. At the practical level, comparisons of spectra provide a basis for the determination of qualitative chemical composition and chemical structure, and for quantitative chemical analysis.
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Since a quantum transition obeys the relation $E = hv$, the change in energy of an ion, atom or molecule associated with absorption or emission of electromagnetic radiation is directly obtained from the measured frequency of the corresponding radiation.

Atoms, ions and molecules absorb or emit characteristically and hence only certain energies of these species are possible. The energy of the photon (quantum of radiant energy) emitted or absorbed corresponds to the difference between two permitted values of the energy of the species, or energy levels. Thus the energy levels may be studied by observing the differences between them. The absorption of radiant energy is accompanied by the promotion of the species from a lower to a higher energy level; the emission of radiant energy is accompanied by falling from a higher to a lower state; and if both processes occur together, the condition is called resonance.

1.2 Applications of laser spectroscopy

1) Investigation of chemical reactions with lasers

The lasers became an important tool for studying elementary chemical processes and for analytical applications. Laser photochemistry is characterized by high selectivity and intensity of the reaction source. The three most important types of reactions in laser-induced chemistry are

a) Electronically or vibronically excited molecules are produced in a bath of reactants, the activation barriers for a reaction is thus reached or surmounted

b) Molecules are ionized by single or multi-photon absorption and they either undergo further reactions with other molecules or unimolecularly decay into fragments.

c) Molecules are dissociated and a high concentration of reactive free radicals are produced by reacting with other molecules.

2) Vibrational relaxation studies

The knowledge of vibrational relaxation of molecules is very important in connection with laser-induced chemistry. When the vibrational energy is stored long enough in the reactant, it leads to a laser initiated process.
3) Study of molecular surface interactions with lasers
4) Laser investigations in the atmosphere

The laser is an ideal instrument for determining the properties of the atmosphere by absorption and scattering processes. Its high spectral density and low divergence are especially useful for such measurements. Lasers with continuous and discrete tunability can be used to measure specific components selectively.

Normally absorption measurements can be performed with low power diode lasers. A remarkable improvement of the detectivity in absorption measurements becomes possible by a heterodyne technique, where a tunable laser is used as a local oscillator and a photodetector as mixer. A suitable amplifier of narrow bandwidth amplifies the signal at the intermediate frequency. This technique (most advantageous in infra red spectral range) yields an increase in sensitivity of several orders of magnitude, allowing appreciable lengthening of the absorption paths [2].

1.3 Use of a tunable laser

Tunable coherent light sources now have very wide applications in the fields of communication, spectroscopy, medicine, biology etc. Tunable diode lasers with narrow linewidths and wide tunability make them ideal light sources for atomic and molecular spectroscopy, which require the laser radiation frequency to coincide with the frequency of a definite quantum transition between two energy levels of the atom or molecule. The sharpness of the frequency and high power per unit solid angle and unit spectral bandpass in a laser beam make it attractive for infrared spectroscopy at very high resolution. Tunable infrared lasers have been used mainly to measure the energy levels due to the vibration and rotation of the molecules in the gas phase at low pressure. Unique characteristics of laser radiation such as high power density, high monochromaticity and tunability are also making them ideal sources for laser spectroscopy. These properties make them very useful for high resolution spectroscopy. Very accurate values of molecular parameters such as internuclear distances, electric dipole moments, vibrational frequencies and internal force fields can be measured using high resolution techniques. Another use
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of laser infrared spectroscopy includes the monitoring of the composition of the atmosphere. The invention of the laser has brought about a drastic change in the spectroscopy of transient molecules. Tunable diode lasers solved the limitation in wavelength coverage. High resolution spectra of transient molecules allow us not only to confirm the presence of these species in reaction systems, but also to monitor their distributions over quantum states; chemical reactions may often result in selective population of molecules in certain levels. High resolution spectra of free radicals provide extremely reliable means of monitoring these species in various environments like in chemical reactions, radio astronomy, atmospheric studies etc. In these studies, the observed spectrum makes it possible to view selectively a particular species in the presence of many others, and one can thus get very specific information on chemical systems by means of high resolution spectra. Molecular spectroscopy has already contributed much to monitor chemically stable species in the atmosphere and short-lived species such as OH, HO$_2$, ClO, SH, NO$_3$ etc. The role of high resolution spectra is very important since they are an indispensable means in unambiguously identifying and monitoring free radicals in various systems and environments. A high resolution molecular spectrum denotes a well resolved rotational structure or it corresponds to rotational transitions of a molecule [3]. Diode laser spectroscopy may be applied to diagnose chemical reaction systems in real time by monitoring the spectra of transient species created or dissipated in systems.

1.4 Diode laser spectrometer

The diode laser consists of a semiconductor p-n junction. When a forward current flows through the p-n junction, laser action is induced by the stimulated carrier-hole recombination emission, with two cleaved facets at the opposite ends of the diode laser as laser mirrors. The strip type double heterostructure has been employed to reduce the threshold current and thus to lower the heat dissipated in the crystal. Either changing the band gap or the index of refraction of the material, both of which are functions of temperature, may tune the oscillation frequency of the diode laser. Therefore the oscillation wavelength may be chosen by adjusting
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the temperature of the diode or by varying the current fed to the diode. Although the current is eventually transformed into heat by ohmic loss, it is much more convenient in fine tuning and modulating the oscillation frequency. The oscillation frequency increases with temperature and current.

Several kinds of modulation techniques may be introduced to make the measurement of absorption lines easier with high sensitivity. Chopping the IR beam and detection of signal by a phase sensitive detector (PSD) is the simplest one. Other modulation techniques include Zeeman modulation, Stark modulation, wavelength modulation, frequency modulation etc.

The IR absorption may be recorded in either of the two modes, “spectroscopy” and “kinetics”. In the spectroscopy mode, the computer receives signals for a certain period (gate width) before and after the laser shot and stores the difference between the two signals while the diode laser is continuously swept as usual. In the kinetics mode, the diode laser emission is set to coincide with an absorption line and the computer stores the time variation of the signal intensity averaged for a number of laser shots.

1.5 Tunable diode laser absorption spectroscopy (TDLAS)

The development of semiconductor diode lasers in the near infrared has been spurred by the development of CD players (diode lasers with 0.78 micrometer) and optical fiber communication (diode lasers at 1.3 and 1.55 micrometers). As technology has improved, lasers have been developed for new applications such as pumping of solid state (0.808 micrometer) and fiber (0.98 micrometer) lasers. In addition to wavelength, other important laser parameters are mode stability, current tunability and frequency drift. Long-term frequency stability is one of the most important parameters for the diode lasers used in industrial gas monitors [4].

Over the past few years, the requirement for accurate and precise monitoring of trace gas constituents in the atmosphere has become increasingly important as a direct result of concerns over the cause and effects of atmospheric pollution. The necessity for reliable tools for trace gas monitoring is obvious, but the type of technique depends very much on the particular application being
addressed and the specific trace gas species of interest. High sensitivity laser spectroscopic techniques are needed to detect the very low mixing ratios or concentrations of trace species ranging from several parts per million to sub parts per trillion levels for carbon monoxide, hydroxyl radical etc. When lead-salt tunable diode lasers (TDL) were first developed in the mid-1960’s they found immediate application as tunable sources for high-resolution infrared laser spectroscopy. The most important application of tunable diode lasers to atmospheric measurements has turned out to be their use in conjunction with a long-path cell to provide high sensitivity local measurements. This technique is commonly referred to as tunable diode laser absorption spectroscopy (TDLAS), a general technique for monitoring most atmospheric trace species. The requirement is that the molecule should have an infrared line spectrum, which is resolvable at the Doppler limit. The principle of TDLAS is absorption spectroscopy using a single isolated absorption line of the species. TDLAS has now established itself as one of the leading techniques for atmospheric analysis of trace gas constituents. Operating at infrared wavelengths, most trace gases except nitrogen and oxygen to be monitored via their characteristic vibrational spectra and the high spectral resolution reduces the possibility of interferences from other species. Theoretical studies on the “differential absorption” studies are reported by Byer et al [5] and differential absorption technique was first applied to pollution detection by Rothe et al [6]. The applications of lead-salt and GaAs based semiconductor tunable diode lasers for atmospheric monitoring are well reviewed by Feher et al [7] and Werle [8].

