ATMOSPHERIC POLLUTION MEASUREMENTS WITH TUNABLE LASERS
EMPLOYING RESONANCE ABSORPTION

by

M.M. Elsherbiny, B.Sc., M.Sc.

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AUTHOR:  
Mohamed Mahmoud Elsherbiny, B.Sc. (E.E.)  
(Alexandria University)  
M.Sc. (E.E.)  
(Alexandria University)

SUPERVISORS: C. K. Campbell, Professor of Electrical and Computer  
Engineering, and  
J. Shewchun, Professor of Engineering Physics

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ABSTRACT

Theoretical and experimental techniques, which are useful in molecular spectroscopic studies and in the development of Laser Absorption Spectrometers (LAS), are described. Both fixed-frequency and tunable lasers have been employed. All the measurements reported are based on either direct or second harmonic absorption techniques.

A commercial CO/CO₂ line-tunable laser has been used to obtain useful criteria for air pollution monitoring via the direct absorption scheme. CO₂ laser absorption measurements on ozone at reduced pressures are reported. Measurements on seventeen NO absorption lines with a CO laser are described. For these, the absolute absorption as a function of pressure has been determined. As a result we have been able to establish accurate values for the absorption of NO at the pertinent CO laser wavelengths. From the best fit between experimental measurements and theoretical calculations we have deduced the separation between the appropriate NO and CO wavelengths, the NO/N₂ pressure broadening, the NO band strength, and the individual NO line strengths.

Using a tunable lead-salt semiconductor diode laser, and employing the direct absorption technique, we have developed a simple method for accurate frequency measurements of ozone absorption lines. This technique is based on employing a tunable semiconductor diode laser, an etalon, and a White cell. We report accurate frequency
measurements of over 100 absorption lines of ozone in the \( \nu_3 \) band, which are near the \( \text{CO}_2 \) laser transitions. Despite the relative simplicity of the technique, we achieved an accuracy of better than 10 MHz in our measurements. This accuracy compares well with that achieved by the more complicated heterodyne techniques of high-resolution spectroscopy. However, these are the first measurements over an entire absorption band using the full resolution of a tunable diode laser.

A LAS, which combines the sensitivity of the acousto-optical methods with the convenience of direct, long-path optical detection, is described. The diode laser is wavelength modulated and the second harmonic detection technique is applied. This technique enables us to detect atmospheric pollutant gases with extremely high sensitivity (3 ppb of a weak absorbing pollutant such as \( \text{SO}_2 \) in its \( \nu_1 \) band or \( 3 \times 10^{-3} \) ppb of a strongly absorbing molecule such as \( \text{CO} \)). This sensitivity is achieved using a frequency-locking technique for the diode. We report on the detection of \( \text{O}_3 \), \( \text{SO}_2 \), \( \text{NH}_3 \), and \( \text{N}_2\text{O} \) pollutants at their ambient levels in air. A very high specificity and virtual elimination of interference effects are obtained by sampling the atmospheric air at reduced pressures.

A remote LAS station, which is considered to be adjunct to the above LAS, has been built. A remote retroreflector and an off-axis telescope near the laser have been employed to achieve a total pathlength of 1.2 km in the atmosphere. We report theoretical and experimental investigations of \( \text{SO}_2 \), \( \text{H}_2\text{O} \), \( \text{NH}_3 \) and \( \text{H}_2\text{O} \) absorption in the region 1100 - 1200 cm\(^{-1}\) at atmospheric pressure. This enabled us to develop a technique,
based on the second harmonic detection scheme, to detect SO$_2$ in the atmosphere with a sensitivity of 50 ppb employing a diode laser emitting in the $v_1$ band of SO$_2$. We report also on spectroscopic studies and absorption measurements for SO$_2$ and H$_2$O in the region 1300 - 1400 cm$^{-1}$. These studies indicate that it is possible to detect SO$_2$ with ambient levels in the atmosphere by employing a diode laser radiating in the $v_3$ band of SO$_2$, near 1331.5 cm$^{-1}$.

In all the above mentioned techniques, theoretical calculations of laser transmission through the atmosphere must be predicted prior to applying such techniques. For this reason, a computer package has been developed and tested. This package generates the absorption line parameters of any molecule, even asymmetric-top molecules, in the vibration-rotation infrared region. The absorption (transmission) can be calculated at any pressure.
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xx
Symbols, Parameters, and Conversion Factors

In the following we have listed the used Conversion factors, constants and definitions in this thesis.

(1) Physical Constants
- h = 6.626 x 10^{-34} Js \quad \text{Planck's constant}
- e = 1.602 x 10^{-19} As \quad \text{Charge of an electron}
- k = 1.381 x 10^{-23} JK^{-1} \quad \text{Boltzmann constant}
- c = 299 792 460 ms^{-1} \quad \text{speed of light in vacuum}

(2) Conversion Factors
- 1 J = 10^7 \text{erg} = 0.239 \text{Cal}
- 1 eV = 1.602 x 10^{-12} \text{erg} = 1.602 x 10^{-19} \text{J}
- 1 W = 10^7 \text{erg s}^{-1}
- 1 \text{Web} / m^2 = 10^4 \text{G}
- 1 \text{bar} = 10^6 \text{dyne cm}^{-2}
- 1^\circ = 17.45 \text{mrad}

(3) Conversion of transmission, T, to optical density, D;
- T = 10^{-D}

(4) Conversion of linewidth given in wavelength (\Delta \lambda) or wavenumber (\Delta \nu) to bandwidth \Delta f
- \Delta f/f = \Delta \lambda/\lambda = \Delta \nu/\nu
(4) cont'd.
\[ \Delta f = c \Delta \nu \]
\[ \Delta \lambda = \Delta \nu \lambda^2 = \Delta f \lambda^2 / c \]

(5) **Units in common usage**
- \( \lambda \) (\( \mu \text{m} \)) = \( 10^4 / \nu \) (cm\(^{-1}\))
- \( E \) (eV) = \( 1.24 \times 10^{-6} \nu \) (cm\(^{-1}\))
- \( f \) (Hz) = \( 3 \times 10^{10} \nu \) (cm\(^{-1}\))
- \( E \) (eV) = \( 1.24 / \lambda \) (\( \mu \text{m} \))
- \( f \) (Hz) = \( 3 \times 10^{14} / \lambda \) (\( \mu \text{m} \))
- \( E \) (eV) = \( 4.14 \times 10^{-15} f \) (Hz)

Following conventional usage, the terms "wavenumber" and "frequency" are used interchangeably, but the individual symbols are quite explicit in their meaning.

(6) **Glossary of Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Area</td>
<td>( \text{cm}^2 )</td>
</tr>
<tr>
<td>( A_e )</td>
<td>Molecular rotational constant</td>
<td>( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>B</td>
<td>Magnetic flux density</td>
<td>( \text{G} )</td>
</tr>
<tr>
<td>( B_e )</td>
<td>Molecular rotational constant</td>
<td>( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>c</td>
<td>Speed of light in vacuum</td>
<td>( \text{cm/s} )</td>
</tr>
<tr>
<td>( C_e )</td>
<td>Molecular rotational constant</td>
<td>( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>d</td>
<td>Mode spacing</td>
<td>( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>e</td>
<td>Electronic charge</td>
<td>( \text{C} )</td>
</tr>
<tr>
<td>( E_i )</td>
<td>Energy level of quantum state</td>
<td>( \text{cm}^{-1} )</td>
</tr>
</tbody>
</table>
Frequency [Hz]

Nuclear spin statistics

Statistical weight

Vibrational energy level [cm^{-1}]

Planck's constant [Js]

Laser Drive current [A]

Laser beam intensity [W # cm^2]

Rotational quantum number

Boltzmann's constant [J/k]

Extinction coefficient [cm^{-1}]

Oblate pseudo-quantum number

Prolate pseudo-quantum number

Depth of pollutant layer [cm, km]

Pathlength [m, km]

Cell length [cm]

Molecular weight [gm]

Refractive index

Number density of molecules [cm^{-3}]

Pressure [atm, Torr]

Laser power [W]

 Electron charge [C]

Total partition function

Rotational partition function

Vibrational partition function
(6) cont'd.

R

Reflectivity

\( R_{ij} \)

Transition dipole matrix element between states \( i \) and \( j \) \([\text{erg}^{1/2} \text{ cm}^{3/2}]\)

S

Integrated spectral line intensity \([\text{cm}^{-2} \text{ atm}^{-1}]\)

T

Absolute temperature [K]

\( T \)

Transmission

V

Vibrational quantum number

V

Voltage [V]

x

Semiconductor alloy composition

y

Variable

z

Pathlength variable [km]

\( \alpha (\nu) \)

Absorption coefficient \([\text{cm}^{-1} \text{ ppb}^{-1}] \) or \([\text{cm}^{-1} \text{ atm}^{-1}]\)

\( |\beta|^2 \)

Vibrational matrix element

\( \beta (\nu) \)

Total extinction coefficient \([\text{cm}^{-1}]\)

\( \gamma_L \)

Lorentz broadening (HWHM) \([\text{cm}^{-1}]\)

\( \gamma_D \)

Doppler broadening (HWHM) \([\text{cm}^{-1}]\)

\( s \)

Thermal diffusivity \([\text{cm}^2 / \text{s}]\)

\( \eta_I \)

Internal quantum efficiency

k

Asymmetric rotor parameter

\( \lambda \)

Wavelength [\mu m]

\( |\mu|^2 \)

Rotational matrix element

\( \nu \)

Wavenumber (or "frequency") of electromagnetic radiation \([\text{cm}^{-1}]\)

\( \nu_0 \)

Wavenumber at line center \([\text{cm}^{-1}]\)
(6) cont'd.

\[ \nu_s \quad \text{Spontaneous - emission frequency \,[\text{cm}^{-1}]} \]

\[ \xi \quad \text{Parameter controlling the emission frequency of semiconductor laser \,[\text{cm}^{-1}]} \]

\[ \omega \quad \text{Central vibrational frequency \,[\text{cm}^{-1}]} \]

(7) PM and LPM definitions

Point monitoring (PM), is where the monitor is placed at one location in the field and it samples the surrounding ambient air. However, the monitor itself contains a long-path absorption cell (White cell).

Long-path monitoring (LPM). Here the monitoring technique is based on long-pathlengths in the atmosphere. This long path is given by twice the distance between the laser source and a remote retroreflector. Hence, the detectable parameter is the average concentration of a pollutant gas over the atmospheric path, and not the concentration at one point into the atmosphere, as in the case of PM.
CHAPTER 1

INTRODUCTION

1.1 Need for a Pollution Monitor

With the increase in industrialization and mechanization, the world has witnessed over the past fifty years a corresponding increase in the pollution of the environment. The atmosphere in particular has been contaminated to an alarming degree by waste from innumerable industrial processes and, especially, the internal combustion engine. Because pollution sources are so diverse, the atmosphere contains hundreds of "unnatural" gases, many of which produce measurable effects on the biological and physical environment.

At this point in time, the degree of pollution in the atmosphere is serious enough to have precipitated government legislation regulating the maximum permissible amounts of pollution levels of industry and vehicles. This requires monitoring the atmosphere to ascertain levels of at least the particularly harmful pollutants.

In Ontario, the Ministry of the Environment compiles an Air Pollution Index for several large urban centres based on the continuous measurement of sulphur dioxide, telemetered from remote stations, and suspended particulate concentrations, determined from 24 hour average values of the soiling index. For a downtown Toronto location (the Index varies according to the character of the particulates), the Index I is
given by:

\[ I = 0.2 \ (30.5 \ \text{COH} + 126.0 \ \text{SO}_2)^{1.35} \]  \hspace{1cm} (1.1)

where COH is the 24 hour running average of the soiling index expressed as a coefficient of haze per 1000 feet of air, while \( \text{SO}_2 \) is the 24 hour running average of sulphur dioxide concentration in parts per million (ppm).

In Hamilton, the Urban Air Environment Group at McMaster University Medical Center is presently conducting a project looking at the effect of environment factors on the respiratory health of school children. It has been found that the combined effect of \( \text{SO}_2 \) and particulates in the ambient air has the more severe effect on respiratory health as compared to the individual effects. It was for this reason that \( \text{SO}_2 \) was monitored (by the McMaster University Air Pollution Laboratory) as a representative of pollutant gases, along with the particulate monitoring. The instrument currently used (by the Ministry of Environment and the group of McMaster University) for \( \text{SO}_2 \) monitoring is based on secondary coulometry and dynamic iodimetric titration. This instrument is a point sampling device in the form of a Beckman Model 906A \( \text{SO}_2 \) analyzer.

Generally, it has been found that the highest levels of pollution can be found in the North-East segment of the City of Hamilton, usually recognized as the industrial sector. When there are prevailing North East or Easterly winds, then the remainder of
the city also has high SO₂ levels.

Techniques for monitoring other gases are available, but all these monitoring instruments are usually based on chemical reaction and laboratory procedures. This limited the applicability of such monitors to one gas or at most an undiscriminated group of gases and is costly in terms of time. Other developments brought about monitors utilizing radiation sources instead of chemical reagents; however, these systems suffered from a lack of suitable sources.

Today, with increased concern over the rapidly deteriorating environment, there is a definite need for a system that is capable of performing far better than the traditional ones. A monitoring system is required that is capable of giving instantaneous measurements of at least four chemically different pollutants on either point or long-path basis. It also should be inexpensive, reasonably mobile, rugged in construction, and simple to operate.

At this time, such a system does not exist. However, the development of the laser, especially, the tunable one, has sparked much interest in solving the problem since, potentially, it can serve as a suitable radiation source.

1.2 The Use of Lasers in Pollution Monitoring

Optical techniques for the monitoring of atmospheric pollution have advantages over the presently-used wet chemical methods, since they can be used for remote sensing and also because they are instantaneous by comparison. Of greatest interest is the infrared (ir) spectral region from about 2 to 20 µm, because nearly all of the
gaseous pollutants have vibration-rotation resonances in this region which can be useful for both absorption and emission measurements [1]. Due to strong absorption of the principal polyatomic constituents of a clean atmosphere, CO$_2$ and H$_2$O, certain bands in this region (2.5 to 2.9 μm, 4.2 to 4.4 μm, 5.5 to 7.5 μm, and 14 to 16 μm) may have to be avoided.

A number of classical optical methods, including the use of selective filters, spectrographs, interferometers, optical correlation and derivative techniques have been explored and shown to hold promise for certain applications [2]. A new dimension to the optical techniques is added by making use of the unique properties of lasers, particularly their high power, directionality, spectral purity, and wavelength tunability.

Three techniques, which involve the use of lasers for various modes of point sampling and remote sensing, have been employed. These techniques are based on 1) Raman scattering, 2) resonance florescence, and 3) absorption. These laser methods have been compared by Kildal and Byer [3], who concluded that the resonance absorption scheme is the least complex and costly one and requires minimal laser power. It lacks depth resolution, but it is the only scheme sensitive enough to detect dispersed pollutants. A more detailed analysis of this scheme, over that performed in [3], has been reported by Rosegren [4].

1.3 Resonance Absorption Scheme

The absorption technique has perhaps the widest range of application because it can be used both for point sampling and remote sensing. For remote long distance measurements, one possible dis-
advantage is the necessity for a remote detector, retroreflector, or scatterer. Wherever this requirement can be met, the technique is advantageous because it is the most sensitive and requires the least amount of laser power, consequently, it promises to be the simplest and least expensive system. For point sampling, laser powers as low as 1 μW can be used, whereas for remote sensing 1 mW should be quite sufficient.

In recent years, a great deal of attention has been given to the use of infrared lasers to measure molecular absorptions over long pathlengths. In general, line-tunable sources (CO₂, CO, DF), have been employed to monitor those gases which have absorption lines in close coincidence with the available output wavelengths of the lasers [5-7]. Semiconductor diode lasers which can readily provide powers in the range mentioned above have proven to be particularly convenient for the absorption technique [8], [9]. To date, the minimum detectable absorption reported using such optical techniques is > 0.1%. This has resulted in applications being limited to gases which occur naturally at high concentrations.

An air pollution detection system must be able to identify and measure the concentration of pollutants. The characteristic resonance frequencies at which a polluting molecule absorbs laser radiation can be used to identify the molecule if there is no ambiguity due to overlapping absorption of other molecules in the atmosphere. The magnitude of the absorbed power of a laser beam propagating through the sample or in the atmosphere at an absorption frequency
of a molecule, is then used to determine the mean concentration of such molecules along the measuring path.

Every absorption line of a molecule in the atmosphere has its own value of center position, width, and intensity. Without a precise knowledge of these parameters, a theoretical determination of absorption coefficient is out of the question, even with a correct knowledge of the dispersing contour. Furthermore, the line parameters depend in a complicated manner on the variable macroconditions of the medium; notably, temperature and pressure (total and partial) of the component gases. All this creates exceptional difficulties in making a quantitative estimate of energy loss of an optical wave due to an individual absorption line. These theoretical calculations along with experimental investigation are required as a starting point in the design of a pollution monitoring system. Hinkley's monograph [10] contains comprehensive theoretical and experimental techniques for atmospheric pollutants monitoring which have been employed during the time period 1968 to 1976.

1.4 Object and Scope of Thesis

Long-path Laser Absorption Spectroscopy (LAS) applications to the detection and spectroscopic studies of pollutant gases are covered in this Thesis. The LAS is used for point sampling of pollutant gases, and provides an important contribution to the concentration of atmospheric pollutants.

Both fixed-frequency and tunable lasers are used and proposed
for atmospheric pollution monitoring. Chapter 2 describes these lasers used in this Thesis: fixed-frequency lasers (CO, CO\textsubscript{2}) are described briefly, while the theory and operation of the tunable Lead-salt Semiconductor Diode Lasers (SDL) are described in detail. Chapter 2 also includes an experimental method for determining diode laser characteristics, including spectral region, tuning ranges, tuning rates, region of single mode operation, and frequency stability. These experimental investigations must be carried out prior to employing the diode laser.

In general, to utilize the LAS technique adequately, it is necessary to accurately know the band spectra of both pollutants and normal atmospheric absorbing gases, together with values of their IR absorption coefficients, \( \alpha \). Therefore, a comprehensive compilation of IR absorption line parameters of the atmosphere constituents, (especially absorbing gases), must be provided. The important line parameters are: central position \( (\nu_o) \), intensity \( (S^0) \), broadening coefficient \( (\gamma) \), and line shape, \( f(\nu, \nu_o) \). Most of this data is coded on two 7 track magnetic tapes, written on a CDC 800 computer, and is available from the Air Force Cambridge Research Laboratory (AFCRL). Also, for a laser spectroscopy air pollutant monitoring station, it is necessary to have a computer package to generate the individual line parameters of the target gas from its molecular constants, especially if the required data is not available or it is, but not accurate enough. The theory used in constructing such a computer package is described in Chapter 3.

Chapters 4, 5, and 6 provide theoretical calculations and
experimental measurements for obtaining the required data mentioned above. This data is useful for the design of any pollutant monitor, based on the resonance absorption scheme. Chapter 4 describes measurements with line-tunable laser (CO₂) on a pollutant gas (O₃) in order to establish some useful criteria for air pollution monitoring via the "direct" absorption scheme. Chapter 5 describes a method for determining the absorption line parameters of a nearest pollutant (NO) line to a line-tunable laser (CO) line. This method is based on the best match between experimental absorption data and theoretical calculations.

In some pollution detection techniques employing line-tunable lasers (e.g., heterodyne radiometers), the separation between the laser line used, and the nearest pollutant absorption line (Δνᵣ) must be known to better than 10 MHz. Chapter 6 describes a simple technique for accurate frequency (wavenumber), ν, measurement of over 100 lines in the ν₃ band of ozone. These measurements are based on the use of a diode laser, White cell, and etalon. The accuracy of these measurements is compared with those obtained using the more complicated laser heterodyne techniques.

Up to this point, experimental and theoretical tools have been examined, for spectroscopic studies of pollutant gases. These studies must be performed (especially in the atmosphere) prior to the design of a detection instrument. Chapter 7 describes the developed Point Monitoring (PM) technique at the McMaster University Air Pollution Laboratory. This technique is based on LAS and second harmonic
detection methods. In this Chapter, the applications of the LAS to the detection of \( \text{SO}_2 \), \( \text{N}_2\text{O} \), \( \text{NH}_3 \), and \( \text{O}_3 \) are described. The LAS sensitivity is compared with the most accurate recent optical techniques. Chapter 7 additionally describes necessary improvements needed to increase the absorption coefficient detection sensitivity from \( 10^{-7} \text{ m}^{-1} \) to \( 3 \times 10^{-8} \text{ m}^{-1} \).

Remote Long-path Monitoring (LPM) yields values for the average pollutant concentration over the path, which are generally more meaningful for regional models than point monitoring. However, LPM is not generally considered to be a substitute for point monitoring, but an adjunct to it. Chapter 8 describes a remote long-path monitoring station for \( \text{SO}_2 \) detection in the atmosphere. This station employs a semiconductor diode laser which radiates in the \( v_1 \) band of \( \text{SO}_2 \), a launching telescope, corner cubes retroreflector, and a second harmonic detection system. The present detection technique enabled us to detect an \( \text{SO}_2 \) concentration as low as 50 ppb in a total pathlength of 1.2 km in the atmosphere. The basic concept shows promise for measuring \( \text{SO}_2 \) concentration as low as 10 ppb in the \( v_1 \) band. This can be achieved by improving the present optical system, and the data processing. Chapter 8 also contains the results of experimental and theoretical investigations which indicate that it is possible to achieve additional improvement in the detection sensitivity by employing a diode laser which radiates in the \( v_3 \) band of \( \text{SO}_2 \).

Chapter 9 describes the LAS system noise and methods for eliminating such noise.
Finally, Chapter 10 contains the summary and conclusions of the presented work in this thesis.
CHAPTER 2

LASERS USED IN THIS THESIS

2.1 Introduction

Resonance absorption pollutant detection can be performed with line-tunable or broadly tunable lasers. Two different schemes for long-path absorption monitoring and spectroscopic investigation have been used in this thesis. One involves the use of line-tunable lasers (CO$_2$ and CO lasers). The other involves the use of tunable lead-salt semiconductor diode lasers. The theory and operation of gas lasers are well known and described elsewhere [11], therefore, in section 2.2, only the CO/CO$_2$ system components and specifications will be described. On the other hand, tunable lead-salt diode lasers, at their present stage, have a variety of important and realizable applications. As the state-of-the-art is advanced, their application range will be expanded considerably. Improved output powers and higher operating temperature appear quite feasible for the near future [12]. In section 2.3 the fundamental theory and operation of such lasers will be described, and a comprehensive comparison between the semiconductor lasers and the other tunable lasers will be demonstrated.
2.2 **Line-Tunable Lasers: CO/CO$_2$ Laser**

The gas laser is one type of device that is capable of generating coherent electromagnetic radiation at wavelengths shorter than those generally considered to be microwave frequencies. The other devices that have this property employ, as an active medium, crystalline solids, glasses, liquids, or semiconductors. The first two experiments in this thesis have been performed with the commercial Molecron C250 CO/CO$_2$ laser. Table 2.1 shows the system component and the laser specifications, while Fig. 2.1 displays a view of the laboratory facility showing the CO/CO$_2$ laser. These two experiments will be described in Chapters 4 and 5 in detail.

2.3 **Tunable Lasers**

2.3.1 **Introduction**

Since the development of the first laser in the early 1960's most applications have relied on their high power and low beam divergence. Wavelength tuning has been of secondary importance. Now the laser has become a powerful tool of spectroscopy over a range extending from submillimeter waves to the vacuum ultraviolet region. The following subsections review the fundamental properties of a lead-salt semiconductor diode laser, which has been used to obtain the data, and to develop the pollutant monitoring techniques in this thesis. A number of tunable lasers can be used for this purpose; these include: spin-flip Raman lasers [13], sum and difference frequency generators [14], parametric oscillators [15], and high pressure gas lasers [16]. Characteristics and properties of this variety of lasers are outside the scope
of the thesis. For comparison, Table 2.2 contains the characteristics of some tunable lasers emitting in the infrared (IR) region.

2.3.2 Lead-Salt Semiconductor Diode Lasers (SDL)

Semiconductor diode lasers are the simplest of the tunable lasers, providing modest continuous powers with narrow line-widths, good frequency stability, and with capabilities for tuning over a wide spectral region. Since the first publication in 1970 of Doppler-limited spectra within the 10.6 µm band of SF₆ by E. D. Hinkley [17], lead-salt semiconductor diode lasers have been employed for high resolution infrared spectroscopy [18], [19].

Over fifteen years ago, J. Butler fabricated the first lead-salt laser [20]; for a number of years subsequently, researchers investigated lead-salt lasers on an R & D basis. But it was not until 1970 that these devices began to be used for ultra-high-resolution spectral measurements.

Structurally, the lead-salt lasers are quite similar to the familiar GaAs lasers, although the wavelength coverage and uses are quite different. The devices are formed using a stripe geometry (Fig. 2.2) to make them lossy in the transverse direction. The diode lasers are fabricated from vapor-grown single crystals of Pb₁₋ₓSnₓTe, Pb₁₋ₓSnₓSe, PbS₁₋ₓSeₓ, Pb₁₋ₓGeₓTe, or Pb₁₋ₓCdₓS semiconducting material by cleaving the crystals into rectangular parallelepipeds of approximate overall dimension 0.12 by 0.05 by 0.03 centimeter. By choosing the alloy composition, x, tunable lasers with wavelengths from less than 3 µm to more than 30 µm can be fabricated.
### TABLE 2.1 \ System Component and Specifications of CO/CO\(_2\) Laser

<table>
<thead>
<tr>
<th>SYSTEM COMPONENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MODEL</td>
</tr>
<tr>
<td>C-250</td>
</tr>
<tr>
<td>CPS-N</td>
</tr>
<tr>
<td>SD-21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specifications</th>
<th>CO(_2) Laser</th>
<th>CO Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grating sine drive</td>
<td>Grating sine drive</td>
</tr>
<tr>
<td>Power Output</td>
<td>10 W</td>
<td>1-4 W</td>
</tr>
<tr>
<td>Output wavelengths</td>
<td>9.17-9.39, 9.43-9.80, 10.13-10.38, 10.44-10.91 (\mu)m</td>
<td>5.1-6.5 (\mu)m</td>
</tr>
<tr>
<td>Mode</td>
<td>TEM(_{oo})</td>
<td>TEM(_{oo})</td>
</tr>
<tr>
<td>Cooling</td>
<td>water</td>
<td>LN(_2)</td>
</tr>
<tr>
<td>Power Stability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>long term (4 hours)</td>
<td>± 2%</td>
<td>± 4%</td>
</tr>
<tr>
<td>short term (1 sec.)</td>
<td>± .2%</td>
<td>± .4%</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>8 mm</td>
<td>6 mm</td>
</tr>
<tr>
<td>1/e(^2) intensity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beam divergence</td>
<td>&lt; 4 m rad</td>
<td>&lt; 3 m rad</td>
</tr>
</tbody>
</table>
FIGURE 2.1
OVERALL VIEW OF THE LASER LAB Laser power supply is in the foreground, laser is in left centre, optical table is in the background. Behind the laser along the wall is the multiple reflection long path cell.
<table>
<thead>
<tr>
<th>Type</th>
<th>Tuning Mechanism</th>
<th>Pump Laser</th>
<th>Active Medium</th>
<th>Wavelength Coverage μm</th>
<th>Highest Resolution cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semiconductor Diode Laser (SDL)</td>
<td>T, p, B</td>
<td>-----</td>
<td>Semiconductor</td>
<td>&lt;1-34</td>
<td>3x10⁻⁶</td>
</tr>
<tr>
<td>Spin-Flip-Raman Lasers (SFR)</td>
<td>B</td>
<td>CO, CO₂</td>
<td>InSb</td>
<td>5-6</td>
<td>3x10⁻⁵</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9-11</td>
<td></td>
</tr>
<tr>
<td>Nonlinear Optical Devices</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parametric Oscillators (OPO)</td>
<td>T₀</td>
<td>YAG, RUBY</td>
<td>Nonlinear Material</td>
<td>&lt;1-11</td>
<td>3x10⁻²</td>
</tr>
<tr>
<td>Diff.-Freq. Generators (DFG)</td>
<td>νₚump</td>
<td>RUBY, Dye, CO₂, Klyst.</td>
<td></td>
<td>3-6</td>
<td>2x10⁻³</td>
</tr>
<tr>
<td>Two-Photon Mixer (TPM)</td>
<td>νₚump</td>
<td>...........</td>
<td>...........</td>
<td>9-11</td>
<td>3x10⁻⁵</td>
</tr>
<tr>
<td>Four-Photon Mixer (FPM)</td>
<td>νₚump</td>
<td>...........</td>
<td>...........</td>
<td>2-24</td>
<td>1x10⁻¹</td>
</tr>
<tr>
<td>Gas Lasers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeeman-Tuned (ZTG)</td>
<td>B</td>
<td>-----</td>
<td>He-Ne, He-Xe</td>
<td>3-9</td>
<td>3x10⁻³</td>
</tr>
<tr>
<td>High-Pressure CO₂</td>
<td>θ, δ</td>
<td>-----</td>
<td>CO₂</td>
<td>9-11</td>
<td>3x10⁻²</td>
</tr>
</tbody>
</table>
Figure 2.2 Schematic diagram of stripe geometry diode laser.
2.3.2.1 Laser Action

Forward bias current flow through a pn junction diode produces a density of minority carriers in excess of the thermal equilibrium density on either side of the pn junction. Laser action results from radiative recombination of these injected minority carriers. The injection luminescence process is illustrated in the energy band diagram of Fig. 2.3. Only a fraction of the injected excess of minority carriers recombine radiatively. The remainder are lost through non-radiative processes such as Auger recombination at impurity or defect-induced centers. Furthermore, a fraction of the generated photons is reabsorbed within the crystal and does not reach the external world. The transitions involved take place between continuous energy bands, rather than discrete states. As a result, the spontaneous emission of semiconductor lasers is much broader than that of atomic or molecular lasers. At low current levels, spontaneous emission is produced, as the current is increased, a threshold current is reached at which stimulated emission gain outweighs electromagnetic loss in one or more modes and laser action occurs. The threshold current density $I_t$ may be expressed as $[11]$:

$$\frac{I_t}{A} = \frac{8\pi^2 qdn^2\Delta\nu}{c^2 n_i} \left[ a + (1/L)2n(1/R) \right]$$ (2.1)
Figure 2.3 Injection luminescence of a pn junction.  
A- Zero bias.  
B- Forward bias.
where

\[ \nu = \text{laser mode wavenumber} \]
\[ d = \text{mode width} \]
\[ \Delta \nu = \text{spontaneous emission line-width} \]
\[ n = \text{refractive index} \]
\[ \alpha = \text{loss constant} \]
\[ L = \text{distance between end faces} \]
\[ R = \text{end face reflectivity} \]
\[ \eta_i = \text{internal quantum efficiency} \]

The output power of an injection laser is given by

\[
P_o = \frac{(1 - I_t) \eta_i h\nu}{q} \left[ \frac{(1/L) \ln (1/R)}{\alpha + (1/L) (\ln 1/R)} \right] \quad (2.2)
\]

Experimentally, it is apparent that the output power of the laser increases much faster than linearly with current. It may be inferred from this observation that since \( \alpha \) does not vary significantly, \( \eta_i \) increases rapidly with current. Maximum observed output power for a single mode was \( P = .5 \text{ mW} \).

