Measurements of submillimetre wavelength radiation emitted by the stratosphere

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SUMMARY

Observations have been made of the submillimetre wavelength radiation emitted by the lower stratosphere, using techniques of Fourier transform spectroscopy, while flying in a Comet 2E aircraft. Using the method of phase-modulation high quality spectra have been obtained at several altitudes over the spectral range 20 to 66 cm⁻¹, and these have enabled identification of many emission lines due to O₂ and O₃, in addition to those of H₂O. Also several unidentified emission lines have been observed. The meteorological applications of this spectroscopic technique are considered. In particular, a direct method of comparing the emission of 'strong' water-vapour and oxygen lines enables a calculation of mixing ratio of water vapour in the stratosphere to be made, and a value of (2.1 ± 0.3) × 10⁻⁴ g/g is derived above an altitude of 12.2 km. A similar comparison for ozone has given an integrated concentration of 0.35 ± 0.10 cm atm in the vertical path above the observer. The merits of these observations in measuring stratospheric mixing ratios are discussed with respect to alternative techniques, in particular with reference to balloon-borne studies.

1. INTRODUCTION

Recent work has shown that, for submillimetric studies of the stratosphere using both atmospheric emission (Bader, Cameron, Gebbie and Burroughs 1967; Gebbie, Burroughs, Harries and Cameron 1968; Eddy, Lee, Lena and MacQueen 1970), and solar radiation (MacQueen, Eddy, and Lena 1969; Eddy, MacQueen, and Lena 1969a) aircraft provide excellent high altitude observation platforms. The observations presented here consist of measurements of the radiation exchange between the atmosphere (temperature T = 220 K) and a thermal radiation detector (temperature T = 300 K). Such measurements will be shown to provide a powerful method of studying the concentration and distribution of water-vapour in the stratosphere, a subject that is of considerable interest and importance in meteorology (Gutnick 1961; Houghton 1963).

The method has been to observe the thermally emitted radiation of the stratosphere in the submillimetre region using Fourier transform spectroscopy. There are several reasons why we have chosen to measure the emission radiation rather than to observe solar radiation attenuated by the atmosphere, chief amongst these being that in the emission method no accurate guidance system is required as in the case of following the sun. This means that a very simple platform can be used for the emission studies. In addition, sky emission also allows one to consider very long atmospheric paths (often desirable for detecting minor constituents) for any length of time whereas in solar work the zenith angle varies very rapidly as the sun approaches the horizon; also, any desired atmospheric path may be obtained by suitable arrangement of the apparatus. One important advantage of using long atmospheric paths, of course, is that the relative contribution of any local water vapour contamination is reduced.

Fourier transform spectroscopy was used in order to exploit the advantages of this method in problems requiring the measurement of weak radiation sources over a wide spectral bandwidth. These advantages are well-known and are usually known as the Fellgett (or Multiplex) advantage (Fellgett 1958), which refers to the possibility of observing many spectral elements simultaneously using an interferometric spectrometer (in contrast to a conventional dispersion spectrometer); and the Jacquinot (or Étendue) advantage (Jacquinot 1960) referring to the large solid angle × area available with an interferometer.
compared with the limited solid angle × area available with the narrow slits necessary in a conventional instrument. These advantages are, clearly, particularly desirable in the present work, and, as will be seen below, the results fully confirm the high efficiency of the Fourier transform technique. One added advantage, of course, is that since observing time is limited (in an aircraft), the ability to increase the spectral resolution in the interferometer without having to decrease the energy throughput by narrowing any slits can be shown to be of value (Jacquinet 1960).

The work presented here in many ways resembles earlier observations (Gebbie et al. 1968) but with one significant modification which makes quantitative stratospheric measurements possible. The modification is the incorporation of phase modulation into the interferometer (as opposed to amplitude modulation previously used) which yields the following two advantages; first, a substantial improvement in performance is obtained (Chamberlain 1970) and, second, it has become possible to resolve closely spaced pairs of emission lines of different atmospheric species, and hence make direct comparison of their emission strengths. These results remove a limitation implicit in our earlier work, namely that the complex process of radiation exchange taking place in the apparatus made the radiometric determination of zero and background levels very difficult, and consequently made the quantitative estimates of water-vapour of only limited value. For these reasons it has now been possible to make accurate qualitative estimates of the concentration of water vapour in the stratosphere, and of the integrated ozone above the observer.