1.5.1 Spectroscopic principles of TDLAS-line strengths and shapes

The intensity of monochromatic radiation of frequency $\nu$ transmitted through a cell containing an absorbing species is given by

$$I(\nu) = I_0(\nu) \exp[-\alpha(\nu)L]$$  \hspace{1cm} (1)

where $I_0$ is transmitted intensity in the absence of an absorbing species, L is the optical path-length within the cell, and $\alpha(\nu)$ is the absorption coefficient. $\alpha(\nu)$ is related to the absorption cross-section $\sigma(\nu)$ by:

$$\alpha(\nu) = \sigma(\nu)N$$  \hspace{1cm} (2)
where $N$ is the concentration of the absorbing species in molecules per unit volume. The cell absorbance, $a$, is defined by $a = \alpha(v) \, L$ and the transmittance by $T = 1 / I_0$.

A given absorption line is characterized by its integrated line strength $S$

$$S = \int_0^\infty \sigma(v) \, dv$$

which is independent of pressure (but not of temperature). The line shape depends on sample pressure. At high pressure, collision broadening dominates giving a Lorentzian line shape:

$$\sigma_L(v) = \frac{S}{\pi} \frac{\gamma_L}{(v - v_0)^2 + \gamma_L^2}$$

where $\gamma_L$ is the half width at half maximum (HWHM), of the line shape and $v_0$ is the line-centre frequency. $\gamma_L$ varies with $P$ and $T$ approximately according to:

$$\gamma_L = \gamma_{L0} \left( \frac{P}{P_0} \right) \left( \frac{T}{T_0} \right)^{1/2}$$

where $\gamma_{L0}$ is the value of $\gamma_L$ at S.T.P ($T_0$, $P_0$)

As the sample pressure is reduced the pressure broadened linewidth decreases until, at pressures below a few mbar, Doppler broadening dominates and the line shape becomes Gaussian:

$$\sigma_D(v) = \frac{S}{\gamma_D} \left[ \frac{\ln 2}{\pi} \right]^{1/2} \exp \left[ -\frac{(v - v_0)^2 \ln 2}{\gamma_D^2} \right]$$

where $\gamma_D$ is the Doppler HWHM given by:

$$\gamma_D = \left[ \frac{2kT \ln 2}{M'} \right]^{1/2} \frac{v_0}{c}$$

where $M'$ is the molecular mass and $c$ is the velocity of light.

For TDLAS the optimum sampling pressure is a compromise between sensitivity (best at high pressure) and selectivity (best at low pressure).

Even for strongly absorbing species, typical line-strengths are such that, an atmospheric concentration of 1 ppbv produces an absorption of only 1 part in $10^7$ over a 10 cm path-length. TDLAS overcomes this problem firstly by using a multi-pass cell to give path-lengths of 100 m or more. Such cells achieve the long path
by using mirrors to fold the optical path, giving typically 100 passes of a 1 m base-length cell. Various types of modulation spectroscopy techniques are employed in which the diode-laser wavelength is modulated over the absorption linewidth at frequencies of anywhere between 100 Hz and 2 GHz. These modulation techniques allow absorptions as low as 1 part in $10^5$ to be measured with a 1 Hz bandwidth.

TDLAS is used in a continuous sampling mode in which air is continually drawn through the multi-pass cell at a pressure of about 30 mbar. Operating at reduced pressure narrows the absorption lines avoiding possible interferences from other species and also reduces the range over which the laser needs to be modulated, which in turn reduces the effects of laser noise. The main features of TDLAS are as follows:

- As a high resolution spectroscopic technique it is virtually immune to interferences by other species - a problem that plagues most competing methods. This ability to provide unambiguous measurements leads to the use of TDLAS as a reference technique against other similar methods.

- The same instrument can easily be converted from one species detection to another by changing the laser and calibration cells. Similarly it is easy to measure several species simultaneously using the same instrument by multiplexing the outputs of several lasers (commonly up to four) through the multi-pass cell. It is a general technique.

- It offers automated measurements at time-constants of a minute or so. It offers *in-situ* monitoring within a very short time with very high sensitivity.

The easily collimated and steered laser beam is ideal for *in-situ*, remote monitoring over an open path thus by-passing many of the problems associated with sampling such as wall losses, condensation or chemical conversions. Multipass cells are commonly employed to increase the absorption pathlength. High sensitivities thus enable fast response measurements of less than 1 second, which is the requirement for measuring rapidly fluctuating concentrations.
TDLAS instruments are complex and expensive, and they require operators with good skills and expertise. The diode lasers themselves can be unreliable and each laser is unique, leading to the need to calibrate the instrument whenever a new laser is installed. Commercially available tunable diode lasers are divided into two classes: lead-salt based tunable diode lasers operate in the mid infrared region approximately from 3–30 micrometers and GaAs based lasers from approximately 0.6–4 micrometers. Operation in the mid IR allows access to most fundamental vibrational bands of the molecules and, combined with long pathlength and harmonic detection, monitoring at the ppb level and below is possible. In the near infrared, overtones and combination bands of molecules can be accessed which are often two to three orders of magnitude weaker than the fundamental bands, yet sub-ppm level sensitivities can still be attained with TDLAS.

The main application of lead-salt based diode lasers has been high resolution infrared spectroscopy of both stable molecules and transient species such as free radicals and ions. GaAs lasers have been developed for different reasons: the shorter wavelength devices are used in compact disc players, bar code scanners and optical guidance systems, the longer wavelength devices (especially at around 1.3 and 1.5 μm for optical fiber communications. Their applications to atmospheric monitoring has been limited due to the lack of spectral coverage and lower sensitivities associated with overtone and combination band transitions but has advantages such as room temperature operation, cost and high power are making them a viable alternative to the lead salt diode lasers for the purpose of atmospheric monitoring. Additionally they can be easily coupled to optical fibres, which is ideal for monitoring remote and possibly dangerous locations without the need for complicated optical arrangements.

Two other uses of TDLs in atmospheric measurements are long-path monitoring and heterodyne spectroscopy. Long-path monitoring replaces the folded path in the multi-pass cell with an open-path, through the atmosphere, to a retro-reflector and back. This gives a path-averaged value of the species concentration, which for some purposes can be an advantage. In heterodyne spectroscopy the diode laser is used as a local oscillator in a heterodyne receiver looking at solar radiation. This allows atmospheric column contents of species to be determined.
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1.6 Description of tunable diode laser spectrometer

1.6.1 Diode laser characteristics, tuning and mode structure

The semiconductor laser chip is a rectangular block of sizes a few hundred micrometer, with a thin active layer of nearly 0.3 micrometer. In most of the laser diodes (except the external cavity versions) the cleaved facets of the laser chip acts as resonator mirrors as mentioned earlier. On increasing the injection current, the power increases and the laser works as an inefficient LED. When the diode starts lasing at a threshold current, the power increases rapidly with current. The wavelength tuning can be achieved by altering the temperature or the injection current of the diode, which results in change in refractive index and cavity length. On increasing the temperature or current, the emitted wavelength in lead salt based diode lasers increases, where as it decreases in GaAs-based diodes.

Lead-salt tunable diode lasers are similar in principle to the more familiar GaAs semiconductor lasers used widely in communications. The simplest form of laser consists of a crystal of a lead-salt semiconductor such as Pb₁₋ₓSnₓSe on which a p-n junction is formed by diffusion of a salt of different stoichiometry into the top surface. The crystal is cleaved to a chip about 300 μm long with front and rear faces about 100 μm square. These front and rear facets form the laser cavity and do not need any reflective coating, as the Fresnel reflection is sufficiently strong. If electrodes are deposited on the top and bottom surfaces and a current of a few hundred milli ampere passed through the junction, lasing action takes place at a wavelength determined by the semiconductor energy gap. This energy gap is temperature dependent and a typical laser can be temperature tuned over about 100 cm⁻¹.

