

A New Method for Making Ground-based Measurements of Stratospheric Species

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ABSTRACT

This report describes the progress made to date in the development of a ground-based tunable diode laser heterodyne spectrometer (TDLHS) operating in the mid-infrared. Details are given of the heterodyne measurements obtained of stratospheric nitric acid from ground level, and the preliminary work to retrieve altitude resolved information for this molecule.

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CONTENTS

	Page
I INTRODUCTION.....	1
II OBJECTIVES.....	1
III BACKGROUND TO HETERODYNE SPECTROMETRY	1
IV SELECTION OF LASERS.....	2
V HETERODYNE DETECTION OF STRATOSPHERIC NITRIC ACID	3
VII PORTABLE NEAR INFRARED SPECTROSCOPIC INSTRUMENT.....	4
VII DISCUSSION AND CONCLUSIONS.....	4
PUBLICATION	5
REFERENCES	5
LIST OF DIAGRAMS	5

Progress Report to the British Council

A New Method For Making Ground-based Measurements of Stratospheric Species

by

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I INTRODUCTION

This progress report describes the results obtained from the joint Anglo-French collaboration between the National Physical Laboratory (NPL) and the Groupe de Spectrométrie Moléculaire Atmosphérique (GSMA) of the Université de Reims. The primary objective of developing a ground-based mid-infrared tunable diode laser heterodyne spectrometer (TDLHS) that is capable of measuring important stratospheric trace species is briefly discussed. Details are given about the tests carried out to select a suitable laser local oscillator (LO) source for the spectrometer. Heterodyne spectra of stratospheric nitric acid are presented together with preliminary efforts to retrieve altitude resolved information for this molecule.

A secondary objective aimed at collaboration to cover portable near infrared atmospheric sensing instruments has emerged from this research.

II OBJECTIVES

Mid-infrared remote sensing instruments have been successfully employed to monitor low concentration molecules that are involved in the chemistry of the stratosphere. The majority of field studies have employed Fourier transform spectrometry (FTS) to detect these species. The objective of this joint project is to develop an instrument that uses the complementary technique of laser heterodyne spectroscopy. The advantages include optimum performance at long wavelengths, a high spectral resolution within a compact instrument, and a high signal to noise ratio to detect gases such as nitric acid which are present at trace levels. HNO_3 was selected as a priority gas because of the important role that it plays in stratospheric ozone depletion.

III BACKGROUND TO HETERODYNE SPECTROMETRY

The heterodyne technique combines incoming solar radiation (of frequency, ν_s) with light from the coherent local oscillator source (of frequency ν_{LO}) located in the instrument. The atmospheric solar spectrum is obtained from the difference frequency which, in this case, is in the radiofrequency region. The solar signal passes through the atmosphere so that some of the light is absorbed at characteristic wavelengths due to the species present. The wavelength of the laser is selected so that it is tunable over the spectral region of interest. By quantifying the

amount of absorption the concentration in the stratosphere can be determined from ground level. Figure 1 gives a schematic diagram of the TDLHS employed to record a spectrum of HNO_3 .

IV SELECTION OF LASERS

This section discusses some of the criteria used to select the diode laser employed to measure stratospheric HNO_3 . It is desirable that the LO should operate at above liquid nitrogen temperatures since this allows the laser to be mounted in a compact dewar and there is no requirement for a helium closed cycle cooler. In practice this is not always possible since it is still technically challenging to fabricate lasers at $11.5 \mu\text{m}$ for the desired target temperature.

The signal to noise ratio heterodyne equations developed by Blaney (1975) and McLroy (1990) can be used to identify the important parameters that govern the performance of a heterodyne spectrometer. With the addition of an extra term for the photomixer dark current, the signal to noise ratio, S_p , as expressed in electrical power is given by:

$$S_p = \frac{\langle i_{IF}^2 \rangle}{\langle i_S^2 \rangle + \langle i_T^2 \rangle + \langle i_D^2 \rangle + \langle i_J^2 \rangle + \langle i_A^2 \rangle} \quad (1)$$

where $\langle i_S^2 \rangle, \langle i_T^2 \rangle, \langle i_D^2 \rangle, \langle i_J^2 \rangle, \langle i_A^2 \rangle$ and $\langle i_{IF}^2 \rangle$ are respectively the mean square currents for shot noise, coherently detected thermal noise, mixer dark current, Johnson noise, IF amplifier noise and signal at the intermediate frequency (difference frequency).

