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THE DETERMINATION OF HNO$_3$ COLUMN AMOUNTS FROM TUNABLE DIODE LASER HETERODYNE SPECTROMETER SPECTRA TAKEN AT JUNGFRUAJOCH, SWITZERLAND

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ABSTRACT

In May of 1991 a Tunable Diode Laser Heterodyne Spectrometer built by the National Physical Laboratory was operated at the International Scientific Station of the Jungfraujoch (46.5°N, 8.0°E, altitude 3.56 km). Nitric acid spectra in the region of 868 wavenumbers were recorded at sunset and sunrise on two separate days at a resolution of 0.0013 wavenumbers with a signal-to-noise ratio of approximately 130:1. A vertical column amount of HNO$_3$ of 1.61×10^{16} molecules/cm^2 was determined using an atmospheric transmission model developed at the University of Denver. The mean of a number of mid-latitude, northern hemisphere profiles was used as the initial profile for the inversion. A comparison of different initial profiles provides information on the sensitivity of the retrieved column amounts to the initial profile. The column amount of 1.61×10^{16} molecules/cm^2 lies within the range of values published in the World Meteorological Organization Report #16 [1986], but is considerably larger than the value of $(0.99 - 1.29) \times 10^{16}$ reported by Rinsland et al. [1991] for June during the period 1986 to 1990.

1. INTRODUCTION

Nitric acid is a trace species of some importance in ozone destruction mechanisms, particularly those related to the catalytic destruction of ozone by chlorine species. It was first measured in the Earth's atmosphere by Murcray et al. [1968] using a balloon-borne grating spectrometer. Subsequently, it has been measured by various techniques including Tunable Diode Laser Heterodyne spectrophotometry (TDLHS). A similar TDLHS system at the University of Denver has previously been used to determine column amounts of ozone [McElroy, et al., 1990, Fogal et al, 1988], and others have also reported Laser Heterodyne Spectrometer (LHS) measurements of atmospheric constituents [Frerking and Muehlner, 1977, Abbas et al., 1978, Hoell et al., 1979, and Okano, et al., 1989]. Laser heterodyne spectrometer theory has been discussed at great length by Blaney [1975], and others, with regards to optimum performance, and the development of a signal-to-noise equation.

2. MEASUREMENT DESCRIPTION

The TDLHS constructed by the National Physical Laboratory (NPL) is configured as a portable instrument which allows it to be transported and setup in various locales such as the International Scientific Station of the Jungfraujoch. This particular site was chosen for its high altitude, its accessibility and also because of its selection as a world network site.

A tunable diode laser heterodyne spectrometer derives its spectra from the product of a local oscillator field, produced by the tunable diode laser, and the signal field which in this case is infrared solar radiation. Thus the detected power has the form

$$P_{REC} = P_{LO} + P_{SUN} + 2\sqrt{P_{LO} P_{SUN}}$$

For these measurements the TDL temperature and current were adjusted such that it lased in an interval centered at 868 cm^{-1}. The intermediate frequency which results from the oscillatory term generated by the mixing of the two fields as described above is filtered by four bandpass filters as follows: 2-5 MHz, 2-10 MHz, 2-20 MHz, and 5-50 MHz. These channels result in a theoretical resolution of 0.00033 cm^{-1}, 0.0006 cm^{-1}, 0.0013 cm^{-1} and 0.003 cm^{-1}. A schematic of the instrument is presented as Figure 1. The TDLHS is provided with a sun seeker so that sunlight may be acquired for the measurement.
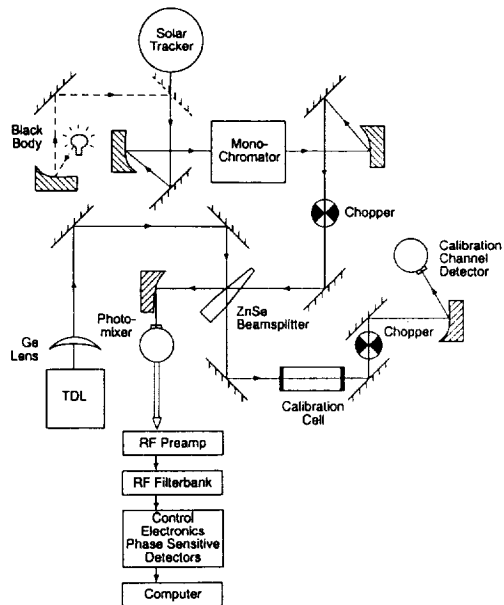
Figure 1: Instrument schematic for the NPL TDLHS system. Note that an etalon could be used in place of the gas cell.

3. DATA ANALYSIS TECHNIQUES

In general, TDLHS spectra require an external method of frequency calibration as there is not a frequency scale implicit in heterodyne detection. For the nitric acid data presented here, the region covered by the TDL was determined by the use of a gas cell containing ammonia. The extent of the mode was then determined by counting the fringes from a germanium etalon. Thus, the TDL was tuned to a known HNO_3 manifold from approximately 868.0 to 868.2 cm^{-1}. The features found in this manifold were then assigned frequencies through the use of a dispersion equation, which is a linear regression relationship between the point numbers of the scan and a well-calibrated interferometer scan of that same manifold, under similar atmospheric conditions and zenith angle. Unfortunately, it 'is not always possible to have the frequency calibration mechanisms in place during scans in which data are taken, due to the noise induced by laser light feeding back into the primary channel as the laser is tuned.