Most of the diodes are manufactured from complex ternary or quaternary compounds of group III–group V elements (GaAs based), group IV–group VI elements (containing different lead salts) or less importantly from group II–group VI elements. The simplest lead salt diode design is the homostructure diode with one n-type and one p-type semiconductor layer, where as in double heterostructure diodes, an n (or p) type semiconductor diode is sandwiched between two layers of opposite material. Another new development is the appearance of PbEuSeTe/PbTe buried heterostructure diode lasers, in which
differently doped layers are deposited by molecular beam epitaxy (MBE). The GaAs based diodes (GaAlAs, InGaAs and InGaAsP) emit laser light in the near infrared region. Most of these have a double heterojunction design. A very promising development in laser production is the strained quantum-well laser. A quantum-well laser is a layer so thin (<20 nm) that carriers are confined to quantum states. Additional lattice mismatches help to reduce threshold current and increase power up to 300 mW. These lasers also have a wider scanning range from 6 nm – 1.55 μm. TDLs are tuned by varying the temperature of the active region. This can be done either by varying the temperature of the cold stage on which the diode is mounted or by varying the laser drive current, which varies the Ohmic heating of the active region.

Single mode operation of the diode laser is another problem to be solved. Two solutions have been successfully used to solve this mode structure problem by incorporating a grating into the semiconductor structure and the diodes are operated near the maximum specified drive current to diminish all but the dominating mode.

- Laser output is single-mode at low drive current and then becomes increasingly multi-mode at higher currents.
- Although the power per mode shows some increase as current increases, the main effect of increased drive current is an increase in the number of modes.
- An individual mode tunes over about 2 cm⁻¹ with power first increasing then decreasing with drive current.

There are some wavelengths that are not accessible at all. This can sometimes be remedied by choosing a different combination of base temperature and drive current but frequently the only solution is to use a different laser.

1.6.2 Optical layout

A typical optical arrangement is briefly described; the strongly divergent laser beam is focused, collimated and split into two or three different beams. Most of the laser power is used in the sample beam to monitor the trace gas interest in either in a multipass cell or in an open arrangement. A second beam is passed through a reference cell for wavelength stabilization and the third beam is passed
through a concentration calibration cell. The invisible infrared beam is normally traced by sending the output of a helium neon laser along the same optical path to aid in alignment, whereas infrared viewers can be used in the near infrared arrangements.

Multipass cells are used for increased absorption and pathlength. A monochromator is only required for multimode lasers where a single mode must be selected from all the others oscillating simultaneously to prevent absorption interferences. High resolution monochromators are not required for this purpose as the mode separation is usually of the order of several wavenumbers.

In general, each beam has a separate detector. For the mid infrared, cryogenically cooled photoconductive or photovoltaic detectors, such as mercury cadmium telluride (HgCdTe or MCT) or indium antimonide (InSb) are most commonly used. Commercially available HgCdTe detectors have high sensitivity and high responsivity in the mid infrared. In the near infrared, much less expensive PIN photodiodes or avalanche germanium, silicon or GaAs photodiodes operating at room temperature are preferred.

The corresponding electronic arrangement consists of a computer that drives the temperature and current controllers. Each of the pre-amplified detector signal is passed to a phase sensitive detector referenced at the wavelength modulated frequency, \( f \). The sample signal is demodulated at \( 2f \) (second harmonic detection) and the signal is processed in a computer. As the second harmonic signal is proportional to the concentration of the trace gas being monitored one possibility is to lock the laser wavelength to the line center and to continuously monitor the peak height above the background level but this is susceptible to background drift. An alternative is to lock the laser to the line center and introduce a slow DC ramp into the feedback loop allowing one to scan from one edge of the line to the other.

The spectroscopic basis of diode laser monitoring is the same as for classical infrared spectroscopy with non-laser sources where the amount of light absorbed by the sample gas are given by the Beer – Lambert law, is recorded as a function of wave number. The resultant lineshape is dependant on pressure. The choice of the absorption line to monitor is important one and several factors must be taken into consideration. The selected line must be well separated from other
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absorptions, both of the same species and of other species, to prevent interferences. This is easier when monitoring at reduced pressure in multipass cells, but problems can arise at higher pressures due to the extensive absorptions of the atmospheric water vapor. A strong line must be selected for increased sensitivity. The identification of the line can be useful for concentration determination, if the line is sufficiently strong to observe in direct absorption. Other information such as line strength, line center wavenumber, linewidth and pressure broadening parameters can be obtained on a wide range of trace gas species of atmospheric interest from databases such as HITRAN [9, 10, 11] or GEISA [12]. A final consideration in the choice of an absorption peak is that the diode laser must tune across the whole line in a single mode.

An absorption spectrum is easily obtained with a diode laser spectrometer by scanning the laser wavelength over an absorption feature and measuring the decrease in laser power, usually with the aid of amplitude modulation with a chopper.

1.6.3 Overall experimental layout

The beam from the TDL housed in the cold head is first collimated and then directed by a sequence of mirrors through the multi-pass White cell and onto the cooled detector as specified earlier. Part of the beam is split off and directed through a line-locking cell and also to a scanning Fabry-Perot interferometer that is used to give an on-line display of the laser mode-structure. A calibration cell can be inserted into the main beam under computer control. A visible He-Ne laser or diode laser beam is combined with the invisible infrared beam to assist in alignment (fig.1.1).

The most important requirement is to minimize optical fringes. Precautions that will reduce the chances of etalon formation include the use of reflective optics where possible, wedging and angling of all windows and anti-reflection coating window and lens surfaces. Similar precautions will also help avoid feedback of scattered or reflected radiation into the laser. Accurate alignment of the TDLAS optical system is important in avoiding optical fringing, and is difficult to achieve due to the invisibility of the beam. Riedel [13] and Fried et al. [14] have discussed the various useful alignment techniques and tools that are in use.

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TUNABLE DIODE LASER SPECTROMETRY

Fig. 1.1. Schematic representation of a TDLA spectrometer
1.6.4 Multipass absorption cell

From the Beer – Lambert law, increasing the pathlength increases absorbance and thus sensitivity. In some cases it is possible to achieve sensitivities in the ppb range in a 1 m absorption cell but more typically several hundred meters pathlengths are required. In order to increase the pathlength in a cell, two arrangements have been applied: White cells and Herriot cells. The limiting factors in the pathlength are the optical surface qualities and reflectivity of the mirrors and in practical applications a few hundred meters are commonly used. In the White cell arrangement [15] the major factor affecting sensitivity is interference fringes, resulting from two images of the entrance focus partially overlapping at the exit [16]. One of the most serious shortcomings of the traditional White cells is that astigmatism limits the attainable pathlength. Herriott cell is more straightforward as it uses a simpler mirror design and the adjustment is also easier. The same number of passes can be accommodated in smaller Herriott cells by using astigmatic mirrors so that the reflections form a Lissajous pattern [17].

1.6.4.a White cell

As the name implies, the original design of multipass absorption cell was given by White [15], but a slightly modified design due to Bernstein and Herzberg (18) is commonly used in TDLAS instruments. A typical cell of this type would have a 1 m mirror separation, a volume of 10 l and a usable path-length of 100 m.

1.6.4.b Herriott cell

The Herriott cell [19, 20] consists of two spherical mirrors separated by nearly their radius of curvature. The optical beam is injected through a hole in one mirror and is reflected back and forth a number of times before exiting from the same hole. Unlike the White cell, the beam remains essentially collimated throughout its traversals of the cell. In the original design the beam traces out elliptical paths on the two mirrors, however this does not give optimum use of the mirror area and thus a modified arrangement using slightly astigmatic mirrors normally used.

A further advantage of the Herriott cell over the White cell is that it is easy to align, since the output beam direction is insensitive to changes in the mirror alignment. Unlike the White cell a Herriott cell can support several independent optical paths, each with a separate entrance and exit hole in the input mirror [21].
This allows multi-species measurements with independent optical channels. There are also other absorption cell designs, like the Welsh cell with four mirrors, plane mirrors multipass cells and Perry cell, which is a two mirror arrangement like a Herriott cell but with the images on both mirrors forming a parabola instead of an ellipse.