The more useful voltage signal to noise, S_v , can be expressed as:

$$S_v = \frac{2\eta C_E (1-r)(B_{IF} \tau)^{1/2} \delta}{1 + 2\eta C_E (1-r)\delta + \frac{1}{I_L} \left[\frac{\bar{I}_n^2}{2e} + I_D \right]} \quad (2)$$

where η = quantum efficiency, C_E = chopper factor, r = beam splitter reflection factor, B_{IF} = Intermediate frequency bandwidth, δ = Bose-Einstein factor for light polarised parallel to the LO, $I_L = rP_L K$ = local oscillator photocurrent, P_L = local oscillator power, K = photomixer responsivity, $= \eta e / h\nu$, with $\bar{I}_n^2 / 2e$ = measured noise equivalent current of the preamplifier and photomixer combination, e = charge on the electron, and h = Planck's constant.

From equation (2) it can be seen that S_v can be increased by maximising η and minimizing I_D and $\bar{I}_n^2 / 2e$. These terms become insignificant if there is sufficient LO power incident on the photomixer to ensure that the LO shot noise dominates over other noise sources. In practice, this condition is not yet realisable with mid-infrared TDLs where typical powers are approximately $100 \mu\text{w}$. Despite this, it is still perfectly possible to achieve an adequate signal to noise ratio to measure stratospheric species.

A further restriction on the specification of the LO is that it must be close to single mode operation at the required wavelength. If this condition is not satisfied excess laser noise in the

radiofrequency region dominates and equation (2) is no longer a good model for the signal to noise ratio in the heterodyne regime.

A number of HNO_3 lasers have first been tested using the direct detection method. A Laser Photonics temperature and current controller was employed to regulate the diode wavelength. The radiation from each laser was passed in turn through a low pressure carbonyl sulphide gas calibration cell and the emerging beam was focussed onto a HgCdTe detector. To obtain absorption spectra each TDL was operated in the current modulation mode so that the output of the detector could be displayed on an oscilloscope. A Polaroid camera was used to record hard copies of the spectra. Relative wavenumber calibration was achieved by substituting the OCS cell in the laser beam with a 0.048 cm^{-1} free spectral range etalon made of germanium.

Figure 2 shows the results obtained for a TDL fabricated by Laser Photonics which was the only device found to have almost single mode coverage over one of the P-branch manifolds of the 5_0^1 band of nitric acid between 868 and 869 cm^{-1} (An FT spectrum from Maki and Wells (1991) was used to identify the OCS calibration features since HNO_3 was measured in the stratosphere). This laser was originally intended to operate at above liquid nitrogen temperatures but it was not possible to reach the target wavenumber region without further cooling.

In order to initially assess the heterodyne performance of the selected TDL, the precision with which a 1600 K glowbar source could be measured at a constant laser current and temperature was determined. The laser output was selected to be near to the nitric acid absorption feature. For 34 microwatts of power incident on the photomixer a SNR of 99 was obtained. When the solar spectrum was recorded there was a factor of three increase in the signal level over the 1600K black-body.

V HETERODYNE DETECTION OF STRATOSPHERIC NITRIC ACID

Heterodyne spectra of nitric acid were acquired using the TDLHS shown in Figure 1. The photomixer employed was made of HgCdTe and had a bandwidth of 310 MHz . The signal was amplified by a matched rf preamplifier of 150 MHz before being split into a bank of four rf filters and detectors. Each of the filters had a different IF bandwidth ($5\text{-}56 \text{ MHz}$, $2\text{-}20 \text{ MHz}$, $0.95\text{-}10 \text{ MHz}$ and $0.27\text{-}4.9 \text{ MHz}$) to enable spectra to be recorded simultaneously at different double-sideband resolutions over a scan range of about 1 cm^{-1} .

The outputs from the rf detectors were fed into four phase sensitive detectors which integrate over a set number of chopper cycles equivalent to a time constant of 0.5s . The signals were fed into an analogue to digital converter before passing to the personal computer controlling the laser scan rate and data collection cycle.

Figure 3 shows a typical solar scan of stratospheric nitric acid with a simultaneous calibration scan, in direct detection, of OCS between 868.3 and 868.75 cm^{-1} . The total scan time was 150 seconds and was recorded at NPL which is located at 51.5°N and 0.5°W .

VII PORTABLE NEAR INFRARED SPECTROSCOPIC INSTRUMENT

The mid infrared work has facilitated further collaboration involving a new instrument for balloon borne *in-situ* stratospheric measurements of key trace gases, and technical discussions are now underway with CNRS, Verrieres Le Buisson, which are synergistic with the other research summarised in this report.