2.3.2.2 Tuning Methods

The lead-salt compounds which are available and have been used for spectroscopy in the 3 \( \mu \text{m} \) to 15 \( \mu \text{m} \) region are shown in Fig. 2.4, along with compositional tuning ranges of the semiconductors and locations.
of some of the molecular-absorption bands which have been studied. Spontaneous-emission frequency $v_s$ varies almost linearly with the alloy composition factor $x$ across most of an alloy's range in the form [21].

$$v_s = v_0 + \xi x$$  \hspace{1cm} (2.3)

The values $v_0$ and $\xi$ in Table 2.3 for the semiconductor can be used to select the appropriate crystal composition to match a particular wavelength. After the wavelength region is selected, the laser may be tuned during its operation by various methods which are described below.

The method chosen for a particular application will depend on factors such as resolution requirements, desired tuning range, cost and convenience. The tuning of a diode laser occurs quasi-continuously with individual modes shifting typically 1-5 cm$^{-1}$. An expression which describes the continuous tuning of a laser mode by varying some external parameter "$y" may be described as follows. The wavelength of the $m^{th}$ mode is given by:

$$\lambda = \frac{2nL}{m}$$  \hspace{1cm} (2.4)

Differentiating,
\[
\frac{d\lambda}{dy} = \left(1 - \frac{2L}{m} \frac{\partial n}{\partial \lambda}\right)^{-1} \left[\frac{2L}{m} \frac{\partial n}{\partial y} + \frac{2n}{m} \frac{\partial L}{\partial y}\right]
\]

\[= \frac{2\Delta\lambda}{\lambda} \left[ L \frac{\partial n}{\partial y} + n \frac{\partial L}{\partial y}\right] \quad (2.5)
\]

where \(\Delta\lambda\) is the mode spacing. The term containing \(\frac{\partial L}{\partial y}\) is generally negligible.

Magnetic field tuning has been demonstrated in many Pb-salt semiconductors [22], [23]. For example, the tuning rate of \(\frac{df}{dB}\) has been measured and found to vary from 0.4 to 2.0 MHz/G.

The widest tuning range in a single tunable laser has so far been achieved with hydrostatic pressure variation. The tuning limit was established by damage to the crystal, and a tuning rate of \(8.4 \times 10^{-6}\) eV/bar was obtained [24].

Temperature tuning utilizes the temperature dependence of the bandgaps of Pb-salt. It is complicated by the fact that, with the present state-of-the-art, pulsed operation of Pb-salt semiconductor lasers is generally required for temperatures greater than about 20°K [101]. To eliminate the need for liquid-helium cooling, a closed-cycle cryogenic cooler has been developed that lowers the temperature to 10°K in 60 minutes. This cryogenic system has been built by Cryogenic Technology Inc., and has been used to control the temperature of the Pb-salt diode lasers employed in this thesis.
TABLE 2.3 Composition-tuning Characteristics of Lead-Salt Lasers [21].

<table>
<thead>
<tr>
<th>Material</th>
<th>$v_o (\text{cm}^{-1})$</th>
<th>$\xi (\text{cm}^{-1})$</th>
<th>Composition Range</th>
<th>Wavenumber Range (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$_{1-x}$ Sn$_x$ Te</td>
<td>1,540</td>
<td>-3,837</td>
<td>$0 &lt; x &lt; 0.32$</td>
<td>1,540 - 312</td>
</tr>
<tr>
<td>Pb$_{1-x}$ Ge$_x$ Te</td>
<td>1,540</td>
<td>14,600</td>
<td>$0 &lt; x &lt; 0.05$</td>
<td>1,540 - 2,270</td>
</tr>
<tr>
<td>Pb$_{1-x}$ Sn$_x$ Se</td>
<td>1,190</td>
<td>-8,780</td>
<td>$0 &lt; x &lt; 0.10$</td>
<td>1,190 - 312</td>
</tr>
<tr>
<td></td>
<td>1,190</td>
<td>5,552</td>
<td>$0.19 &lt; x &lt; 0.40$</td>
<td>312 - 1,562</td>
</tr>
<tr>
<td>Pb$_{1-x}$ S$_x$ Se$_x$</td>
<td>2,295</td>
<td>-1,105</td>
<td>$0 &lt; x &lt; 1$</td>
<td>2,295 - 1,190</td>
</tr>
<tr>
<td>Pb$_{1-x}$ Cd$_x$ S</td>
<td>2,295</td>
<td>29,396</td>
<td>$0 &lt; x &lt; 0.058$</td>
<td>4,000 - 2,295</td>
</tr>
</tbody>
</table>
Figure 2.4 Wavelength coverage for several lead-salt diode lasers. Also shown are some gases that have been studied with diode lasers (present work are marked by *).
Current tuning is a manifestation of temperature tuning which utilizes the joule heating caused by the diode current flow. Continuous tuning of a single mode has been achieved, and a continuous tuning range of about 1 cm\(^{-1}\) is observed during the present research. Current tuning may be used in conjunction with other tuning methods as a fine tuning control or to extend the tuning range.

The usefulness of the current tuning may be enhanced by superimposing a small ac ripple onto the dc bias current. The ac component allows synchronous detection to be used, or the resulting small laser frequency variation may be applied to differential spectroscopy.

In a typical monitoring application, several Pb-salt diode lasers would be used, each tailored to emit in a strongly absorbing infrared region of one of the pollutant gases. This arrangement is necessary because of the limited current tuning range of these lasers, and desirable because it provides for increased specificity. The small size of these lasers makes it possible for several to be mounted into the same cold head.

2.3.2.3 The Lead-Salt Diode Laser System

An operating system has been assembled to provide a convenient source of tunable radiation from any diode laser system. A block diagram of the system assembly is given in Fig. 2.5. The major components consist of a closed-cycle liquid helium temperature cryocooler (CTi Model 21), a laser diode temperature control unit (Lake Shore Cryotronics Model DTC 500) and a laser power supply and
control unit (Laser Analytics Model LPS-2). This overall package allows the temperature of the laser diode mounting system to be controlled to within a few millidegrees at average temperatures ranging upwards from 11°K. At present, a particular PbSnSe diode laser (acquired from Laser Analytics) is mounted on the cold head of the cryocooler (see Figures 2.6 and 2.7), but the system is sufficiently versatile to permit the easy installation of other alloy lead-salt combination diode lasers directly into the system. The particular diode presently installed in the cryocooler package has an alloy composition (12% Sn) selected to produce laser wavelengths spectrally matched to some strong absorption lines in the ν₁ band of SO₂. The characteristics of this particular diode have been investigated, and are reported below. It is expected that the output power, laser mode and tuning characteristics will be typical of those obtained with diodes operating at other wavelengths (e.g., O₃ monitoring diode).

The conjunction of laser and cryocooler control units permits the average temperature of the cold head to be selected, independent of the drive current applied to the continuously operating diode laser. This feature is crucial to the provision of a convenient, repeatable means of tuning the wavelength of the laser mode output. The base temperature of the cold head broadly determines the average wavelength of the diode laser output. Relatively small changes in the current drive to the diode subsequently provide the means of "fine tuning" the wavelength of laser emission about the base value fixed by the cold head temperature. The necessary electronic systems to
Figure 2.5 Block diagram of tunable diode laser system showing three major components: refrigeration unit and cold head, temperature controller, and laser power supply.
Figure 2.6  A view of the cryocooler head in which the semiconductor diodes are located. The infrared transmitting window through which the laser output is emitted can be seen in the background.
Figure 2.7 A close-up of the cryocooler cold head, taken from the direction of the output window. The lead-salt diode laser can clearly be seen highlighted in its mounting in the lower central part of the photograph.
provide the base temperature of the diode and the current drive for
fine tuning are shown in Fig. 2.8 which also illustrates the
compactness of the system. The small changes in diode current are
generated by the laser drive unit; two modes of operation are
available: a slow scan mode in which the current is slowly varied
over a range of up to 200 mA (the drive current itself is from 0.6 to
2A), or a modulation mode in which a sawtooth, triangular or sinusoidal
current modulation can be applied at a rate varying from 50 Hz to 1 kHz.
The latter mode of operation is particularly suitable for the sensing
of rapid changes in laser radiation absorption, such as would be
employed in a fast-time response detection system for monitoring small
scale fluctuations in atmospheric pollutant gases. The base temperature
range from 11°K to 40°K allows an overall change in average (inverse)
wavelength of diode emission by approximately 80 cm\(^{-1}\) (1080 cm\(^{-1}\) to
1160 cm\(^{-1}\)). Fine tuning by variation of diode drive current produces
a tuning range for a particular mode of roughly 1 cm\(^{-1}\) at a given cold
head temperature. The threshold current of the laser diode is a
function of the base operating temperature. The threshold bias current
was found to increase from 0.65 to 1.5 amps as the base temperature was
increased from 11°K to a maximum of 40°K. Under typical operating
conditions the laser output was measured with a HgCdTe infrared
detector (see Fig. 2.9).

Figure 2.10 shows the output obtained from the diode laser
as a function of wavelength. The diode was operated at low base
temperature (16°K) and a high drive current. As expected under these
circumstances, a number of laser modes operate simultaneously. The laser mode spectrum so produced was measured with a 1/2 metre Jarrell/Ash scanning spectrometer (Model 82-000). The width of the peaks shown in Fig. 2.10 reflect the resolution setting of the spectrometer (~75Å). Of course, this does not reflect the width of each individual laser mode, which is a great deal smaller (~10⁻⁴ cm⁻¹ which is ~0.01Å) than the spectral resolution. Observe that, even for operation well above threshold, only a few laser modes oscillate. Furthermore, these modes are well separated in wavelength and so one of them can easily be selected using a spectrometer with a very modest resolution.

Figure 2.11 shows the output of the diode laser at a higher temperature (250K) and relatively high drive current. Nevertheless, only a single mode oscillates. Once more, the width of the peak shown in the figure merely reflects the resolution of the spectrometer. In this figure, the single mode output is shown for several different currents. Observe the change in wavelength of the peak as the diode drive current is changed, directly reflecting the "fine tuning" of the laser diode wavelength.

Finally, a particularly important characteristic of the diode laser is the extent to which, at a given base temperature and drive current, the output wavelength remains constant. Figure 2.12 shows the results of a direct test of this stability obtained on an X-Y recorder. In this experiment, the laser beam was used to probe the multi-pass White cell (see Chapter 4) which contained a trace of SO₂ in a few Torr of nitrogen. The diode current was fine-tuned until a particular, sharp resonance line was detected. At some point,
tuning was discontinued and the X-Y recorder was switched to time base. Any tendency of the laser wavelength to drift would show up as a decrease or increase in the absorption as a coincidence is lost between the laser radiation and that point on the resonant absorption line. No such effect was observed over a period of several seconds. Three different diode lasers are used in this thesis. Table 2.4 contains the listing of these diodes along with its applications.

**TABLE 2.4 Listing of the Diode Lasers Used in this Thesis**

<table>
<thead>
<tr>
<th>SDL</th>
<th>Range cm⁻¹</th>
<th>Application</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSnSe</td>
<td>1050 - 1160</td>
<td>Atmospheric Monitoring of SO₂, Point Monitoring of SO₂, NH₃, and N₂O</td>
<td>8</td>
</tr>
<tr>
<td>PbSnSe</td>
<td>1030 - 1070</td>
<td>Point Monitoring of O₃</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High resolution spectroscopy of O₃</td>
<td>6</td>
</tr>
<tr>
<td>PbSnSe</td>
<td>1300 - 1380</td>
<td>Laboratory Studies of atmospheric SO₂ monitoring possibility</td>
<td>8</td>
</tr>
</tbody>
</table>
Figure 2.8  A view of the lead-salt diode laser control system. The helium transfer lines and cryocooler head can be seen on the optical table behind the controller.
Figure 2.9  A view of the optical table showing the beam transport systems for both the semiconductor diode and the CO/CO$_2$ lasers. The He-Ne laser is used for optical alignment and the spectrometer for wavelength determination.
Figure 2.10 Output spectrum from PbSnSe diode laser operating at 16 °K and diode current of 1.8107 A.
Figure 2, 11 Output spectrum from PbSnSe diode laser operating at 25°K and for various diode currents as shown.
Figure 2.12 Typical result of diode-laser frequency stability experiment. The laser is scanned first through gas absorption lines (left part). Then, the scanning is stopped and the recording apparatus (X-Y recorder) is switched to time base. Note that in 20s the stability is better than 0.25 MHz.
CHAPTER 3

THEORY OF MOLECULAR ABSORPTION OF INFRARED LASER RADIATION

3.1 Introduction

In this Chapter, we consider the required data and modelling, necessary to predict the molecular absorption of narrow linewidth laser radiation.

Beer's law for the linear propagation of monochromatic radiation of frequency (wavenumber) $\nu$ in a homogeneous and isotopic medium is of the form

$$\frac{d}{dz} I(z, \nu) = -\beta(\nu) I(z, \nu) \tag{3.1}$$

Where $z$ is the direction of propagation, $I(z, \nu)$ is the intensity of the radiation, and $\beta(\nu)$ is the extinction coefficient. The extinction coefficient is the sum of the total absorption coefficient and total non-forward scattering coefficient. The transmittance, $T$, over a path of length $L$ is then given from the above Equation by

$$T(L, \nu) = \frac{I(L, \nu)}{I(0, \nu)} = \exp \left[ -\beta(\nu) L \right] \tag{3.2}$$
The effects of aerosol absorption and scattering or the effects on propagation due to refractive index changes arising from turbulence will not be considered. Also, only the region from 1 to 25 μm will be considered. Here the molecular absorption is primarily due to vibrational overtones and combination bands at the short wavelength end, vibrational fundamental in the middle of this range, and pure rotation at the long wavelength end. The principal absorbers are the most abundant isotopes of H₂O and CO₂ and secondarily, but important in those regions away from strong absorptive transitions of the above molecules, are CH₄, CO, O₃, N₂O, NO, NO₂, SO₂, and HNO₃ as well as the less abundant isotopes of H₂O and CO₂.

The important parameters of a calculation of molecular absorption in the atmosphere relate to a detailed knowledge of line positions, intensities, pressure broadening coefficients, and line shapes. This data has been accumulated and refined since the inception of infrared molecular spectroscopy in the 1930's. The improvement in available data has over the years been most significant. With accurate spectroscopic information one can calculate for various model atmospheres the expected laser transmittance.

Data on individual vibration-rotation lines that are useful for atmospheric transmission calculations in the infrared have been compiled in a systematic fashion over the last ten years. The most accurate data on spectral line parameters has been compiled on magnetic tapes by AFCRL [25]. The molecules included in the compilation are H₂O, CO₂, O₃, N₂O, CO, CH₄, O₂, and recently SO₂, NO, NO₂, and HNO₃ [26].
Since the improvement of accuracies in the molecular constants have become more and more significant over the years, it has been found that for a laser spectroscopy air pollution monitoring station, it is necessary to have a computer package to generate the individual line parameters of the target gas from its molecular constants, especially if the required data is not available or it is, but not accurate enough. In the following sections, the wavelength regions of different gases and their mixing ratios in the atmosphere, the theory of evaluating the individual line parameters, and the transmittance calculations will be considered.

3.2 General Characteristics of Absorption Spectra of Atmospheric Gases

The main absorbing gases in the atmosphere in the infrared are water vapor, carbon dioxide, ozone, and oxygen. The atmosphere contains minor constituents that also absorb radiation in the infrared region. These are primarily carbon monoxide, methane, and nitrogen oxides. In addition, various gases of industrial origin are present in localized regions, and these can absorb optical radiation. In this section the absorption spectra and the mixing ratios of gases existing in the atmosphere on a planetary scale will be considered [10].

\[ H_2O, \text{ mixing ratio of } 1.3 \times 10^{-7} \text{ to } 4.5 \times 10^{-2} \]
The vibrational-rotational spectrum of $H_2O$ contains three main bands $v_1$, $v_2$, and $v_3$ with centers at 3657.05, 1594.78, and 3755.92 cm$^{-1}$, respectively, and overtones, combination, and hot bands in the infrared. The most intensive and broad vibration-rotation band of $H_2O$ is the main $v_2$ band with center near 6.3 $\mu$m. The laser used for pollutant monitoring must be tuned away from the completely absorbing regions (non-window): 5.5 - 7.5 $\mu$m, and 2.6 - 3.3 $\mu$m by $H_2O$.

$\text{CO}_2$: mixing ratio at sea level: $3.18 \times 10^{-4}$

The vibration of $\text{CO}_2$ contains three main modes $v_1$, $v_2$, and $v_3$. $v_1$ is optically inactive - because of symmetry its dipole moment remains constant during vibrations. Centers of the main $v_2$ and $v_3$ vibration-rotation bands are located near 667.40 and 2349.16 cm$^{-1}$, respectively. The non-window regions are from 13.5 to 16.5 $\mu$m, and from 4.2 to 4.4 $\mu$m.

$\text{O}_3$: mixing ratio: $(2 - 7) \times 10^{-8}$

All three main vibration frequencies of $\text{O}_3$ are active in absorption. $v_1 = 1110$ cm$^{-1}$, $v_2 = 710$ cm$^{-1}$, and $v_3 = 1043$ cm$^{-1}$. The $v_1$ band is very weak and completely overlaps the $v_3$ band. The strongest absorption band of ozone, with its center near 9.6 $\mu$m, with a width of approximately 1 $\mu$m, absorbs half the solar radiation (non-window).
\( N_2O \): mixing ratio: \((2.7 - 3.5) \times 10^{-7}\)

All three main oscillation frequencies of \( N_2O \): \( \nu_1 = 1285.6 \text{ cm}^{-1} \), \( \nu_2 = 588.8 \text{ cm}^{-1} \), and \( \nu_3 = 2223.5 \text{ cm}^{-1} \), are active in the infrared.

\( CH_4 \): mixing ratio: \((1.0 - 1.4) \times 10^{-6}\)

A high degree of molecular symmetry causes strong degeneracy of the vibrational energy levels. The molecule has only four basic oscillations differing in frequencies while the \( \nu_1 \) and \( \nu_2 \) frequencies are optically inactive. The centers of the basic \( \nu_3 \) and \( \nu_4 \) vibration-rotation bands are close to \( 3020.3 \text{ cm}^{-1} \) and \( 1306.2 \text{ cm}^{-1} \), respectively.

\( CO \): mixing ratio: \((0.5 - 2.5) \times 10^{-7}\)

The basic vibration-rotation band is close to \( 2143.2 \text{ cm}^{-1} \), centers of the second, third, and fourth overtones are near \( 4260.1, 6350.4, \) and \( 8414.5 \text{ cm}^{-1} \), respectively. Other minor constituents [27] are:

\( NO \): mixing ratio: \( 10^{-8} - 10^{-6}\)

Band \( 1-0 \) : \( 1876 \text{ cm}^{-1}\)

\( NO_2 \): mixing ratio: \( 10^{-9} - 10^{-6}\)

Band \( \nu_3 \) : \( 1621 \text{ cm}^{-1}\)
\[ HNO_3: \text{mixing ratio: } 2.4 \times 10^{-9} \]
\[ \text{Band } v_9 = 896 \text{ cm}^{-1} \]
\[ \text{NH}_3: \text{mixing ratio: } <10^{-6} \]
\[ \text{Band } v_2 = 933 \text{ cm}^{-1} \]
\[ \text{SO}_2: \text{mixing ratio: } (0.5 - 7.2) \times 10^{-9} \]
\[ \text{Bands: } v_1 = 1151 \text{ cm}^{-1} \]
\[ v_2 = 518 \text{ cm}^{-1} \]
\[ v_3 = 1362 \text{ cm}^{-1} \]

3.3 Calculation of Absorption Coefficients

The absorption of laser radiation by a gas may be expressed in terms of the absorption coefficient, \( \alpha(\nu) \). For frequencies (wavelengths) \( \nu \) near a resonant absorption centered at frequency \( \nu_0 \), \( \alpha(\nu) \) is given by

\[ \alpha(\nu) = S^0 \rho f(\nu, \nu_0) \quad (3.3) \]

where \( S^0 \) is the line intensity (to be defined below), \( \rho \) is the partial pressure of the absorber, and \( f(\nu, \nu_0) \) is the normalized lineshape function, which expresses the fact that the resonance has finite width.

At atmospheric pressure (in the lower region of the atmosphere), broadening of spectral lines is mainly due to collisions between molecules. The line contour determined by these effects is called dispersion and, in the absence of power saturation, may be written as \([28]\).
\[ f(\nu, \nu_0) = \frac{1}{\pi} \frac{\gamma_L}{(\nu-\nu_0)^2 + \gamma_L^2} \]  

(3.4)

Where \( \gamma_L \) is the line-halfwidth, which is one-half the linewidth between points \( \nu_1 \) and \( \nu_2 \) satisfying the condition

\[ a(\nu_1) = a(\nu_2) = \frac{a(\nu_0)}{2} \]  

(3.5)

This linewidth is caused by collisions between the molecules and is proportional to the pressure and temperature. For the case of a gas mixture,

\[ \gamma = \sum_j \gamma_j \hat{p}_j \]  

(3.6)

where \( \gamma_j \) is the pressure broadening constant of the jth component of the mixture for the spectral line in question, and \( \hat{p}_j \) is the partial pressure of the jth component. The values of \( \gamma_L \) for atmospheric gases are of the order of \( 0.01 - 0.1 \) \( \text{cm}^{-1} \).

Since the line intensity, \( S^0 \), is also proportional to the pressure, the peak absorption at resonance \( a(\nu_0) \), obtained by combinations of Equations 3.4 and 3.3, is pressure independent. It is therefore a convenient parameter to characterize the magnitude of absorption.

Under these conditions, the peak absorption is given by

\[ a(\nu_0) = \frac{S^0}{(\pi \gamma_L^0)} \]  

(3.7)
Spectral-line broadening is also produced by the Doppler effect. At reduced pressures, and assuming thermodynamic equilibrium for the translational degrees of freedom of a molecule, and Maxwellian velocity distribution of the molecules, then for spectral line contour for which broadening is due to the Doppler effect only, the following expression is obtained [28].

\[
f(\nu, \nu_0) = \left(1/\gamma_D\right) \left(\ln 2/\pi\right)^{1/2} \exp \left[-(\nu-\nu_0)^2(\ln 2)/\gamma_D^2\right]
\]

(3.8)

where,

\[
\gamma_D = (\text{HWHM}) = \left(v_0/c\right) \left(2kT \ln 2 / m\right)^{1/2}
\]

(3.9)

\[
\approx 3.58 \times 10^{-7} \left(T/\text{m}\right)^{1/2} \nu \text{ cm}^{-1}.
\]

Calculations show that the value of \(\gamma_D\) for atmospheric gases is approximately within the limits from \(\gamma_D = 6 \times 10^{-2} \text{ cm}^{-1}\) (for \(O_2\) lines near .2 \(\mu\)m) to \(\gamma_D = 3 \times 10^{-4} \text{ cm}^{-1}\) (\(H_2O\) vapor lines near 50 \(\mu\)m).

In the stratosphere (between 15 and 30 km), the ambient pressure varies from 10 to 90 Torr, such that the spectral lines in the infrared are for the most part, neither fully Lorentzian nor Gaussian in shape, but a convolution of the two—known as the Voigt lineshape, and may be written as [28]:
\[ 
\alpha(v, v_0) = \frac{\alpha_0 A}{\pi} \int_{-\infty}^{\infty} \frac{\exp\left(-\frac{x^2}{A^2 + (\omega - x)^2}\right)}{A^2} \, dx \tag{3.10} 
\]

where,

\[ 
\alpha_0 = \frac{S_0 \rho}{\gamma_D} \left( \ln \frac{2}{\pi} \right)^{\frac{1}{2}}, 
\]

\[ 
A = \frac{\gamma_L}{\gamma_D} \left( \ln 2 \right)^{\frac{1}{2}}, 
\]

\[ 
\omega = \frac{v - v_0}{\gamma_D} \left( \ln 2 \right)^{\frac{1}{2}}. 
\]

For the limiting case where \( |v - v_0| \gg \gamma_L \) and \( \gamma_D \)

\[ 
\alpha(v_0) = \frac{S_0 \rho \gamma_L}{\pi (v - v_0)^2} \left[ 1 + \left( \frac{3}{2} A^2 - 1 \right) \left( \frac{\gamma_L}{v - v_0} \right)^2 + \left( \frac{15}{4 A^2} - \frac{5}{2} + 1 \right) \left( \frac{\gamma_L}{v - v_0} \right)^4 + \ldots \right] 
\tag{3.11} 
\]

In the case of a number of overlapping lines, the absorption coefficient is the sum over all the individual contributing lines.

The intensity of a spectral line is expressed as an integral of the absorption coefficient over all frequencies.
\[ S = \int_{-\infty}^{\infty} a(v) \, dv \quad (3.12) \]

In principle, the intensity may be evaluated by the application of quantum theory of Einstein transition probabilities. Thus the intensity of absorption for the transition \( i \) to \( j \) is [21],

\[ S_{ij} = \left( \frac{8\pi^3 v_{ij}^3}{3hc} \right) \left( \frac{N_i}{g_i N} \right) \left[ 1 - \exp \left( \frac{hc v_{ij}}{kT} \right) \right] \times |R_{ij}|^2 \quad (3.13) \]

where \( v_{ij} \) is the transition frequency (wavenumber), \( N_i/N \) is the fractional number density in state \( i \) with statistical weight \( g_i \), \( |R_{ij}|^2 \) is the square of the matrix element of the dipole moment. The fractional number density may be rewritten in terms of energy level \( E_i \) of state \( i \) and the total partition function \( Q \) as

\[ \frac{N_i}{g_i N} = Q^{-1} \exp \left[ \frac{-E_i}{kT} \right] \quad (3.14) \]

The partition function is given as the product of the vibrational and rotational partition function, i.e.

\[ Q = Q_v Q_r \quad (3.15) \]

Using the harmonic oscillator approximation, the vibrational partition
function is expressed by

\[ Q_v = \frac{d_1}{\Pi} \left[ 1 - \exp \left( -\hbar \omega_1 / kT \right) \right]^{-1} \]  

(3.16)

where \( \omega_1 \) is the fundamental vibrational frequencies of degeneracy \( d_1 \).

The calculation of absorption coefficients for specific molecules, using Eqn. (3.3), depends upon the molecular symmetry. The appropriate line intensity formulas for the asymmetric top and linear molecules are described in the following subsections.

3.3.1 Asymmetric Top Molecules

A number of atmospheric gases are asymmetric top rotors with \( C\gamma_4 \) molecular symmetry. For these molecules, the rotational states are identified by the quantum numbers \( J(K_p, K_o) \), where \( J \) is the rotational quantum number and \( K_p \) and \( K_o \) are pseudo-quantum numbers describing the projection of \( J \) on the symmetry axis for the limiting prolate and oblate symmetric tops respectively.

The energy levels associated with these states cannot be obtained in closed form but can be calculated by a Computer diagonalization of the rotational Hamiltonian. A subroutine subprogram has been developed in this study, and proved to be very efficient. This program calculates the energy levels and hence the frequency of any transition from \( J = 0 \) up to \( J = 45 \) for any asymmetric molecule following the general theory described by King et al [30]. In order
to obtain results of sufficient accuracy, it is necessary to include contributions to the Hamiltonian due to centrifugal distortion [31].

In calculating the absorption coefficient due to individual lines, the most difficult problem in line intensity calculations is the determination of $|R_{ij}|^2$. Neglecting the interaction between vibration and rotation we obtain the dipole matrix element as the product of the vibrational and rotational matrix element:

$$|R_{ij}|^2 = |\mu|^2 |\beta|^2$$  \hspace{1cm} (3.17)

The rotational matrix element $|\mu|^2$ cannot be given as a simple function of the rotational quantum number because of the asymmetric nature of the molecule. A subroutine subprogram has been developed in this study which calculates the matrix element for arbitrary $\kappa$ and for any transition. The theory used is the same as that described by Cross et al [32].

The vibrational matrix element $|\beta|^2$ for a complex molecule is very difficult to calculate and it is customary to obtain the matrix element through a measured quantity. This matrix element is related to the integrated absorption coefficient through the relations

$$|\beta|^2 = (v_1 + 1) |\beta_0|^2$$  \hspace{1cm} (3.18)
where $|\beta_0|^2$ for the fundamental transition, and the integrated absorption coefficient $\alpha$ at temperature of $T_0$ may be expressed as

$$
\alpha = \frac{8\pi^3}{3\hbar c} \frac{N_{\text{v}} T_0}{Q_v} |\beta_0|^2 \sum_{v_1, v_2, \ldots} \omega_v (v_1 + 1) \exp \left[ \frac{\hbar c G_0 (v_1 v_2 \ldots)}{k T_0} \right] x
$$

$$
\left[ 1 - \exp \left( \frac{\hbar c \omega_v}{k T_0} \right) \right].
$$

(3.19)

As an example, consider the first band $v_1$ in the three bands $v_1, v_2,$ and $v_3$ of a triatomic molecule

$$
G_0 (v_1 v_2 v_3) = G (v_1 v_2 v_3) - G(000),
$$

where $G(v_1 v_2 v_3)$ is the vibrational energy [33], and

$$
\omega_v = G_0 (1 v_2 v_3) - G_0 (0 v_2 v_3)
$$

The rotational partition function can be written to sufficient accuracy using the semi-classical expression
\[ Q_r = \left[ \frac{\exp\left(\sqrt{B_e C_e} \frac{\hbar c}{4kT}\right)}{A_e B_e C_e \frac{kT}{\hbar c}} \right]^3 \left[ 1 + \frac{1}{12} \left( 1 - \frac{B_e C_e}{A_e} \right) \frac{\hbar c}{B_e C_e} \right] \] (3.20)

where \( A_e, B_e, \) and \( C_e \) are the rotational constants.

Finally, it is necessary to consider the effects of the nuclear spin statistics on the level population. In the case of the molecules \( \text{SO}_2, \text{O}_3, \) and \( \text{NO}_2, \) this factor is unity for the allowed states which are \( J(e, e) \) and \( J(o, o), \) where \( e \) and \( o \) specify the parity of \( K_p \) and \( K_o. \)

In the case of \( \text{H}_2\text{S} \) and \( \text{H}_2\text{O} \) the factor is \( g = 1/4 \) for the states \( (e, e) \) and \( (o, o) \) and is \( g = 3/4 \) for the states \( (e, o) \) and \( (o, e). \)

These factors, the molecular constants, the total band strength, and the selection rules are the input data to run the two subroutine subprograms for the line position and intensity calculations.