The choice of material for the sampling system and multipass cells must be a consideration for polar molecules that easily adsorb onto surfaces (\(\text{NH}_3\), \(\text{H}_2\text{O}\), \(\text{HNO}_3\), \(\text{H}_2\text{O}_2\) etc) as well as reactive species (HF-Glass, \(\text{SO}_2\)-Stainless steel). These effects can be somewhat reduced by high pumping speeds. The optimum pressure in the measurement is dependent on the arrangement and is the result of two factors: pressure broadening and the increase of the amount of sample on increasing the pressure. Values of around 10–100 torr usually present a reasonable compromise. For measuring the changes in concentration in a multipass cell, the response time of the gas handling system has to be considered which is dependent on pump speed, measurement pressure, dimensions adsorption properties, and it can be as much as several seconds.

The design requirements for the multi-pass cell are as follows:

- **Long path-length**: Long total path-length to give high sensitivity
- **Compact design**: The multi-pass cell is often the largest component and can determine the overall dimensions of the instrument.
- **Low volume**: This is needed to give a fast response time for flux measurements and is also useful in lower bandwidth measurements since it allows sample and background spectra to be alternated more rapidly which in turn helps to reduce the effects of optical fringes also.
- **High overall transmission**: This is particularly important in modulation spectroscopy systems that are usually detector or shot noise limited.
- **Freedom from optical fringing**: The optical fringes in the multi-pass cell arise when the output beam from the cell contains some radiation that has traversed a smaller number of passes than the main beam.
- **Ability to easily vary the number of passes**: The higher the number of passes, the greater the path-length and hence the higher the instrument sensitivity. However a high number of passes increases the amplitude of optical fringes and also decreases the overall transmission and hence the power of the signal. The ability to optimize
the number of passes is thus important for any system and is particularly important in frequency modulation systems where this optimum number of passes will vary with the power of the laser being used.

*Freedom from optical aberrations:* This is important, firstly in avoiding optical fringes and secondly in ensuring that the beam can be focused to a spot smaller than the detector element.

*Lack of memory effects:* Lack of memory effects due to adsorption of the monitored species on the internal surfaces. This is mainly a problem with polar molecules such as HNO₃ and NH₃. Use of glass and Teflon construction helps to minimize the problem and metals should be avoided.

### 1.6.5 Multi-species operation

In practical applications it is often necessary to monitor several different gases simultaneously. The gases must have strong absorptions over a narrow wavelength range to record their spectra within one laser mode. A solution to this is to operate the laser in different modes for different species or even to have several lasers with the beam passed through the absorption path alternately [22]. This method is called time multiplexing and its major disadvantage is the low time resolution of the order of minutes.

Because of the limited tuning range of an individual laser, multi-species operation usually requires a separate laser for each species. In the most common approach the collimated beams from these lasers are sequentially directed along the optical path through the instrument by either a rotating selecting mirror on a galvanometer drive or by individual "pop-up" mirrors for each laser. A different approach is wavelength multiplexing where two laser beams are combined. They are detected with two detectors each of which is only sensitive to one of the wavelengths.

If a Herriott cell is used as the multi-pass cell then its ability to provide several independent optical paths allows truly simultaneous measurements of several species by using separate optical channels for each. In such a system only the sampling system, Herriott cell, and data acquisition system are common to each species-measurement. The four-species ALIAS [21] and the proposed two-species ARGUS [22] instruments use these systems.
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1.6.6 Optical fringes

Most TDLAS systems are limited in sensitivity not by laser or detector noise but by optical fringes superimposed on the measured spectrum. These result from unwanted etalons formed by reflections and scattering in the optical system and they appear in the form of an approximately sinusoidal variation of the background signal. This is true both for the direct absorption signal and for the various orders of modulation spectra [23]. These fringes can be reduced by careful optical design and adjustment, but it is usually difficult to reduce the fringe amplitude to a level much below that equivalent to an absorbance of $10^{-4}$ [24]. In order to achieve sensitivities in the $10^{-5}$ to $10^{-6}$ range some method of reducing the effect of the fringes must be found. These techniques can be categorized as follows: (i) mechanical modulation or dithering of the etalon spacing (ii) modified modulation schemes (iii) background subtraction and (iv) post-detection signal processing.

1.6.7 Sampling and calibration

1.6.7.a Sampling system

A high-speed rotary pump sucks air through the multi-pass cell at reduced pressure. A valve on the cell inlet controls this pressure, which is normally servo-controlled to maintain a fixed cell pressure. Polar species such as HNO$_3$, HCl and NH$_3$ are readily adsorbed onto the surfaces of the inlet system and multi-pass cell. This leads to memory effects due to subsequent out gassing, which can persist for days after high concentrations have been sampled. Metals give the worst adsorption problems. PTFE (polytetrafluoroethylene) and glass are the preferred materials for most species and these materials need to be used for the whole of the inlet system including the valves. The multi-pass cell also needs to be of glass or lined with PTFE. Other measures like high throughput and trace heating of the inlet tubing [25] help to reduce adsorption problems.

1.6.7.b. Calibration methods

The best and most direct calibration method is to attach calibrant and zero air sources to the instrument inlet. This method has the advantage of calibrating the entire signal processing chain and also corrects for any loss of species due to surface adsorption (to the extent that this loss is proportional to concentration). In
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general oven-stabilized permeation sources are preferred although dilution of standard gas mixtures can be used. For polar species calibration concentrations should be comparable with levels being measured because adsorption losses can be non-linear. Ideally zero air should be obtained by scrubbing from the ambient air only the species being monitored. In this way the background spectrum will contain any interferences from other atmospheric species, and these will then be subtracted off the sample spectrum. The zero air should contain levels of the monitored species well below the required detection limit since all measurements will be relative to this zero air level. Alternatively the level can be established in a separate experiment and a correction applied. Because of the inherent linearity of the TDLAS technique a single point calibration is sufficient.

Direct calibration can be time consuming especially for polar species with long equilibrium times. Because of this it is often convenient to use a sealed calibration cell as a transfer standard. This cell contains a sufficient concentration of the species being measured to give a strong signal when inserted into the optical path between the multi-pass cell and the detector (but low enough to still be in the linear response regime). The cell is filled with buffer gas to the same pressure as the multi-pass cell so that the lineshape is the same. This procedure corrects for most instrumental drifts without requiring frequent primary calibrations. In principle TDLAS measurements can be calibrated absolutely using the known absorption line strength and HWHM.

1.6.8 Data processing and experimental control

Whilst no two TDLAS systems are alike, the data processing and experimental control system is typical and serves to illustrate the principles. The laser frequency is ramped through the absorption line at 100 Hz and the resulting second harmonic spectra are averaged in the microprocessor-controlled signal-averager. On completion of the desired number of scans the averaged spectrum is transferred to the PC for further processing.
1.6.9 Sensitivity and precision limits

1.6.9.a Sensitivity

Sensitivities in the sub-ppb range have been achieved for many trace gases with lead salt diode lasers. In the near infrared, ppm and sub-ppm sensitivities can be demonstrated.

A TDLAS system can be operated either with the laser wavelength fixed at the point of maximum harmonic signal (often at line-centre) or with the laser repetitively scanning through the line and building up a spectrum by accumulating the scans in a signal averager. The first method theoretically gives the highest sensitivity for a given bandwidth because it gives maximum duty factor on the point of maximum signal. However unless fast response is needed (e.g. for flux measurements) the second method has overwhelming advantages because it avoids various systematic errors, which can affect the fixed wavelength technique. These include residual etalon fringes and a residual amplitude modulation (RAM) offsets which drift with time, and interferences from nearby absorption lines of other species. Scanning over the line also gives increased confidence in the measurement because the characteristic feature of the measured species is clearly seen and unwanted spectral features due to interfering species or etalon fringes can be identified.

