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THE GROUND-BASED MEASUREMENT OF OZONE IN THE 9.6 MICRON BAND

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ABSTRACT

Stratospheric ozone has been measured using infrared emission spectroscopy of the 9.6 micron band. Thermal emission spectra of the zenith sky were measured from the ground. The spectra show the presence of the 1020 cm^{-1} spectral feature of ozone on clear days. The spectra were measured with a BOMEM model 100 emission interferometer with a resolution of 4 cm^{-1}. This feature corresponds to a mixing ratio of 5 ppmv if the ozone is assumed to be uniformly distributed in the stratosphere from 25 to 35 km. The development of an inversion algorithm to derive the altitude distribution of the ozone in 3 layers is described. These measurements have been conducted from Peterborough, Ontario since June 1991; further investigations are planned to study the comparisons with Dobson and LIDAR ozone measurements.

1. INTRODUCTION

The infrared method for measuring ozone fell into disuse after the initial development in the 1950s; the infrared technique has been described in detail by Craig (1965). In this paper we describe a new application of the modern infrared technique that will complement the Umkehr method. The latter method is insensitive to tropospheric ozone, whereas the former technique is sensitive. The development of modern instrumentation and atmospheric inversion methods makes this a useful technique worth reviving again to be used in concert with the Umkehr method.

Infrared thermal emission spectra from the clear zenith sky have been monitored for the period of June 1991 to May 1992 at Peterborough, Ontario, using FTIR emission spectroscopy. The 9.6 micron band feature of ozone has been analyzed quantitatively using a radiative transfer model to infer the stratospheric ozone as well as the tropospheric ozone amounts. Six emission spectra, representative of seasonal variations over the measurement period, have been subjected to this analysis to determine the potential for this technique. Preliminary results indicate this analysis provides useful information on the altitude distribution of tropospheric, lower-stratospheric and upper-stratospheric ozone.

2. EXPERIMENTAL

All of the thermal emission spectra have been measured using a Bomem M100 Michelson interferometer with a resolution of 4 cm^{-1}. The interferometer is a two-entrance port instrument equipped with a deuterated triglycine sulphate high-speed (pyroelectric) detector. In order to collect an emission spectrum, one observation port was used as a reference, which received negligible radiation from a cold dewar of liquid nitrogen. The second port collected the vertically incident zenith sky radiation. A typical spectrum consisted of an average of 100 interferograms, providing a good signal-to-noise ratio of better than 30:1.

A three-layer model was developed to simulate the Planck blackbody emission from each layer and the transmission through each layer from the layer above. A forward calculation of the radiance was performed. An inversion was then conducted by iterating using ratio feedback (Chahine, 1972; Rodgers et al., 1988).

3. RESULTS AND DISCUSSION

A thermal emission spectrum of the clear zenith sky is shown in Figure 1. Various features from ozone, trichlorofluoromethane (CFC-11), dichlorofluoromethane (CFC-12), nitrogen dioxide and carbon dioxide are identified on the spectrum. The ozone band is located between 990 and 1070 cm^{-1}. Sky emission spectra displaying the ozone band are presented in Figure 2(a-e) and Figure 3 for six clear days representative of the period from June 1991 to May 1992. This band corresponds to a mixing ratio of 5 ppmv if the ozone is assumed to be uniformly distributed in the stratosphere from 25 to 35 km. The ozone emission feature calculated from the MODTRAN radiation code is shown for comparison in Figure 3. This simulation incorporated summer, mid-latitude temperature and density profiles. Features existing outside the band are primarily associated with water vapour, as determined from MODTRAN. The observed radiances at 990, 1000, 1010 and 1030 cm,$^{-1}$ which divide the band approximately equally, have been inverted into three layers at 500 mb (troposphere), 100 mb (lower stratosphere) and 30 mb (upper stratosphere) by an algorithm based on the Chahine method of relaxation (Chahine, 1972). The 990 cm^{-1}