The Computer program for such evaluations, as devised by the author, contains three main subroutines:

(1) A subroutine for generating line positions,
(2) A subroutine for generating line intensities,
(3) A subroutine for calculating the absorption coefficient at any selected wavenumber, and any pressure due to all the contributing absorption lines.

3.3.2 Linear Molecules

For diatomic and linear polyatomic molecules the calculations of the individual line positions and intensities are straightforward
and available elsewhere [31].

3.3.3 Linewidths

Calculations of the linewidth parameter $\gamma_L$ based on collisional models are quite complex and available for only a few cases of interest. Hence, if accurate absorption coefficients are desired, it is usually necessary to use experimentally determined values for $\gamma_L$. Because of the limitations of the available data, in most of the calculations reported in this thesis, average values of $\gamma_L$ were assumed for each molecule independent of the transition involved. Calculations and/or measurements of linewidth for $N_2$ and air diluted mixtures have been given for a number of gases in the literatures [34-38].

3.4 Results and Discussion

In the wavelength range from 2 to 20 $\mu$m, absorption by atmospheric gases is mainly due to vibration-rotation bands, the strongest of which are in the infrared spectral region. It is clear that very intensive absorption in the center of certain bands practically excludes the possibility of applying these regions for the purpose of laser monitoring of the atmosphere, irrespective of whether the wavelength of the laser radiation is near the central part of the absorption line of the gas, or is between strong lines of central part of the absorption band. Within strong absorption bands, laser monitoring can be accomplished only in the upper layers of the atmosphere or by point monitoring (extracting an air sample at reduced pressures). In both cases the neighbouring lines are
separated and there is no overlapping.

The most useful wavelengths for laser monitoring are generally those in intervals between absorption bands, or microwindows of atmospheric transparency. In order to perform laser monitoring of the atmosphere, it is necessary to have quantitative information on absorption coefficients in the very atmospheric transparency microwindows located close to the wavelength of the laser radiation, along with information on absorption due to nearly spectral lines of atmospheric gases. Figure 8.7 (see Chapter 8) shows the required quantitative information about the atmospheric gases for the region from $1100 \text{ cm}^{-1}$ to $1200 \text{ cm}^{-1}$. These traces in Fig. 8.7 are the output of our computer package. The upper trace is the transmission due to 1% of $\text{H}_2\text{O}$ in the air at total pressure of one atmosphere, and with total pathlength of $L = 1 \text{ km}$. The other traces are the absorption coefficient for different atmospheric gases absorbing in this region. The optimum laser wavelength regions are determined first, in order to avoid strong absorption due to $\text{H}_2\text{O}$. Secondly the selected wavelength region must be at maximum absorption due to the target gas and minimum absorption due to the other gases. This Figure will be used for $\text{SO}_2$ monitoring in the atmosphere in Chapter 8.
CHAPTER 4

RESONANCE ABSORPTION MEASUREMENTS
WITH FIXED-FREQUENCY LASERS: USEFUL CRITERIA

4.1 Introduction

As mentioned in Chapter 3, every absorption line of a molecule in the atmosphere has, generally speaking, its own value of center position, width, and intensity. Without precise knowledge of these parameters, a theoretical determination of absorption coefficient is out of the question, even with correct knowledge of the broadening contour. The measurements of absorption coefficients of different gases, or performing high resolution spectroscopic studies with tunable lasers seem to be good solutions to this problem. A laser beam has a very low divergence and can thus be passed through a sample of target gas many times to enhance its absorption at concentrations equal to the ambient levels.

In this Chapter, measurements with line-tunable CO$_2$ laser, whose emission wavelengths are stable and well known, will be demonstrated. Section 4.2 contains measurements with a CO$_2$ laser on ozone in order to establish some useful criteria for pollution monitoring via the direct absorption scheme. The measurements of absorption coefficient $\alpha$ and the pressure dependence of the extinction coefficient $k_\nu(p)$ at frequencies $\nu$ corresponding to the P(8) to P(36) vibration-
rotation lines of the CO$_2$ laser will be described and compared with theory.

Of the laser techniques mentioned in Chapter 1, the resonance absorption approach appears to be the least sophisticated in experimental design, least costly, and most straightforward in providing optical information on gaseous pollutants. However, the applicability of this approach has appeared to be limited for two reasons: (a) the lack of frequency matching of available laser lines from fixed frequency lasers with lines from the vibrational-rotational spectrum of the target gas; (b) interference with the absorption signal by neighboring lines of other gas species as a result of Lorentz broadening of absorption lines at atmospheric pressure. The first of these problems has been potentially removed with the development of tunable lasers (as described in Chapters 6, 7 and 8). In the second area, the question of line interference has not been answered because of a lack of experimental and theoretical investigation. It is this second area that this Chapter is addressed to. The following questions are the main object of this Chapter: (1) If a fixed frequency laser is used, how close a line match is required to the principal gas species absorption line? (2) What is the width of the frequency band around the laser line in which spectral line absorptions due to other gases will cause a significant error in concentration measurements? (3) What is the minimum absorption intensity of foreign gas species lines above which they will play a significant part, if they are in the range described in (2)? (4) If fixed frequency detection
is employed, is more than one line required in order to ensure that
the absorption reading is solely due to the gas species, and if so,
how many such lines are required?

To answer such questions a "tunable" CO₂ laser has been
employed as a light source. This laser is tunable in the sense that
it employs a diffraction grating for line selection and thus offers a
large number of lines that can be matched up in varying degrees with
the absorption lines of target gas.

The growing concern about the hazardous effects of ozone on
human respiratory [39] and visual systems [40] has pointed to the need
for an efficient scheme for monitoring this pollutant gas in the
atmospheric ambient. Due to the overlap between the ozone absorption band
and the CO₂ laser emission band, the CO₂ laser has been employed in some
optical monitoring investigations on ozone [41 - 43]. However, ozone
is a complicated molecule and has a concomitant complex multiline
absorption spectrum. An examination of the ozone vibrational-rotational
spectrum [44] indicates that at room temperature and pressure there
can be significant absorption due to lines with centers as far away
as 0.1 cm⁻¹.

Therefore, the observed absorption of a laser line can be due
to contributions from several ozone lines. The effects due to fre-
quence mismatch, line broadening, and numbers of lines contributing are
then all mingled together. A study of the ozone system in more detail
was expected, therefore, to shed light on the various questions raised
in the previous paragraph. Although the frequency mismatch between
the CO₂ laser lines and the ozone lines is fixed, the line broadening can be reduced by lowering the pressure of the gas. This will be employed to yield useful information on the establishment of criteria for monitoring pollutants with lasers.

4.2 Experimental Technique

Room temperature measurements of resonance absorption were made on ozone in the 9.4 μm wavelength region using CO₂ laser radiation. A schematic diagram of the apparatus is shown in Figs. 4.1 and 4.2. The CO₂ laser used was a Molecron model C250 (see Fig. 2.1), coupled with a model SD-20 diffraction grating for spectral line selection. The spectral lines used in this work were P(8) - P(36) in the 00⁰₁ - 02⁰₀ band. The designation of each line was confirmed by using an Optical Engineering model 16-A CO₂ laser spectrum analyzer.

The absorption chamber (see Fig. 4.3) was a multipass White-type cell [45] consisting of a 5 m long stainless steel tube of 15 cm diam. Both the entrance and exit windows were made of BaF₂. A mechanical assembly at the chamber ends supported the concave gold-plated mirrors of 5 m radius of curvature. Orthogonal kinematic mounts on these mirrors allowed the adjustment of the optical path, with lengths from 20 m to 1000 m in intervals of 20 m. However, for optimum SNR and stability of the optical path, a pathlength of 400 m was used for most measurements in this Chapter. The absorption chamber was equipped with vacuum facilities to permit measurements at controlled pressures in the 0.015 - 1 atm. range.
Figure 4.1 Schematic diagram of the system used for resonance absorption measurements on ozone.
FIGURE 4.2.

OPTICAL BENCH IN THE LASER LAB  Laser light follows the path drawn in: past the alignment mirror (normally withdrawn) to concave mirror A, to B, through the asbestos pinhole, to C, to concave mirror D, to E, to F, then to concave mirror G (which focuses the beam into the long path cell H). It re-emerges to concave mirror I, to J, and finally to the detector K.
Figure 4.3 View of laboratory facility showing stainless steel absorption chamber (variable path length, multiple-reflection White Cell) in which various atmospheres are simulated, as well as instrumentation for absorption detection and data processing.
Optical alignment for the system was achieved by using a He - Ne (6328-A) laser whose optical path was made to coincide with that of the CO₂ laser, (see Figure 4.2). The CO₂ laser radiation was attenuated before being detected by a Hewlett-Packard (H-P) Model 8334 A radiation flux detector that was coupled with a H-P Model 8330 A radiant flux meter.

Ozone was generated by an electrical discharge across pure oxygen. The ozone was then diluted with room air in a chamber. The concentration of ozone in the resultant mixture used for this work was in the 0.05 - 2 ppm range. Ozone-air mixtures and pure N₂ were alternatively introduced into the absorption chamber in order to determine the transmitted radiation intensity. Since ozone decayed with time, a continuous flow method was used. The ozone concentration was monitored by a MAST model 724-2M ozone meter that was calibrated against a neutral buffered KI method. For resonance measurements at 1 atm pressure, the ozone meter placed at either the gas inlet or outlet line showed no observable change in its reading. For measurements at reduced pressures, the ozone meter was placed at the gas inlet line where the pressure was 1 atm. The error in ozone concentration determination was within ± 3%.

4.3 Data Analysis and Results

The transmission T(ν) was obtained from the ratio of measured transmitted light intensities for the ozone-air mixture and for pure N₂. Using the following expression
- ln T(ν) = k(ν) L  \quad (4.1)

Experimental values of the extinction coefficient k(ν) were deduced for a total pathlength L. The absorption coefficient

\[ \alpha(ν) = \frac{k(ν)}{p_{O_3}} \quad (cm^{-1} \ atm^{-1}) \quad (4.2) \]

of ozone was then determined for each of the P(8) - P(36) laser lines in the 00'1 - 02'0 band. For each laser frequency, α was found to be constant over the ozone concentration range of 0.05 - 2 ppm. The variation of α with ν for measurements at 1 atm is shown in Fig. 4.4 Patty et al. [42] have reported similar results for ozone. Despite some differences in the experimental approach and the range of ozone concentrations used (the range used by Patty was 10 - 80 ppm) the absorption coefficients obtained in both cases were in agreement to within the experimental error of ± 10%.

Using the theoretical considerations in Chapter 3, α(ν) was calculated using only the nearest ozone line to the corresponding P branch laser line. These results, which are presented in Fig. 4.4, indicate that significant absorption is present due to other neighboring ozone lines. For these calculations, CO₂ wavelengths given by Baird et al [46] and ozone wavelength compilations by Clough and Kneizys [47] were used. Further calculations were carried out using up to six neighboring ozone lines with frequencies separated from
Figure 4.4 Experimental and theoretical plots of absorption coefficients as a function of CO₂ laser wavelength for P(8) to P(36) lines in the 00₁⁺₁-02₂⁺₂ [2] band. Temperature=22°C and pressure=1 atm. The multi-line theoretical curve has been normalized to the experimental curve of P(8) and the single nearest line curve is appropriately scaled with respect to that point.
the laser line by as much as 0.25 cm⁻¹. The ozone lines used are
given in Table 4.1. The results are also presented in Fig. 4.4 and
indicate good agreement (to within experimental error) between
experiment and theory. Note that the multiline theoretical curve has
been normalized to the experimental curve at P(8) and the single nearest
neighbor curve appropriately scaled with respect to that point. Calcu-
lations of absolute absorption coefficients always lead to numerical
values higher than observed. The implications of these data, insofar
as considerations for a practical pollution monitoring system using
direct absorption with single line lasers are concerned, is that even
with an exact laser-pollutant absorption line match, absorption lines
of any species within about 0.1 cm⁻¹ can contribute significantly
to the absorption process if their absorption intensity is not more
than an order of magnitude below that for the nearest neighbor line.
Consequently, in constructing a pollution monitoring system using
fixed frequency detection, care must be exercised in the selection of
the laser line and gas absorption frequency so as to ensure that
there are no other neighboring absorption lines of significant strength
within about ±0.10 cm⁻¹. In practice this may be difficult to
realize as the ozone data presented here seem to indicate. To test
this hypothesis further, measurements as function of pressure were
also carried out and are presented next.

Typical experimental results of resonance absorption measure-
ments at pressures in the 0.015 - 1 atm range are shown in Figs.
4.5 - 4.7. The extinction coefficient k(v) has been normalized with
TABLE 4.1 Listing of CO\textsubscript{2} Laser Lines from the P Branch of the 00°1-02°2 Band Along with Nearest Neighbor Ozone Lines.

<table>
<thead>
<tr>
<th>CO\textsubscript{2} Laser Line Frequency in cm\textsuperscript{-1}</th>
<th>Difference of Nearest Ozone Line Frequency to CO\textsubscript{2} Laser Line in cm\textsuperscript{-1} (Intensity of Ozone Line in cm\textsuperscript{-2} atm\textsuperscript{-1} at T = 300°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(8) : 1057.3001</td>
<td>+0.0002 +0.0077 +0.0710</td>
</tr>
<tr>
<td></td>
<td>(0.33) (0.81) (0.78)</td>
</tr>
<tr>
<td>P(10) : 1055.6251</td>
<td>-0.0032 +0.0428 +0.0846 +0.0940</td>
</tr>
<tr>
<td></td>
<td>(0.01) (0.15) (0.06) (0.03)</td>
</tr>
<tr>
<td>P(12) : 1053.9235</td>
<td>+0.0008 +0.0220 +0.0546</td>
</tr>
<tr>
<td></td>
<td>(0.90) (0.21) (1.35)</td>
</tr>
<tr>
<td>P(14) : 1052.1956</td>
<td>-0.0059 -0.0493 +0.0614 +0.0640 +0.0765</td>
</tr>
<tr>
<td></td>
<td>(0.25) (0.72) (0.35) (0.52) (1.16)</td>
</tr>
<tr>
<td>P(16) : 1050.4413</td>
<td>-0.0445 +0.0978</td>
</tr>
<tr>
<td></td>
<td>(1.48) (0.92)</td>
</tr>
<tr>
<td>P(18) : 1048.6609</td>
<td>+0.0175 +0.0509 +0.0690</td>
</tr>
<tr>
<td></td>
<td>(0.60) (0.12) (0.90)</td>
</tr>
<tr>
<td>P(20) : 1046.8545</td>
<td>-0.0588 -0.0534 -0.0521 +0.0429</td>
</tr>
<tr>
<td></td>
<td>(0.03) (0.15) (0.15) (0.39)</td>
</tr>
<tr>
<td>P(22) : 1045.0219</td>
<td>+0.1295 +0.1539</td>
</tr>
<tr>
<td></td>
<td>(0.48) (0.66)</td>
</tr>
<tr>
<td>P(24) : 1043.1635</td>
<td>-0.1190 +0.0244</td>
</tr>
<tr>
<td></td>
<td>(0.03) (0.03)</td>
</tr>
<tr>
<td>P(26) : 1041.2791</td>
<td>+0.0964 -0.0587 -0.0215</td>
</tr>
<tr>
<td></td>
<td>(0.01) (1.38) (0.24)</td>
</tr>
<tr>
<td>P(28) : 1039.3693</td>
<td>-0.0403 +0.0229 -0.0179 -0.0130 +0.0385 +0.0724</td>
</tr>
<tr>
<td></td>
<td>(0.25) (0.55) (0.25) (0.12) (0.08) (0.68)</td>
</tr>
<tr>
<td>P(30) : 1037.4342</td>
<td>-0.0824 +0.0323 +0.0166 +0.0112 +0.0326 +0.0592</td>
</tr>
<tr>
<td></td>
<td>(0.42) (0.03) (0.12) (0.27) (0.01) (0.06)</td>
</tr>
<tr>
<td>P(32) : 1035.4737</td>
<td>-0.0604 -0.0517 +0.0461 +0.0265 +0.0343 +0.0438</td>
</tr>
<tr>
<td></td>
<td>(0.06) (0.01) (0.03) (0.01) (0.03) (0.01)</td>
</tr>
<tr>
<td>P(34) : 1033.4883</td>
<td>-0.0541 -0.0430 -0.0104 +0.0087 +0.0465</td>
</tr>
<tr>
<td></td>
<td>(&lt;0.01) (&lt;0.01) (0.02) (0.01) (&lt;0.01)</td>
</tr>
<tr>
<td>P(36) : 1031.4776</td>
<td>-0.1054 -0.0999 -0.0191 -0.0186 -0.0175 +0.0158</td>
</tr>
<tr>
<td></td>
<td>(1.40) (&lt;0.01) (&lt;0.01) (0.30) (0.82) (&lt;0.01)</td>
</tr>
</tbody>
</table>
respect to the value at 1 atm. Although data were obtained for all
fifteen lines in the P(8) - P(36) band, it was found that the curves
could be sorted according to their shapes into three categories. These
categories were determined basically by the magnitude of the frequency
separation of the laser line from its nearest neighbor ozone line ($\Delta \nu_n$)
provided the absorption strength of the nearest neighbor was greater
than 0.1 cm$^{-2}$ atm$^{-1}$. In those situations where the absorption strength
was less than 0.1 cm$^{-2}$ atm$^{-1}$ there were two cases: (a) the next
nearest neighbor would be chosen provided it also was within the criterion
and (b) the nearest neighbor would still be chosen in spite of the criterion
because other nearest neighbors also had low absorption strengths.
The categories and lines in each are enumerated in Table 4.2.

The special cases are marked with an asterisk. For example,
for P(10) $\Delta \nu_n = 0.0032$, but the absorption strength $s^0 = .01$, whereas
the next nearest neighbor $\Delta \nu_n = 0.0428$ along with a strength of $s^0 = .15$,
and so it is chosen. Typical curves for each category are given in
Figs. 4.5 - 4.7.
Figure 4.5 Plot of normalized extinction coefficient, $k_\nu/k_\nu(1\text{ atm})$, as a function of ozone partial pressure for the P(8) CO$_2$ line: (a) theoretical curve using nearest neighbor ozone line only; (b) theoretical curve using neighbors listed in Table 4.1 and experimental points. Temperature=22\degree C,
Figure 4.6 Plot of normalized extinction coefficient, $k_y/k_y (1 \text{ atm})$, as a function of ozone partial pressure for the P(30) CO$_2$ line:

(a) theoretical curve using nearest neighbor ozone line only;
(b) theoretical curve using neighbors listed in Table 4.1 and experimental points. Temperature is 22°C.
Figure 4.7: Plot of normalized extinction coefficient, $k_y/k_y(1\text{atm})$, as a function of ozone partial pressure for the $\mathcal{P}(14)\text{ CO}_2$ line: (a) theoretical curve using nearest neighbor ozone line only; (b) theoretical curve using neighbors listed in Table 4.1 and experimental points. Temperature is 22°C.
TABLE 4.2 Categories and Lines

$\Delta \nu_n < .001 \text{ cm}^{-1}$

$0.001 \text{ cm}^{-1} < \Delta \nu_n$

$\Delta \nu_n > .01 \text{ cm}^{-1}$

and

$\Delta \nu_n < .01 \text{ cm}^{-1}$

<table>
<thead>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P(14)$</td>
<td>$P(16)$</td>
<td>$P(18)$</td>
<td>$P(20)$</td>
<td>$P(22)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
A theoretical variation of $k(\nu)_p / K(\nu)_{1 \text{ atm}}$ was generated for each laser line using the theory described in Chapter 3 with numerical values from Refs [46] and [47]. This was done first using only the nearest neighbor ozone line and then the neighboring lines listed in Table 4.1. The results of these calculations are shown in Figs. 4.5 - 4.7. In the calculations using only the nearest neighbor ozone line, the discrepancy between experimental data and theory is quite large. This again illustrates the hypothesis advanced earlier that neighboring lines within $\pm 0.1 \text{ cm}^{-1}$ have a significant effect on total absorption even when the match between laser lines and nearest gas absorption line is quite close, as in the case of P(8). When lines within $\pm 1 \text{ cm}^{-1}$ are included in calculations, the agreement between theory and experiment is quite good.

As seen in Figs. 4.5 - 4.7, when the pressure is reduced, the discrepancy between the nearest neighbor curve and the multiline curve is reduced. The number of ozone lines contributing to the absorption of a CO$_2$ laser line depends on the frequency separation of the ozone lines and on the Lorentz-half-width $\gamma_L$ (which is $\approx 0.08 \text{ cm}^{-1}$ at 1 atm). Since $\gamma_L$ decreases approximately linearly with pressure, the ozone lines farthest from the laser line will, in sequence, become less important, and the nearest neighbor and multiline calculations must merge at low pressures. It should be noted that despite an uncertainty of approximately 0.003 cm$^{-1}$ in each laser line, only the frequency corresponding to the center of the appropriate rotation line was used in the calculation of $k(\nu)_p$. This simplifying process did not affect the validity of the
theory for the case of significant frequency mismatch of laser and ozone lines. Even for the case of closely matched lines, such as P(8) or P(12), the error due to neglecting the finite spread of the laser line would only be noticeable at \( p < 0.1 \text{ atm} \). However, the decreasing accuracy in the experimental determination of \( k(\nu)_p \) at pressures below 0.1 atm may prevent one from making this observation.

4.4 Discussion

For all fifteen laser frequencies considered here, \( k(\nu)_p \) was found to decrease monotonically with decreasing pressure. In the theoretical framework of collision and Doppler broadenings, the variation of \( k(\nu)_p \) at high pressures can be interpreted primarily in terms of the changes in Lorentz half-width \( \gamma_L \) and in the partial pressures of the gases. Should the absorption of a laser line be due to a very closely matched ozone line alone, \( k(\nu) \) would not decrease much with decreasing \( p \) until the onset of the Doppler broadening. This behaviour is shown in the calculated nearest-neighbor-only curve for P(8) in Fig. 4.5. On the other hand, should the absorption be mainly due to some poorly matched ozone lines, \( k(\nu) \) would drop very rapidly as \( p \) decreases. This is illustrated in Fig. 4.7 for the single nearest neighbor curve of P(14).

The three categories depicted in Figs. 4.5 - 4.7 each show a characteristic curve shape with pressure. For the category of a closely matched laser-ozone-line pair as in Fig. 4.5 for P(8), the sign of \( \frac{d^2k(\nu)}{dp^2} \) changes from negative to positive and then negative as \( p \) gradually decreases over the whole pressure range used. The
reason for this is, of course, the contribution due to the two other nearest neighbors \( \Delta \nu_n = 0.008 \text{ cm}^{-1} \) and \( \Delta \nu_n = 0.071 \text{ cm}^{-1} \), which have strengths greater than the nearest neighbor \( \Delta \nu_n = 0.0002 \text{ cm}^{-1} \). The second category \( (0.001 \text{ cm}^{-1} < \Delta \nu_n < 0.01 \text{ cm}^{-1}) \) yields curves that are similar to the category of closely matched lines, but the effect on \( k(v) \) due to the larger frequency mismatch is readily noticeable. A frequency mismatch of \(-0.01 \text{ cm}^{-1}\) is not small enough to overcome the narrowing of the Lorentz half-width, but not large enough to cause a rapid decrease of \( k(v) \) at low pressures. For either P(30) or P(34), the laser line is evenly sandwiched between its two nearest ozone lines. This coincidence helps to maintain their marginal contributions to \( k(v) \) even at lower pressures. In the final category of a large mismatch \( (\Delta \nu_n > 0.01 \text{ cm}^{-1}) \) as in Fig. 4.7 for P(14), the sign of \( d^2 k(v) / dp^2 \) changes from negative to positive as \( p \) decreases. For each laser line in this category, the frequency mismatch is large enough to cause a rapid decrease with reduced pressure. It is interesting to note that the absorption coefficient for P(14) at \( p = 1 \text{ atm} \) (see Fig. 4.3) is comparable to P(8) or P(12) where \( \Delta \nu_n < 0.001 \text{ cm}^{-1} \). Again this supports the argument that absorption lines of any gas species within ± 0.1 cm\(^{-1}\) of the laser line will contribute significantly to the absorption process provided their intensities are not more than one order of magnitude below that of the main gas line being scrutinized.
CHAPTER 5

RESONANCE ABSORPTION MEASUREMENTS WITH A FIXED-FREQUENCY LASER: SPECTROSCOPIC DATA FOR POLLUTION MONITORING

5.1 Introduction

In Chapter 4 the matching between the line-tunable CO₂ laser and the ozone absorption lines was explored to establish some useful criteria for air pollution monitoring via the direct absorption scheme employing a fixed-frequency laser. This was achieved mainly because of the fact that, all the required knowledge about the laser line positions, and the individual pollutant gas absorption line parameters are well known to the desired accuracy. However, in the case where accurate values of the absorption line parameters, or a tunable laser with its calibration method are not available, the line-tunable laser with very accurately measured transition frequencies, can be employed to estimate the position, strength, and width of the nearest absorption line to a particular laser emission line with enough accuracy to perform studies or monitoring at atmospheric pressure.

In this Chapter, a line-tunable CO₂ laser is employed to carry out laboratory measurements of NO absorption in a White cell. This laser is tunable in the sense that a diffraction grating is used for selecting discrete CO₂ laser frequencies. Absorption by NO is observed on seventeen CO₂ laser transitions. The absorption coefficients
of these transitions are determined by measuring the transmission when the White cell was evacuated (or filled with pure N₂) and when filled with an appropriate NO - N₂ mixture. The separation \( (\Delta \nu) \) between each CO and relevant absorbing NO transition, the pressure broadening parameter \( (\gamma_L^0) \), and the integrated absorption \( (S^0) \) for the seventeen lines are determined by matching the experimental data to the theoretical calculation.

5.2 Theory

The theory is similar to that used for Chapter 4, and described in Chapter 3. The absorption coefficient for NO is evaluated using

\[
\alpha(\nu) = \frac{k(\nu)}{P_{NO}}
\]  

(5.1)

where \( P_{NO} \) is the partial pressure of NO in the mixture.

The NO molecule is a simple molecule which has an odd number of electrons and a non-zero electron angular momentum. The electronic orbital and spin angular momenta are strongly coupled to give a total electron angular momentum of either 1/2 or 3/2. The electronic ground state is actually a doublet, and the substates, classified as \( ^2\Pi_{1/2} \) and \( ^2\Pi_{3/2} \) are separated by a spin orbit splitting of about 124 cm\(^{-1} \) [49]. The ir band of NO consists of two superimposed sub-bands, one associated with each ground substate. The rotational energies of these two substates can be represented by using different effective rotational constants for each substate; the conventional rotational constants of the molecule are just the average of the effective constants. The vibrational
constants are not as well established, and there is disagreement between the various published values [50-52]. These values are adequate for this technique, where it is only necessary to obtain reasonably accurate parameters for the target gas (NO). The wave-numbers are calculated using the approach outlined in Ref. [53]. This allows identification of relevant absorbing lines and provides a starting point for comparison between theory and experiment.

Individual line strengths are calculated using

$$S_{v,J} = S_1 H(v, J)$$  \hspace{1cm} (5.2)$$

which is derived from Ref. [53]. Here $S_1$ is the fundamental band strength of NO, and $H(v, J)$ is the appropriate weighting function of the transition. The fundamental band strength $S_1$ may be calculated using

$$\alpha(v) = S_1 H(v, J) \ f(v-v_0) / p_{NO}.$$  \hspace{1cm} (5.3)$$

derived from Eqs. 5.2, and 5.3.

5.3 Experimental

The instrumentation and alignment techniques used are identical to those described in Chapter 4, except that the liquid-nitrogen-cooled CO plasma tube was employed in the Molecron model C250 laser. Oscillation was observed on approximately fifty transitions in the 5.16 -
5.6 μm range. Significant absorption was observed on seventeen of these.

Measurements were carried out employing a 934 ppm (by volume) NO in N$_2$ mixture supplied by Matheson. This was diluted with high-purity N$_2$ as required. As a check on reliability, all measurements were repeated using a different cylinder (93.5 ppm) obtained from AIRCO.

5.4 Data Analysis and Results

The transmission $T(\nu)$ and the absorption coefficient $\alpha(\nu)$ were evaluated using Eqs. (4.2) and (5.1), respectively. Values of $\alpha(\nu)$ for the seventeen lines, shown in Fig. 5.1, are based on measurements taken at 1 atm total NO-N$_2$ pressure. Also shown in Fig. 5.1 are the two values obtained by Chackerian and Weisbach [54]. Despite some differences in experimental approach (the nitric oxide was placed in an intralaser-cavity absorption cell), the absorption coefficients obtained in the two cases are in reasonably good agreement.

Absorption measurements were also made using total gas pressures ranging from 20 Torr to 760 Torr. The following procedure was employed to give theoretical fit to the measured absorption coefficients. The separation of the NO lines [R(1.5)$_{1/2}$ and R(1.5)$_{3/2}$] from the CO-laser line [P(13) 9-8 band] are known to high precision [55] and consequently were taken as reference separations. These reference separations were used to determine the pressure broadening parameter ($\gamma^0_L$) by matching the theoretical and experimental normalized extinction coefficients. This normalization procedure avoids the need to know the individual line strengths. Data were taken over a range of pressures and were fitted
by using the least squares technique. Results of this procedure are
displayed as curve b in Fig. 5.2 and yield a value of $\gamma^o_L = 0.052 \pm$
0.002 cm$^{-1}$ atm$^{-1}$. Note that the quoted error represents the limit for
which there is no significant deviation in the fit between measure-
ment and theory. The two other plots depicted in Fig. 5.2 correspond
to a best fit of the theory presented earlier to the experimental data
obtained for the $R(6.5)_{1/2}$ and $R(18.5)_{3/2}$ lines of NO. The three
plots shown in the figure are representative of the types of variation
of the extinction coefficient with pressure observed on the remaining
lines. Curve a is typical of the variation obtained when the absorbing
NO line and the CO laser wavelength are close to coincidence; curves
b and c correspond to increasing separation between the laser wave-
length and molecular resonance line. The best fits between experi-
mental observation and the theoretical model illustrated in plots a
and c, and those for all other absorbing transitions, were obtained
as follows. The parameter $\gamma^o_L$ was initially assumed to have the value
$\gamma^o_L = 0.052$ cm$^{-1}$ atm$^{-1}$ determined above. Next, $\Delta v$ (separation between
the NO and appropriate CO transitions) was adjusted until the best fit
was obtained between theory and experiment. Finally, the procedure was
repeated for small changes in $\gamma^o_L$. Both $\Delta v$ and $\gamma^o_L$ were determined
from the one curve giving the best fit to the experimental data.
Results for the values of $\Delta v$ and $\gamma^o_L$ obtained in this way were presented
in Tables 5.1 and 5.2 respectively. For purposes of comparison values
deduced from NO measurements by other workers are also displayed. The
CO laser wavenumbers required for this have been measured directly
using harmonic mixing techniques, and so they are known to high
precision [56].