1.6.9.b Precision and Accuracy

For measurements of trace species, sensitivity is usually more important than accuracy, and the 10 - 20% accuracy of most systems is normally adequate. However when monitoring the more abundant long-lived species such as CO, CH₄, and CO₂ high accuracy is often needed [14]. TDLAS accuracy depends firstly on the calibration procedure and secondly on instrument drift between calibrations. Calibration usually involves injecting a calibration mixture and also a zero air sample into the instrument inlet.

1.6.10 Modulation spectroscopy

The modulation technique employed in the majority of the applications is wavelength modulation spectroscopy (WMS, also called derivative spectroscopy). The laser wavelength is modulated by rapidly varying the drive current at a frequency f (typically up to several kHz), while being slowly tuned across the
absorption line. The crucial difference is that for FMS the modulation frequency is equal to or greater than the absorption linewidth whereas for WMS the modulation frequency is much less than the linewidth. Thus FMS uses modulation frequencies of around 500 MHz and WMS frequencies of around 50 kHz. A phase sensitive detector at the modulation frequency or the harmonics of this then demodulates the resulting signal. Detection is usually done at the first or second harmonics of the modulation signal (hence harmonic detection), which is called ‘1f’ or ‘2f’ detection respectively. Unfortunately, modulating the wavelength rapidly over several absorption linewidths also results in RAM due to the variation of laser power with current.

The benefits of modulation spectroscopy in TDLAS are firstly, it produces a signal, which is directly proportional to the species concentration, rather than the small change in a large signal that occurs with a conventional absorption measurement, and this reduces drift. Secondly it allows the signal to be detected at a frequency at which the laser noise (one of the two main factors limiting sensitivity) is much reduced.

1.6.11 Harmonic detection

Figure 1.2 illustrates the direct, first, and second harmonic absorption line shapes. As shown, second harmonic detection produces a zero baseline signal, thus eliminating the necessity of measuring small differences between two large intensities, I and I₀, as is the case for direct absorption.

Further advantages of second harmonic detection over direct absorption are:

1. the elimination of a strongly sloping background often present in direct absorption
2. reduced susceptibility to low frequency noise due to the kHz detection regime and
3. enhanced discrimination against signals that do not have a strong wavelength dependence such as the broad absorption tails of ambient H₂O vapor. Employing second harmonic detection, minimum detectable absorbances (ln I₀/I) of 10⁻⁵ to 10⁻⁶ are frequently obtained in TDLAS systems using total pathlengths around 100 m. This corresponds to
minimum detectable concentrations ranging between a few parts-per-trillion (pptv) to parts-per-billion (ppbv), depending upon the absorption cross section. Unlike direct absorption, many instrument and experiment-dependent factors must be taken into account when deducing absolute concentrations from the measured second harmonic response. As a result, accurate quantitative analysis employing second harmonic detection is most frequently accomplished using calibration standards.

Figure 1.2 Direct, first and second harmonic line shapes
1.6.12 Signal to noise ratio

The noise is due to several factors like the signal independent thermal noise, the detector shot noise from the incident photons and laser excess noise caused by laser mode competition and stray optical feedback. Mechanical vibrations also may cause noise. The largest influence on noise in diode laser monitoring systems is Fabry–Perot interference fringes or “etaloning” caused by reflection off optical surfaces in the beam such as monochromator slits or cell windows, the fringe spacing being equal to the free spectral range of the etalon. Placing optical components at an angle, by careful optical alignment and the use of antireflection coatings can reduce their magnitude.

In modulation spectroscopy the signal is directly proportional to the laser power, incident on the detector, in the mode being absorbed. The noise arises from four sources: detector shot noise, detector thermal noise, laser excess-noise and RAM offset noise. We consider these in turn.

*Detector shot noise* corresponds to the photon noise on the laser power incident on the detector \((P)\). The noise power is proportional to \(\sqrt{P}\) and has a white noise frequency spectrum.

*Detector thermal noise* is the signal-independent noise of the detector and preamplifier and depends on the type of detector used. This noise also has a white noise spectrum.

*Laser excess-noise* is the laser noise within the measurement bandwidth centered on the detection frequency. This noise is laser dependent and is influenced by mode competition and by optical feedback to the laser due to scattering from components in the optical system. The frequency at which the laser excess-noise reduces to below the shot noise is laser dependent.

*RAM offset noise.* The RAM offset carrying the low frequency laser excess-noise through to the mixer or lock-in amplifier output causes it.

1.6.13 Sweep integration

Some TDLAS measurements have used sweep integration of the direct absorption spectrum instead of modulation spectroscopy. In the sweep integration, the absorption line is scanned over repeatedly many times and the signal averaged to produce a direct absorption signal. In this technique the output from the detector
measuring the transmitted radiation is fed directly into a signal averager [26, 27]. The laser wavelength is not modulated but is instead swept repeatedly across the absorption line of the species being detected. A direct absorption spectrum of the species is thus built up. Sweep integration has been shown to be more stable than harmonic methods due to rapid baseline subtraction for systems under harsh environmental conditions and has a strictly linear response. It has also claimed an order of magnitude more than “2f” detection although it has not been used as widely.

1.6.14 Choice of absorption line

Several factors are to be considered while choosing the absorption line. A strong line is required for trace gas monitoring, to give high sensitivity in the experiment. Because the tuning range of a diode laser is not always continuous, a particular absorption line might not be accessible. It is important to choose a wavelength with several strong lines within the tuning range of the laser (typically 100 cm\(^{-1}\)) so that there is a high probability that at least one strong line will always be accessible. The line should, if possible be isolated from other lines of the same species, but this is not an absolute requirement and can prove difficult to achieve for the more complex molecules. The line should also be isolated from interfering lines due either to other trace species or to the more abundant atmospheric constituents such as H\(_2\)O, CO\(_2\) or O\(_3\). H\(_2\)O causes the most problems because it absorbs over a large part of the infrared region and it has a relatively high and variable concentration.

Because TDLAS operates at reduced pressure it is not restricted in wavelength to the so-called atmospheric windows such as 3.4-5 \(\mu\)m and 8-13 \(\mu\)m. However when operating outside these window regions it is not always possible to arrange for the absorption due to the tails of strong H\(_2\)O or CO\(_2\) lines to be small compared to the absorption due to the line being measured. The line being measured can be easily instrumentally distinguished from the slow variation with wavelength of the absorption due to the wings of the strong lines.

The task of choosing the operating wavelength is made easier by the existence of spectral-lines databases of which the most popular is the HITRAN compilation [9-11]. The database is available on magnetic tape, PC-format floppy
disks, and CD ROM together with software to produce spectral plots for any combination of species and at any temperature and pressure. This currently covers a total of 709,000 transitions over a frequency range of 0-23,000 cm\(^{-1}\) and includes data on the following species (although not on all bands of each species): H\(_2\)O, CO\(_2\), O\(_3\), N\(_2\)O, CO, CH\(_4\), O\(_2\), NO, SO\(_2\), NO\(_2\), NH\(_3\), HNO\(_3\), OH, HF, HCl, HBr, HI, ClO, OCS, HCHO, HOCI, N\(_2\), HCN, CH\(_3\)CI, H\(_2\)O\(_2\), C\(_2\)H\(_2\), C\(_2\)H\(_6\), PH\(_3\), COF\(_2\), SF\(_6\), H\(_2\)S. For each line the data includes wavenumber, line strength, Lorentzian half width and lower state energy.

1.7 Applications of TDLAS for atmospheric measurements

The aim of diode laser trace gas monitoring is to establish absolute concentrations. These can be measured directly from the absorbance and the lineshape information using published line strengths and widths [10] at a given pressure and pathlength. For harmonic detection, it is also necessary to relate the harmonic lineshape to the normal absorption lineshape, which can be done either by mathematical treatment using the experimental modulation depth or by determining the proportionality constant between the measured absorbance of an arbitrary amount and the second harmonic signal. Absolute concentration can be obtained indirectly by comparing with known concentrations, which can either be purchased commercially or can be determined for a similar concentration by wet chemistry or gas chromatography.