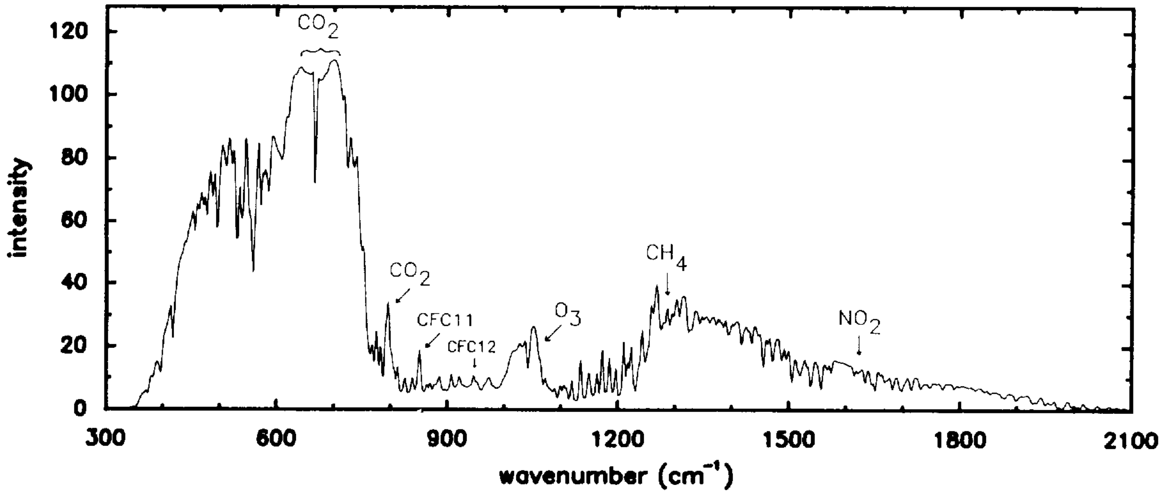

Figure 1: A typical thermal emission spectrum of the zenith sky on May 19, 1992. Various emission features are identified.

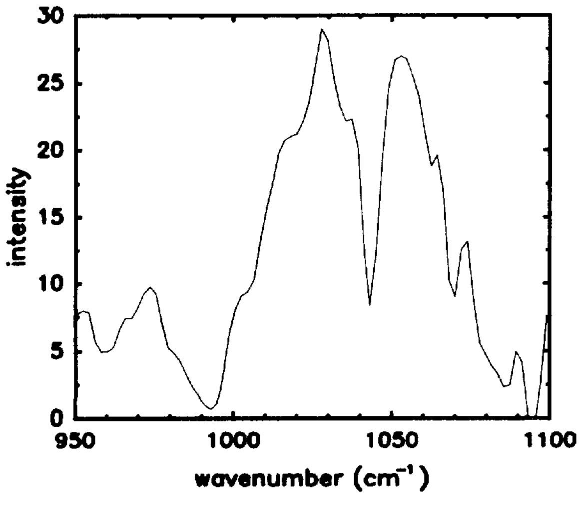

Figure 2a: The 9.6 μ ozone band for July 9/91.

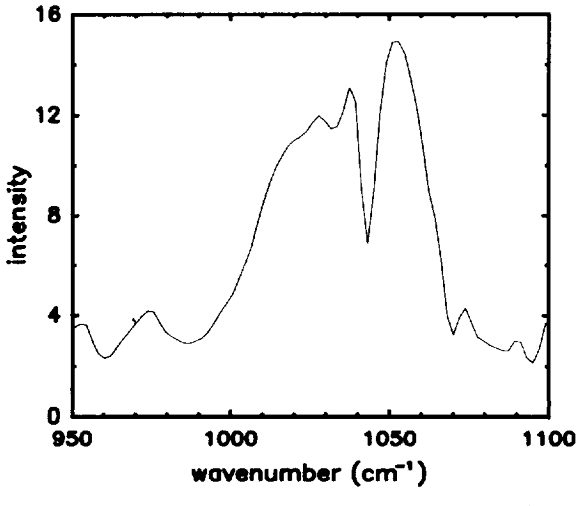

Figure 2b: The 9.6 μ ozone band for Nov. 4/91.

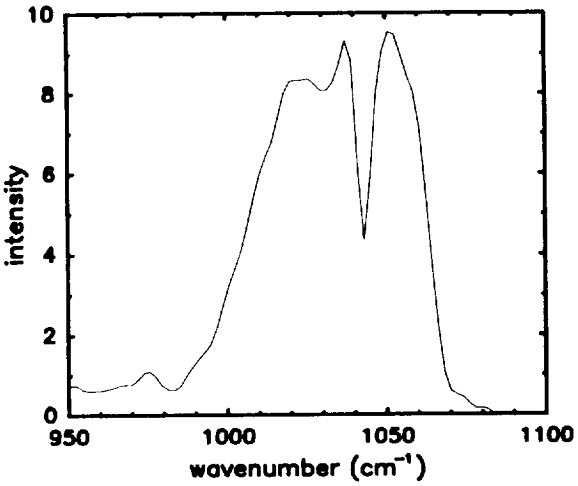

Figure 2c: The 9.6 μ ozone band for Jan. 16/92.

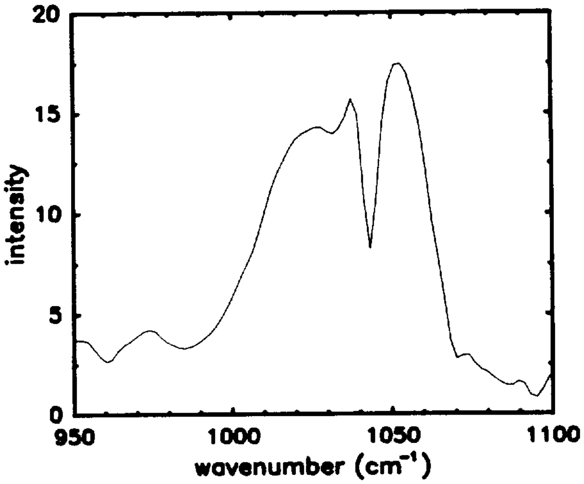

Figure 2d: The 9.6 μ ozone band for Mar. 19/92.