2. Experimental details

The experiments reported here were conducted during the period 10 to 14 November 1969 in the Comet 2E aircraft of Radio Flight, RAE Farnborough, England, while flying at altitudes up to 12-2 km. The experimental arrangement is shown in Fig. 1. A standard NPL-Grubb-Parsons Michelson interferometer was positioned inside an aluminium enclosure which could be flushed with dry nitrogen. The interferometer has been described

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Figure 1. Plan of the experimental system. W is the polypropylene/aluminium window in the fuselage of the aircraft; X is the position of the silvered reflector used to couple in the black body source Y; B is the beamsplitter of the interferometer; M₁ is the moving mirror mounted on a stepped micrometer; M₂ is the oscillating mirror used for phase modulation; D is the Golay cell detector. The enclosure E could be flushed with dry air if necessary (see text).
in detail elsewhere (Chantry, Evans, Chamberlain and Gebbie 1969) and it is only necessary to discuss the incorporation of phase-modulation (PM) into this system. In order to obtain sinusoidal PM it is necessary to mount one of the interferometer mirrors (usually the fixed mirror in a standard system) on a loudspeaker coil and apply a sinusoidal voltage to the coil. It can be shown (Chamberlain 1971) that for a modulation of amplitude $p$ and frequency $f$ given by

$$p(t) = p_0 \sin(2\pi ft),$$

then for an instrument with no dispersive element, the interferogram is given by the expression

$$V_\phi(y) = 2k_\phi \int_0^\infty \psi(\sigma, p_0)p(\sigma) \sin(2\pi y \sigma) d\sigma,$$

where $\psi(\sigma, p_0)$, the PM characteristic function, is proportional to a Bessel function of the first kind:

$$\psi(\sigma, p_0) = 2J_1(2\pi \sigma p_0).$$

$k_\phi$ is a constant dependent on the details of the synchronous detection, $p(\sigma)$ is the power spectrum of the energy reaching the detector, $\sigma$ is the radiation wave-number (cm$^{-1}$) and $y$ is the optical path-difference (cm). The first maximum of the function (3) is chosen to coincide with the maximum of the beam-divider characteristic by adjustment of $p_0$ (Chamberlain 1971).

The Fourier transform of the interferogram $\psi_\phi(y)$ gives a power spectrum $B_{\phi}(\sigma)$ that is related to the standard amplitude-modulation (AM) power spectrum $B_\alpha(\sigma)$ by the expression

$$B_{\phi}(\sigma) = \frac{k_\phi}{k_\alpha} \psi(\sigma, p_0)B_\alpha(\sigma).$$

The presence of the multiplicative PM characteristic function does not interfere with the analysis of the spectra, but, in fact, improves their quality in some respects. The advantages of PM (namely the more efficient use of the available radiation, and the removal of problems associated with multiplicative noise) are considered in detail by Chamberlain (1971).

The interferograms are recorded on paper tape and Fourier transformed by a numerical sine routine, as opposed to a cosine routine in the AM case. Zero-path-difference is defined by the zero-crossing point between the maximum and minimum values of recorded signal (Fig. 2). Phase errors occurring as a result of incorrectly locating this zero-path-difference point (Vanasse and Sakai 1967) are negligibly small because the PM interferogram

![Interferogram signal](figure2.png)

**Figure 2.** An example of the interferograms obtained. The case shown is 'double-sided' and should be antisymmetric about zero path difference, in the absence of noise.
is a rapidly varying linear function in this region, and the zero ordinate position can be very accurately located.

Initially it was intended to calibrate the system radiometrically and provision was made to mount a 45° reflecting membrane at position X (see Fig. 1) which allowed the interferometer to look at a calibration source placed at Y. Since the technique used to obtain stratospheric mixing ratios (see below for a description) is independent of such calibration this arrangement was chiefly used to check the adjustment of the interferometer in the aircraft.

The path of the radiation is indicated in Fig. 1; the radiation exchange between the interferometer and the sky is transmitted by means of a 350 mm diameter Cassegrain telescope through a window W, constructed of aluminium and polypropylene, the transparent section of the window consisting of four circular apertures 125 mm in diameter and 16 mm thick. The transmission spectrum of the polypropylene is shown in Fig. 3. This window replaced one of the usual passenger windows in the Comet. These windows allow observations to be made only at a range of angles close to the horizon and an angle of 10° above the horizontal was chosen as optimum for the optical axis. This meant that the effective emission path was 5-6 times the vertical path and proved to be well suited to the atmospheric conditions encountered. The detector was a Golay cell, as in the earlier work (Gebbie et al. 1968).