TDLAS has been used for atmospheric measurements of CH\(_4\) [28] CO [29], HCl [30], HCHO [31], H\(_2\)O\(_2\) [28, 31], H\(_2\)O [32,33], HNO\(_3\) [34], NO [34], NO\(_2\) [25, 31, 34], N\(_2\)O [35], OCS [14], and SO\(_2\) [34, 36]. With the single exception of one of the H\(_2\)O measurements [32], which used sweep integration, all the above measurements used second-harmonic wavelength modulation spectroscopy. Some representative applications of TDLAS to atmospheric measurements are

1.7.1 Open path measurements

Open-path or long-path monitoring, in which the multi-pass cell is replaced with an open atmospheric path to a remote retro-reflector and back, was the first application of lead-salt lasers to atmospheric monitoring [37, 38]. The technique has the great advantage that there are no sampling problems, also in some
applications the path-averaged concentration which this method gives is more useful than the point measurement provided by conventional TDLAS. However, there are also several disadvantages like the measurement at atmospheric pressure produces wider absorption lines which lead to interference problems due to nearby lines of other atmospheric species, variation of laser power with greater modulation, greater noise, difficulty in getting zero air baseline or back ground spectrum, less sensitivity etc. Despite these problems open-path measurements have produced useful measurements.

An interesting example of the application of long-open-path monitoring to stratospheric measurements is found in the BLISS system [39-41], which was developed at the Jet Propulsion Laboratory (NASA, U.S.A). The system has made many flights and species measured include NO, NO2, O3, CH4, H2O, CO2, HCl, HNO3, and N2O [40 - 42]. In open path measurement the detector is either situated some way from the laser source or a retro reflector is used which returns the beam to the detector, near the source. Unlike multi pass cells, open path monitoring provides unique, in-situ, direct information on gas concentrations over large areas. Unfortunately new problems arise such as pressure broadening, which seriously limit the sensitivity, as well as weather effects, scattering on dust particles, and atmospheric turbulence. The aim of the retro reflector is to return the laser beam parallel to the incoming beam. The most often used design is the corner-cube with three mirrors mounted perpendicularly.

1.7.2 Stratospheric measurements

Whilst TDLAS has mainly been used for tropospheric measurements interest in its use in the stratosphere is increasing. Recently instruments using multi-pass cells have been developed for use on stratospheric research aircraft such as the NASA ER-2. ATLAS [35] is a conventional single-species instrument for the ER-2, which has measured nitrous oxide as a tracer species during the Antarctic AAOE experiment [43, 44] and the arctic AASE expedition. ALIAS [21] is a more radical design which is mounted in an un-pressurized external pod of the ER-2. It has a compact optical layout using a Herriott cell with four independent optical channels, giving it the capability of simultaneous four-species measurements.
1.7.3 Flux measurements

Accurate gas fluxes can be determined using the method of eddy correlation. In this, the three components of the wind velocity are correlated with fast concentration measurements to yield the net flux of the gas normal to the surface. The wind velocity can be measured with three axis sonic anemometers and the gas concentrations with lead salt or GaAs type diode lasers.

1.7.4 Laser heterodyne measurements

Heterodyne radiometers using TDLs as the local oscillator can be used to probe the atmosphere by measuring the spectra of the sun, moon, or planets. Column contents of atmospheric species can be determined from their absorption of the solar, or other spectrum. Instruments of this type have been used to measure N$_2$O, O$_3$, CH$_4$, and CO$_2$ [45 - 47].

1.8 TDLAS as gas sensors and trace gas detection technique

Laser optical sensors in the near and mid infrared spectral region are now at the threshold of routine applications in gas analysis and increasingly these sensors are transformed to industrial and monitoring applications wherever sensitive, selective and fast analysis is required. With increasing complexity of the process, online gas analysis is becoming a key issue in automated control of various industrial applications such as combustion diagnostics, investigation of aero-engines and automobile exhaust measurements. Other challenges are online analysis of high purity process gases, medical diagnostics and monitoring of agricultural and industrial emissions. The need to meet increasingly stringent environmental and legislative requirements has also led to the development of analyzers to measure the concentrations of a variety of gases based on near and mid infrared absorption spectroscopy [8].

The features of diode laser spectroscopy rendering it such a valuable technique for gas analysis is: it is specific and as a high resolution spectroscopic technique, it is virtually immune to interference by other species – a problem that plagues most competing methods. This ability to provide unambiguous measurements leads to the use of TDLAS as a reference technique against which other methods are often compared. It is a technique universally acceptable to all
smaller IR active molecules and the same instrument can easily be converted from one species to another by changing the laser and the calibration gases. The time resolution of TDLAS measurements can be traded off against sensitivity and this allows very fast measurements with millisecond time resolution. In order to improve sensitivity, various types of direct and modulation spectroscopy have been employed. These techniques allow absorption as low as one part in 10⁶ to be measured within a 1 Hz bandwidth. In combination with optical multipass cells, this is equivalent to detection limits of around 20 pptv for the most strongly absorbing species and better than 1 ppbv for almost all species of interest [8].

Werle et al [48] describes spectroscopic gas analyzers based on indium-phosphide, antimonide and lead-salt diode lasers. In this paper, the currently available semiconductor lasers for spectroscopy in the near infrared and mid infrared regions based on direct band-to-band transitions as gallium arsenide, indium-phosphide, antimonides and lead salt containing compounds are discussed with main features of different tunable diode laser absorption spectrometers for trace gas analysis. Measurements of atmospheric carbon dioxide with a room temperature 2 μm indium-phosphide laser, applications of antimonide lasers for methane and formaldehyde sensing in the 3–4 μm range and a fast chemical sensor for methane flux measurements based on lead salt diode lasers operating near 7.8 μm are also presented. Vicet et al [49] reported trace gas detection using antimonide based quantum well diode lasers. Widely tunable GaInAsSb/AlGaAsSb quantum well (QW) lasers have been grown by molecular beam epitaxy (MBE) on GaSb substrates. Their emission wavelength from 2.0 – 2.5 μm make them suitable for detection of many gas species in the wavelength range, which corresponds to an atmospheric transmission window. Using these devices an experimental setup for open path detection has been developed.

Trace gas detection is of great interest in industrial process control and pollution monitoring. Gas detection systems based on TDLAS provides that the lasers emit at a single frequency and are able to work at room temperature in continuous wave (cw) regime. In order to improve the sensitivity of the TDLAS measurement techniques such as heterodyne detection, wavelength (2f – WMS) and frequency (FMS) modulation spectroscopy are used [50] in combination with multipass cells increasing the absorption path. Many atmospheric pollutants as well
as some gaseous species involved in industrial process have strong absorption lines in the spectral region between 2.0–2.5 µm. The 2.3 µm window is especially interesting for gas analysis because it corresponds to a transmission window of the atmosphere where gas traces can be measured without the interfering effect of water vapor absorption. The advantage of this spectral region compared with longer wavelengths is the possibility to develop high quality semiconductor lasers and detectors that are able to operate at room temperature.

A novel single frequency stabilized Fabry – Perot (SFP) laser diode with an emission wavelength at 1590 nm for H2S gas sensing is reported by Weldon et al [51]. The application of this device to spectroscopic based H2S sensing is demonstrated by targeting absorption lines in the wavelength range 1588 ≤ λ ≤ 1591 nm. Using wavelength modulation spectroscopy (WMS) a low detection limit of 120 ppm mHz1/2 was estimated while targeting the absorption line at 1590.08 nm. The results demonstrate the potential of the stabilized FP laser diode at this wavelength as a tunable, single frequency source for spectroscopic based gas sensing. The application of a multi-laser tunable diode laser absorption spectrometer for atmospheric trace gas measurements at sub-ppbv levels is reported by Kormann et al [52]. This paper describes the application of a three-laser tunable diode laser absorption spectrometer (TDLAS) called “tracer in-situ TDLAS for atmospheric research (TRISTAR) to measure nitrogen dioxide (NO2), formaldehyde (HCHO) and hydrogen peroxide (H2O2).