VII DISCUSSION AND CONCLUSIONS

One of the aims of this project is to derive some altitude resolved information from heterodyne spectra. A method for obtaining such data was first suggested by Blatherwick et al (1991). It relies on the fact that the widths of the absorption lines in the mid-infrared are strongly influenced by pressure and are therefore height dependent. In this spectral region the pressure broadened linewidth (FWHM) for HNO₃ varies from approximately 0.017 cm⁻¹ at 20 km to approximately 0.0035 cm⁻¹ at 30 km.

In a preliminary study the atmospheric heterodyne spectrum of nitric acid was analysed using the software developed at the Université de Reims. A synthetic spectrum was generated using the parameters of A Goldman (1995) and an initial profile derived from the ATMOS/Spacelab 3 data in 1985. Using a non-linear least squares method the synthetic spectrum was scaled until it matched the recorded data. The fit is shown in Figure 4. The analysis yielded a total column amount of 1.5×10^{16} molecule cm⁻² which is a reasonable value for this species. The vertical profile obtained is shown in Figure 5 and has the expected maximum HNO₃ concentration between 20 and 25 km.

In conclusion, the Anglo-French collaboration has successfully enabled a high resolution heterodyne spectrum of stratospheric nitric acid to be recorded from ground level. The total column amount has been determined and a start has been made to obtain altitude resolved data for this species. It has also been beneficial in opening up a further related area - that of stratospheric sensing using near infrared diode laser spectroscopy and closer links are being established as a result of the synergistic nature of the ongoing research. Finally, this project has enabled there to be a close interaction between the two groups which has been particularly beneficial in the training of new young scientists in this area of research.

PUBLICATION

A poster was presented at the 1998 5th Symposium on Gas Analysis by Tunable Diode Lasers Freiburg, Germany.

REFERENCES

1. Blaney, T. G., 1975, Space Science Reviews 17, 691-702
2. McIlroy, C. T., et al., 1990, J. Geophys. Res. 95D, 5567-5575
3. Blatherwick, R. D., et al., 1991, Remote Sensing of Atmospheric Chemistry SPIE 1494, 203-210

LIST OF DIAGRAMS

- Figure 1: Schematic Diagram of Tunable Diode Laser Heterodyne Spectrometer.
- Figure 2: Diode laser OCS Absorption Spectrum.
- Figure 3: Scan of Atmospheric HNO₃ with Calibration Scan of OCS.
- Figure 4: Fit of Recorded Stratospheric HNO₃ Heterodyne Spectrum with Synthetic Spectrum
- Figure 5: Vertical Profile of HNO₃ Derived from Heterodyne Spectrum.

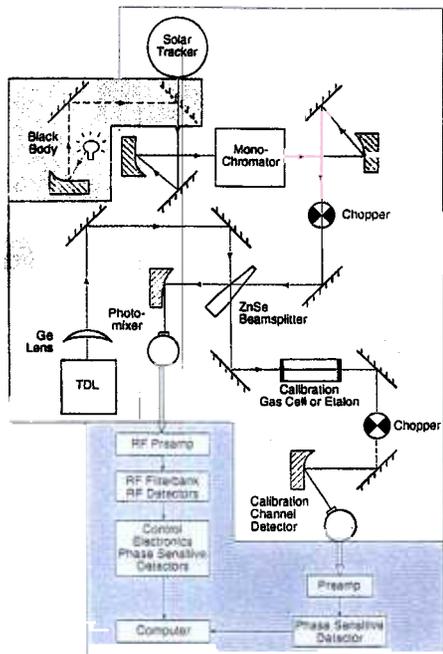
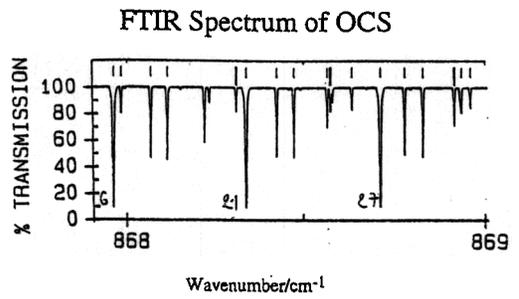
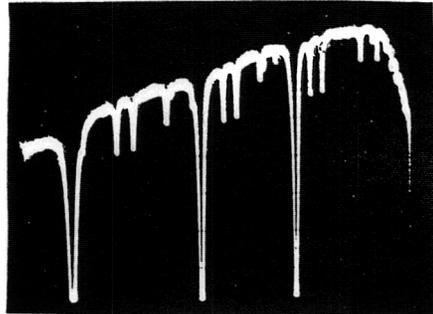