As mentioned earlier, the enclosure containing the interferometer could be flushed with dry nitrogen. However, it was found that by turning the cabin humidifiers off before and during the flight the humidity rapidly fell to a level that was insignificant in the analysis of the results: typically the relative humidity fell to below 5 per cent within the first hour of the flight. It was found that the contribution of the cabin water-vapour never exceeded 5 per cent of the total emission measured even at the highest altitude when observing the lowest concentrations of atmospheric water-vapour (Houghton 1966). Despite these low values of cabin humidity, it was found that a thin film of ice was formed on the inside surface of the window during the early parts of the flight. This deposit did not have any observable effect on the sky signal, and was removed before the start of each run. After about one hour flying at altitude no further ice deposits were noticeable. This was more of a problem during the first two flights when the humidity did not fall so rapidly. However, the results that have been used in the quantitative measurement of stratospheric humidity (Table 1) were in all cases obtained towards the end of the long flights, i.e. after at least two hours flying, and so the effect on the quantitative analysis is negligible. Further-
TABLE 1. DETAILS OF FLIGHT CONDITIONS DURING OBSERVATIONS

<table>
<thead>
<tr>
<th>Date</th>
<th>Time at start of run</th>
<th>Position at start and end of run</th>
<th>Mean Altitude (km)</th>
<th>Temperature T (°C)</th>
<th>Height of tropopause (km)</th>
<th>Run number N</th>
<th>Max. res. (cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 November 1969</td>
<td>11:40</td>
<td>50°30N 06°00W</td>
<td>10:0</td>
<td>−60</td>
<td>9:5</td>
<td>1</td>
<td>0:5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50°40N 04°45W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 November 1969</td>
<td>12:45</td>
<td>50°40N 01°45W</td>
<td>10:9</td>
<td>−48</td>
<td>9:5</td>
<td>2</td>
<td>0:33</td>
</tr>
<tr>
<td>12 November 1969</td>
<td>13:10</td>
<td>54°40N 04°30W</td>
<td>11:1</td>
<td>−48</td>
<td>9:5</td>
<td>3</td>
<td>0:5</td>
</tr>
<tr>
<td>12 November 1969</td>
<td>14:00</td>
<td>56°20N 02°30W</td>
<td>12:2</td>
<td>−50</td>
<td>9:5</td>
<td>4</td>
<td>0:33</td>
</tr>
<tr>
<td>13 November 1969</td>
<td>14:20</td>
<td>56°20N 02°30W</td>
<td>9:1</td>
<td>−58</td>
<td>8:8</td>
<td>5</td>
<td>0:5</td>
</tr>
<tr>
<td>14 November 1969</td>
<td>11:25</td>
<td>51°15N 02°30W</td>
<td>12:2</td>
<td>−51</td>
<td>9:4</td>
<td>6</td>
<td>0:5</td>
</tr>
<tr>
<td>14 November 1969</td>
<td>12:13</td>
<td>51°03N 07°27W</td>
<td>12:2</td>
<td>−51</td>
<td>9:4</td>
<td>7</td>
<td>0:33</td>
</tr>
</tbody>
</table>

SYNOPTIC CONDITIONS

12 November 1969 Deep depression centred in North Sea, with associated polar troughs and minor polar lows crossing British Isles
13 November 1969 Same as 12 November 1969, with depression moving north-east and slowly filling
14 November 1969 Unstable low pressure complex still maintained over British Isles

more, it is known (Bertie and Whalley 1967) that the spectrum of ice does not exhibit any sharp features (Δσ < 5 cm⁻¹) in the submillimetre region while all the lines considered in the analysis are narrow (Δσ < 1 cm⁻¹), so that no confusion is possible due to this effect.

3. EXPERIMENTAL RESULTS

(a) Spectroscopic analysis

The details of the flight conditions during observations are given in Table 1, and the spectra will all be referred to in terms of the run number. An example of the high signal-to-noise ratio obtained during this work is shown in Fig. 2 (Run 4 Table 1). Typically the signal-to-noise ratio was of the order of 40, and this may be gauged in Fig. 2, where the double-sided interferogram should be antisymmetric about zero-path-difference; from a consideration of the Figure this can be seen to be the case out to path-differences of the order of 5 mm. The spectra evaluated here have, apart from run 4, been obtained from single-sided interferograms equivalent to the portion of Fig. 2 which occupies positive path-difference. This was because of the need to keep to a minimum the observation time required to record a set of data to a given spectral resolution.