In general, the present results for Δν are in reasonably good agreement with the more recent experimental work [57] and with the calculated values [58]. The latter values of Δν were found from a new compilation of NO transition wavenumber obtained by fitting the molecular constants to the best available data. The generally good agreement between the values of Δν deduced from our experiment and those determined from Johns' NO wavenumbers has motivated to the interpretation of the experimental data in an alternate fashion. The values of Δν determined from Johns' work were taken to be correct. The best fit between theory and experiment was carried out by variation of the pressure-broadening parameter (γ_L^o) alone. In this way, the values of γ_L^o have been determined to an accuracy limited mainly by the precision of the wavelength data for the NO lines. The set of values of γ_L^o so determined, as well as those determined by the previous approach, is given in Table 5.2 [(11) and (1), respectively]. The agreement obtained between the line broadening parameters determined by the two methods for treating the data is moderately good in most cases. However, for the line designated as R(12.5)_1/2 (using the Johns' NO wavelength tabulation), it was not possible to obtain a fit between theory and experiment for any reasonable line-broadening parameter. This indicates that the predicted position of this particular NO line is significantly in error. In a more general way, there is a lack of obvious correlation between the γ_L^o values obtained using the fixed Δν approach and molecular state angular momenta. This is some
indication that the present accuracy of the wavelength data for the NO lines is not sufficient to give high-precision values of \( \gamma_L \). Better values for these parameters are expected from the present experimental data when more accurate values of the target gas resonance lines become available. However, a different technique, which is proved to be very accurate, is achieved and will be described in Chapter 6.

The measurements of extinction coefficient as a function of pressure were normalized to the values observed at atmospheric pressure before fitting to the theory. The value of the extinction coefficients, together with a knowledge of the partial pressure of NO, allows the various line strengths to be calculated using Eq. (5.3). Figure 5.3 is a plot of the line strengths obtained in this way against wavenumber. Also shown are experimental values from Abels and Shaw [59] and the relative variation of the line strength expected theoretically (using the computer program package described in Chapter 2). The theory has been normalized to agree with the experimentally determined band strength. As can be seen, the agreement between experiment and theory is very good. The value of the band strength obtained is given in Table 5.3, which also shows a sampling of values obtained by other investigators. The agreement with the earliest and more recently, reported measurement is good.
Figure 5.1 Absorption of the seventeen CO laser wavelengths. Present measurements are represented by ●; those of Chackerian and Weisbach[54] by ○.
Figure 5.2 Typical best fit data for the normalized extinction coefficient. The plotted points are experimental, the solid curves theoretical. Curve b represents the combined R(1,5)\(1/2\) and R(1,5)\(3/2\) NO absorption. Curves a and c represent the R(18,5)\(3/2\) and R(6,5)\(1/2\) NO absorption, respectively.
Figure 5.3 NO strengths at 300 K. The solid line is based on suitably normalized values from Johns[58]. Present data points are represented by O; those of Abels and Shaw[59] by ▲.
TABLE 5.1  Different $\Delta \nu_n$ Values Between Selected CO Laser Lines and the Nearest NO line (in cm$^{-1}$)

| CO line (cm$^{-1}$) | NO line | Hakuta$^5_5$Vehara (obs.) | Johns (calc.)$^a$ $\Delta \nu_n$ [58] | This work (obs.) $|\Delta \nu_n|$ |
|--------------------|---------|--------------------------|--------------------------------------|-------------------------------|
| 1935.4818          | R(18.5) $3/2$ | --                       | -0.016                              | 0.014                         |
| 1931.6929          | R(17.5) $1/2$ | --                       | -0.037                              | 0.061                         |
| 1927.2959          | R(15.5) $3/2$ | --                       | +0.019                              | 0.045                         |
| 1917.8611          | R(12.5) $1/2$ | --                       | -0.008                              | 0.032                         |
| 1909.8776          | R(9.5) $3/2$  | --                       | +0.094                              | 0.074                         |
| 1900.0427          | R(6.5) $1/2$  | --                       | -0.034                              | 0.042                         |
| 1884.3492          | R(1.5) $1/2$  | --                       | +0.049                              | 0.044                         |
| 1884.3492          | R(1.5) $3/2$  | 0.0280$^b$               | +0.026                              | 0.026                         |
| 1874.4517          | Q(9.5) $3/2$  | --                       | +0.026                              | 0.041                         |
| 1870.6135          | Q(17.5) $3/2$ | --                       | -0.072                              | 0.077                         |
| 1863.6344          | P(3.5) $3/2$  | 0.0484$^b$               | -0.049                              | 0.047                         |
| 1860.1468          | P(4.5) $3/2$  | 0.0274$^b$               | +0.028                              | 0.04                           |
| 1856.4449          | P(5.5) $3/2$  | --                       | -0.074                              | 0.072                         |
| 1842.8159          | P(9.5) $1/2$  | --                       | -0.115                              | 0.079                         |
| 1841.8411          | P(9.5) $3/2$  | --                       | +0.065                              | 0.061                         |
| 1830.4125          | P(12.5) $3/2$ | --                       | +0.048                              | 0.052                         |
| 1812.7522          | P(17.5) $1/2$ | --                       | +0.116                              | 0.076                         |
| 1794.4241          | P(21.5) $3/2$ | --                       | +0.064                              | 0.061                         |

$^a$ The calculated difference is for the average value of the two $\Lambda$-doubled components.

$^b$ Measurements obtained from laser magnetic resonance spectroscopy.
TABLE 5.2 Experimental Halfwidths (HWHM) \( \gamma_L^0 \) at 300°K (in cm\(^{-1}\) atm\(^{-1}\))

<table>
<thead>
<tr>
<th>NO line</th>
<th>Abels and Shaw [59]</th>
<th>Richton [60]</th>
<th>Present work (1)</th>
<th>Present work (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(18.5)(3/2)</td>
<td>0.050</td>
<td>0.053</td>
<td>0.055</td>
<td></td>
</tr>
<tr>
<td>R(17.5)(1/2)</td>
<td>0.041</td>
<td>0.051</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>R(15.5)(3/2)</td>
<td>0.056</td>
<td>0.048</td>
<td>0.065</td>
<td></td>
</tr>
<tr>
<td>R(12.5)(1/2)</td>
<td>0.058</td>
<td>0.047</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>R(9.5)(1/2)</td>
<td>0.058</td>
<td>0.054</td>
<td>0.043</td>
<td></td>
</tr>
<tr>
<td>R(6.5)(1/2)</td>
<td>0.058</td>
<td>0.051(^a)</td>
<td>0.050</td>
<td>0.066</td>
</tr>
<tr>
<td>R(1.5)(1/2)</td>
<td>--</td>
<td>0.058(^a)</td>
<td>0.050</td>
<td>0.052</td>
</tr>
<tr>
<td>R(1.5)(3/2)</td>
<td>--</td>
<td>--</td>
<td>0.050</td>
<td>0.052</td>
</tr>
<tr>
<td>Q(9.5)(3/2)</td>
<td>--</td>
<td>--</td>
<td>0.050</td>
<td>0.062</td>
</tr>
<tr>
<td>Q(17.5)(3/2)</td>
<td>--</td>
<td>--</td>
<td>0.054</td>
<td>0.066</td>
</tr>
<tr>
<td>P(3.5)(3/2)</td>
<td>0.055</td>
<td>0.050</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>P(4.5)(3/2)</td>
<td>0.059</td>
<td>0.051</td>
<td>0.065</td>
<td></td>
</tr>
<tr>
<td>P(5.5)(3/2)</td>
<td>0.058</td>
<td>0.049</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>P(9.5)(1/2)</td>
<td>0.058</td>
<td>0.052</td>
<td>0.062</td>
<td></td>
</tr>
<tr>
<td>P(9.5)(3/2)</td>
<td>0.059</td>
<td>0.05</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>P(12.5)(3/2)</td>
<td>0.057</td>
<td>0.05</td>
<td>0.061</td>
<td></td>
</tr>
<tr>
<td>P(17.5)(1/2)</td>
<td>0.061</td>
<td>0.05</td>
<td>0.062</td>
<td></td>
</tr>
<tr>
<td>P(21.5)(3/2)</td>
<td>--</td>
<td>0.049</td>
<td>0.051</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Assuming the values in Ref.[60] are quoted for the full widths.
<table>
<thead>
<tr>
<th>Investigator(s)</th>
<th>Band Strength cm$^{-2}$ atm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Havens (1938)</td>
<td>121</td>
</tr>
<tr>
<td>Dinmore and Crawford (1949)</td>
<td>145 ±29</td>
</tr>
<tr>
<td>Penner and Weber (1953)</td>
<td>70 ±7</td>
</tr>
<tr>
<td>Vincent - Geisse (1954)</td>
<td>82</td>
</tr>
<tr>
<td>Schurin and Clough (1963)</td>
<td>111 ±7</td>
</tr>
<tr>
<td>James (1964)</td>
<td>138 ±6</td>
</tr>
<tr>
<td>Breeze and Ferriso (1964)</td>
<td>76 ±7</td>
</tr>
<tr>
<td>Fukuda (1965)</td>
<td>70 -77</td>
</tr>
<tr>
<td>Ford and Shaw (1965)</td>
<td>115 ±9</td>
</tr>
<tr>
<td>Abels and Shaw (1966)$^5$</td>
<td>122 ±6</td>
</tr>
<tr>
<td>Varanasi and Penner (1967)$^{61}$</td>
<td>128 ±10</td>
</tr>
<tr>
<td>Present Study (1976)</td>
<td>124 ±9</td>
</tr>
</tbody>
</table>

**Note:** The first nine values are taken from Varanasi and Penner [61] and are referenced therein.
CHAPTER 6

RESONANCE ABSORPTION MEASUREMENTS
WITH TUNABLE SEMICONDUCTOR DIODE LASERS:
HIGH RESOLUTION SPECTROSCOPIC TECHNIQUE

6.1 Introduction

The development of tunable lasers with emission between 1 and 30 micrometers has provided spectroscopists with much higher resolution than has been possible in the infrared "fingerprint" region, which is rich in characteristic molecular vibration-rotation lines.

This Chapter describes a developed technique for accurate frequency measurements. Over 100 lines in the \( v_3 \) band of ozone have been measured. These measurements, taken with a laser absorption spectrometer based on a tunable semiconductor diode laser, are accurate within 3-10 MHz. Throughout this series of measurements, only those ozone lines that are important for monitoring instruments based on \( \text{CO}_2 \) lasers, are determined. Hence, measurements of the frequencies, of those reasonably strong ozone lines that lie within 6 GHz of the laser lines in the 9.4 \( \mu \text{m} \) region, have been made. These laser lines include most of the \( ^{12}\text{C}^{16}\text{O}_2 \) lines and, in addition, selected isotopic and sequence lines, particularly those in close coincidence (<300 MHz) with ozone lines. Diode lasers have been used previously to measure some individual absorption lines with accuracies of 15 MHz [62] and to analyze absorption bands with much reduced accuracies [63].
However, this is one of the first reported measurements over an entire absorption band using the full resolution of the tunable diode laser.

Thus far, detection of ozone based on CO$_2$ lasers is discussed in Chapter 4. Such lasers are suitable if long pathlength propagation through the atmosphere is employed. For short pathlengths or for point monitoring of ozone (as will be described in next chapters), tunable diode lasers possess many advantages. For example, a tunable diode laser does not have to rely on chance coincidences between discrete laser lines and target gas absorption lines. An appropriate diode laser can be tuned to the line center of any strong ozone line and to a wavelength region that avoids interference from other atmospheric species, particularly CO$_2$ and water vapor (instruments based on CO$_2$ lasers usually probe the atmosphere at several different frequencies in order to allow for interfering species).

6.2 Experimental Method

Figure 6.1 is a schematic diagram of the laser absorption spectrometer. A PbSnSe diode (Laser Analytics, Inc.) is mounted on the tip of a cold head, which is cooled by a closed-cycle He refrigerator. The diode temperature, which determines the approximate laser emission wavelength, can be set and controlled accurately in the 10-70° K range (employing the technique described in Chapter 2). Fine tuning of the wavelength is obtained by varying the diode current. A 1030-1070 cm$^{-1}$ range was readily available from the diode laser used in the present measurements. The laser output is collected by a 5 cm focal length lens, then chopped at 150 Hz by a mechanical chopper, and finally
focused into the 5 m base-pathlength multiple traversal (White) cell (described in Chapter 4). The output beam from the White cell passes through the 0.5 m spectrometer (to separate the longitudinal modes of the diode) and is then focused onto a HgCdTe, LN$_2$ cooled, detector. A PAR-Lock-in Amplifier Model 126 and an HP (X-Y) recorder model 74004B are used to record the laser power as a function of diode current. As indicated in Fig. 6.1, a germanium etalon (described in Sec. 6.3) can be inserted in the laser beam to provide a series of wavelength calibration fringes. There is also a provision for using the CO$_2$ Molelectron laser discharge tube in the laser beam. This allows one to use gain measurements on selected CO$_2$ sequence lines [64], for example, as a method of obtaining additional reference lines.

Generally, an optical pathlength of 300 m in the White cell was used. Although not essential, such a long pathlength allows the use of low concentrations of ozone. Ozone, generated by flowing air through a simple UV ozone generator, was introduced into the White cell at a reduced pressure (~3 Torr). The ozone concentration in the cell was estimated to be 10 ppm, based on the measured absorption of the strong ozone lines. The diode laser beam passes through this mixture of ozone and air in the White cell, through the 0.5 m scanning spectrometer, and finally onto the detector. The spectrometer serves two functions. Initially, it is used to select a single diode mode in the wavelength region of interest. For example, the spectrometer is set to pass IR radiation at 1053.9 cm$^{-1}$ [i.e., near the P(12) CO$_2$ laser line]. The diode temperature and current are then varied until
maximum detector output is achieved. Finally, a recording is made of absorption vs diode laser current in this wavelength region. The spectrometer now acts as a filter to reject any undesirable laser modes that may be present (these are generally separated by at least 2 cm\(^{-1}\) and, therefore, are easily rejected by a 0.5 m spectrometer).

It is easy to produce high-resolution recordings with a good diode laser. The main problem in high-resolution diode-laser spectroscopy is the accurate calibration of the wavelength scale. The usual procedure is to measure the separation between an unknown absorption line and a known reference line [62, 63]. Fortunately, CO\(_2\) provides numerous reference lines in the 9 μm wavelength region, and these have been measured with extremely high accuracy [65]. The upper traces in Fig. 6.2 show the P(12) CO\(_2\) reference line together with ozone lines obtained by adding a trace of CO\(_2\) to the air-ozone mixture entering the White cell. The high sensitivity of the apparatus also enables one to use isotopic variation of CO\(_2\) to provide additional reference lines. Both the \(^{13}\)C\(^{16}\)O\(_2\) and \(^{16}\)O\(^{12}\)C\(^{18}\)O forms of CO\(_2\) can easily be detected in absorption using a 300 m pathlength in naturally occurring CO\(_2\) (\(\sim 5\) Torr total pressure of CO\(_2\)). The frequencies of these isotopic laser lines have been measured to high accuracy by Freed et al. [66, 67]. In addition, the CO\(_2\) Molecule discharge has been employed to generate the CO\(_2\) sequence lines [68] as further references. As a result, it was very easy to find a CO\(_2\) reference line within 0.4 cm\(^{-1}\) of any ozone line.
Figure 6.1 Schematic diagram of laser absorption spectrometer (LAS). $L_1$ and $L_2$ are the laser output and detector input lenses, respectively.
Figure 6.2 Typical example of data taken with the tunable diode laser. For the upper scans, a mixture of 10 ppm ozone in air, together with a trace of CO₂, flows at 3Torr total pressure through the White cell (300 m pathlength). The lower scans show reference fringes obtained with a germanium etalon.
6.3 **Accuracy of Measurements**

The final step in determining the accurate wavenumber of an ozone line, from data such as shown in Fig. 6.2, is to measure its separation from the reference CO₂ line. For this, an uncoated solid germanium etalon was employed, this solid germanium was nominally 7.650 cm long with a finesse of approximately 3. The etalon was placed in the diode laser beam and provided calibration fringes as shown at the bottom of Fig. 6.2. The separation between a pair of absorption lines was measured by counting the number of etalon fringes. The main aim was to measure the ozone line frequencies to an accuracy of better than 10 MHz, which corresponds to less than two hundredths of an etalon fringe. Care in etalon stabilization and systematic checking of the apparatus were, therefore, required.

First the stability of the laser, detector, and X-Y recorder were evaluated by comparing many successive traces of the type shown at the top of Fig. 6.2 or in Fig. 6.3. A comparison of the positions of the absorption lines on successive traces showed that the maximum uncertainty in the line was less than 3 MHz over a period of about an hour. Chapter 2 contains a different experiment to evaluate the laser stability (see Fig. 2.11). Next, the etalon stability was checked. Initially, it was found that thermal changes cause the fringes to drift as much as half a fringe (i.e., 240 MHz) from scan-to-scan. This corresponds to a 0.08°K temperature change, based on calculations using the data in Edvin et al. [69]. Consequently, the etalon was enclosed within a heavy copper cylinder whose temperature
was stabilized by flowing water from a temperature controller through the cylinder walls. This resulted in a random shift of \( \sim 0.05 \) fringes in periods of up to an hour, corresponding to the average etalon temperature remaining constant to better than \( 0.008^\circ \) K. The very good reproducibility enabled the measurement of absorption lines and then etalon fringes on successive scans with negligible loss of accuracy. Figure 6.3 illustrates the scan of a reference \( \text{CO}_2 \) line in gain, an ozone absorption line, and the etalon fringes, using a single diode-laser beam. Note that the use of successive scans enables the placement of the etalon in the diode-laser beam before it enters the spectrometer. Placing the etalon after the spectrometer in a two-beam system can lead to errors due to a changing angle of incidence at the etalon as the diode wavelength is changed [62, 70]. A recent publication [71] describes a technique for the simultaneous recording of both the spectrum and the etalon fringes. This technique, which avoids errors due to changing angle of incidence, requires additional instrumentation but does not require such a high degree of stability from scan-to-scan.

The usual measurement procedure was to take several recorder scans with ozone or \( \text{CO}_2 \) in the White cell, then several scans with the cell evacuated and the etalon in the beam. Finally, the initial scans were repeated as a check of stability. The scans were carefully measured by hand, with an estimated accuracy of 0.01–0.02 fringes (depending on the quality of the lines). This accuracy is based on the reproducibility of many successive measurements. To check for
systematic errors, initial series of measurements on CO₂ lines of known separation are made. The results of these measurements are given in Table 6.1. The etalon fringe separation [0.016271 (3) cm⁻¹] was calibrated by measuring the number of fringes between the P(16) and P(14) laser lines of $^{12}C^{16}O_2$ using a single diode-laser mode. The agreement between the present measurements and the values calculated from heterodyne data is very good, particularly as the available frequency measurements on the $^{13}C^{16}O_2$ isotope lines and the 0002 sequence lines may be in error by a few megahertz [56, 68]. Based on the above agreement and on the reproducibility of the measurements, the accuracy was estimated to range from ±3 MHz for very closely separated lines to ±10 MHz for absorption lines separated by about 25 fringes (0.4 cm⁻¹).

It is worthwhile to compare the accuracies using the present relatively simple technique with those obtained using laser heterodyne techniques. Accuracies of ±15 MHz and ±3 MHz have been achieved employing tunable lasers [72] and CO₂ lasers [73], respectively, to determine spectral line centers. The accuracy reported in this work compares favorably with these values. Note that the heterodyne techniques are limited to measurements of absorption lines that lie within a detector bandwidth (~2 GHz) of the reference CO₂ lines [72, 73]. No such limitation exists with the present method.

The accuracy of the present measurements is still limited by residual drifts of the etalon fringes. Better temperature stabilization or the use of an air-spaced actively-locked etalon
will remove this limitation. The estimated accuracy of a tunable
diode laser, in combination with a stabilized etalon, would then be
limited simply by the accuracy with which one can judge the line
center (1-3 MHz). Finally, it should be possible to automate much
of the measurement procedure.

6.4 Results and Discussions

The diode laser used in the present work was operated in the
1030-1070 cm⁻¹ range. By using regular and isotopic forms of CO₂ as
references, frequency measurements of over 100 ozone lines in this
wavenumber region were made. These lines are more than sufficient
for a detailed band analysis of the ν₃ band of ozone; such an analysis
is underway but it is outside the scope of this thesis. Table 6.2 is
a comprehensive list of relatively strong ozone lines that lie close
to the important 9.4 μm laser lines of ¹²C₁₆O₂, to other CO₂ isotopes,
and to the CO₂ sequence lines. These measured lines all lie within
0.4 cm⁻¹ of the appropriate CO₂ lines and usually have intensities
greater than 1 x 10⁻²¹ mole⁻¹ cm⁻¹. The present technique enabled
the measurements of approximately 55% of the lines satisfying these
conditions at the listed CO₂ reference lines. The balance of the lines
was either overlapped, or else the laser power was too low for carrying
out accurate measurements. The listed line strengths are taken from
Barbe et al. [74]. The measured wavenumbers are in good agreement with
Barbe et al. when their experimental uncertainties (up to 0.003 cm⁻¹)
are taken into account.
In the regions covered by the diode laser, it was found that all ozone lines with intensities greater than $1 \times 10^{-21}$ mole$^{-1}$ cm$^{-1}$ (i.e., lines within 1/30th of the line strength of the strongest lines) could be identified with $v_3$ lines listed by Barbe et al. There is no evidence of hot band or isotope lines with significant line strength. This observation agrees with the results of Barbe et al. [74].

The data in Table 6.2 is essential for comparing experimental and theoretical estimates of ozone absorption as a function of pressure (as described in Chapter 4), [75 - 77]. The wavenumbers in this table are also sufficiently accurate to be used with solar heterodyne radiometers in the measurement of both tropospheric and stratospheric ozone. Airborne instruments employing differential absorption based on CO$_2$ lasers require a close coincidence between the ozone line and the CO$_2$ laser line. Such CO$_2$ lines, which are indicated by an asterisk in Table 6.2, include various isotope and sequence lines. Despite the additional complexity in obtaining lasing on the rare isotope or sequence lines of CO$_2$, these may prove more practical for stratospheric monitoring of ozone, as they suffer negligible absorption by atmospheric CO$_2$.

The present sensitivity depends upon the accuracy of the reference lines. All the laser lines have been measured with accuracy better than 1 MHz, however, some absorption lines of particular gases has been measured with moderate accuracies. These measured lines could be used as reference lines to measure the inaccurate absorption lines which are in coincidences. Table 6.3 contains a listing of wavenumbers, and the estimated accuracy, that can be used as reference lines [78].
Figure 6.3 Representative diode scans. For these, the diode laser beam is passed through a CO$_2$ discharge, through an ozone-air mixture in the White cell, and finally through the germanium etalon.
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CHAPTER 7

HIGH SENSITIVITY POINT MONITORING (PM) OF ATMOSPHERIC GASES EMPLOYING TUNABLE DIODE LASERS

7.1 Introduction

Chapters 4 and 5 have been concerned with line-tunable laser sources (CO₂, CO) which were employed to monitor those gases which have absorption lines in close coincidence with the available output wavelength of the lasers [79-82]. Some work on longpath atmospheric absorption has also been reported using tunable diode lasers [10]. Both of these techniques have shown considerable success, but have been somewhat limited in sensitivity. This has resulted in applications being limited to gases which occur naturally at high concentrations. Much greater absorption sensitivities can be attained using acousto-optical techniques [83-85], but the effective pathlength in typical spectrophone cells is less than 1 m. In addition, this approach suffers from interferences from unwanted molecular species, and is somewhat difficult to calibrate [84], [85].

In the present chapter, a laser absorption spectrometer which combines the sensitivity of the acousto-optical methods with the convenience of direct, longpath optical detection is described. The system is exactly the same one described in Chapter 6. With this system, we can detect absorptions with sensitivity of 3 x 10⁻⁸.
This corresponds to concentrations of 1 part per billion (ppb) of a weakly absorbing molecule such as SO₂ (v₁ band), or 3 x 10⁻³ ppb of a strongly absorbing molecule such as CO. This sensitivity, combined with the wavelength tunability of diode lasers, permits trace amounts of almost any gaseous molecular species to be monitored. For example, two diodes have been employed in the present work, which have the capability of detecting ambient levels of many gases commonly found in the atmosphere, such as SO₂, N₂O, H₂O, CO₂ and O₃. Furthermore, the present technique does not suffer from interference from unwanted molecular species, and can be easily calibrated even at the ppb concentration level.

Section 7.2 of this Chapter describes the experimental arrangement, while Section 7.3 explains the modulation techniques used to achieve a high sensitivity. In section 7.4 the applications of the present system to detect O₃, NH₃, and SO₂ in the atmosphere are demonstrated.

7.2 Experimental Apparatus

The apparatus employed is illustrated schematically in Fig. 7.1, and is described in detail in Chapter 6. For point monitoring, two important modifications have been made. In the first modification, in addition to the drive current supplied to the diode, a small high-frequency current modulation is superimposed. This results in a high-frequency modulation (kHz range) of the diode wavelength and it is this modulation which enables us to achieve such high sensitivity. The
second modification involves splitting off a portion of the diode laser beam and directing it to a second HgCdTe detector (Detector B in Fig. 7.1). This second beam is used to lock the laser wavelength to the molecular absorption line under investigation. The first diode laser used for the measurements is a Pb_1-xSn_xSe diode supplied by Laser Analytics, (1% Sn) which was selected to give an output covering the range 1050 cm\(^{-1}\) to 1150 cm\(^{-1}\), which spans the \(\nu_1\) absorption band of SO\(_2\). The second diode is the same one as in Chapter 6 which spans the \(\nu_3\) absorption band of O\(_3\).

7.3 Experimental Technique

The first step in attaining the high sensitivity detection of any gas is to determine an operating region in which the laser operates in a single mode, and tunes through several strong absorption lines of the gas under investigation. Accordingly, this gas is placed into the 5 m base White cell if it is available in low concentration (e.g., SO\(_2\) source gas employed was supplied by Matheson with 1% SO\(_2\) in dry nitrogen, and ozone which was generated by uv source to obtain ozone with 10 ppm in air). After the gas sample was placed into the laser beam a search was made for strong absorption lines. Using the spectrum available in the literature as a guide, we were able to find several strong lines for each gas. For SO\(_2\), we employed the first diode, a relatively strong concentration of SO\(_2\) is placed in the 5 m White cell, and scanned those wavelength regions covered by the diode laser. The
Figure 7.1 Schematic diagram of the Laser Absorption Spectrometer.
gas sample was introduced at a pressure $p = 10$ Torr and pathlength $L = 60$ m. This mixture produces $\sim 80\%$ absorption on the stronger $SO_2$ lines, as can be seen in Fig. 7.2. The lower trace was obtained from experimental results using conventional detection techniques. The diode laser beam was chopped at 150 Hz and synchronously detected by the HgCdTe detector (A in Fig. 7.1) and a lock-in amplifier. The diode wavelength was tuned over $\sim 1$ cm$^{-1}$ using a combination of temperature and current tuning. Throughout this wavenumber region, the diode was operated in a single mode, thus eliminating the need for a mode-selecting monochromator. The resolution of the diode laser is much less than a Doppler width, but a major problem with all diode-laser spectroscopy is to obtain absolute wavenumber calibration. To some extent we were able to overcome this problem, by using as our reference the accurately-known wavenumbers of several absorption lines of $N_2O$ which lie in this region [26]. We are able to estimate the wavenumbers, $\nu$, of the $SO_2$ lines in Fig. 7.2 to better than 0.01 cm$^{-1}$. This enables us to make an accurate comparison with the theoretical predictions of [26] shown in the upper half of Fig. 7.2. In general, the agreement is good, with the predicted wavenumbers rarely being more than 0.01 cm$^{-1}$ different from the experimental measurements. The experimental intensities also agree with the theoretical predictions to better than 20% on the strong lines. Observe, however, that many weak $SO_2$ absorption lines (a few are indicated by *) which are obtained experimentally, are not predicted from the theoretical compilation. Some of these weak $SO_2$
lines were confirmed to relate to $^{34}\text{S}^{16}\text{O}_2$ isotope and the first hot band of $^{32}\text{S}^{16}\text{O}_2$. This was achieved by using our computer package to generate the whole spectrum of $^{32}\text{S}^{16}\text{O}_2$ and its isotopic species employing the molecular constants in Ref. [33]. Experimentally (and theoretically), the two strong lines near 1142.0 cm$^{-1}$ were found to be amongst the strongest in the band (indicated by R). They were therefore selected for more detailed study and for SO$_2$ detection.

For NH$_3$, we employed the same diode laser, which was used in defining SO$_2$. A 10 cm$^3$ sample cell containing pure ammonia at pressure $p < 1$ Torr was introduced into the laser beam, and a search was made for strong absorption lines. Using the spectrum compiled by F. W. Taylor [87] as a guide, we were able to find several strong lines near 1140 cm$^{-1}$, as shown in Fig. 7.3. For this data the diode wavenumber is tuned by varying the current, the laser beam is chopped, and conventional amplitude detection is employed. For O$_3$, we employed the same diode which was used in ozone high resolution spectroscopy (Chapter 6). We chose to operate the diode laser in the 1052 cm$^{-1}$ region where it was single mode, and tuned through several strong absorption ozone lines. The upper trace of Fig. 7.4 is a scan of a relatively high concentration of ozone (using the same technique as in Chapter 6), taken with the chopper in the laser beam, and employing conventional amplitude detection. The chopper was then removed from the system and a small frequency modulation was superimposed on the diode current ramp. Next, the detector signal is synchronously detected at the modulation frequency. Figure 7.4 (lower scan) shows
the recorded second harmonic signal. This second harmonic technique results in a substantial reduction in noise as described by Reid et al. [75], and enables us to detect absorption coefficients with sensitivity as high as $3 \times 10^{-8} \text{ m}^{-1}$ [77].

7.4 \( \text{O}_3 \) Detection and Results

Ambient ozone levels in air are detected by scanning at high sensitivity. For our measurements, air from above the roof of the laboratory building was passed through the White cell at reduced pressure ($p = 20$ Torr), and the diode laser scanned over the same wavenumber region as in Fig. 7.4. The data is shown in Fig. 7.5 where four strong ozone lines can be clearly seen, as well as several additional lines. The very strong line at 1052.196 cm\(^{-1}\) is easily identified as the P(14) line of CO\(_2\). One of the other additional lines is probably the $^{3}S_5 \rightarrow ^{3}P_4$ line of HDO, listed at 1052.144 cm\(^{-1}\) on the AFCRL compilation of [25]. The remaining two lines are caused by some unidentified constituent of the air above our laboratory.