Figure 1: Schematic Diagram Of Tunable Diode Laser Heterodyne Spectrometer



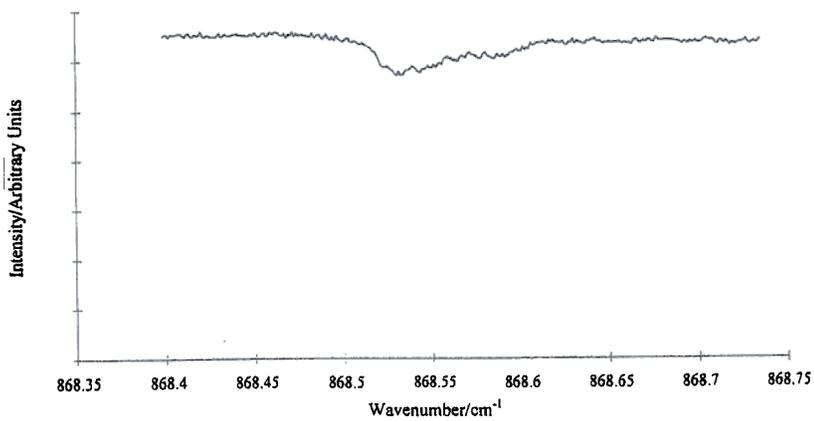
Diode Laser Absorption Spectrum of OCS (Direct Detection)