To identify as many atmospheric lines as possible all the spectra computed to a resolution of 0.5 cm⁻¹ were averaged to give the maximum signal-to-noise ratio, and the result is shown in Fig. 4. The spectra are shown with atmospheric emission in the negative sense, while detector emission is shown in the positive sense. This is because in the interferogram the greater part of the observed signal is due to detector emission and it was found less confusing to show this emission in the positive sense despite the fact that all the important information is contained in the measured atmospheric emission. Many of the lines observed have already been identified in recent solar absorption studies (Eddy, MacQueen and Lena 1969a). However, the present results were obtained at a much larger zenith angle than those of Eddy, MacQueen and Lena (1969a), and this, together with the fact that our flights were conducted well above the Arctic tropopause (thus at a very low humidity level) has resulted in the water vapour lines being of comparable intensity, but
those due to oxygen and ozone being much stronger than in the solar studies. The theoretical positions of the water-vapour lines are shown by vertical lines at the top of the diagram, and the lengths are proportional to the square root of the theoretical line strengths (see Section 3(b)). It can be seen that there is excellent agreement in both position and strength between experiment and theory. The positions and relative strengths of the magnetic dipole rotation spectrum of oxygen are also indicated, as are the principal lines of ozone (the Q branches), and again the agreement between theory and experiment is very good. Also indicated are a number of unidentified emission features (cross-hatched) which

<table>
<thead>
<tr>
<th>Observed feature (cm⁻¹)</th>
<th>Relative strength*</th>
<th>Possible assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.5 (E)</td>
<td>S</td>
<td>Gas (cm⁻¹)</td>
</tr>
<tr>
<td>24.70 (E)</td>
<td>W</td>
<td></td>
</tr>
<tr>
<td>26-80</td>
<td>M</td>
<td>N₂O 26.76</td>
</tr>
<tr>
<td>28.75 (E)</td>
<td>S</td>
<td>CO 26.95</td>
</tr>
<tr>
<td>29.60 (E)</td>
<td>S</td>
<td>N₂O 28.50</td>
</tr>
<tr>
<td>31.10</td>
<td>M</td>
<td>HDO 29.77</td>
</tr>
<tr>
<td>31.75</td>
<td>M</td>
<td>N₂O 31.00</td>
</tr>
<tr>
<td>34.85</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>44-90 (E)</td>
<td>W</td>
<td>HDO 45.14</td>
</tr>
<tr>
<td>45-40 (E)</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>49-95 (E)</td>
<td>W</td>
<td></td>
</tr>
<tr>
<td>51-50</td>
<td>W</td>
<td></td>
</tr>
</tbody>
</table>

* Strengths classified as S—strong; M—medium; W—weak
E=observed by Eddy et al. (1969a)
have reproducibly been observed in the results, but which cannot be consistently assigned to known atmospheric dipolar molecules. (Details of these are given in Table 2.)

The increased atmospheric path, compared with earlier work has enabled certain oxygen and ozone features to be resolved for the first time. In particular, the oxygen transition $K = 5 \rightarrow 7, J = 6 \rightarrow 7$ at 39.36 cm$^{-1}$, and the ozone $Q_2$ branch at 45.56 cm$^{-1}$ are resolved. In addition, three runs (Table 1, Nos. 2, 4 and 7) have been recorded to a resolution limit of 0.33 cm$^{-1}$ and the region 35 to 42 cm$^{-1}$ is shown in Fig. 5. This spectrum,

![Figure 5](image)

Figure 5. The average of three atmospheric spectra (curve b), resolution 0.33 cm$^{-1}$. A laboratory absorption spectrum (curve a), resolution 0.25 cm$^{-1}$ is shown for comparison. The positions and strengths of H$_2$O, O$_2$ and O$_3$ lines are indicated as in Fig. 4.

apart from showing the 39.36 cm$^{-1}$ oxygen line more clearly resolved, shows that at this increased resolution other features are beginning to appear, namely, the oxygen line at 37.35 cm$^{-1}$, and the water line (2$_1$ -- 3$_{-1}$) which can be inferred on the low frequency side of the strong water line at 38.80 cm$^{-1}$. This result shows that atmospheric emission spectroscopy can be used to make relatively high resolution (i.e. 0.4 to 0.2 cm$^{-1}$) studies
of submillimetre transmission of the stratosphere with the moderately simple system used in this work.