Figure 7.5 clearly illustrates one of the problems of using CO\(_2\) lasers for differential absorption measurements to monitor atmospheric ozone. If the P(14) CO\(_2\) line is used as a probe, most of the atmospheric absorption of the laser beam will be caused by the atmospheric CO\(_2\), with only a small contribution from ozone. There can also be additional interferences from HDO, and possibly from the unknown lines (neither O\(_3\) nor HDO) observed near 1052.0 cm\(^{-1}\). Clearly, a complicated calibration procedure is required to account for such interferences.
Our LAS does not suffer from such complications, as the tuning ability of the diode laser enables us to concentrate on those ozone lines which are free from interferences. For example, to monitor ozone in the air, it is sufficient to scan over one isolated ozone line, as shown in Fig. 7.6A. This scan is taken with a 3 s time constant to improve the signal-to-noise ratio. For comparison, we show in Fig. 7.6B the P(14) CO$_2$ line as observed in air. For the latter, the instrumental sensitivity was reduced by a factor of 20. These lines correspond to A and B in Fig. 7.5. No attempt was made to accurately calibrate the ozone concentrations observed in Fig. 7.5 and 7.6, or to ensure that our samples of air remained uncontaminated by nearby vehicle and air-conditioner exhausts. These scans were simply taken to illustrate the technique and sensitivity. However, one can obtain a reasonable estimate of the ozone concentration by comparing the measured absorption with the known line strength of the observed ozone lines [74]. This procedure gives an ozone concentration of 35 ppb. As a check on this calculation, we compare the measured ozone absorptions directly with the absorption observed on the P(14) CO$_2$ line. If the atmospheric CO$_2$ concentration is assumed to be 330 ppm, we estimate that the ozone concentration is 38 ppb, in good agreement with the previous calculation. It follows that the noise level shown in Fig. 7.6 corresponds to ~0.5 ppb ozone in air.
Figure 7.2 Experimental and theoretical transmission spectra for SO$_2$ in the region 1142 cm$^{-1}$. A pathlength of 60 m is used, with a 1000 ppm mixture of SO$_2$ in N$_2$ at a total pressure of 10 Torr. A few of weak absorption lines (marked by *) which are not predicted by the theoretical compilation of [25].
Figure 7.3 Detection of 10 ppb NH$_3$ in air. A conventional high resolution scan of NH$_3$ near 1140 cm$^{-1}$. Pressure is <1 Torr, and cell length of 10$^3$ cm are used. These are the same lines used in NH$_3$ detection in Fig. 7.7.
Figure 7.4 High-resolution ozone spectrum near 1052 cm\(^{-1}\). The upper scan is taken with conventional amplitude detection; second harmonic detection is employed for the lower scan. A mixture of 10 ppm ozone in air is flowed through the White cell (240m pathlength) at total pressure of 20Torr.
Figure 7.5 Detection of atmospheric ozone. This second harmonic scan is taken over the same wavelength region as in Fig. 7.4 and employed the same pathlength and total pressure. A 1 sec time constant is used. The additional lines are described in the text. The estimated ozone concentration is 33 ppb. Note that line A and line B are repeated in Fig. 7.6 but in different scale, and the instrumental sensitivity is reduced by a factor of 10 for line B.
Figure 7.6 Selected lines from Fig. 7.5 taken under the same conditions, except that the instrumental sensitivity for B is a factor of 20 lower than A. The absorption coefficient of the central ozone line is $5 \times 10^{-6} \text{m}^{-1}$. 
7.5  \( \text{NH}_3 \) Detection and Results

To detect ammonia in the air, one only needs to scan the selected wavenumber region with very high sensitivity. To obtain sufficiently high sensitivity, the diode wavelength has a small 1 KHz frequency modulation superimposed upon it, and the laser beam is passed through the 5 m White cell to provide a total pathlength of 200 m. Figure 7.7 shows the signal obtained at 2 kHz from \( \text{H}_2\text{CdTe} \) detector A, for the same lines in Fig. 7.3. Figure 7.7 clearly illustrates the capability of the system to detect the ammonia in air. There are two additional absorption lines present in this air scan. These were identified as the P(34) (02\(^0\)0 - 00\(^0\)0) and the P(24) D (03\(^1\)0 - 01\(^1\)0) lines of \( \text{N}_2\text{O} \) at 1140.606 cm\(^{-1}\) and 1140.747 cm\(^{-1}\) respectively [25]. Using the calibration procedures outlined in section 7.7, the ammonia concentration in the laboratory was determined to be 10 ppb.

Figure 7.7 displays a very convincing demonstration of the detection of ammonia in air, but there is actually no need to scan over several absorption lines. A single isolated line is sufficient to monitor a given gas. One can then increase the sensitivity by scanning very slowly over a single line, and using a long time constant to reduce noise.

7.6  \( \text{SO}_2 \) Detection Employing a Locking Technique

To ensure that the diode wavelength does not drift during a very slow scan, we have found it convenient to lock the laser wavelength to the relevant absorption line using a beam splitter and the second
HgCdTe detector B. A short cell (Cell 2 in Fig. 7.1) containing pure gas (ammonia or \( \text{SO}_2 \)) at low pressure is placed in this beam, and first harmonic detection is used to give a derivative line-shape. Figure 7.8 shows the first derivative and second derivative of an absorption line. The laser wavelength is then locked to the line center, \( P \), using conventional servo techniques. The wavelength can be scanned by introducing a slow dc ramp into the feed-back loop. This dc shifts the locking point from line center, and allows one to scan slowly from one edge of the line to the other. Another advantage of locking the laser wavelength using a short cell of pure gas is that it confirms the identification of the absorption line being measured in the air. Locking has been carried out on isolated lines in \( \text{NH}_3 \), \( \text{SO}_2 \), and \( \text{N}_2\text{O} \), while monitoring the same absorption lines in air using detector A. Figure 7.9 shows a typical scan when locked to an \( \text{SO}_2 \) line at 1141.91 cm\(^{-1}\). A time constant of 10 s was used for this trace. The noise level corresponds to \( \approx 2 \text{ ppb} \text{ SO}_2 \) or an absorption sensitivity of \( 6 \times 10^{-8} \text{ m}^{-1} \).

It takes several minutes to complete the scan shown in Fig. 7.9. A more effective utilization of this time is simply to lock at point \( P \) and measure the voltage offset, \( s \), from the baseline. In this manner one can conveniently use time constants as long as 100 s, and continuously monitor changing levels of gas concentration. Figure 7.10 is typical of the results obtained. The diode laser is locked to the center of an \( \text{SO}_2 \) absorption line, and the second harmonic signal at detector A is recorded on chart paper as the gas mixture
in the 5 m White cell is varied. The baseline level is obtained by
flowing pure N₂, or simply by evacuating the cell. The system
response is calibrated using a known N₂/SO₂ mixture, and the SO₂
concentration in air can easily be determined as 8 ppb. In Fig. 7.10,
the noise level corresponds to \( \sim 1 \) ppb SO₂, or an absorption sensitivity
of \( \sim 3 \times 10^{-8} \text{ m}^{-1} \). These results are typical of the day-to-day
operation of the instrument. We have monitored atmospheric SO₂
concentrations for periods of several hours at a time, and the diode
laser has been in trouble-free operation for many months. To change
from one gas to another, the diode temperature and current are changed
slightly to shift to the correct wavelength, and the gas in sample cell
2 is changed. N₂O was monitored on the overlapping P(28) (0²O⁰ - 00⁰O)
and P(18) C (03¹O - 01¹O) lines at 1145.334 cm⁻¹ [25] with a sensitivity
of \( \sim 1 \) ppb. The NH₃ lines at 1140 cm⁻¹ are much stronger ir transition
than those of SO₂ or N₂O in the same wavelength region, and the LAS
can detect less than 0.1 ppb NH₃ in air.

7.7 Linearity and Calibration

An important property of any practical pollution monitoring
instrument is that its response should be linear, and that it should
be easily calibrated. The LAS is based on the measurement of optical
absorption, and for the very small optical densities involved, Beer’s
law should ensure linearity of response. Nevertheless, this linearity
was checked under practical conditions. The diode laser was locked to
an SO₂ absorption line, and calibrated SO₂ in N₂ mixtures were passed
through the White cell. The results are shown in Fig. 7.11. The calibrated mixtures were prepared from an 820 ppb SO₂ in N₂ mixture supplied by Airco Industrial Gases. This standard mixture was then diluted with pure N₂ using a carefully calibrated flow-meter system. Within experimental error, the LAS response was linear over the entire range from 20 to 820 ppb. The experimental error was small, being approximately 1 or 2% of the higher concentrations (limited by the resetability of the flowmeters) and ±1 ppb at the lower concentrations. These flowmeter results confirm the linearity of the LAS. The absolute calibration clearly depends on the accuracy and stability of the concentration of SO₂ in the standard mixture. The Airco mixture was supplied in a specially coated aluminum cylinder designed to minimize concentration changes with time and temperature [88]. Nevertheless, SO₂ mixtures in the ppb range are notoriously difficult to prepare and store, and an independent check on the calibration is in order. Fortunately, the system can be directly calibrated for mixtures in the ppb range using high SO₂ concentration mixtures which do not suffer from the same preparation and storage problems. Over an interval of several months, two cylinders of ~1000 parts per million SO₂ in N₂ were obtained from Matheson Gas Products. These mixtures were passed, at the same pressure as in the multi-pass cell, through a 10 cm cell placed in front of the 5 m White cell (cell 1 in Fig. 7.1). With the White cell set for a 160 m pathlength, the system response is equivalent to a mixture of ~625 ppb flowing through the White cell. These results are also indicated in Fig. 7.11.
The very good agreement obtained with mixtures from two different suppliers, and differing in nominal concentration by 3 orders of magnitude, confirms the absolute calibration of the LAS for the monitoring of SO₂. In principle, one could even eliminate the necessity of obtaining calibrated mixtures by making absorption lines in pure SO₂, i.e., the LAS can be entirely calibrated by optical methods.

The usefulness of these calibration techniques were particularly well illustrated when we attempted to measure the concentration of NH₃ in air. Rough calculations based on the results of Fig. 7.7, and the theoretical linestrengths of the NH₃ lines [90], indicated that the measured NH₃ concentration was ~10 ppb. However, the most dilute concentration commercially available was 50 ppm NH₃ in N₂. By using this mixture in cell 1, and setting the White cell to a 200 m pathlength, we were able to simulate a 25 ppb mixture. This calibration enabled us to determine that the local NH₃ concentration fluctuated in the 6 to 8 ppb range. When the system sampled laboratory air, a somewhat higher reading was obtained due to NH₃ given off by laboratory personnel. If anyone stood close to the air intake tube, the NH₃ emitted by the human body would derive the system off scale. No particular care was taken to eliminate such contamination effects from the measurements taken of the local atmosphere. Hence, the true background level may be somewhat lower than 6-8 ppb NH₃.
Figure 7.7 Detection of 10 ppb NH$_3$ in air. Typical results of an LAS scan over the same wavelength region, as in Fig. 7.3, in air. Pathlength is 200m in air at 20 Torr, with a time constant of 3 sec. The air scan contains two additional lines due to N$_2$O. One is indicated at 1140.747 cm$^{-1}$. A second stronger N$_2$O line is coincident with the NH$_3$ line at 1140.606 cm$^{-1}$.
Figure 7.8 Transmission, first, and second derivative assuming Lorentzian line shape; $\gamma_L$ denotes HWHM for the absorption line. $W$ denotes the inflection point location ($W = \pm \gamma/\sqrt{3}$). $P$ is the locking point.
Figure 7.9 Slow scan over the $SO_2$ line at 1141.91 cm$^{-1}$.
Pathlength in air is 200m, at 1 torr pressure, and a time constant of 10 sec is used. All the results are taken by locking at point $P$ and measuring the voltage offset $S$. 
Figure 7.10 A plot of voltage offset $S$ with the diode laser at the center of an $SO_2$ line. Pathlength in the 5m White cell is 160m, and the gas mixture in the cell is varied with time. Under these conditions, the speed of response of the LAS is limited by the 100 sec time constant used with lock-in amplifier A.
Figure 7.11 Linearity and calibration of LAS. The points marked are obtained using a 160m pathlength in mixtures prepared from a standard 820ppb SO$_2$ in N$_2$ mixture supplied by Airco. This standard mixture was then diluted with pure N$_2$ using calibrated flowmeters. The two points marked x correspond to 973ppm and 1123ppm SO$_2$ in N$_2$ mixtures supplied by Matheson. These high concentration mixtures are placed in sample cell 1, with a pathlength of only 9.5cm.
CHAPTER 8

REMOTE LONG-PATHLENGTH STATION
FOR SO₂ DETECTION

8.1 Introduction

The use of a Laser Absorption Spectrometer (LAS), and gas samples at reduced pressures enabled us to detect absorption coefficients, in the laboratory, with sensitivity of \(3 \times 10^{-8} \text{ m}^{-1}\). The performance of the LAS using a shorter White cell has recently been demonstrated, Reid et al [77] obtained a commercial multipass cell (Wilks Variable Long Path Gas Cell) with a single pathlength of 0.75 m, and a capability of pathlengths up to 50 m. This cell was operated with a total pathlength of 40.5 m. Typical results for the detection of SO₂, N₂O, and NH₃ are shown in Fig. 8.1. The Wilks cell is a factor of 7 times shorter in length than the 5 m White cell, and was expected to be a factor of 7 less sensitive. However, it is found that the better mechanical stability of the Wilks cell helps to compensate for the loss of pathlength, and the experimental sensitivity is only reduced by 2. This can be clearly seen by comparing the results for SO₂ in Figs. 7.10 and 8.1. The sensitivity of the LAS using the short Wilks cell is 2.3 ppb of SO₂ or N₂O, and .1 - .2 ppb NH₃. These figures apply to continuous monitoring, (with a 100 S time constant), and to absorption

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Figure 8.1 LAS performance with 40.5 m pathlength in Wilks White cell. The cell is filled successively with pure N₂, air, and pure N₂, at a total pressure of 20 Torr. The diode laser is locked in turn to SO₂, N₂O, and NH₃ lines near 1140 cm⁻¹, and a 100 s time constant is employed.
coefficients sensitivity $10^{-7} \text{ m}^{-1}$. A prototype portable Point Monitoring (PM) instrument which has been designed in the McMaster University Air Pollution Laboratory is now monitoring $\text{SO}_2$ in Hamilton with great success. This instrument permits the gas pressure to be reduced until the Doppler-broadened ir absorption structure is revealed, thereby making possible very high specificity. However, it is difficult to eliminate entirely the problems associated with the PM of reactive gases such as NO and $\text{SO}_2$, which can be changed during the sampling procedure.

In the present Chapter the use of a LAS in remote Long-Path Monitoring (LPM) is described. Although, LPM sensitivity at the present time is not high as in PM, it has several advantages over PM. LPM produces average values for the pollutants concentration over the path. These average values are of greater overall significance in the ambient air analysis than are point values. In addition, the LPM eliminates entirely the problems associated with the sampling procedure. Furthermore, it is more meaningful for regional data than PM, as well as being more economical in manpower and equipment. Generally, however, remote monitoring is not considered to be a substitute for point monitoring, but an adjunct to it. Nevertheless, in some cases remote sensing represents the only economical or technically feasible technique.

The feasibility of remote long-path laser monitoring of atmospheric pollutants by a derivative absorption techniques has recently been demonstrated by Ku et al. [89] and redesigned for
improved performance by Chaney et al [9]. The capability of this technique is limited for simple molecule detection such as CO.

We report here the first remote long-path monitoring technique for SO\textsubscript{2} detection employing a second harmonic resonance absorption scheme. This technique enabled us to detect SO\textsubscript{2} concentrations as low as 50 ppb employing a diode laser emitting in the ν\textsubscript{1} band of SO\textsubscript{2}, and a total pathlength of 1.2 km in the atmosphere which was obtained by using corner cube retroreflectors and an off-axis launching telescope. The basic concept shows promise for measuring SO\textsubscript{2} concentrations as low as 10 ppb in the ν\textsubscript{1} band. This can be achieved by improving the present transmitter-receiver optical system, and the data processing. We also report on absorption data at atmospheric pressure for SO\textsubscript{2}, N\textsubscript{2}O, NH\textsubscript{3}, H\textsubscript{2}O and O\textsubscript{3} in the region 1100 – 1200 cm\textsuperscript{-1}. This data is a useful starting point for designing single- or multi-species LPM systems.

The present Chapter includes theoretical and experimental investigations indicating that additional improvements in sensitivity should result from operating in the ν\textsubscript{3} band of SO\textsubscript{2}. However, greater care is required in this region (1300 – 1400 cm\textsuperscript{-1}) because of interference from atmospheric H\textsubscript{2}O.

8.2 Experimental Apparatus

Figure 8.2 is a schematic diagram of the experimental apparatus; while Fig. 8.3 shows a view of the laboratory optical table. The same PbSnSe diode laser (used in PM of SO\textsubscript{2} in Chapter 7) is mounted on the tip of the cold head (described in Chapter 2). The laser output is
Figure 8.2. Schematic diagram of the LAS used for remote detection.
Figure 8.3  A view of the laser laboratory showing the optical table, and the optical components; (foreground) from the left He-Ne red laser, He piping, the cold head, the spectrometer, and the CO/CO₂ laser head; (background) from the left the launching telescope, the focussing mirror, the beam-splitter, the calibration (10 cm) cell, detector input lens, the detector, and the 5 m White cell. Also showing, on the laboratory wall, the launching hole, and a mirror which may be used to obtain the zero-pollutant reference signal.
collected by a 5 cm focal-length germanium (Ge) lens, and divided into two beams by a Ge beam-splitter. The reflected beam is focussed by a 2.5 cm focal-length Ge lens at the focal point of a launching telescope (off-axis Hardin Optical Co.). The latter has a 12.5 cm clear aperture and employs an off-axis parabola of 63 cm focal-length. One may use a focussing mirror instead of the 2.5 cm focal-length lens. However, we have found that greater care is required for the configuration that employs a focussing lens, because the reflection from the lens back to the beam-splitter results in a large false signal at the signal detector, and may cause fringes to appear as an optical noise, and also because the Ge lens will not be transparent to the visible beam used for the alignment.

Two mirrors (6 mm x 200 x 250 plate glass) are used to send the expanded beam (12 cm dia.) 28 m to the roof of the laboratory; one to direct the beam vertically and one to dodge past existing piping. The beam is confined to a 15 cm stove-pipe for 23 m vertically. A small over pressure in the building causes a flow of air up the pipe. Approximately 13 cm of clear aperture is available.

A third mirror on the roof, of the same type, is used to direct the beam to targets (see Fig. 8.4). This mirror (aiming mirror) can be remotely controlled from the laser laboratory for fine alignments.

Several methods are available for returning the laser beam
Figure 8.4 A view of the laser beam launch station located on the roof of the McMaster University Medical Centre.
towards its origin. We chose corner reflectors, as a target, because they are compact and require no alignment or maintenance, while "Cat's eye" retroreflector systems are large and subject to misalignment. However, for large permanent installations, "Cat's eyes" are best in offering large aperture at low cost, but for experimental work, inexpensive corner cube retroreflectors are quite adequate. Five small corner cubes, each of 5 cm size, obtained from Edmund Scientific are placed beside each other on a wooden plate and mounted in a wooden box. This box was placed on the roof of another building (Arts II) facing the laboratory roof and the aiming mirror. The distance between the aiming mirror and the retroreflector is 590 m (see Fig. 8.5).

To facilitate precise aiming of the IR beam, the roof mirror is rebuilt with electric motors to provide a very fine motion (as shown in Fig. 8.6). The motion is slow, but not so slow as to prevent motions of several degrees. The drive rate, in both axes, for the beam reflected from the mirror, is 42 µ rad/sec. Backlash is about 2.5 µ, and motor stop time is about 1.5 s. The motors are controlled from the laboratory by toggle switches.

Several techniques were conceived and tried out, to find the simplest method of aiming the diode laser IR beam to the distant retroreflector target. A small mirror (1 cm diameter) was placed near the focal point of the launching telescope, away from the beam, and an eye-piece was used to see the image of the target. The He-Ne laser was sent through the beam path and the required adjust-
ment of the optical components on the optical table was made to focus the He-Ne laser beam on the retroreflector image. The beam is returned by the retroreflector along the same path, through the beam-splitter, and then focused on the HgCdTe signal detector. As a part of the alignment, a retroreflector is placed near the telescope and the detector position is adjusted to obtain a maximum signal. If this is done carefully, a retroreflected signal will be detected when the diode laser beam is launched through the atmosphere. The roof mirror is then used to maximize this signal.

8.3 Experimental Technique

The laser beam is chopped mechanically at ~900 Hz, while the drive current to the diode is simultaneously modulated at a higher frequency, \( f = 5 \text{ kHz} \). The output of the detector is fed into two lock-in amplifiers. One of them is for synchronous detection at twice of the modulation frequency (second harmonic detection); while the other is for synchronous detection of the chopped signal. The outputs from the two lock-in amplifiers are fed to a ratio meter to obtain \( \Delta I(v)/I(v) \), where \( I(v) \) is the chopped component and \( \Delta I(v) \) is the frequency-modulated component detected at \( 2f \). These signals are related to the transmitted signal and its second harmonic, respectively. The output of the ratio meter is fed to the Y axis of an X-Y recorder. The X axis signal is proportional to the diode current, hence it is related to the wavelength of the diode power.

The second beam, which is the transmitted part through the
Figure 8.5 Schematic diagram of the launch station on the roof of the laboratory and the retroreflector system on the roof of the Arts Building some 600 m away.
Figure 8.6 A view of the large mirror mount located within the launch station on the roof of the McMaster University Medical Centre. The chain drive to the mirror mount angular alignment adjustment controls can be clearly seen.
beam-splitter, can be focussed into the 0.5 m spectrometer, or into the 5 m White cell. This beam enabled us to perform the measurements described next.

8.3.1 White Cell Experiment: $v_1$ Band Results

The following results were obtained by employing the diode laser emitting in the $v_1$ band of $SO_2$, the 5 m White cell, and gas samples of known concentrations. The first step in the detection of any (absorbing) gas concentration in the atmosphere is to obtain a wavelength region which contains strong absorption lines of the target gas and minimal absorption due to other gases. This was achieved by using the line parameter compilation of Ref. [25] as an input to our computer program to generate the desired transmission spectra in the region $1100 - 1200 \text{ cm}^{-1}$. Some results are shown in Fig. 8.7. Here, the upper curve represents the transmission of $H_2O$ due to 1% of $H_2O$ in air and a total pathlength of $L = 1 \text{ km}$ (i.e., $CL = 1000 \text{ cm}$). The remaining curves represent the normalized absorption coefficients for several important absorbing gases. The maximum value of the absorption coefficient for each gas is given in Table 8.1. Also shown in Table 8.1 is the minimum detectable concentration of each gas in the spectral region $1100 - 1200 \text{ cm}^{-1}$. This concentration is calculated using Eqn. 3.2 and the strongest absorption coefficient value of each gas. It is assumed that a pathlength of 1.2 km is employed, and that an absorption of 0.3% can be measured. Our experience indicates that the latter is a reasonable criterion for a practical monitoring system. Figure
Figure 8.7 A theoretical curve of H$_2$O transmission and absorption coefficients of different gases in the atmosphere. The value of CL (concentration times pathlength) used for generating H$_2$O curve is 1000 cm. These traces with Table 8.1 are used in selecting the optimum wavelength region for gas detection in the presence of the others.
8.7 and Table 8.1 contain sufficient data for determining the optimum spectral region in which to detect a particular gas in the presence of others.

**TABLE 8.1** Minimum detectable concentration of different pollutant gases in the region 1100 - 1200 cm\(^{-1}\) at atmospheric pressure. The results are quoted for a minimum detectable absorption of .3%.

<table>
<thead>
<tr>
<th>Pollutant Gas</th>
<th>Maximum Absorption Coefficient (cm(^{-1}) atm(^{-1}))</th>
<th>Minimum Detectable Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_2)</td>
<td>2.3</td>
<td>10</td>
</tr>
<tr>
<td>O(_3)</td>
<td>.5</td>
<td>50</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>1.2</td>
<td>20</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>52</td>
<td>.5</td>
</tr>
</tbody>
</table>

For SO\(_2\) detection, the spectral region 1160 - 1161 cm\(^{-1}\) has been chosen, where the absorption coefficients of other gases are minimum or approximately constant with the wavelength. In
addition, this spectral region was covered by our diode laser which was operating in a single mode. Figure 8.8 shows typical results of the conventional direct transmission scan of the diode current over the selected spectral region. The four scans A, B, C, and D were taken at total pressure of 10, 100, 400, and 760 Torr, respectively to illustrate the broadening of the absorption lines due to increasing the total pressure. A value of CL = .7 cm was used for all the four scans, where C is the concentration of the SO₂/N₂ mixture introduced into the White cell at a pathlength L. After the operating diode current (which is required to scan the diode over the absorption dip, marked by * in Fig. 8.8) is determined, the synchronous detection is switched to the second harmonic one. It was found that a 100 mA current was required to scan our diode over this absorption dip.

To apply the second harmonic detection technique adequately, the modulation frequency and amplitude must be adjusted for the largest 2f signal and minimum noise for a low concentration of SO₂. This was achieved by introducing 1 Torr from an 973 ppm SO₂ in N₂ mixture, and 759 Torr of dry N₂ supplied by Matheson, into the White cell at 40 m pathlength. This combination of SO₂ concentration and pathlength is equivalent to 43 ppb of SO₂ in 1.2 km. The amplitude of the frequency modulation which is necessary to scan our diode over an absorption line at reduced pressure is ~ 200 mV at f = 3 kHz. In the case of atmospheric pressure, the optimum amplitude of modulation is 3 V, at f = 5 kHz, and near 1160.8 cm⁻¹. This amplitude
Figure 8.8 Typical results of scanning the laser current over the selected region for $\text{SO}_2$ detection ($1160.8 \text{ cm}^{-1}$). A, B, C, and D are taken at 10, 100, 400, and 760 Torr total pressure, respectively. The CL value used for $\text{SO}_2$ mixture is 0.7 cm. Note the region marked by * is the selected region which shows maximum absorption. This region is used for $\text{SO}_2$ detection in the atmosphere.
depends on the width of the absorption dip which may vary for different spectral region.

Since the amplitude of the frequency modulation signal is relatively large, the probability of modulating a curvature portion of the diode laser power is high. This results in a high background (B.G) (i.e., zero-pollutant) signal which is not related to the absorbing pollutant. However, the B.G signal can be measured by scanning the diode current over the same region with the White cell filled with pure N₂, or completely evacuated. We found that the detection sensitivity, depends on how accurate one can produce and measure this zero-pollutant signal and subtract it from the pollutant signal. Figure 8.9 shows the system responses due to 492 ppb, and 246 ppb of SO₂/N₂ mixtures in 1.2 km. Each of these responses is the result of a 2f signal normalization by its chopped signal, and subtraction of its normalized background signal.

During our measurements, two standard SO₂/N₂ mixtures were used: 973 ppm and 1123 ppm of SO₂ in N₂, supplied by Matheson. However, for checking the system linearity, one can employ one standard mixture and change the White cell pathlength to obtain different combinations of CL. From Fig. 8.9, and several measurements which were taken at different CL values, it is found that, the system response is linear and this linearity is valid up to 500 ppb of SO₂ in 1.2 km. This applies only for the spectral region near 1160.8 cm⁻¹ and may not be true for different regions.

According to the above calibration procedure, we have prepared
Figure 8.9 A typical result of the second harmonic signal. The diode laser is scanned over the selected region shown in Fig. 8.8. Scan A is taken with the White cell filled with a mixture of 492 ppb of SO$_2$ in 1.2 km. Scan B is taken after reducing the pathlength used in Scan A by a factor of 2.
two $\text{SO}_2/\text{N}_2$ mixtures in 10 cm short cells; one is equivalent to 83 ppb of $\text{SO}_2$ in 1.2 km, while the other is calibrated to be equivalent to 1 ppm of $\text{SO}_2$ in 1.2 km. Two ratios of the system responses to these concentrations are determined experimentally, and we define:

$$R_1 = \frac{\text{normalized 2f signal due to 1 ppm}}{\text{normalized 2f signal due to 83 ppb}}$$  \hspace{1cm} (8.1)

$$R_2 = \frac{\text{normalized (2f signal due to 1 ppm + B.G.)}}{\text{normalized (2f signal due to 83 ppb + B.G.)}}$$  \hspace{1cm} (8.2)

The above mixtures, along with the calculated ratios ($R_1$ and $R_2$), are used in the adjustment and calibration of the system during the atmospheric measurements.

To check against $\text{H}_2\text{O}$ and other interferences experimentally, the 83 ppb small cell is placed into the beam, and the White cell (at 400 m pathlength) was evacuated and filled with pure $\text{N}_2$. Then the diode current is scanned over the absorption region, and the 2f signal is recorded. After that, the White cell is evacuated and filled with 1 atm of the roof air. This roof air was flowing through two stages in cascade before it enters the White cell: (1) a tube filled with a ground charcoal to absorb the ambient $\text{SO}_2$; (2) a tube contains a small wet cloth to increase the $\text{H}_2\text{O}$ concentration in the White cell. Then the diode current is scanned and the response is recorded again. Typical results of the above measurements are shown in Fig. 8.10. These traces indicate that there are no inter-
Figure 8.10 Check against interference effects: the 4 second harmonic scans are taken by scanning the laser over the SO₂ absorption dip shown in Fig. 8.8 (marked by *). Note that there is no effect due to the air in the selected region (marked by *).
ference effects in the selected absorption region (marked by * in Figs. 8.10 and 8.8).

Finally, as a word of caution, the accuracy of 2f signal measurement depends on how accurate one can adjust the phase on the 2f lock-in amplifier. It was found that this adjustment may be performed at low pressures, which is accurate and easier. Since the phase setting depends only on the frequency of the modulation, it is only necessary to increase the amplitude of the modulation in the case of measurement at atmospheric pressure.

8.3.2 Atmospheric Measurements (ν₁ Band)

All the measurement results reported in the preceding subsection have been achieved by employing the transmitted beam through the beam-splitter (see Fig. 8.2), and the 5 m White cell. Now, for measurements into the atmosphere, we have employed the reflected beam from the beam-splitter. This beam is launched through the atmosphere by the telescope, and returned back (to a signal detector behind the beam-splitter) by a remote retroreflector. The total pathlength into the atmosphere employing the present optical setup is 1.2 km. The returned signal is synchronously detected at twice the modulation frequency by a lock-in amplifier, and at the chopped frequency by another one. Long-term effects due to atmospheric turbulence and scattering unrelated to absorbing molecules are eliminated electronically by rationing the 2f and the chopped signals, since both are proportionately affected by such influences.

A small cell (10 cm long) is placed permanently into the
Figure 8.11 Atmospheric SO\textsubscript{2} measurements: the shown scans are taken by scanning the laser over the region near 1160.8 cm\textsuperscript{-1}. Each trace is the ratio of the 2f signal and the chopped signal. The time constant on the Lock-in amplifier is 10 sec. The estimated detectable limit is 50 ppb of SO\textsubscript{2}. Traces B and C are taken with the instrumental sensitivity increased by a factor of 10.
\[ Y_C = \text{the system response in curve C} \]
\[ = B.G + S_{N_{\text{atm}}} \tag{8.5} \]

where, B.G is the zero-pollutant response (background), and \( S_{N_{\text{atm}}} \) is the response due to atmospheric pollutant \( N_{\text{atm}} \) assuming zero background.