A portable diode laser based sensor for NH3 detection using vibrational overtone spectroscopy at 1.53 µm is reported by Claps et al [53]. Use of fiber coupled optical elements makes such a trace gas sensor rugged and easy to align. On-line data acquisition and processing requiring less than 30 sec can be performed with a laptop PC running labVIEW software. The gas sensor is primarily used for NH3 concentration measurements with a sensitivity of 0.7 parts per million. The feasibility of simultaneous, real-time measurements of NH3 and CO2 concentrations is also reported.

The measurements of CO, CO2, OH and H2O in room temperature and combustion gases by use of a broadly current tuned InGaAsP diode laser is reported by Upschulte et al [54]. This paper reports a new laser technology that achieve nearly 100 nm quasi-continuous tuning with only injection current control
in a four section grating coupler sampled reflector laser is used to detect CO and CO$_2$ simultaneously in the room temperature gas mixtures. The same grating coupler sampled reflector laser is used to perform in-situ measurements of CO, H$_2$O and OH in the exhaust gases of a CH$_4$ air flame. A diode laser sensor is applied to monitor CO, CO$_2$ and CH$_4$ in combustion gases with absorption spectroscopy and fast extraction sampling techniques is reported by Mihalcea et al [55]. Species concentrations above a laminar, premixed, methane - air flame are determined from measured absorption in a fast flow multipass cell containing probe sampled combustion gases; good agreement is found with calculated and chemical equilibrium values.

Two tunable infrared laser differential absorption spectroscopy (TILDAS) technique is used to measure the N$_2$O emission levels of on-road motion vehicles exhausts by Jimenez et al [56]. They have used two different TILDAS based techniques to measure the N$_2$O/CO$_2$ emission ratios of on-road motor vehicles. Average N$_2$O/CO$_2$ emission ratios for each TILDAS technique are comparable and their distributions are similar, even though the measurement circumstances are quite different.

The principal gas sensor technologies are based on absorption spectroscopy of fundamental bands in the 3–25 µm spectral region and NIR vibrational overtone and combination bands from 1–3 µm. Common radiation sources include continuous wave (CW) diode lasers (GaAs based, antimonide based and lead salt based), parametric frequency conversion devices (difference frequency generation and optical parametric oscillators) gas lasers (CO and CO$_2$) and quantum cascade lasers. Telecommunication distributed feedback (DFB) diode lasers are ideally suited for overtone spectroscopy of molecules with chemical bonds such as C-H, O-H and N-H in the NIR region (0.78–2.5 µm). Overtone spectroscopy exhibits absorption line strengths that are typically approximately one to two orders of magnitude weaker than those of fundamental vibrations in the mid IR. To obtain the required sensitivity in the NIR, longer absorption pathlengths and optical balancing of laser noise are required. For this purpose, a compact multipass cell configured for a 36 m total optical pathlength and an auto balance detection technique is used [57]. Other groups have used cavity-enhanced spectroscopy to monitor ro-vibrational overtone and combination band transition [58, 59].
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The spectrum of the weakly bound complex Ar-CH₄ in the 7 μm region is discovered, analyzed and compared with a spectrum predicted by ab initio calculations by Wangler et al [60]. Probing a supersonic gas expansion with a tunable diode laser did the measurements. Several bands of Ar-CH₄ associated with different ro-vibrational transitions of the ν₄ vibration of CH₄ are recorded and analyzed in the spectral region 1295–1330 cm⁻¹. The experimental results show close agreement with the ab initio calculations.

1.9 Isotope detection and measurements

Tunable diode lasers are used in isotope separation processes also. Lithium isotope separation with TDL is reported by Olivares et al [61]. A laser isotope separation study of lithium has been performed with two-step excitation involving UV laser radiation and a visible tunable diode laser. The method yields a high degree of selectivity by tuning the narrow linewidth diode laser to the D₁ or D₂ levels of the lithium atom. Selective laser excitation is simplified by the use of the tunable diode laser and the overall approach benefits from the applications of a compact mass selector that includes a precision magnetic sector and an ion beam that is designed specifically for light atoms such as lithium.

High precision isotopic ratio measurement system for methane by using a near infrared diode laser absorption spectroscopy is reported by Yamamoto et al [62]. They demonstrate that the absorption spectroscopic method could be applied to a precise δD (an index of ¹²CH₃D/¹²CH₄) and δ¹³C (an index of ¹³CH₄/¹²CH₄) analysis for methane samples of natural isotopic abundance. The measurements are performed on choosing an appropriate absorption line pair whose absorption coefficients have nearly the same temperature dependences. This minimizes the temperature effects. They measured ¹²CH₃D/¹²CH₄ ratio by using near-infrared external cavity diode lasers and a new type of multipass cell. The δD value can be determined from the ¹²CH₃D/¹²CH₄ signal – intensity ratio with a fine correction by taking into account of the interference of ¹³CH₄ lines. Similarly the δ¹³C value is determined from the ¹³CH₄/¹²CH₄ signal intensity ratio, which is measured by using distributed-feedback laser and a modified Herriott-type cell and corrected for the abundance ¹²CH₃D.
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In absorption spectroscopy, in contrast different isotopic molecular species can be distinguished easily irrespective of their masses if appropriate absorption lines are selected. Then the abundance ratio is determined by comparing the ratio of the absorbances of the selected absorption lines in the same sample gas with that in the standard gas of known isotopic composition. There are related works for isotope analyses by spectroscopic methods using lead salt diode laser in the mid infrared [63], a DFB (Distributed feed back) single mode laser in NIR [64], a 3.3 μm He-Ne laser [65], a colour center laser [66] a quantum cascade laser [67] in 8 μm region and FTIR spectrometer.

1.10 TDLAS in industrial gas monitoring

Gas monitoring in the process industry using diode laser spectroscopy is reported by Linnerad et al [68]. Gas monitors for industrial applications must have high reliability and require little maintenance. Monitors for in-situ measurements using tunable diode laser absorption spectroscopy in the near infrared can meet these requirements. Over the last few decades there has been increasing concern about man made pollution of the atmosphere. The dilution of pollutants in the atmosphere makes the concentrations very low, often below 1 ppb, and therefore difficult to measure.

TDLAS is one of the emerging techniques used in pollution and trace gas detection. In recent years new techniques has emerged such as Fourier Transform Infrared (FTIR), Differential optical absorption spectroscopy (DOAS), Laser Induced Fluorescence (LIF) and tunable diode laser absorption spectroscopy (TDLAS). Tunable diode lasers (TDL) have line widths of only a few MHz or less and are therefore well suited for high resolution spectroscopy. In the near infrared (NIR, 0.8–3 micrometers) we have the first and second overtones of the rotational/vibrational modes of the trace gases and there are commercial semiconductor lasers available that operates at room temperatures.

Due to short response time, industrial TDLAS monitors are ideal as process control tools in processes requiring a fast response, and they are also well suited for continuous emission monitoring of gases such as HCl and HF where the
maximum permissible emission levels are in the low ppm range. Some typical examples are presented below

1) Process control
   a) O₂ measurement
   b) NH₃ measurement
   c) CO measurement
   d) H₂S measurement
2) Emission monitoring
   a) CO, NO, NO₂, SO₂
   b) HF, HCl, NH
3) Measurement of O₂, CO and HCl from a waste incinerator
4) Measurement of HF in a primary aluminium smelter
5) Measurement of NH₃ at a coal fired power plant with SCR abatement system.

Sandstrom et al [69] reported TDLAS application for simultaneous contact free measurement and monitoring of the oxygen concentration as well as the gas temperature in a reheating furnace. During the production, the tunable diode laser spectrometer measured *in-situ* across the preheating zone and the soaking zone in the furnace. The oxygen concentration and gas temperature in the furnace environment were simultaneously monitored and instantaneous variations in these parameters could be easily recorded and subsequently correlated to actual changes in the process. Compared with the conventional measurement methods, TDLS technique have much shorter response time and hence it can be used for energy savings as well as product quality improvements by controlling the burners in the reheating furnace.