In Tables 2 and 3 the assignment of the observed features in the 0.5 cm\(^{-1}\) resolution spectrum are given. The water vapour lines are not included, and many of the assignments

<table>
<thead>
<tr>
<th>Gas</th>
<th>(measured) (cm(^{-1}))</th>
<th>(calculated) (cm(^{-1}))</th>
<th>Transition (K_f J_1 \rightarrow K_f J_2)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>23.73</td>
<td>23.663</td>
<td>3.3 \rightarrow 5.4</td>
<td>Too strong for O(_2) alone</td>
</tr>
<tr>
<td></td>
<td>25.82</td>
<td>25.819</td>
<td>3.4 \rightarrow 5.4</td>
<td>Blend with O(_3)</td>
</tr>
<tr>
<td></td>
<td>27.85</td>
<td>27.831</td>
<td>3.4 \rightarrow 5.5</td>
<td>Blend with H(_2)O</td>
</tr>
<tr>
<td></td>
<td>35.48</td>
<td>35.396</td>
<td>5.5 \rightarrow 7.6</td>
<td>Blend with H(_2)O</td>
</tr>
<tr>
<td></td>
<td>37.364</td>
<td>39.362</td>
<td>5.6 \rightarrow 7.6</td>
<td>Blend with H(_2)O</td>
</tr>
<tr>
<td></td>
<td>46.914</td>
<td>48.929</td>
<td>7.7 \rightarrow 9.8</td>
<td>Blend with H(_2)O</td>
</tr>
<tr>
<td></td>
<td>50.82</td>
<td>50.877</td>
<td>7.8 \rightarrow 9.9</td>
<td>Blend with H(_2)O</td>
</tr>
<tr>
<td></td>
<td>58.414</td>
<td>58.420</td>
<td>9.9 \rightarrow 11.10</td>
<td>Blend with H(_2)O</td>
</tr>
<tr>
<td></td>
<td>60.457</td>
<td>62.371</td>
<td>9.10 \rightarrow 11.10</td>
<td>Blend with H(_2)O</td>
</tr>
<tr>
<td>O(_3)</td>
<td>21.78</td>
<td>21.78</td>
<td>Q(_2) branch</td>
<td>Blend with O(_2)</td>
</tr>
<tr>
<td></td>
<td>27.88</td>
<td>27.88</td>
<td>Q(_2) branch</td>
<td>Blend with O(_2)</td>
</tr>
<tr>
<td></td>
<td>34.11</td>
<td>34.11</td>
<td>Q(_2) branch</td>
<td>Blend with O(_2)</td>
</tr>
<tr>
<td></td>
<td>46.56</td>
<td>46.56</td>
<td>Q(_3) branch</td>
<td>Blend with O(_2)</td>
</tr>
<tr>
<td></td>
<td>52.71</td>
<td>52.71</td>
<td>Q(_4) branch</td>
<td>Blend with O(_2)</td>
</tr>
<tr>
<td></td>
<td>64.80</td>
<td>64.80</td>
<td>Q(_{10}) branch</td>
<td>Blend with O(_2)</td>
</tr>
</tbody>
</table>

* Not previously observed in the atmosphere

in Table 2, we stress, are very tentative. To identify features above 52 cm\(^{-1}\) only two runs have been used (Nos. 6 and 7), because these were the only observations that gave a good response up to 66 cm\(^{-1}\). This is probably associated with the problem of ice on the window.

![Figure 6](image_url)

**Figure 6.** A comparison of a stratospheric spectrum (continuous curve), resolution 0.5 cm\(^{-1}\) and, a laboratory absorption spectrum, resolution 0.25 cm\(^{-1}\) (broken curve) showing the O\(_2\) and O\(_3\) lines between 46 and 65 cm\(^{-1}\) in the former case.
in the early flights. In order to provide additional evidence of identification of lines in this spectrum a comparison has been made (Fig. 6) with a laboratory absorption spectrum obtained in a 7.5 m multipass 'White' cell. The laboratory conditions of 120 m path-length, and 1.5 Torr water vapour pressure gives an equivalent water vapour amount to that encountered in the stratospheric measurements, and it is evident that the equivalence of laboratory absorption and atmospheric emission in the case of water lines is very good indeed (Fig. 6).