From Eqns (8.3 - 8.5) and 8.1, the minimum detectable SO\(_2\) concentration is given by

\[ N_{\text{min}} = \frac{N_B}{n} \sum_{i=1}^{n} \left( \frac{Y_{A_i}}{Y_{B_i}} - \frac{Y_{C_i}}{Y_{C_i}} - R_1 \right) \tag{8.6} \]

where \( n \) is the number of measurements which have been taken, and \( N_B \) is equal to 83 ppb. The value \( N_B \) depends on \( N_{\text{min}} \) through the relation \( N_B > N_{\text{min}} \). Primary calculations of the SNR indicated that \( N_{\text{min}} = 50 \) ppb, and for this reason, we have chosen \( N_B = 83 \) ppb.

The atmospheric SO\(_2\) concentration, \( N_{\text{atm}} \), is calculated using Eqns 8.1 to 8.3, and is given by:

\[ N_{\text{atm}} = N_B \left( \frac{R_2 \cdot Y_B - Y_A}{R_2 - 1} \right) \frac{1}{Y_B - Y_C} \pm N_{\text{min}} \tag{8.7} \]

where \( R_1 \) and \( R_2 \) are defined by Eqns 8.1 and 8.2, respectively.
We report here a sensitivity of 50 ppb for SO$_2$ detection employing a diode laser emitting in the $v_1$ band of SO$_2$. The present sensitivity is not high enough to monitor SO$_2$ in ambient levels ($\sim 10$ ppb), but it is quite enough to monitor SO$_2$ in stacks and at flare levels. However, the present basic concept shows promise for measuring ambient levels. This can be achieved by:

1. Improving the present transmitter-receiver optical system.

Eng et al [90] concluded that, a large retroreflector allows a greater reduction of noise due to atmospheric turbulence by aperture averaging. Therefore, a 30 cm diameter Cat's eye retroreflector, which has a beam divergence of about 0.15 mrad, is recommended for this application.

2. Data processing, and fully-controlled measurements. Since the amplitude resolution of the analog ratioing system used was only about two parts in $10^3$. This can be improved by using a higher resolution ratio meter or a digital ratioing system. Also, employing a digital system will enable one to perform all the repeatable scans and background subtraction accurately.

Theoretical calculations and laboratory measurements (described in the next section) indicate that additional improvements in SO$_2$ detection sensitivity should result from employing a diode laser emitting in the $v_3$ band of SO$_2$.

8.4 $v_3$ Band Measurements

Recently, Laser Analytics has fabricated a diode laser emitting in the $v_3$ band of SO$_2$ (1350 cm$^{-1}$). This laser is 10
times more powerful than any diode laser previously used in our laboratory. Its threshold current is relatively constant with temperature. A typical value is 0.25 A, and it is easy to find a single mode operation anywhere in the range from 1300 cm\(^{-1}\) to 1380 cm\(^{-1}\) with a continuous tuning range of \(\approx 0.5\) cm\(^{-1}\). In addition, the SO\(_2\) absorption line intensities in the \(\nu_3\) band is about 8 times more stronger than the absorption lines in the \(\nu_1\) band. These combined characteristic features of the diode laser and the SO\(_2\) absorption have been exploited to improve the sensitivity of point and long-path monitoring. Great care is required because of the overlapping of very strong H\(_2\)O absorption lines in this region. However, since the point monitoring technique permits the gas sample to be extracted at reduced pressure, it is easy to select a strong absorption line of SO\(_2\), free from any overlapping H\(_2\)O absorption lines.

We tried to exploit these characteristic features and perform theoretical and experimental investigations about the possibility of launching this laser beam into the atmosphere and detect SO\(_2\) in ambient levels (10 ppb).

8.4.1 Calculations

The transmission spectra of H\(_2\)O in the region from 1320 cm\(^{-1}\) to 1380 cm\(^{-1}\) was generated using our computer program. The value of pathlength times concentration used in these calculations was CL = 1200 cm. The individual line parameters of H\(_2\)O were taken from AFRCL compilations [25] after making the necessary corrections. It
was found, from several observations, that the H$_2$O lines wavenumbers in this spectral region must be shifted a value of $\sim 0.03 \text{cm}^{-1}$ towards lower wavenumbers. Our theoretical calculations indicate that the only relatively wide microwave region is the one near 1331.5 cm$^{-1}$, where the transmission of H$_2$O is about 50% for an interval of about 0.5 cm$^{-1}$. Figure 8.12 shows the calculated absorption spectra in the spectral region 1330 - 1334 cm$^{-1}$. The absorption spectra of H$_2$O (heavy curve) was generated using CL = 1200 cm, while the other three curves are the absorption spectra of SO$_2$, CH$_4$, and N$_2$O generated using CL = .12 cm for each gas. Note that decreasing the total pathlength will improve the H$_2$O transmission, but at the same time it will lower the detection sensitivity. Therefore, a study is required to determine the optimum pathlength prior to designing a system, employing this diode laser, for pollutant detection in the atmosphere. Our observations and calculations indicate that an optimum pathlength of about 500 m is sufficient to increase the atmospheric detection sensitivity to 10 ppb of SO$_2$ in the $v_3$ band.

8.4.2 Experimental Results and Discussions

Figure 8.13 is a typical direct scan of the diode laser current over the theoretically selected region 1330.8 - 1331.8 cm$^{-1}$. This scan was achieved by placing a small 10 cm cell containing a trace of pure SO$_2$ at $\sim 1$ Torr into the laser beam, and synchronously detecting the "direct" transmission at the chopper frequency. The wavenumbers in this region were calibrated by the aid of SO$_2$ line
Figure 8.12 Theoretical curves of the $\text{H}_2\text{O}$ absorption, and $\text{SO}_2$, $\text{N}_2\text{O}$, and $\text{CH}_4$ absorption in the microwindow near 1331.5 cm$^{-1}$. These curves show the possibility of detecting $\text{SO}_2$ in the atmosphere employing diode laser radiating in the $\nu_3$ band of $\text{SO}_2$. The $\text{H}_2\text{O}$ curve is calculated using $C_1 = 1200$ cm$^{-3}$, and all the absorption curves are calculated using $C_1 = 0.12$ cm. The wavelength marked by $\ast$ is the proposed region for atmospheric $\text{SO}_2$ monitoring with expecting sensitivity of 10 ppb.
Figure 8.13: A typical direct scan of the diode laser current over the proposed region in Fig. 8.12. This scan is taken by placing a 10 cm cell containing trace of SO2 at 1 Torr. Note that there are 3 groups of SO2 lines, a, b, and c, each group may produce an absorption dip at atmospheric pressure. The regions b and c are the same regions in Fig. 8.14 marked by 1 and 2, respectively.
parameters listed in Ref. [26]. Figure 8.13 illustrates three groups of \( \text{SO}_2 \) lines a, b, and c, each group may produce an absorption dip at atmospheric pressure. Figure 8.14 shows the transmission of \( \text{SO}_2/\text{N}_2 \) mixture introduced into the white cell with a CL = .03 cm. The four curves, from the top, illustrate the broadening of the absorption lines with increasing pressure from 10 to 100, 400, and 760 Torr, respectively. Note that there are two absorption dips, marked by 1 and 2 which belong to the absorption lines groups b and c in Fig. 8.13, respectively. One absorption dip, 1, near 1331.35 cm\(^{-1}\); while the other, 2, near 1331.63 cm\(^{-1}\). Employing the second harmonic detection technique (described in subsection 8.3.1) on the absorption region, marked by 2, enabled us to measure a known \( \text{SO}_2 \) concentration in the white cell with a sensitivity of better than 1 ppb in 1 km.

8.4.3 \( \text{H}_2\text{O} \) Interference Effects

To check experimentally against \( \text{H}_2\text{O} \) interference, the diode laser current is scanned across the selected spectral region with the white cell at 400 m, and filled with room air. Figure 8.15 shows typical direct scans for total pressures (of the room air) of 25 Torr (top scan), and 760 Torr (middle scan). The lower scan was taken with a small 10 cm cell, containing pure \( \text{SO}_2 \) at \( p < 1 \) Torr, placed into the beam, for wavenumbers calibration. Note that there is an absorption dip due to \( \text{H}_2\text{O} \) (marked by * in the middle scan). Comparing Figs. 8.14 and 8.15, it is clear that the two absorption dips marked by * (due to \( \text{H}_2\text{O} \)) and 2 (due to \( \text{SO}_2 \)) are overlapped;
Figure 8.14 Typical direct scans of the diode laser current over the regions b and c in Fig. 8.13 near 1331.5 cm\(^{-1}\). The four curves from the top are taken at 10, 100, 400, and 760 Torr total pressure, respectively. The value of cl used is 0.03 cm.
Figure 8.15 Typical direct scans showing the H$_2$O effect in the proposed region near 1331.5 cm$^{-1}$. Note that there is H$_2$O absorption dip (marked by *) overlapping the absorption dip (marked by 2) in Fig. B.14. The absorption dip marked by 1 is free from H$_2$O absorption dips. The pathlength used was 400 m.
while the absorption dip marked by 1 is free from H₂O absorption dips.

This may not be true at higher CL values of H₂O. However, by scanning the diode current back and forth between these two SO₂ absorption dips 1 and 2, and by knowing the relative absorption coefficients of H₂O and SO₂ at these two regions, one can estimate the SO₂ and H₂O in the path simultaneously. This may be achieved by applying the novel Detection and Estimation Techniques using Linear Weights described by Morgan [91]. The linear weights may be implemented as hardware (analog detection), or as software (digital processing). To demonstrate the absorption effects due to H₂O and SO₂ in these two spectral regions, we employed the White cell at 400 m and the small 10 cm cell which contains 83 ppb of SO₂ in 1.2 km as following:

It is possible to apply a ramp current from an external generator to the laser power supply. The function of this ramp current (together with the frequency modulation) is to produce repeated 2f scans automatically as shown in Fig. 8.16. The crucial parameters of this ramp are: (1) its frequency which control the scanning rate, (2) its amplitude which, together with the setting current value on the laser power supply, control the scanned spectral region. Applying this ramp technique, one can adjust the LAS to monitor a pollutant in the atmosphere continuously. The upper traces in Fig. 8.16 are typical scans over the spectral region marked by 1 in Fig. 8.14; while the lower traces in Fig. 8.16 are for the region marked by 2. The results in Fig. 8.16 agreed with the results in Fig. 8.15 in the sense that, the spectral region marked by 1 is free from H₂O.
Figure 8.16 A typical repeatable 2f scans over the absorption dips 1 and 2 (see Fig. 8.14). The upper traces are taken in the region 1; the lower are in the region 2. B.G. is the background signal (zero-pollutant signal) taken by flushing the White cell with dry N₂. The instrumental sensitivity is increased by a factor of 2 in the lower traces.
interference. In Fig. 8.16, the background scans (B.G.) were taken when the White cell was evacuated completely and no \( \text{SO}_2 \) in the beam path. The \( \text{SO}_2 \) scans were achieved by placing a small 10 cm cell (83 ppb) in the beam, or by introducing a known mixture of \( \text{SO}_2/N_2 \) into the White cell (20 ppb). The roof air scans were generated when the White cell, at 400 m pathlength, was filled with 1 atm of roof air. The latter was passing through a small tube filled with ground charcoal to absorb the ambient \( \text{SO}_2 \) before it enters the White cell.

The reported data in the present section may be considered as a starting point for the design of an \( \text{SO}_2 \) monitor in the atmosphere employing a diode laser emitting in the spectral region near 1331.5 cm\(^{-1}\). Due to overlapping by \( \text{H}_2\text{O} \) absorption, we recommend the use of a fully-controlled instrument and data processing. This may be achieved by following the automatic technique which is described by Max et al [92]. The present investigations show promise for monitoring \( \text{SO}_2 \) and \( \text{CH}_4 \) ambient levels in the atmosphere employing a lead-salt semiconductor diode laser radiating in the spectral region near 1332 cm\(^{-1}\).
CHAPTER 9

NOISE REDUCTION AND SYSTEM IMPROVEMENTS

9.1 Introduction

The feasibility of laser monitoring of atmospheric pollutants by the resonance absorption technique has been demonstrated in Chapter 7 for point monitoring, and in Chapter 8 for long-path monitoring. Generally, the sensitivity of a LAS is limited by the ability to detect a small change in the transmitted signal. The major sources of signal fluctuations which limit sensitivity are:

1. noise due to atmospheric turbulence;
2. laser source noise;
3. optical feedback;
4. signal level fluctuations due to changes in the transmittance of the atmosphere;
5. laser frequency fluctuations.

By eliminating the effects due to the above noise sources, much higher detection sensitivity than that at the present can be achieved. Noise analysis and reduction is described in the following sections.

9.2 Advantages of Employing Harmonic Detection Technique

Figure 9.1 represents several scans over two SO₂ lines in the 1141.9 cm⁻¹ region [75]. The SO₂/N₂ mixture used in the White Cell has
been diluted with $N_2$, and the absorption at the stronger line is now only 10%. It can be seen that, for small absorptions, the direct amplitude detection method (upper scan) produces a very noisy trace. The chief source of this noise is power fluctuations in the laser beam caused by mechanical vibrations of the diode, and consequent beam wander in the optical path. For the purposes of Fig. 9.1, a small aperture was placed in the beam path to enhance such power fluctuations. The regular nature of the "noise" is caused by the cycling of a piston in the diode cold head. It is obvious that direct detection techniques using a mechanical chopper are very susceptible to any type of power fluctuations in the laser beam. Other disadvantages of this technique are the strongly sloping background signal, which make it very difficult to identify small absorptions, and the vulnerability of the scheme to small drifts in the laser output power, in addition to the fact that it is impossible to accurately locate the line center for high resolution spectroscopy (described in Chapter 6). All these problems can be avoided by modulating the diode current at kHz frequencies. We report here an optimum modulation frequency of 3 kHz for point monitoring, and 5 kHz for long-path monitoring. Signals detected at the first and second harmonic of the modulation frequency are also shown in Fig. 9.1. Note the dramatic improvement in SNR in each case. However, it is clear that the second derivative technique results in least noise. This is related to the strongly sloping background in the upper scan of Fig. 9.1. This slope produces a significant dc offset in the first harmonic scan, and the magnitude of this offset is proportional to the laser
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Figure 9.1 Comparison of the three detection schemes at low $SO_2$ concentrations. The three traces are taken under the same experimental conditions. Note the dramatic noise reduction with second harmonic detection. After [75].
power incident on the detector. Hence, the first harmonic technique is still somewhat susceptible to fluctuations in the laser power. In contrast, detection at the second harmonic produces negligible dc offset, and further reduces the effect of laser power fluctuations. Also, the fact that the second harmonic signal swings around zero greatly facilitates subsequent signal processing. Another advantage of modulating the laser is that, the first or the second harmonic signal can be used to stabilize the laser frequency. The frequency instability, or drift in operating frequency (wavelength), is due primarily to changes in room temperature. Even though the cold finger on which the diode laser is mounted is precisely controlled, the diode temperature will vary with room temperature due to the variation in the radiation falling on the diode. This problem was not apparent when the LAS was used in a temperature-controlled laboratory, but it became very apparent when the portable system was monitoring SO$_2$ in the field. The conclusion was that the laser frequency had to be controlled at a given frequency on the SO$_2$ absorption line being used for the measurements. This was achieved by employing the locking technique (described in Chapter 7) on the first harmonic or the technique used on the second harmonic as described by Chaney et al [9].

In harmonic detection, the modulation amplitude must be adjusted to give the largest signal, consistent with no undue broadening of the linewidth. This corresponds to a diode wavelength modulation of the order of the FWHM of the pollutant absorption lines (PM), or absorption dip (LPM). Detection at the first and second harmonic of
the modulation frequency is often referred to as taking the first and second derivative of the upper scan in Fig. 9.1. However, a much smaller amplitude of modulation is required for a true derivative signal as described by McClenny et al [93]. The three traces in Fig. 9.1 were taken for the same absorption conditions. Note that the maximum excursion of the harmonic signals from zero is approximately equal to the magnitude of the direct absorption signal in the upper scan. This results from the fact that the direct absorption amplitude represents the maximum swing which can be obtained in a signal transmitted through the absorbing medium. So, from this point of view, we neither lose or gain signal by using the diode modulation techniques.

9.3 Background Signals (Zero-Pollutant-Signal)

For the reasons mentioned above, we have chosen to concentrate on increasing the detection sensitivity using second-harmonic detection. The detection limit of a LAS can be determined by trying to detect a standard low concentration of a pollutant gas. In an initial series of experiments at reduced pressures employing the diode laser setup shown in Fig. 7.1, Reid et al [75] arranged for the total $SO_2$ absorption in the beam path to be $\approx 10^{-4}$, and tried to detect this using the second harmonic technique. The traces shown in Fig. 9.2 are typical of early results. All traces represent the output of the lock-in amplifier (A in Fig. 7.1) with the second harmonic of the diode modulation frequency as reference, and a time-constant of one second. The upper trace was taken with the laser beam blocked, and represents detector
Figure 9.2 Lock-in amplifier output using the second harmonic detection scheme. In the absence of modulation, sensitivity is limited by detector noise. When a 1 kHz modulation is applied to the diode current, the interference fringes in the bottom trace appear. These fringes result from an etalon formed by two anti-reflection coated lenses in the beam path. The etalon spacing is 38 cm, with an effective reflectivity of $10^{-3}$. After [75].
noise. The next trace was taken with the laser beam falling on the detector, but with no modulation applied to the diode. Note that there is only a small increase in noise, even though approximately 10 µW of power was incident on the detector. This gave a potential maximum SNR value of $>10^6$ with the employed detector. Unfortunately, when modulation was applied to the diode, the bottom trace was obtained. These fringes have amplitudes much greater than detector noise, and correspond to interferences between scattered and reflected beams in the optical path. In a sense, the diode wavelength was being tuned through a series of Fabry-Perot fringes. By measuring the fringe spacing and amplitude we were able to determine the physical elements involved in the "etalon". The fringes in Fig. 9.2 were caused by two anti-reflection coated lenses in the beam, with a lens spacing of 38 cm and effective etalon reflectivity $\approx 10^{-3}$.

For detection at atmospheric pressure, we mentioned in Chapter 8 that the sensitivity depends on how accurately one can produce and measure the background (zero-pollutant) signal. The relatively large amplitude of modulation applied at 1 atm produces a large background signal which is not the case at reduced pressures. Therefore, greater care is required to ensure that the resulting signal is a true background due to the laser behaviour and not a wide fringe caused by optical components. To perform these measurements, the White cell was filled with 1 atm of pure $N_2$, and the laser (which was emitting in the $v_3$ band of $SO_2$) was scanned over a spectral region.
(e.g., the region marked by 2 in Fig. 8.14) with the modulation on.

Figure 9.3 shows typical 2\( \times \) scans of the diode laser over this region. Traces marked by 1, 2, and 3 were taken with the White cell at 40, 200, and 300 m pathlengths, respectively. Trace 5 was taken at 100 m. It is clear that these traces are not true background but are results of fringes. By measuring the fringe spacing, we found that the only possible physical elements which may cause these fringes were the diode collecting 5 cm lens and a reflecting surface deep inside the cold head. We have confirmed this by blocking part of the beam between the collecting lens and the cold head window. Traces 4, 6, and 7 are the results of blocking part of the beam at different positions. Comparing these traces in Fig. 9.3, we conclude that the left part of the beam is responsible for creating such fringes. Similar fringes were observed involving the windows of the small 10 cm cell, and other optical components in the laser beam.

It is necessary to carefully design the optical beam handling and the absorption cell to minimize such effects. Careful design of the absorption cell, together with slight angular misalignment of the optical elements in the beam path, allows the reduction of these effects.

9.4 Atmospheric Measurements Noise

In the case of pollutants detection in the atmosphere (see Fig. 8.2), the fringes caused by multi-pass White cells do not exist. The total pathlength (1.2 km) is obtained by the laser beam round
Figure 9.3 Different lock-in amplifier outputs with the modulation on. The top three scans 1, 2, and 3 are taken over the region 1331.5 (see Fig. 8.13) with the White cell at 40, 200, and 300 m pathlength, respectively. All the four traces 4, 5, 6, and 7 are taken with the White cell at 100 m. All the seven scans shown are taken with the White cell filled with dry nitrogen. The difference between these scans in the bottom is the result of blocking part of the laser beam before it enters the 5 cm collecting lens. Note that scan No. 6 is the optimum one and resulted by blocking the part of the beam which creates the shown fringes in scans 4, 5, and 7.
trip into the atmosphere. However, such fringes may be produced by other optical components (e.g., small 10 cm cell, and between the beam-splitter and detector lens), but it is easy to eliminate these fringes. Also, great care is required (to eliminate fringes) when a retroreflector is used near the laser to obtain the background (zero-pollutant) signal. In the following we describe other sources of noise rather than these fringes.

9.4.1 Vibration and Stability

The mounts for shaft mirrors (see Fig. 8.2) were worked to rest on stubby triangular bases; this improved stability to what is probably the limit attainable in the laser laboratory building at McMaster University Medical Centre (MUMC). From beam alignment experiments, it physically appears that MUMC is fairly stable during the night, but bends a few minutes of arc at about 8:30 a.m. and continues to move around until 10:30 p.m. However, if the building is to be seriously used as a laser base, experiments should be made to characterize total image motion and vibration, and to separate building motion from atmospheric effects. In Fig. 9.4, a possible coaxial system for diode lasers is shown. Once aligned, the entire unit is pointed at distant targets. Such a unit could be reasonably portable, compact, and separated from the building vibrations. Coaxial optics offer some advantages over beam-splitters, since there is no scattered light from a partial mirror and the system operates at any wavelength. However, the aperture of the transmitter (or receiver) is restricted to 1/2 or 1/3 that of the other, and the central part of the beam is
Figure 9.4 A possible coaxial beam launching and receiving telescope containing the semiconductor diode source and detector in one unit. A proposed portable system.
9.4.2 Beam Focus

It is important to focus the outgoing laser beam on the retroreflector if maximum energy is to be intercepted by the retroreflector. However, early experiments (employing the Molecron CO$_2$ laser) suggested that the focussed beam might scintillate more than a defocussed beam, presumably caused by the focussed beam wandering off the retroreflector entirely or partly. Thus it was necessary to measure both returned power and noise as a function of focus. It was found that power rises sharply at the best focus, while noise, measured as the peak to peak variation in 120 seconds divided by the average total power, is roughly constant. Under markedly different conditions of turbulence, this may not be true.

9.4.3 Scintillation

Although the second harmonic detection technique, together with the ratioing technique has been proved to be the only feasible method for the reduction of laser power fluctuations falling on a detector, we have found that it is necessary to describe the atmospheric scintillation.

The intensity of a laser beam propagating in the atmosphere is randomly amplitude modulated. Reviews of the literature dealing with this scintillation problem are given in [94] and [95]. Experimental results about CO$_2$ laser radiation propagation are given in [96]. The variance of $\sigma^2_I$ of the natural logarithm of the normal-
ized radiation intensity $\log_e I(\lambda R) / I(\lambda R)$ as a function of range $R$ and wavenumber $\nu$ is, by theory, predicted to be

$$\sigma^2_T = \begin{cases} 12.8 C_n^2 l_o^{-7/3} R^3, & (\lambda R)^{1/2} << l_o \\ 1.23 C_n^2 \nu^{7/6} R^{11/6}, & l_o << (\lambda R)^{1/2} L_o \end{cases} \quad (9.1)$$

where $l_o$ is the inner and $L_o$ the outer scale size of the turbulence and $\lambda$ is the wavelength of the laser beam. Plane wave propagation in a homogeneous medium and detection in a point have then been assumed. Typical values of $l_o$ and $L_o$ are $3 \times 10^{-3}$ m and 10 m, respectively, suggesting a wide range in which Eqn. 9.1 shall hold.

The present launching system when employing a cat's-eye retroreflector will be considered to have transmitting and receiving optics with large aperture areas. This means that the variance of $I(\lambda R) / I(\lambda R)$ is reduced due to aperture averaging (see [94], [95]). For example, at 10 $\mu$m, a 30 cm diam beam is about 3.5D, where D, the transverse correlation distance of the log intensity, is approximately given by the first Fresnel zone diameter $(2 / \pi \lambda R)^{1/2}$. $R$ is the range. For the above conditions, a reduction of about 80% in atmospheric turbulence noise is possible for an average value of the turbulence parameter $C_n^2 = 1 \times 10^{-4}$ m $^{-2/3}$. The noise reduction is more than two times as great as that for a 10 cm beam retroreflected by a 10 cm corner-cube retroreflector.

Figure 9.5 shows the effects of increasing the retroreflector area on the SNR.
Figure 9.5 Typical results showing the effect of increasing the retroreflector area. Note that as the area of the retroreflector is increased the scintillation decreased.
CHAPTER 10

SUMMARY AND CONCLUSIONS

Employing the resonance absorption scheme, we report theoretical and experimental techniques which are useful in molecular spectroscopic studies and in the development of a Laser Absorption Spectrometer (LAS). This LAS marks a significant step forward in the application of a tunable laser to point and long-path monitoring of atmospheric pollutants.

We have described, in Chapter 1, the advantages of using lasers as a light source in optical monitoring techniques in general, and in a resonance absorption scheme in particular. The latter is advantageous because it is the most sensitive and requires the least amount of laser power. Consequently, it promises to be the simplest and least expensive system.

Both fixed-frequency and tunable lasers have been employed in this Thesis. The distinction between tunable and fixed-frequency lasers is not as clear as one might first believe. A reasonable definition of a tunable laser is one that is continuously tunable over 1 cm⁻¹ or more and has a total tuning range of hundreds of cm⁻¹; a fixed-frequency laser is one that cannot be tuned over more than a small fraction of a cm⁻¹ (e.g., ~ 0.002 cm⁻¹ for a low-pressure CO₂
laser transition). A fixed frequency laser may often be step-tuned from one transition to another - and for this reason these lasers seldom match perfectly with the absorption lines of molecules to be detected. With the availability of tunable ir lasers, it is possible to ideally match pollutant absorption lines. The most useful type of tunable laser for pollution monitoring is the lead-salt semiconductor diode laser because it is simple, and can be made to emit in the infrared "fingerprint" region of most molecules. In addition, it has a narrow linewidth. Very recently, Preier [97] reviewed the fundamental material properties, device technology, laser properties, and applications of lead-salt diode lasers.

In Chapter 2, we described the lasers which have been used in this thesis. An experimental technique for determining semiconductor diode laser characteristics is described. These characteristics (e.g., wavelength coverage, tuning rates, single mode operating regions, and frequency stability) are very important parameters which must be known prior to applying such lasers.

As a starting point in the design of a resonance absorption pollution monitor (especially one which employs a fixed-frequency laser), theoretical calculations of laser transmission through the atmosphere must be carried out. To perform such calculations, it is necessary to know accurately the band spectra of both pollutant gases and normal atmospheric absorbing gases, together with values for their ir absorption coefficients. We review the molecular absorption theory in Chapter 3. This theory enabled us to develop a computer software
package which proved to be both accurate and efficient. The three main subroutine subprograms, written in Fortran IV, are as follows:

(1) A subroutine for generating molecular absorption lines positions,

(2) A subroutine for generating lines intensities,

(3) A subroutine for generating absorption (transmission) spectra of any gas within a selected wavelength region, and at any pressure.

Much of the data which can be generated by the first two subroutines is available in the literature. However, the available data is often in a form which cannot be used directly, is not available, or is not accurate enough. Therefore, it is necessary for an air pollution laboratory to have such programs to generate the individual line parameters of a gas from its molecular constants. New data can be obtained experimentally, for special cases, and for relatively narrow spectral regions, by employing lasers. One of our computer subroutine subprograms has been used recently by Taylor et al [98] to generate the CO₂ laser gain code at multiautmosphere pressures.

To establish some useful criteria for pollution monitoring via the "direct" resonance absorption scheme, measurements on ozone with a line-tunable CO₂ laser have been performed and reported in Chapter 4. We conclude that, if fixed frequency laser systems are employed, a frequency mismatch of up to Δν₀ = 0.001 cm⁻¹ can easily be tolerated provided that there are no neighboring absorption lines due to foreign species within ± 0.1 cm⁻¹, or that the absorption intensity of such foreign species lines is more than an order of magnitude less than the intensity of the gas species being monitored. Reduced pressure
measurements, such as employed in Chapter 4 on ozone, are a useful experimental tool for establishing such criteria. Whether these criteria can be met for every pollutant gas is in doubt, as the measurements on ozone indicate. The density of ozone absorption lines is so great that it appears impossible to find a region where nearest neighbor contributions can be neglected. Although these nearest neighbors are all part of the ozone system, they can serve to represent the effect of interfering foreign species lines. If fixed frequency laser systems are to be effectively employed, monitoring likely has to be carried out at, e.g., two CO$_2$ transitions such as P(8) and P(12). Thus, the ratio of the absorptions at the two transition frequencies would probably serve as a positive identification of the ozone species. However, the ability to match laser lines with gas species lines to within 0.001 cm$^{-1}$ (30 MHz) may prove difficult for the majority of gases that one would want to detect as pollutants. Consequently, a fully-tunable laser system is probably the best route to follow, with a scan through two or more adjacent absorption lines to ensure that the effects of interference from foreign species is eliminated.

As mentioned previously, the use of "direct" absorption laser techniques for monitoring of a pollutant gas requires an accurate knowledge of a number of spectroscopic parameters. In particular, it is important to have good values for the location and the absorption of suitable pollutant transitions. To provide such information on NO, we have exploited the coincidences between CO laser lines and NO.
absorption lines to experimentally perform spectroscopic studies. In Chapter 5, we have reported measurements on seventeen NO lines which showed significant absorption with the line-tunable CO laser source. The absolute absorption as a function of pressure has been determined. As a result, we have been able to establish accurate values for the absorption of atmospheric NO at the pertinent CO laser wavelengths. For the experimental data we have also deduced the separation $|\Delta v_n|$ between the appropriate NO and CO wavelengths, the NO/$N_2$ pressure-broadening, the NO band strengths, and the individual NO line strengths. A knowledge of both the absorption and the pressure-broadening parameters is essential for pollutant sensing using either long atmospheric paths or point monitoring employing a multi-pass absorption cell operating at reduced gas pressure. We have determined all the available NO lines suitable for use with the CO laser. Further research is required to establish regions free of interference from other atmospheric gases when direct atmospheric monitoring is employed. However, the data presented in Chapter 5 are sufficient to design a point monitoring system, which is less susceptible to interference from other gases. In particular, water vapor (which is the source of considerable interference over long-pathlengths in this wavelength region) is easily removed prior to measurement.