Once the spectrum has been assigned a usable frequency scale, it is compared to a modelled spectrum. The difference is calculated, and the model is adjusted until it agrees with the experimental spectrum to within some pre-determined tolerance. The tolerance is nominally set by the signal-to-noise ratio of the data,

which is calculated as the standard deviation divided by the mean over a region in which the signal is constant, weighted by the theoretical noise performance as follows

$$\% \ of \ theoretical \quad \frac{1}{* \ actual}$$

The modelling itself is accomplished through the use of radiation code developed at the University of Denver, which has been adapted to run on a PC-type computer. An atmospheric ray-tracing calculation is carried out followed by a line-by-line calculation. The line parameters are taken from the Hitran database [Rothman et al., 1987] with corrections made to the HNO_3 parameters [A. Goldman, private communication] in the 860-880 wave number region. A background atmosphere calculation containing water vapor and carbon dioxide as absorbers is first carried out. This is followed by a calculation for the nitric acid. The two are then added, and if needed the nitric acid calculation is adjusted through adjustments to its initial profile until the sum of the two accurately represents the experimental spectrum to within the prescribed tolerance. The original initial profile was calculated using the average of a number of mid-latitude northern hemisphere profiles as published in the World Meteorological Organization report #16 [1986].

4. RESULTS AND DISCUSSION

The nitric acid manifolds in this region are not very strong absorptions. Thus, large solar zenith angles are needed in order to provide features that can be easily calibrated and that are large enough that differences between modelled and measured radiances can be measured with confidence. However, this same scenario makes the calibration of the spectra more difficult as the features tend to be broad, leading to some uncertainty in assigning the frequencies. On the other hand, at small zenith angles the weak absorptions are not easily identified. Thus, we cannot calibrate the frequencies as well as we would like to, which results in some error over the manifold. However, the gross structure does match up quite well. Furthermore, there is the possibility that the Hitran HNO_3 line parameters may require further adjustments. There is also a background envelope to deal with, which is due mainly to the shape of the bandpass function of the solar grating. The laser mode also has an envelope, but this can be removed by subtracting the signal from the laser

monitor channel. This procedure also removes noise directly resulting from excursions in the laser intensity (ie: changes on the order of few current steps). The grating function can be removed either by studying the shape of a blackbody scan over the same region, or by an ad hoc approximation to the shape. The latter was performed here, due to the lack of an appropriate blackbody scan.

Scans at large zenith angles were obtained on two different days, the 7th and 13th of May, 1991. Presented here are four different scans from the 7th of May. The analysis of these scans returned a column amount of 1.61×10^{16} molecules cm^{-2}. These four scans are shown in Figure 2. A similar analysis of data from the 13th showed the column to be 1.65×10^{16}. The modelled atmosphere was given 8 layers, and pressure and temperature profiles were taken from the nearest radiosonde location for the two days in question. The residuals for the comparison of scan 11921126 and its modelled spectrum is shown in Figure 3.

The initial mixing ratio profile was moved upwards and downwards in steps of 2 km in order to test the sensitivity of the modelled spectra to the initial profile. The results are shown in Figure 4. The column amount was allowed to vary as the profile was moved. After the spectra were scaled to provide the best fit, it was clear that there were noticeable differences between the modelled *and experimental spectra for a change of 4 km. When the profile was moved upwards 4 km, the lines in the manifold were much more clearly resolved than shown in the experimental spectra. Conversely, when the profile was moved downwards 4 km we see that other features are somewhat less resolved. Moving the profile upwards 2 km, produces modelled spectra that very clearly resolve the complex indicated by the arrow. This is not so clearly resolved in the experimental spectra. When the profile is moved downwards 2 km, the modelled spectra provide the best fit to the experimental spectra. Thus, we arrive at a representative profile for these measurements to within 2 km. This move downwards increased the total column amount from 1.25 $\times$ 10^{16} to 1.61 $\times$ 10^{16} molecules cm^{-2}.