Of particular interest in these observations are the three ozone lines at 45.6, 52.5 and 64.9 cm⁻¹ which are in close proximity to well defined water lines at 47.1, 53.4 and 64.0 cm⁻¹; these lines are obviously suitable for comparison of water and ozone concentrations in the stratosphere (Section 3(b)). In the case of oxygen and ozone the position of the observed lines is compared with the theoretical predictions (Gebbie, Burroughs and Bird 1969; Gora 1959) and the agreement is found to be very good. This is a further indication of the good spectroscopic performance of the instrument.

As mentioned earlier, the identifications of the cross-hatched lines in Fig. 4 are exceedingly tentative. A number of the features have been observed by Eddy et al. (1969a) (indicated in Table 2), and these authors have also had difficulty in consistently explaining all these features, and have proposed that they might be due to some as yet unidentified atmospheric species, possibly produced by solar radiation. We cannot really add to this conclusion, save only to say that the features are definitely of atmospheric origin. However, special note must be made of the anomalously strong emission at 23.5 cm⁻¹, which is commented on by Eddy et al. and which has also been inferred from work at lower altitudes (Gebbie, Chamberlain and Burroughs 1968). This feature is far too strong to be explained in terms of the O₂ line at 23.9 cm⁻¹ or known minor constituents (see Table 2, e.g. N₂O, NO, HDO, or (H₂O)₂); one of the few remaining stratospheric constituents that has not been investigated in the submillimetre region is the recently observed HNO₃ molecule (Murcray, Kiley, Murcray and Williams 1968, 1969). It is suggested that, as a result of the large mass of the molecule, it will give rise to a pure rotation spectrum centred at low wave-number. Moreover, the absorption is expected to be intense since the dipole moment of the molecule is large (2. 16 D). The figures given by Murcray, Kiley, Murcray and Williams (1969), lead to an equivalent path of HNO₃ for our observations of 5 x 10⁻³ cm atm, and bearing in mind the magnitude of dipole moment it can be expected that HNO₃ should emit strongly in the submillimetre region. A laboratory study of the submillimetre spectrum of HNO₃ vapour would therefore seem to be a matter requiring urgent attention.

Finally, it should be noted that we find very little evidence for the existence of the water vapour dimer in these spectra. We have made observations at sea-level (Harries and Burroughs 1970) and at an altitude of 3.58 km (Burroughs and Chamberlain, to be published) and from these measurements have concluded that the dimer feature at 7.5 cm⁻¹ has considerable structure (Harries and Burroughs 1970). As a result of this conclusion, it is believed that the higher frequency components of the dimer spectrum (at 22, 35 and 49 cm⁻¹) will be rather diffuse, and hence not easily observed as discrete lines in the present work. However, Eddy et al. (1969a) present good experimental evidence to support the conclusion that a feature at 49.5 cm⁻¹ can be attributed to the water dimer. In our results this feature is not at all obvious (Fig. 6), but it may well be that the different atmospheric conditions prevailing during these two flights can effectively explain this discrepancy. Moreover there is little evidence of the feature in our laboratory observations (Fig. 6), though there is an unexplained feature at 50.2 cm⁻¹ that may be associated with this molecule. However, again our atmospheric observations (Harries and Burroughs 1970; Burroughs and Chamberlain, to be published) as well as our laboratory measurements (Harries, Burroughs and Gebbie 1969) indicate that an essential requirement for observing dimeric lines is low temperature, and so the laboratory spectrum shown in Fig. 6 (obtained at 20°C) is not necessarily inconsistent with the stratospheric results of Eddy et al. (1969).
(b) Quantitative analysis of water vapour and ozone concentrations

In order to present details of the quantitative analysis, we have considered two averages each of two spectra, respectively Runs 2 and 3 (mean altitude 11.0 km), and Runs 6 and 7 (altitude 12.2 km). These results are shown in Fig. 7. It can be seen that for the most part the reproducibility is very high, except at low-wave-numbers ($\sigma < 24$ cm$^{-1}$) where several noise sources, including that due to the roll of the aircraft, may become significant. The importance of these guidance errors will be considered later. The results

![Graphs showing detector emission and atmospheric emission comparisons.](image)

Figure 7. The results obtained at altitudes of 11.0 km (Runs 3 and 4) (continuous curve) and 12.2 km (Runs 6 and 7) (broken curve) resolution 0.5 cm$^{-1}$, which have been used to calculate the humidity mixing ratio of the stratosphere. The pairs of H$_2$O and O$_3$ lines which have been used may be found in Table 4.
presented in Fig. 7 are the direct outputs of the computer, so that the difference in emission at the two altitudes is directly compared. It can be seen that the amount of water vapour emission is reduced with altitude as would be expected. However, it was found that the direct use of these outputs to measure the absolute concentration of stratospheric water was not the most accurate method. This is because, first, there is a considerable calibration problem in defining background and zero intensity levels in such a radiometrically complicated system; second, the amplitude of the PM was adjusted at different altitudes to give the maximum signal, with a resultant slight change in the spectral response of the interferometer between the various levels. For these reasons, it was important to find a method of measuring water vapour which was not affected by these quantitative limitations of the interferometer.