As already explained, frequency modulation, baseline reduction methods, line locking, reduction in interference fringes, reduction in random noise and choice of integration time, usage of optical fibers, diode laser optoacoustic trace gas monitoring, heterodyne measurements etc are some of the advanced techniques used in trace gas detection using TDLAS.
1.11 TDL based molecular spectroscopy

Spectroscopy in the infrared, visible and ultraviolet regions serves qualitative and quantitative purposes. The quantitative analysis of the material is done through the radiation that the material is absorbs or emits. Qualitative analysis is made possible by the fingerprint nature of the spectra: they are highly characteristic of the material concerned. Quantitative analysis can be carried out in cases where relative intensities are accurately measurable. The quantitative analysis in these regions is a very powerful and accurate tool for the investigation of atomic and molecular structure. This includes not only the determination of molecular geometry in ground electronic state but also how molecules behave when they vibrate and rotate and how both atoms and molecules change when they are in excited electronic states. Low-resolution spectra is used for analytical purposes, where as high resolution spectra is used for obtaining more and more accurate structural information.

Microwave and millimeter wave spectroscopy are intrinsically high resolution techniques because of the highly monochromatic nature of the sources and the very small linewidths of the transitions involved. The development of continuously tunable backward wave oscillators, tunable lasers and tunable diode lasers are useful in high resolution studies in other regions also [70].

High-resolution spectroscopy requires the narrow-bandwidth excitation sources that are only achievable with lasers. Studies in the visible spectral region typically use a tunable dye laser and studies in the near ultraviolet and near infrared are becoming more common as frequency doubling and wave-mixing methods improve. Mid infrared and Near-infrared tunable diode lasers are also used for high-resolution vibrational spectroscopy.

Super high-resolution studies also require cooling of the molecules to remove spectral congestion and to reduce the Doppler width of the transitions. Gas-phase studies use free-jet expansions or molecular beams to cool molecules to very low temperatures. The major application of TDLAS is high resolution recording of vibrational rotational spectra of molecules in the gas phase [71]. The major uses are summarized below.
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i. Investigation and analysis of fundamental and vibrational-rotational bands of chemically stable molecules, line assignments, determination of precise spectroscopic constants and molecular structure

ii. Study of rotational fine structure of molecular spectra

iii. Investigation of individual line parameters- profiles, intensities widths and also coefficients of broadening and shifts

iv. Spectroscopy of transient species, in particular, free radicals and molecular ions

v. Investigation of absorption by molecules in excited states

vi. Study of dynamic molecular process

Tunable diode laser absorption method is used to study the fine structures in many molecules corresponding to interactions between different forms of molecular motion (electronic, vibrational and rotational). The molecules whose fine structures are studied using lead salt diode lasers include H2, CO, NO, HCl, LiF, CO2, N2O, H2S, OCS, O3, NH3, C2H2, CH4, CF4, CCl4, SiF4, HCOOH, HNO3, CH3CN, C4H2, SF6, C2H6, C6H5Cl, C6H8 etc., [71].

1.12 High resolution overtone spectroscopy – some reported works

With the recent developments in high resolution FTIR spectrometers, tunable diode laser spectrometers and other high sensitivity laser based techniques like photothermal methods, NIR overtone spectral analysis have now become an important tool for molecular structural studies and for applications like trace gas monitoring.

The local mode effects on the high resolution overtone spectra of H2S near 12500 cm⁻¹ are reported by Vaittinen et al [72]. The overtone spectrum is studied by intracavity laser absorption spectroscopy in the wavenumber region 12270 – 12670 cm⁻¹. The rovibrational analysis has provided upper state rotational parameters for the three interacting vibrational states. A local mode type behavior is evidenced by the values of rotational parameters.

Becucci et al [73] studied the high resolution optothermal spectra of pyridine S0 – S1 electronic transition. Rotational profile measurement for several vibronic bands revealed severe homogeneous broadening, with linewidths of the
order of 3 – 5 GHz. The rotational constants of pyridine in the excited state $S_1$ vibronic levels were extracted by a band contour analysis and the values obtained are in good agreement with results from ab initio calculations.

Held et al [74] studied the high resolution FTIR spectroscopy first overtone of N-H stretch and the fundamental of C-H stretch in gas phase pyrrole. The first overtone N-H stretch is rotationally analyzed using an asymmetric top model and was found to exhibit two separate perturbations. These perturbations produce line splitting and anomalous intensity patterns in the spectrum. The C-H fundamental stretches are also analyzed. A combined high resolution and theoretical study of the rovibrational spectrum of hydroxylamine is carried out by Luckhaus et al [75]. They reported the ro-vibrational spectrum of hydroxylamine (NH$_2$OH) recorded by interferometric Fourier transform spectroscopy with a resolution up to 0.004 cm$^{-1}$ close to the Doppler limit at room temperature, in the spectral range of 800 cm$^{-1}$ up to the visible region. A detailed rotational analysis of all the fundamentals and numerous overtones up to 10500 cm$^{-1}$ are also done.

Photoacoustic spectroscopy is used in high resolution vibrational overtone studies by Douketis et al [76]. The high resolution vibrational overtone spectrum of H$_2$O$_2$ vapor between 7400 and 7600 Å is recorded under both bulk gas and supersonic beam conditions. An absorption band corresponding to a $\Delta V = 4$ of O-H stretch is observed in this spectral region. Rotational analysis indicated that it is a hybrid band with mainly parallel character. Spectral linewidths are found to be Doppler limited in all cases.

The photoacoustic spectra of stannane with its rotations and local modes is reported by Zhan et al [77]. The fifth and the seventh stretching vibrational overtone bands of a monoisotopic stannane sample have been recorded with Doppler limited resolution using intracavity photoacoustic technique using a titanium:sapphire ring laser. The rotational fine structures of these bands have been analyzed with the symmetric top energy formula and a spherical top Hamiltonian and about 200 rotation-vibration transitions have been assigned for both the systems.

High resolution infrared emission spectrum of sodium monofluoride is recorded with a high resolution Fourier transform spectrometer and reported by Muntianu et al [78]. They observed a total of 1131 vibration – rotation transitions.
from the $v=1\rightarrow0$ to $v=9\rightarrow8$ vibrational bands and assigned. The high resolution spectral analysis of $^{13}\text{CH}_3\text{OH}$ in the excited torsional states are reported by Mukhopadhyay et al [79]. They did a theoretical analysis of $^{13}\text{C}$ substituted methanol to include a large number of spectral lines with the help of microwave and Fourier transform for infrared spectral lines involving up to the second excited torsional state ($n=2$) in the ground vibrational state and the effective Hamiltonian parameters were determined.

Long path length, high resolution Fourier transform spectrometer measurements for water which covered the near infrared, visible and near ultra violet regions are reported by Carleer et al [80]. Transitions in the range 13100 – 21400 cm$^{-1}$ are analyzed using line lists computed using first principle calculations. The newly observed 15 overtone and combination bands of water and the energy levels for these were presented. High resolution spectra of H$_2^{16}$O vapor covering the region 11610 – 12861 cm$^{-1}$ are reported by Toth [81]. The line positions and strengths of 933 lines which include vibration – rotation transitions were reported. New water vapor line parameters in the 26000 – 13000 cm$^{-1}$ region with a high resolution Fourier transform spectrometer combined with a long path absorption cell are reported by Coheur et al [82]. Naus et al [83] reported the high resolution cavity ring down spectrum of water vapor in the range 555 – 604 nm. The spectrum contained 1830 lines calibrated against iodine standard with an accuracy of 0.01 cm$^{-1}$.

1.13 The present work

We have setup a narrow band near infrared tunable diode laser based absorption spectrometer. The spectrometer is automated by interfacing with LabVIEW software and is successfully used for recording the rotationally resolved second OH overtone spectra of some alcohols. We could reproduce the reported rotational structures of OH second overtone bands of water and methanol, which are thus used for the calibration of the spectrometer. The details of the experimental configuration, spectral calibration and spectral measurements are described in detail in the following chapters.
References


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