The technique reported in Chapter 5 is a useful tool when a tunable laser is not available. However, for some applications, as in the case of employing CO$_2$ laser in ozone detection in the atmosphere, the linewidths of ozone have a HWHM of $\sim$ 30 MHz. Therefore, their
line-center frequencies must be known to better than 10 MHz if the
absorption data are to be used properly. For this reason, we have
developed a simple technique for high resolution spectroscopy. This
technique is described in Chapter 6, where we report the accurate
frequency measurement of over 100 lines in the \( v_3 \) band of ozone.
These measurements were made with a tunable diode laser, a multi-pass
absorption cell, and a temperature-stabilized germanium etalon.

Despite the relative simplicity of the technique, we achieved an
accuracy of better than 10 MHz in our measurements. This accuracy
compares well with that achieved by the more complicated heterodyne
techniques of high-resolution spectroscopy. In our measurements we
have primarily concentrated on those ozone lines that are close to
CO\(_2\) laser lines. We have measured the frequencies of those reasonably
strong ozone lines that lie within 6 GHz of the laser lines in the 9.4
\( \mu \)m region. These laser lines include most of the \( ^{12}C^{16}O_2 \) lines and,
in addition, selected isotopic and sequence lines, particularly those
in close coincidence (< 300 MHz) with ozone lines. Diode lasers have
been used previously to measure some individual absorption lines with
accuracies of 15 MHz, and to analyze absorption bands with much
reduced accuracies. However, we report here the first measurements
over an entire absorption band using the full resolution of our
tunable diode laser. The data reported in Chapter 6 is more than
sufficient for a detailed band analysis of the \( v_3 \) band of ozone.
At present, the accuracy of our measurements is still limited by
residual drifts of the etalon fringes. Better temperature stabiliz-
ation or the use of an air-spaced actively-locked etalon will remove
this limitation. The estimated accuracy of a tunable diode laser, in combination with a stabilized etalon, would then be limited simply by the accuracy with which one can judge the line center (1-3 MHz). Finally, it should be possible to automate much of the measurement procedure.

Up to this point, experimental and theoretical techniques have been demonstrated for spectroscopic studies of pollutant gases. These studies must be performed prior to the design of any pollution monitor based on the resonance absorption scheme. In Chapter 7, a laser absorption spectrometer which combines the sensitivity of acousto-optical methods with the convenience of direct, long-path optical detection has been demonstrated. This LAS employs tunable lasers and a second harmonic detection technique which has been developed at McMaster University Air Pollution Laboratory (MUAPL) [75]. A dramatic reduction of the system noise was achieved by using the second harmonic detection technique. A sensitivity of $3 \times 10^{-8} \text{ m}^{-1}$ is attained. This extremely high sensitivity was reached after locking the diode laser wavelength at the absorption line center and employing longer time constant. We have demonstrated the use of LAS for point monitoring of ambient concentrations of ozone at a sensitivity of 0.5 ppb, employing the same diode laser which was used in Chapter 6, and with the White cell set at 200 m. Employing another diode laser (discussed in Chapter 2), we have detected $\text{SO}_2$, $\text{N}_2\text{O}$, and $\text{NH}_3$ in the atmosphere with sensitivities of 2, 3, and 0.2 ppb, respectively. Furthermore, the present technique does not suffer from interference from unwanted molecular species, and
can be easily calibrated even at the ppb concentration level. The LAS was zeroed by evacuating the White cell, and calibration was checked using a short cell containing a relatively high concentration mixture. At this time, a fully portable instrument is under development at the MUAPL. This instrument is based on a tunable semiconductor diode laser, and a relatively small commercial White cell capable of 50 m maximum pathlength.

Point monitoring (PM) permits the gas pressure to be reduced until the Doppler-broadened IR absorption structure is revealed, thereby making possible very high specificity along with the very high sensitivity. The present sensitivity of the LAS is more than sufficient for many practical applications, and we are still far from the ultimate limit given by detector noise. However, it is difficult to eliminate entirely the problems associated with PM of reactive gases such as NO and SO₂, which can be changed or converted during the sampling procedure. Remote long-path monitoring (LPM) yields values for the average pollutant concentration over the path, which is generally more meaningful for regional models than point monitoring. In addition, the LPM eliminates entirely the problems associated with the sampling procedure. However, LPM is not generally considered to be a substitute for point monitoring, but an adjunct to it. Nevertheless, in some cases, remote sensing represents the only economical or technically feasible technique.

A long-path station for monitoring atmospheric pollutants has been built and tested. Chapter 8 describes such a station
using a second harmonic technique which has been modified to apply on an absorption dip instead of an isolated absorption line. At atmospheric pressure a number of pollutant absorption lines may combine to form an absorption dip of any shape and a relatively wide halfwidth (≈ 0.2 cm⁻¹). Therefore, the amplitude of the frequency modulation applied to the diode laser is about 15 times more than the one applied at reduced pressures on an isolated absorption line (these values are valid only at 1160.8 cm⁻¹ in the ν₁ band of SO₂, and may be different for another gas or region).

The large modulation amplitude resulted in a high zero-pollutant reference signal (background signal). This background signal must be measured accurately in order to attain high detection sensitivity. The response of the system to a pollutant concentration is the result of subtracting two signals, one with zero-pollutant, and the other with the pollutant present. The zero-pollutant reference signal may be obtained by one of the following techniques:

1) Employ another retroreflector near the laser in a laboratory or in a van (portable type station). The resulted pathlength L is essentially equal to zero. Hence, the recorded system response is due to zero-pollutant concentration.

2) Tune the diode laser current away from the absorption line. This technique is valid only for monitoring simple, linear, or symmetric-top molecules such as NO, CO, CO₂, N₂O, NH₃, ... etc., where the absorption lines at atmospheric pressure are separated from each
other and the absorption between two adjacent lines is approximately constant or zero.

(3) Employ two short 10 cm cells containing two known pollutant gas concentrations. Chapter 8 describes this technique, which has been used for background compensation.

In Chapter 8, we report theoretical and experimental absorption data for $\text{SO}_2$, $\text{N}_2\text{O}$, $\text{H}_2\text{O}$, $\text{NH}_3$ and $\text{O}_3$ in the spectral region 1100-1200 cm$^{-1}$. This data is useful as a starting point in the design of a long-path pollution monitor of single- or multi-pollutants into the atmosphere. Our calculations and observations indicate that the selected region near 1160.8 cm$^{-1}$ is relatively free from $\text{H}_2\text{O}$ interference effects. Here, an $\text{H}_2\text{O}$ concentration variation from 25% R.H. to 75% R.H. is equivalent to 5 ppb of $\text{SO}_2$ in 1.2 km. These values may be different for other spectral regions.

The non-perfect reproducibility of the system response to a known low concentration of $\text{SO}_2$ give a limit of 50 ppb on the minimum detectable $\text{SO}_2$ concentration. This concentration is the average value over a 600 m pathlength (one way); the total pathlength which was used in our calculations was 1.2 km (round trip). This pathlength was achieved by employing an off-axis telescope at the laboratory and 5 small corner cubes for the retroreflector placed on the roof of another building at 600 m distance from the laboratory roof building. The most serious limitation was due to the laser beam wandering. This can be reduced by using larger retroreflector. Our calculations and observations indicate that it is possible to
obtain a detection sensitivity of 10 ppb of $\text{SO}_2$ in 1.2 km, employing a diode laser radiating in the $v_1$ band of $\text{SO}_2$. This higher sensitivity can be achieved by improving the present transmitter-receiver optical system (e.g., switching to a Cat's eye retroreflector system and data processing (e.g., digitalization of the data for processing with a computer).

Chapter 8 also contains theoretical and experimental investigations of $\text{SO}_2$, $\text{CH}_4$, $\text{H}_2\text{O}$, and $\text{N}_2\text{O}$ in the region 1300-1400 cm$^{-1}$ ($v_3$ band of $\text{SO}_2$). These investigations indicate that it will be possible to achieve additional improvement in the detection sensitivity by employing a diode laser emitting in the $v_3$ band of $\text{SO}_2$. We report an optimum microwindow spectral region near 1331.5 cm$^{-1}$ for $\text{SO}_2$ monitoring in the atmosphere. We report also an optimum pathlength of 500 m and two spectral regions near 1331.35 cm$^{-1}$ and 1331.63 cm$^{-1}$. The first region is free from $\text{H}_2\text{O}$ interference effects with 500 m pathlength; the other region suffers from $\text{H}_2\text{O}$ interference effects. However, one can scan the diode over these two regions and apply an analytical technique to estimate $\text{H}_2\text{O}$ and $\text{SO}_2$ concentrations simultaneously.

The feasibility of laser monitoring of atmospheric pollutants by the resonance absorption technique has been demonstrated in Chapter 7 for point monitoring, and in Chapter 8 for long-path monitoring. The attained detection sensitivities were achieved after employing the second harmonic detection technique and eliminating the effects due to system noise sources. These
sources are described in detail in Chapter 9, where we demonstrate the advantages of employing the second harmonic technique. The main advantage of applying such a technique is the dramatic reduction of the noise which results from laser power fluctuations. However, modulating the diode laser resulted in another kind of noise which is due to optical feedback (fringes). We describe these fringes in Chapter 9, along with a method of eliminating such fringes.

Atmospheric noise, other than that mentioned above, is described in Chapter 9. Long-term effects due to atmospheric turbulence and scattering unrelated to absorbing molecules are eliminated electronically by rationing the second harmonic and the chopped signals, since both are affected similarly by such influences. Finally we describe in Chapter 9 the possibility of improving the stability, sensitivity, and portability of our atmospheric monitoring system.
APPENDIX A

CALCULATIONS OF PARAMETERS OF ABSORPTION LINES FOR ASYMMETRIC ROTORS

"AROTOR" is a Fortran IV computer program which we have developed to generate line positions and intensities of any asymmetric rotor molecule (e.g., SO₂, H₂S, O₃, H₂O, NO₂, etc.). The inputs to the program are the molecular constant, the band strength, the axis of rotation, and the selection rules of the molecule under consideration.

Definitions of Variables

Section Al. The inputs to the program are read in this section as following:

VK1, VK2: Lower and upper state value of κ, respectively.
OMG: Band center (cm⁻¹).
OSO: Abundance of isotopic species (percentage).
SP: Total band strength (cm⁻² atm⁻¹).
Q: Total partition function value.
GO: Lower state vibrational energy (cm⁻¹).
TEMP: Temperature °K.
CEX: constant = kT/h.
IBAND: Number of bands to be performed.
IAXIS:  Rotation axis:  a, b, or c.
IAXIS = 1  for a,
IAXIS = 2  for b, and
IAXIS = 3  for c.

JI:  The minimum value of J (Quantum number).

JF:  The maximum value of J.

C1:  \((A_v - C_v)/2\) of the lower state \((\text{cm}^{-1})\).

C2:  \((A_v + C_v)/2\) of the lower state \((\text{cm}^{-1})\).

C3 and C4 are the same as C1 and C2, respectively, but for the upper state. Here, \(A_v, C_v\) are the molecular vibrational constants.

**Section A2**

IITOT:  Number of all P, Q, and R transitions.

ML(1):  J number of a lower state, while

ML(2):  J number of its upper state.

ICC:  equal to 0 for Q branch, 1 for R or P branch.

This section generates also the constants H, F, G, and A as described in Table II of reference [30]. We have used type II^4 in our calculations.

**Section A3**

In this section, the submatrices \(E^+, E^-, O^+, \) and \(O^-\) are generated into the subroutine subprogram "SUBMTX" for the lower and upper states. This subroutine evaluates also all the eigenvalues of each matrix. The theory used to generate these matrices is in
reference [30]. The outputs of "SUBMTX" are:

TEPD, AB1D: $E^+$ matrix and its eigenvalues, respectively, for the lower state.

TEND, AB2D: Same for $E^-$.  

TOPD, AB3D: Same for $O^+$.  

TOND, AB4D: Same for $O^-$.  

For all the above and following definitions, we have replaced the last character, D, by U for the same calculations but for the upper state. For example, TEPD is $E^+$ matrix for the lower state, while TEPU is $E^+$ for the upper state.

ABTOD, ABTOTU: Arrays contains all the eigenvalues of the four submatrices $E^+$, $E^-$, $O^+$, and $O^-$.  

BD, BU: Are outputs of the subroutine "ORD" which arrange the arrays ABTOD and ABTOTU in descending order.

Subroutine "ARRGE" is used in this section to provide each one of the matrices $E^+$, $E^-$, $O^+$, and $O^-$ with its row and column values of $K_{-1}$ and $K_{+1}$ as following:

NK1D: $K_{-1}$ for the lower state of $E^+$.  

NK2D: $K_{-1}$ for the lower state of $E^-$.  

NK3D and NK4D are for $O^+$ and $O^-$, respectively.  

NP1D, NP2D, NP3D, NP4D are for $K_1$ of the lower state of $E^+$, $E^-$, $O^+$, $O^-$, respectively.  

BEPD: Arranged eigenvalues of $E^+$ in the lower state, while BEND, BOPD, BOND are the same for $E^-$, $O^+$, $O^-$ in-the
lower state.

Subroutine "FINSUB" generates the final matrix $T$ which is described in reference [30].

The generated matrix is "AAV" for each of the matrices $E^+$, $E^-$, ..., then each one is stored in its array. For example, AAV of $E^+$ is stored in the array TEPD, AAV of $E^-$ in the array TEND, ... etc.

Note: In the above definitions, the last character D or U indicates that the calculations are in the lower or upper state.

Section A4

Up to this point, we have calculated the matrices $T$ and $T'$ described in references [30, 32]. To calculate the rotational dipole matrix $|\mu|^2$, we have used the following equation [32],

$$|\mu|^2 = T_1' \Phi_F G T_2$$

$\Phi_F G$ is the symmetric direction cosines matrix. We have followed the theory described in [99] to calculate $\Phi_F G$. Eighteen different matrices were used according to Table 1 in reference [99]. These eighteen matrices could be constructed using five different subroutines "R1", "R2", "R3", "Q1", and "Q2". These subroutines are classified with respect to the selection rules and the rotation axis IAXIS as described in Fig. 1 in [99]. Subroutine "FROAST" performs the last calculation which is defined above. This subroutine generates all the desired line positions and strengths for the given transitions. This data needs to be sorted in ascending or descending order with
respect to line positions.

A typical output of "AROTOR" is shown in Fig. A-1 for the \( v_3 \)
band of \( {^{32}}S\; {^{16}}O_2 \) molecule. The molecular constants and the absorption
data are the same as in reference [100]. Where,

\[
J = \quad \text{Lower state } J \text{ number.}
\]

\[
J_1 = \quad \text{Upper state } J \text{ number.}
\]

\[
K = K_{-1}
\]

\[
\text{FREQUENCY} = \quad \text{Transition frequency } J \rightarrow J_1 \ (\text{cm}^{-1}).
\]

\[
\text{ROTA. STR.} = \quad \text{Rotational dipole matrix element.}
\]

\[
\text{RELAT. STR.} = \quad \text{Relative strength.}
\]

\[
\text{ABS. STR.} = \quad \text{Absolute strength } (\text{cm}^{-2} \text{ atm}^{-1} \times 1000).
\]

\[
\text{LOW ENG.} = \quad \text{Lower state energy } (\text{cm}^{-1}).
\]

\[
\text{UPP. ENG.} = \quad \text{Upper state energy } (\text{cm}^{-1}).
\]

\[
\text{EIG. LOW.} = \quad \text{Eigenvalue used in lower state.}
\]

\[
\text{UPP. EIG.} = \quad \text{Eigenvalue used in upper state.}
\]

\[
\text{LINE ISOTOPIC} = \quad \text{Isotopic identification, 3216 is for } {^{32}}S\; {^{16}}O_2, \text{ while}
\]
\[
001 \text{ refers to } v_1 v_2 v_3 \text{ and } v_3 = 1 \text{ for the } v_3 \text{ band.}
\]
PROGRAM ARYOR. INPUT, OUTPUT, TAPES=INPUT, TAPES=OUTPUT
DIMENSION AAI(25, 26)
DIMENSION V(2), NI(2)
DIMENSION F(25, 26)
DIMENSION TEPD(26, 26), TEND(26, 26), TOPD(26, 26), TOND(26, 26)
DIMENSION TEPU(26, 26), TENU(26, 26), TOPU(26, 26), TOUN(26, 26)
DIMENSION AB(26), AB2D(26), AB3D(26), AB4D(26)
DIMENSION ABS(26), ABSU(26), ABSU(26), ABSU(26)
DIMENSION AB1U(26), AB2U(26), AB3U(26), AB4U(26)
DIMENSION ABOJ(101), ABUJ(101), BBO(101), BB(101)
DIMENSION BEPD(26), BEPU(26), BOPD(26), BOND(26)
DIMENSION BENU(26), BENU(26), BOPU(26), BONU(26)
DIMENSION N1K(26), N1PD(26), N12K(26), N12D(26), N13D(26), N1P3D(26)
DIMENSION N1KU(26), N1PU(26), N1KU(26), N1K2U(26), N12U(26)
DIMENSION N1KU(26), N1P3U(26), N14U(26), N1PU(26)
DIMENSION N1KU(26), N1PD(26), N12K(26), N12D(26), N13D(26), N1P3D(26)

C

SECTION A1

C

WRITE(6, 1)
JELAT STR *, 3X, *, ABS STR *, 3X, *, LOW ENG *, 3X, *, UPP ENG*, 3X, *, EIG LOW*
2, 3X, *, UPP EIG*, 3X, *, EIG LOW*, 3X, *, LINE ISO TOPIC*)
READ(5, *) IAXIS, IBANDS
READ(5, *) OSO, CEH, ON, TEMP
DO 1020 1K5=1, IBANDS
READ(5, *) JF, J1, C1, C2, C3, C4
READ(5, *) V1, V2, SP, OME, GO, IDNT
SO=OSO=SP/100.
ITRAC=IDNT
C

SECTION A2

C

NI=(JF-JI)+1
N2=NI-1
11TOT=3*JF-3*J1+1
DO 7777 1K1=1, 11TOT
1F(1K1.LE.N1) GO TO 1919
GO TO 2929
1919 NI(1)=JI-1+IK1
NI(2)=NI(1)
1CC=0
GO TO 5959
2929 IF(1K1.LE.(NI+N2)) GO TO 3939
GO TO 4949
3939 NI(1)=IK1-NI-J1-1
NI(2)=NI(1)+1
1CC=0
GO TO 5959
4949 NI(2)=IK1-(NI+N2)+J1-1
NI(1)=NI(2)+1
1CC=1
5959 VL(1)=VK1
VL(2)=VK2
DO 9010 1K=1, 2
J=NI(1)
VK=VL(1K)
1=1.
F=0.
C=VK
A=0.
C=VK
C

SECTION A3

C

IF(1K.EQ.2) GO TO 9000
CALL SUBNTXU,F,C,G,J,TERF, TEND, TOPD, TOND, NEPD, NEND, NOPD, NOND, AB1D
1, AB2D, AB3D, AB4D)
GO TO 9010
9000 CALL SUBNTXU,F,C,G,J,TERP, TENU, TOPU, TOUN, NEPU, NENU, NOPU, NOUN, AB1U
1, AB2U, AB3U, AB4U)
9010 CONTINUE
DO 9100 1=1, NEPD
9100  ABDTOD(1) = ABD1D(1)  
   DO 9200  I=1, NEND  
9200  ABDTOD(I+NEPD) = ABD2D(1)  
   DO 9300  I=1, NOND  
9300  ABDTOD(I+NEPD+NEND) = ABD4D(1)  
   DO 9400  I=1, NORD  
9400  ABDTOD(I+NEPD+NEND+NORD) = ABD3D(1)  
    J0=1(I)  
    JO=2*J+1  
    J1=1(I+1)  
   DO 9101  I=1, NEPU  
9101  ABDTOD(I) = AB1U(I)  
   DO 9201  I=1, NENU  
9201  ABDTOD(I+NENPU) = AB2U(I)  
   DO 9301  I=1, NOUN  
9301  ABDTOD(I+NENPU+NENU) = AB4U(I)  
   DO 9401  I=1, NOUN  
9401  ABDTOD(I+NENPU+NENU+NOUN) = AB3U(I)  
    J01=2*J1+1  
    CALL ORU(ABDRTOD, BD, JO)  
    CALL ORU(ABDRTOD, BU, J01)  
    CALL ARPJE(J, BD, BEPD, BEND, BPDP, BOND, NK1D, NP1D, NK2D, NP2D, NK3D, NP3D,  
         NK4D, NP4D, NEPU, NEND, NORD, NOND)  
    CALL ARPJE(J1, BU, BEPU, BENU, BPDU, BOND, NK1U, NP1U, NK2U, NP2U, NK3U, NP3U,  
         NK4U, NP4U, NEPU, NENU, NOUN, NONU, NOND)  
    CALL FINSUB(TEPD, NEFD, BEPD, BAV)  
1002  DO 1111  IR=1, NEFD  
1111  DO 1111  IC=1, NEFD  
      1C=IC  
1111  TEPD(IR, IC) = AAV(1R, IC)  
    CALL FINSUB(TEPD, NEPU, BEPU, BAV)  
1004  DO 1112  IR=1, NEPU  
1112  DO 1112  IC=1, NEPU  
      1CR=IC  
1112  TEPD(IR, IC) = AAV(1R, IC)  
    CALL FINSUB(TEND, NEND, BAV)  
1006  DO 2220  IR=1, NEND  
2220  DO 2220  IC=1, NEND  
      1CR=IC  
2220  TEND(IR, IC) = AAV(1R, IC)  
    CALL FINSUB(TEND, BAV)  
1008  DO 2229  IR=1, NAVA  
2229  DO 2229  IC=1, NAVA  
      1CR=IC  
2229  TEND(IR, IC) = AAV(1R, IC)  
    CALL FINSUB(TEND, BAV)  
3333  DO 3333  IR=1, NOPD  
3333  DO 3333  IC=1, NOPD  
3333  TOPD(IR, IC) = AAV(1R, IC)  
    CALL FINSUB(TOPD, NPOD, BPOD, BAV)  
3333  DO 3334  IR=1, NOPU  
3334  DO 3334  IC=1, NOPU  
3334  TOPU(IR, IC) = AAV(1R, IC)  
    CALL FINSUB(TOPU, NPOU, BPOU, BAV)  
4444  DO 4444  IR=1, NOND  
4444  DO 4444  IC=1, NOND  
4444  TOND(IR, IC) = AAV(1R, IC)  
    CALL FINSUB(TOND, NONU, BOND, BAV)  
4444  DO 4445  IR=1, NONU  
4445  DO 4445  IC=1, NONU  
4445  TOND(IR, IC) = AAV(1R, IC)  
C  
C  
CCCC  
SECTION A4  
C  
L=1CC  
IF(I(AAXIS.FQ.1)) GO TO 9991  
IF(I(AAXIS.FQ.2)) GO TO 9993  
IF(JN.EQ.3I) GO TO 9991  
CALL Q1(J, 0, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1)  
CALL FROSTX(NK1D, NP1D, NK3U, NP3U, J, J, TEPD, TOPD, BEPD, BPOD, F1, M, N, L)  
CALL Q1(J, 0, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1)
CALL FRQA$TY (NK2D, NP2D, NK4U, NP4U, J, J1, TEND, TONU, BEND, BONU, FI, M, N, L)
GO TO 7770
8881 IF (ICC.EQ.1) GO TO 8882
CALL R2(1,1,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK1D, NP1D, NK4U, NP4U, J, J1, TEPD, TONU, BEND, BONU, FI, M, N, L)
CALL R2(2,1,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK2D, NP2D, NK3U, NP4U, J, J1, TEND, TOPU, BEND, BONUP, FI, M, N, L)
CALL R2(2,2,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK3D, NP3D, NK4U, NP4U, J, J1, TEND, BOPD, BEND, BONU, FI, M, N, L)
CALL R2(1,1,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK4D, NP4D, NK1U, NP1U, J, J1, TEND, TEPF, BOND, BEND, BONP, FI, M, N, L)
GO TO 7770
8882 CALL R3(1,1,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK4U, NK1D, NP1D, NK4U, NP4U, J, J1, TEPD, TONU, BEND, BONU, FI, M, N, L)
CALL R3(2,1,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK3U, NP3U, NP4D, NP4D, J, J1, TOPU, BEND, BOND, BONP, FI, M, N, L)
CALL R2(1,2,1,1,1,M,1,N,1,F1)
CALL FRQA$TY (NK4U, NP4U, NK3D, NP4D, J, J1, TEPD, BOND, BONP, FI, M, N, L)
GO TO 7770
9993 IF (J.NE.J1) GO TO 7771
CALL R4(1,1,1,1,1,N,1,N,1,J,FI)
CALL FRQA$TY (NK1D, NP1D, NK4U, NP4U, J, J1, TEPD, TONU, BEND, BONU, FI, M, N, L)
CALL R4(2,1,1,1,1,N,1,N,1,J,FI)
CALL FRQA$TY (NK2D, NP2D, NK3U, NP3U, J, J1, TEND, TOPU, BEND, BONUP, FI, M, N, L)
GO TO 7770
7771 IF (ICC.EQ.1) GO TO 7772
CALL R2(1,0,1,1,1,N,1,N,1,J,FI)
CALL FRQA$TY (NK1D, NP1D, NK3U, NP3U, J, J1, TEPD, TOPU, BEND, BONP, FI, M, N, L)
CALL R2(2,0,1,1,1,N,1,N,1,J,FI)
CALL FRQA$TY (NK2D, NP2D, NK4U, NP4U, J, J1, TEND, TONU, BEND, BONU, FI, M, N, L)
CALL R3(1,0,1,1,1,N,1,N,1,J,FI)
CALL FRQA$TY (NK3D, NP3D, NK1U, NP1U, J, J1, TOPD, TEPF, BOPD, BEND, BONP, FI, M, N, L)
CALL R3(2,0,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK4D, NP4D, NK2U, NP2U, J, J1, TOND, TEND, BEND, BONP, FI, M, N, L)
GO TO 7770
7772 CALL R3(1,0,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK1U, NP1U, NK3D, NP3D, J, J1, TEPD, TOPD, BEND, BONP, FI, M, N, L)
CALL R3(2,0,1,1,1,M,1,N,1,J,FI)
CALL FRQA$TY (NK2U, NP2U, NK4D, NP4D, J, J1, TEND, TONU, BEND, BONU, FI, M, N, L)
CALL R4(1,0,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK3U, NP3U, NK1D, NP1D, J, J1, TOPU, TEPD, BOPD, BEND, BONP, FI, M, N, L)
CALL R4(2,0,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK4U, NP4U, NK2D, NP2D, J, J1, TOND, TEND, BEND, BONU, FI, M, N, L)
GO TO 7770
9999 IF (J.NE.J1) GO TO 6661
CALL R2(1,2,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK1D, NP1D, NK2U, NP2U, J, J1, TEPD, TEND, BEND, BONU, FI, M, N, L)
CALL R2(2,1,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK2D, NP2D, NK3U, NP4U, J, J1, TOPD, TONU, BOPD, BONU, FI, M, N, L)
GO TO 7770
6661 IF (ICC.EQ.1) GO TO 6662
CALL R1(0,1,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK1D, NP1D, NK1U, NP1U, J, J1, TEPD, TEPF, BEND, BEND, FI, N, L)
CALL R1(1,2,1,1,1,N,1,N,1,F1)
CALL R1(1,3,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK3D, NP3D, NK4U, NP4U, J, J1, TEND, BONU, BEND, FI, N, L)
CALL R1(2,4,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK2D, NP2D, NK2U, NP2U, J, J1, TEND, TEND, BEND, BONU, FI, M, N, L)
GO TO 7770
6662 CALL R2(1,0,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK1U, NP1U, NK1D, NP1D, J, J1, TEPD, TEPD, BEND, BEND, FI, N, L)
CALL R1(2,1,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK3U, NP3U, NK3D, NP3D, J, J1, TOPU, TOPD, BOPD, BOPD, FI, N, L)
CALL R1(1,3,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK4U, NP4U, NK4D, NP4D, J, J1, TONU, TOND, BONU, BOND, FI, N, L)
CALL R1(2,4,1,1,1,N,1,N,1,F1)
CALL FRQA$TY (NK2U, NP2U, NK2D, NP2D, J, J1, TEND, TEND, BEND, BEND, FI, N, L)
7770 CONTINUE
1020 CONTINUE
9770 STOP
END
SUBROUTINE FROASTXY(N1D,N2D,N1U,N2U,J1,TD,TU,B1D,B2U,F1,F2,N,IO)
DIMENSION R(1:1),R(2:1),R(1:1),R(2:1)
DIMENSION P(26,1),T(26,1),TU(26,1)
DIMENSION R(26,26),RC(26,26)
DIMENSION B1D(1),B1U(1),B2D(1),B2U(1)
DIMENSION J1(150),J2(150),K1(150),K2(150)
DIMENSION EEDX(150),ESX(150),SS1(150)
DIMENSION EEDY(150),AAA1(150),AAAXY(150)
DIMENSION FF(150),LJ1(150)
DIMENSION SSRN(150)
COMMON /ABC/ IT,TRAC
COMMON /AAA/ C1,C2,C3,C4,OMC,SO,CEX,QR,VK1,VK2,CO

C
202  JD=J*(J+1)
    JD=J*(J+1)
    DO 100 IR=1,N
        IR=1,N
        RC(IR,IC)=0.
100  IF(J.EQ.J1) GO TO 300
    IF(J.GT.J1) GO TO 400
        CO=1./((4.*J*(J+1))
    GO TO 500
300  CO=(2.*J+1)/(4.*J*(J+1))
    GO TO 500
400  CO=1./((4.*J))
500  DO 600 IR=1,N
    DO 600 IR=1,N
        DO 600 IC=1,N
            DO 600 IC=1,N
            R(REC,IR,IC)=R(REC,IR,IC)+TD(I,IR)*F1(I,IC)
        DO 600 IC=1,N
        DO 600 IR=1,N
400  RC(REC,IR,IC)=RC(REC,IR,IC)+R(REC,IR,IC)*TU(REC,IR,IC)
700  I=I+1
100  CONTINUE

300  K1=N1D(IR)
    K2=N2D(IR)
    K3=N1U(IC)
    K4=N2U(IC)
    IF(J.EQ.K1) GO TO 2001
    IF(J.EQ.K2) GO TO 2001
    IF(J.EQ.K3) GO TO 2001
    IF(J.EQ.K4) GO TO 2001
    VKP=ABS(VKP)
    VKN=ABS(VKN)
    IF(VKN.GT.2.0*VKP.GT.3) GO TO 800
    KT=KN+KP