In a recent publication (Burroughs and Harries 1970) we have presented details of a method that allows atmospheric mixing ratios to be calculated, while avoiding the radiometric limitations of the spectroscopic system. The principal requirement of this technique is to be able to observe the magnetic dipole rotation lines of oxygen, which have been theoretically predicted (Tinkham and Strandberg 1955a) and experimentally observed (Gebbie, Burroughs and Bird 1969). As these lines are of known strength, and the distribution of oxygen in the stratosphere can be assumed to have a constant mixing ratio without any significant error, these lines are ideally suited to a comparison with adjacent water lines in order to measure the mixing ratio of the latter. Furthermore, it should be noted that since these lines are approximately 10³ times weaker than adjacent water lines they are particularly suited to the measurement of stratospheric water vapour mass mixing ratios that are typically of the order of $10^{-3}$ to $10^{-6}$ g/g (Gutnick 1961; Murcay, Kyle and Williams 1969; Pick and Houghton 1969). Burroughs and Harries (1970) have shown that for a pair of strong emission lines that are close together (i.e. separated by less than 5 cm⁻¹ so that the increase with wave-number of the Planck black-body emission function is largely compensated for by the decrease with wave-number of the transmission of the instrument), then the mass mixing ratio of the gas to be measured is given by

$$\mu = \left( \frac{E_n}{E_\alpha} \right)^2 \cdot \frac{S_\alpha \Delta \alpha_{\alpha} M_n k_{\alpha}}{S_n \Delta \alpha_n M_\alpha k_n} \cdot (5)$$

where $E_n$ and $E_\alpha$ are the integrated emission areas of the two lines, $S_n$ and $S_\alpha$ are the line-strengths of the two lines, $\Delta \alpha_n$ and $\Delta \alpha_{\alpha}$ are the half-widths of the lines, $M_n$ and $M_\alpha$ the molecular weights of the gas n and O₂, and $k_n$ and $k_\alpha$ are the mean densities of oxygen and air in the observation path. Eq. (5) is based on the assumptions that the atmosphere is approximately isothermal over the observation path and the mixing ratio is constant over this distance. The radiation emitted in a typical line originates in the layer of about 5 – 10 km thick above the aircraft (i.e. the emission falls by 1/e in about this distance), and this defines the effective 'observation path'. Both the above assumptions are valid in the case of water vapour in the lower stratosphere but for ozone the assumption of a constant mixing ratio is not valid. For the present analysis, which is principally concerned with the measurement of water vapour, it is considered reasonable to use Eq. (5) in this work. The use of theoretical line-parameters ($S_n$, $S_\alpha$, $\Delta \alpha_n$, $\Delta \alpha_{\alpha}$) has been justified on the basis that microwave measurements on atmospheric gases have indicated reasonable agreement between theory and experiment; the limitations in using the theoretical values will be considered below in terms of the analysis of specific gases.

(i) Water vapour. Several pairs of oxygen and water vapour lines have been used to calculate the mass mixing ratio $\mu$ at two flight altitudes (11.0 and 12.2 km). These pairs are listed in Table 4, and are shown in Fig. 5 and 6. Table 4 gives the ratios of the integrated emission areas and the values of the mixing ratio derived from each pair of lines. In these calculations we have used the following constants, $M_{H_2O} = 18$, $M_\alpha = 32$, $k_\alpha/k_n = 0.231$ (Allen 1955); a value of $\Delta \alpha_{H_2O} = 0.066$ cm⁻¹ atm⁻¹ at 220°K has been used, arrived at from a combination of the results of Tinkham and Strandberg (1955b) and of Hill and Gordy (1954); for $H_2O$ at 220°K, a representative value of $\Delta \alpha_{H_2O} = 0.12$ cm⁻¹
atm⁻¹ has been taken from the work of Benedict and Kaplan (1959, 1964). Values of
$S_{H_2O}$ have been calculated using the line-strengths given by Yunker and Querfeld (1963)
and values of $S_{O_2}$ have been taken from Gebbie et al. (1969). The theoretical expressions
for the temperature dependences of the various parameters (line half-width, strength)
have been used (Herzberg 1945). Since we are concerned with the ratios of these parameters
(Eq. (5)) any systematic errors in the theoretical values will tend to be cancelled out. A
rough check on the reliability of these data for O₂ has been carried out by estimating the
amount of O₂ above the observer from the absolute equivalent widths of the O₂ lines. This
analysis for the three strongest O₂ lines at 25.8, 48.9 and 60.5 cm⁻¹ yields a result of
0.34 ± 0.05 km atm compared with the calculated value of 0.31 km atm (calculated
assuming an exponential atmosphere and a mean stratospheric temperature of 240°K).
The agreement indicates that the O₂ data used is accurate to better than ± 10 per cent.
This comparison is, of course, limited by the very problems that beset an absolute deter-
mination of concentration (problems of measurement of equivalent width, of assuming a
scale height and so on) which we hope to avoid by using Eq. (5). However, it is of use in
adding to the confidence with which we may use the available spectroscopic data for O₂
in this work.