Laser #4013-15
T=79.5K

Figure 2: Diode Laser OCS Absorption Spectrum

HNO₃ Atmospheric Heterodyne Spectrum



Simultaneous OCS Calibration

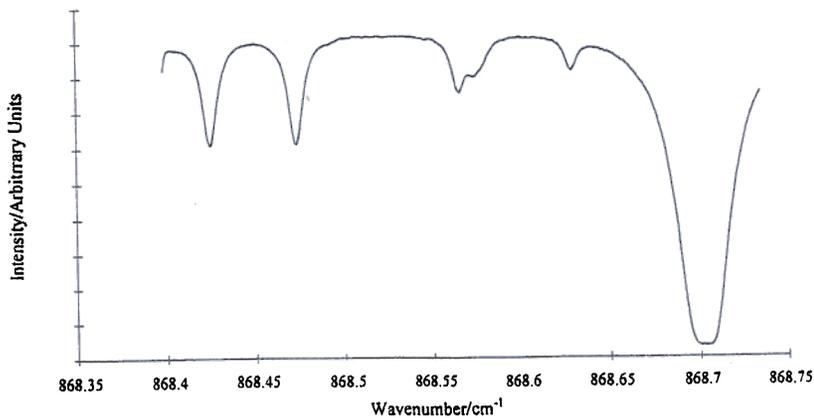


Figure 3: Scan Of Atmospheric HNO₃ With Calibration Scan Of OCS

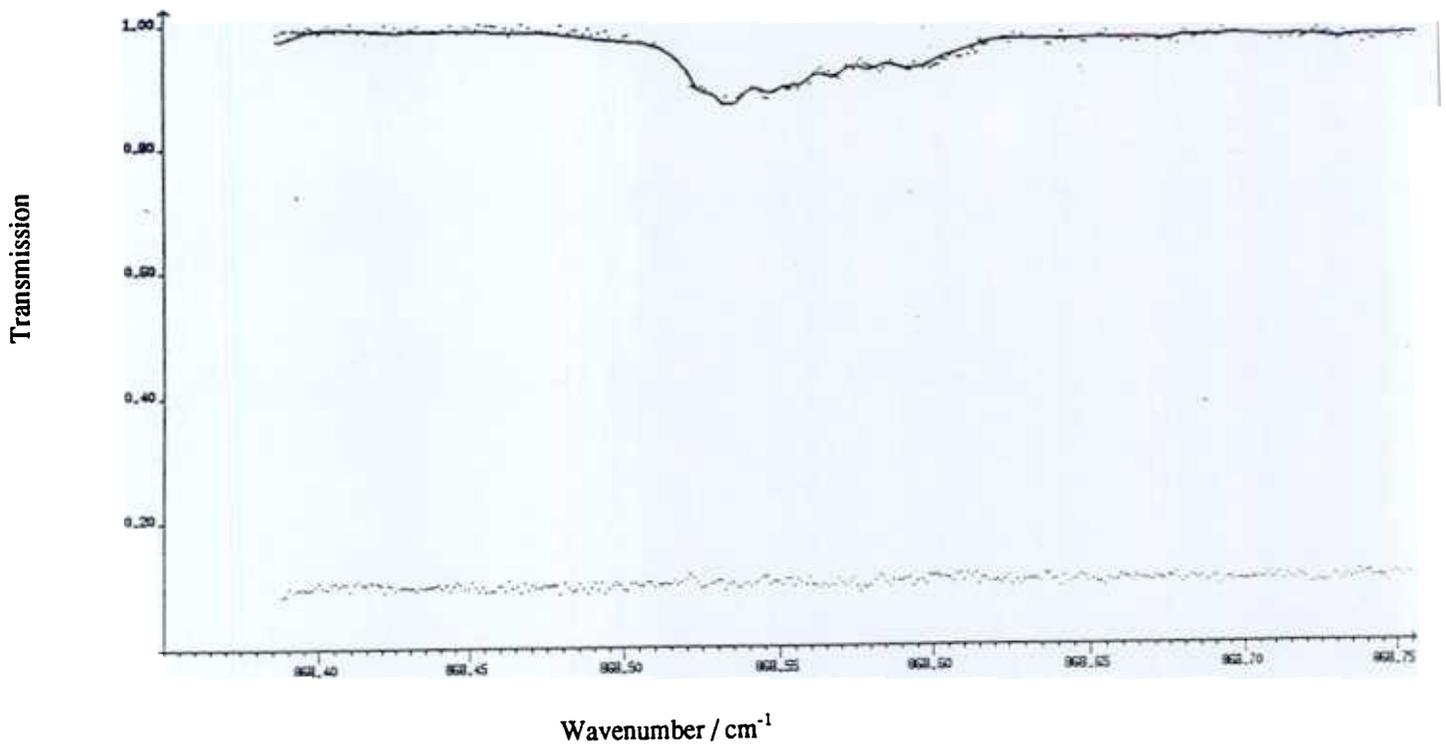


Figure 4: Fit Of Recorded Stratospheric HNO₃ Heterodyne Spectrum With Synthetic Spectrum

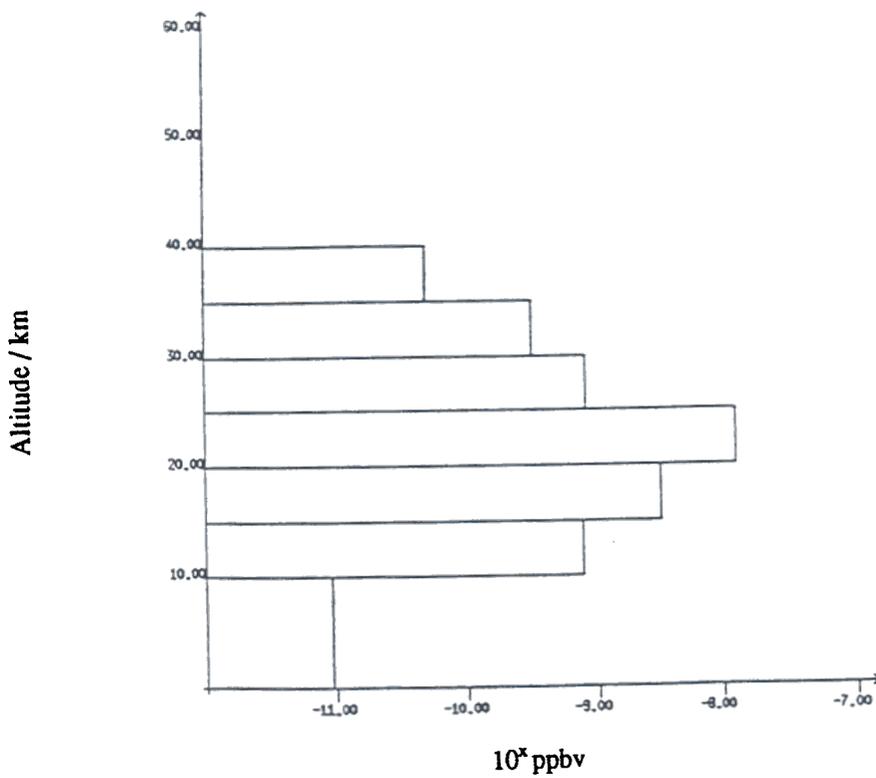


Figure 5: Vertical Profile Of HNO₃ Derived From Heterodyne Spectrum