5. CONCLUSIONS

The good agreement between the modelled spectra and the experimental spectra indicates the initial profile, which is an average of many previously determined northern, mid-latitude profiles, is a good approximation to the actual HNO_3 vertical distribution. This is further substantiated by somewhat different modelled spectra produced when
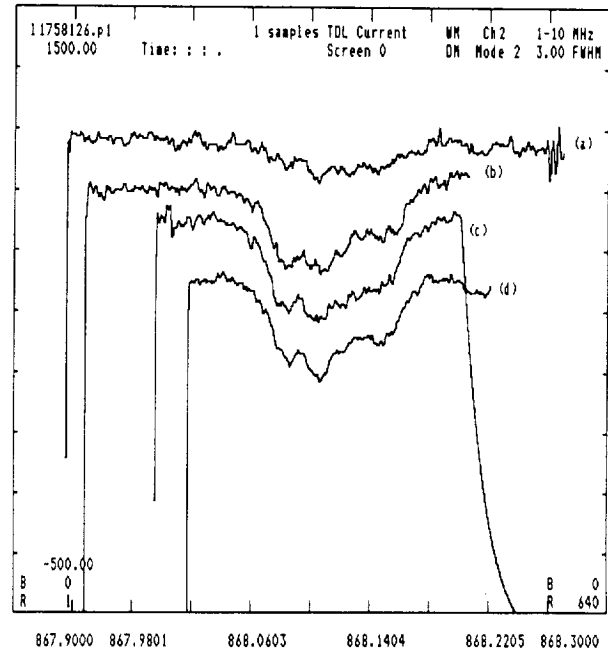
Figure 2: Four TDLHS scans taken on 7 May 1991. Scan (a) has a zenith angle of 73.37°, (b) has a zenith angle of 86.35°, (c) has a zenith angle of 87.15° and (d) has a zenith angle of 88.73°. All scans have been filtered with a 3 point FWHM triangular filter.
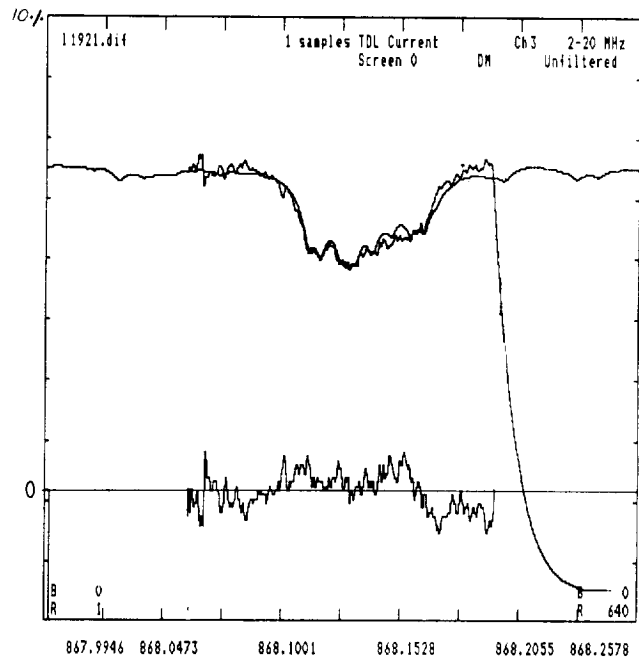
Figure 3: A comparison of scan (c) taken at 87.15° with a spectrum produced by the University of Denver model. The residuals are plotted on a scale of -2.5 to 10 % of full scale.

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11921up4.s1        Point number  WH   Synthetic
1900.00            Screen 0      OH   Unfiltered

-100.00

R 1921                                  R 2560
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867.9000 867.9801   868.0603   868.1404   868.2205 868.3000
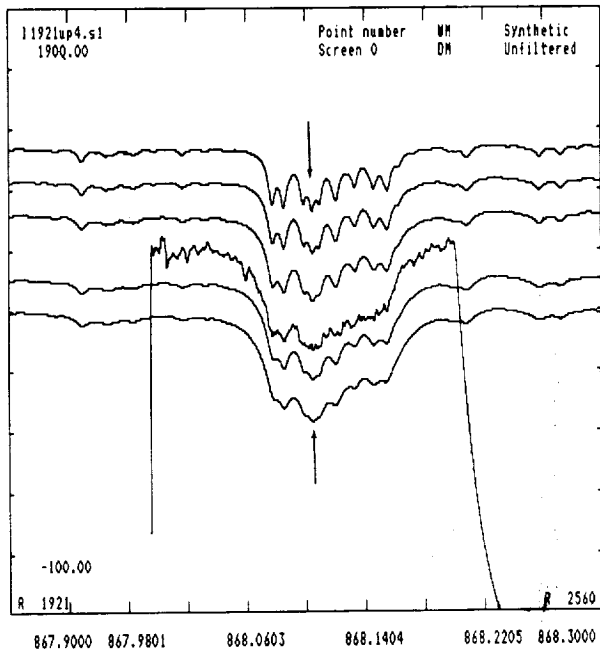
Figure 4: A comparison of the spectra resulting from moving the profiles upwards and downwards in 2 km increments. Curve (a) is the initial profile moved upwards 4 km, (b) up 2 km, (c) initial profile, (d) the experimental spectrum at a zenith angle of 87.15°, (e) initial profile moved down 2 km, and (f) moved down 4 km.

that profile is displaced vertically upwards and downwards. While this approach is not strictly speaking an inversion approach, this type of comparison between modelled and experimental spectra, can increase the accuracy of column amounts of HNO_3. The differences found by moving the profile upwards and downwards demonstrate that high-resolution spectra provide usable altitude distribution information on the scale of 2 km.

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