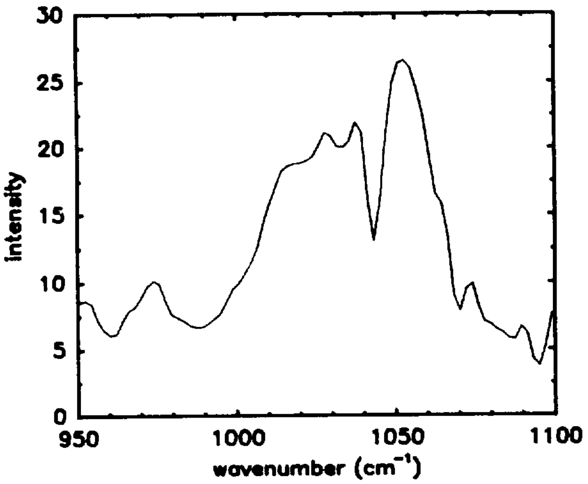

Figure 2e: The 9.6 μ ozone band for May 19/92.

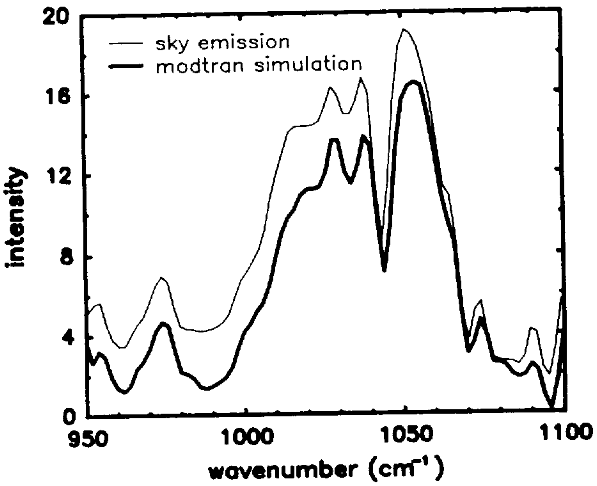

Figure 3: The comparison of an observed spectrum for Sept. 27/91 with a MODTRAN simulation. This band was normalized to the peak height of the experimental curve and displaced for clarity.

radiance is used to correct for the water vapour continuum. Climatological temperatures have been used for the seasonal variations of the three layers. Representative temperatures for the three layers in September are 270, 210 and 250 K. The results of the distribution of ozone in the three layers are tabulated in Table 1. A comparison with the climatological ozone from Toronto (Kerr, 1991) is shown in the last column of the Table. In addition, the total ozone column was determined and these preliminary results agree, in most cases, to within 5% of the climatological ozone for Toronto, Ontario; hence, these preliminary results indicate that this procedure is promising for providing the ozone distribution.

The inversion is quite sensitive to the amount of tropospheric ozone and to tropospheric temperature. Blackbody emission varies as T^4, hence the method is about $({}^{275}/_{220})^4$ or 2.4 times more sensitive to tropospheric ozone than stratospheric ozone.

The tropospheric temperature profile is easily obtained from radiosonde measurements in Southern Ontario. It could also be derived from the $15\mu m$ CO_2 band, although this would require further algorithm development.

It is estimated that the errors in the determination of the ozone amounts in the

Date	Troposphere Ozone (mm)	Lower-stratosphere Ozone (mm)	Upper-stratosphere Ozone (mm)	Total Ozone (mm)	Climatological Ozone (mm)
09/07/91	0.74	1.09	1.96	3.79	3.65
27/09/91	0.16	1.86	0.73	2.75	3.15
04/11/91	0.24	1.92	0.85	3.01	3.15
16/01/92	0.15	1.85	1.12	3.12	3.85
19/03/92	0.28	2.46	1.36	4.10	4.10
19/05/92	0.26	2.48	0.90	3.64	3.80

Table 1: Preliminary results showing the seasonal variation of inverted ozone layer amounts.

three layers are smaller than 15%. Part of this error could be reduced by using measured temperatures instead of climatological temperatures. Radiance errors are estimated to be about 3% for a signal-to-noise ratio of 30:1. The inversion algorithm multiplies these by about a factor of 3, so that the errors in the inverted ozone amounts are about 9%. The temperature error contribution is estimated to be about 8%; therefore the r.m.s. combined error in the ozone amount is about 15%.

4. CONCLUSIONS

Thermal emission spectra of the clear zenith sky have been measured since June 1991 at Peterborough, Ontario on a regular basis. By analyzing quantitatively the emission features at 990, 1000, 1010 and 1030 cm^{-1} with a radiative inversion model, the amount of ozone in 3 layers at 500, 100 and 30 mb has been determined.

The total ozone column also has been determined and is in fairly good agreement with the climatological ozone for Toronto, Ontario. Hence, these preliminary results suggest that the technique is promising for future analysis. An improvement in agreement is expected when measured upper air temperatures from radiosondes are used in the inversion model.

This method is most sensitive to tropospheric ozone, thereby complementing the Umkehr method and making this procedure valuable for the remote sensing of tropospheric ozone concentrations.

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