1002  BB=B1D(IR)
    BU=R2U(IC)
    IF(I.EQ.1) GO TO 2001
    ED1=C1+J1*2*BB
    EU2=C3*J1+4*BU
    AA1=KD
    AA2=BU
    GO TO 3001
2001  ED1=C1+J1*2*BU
    EU2=C3*J1+4*BU
    AA1=BU
    AA2=BU
3001  F1=OMC*EU2-ED1
    S=DP(I,IC)+2*CO
    IF(S.LE.1.0) GO TO 800
    IF(K1.RE.10(K1)) GO TO 900
    C=.25
    GO TO 800
900  C=.75
800  EDE=ED1+CO
    S1=S+5*F1*EXP(-EDE/CNX)=1000.*C/(3.1415927*QR*OMC)
    SR=S-5*F1*EXP(-EDE/CNX)/OMC
    ICOUNT=ICOUNT+1
    I=ICOUNT
SUBROUTINE Q1(IA, IB, IM, MR, MC, J, FI)
DIMENSION F1(26, 1)
DO 500 IR = 1, MR
DO 500 IC = 1, NC
500  F1(1R, IC) = 0.
IF (IA, EQ, 2) GO TO 700
DO 800 IC = 1, NC
IQ = 2*IC - 3
F1(IC, IC) = J*X(J+1)-10*X(IQ+1)
800  F1(IC, IC) = SQRT(F1(IC, IC))
F1(1, 1) = F1(1, 1)*SQRT(2.)
GO TO 900
700  DO 100 IC = 2, NC
IQ = 2*IC - 2
IF (IC) = J*X(J+1)-10*X(IQ+1)
100  F1(1R, IC) = SQRT(F1(1R, IC))
900  IF (IA, EQ, 2) GO TO 200
DO 500 IR = 2, NR
IC = 1
IQ = 10+IC-2
IF (IB, EQ, 0) GO TO 400
FAC = -1.
GO TO 510
400  FAC = 1.
510  F1(IR, IC) = J*X(J+1)-10*X(IQ+1)
300  F1(IR, IC) = FAC*SQRT(F1(IR, IR-1))
GO TO 610
200  DO 710 IR = 1, NR
IQ=2*IR-1
IF(IR, IR=J*(J+1)-IQ*(IQ+1)
IF(IR, EQ.0) GO TO 810
FAC=1.
GO TO 710
810 FAC=1.
710 IF(IR, IR=FAC*SQR(FI(IR, IR))
610 DO 111 IR=1, MR
DO 111 IC=1, NC
111 IF(IR, IC)=FI(IR, IC)*IN
RETURN
END
SUBROUTINE R2(A, IA, IB, IM, M, J, FI)
DIMENSION FI(26, 1)
DO 600 IR=1, N
DO 600 IC=1, N
IF(IR, IC)=0,
IF(A, EQ.2) GO TO 700
DO 500 IR=1, M
IQ=2*IR-2
FI(IR, IR)=(J1+IQ)*(J1+IQ+1)
IF(IR, EQ.0) GO TO 1000
FAC=1.
GO TO 2000
1000 FAC=1.
2000 IF(IR, IR)=FAC*SQR(FI(IR, IR))*IN
600 CONTINUE
DO 1100 IR=2, N
1C=IR-1
IQ=IR+IC-2
FI(IR, IC)=(J1-IQ)*(J1-(IQ+1))
1100 FI(IR, IC)=SQR(FI(IR, IC))*IN
FI(1, 1)=FI(1, 1)*SQR(2)
RETURN
700 DO 1200 IR=1, N
IQ=2*IR-1
FI(IR, IR)=(J1-IQ)*(J1-(IQ+1))
1200 IF(IR, IR=IN*SQR(FI(IR, IR))
-DO 1300 IC=2, N
1R=IC-1
IQ=2*IC
FI(IR, IC)=(J1+IQ)*(J1+IQ-1)
SI=SQR(FI(IR, IC))
IF(IR, EQ.0) GO TO 1400
FAC=1.
GO TO 1500
1400 FAC=1.
1500 FI(IR, IC)=FAC*S1*IN
1300 CONTINUE
RETURN
END
SUBROUTINE G2(I, IRD, MR, MC, J, FI)
DIMENSION FI(26, 1)
IF(I, EQ.2) GO TO 700
MR=IFIX(0.5*(J+2))
OC=IFIX(0.5*J)
DO 500 IR=1, MR
DO 500 IC=1, NC
500 FI(IR, IC)=0.
GO TO 600
700 MR=IFIX(0.5*(J+2))
MC=IFIX(0.5*(J+1))
DO 600 IR=1, MR
DO 600 IC=1, NC
600 IF(IR, IC)=0.
200 DO 900 IR=1, MR
DO 900 IC=1, NC
MM=IR-1C
IF(IN, NE.1) GO TO 900
FI(IR, IC)=4.*((IR+2.)*(IR-2))**2
900 CONTINUE
END
SUBROUTINE R1 (IR, ID, J, M, N, PI)
DIMENSION FI(26, 1)
C0 TO (100, 200, 200, 400), ID
100 N = IFIX(0.5*(J+3))
N = IFIX(0.5*(J+2))
C0 TO 500
200 N = IFIX(0.5*(J+2))
N = IFIX(0.5*(J+1))
C0 TO 500
400 N = IFIX(0.5*(J+1))
N = IFIX(0.5*J)
500 DO 600 I = 1, N
DO 600 K = 1, M
600 FI(I, K) = 0.
DO 700 I = 1, N
DO 700 K = 1, M
IF(I .NE. K) GO TO 700
IQ = 1
FI(I, 1) = 4.*(J**2-(IR+2*IQ)**2)
700 CONTINUE
RETURN
END
SUBROUTINE ARRCG(J, D0, B1, B2, B3, B4, NK1, NP1, NK2, NP2, NK3, NP3, NK4, NP4, IR, N2, N3, N4)
DIMENSION BO(1), BI(1), B2(1), B3(1), B4(1), N1(101), N2(101)
DIMENSION NK1(1), NP1(1), NK2(1), NP2(1), NK3(1), NP3(1)
DIMENSION NK4(1), NP4(1)
J0 = 2*(J+1)
CALL ACG(J, N1, N2)
IF(J .EQ. 10(J)) GO TO 1000
DO 200 I = 1, N1
K = 4*I-2
B1(1) = BO(K)
NK1(1) = N1(K)
200 NP1(1) = N2(N1)
DO 300 I = 1, N2
K = 4*I-1
B3(1) = BO(K)
NK3(1) = N1(K)
300 NP3(1) = N2(N3)
DO 400 I = 1, N3
K = 4*I-3
B2(1) = BO(K)
NK2(1) = N1(K)
400 NP2(1) = N2(N2)
DO 500 I = 1, N4
K = 4*I-1
B4(1) = BO(K)
NK4(1) = N1(K)
500 NP4(1) = N2(N4)
RETURN
1000 DO 600 I = 1, N1
K = 4*I-3
B1(1) = BO(K)
NK1(1) = N1(K)
600 NP1(1) = N2(N1)
DO 700 I = 1, N2
K = 4*I-1
B2(1) = BO(K)
NK2(1) = N1(K)
700 NP2(1) = N2(N2)
DO 600 I = 1, N3
K = 4*I-2
B3(1) = BO(K)
NK3(1) = N1(K)
600 NP3(1) = N2(N3)
DO 900 I = 1, N4
K = 4*I-1
B4(1) = BO(K)
NK4(1) = N1(K)
900 NP4(1) = N2(N4)
RETURN
END
SUBROUTINE SUBMTK(H,F,C,J,TEP,TEN,TOP,TON,NEP,REN,ROP,RON,AB1,AB1,AB2,AB3,AB4)
DIMENSION AB1(1),AB2(1),AB3(1),AB4(1)
DIMENSION Z(26,26),W(40)
DIMENSION TEP(26,1), TEN(26,1), TOP(26,1), TON(26,1)
DIMENSION A1(26,26), A2(26,26), A3(26,26), A4(26,26)
DIMENSION G1(26), C2(26), C3(26), C4(26), C5(26)
DIMENSION N(40)
COMPLEX W
NZ=26
JD=J*(J+1)
A*=F*JD
IF(J.EQ.10(J)) GO TO 3333
N1=(J+1)/2
N2=(J-1)/2
N3=N1
N4=N1
GO TO 2222
3333 N1=(J+1)/2
N2=J/2
N3=N2
N4=N2
2222 DO 1000 IR=1,N1
DO 1000 IC=1,N1
TEP(1R,1C)=0.
1000 DO 1001 IR=1,N2
DO 1001 IC=1,N2
1001 DO 1002 IR=1,N3
DO 1002 IC=1,N3
TOP(1R,1C)=0.
3000 A3(IR,IC)=0.
DO 4000 IR=1,N4
DO 4000 IC=1,N4
1000 A4(IR,IC)=0.
C
BB=C-F*JD
CC=H*FN(J,0)*X.5
BG1=BB+CC
BG2=BB-C
DO 1001 IR=2,N3
IC=IR-1
L=2*IC
TR=FN(J,L)*X*IC
A3(IR,IC)=SQRT(TR)
1001 TOP(1R,1C)=TR
JC=1
DO 1002 IR=2,N3
TR=A*(IR+JC)*2*IC
A3(IR,IR)=TR
TOP(1R,1C)=TR
1002 JC=JC+1
DO 1003 IC=2,N3
IC=IC-1
A3(IR,IC)=1.
1003 TOP(1R,1C)=1.
A3(1,1)=HC1
TOP(1,1)=HC1
DO 1004 IR=1,N4
DO 1004 IC=1,N4
1004 TOP(1R,1C)=TOP(1R,1C)
A4(IR,IC)=A3(1R,1C)
TOP(1,1)=BC2
A4(1,1)=BC2
DO 1005 IR=2,N1
IC=IC-1
L=2*IC
TR=FN(J,L)*X*IC
A1(IR,IC)=SQRT(TR)
1005 TEP(LR, IC)=TR
           JC=1
           DO 1006 L=1, N1
           TR=A*(L+JC)**2*C
           A1(L,L)=TR
           TEP(L,L)=TR
1006 JC=JC+1
           A1(2,1)=SQR(2.)*A1(2,1)
           TEP(2,1)=2.*TEP(2,1)
           DO 1007 IC=2, N1
           IR=IC-1
           A1(IR, IC)=1.
1007 TEP(IR, IC)=1.
           NM=NM-1
           DO 1008 IR=1, NM
           IC=IR+1
           A2C(IR, IC)=1.
1008 TEP(IR, IC)=1.
           DO 1009 IR=1, N2
           I=(2*I)**2
           TR=IP*C+A
           A2C(IR, IR)=TR
1009 TEP(IR, IR)=TR
           DO 2001 IR=2, N2
           IC=IR-1
           I=2*IC+1
           TR=FM(J, I)**2*T
           A2C(IR, IC)=SQR(2.*TR)
2001 TEP(IR, IR)=TR
           NER=N1
           NEN=N2
           NOP=N3
           NON=N4
           T=4B.
           FX=2.*(-T)
           CALL EA02B(N1, 26, A1, C1, C2, C3, C4, C5, FX)
           DO 3001 IP=1, N1
1001 AR(IP)=A1(IP, IP)
           CALL EA02B(N2, 26, A2, C1, C2, C3, C4, C5, FX)
           DO 3002 IP=1, N2
1002 AR(IP)=A2(IP, IP)
           CALL EA02B(N3, 26, A3, C1, C2, C3, C4, C5, FX)
           DO 3003 IP=1, N3
1003 AR(IP)=A3(IP, IP)
           CALL EA02B(N4, 26, A4, C1, C2, C3, C4, C5, FX)
           DO 3004 IP=1, N4
1004 AR(IP)=A4(IP, IP)
           RETURN
           END
           FUNCTION 10(L)
           Y=FLOAT(L)
           Z=Y**2.
           M=Z
           M2=M*M
           I0-M12
           RETURN
           END
           SUBROUTINE ODR(X, Y, J0)
           DIMENSION X(J0), Y(J0)
           J=1
20          TERN=-1.E20
           DO 10 I=1, J0
           IF(X(I).GT. TERN) GO TO 20
           GO TO 10
20          TERN=X(I)
           J=J+1
           IF(J.GT.J0) GO TO 2222
           GO TO 30
2222 RETURN
           END
SUBROUTINE FINSUB(T,N,TB,AAV)
DIMENSION AL(26,26),AN(26,26),AY(26,26),AP(26,26),R(26,26)
DIMENSION T(26,1),TB(1),AAV(26,1),VKN(26),VBM(26)
C
C
NORD*N
VKN=T(1,1)
DO 5000 IR=2,N
IC=IR-1
5000 VBM(IC)=T(IR,IC)
DO 5001 IR=2,N
11=IR-1
5001 VKN(I1)=T(IR,IR)
DO 1000 IR=1,N
DO 1000 IC=1,N
AL(IR,IC)=0.
1000 AN(IR,IC)=0.
AL(1,1)=1.
IF(N.LT.2) GO TO 1002
TERM=1.
DO 1001 I=2,N
TERM=TERM*SDRT(VBM(I-1))
1001 AL(I,1)=TERM
1002 DO 1003 I=1,N
1003 AV(1,1)=1.
IF(N.LT.2) GO TO 1007
DO 1004 I=1,N
AVC(2,I)=(VKN-TB(I))
1004 AVC(2,I)=AV(2,I)
IF(N.LT.3) GO TO 1007
DO 1005 I=1,N
AVC(3,I)=(VKN(1)-TB(I))*(-AV(2,I))-VBM(I)
1005 AVC(3,I)=AV(3,I)
IF(N.LT.4) GO TO 1007
DO 1006 J=4,N
SIG=(-1)**(J-1)
DO 1006 I=1,N
AVC(J,I)=AVC(J,I)*SIG
1006 AVC(J,I)=AVC(J,I)*SIG
1007 DO 1008 IR=1,N
1008 DO 1009 IC=1,N
1009 R(IR,IC)=0.
1008 DO 1009 KC=1,N
1009 T(I)=0.
1009 R(KR,KC)=R(KR,KC)+AL(KR,1)*AV(1,KC)
DO 1011 I=1,N
SUN=0.
DO 1011 J=1,N
1010 SUN=SUN*R(J,1)**2
1011 AN(I,1)=1./SORT(SUN)
DO 1012 IR=1,N
1012 IC=1,N
1012 AAV(IR,IC)=0.
DO 1012 KR=1,N
1012 AAV(IR,IC)=0.
DO 1012 KC=1,N
1012 AAV(IR,IC)=0.
DO 1013 I=1,N
1013 AAV(KR,KC)=AAV(KR,KC)+R(KR,1)*AN(I,KC)
RETURN
END

FUNCTION TH(M,N)
TH=(M*(M+1)-N*(N+1))*(M*(M+1)-N*(N-1))/4.
RETURN
END
SUBROUTINE R3(IA,IB,IM,M,N,J1,FI)
DIMENSION FI(26,1)
DO 600 IR=1,M
DO 600 IC=1,N
600 FI( IR, IC )=0.
IF( IA .EQ. 2 ) GO TO 700
DO 800 I=1,M
IQ=2*I-2
FI( I, I )=(J1-IQ)*(J1-(IQ+1))
FI( I, I )=SQRT(FI( I, I ))*IM
800 CONTINUE
FI( I, I )=FI( I, I )*SQRT(2.)
DO 900 IC=2,N
IR=IC-1
IQ=IR-IC-2
FI( IR, IC )=(J1+IQ)*(J1+(IQ+1))
SI=SQRT(FI( IR, IC ))
IF( IB .EQ. 0 ) GO TO 1000
FAC=-1.
GO TO 900
1000 FAC=1.
900 FI( IR, IC )=FAC*SI*IM
RETURN
700 DO 1100 I=1,M
IQ=2*I-1
FI( I, I )=(J1-IQ)*(J1+(IQ+1))
SI=SQRT(FI( I, I ))
IF( IB .EQ. 0 ) GO TO 1200
FAC=-1.
GO TO 1100
1200 FAC=1.
1100 FI( I, I )=FAC*SI*IM
DO 1300 IR=2,M
IC=IR-1
IQ=IR-IC-1
FI( IR, IC )=(J1-IQ)*(J1-(IQ+1))
SI=SQRT(FI( IR, IC ))
1300 FI( IR, IC )=IM*SI
RETURN
END
SUBROUTINE AHC(J,N1,N2)
DIMENSION N1(1),N2(1)
I=1
N2=0
N1=0
1000 N1( I )=J-N1
N2( I )=N2
N1( I +1 )=N1( I )
N2( I +1 )=N2( I )+1
N2=N2+1
I=I+2
IF( I .GT. 2*J ) GO TO 1001
GO TO 1000
1001 N1( 2*J+1 )=0
N2( 2*J+1 )=J
RETURN
END
APPENDIX B

SUBROUTINE SUBPROGRAM FOR MOLECULAR SPECTRA GENERATION

"ABSORP" is a computer program which we have developed to plot the absorption spectra in a selected wavelength region at any pressure. The resolution of the scanning is assumed to be infinity which is suitable for employing lasers (i.e., the line-width of the laser is much smaller than the narrowest absorption line-width of the considered molecule).

List of Variables

FMAX: Is the upper frequency limit of the spectral region (cm⁻¹).

FMIN: Is the lower frequency limit (cm⁻¹).

P: The total pressure of the gas or the mixture (Torr).

WDO: Doppler-broadening HWHM per 1 cm⁻¹.

WLO: Lorentz-broadening HWHM (at P = 760 Torr), cm⁻¹.

NO: Number of absorption lines in the selected spectral region.

F(I): Absorption line positions, I = 1 ... I = NO, in cm⁻¹.

S(I): Absorption line intensity (cm⁻² atm⁻¹).
W(I)  

HWHM (Lorentz) for transition I if it is available (cm⁻¹).

For most of the calculations we have considered W(I) having the same value (i.e., equal to WLO).

The above parameters are inputs to "ABSORP". F(I), S(I), and W(I) may be available in the literature or can be calculated by "AROTOR" in Appendix A.

DFMX:  

Is a frequency limit around any absorption line, at which the absorption is to be considered as zero, i.e., absorption at (F(I) ± DFMX) equal 0.

FFO(I), SSO(I), WWO(I), I = 1, N, are parameters of the contributing absorption lines in the selected spectral region (i.e., from FMIN to FMAX).

The calculations of the absorption coefficient, Y(M), at a frequency, X(M), due to all contributing absorption lines depends on the total pressure. We have divided the pressure scale, from 1 Torr and below up to 760 Torr, to three regions: 1) P < 10 Torr, the profile used is purely Doppler. 2) P > 40 Torr, the profile is mainly Lorentzian, and 3) between 10 and 40 Torr we have used Voigt profile. We have checked the transitions from one profile to another.

The calculation of Y(M) is done at each frequency by adding the absorptions of all the contributing lines, then increment the frequency by DF and repeat the calculations. Now, we have an (X, Y) array of size NN. Y(I) must be normalized to its maximum value, YN.
Plotting the results depends upon the available plotting subroutines, the plotting statements listed in Appendix B may be only useful at McMaster University Computer Center. We have used the following subroutines from the Computer Center library:

1) "EA02B" for eigenvalues generation of any symmetrical matrix of N×N.

2) "PLOT" used to plot a continuous curve between the points Y(I) at X(I).

3) "UNITT0" to convert from data point to plotter units.

4) "INCH TO" to convert from inches to data points.

A typical output of "ABSORP" is shown in Fig. 8.7.
PROGRAM ABSORB (INPUT, OUTPUT, TAPE3=INPUT, TAPE6=OUTPUT)
DIMENSION F(3000), S(3000), W(3000)
DIMENSION FO(1000), SO(1000), Wo(1000)
DIMENSION FO(1000), SO(1000), WO(1000)
DIMENSION X(4000), Y(4000)
DIMENSION Xs(2), Ys(2)

READ(5, *) FMAX, FMIN, P, WO, WO, NO
READ(5, 101) (F(I), S(I), W(I), I=1, NO)

101 FORMAT(3 F10.4)

PICK UP ALL THE LINES IN THE SPECTRAL REGION

FLMT = (P/100.) * WLO
DFMN = 2. * FLMT

J = 1
DO 100 I = 1, NO
IFC (F(I) .GT. (FMAX + FLMT) .OR. F(I) .LT. (FMIN - FLMT)) GO TO 100
FOC(J) = F(I)
SOC(J) = S(I)
WOC(J) = W(I)
J = J + 1
100 CONTINUE

N = J - 1

ORDERING THE LINES IN INCREASING WAY

L = N
200 CONTINUE
200 CONTINUE

TERM = 0
DO 300 I = 1, L
IFC (FO(I) .GT. TERM) GO TO 300
TERM = F(I)
N = I
300 CONTINUE

FFO(J) = FO(N)
SSO(J) = SO(N)
WOO(J) = WO(N)
FOC(N) = FOC(L)
SOC(N) = SOC(L)
WOC(N) = WOC(L)
L = L - 1
IFC (L .EQ. 0) GO TO 400
GO TO 200

CALCULATING THE ABSORPTION COEFFICIENT AT DIFFERENT FREQUENCY

THE LINE PROFILE WILL DEPEND ON THE PRESSURE 1) P.LT. 10 TERR
   DOPPLER BROADEN. 2) P.LT. 40 TERR IT WILL BE WOIGT PROFILE 3)
   P.GT. 40 IT WILL BE COLLISION BROADEN.

400 J = 1

500 MM = (J - 1) * 4
DF = (FFO(J+1) - FFO(J)) / 5.
DO 600 K = 1, 5

N = K * J - 1 + M
X(K) = FFO(J) + DF * (K - 1)

FRO = X(N)

SUN = 0.
DO 990 I = 1, N

XX = AIMS * FRO - FFO(I)
IFC (XX .GT. DFMO) GO TO 500
SS = SSOC(I)
WOO = WLO * P / 760.
WD = WDO * FFO(I)

IFC (P .LT. 10.) GO TO 600
IFC (P .LT. 40.) GO TO 700

P10F = SS * XX * P / (3.1415927 * 760. * (XX**2 + WO**2))
GO TO 800
600 PROPSWP*ALOC(2.)**.5*EXP(-XW**2*ALOC(2.)/WD**2)/(WD*3.1415927**.5*760.)
GO TO 800
700 XW=XW*ALOC(2.)**.5/WD
YW=YW*ALOC(2.)**.5/WD
PROPSWP=PROPSWP*(XW,YW)/(760.*3.1415927**.5*WD)
800 SUMP=SUMP+PROPSWP
900 CONTINUE
YD=YD+SUMP
J=J+1
IF(J.GT.(J-1)) GO TO 1000
GO TO 500
1000 NN=(N-1)*5+1

C Calculate the max. absorption coefficient Yn=Y(1) max. and then
C Normalize all the abs. to Yn
C
TERM=0.
DO 1100 J=1,NN
IF(Y(J).LT.TERM) GO TO 1100
TERM=Y(J)
M=J
1100 CONTINUE
YN=Y(1)
DO 1200 I=1,NN
1200 Y(I)=Y(I)/YN

C Now we have Nn points of X and Y and the following steps for plot
C Nn points the following depends on the computer used and is only
C when using CDC MACH1 COMPUTER
C
XS(1)=FMAX
XS(2)=FMIN
YS(1)=1.
YS(2)=0.
XL=5.+20.
YL=3.+6.5
XNDIV=20.
YNDIV=5.
CALL HAP(XS,YS,2,XL,YL,XNDIV,YNDIV)
CALL CURVE(X,Y,NN)
CALL PLOT(G,0.0,999)
STOP
END

SUBROUTINE CURVE(X,Y,N)
DIMENSION X(1),Y(1)
N=1
XI=X(1)
YI=Y(1)
CALL UNITTO(XI,YI,XX,YY)
CALL PLOT(XX,YY,3)
DO 100 I=1,NN
CALL UNITTO(X(I+1),Y(I+1),XI,YI)
CALL PLOT(XI,YI,2)
100 CONTINUE
RETURN
END
SUBROUTINE MAP (X, Y, M, XL, YL, XDIV, YDIV)
DIMENSION X(M), Y(M)
CALL PLOT(0., 0., -3)
CALL DATE(D1)
CALL LETTER(10., 3, 279., 1., 10., 10, HELSHERBINY)
CALL LETTER(10., 3, 279., 2., 10., D1)
CALL PLOT(5., 0.0., -3)
XNARC=6.
YNARC=3.
CALL FACTOR(M, X, Y, XL, XMARC, YMARC)
CALL PLOT(XMARC, YMARC, 3)
CALL PLOT(XL, YMARC, 2)
CALL PLOT(XL, YL, 1)
CALL PLOT(XMARC, YL, 1)
CALL PLOT(XMARC, YMARC, 1)
YSTEP=(YL-YMARC)/YDIV
XOR=XMARC
YOR=YMARC
NDIVX=1IFX(XNDIV+1.)
NDIVY=1IFX(YDIV+1.)
DO 100 KY=1, NDIVY
CALL PLOT(XOR, YOR, 2)
CALL PLOT(XOR, YOR, 3)
CALL PLOT(XL, YOR, 2)
CALL INCITO(XMARC, YOR, XP, YP)
ENCODE(5., 3., YD) YP
CALL LETTER(5., 1., 6., 4., 1., YOR, .05, YD)
YOR=YOR+YSTEP
100 CONTINUE
IRSTEP=(XL-XMARC)/XDIV
DO 200 KN=1, NDIVX
CALL PLOT(XOR, YMARC, 3)
CALL PLOT(XOR, YMARC+1, 2)
CALL PLOT(XOR, XL-1, 3)
CALL PLOT(XOR, YL, 2)
CALL INCITO(XOR, YMARC, XII, YD)
ENCODE(7., 4., XD) XII
 CALL LETTER(7., 1., 0., 0., XOR, -2.2, 815., XD)
XOR=XOR+NSTEP
200 CONTINUE
RETURN
3 FORMAT(FG, 2)
4 FORMAT(F7.2)
END
FUNCTION RO(X,Y)
CONEQ(W(10),T(10),U2
W(1) = 6.6224367E-1
W(2) = 2.8667580E-1
W(3) = 1.0901720E-1
W(4) = 2.4810520E-2
W(5) = 3.2437334E-3
W(6) = 2.2853866E-4
W(7) = 8.602854E-6
W(8) = 1.8806937E-7
W(9) = 4.39930499E-10
W(10) = 2.22999356E-13
T(1) = 0.23554078
T(2) = 73747329
T(3) = 2.9476227
T(4) = 3.7985771
T(5) = 2.254974
T(6) = 2.7890669
T(7) = 3.3478548
T(8) = 3.9476408
T(9) = 4.6038245
T(10) = 5.3974989
Y2 = Y2 * 2
IF(Y.LT.1.0.AND.X.LT.4.0.R.Y.LT.1.8/(X+1.) GO TO 333
IF(Y.LT.2.5.AND.X.LT.4.0) GO TO 222
111 R0=R1(X,Y)
RETURN
222 R0=R2(X,Y)
RETURN
333 R0=R1(X,Y)
RETURN
END
FUNCTION R1(X,Y)
DIMENSION C(34)
F3(T) = EXP(T+2-X)*X2
Y2 = Y2 * 2
IF((X+2-Y2).GT.70.) GO TO 22
U1 = EXP(-X+2-Y2)*COS(2.*X+Y)
GO TO 65
22 U1 = 0.0
55 IF(X.GT.5.) GO TO 1111
C(1) = 1.9999999997
C(2) = 1.64900099999299
C(3) = 1.5539999999999
C(4) = 1.21666666666664
C(5) = 0.98769879999904
C(6) = 0.9583141248087
C(7) = 0.93621573016249
C(8) = 0.9205497464398
C(9) = 0.91196011635
C(10) = -0.5623198727E-2
C(11) = -0.2648763417E-2
C(12) = -0.1173267076E-2
C(13) = 0.4899519781E-3
C(14) = 1.933636801E-3
C(15) = 0.7258774668E-4
C(16) = 0.2365812E-4
C(17) = 0.0666763684E-5
C(18) = 0.027676397E-5
C(19) = 0.856673627E-6
C(20) = 0.031843374E-6
C(21) = 0.79395221E-7
C(22) = 1.91732287E-7
C(23) = 4.9102846E-8
C(24) = -1.244733E-8
C(25) = 2.9997777E-9
C(26) = -6.96450E-10
C(27) = 1.56225E-10
C(28) = -4.3997E-11
C(29) = -7.116E-12
C(30) = -1.447E-12
C(31) = -2.87E-13
C(32) = -3.35E-14
C(33) = .4E-14
C(34) = -.2E-15
BNO1 = 0.00
BNO2 = 0.00
XI = X/5.00
COEF = 4.00*X1**2 - 2.00
DO 20 I = 1, 34
II = 35 - I
BN = COEF + BNO1 - BNO2 + CI(II)
BNO2 = BNO1
20 BNO1 = BN
330 F = X1*(BN-BNO2)
460 DNO1 = 1.0 - 2.0*X1*F
1100 DNO2 = F
CO TO 1200
1111 DNO1 = -(1.5)**2 + .75/(**4 + 1.875/3**6 + 6.5625/3**8 + 29.53125/3**10 + .162
14210/3**12 + 1055.7421/3**14)
DNO2 = (1.00 - DNO1)/(2.**D)
1200 FUNCTION Y = DNO1
IF(Y .LE. 1.0E-08) GO TO 2500
Q = 1.0
YN = Y
DO 2000 I = 2, 50
DN = ((Y*DNO1 + DNO2) * (-2.) ) / FLOAT(I)
DNO2 = BNO1
DNO1 = BN
IF(MOD(I,2)) 2000, 2000, 1500
1500 Q = Q
YN = YN*Y2
G = DN*YN
FUNCTION Q = G/FUNCT + Q*G
IF(ABS(G/FUNCT) .LE. 1.0E-08) GO TO 2500
2000 CONTINUE
2500 R1 = U1 - 1.02637917*FUNCT
RETURN
END
FUNCTION R2(X,Y)
COMMON V(10), T(10), Y2
C = 0.0
DO 100 I = 1, 10
RN = T(I) - X
S = T(I) + X
100 C = C + (4.**T(I)**2 - 2.) * (RR*ATAN(RR/Y) + S*ATAN(S/Y) - .5*Y*(ALOG(Y2+RR**2
I) + ALOG(Y2+S**2))) * W(I)
R2 = 0.316309886*C
RETURN
END
FUNCTION R3(X,Y)
COMMON W(10), T(10), Y2
C = 0.0
DO 100 I = 1, 10
100 C = C + (1.0E0/((X-T(I))**2 + Y2) + 1.0/((X+T(I))**2 + Y2)) * W(I)
R3 = 0.316309886*Y*C
RETURN
END
The following are subroutines available from the author and not listed here:

1) Subroutine for absorption lines generation of symmetric-top molecules.

2) Subroutine for diatomic molecules.

3) Subroutine for CO$_2$ laser gain spectra including all the hot bands, the isotopic species bands, and their sequence bands.
REFERENCES


and

[26] L. S. Rothman, S. A. Clough, R. A. McClatchey, L. G. Young, D. E. Snider, and A. Goldman (SO\( \text{O}_2 \), NO, CH\( \text{H}_4 \), ...) 1977 Magnetic Tape, "AFCRIL Atmospheric absorption line parameters' compilation".

These two tapes are available from National Climatic Center of NOAA, Federal Building, Asheville, North Carolina 28801, each tape can be purchased from them for a service charge of $60.00.


and


OR

[101] "Widely-tunable" lasers, while operating CN at temperatures above 77°K are available commercially, but are quite expensive.