It has been argued that the position of the background level (i.e. the level of detector
emission in the absence of atmospheric emission) is not important in these calculations,
and to support this case we show the pair of lines at 25.1 and 25.8 cm⁻¹ (Fig. 8). These

![Figure 8. The three cases which have been used to investigate changes in the assumed background envelope of the spectra. The H₂O line at 25.1 cm⁻¹ and the P, O₂ line at 25.8 cm⁻¹ have been used to obtain the mixing ratio in this case (see text).](image)

lines have been chosen because the background level is varying most rapidly in this region
(Fig. 4), and the lines are likely to show the greatest variation with the specific choice of
the background. It may be seen from the Figure that we have used three background levels
to show the two extreme cases (1 and 3) and the most probable position (2), and we have
computed the integrated areas of the two lines in each case. To allow for the varying
response of the instrument over the spectral range, we have divided the integrated areas
by the magnitude of the background level (defined from the computed zero-level in the
spectrum); that is, we have used the full expression for the equivalent widths (Goody 1964)
of the emission lines in the regions of large gradients of spectral intensity. For the lines shown in Fig. 8 this procedure produces three values for the mixing ratio; (a) $1.7 \times 10^{-6}$ g/g; (b) $1.9 \times 10^{-6}$ g/g; (c) $2.2 \times 10^{-6}$ g/g to yield a mean value of $(1.9 \pm 0.3) \times 10^{-6}$ g/g. Such an error is certainly acceptable particularly since we are able to reduce it considerably by averaging the results of calculations based on all the suitable pairs of lines available in the spectral range considered (Table 3). It must be stressed that the error quoted in the above test case is an extreme estimate, and that for the majority of the lines used, the background level is flat enough not to require any correction (Fig. 7). In these cases, therefore, the error from this source is very small.

As a result of these calculations the following values of the mass mixing ratio $\mu$ have been obtained for the stratosphere above the altitudes of 11.0 km (Runs 2 and 3) and 12.2 km (Runs 6 and 7) respectively:

\[
\begin{align*}
11.0 \text{ km} & \quad \mu = (3.9 \pm 0.8) \times 10^{-6} \text{ g/g} \\
12.2 \text{ km} & \quad \mu = (2.1 \pm 0.3) \times 10^{-6} \text{ g/g}.
\end{align*}
\]

The errors quoted represent the root mean square deviations calculated from the scatter obtained (Table 4) from the different pairs of lines, and no allowance has been made here for any systematic error arising from the line-parameters. The problem of systematic errors will be considered in conjunction with a discussion of how these values of $\mu$ compare with other measurements. It should be noted that the increased error in the value of $\mu$ obtained at an altitude of 11.0 km arises largely from the reduced spectral range considered (Fig. 7), so that fewer pairs of lines are accessible to measurement (Table 4).

### TABLE 4. Calculation of $\text{H}_2\text{O}$ mixing ratio

<table>
<thead>
<tr>
<th>Lines used</th>
<th>$\text{H}_2\text{O}$ (cm$^{-1}$)</th>
<th>$\text{O}_2$ (cm$^{-1}$)</th>
<th>ratio of areas</th>
<th>Mixing ratio ($\times 10^{-6}$ g/g)</th>
<th>Mean mixing ratio ($\times 10^{-6}$ g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Altitude 12.2 km</td>
<td></td>
</tr>
<tr>
<td>25.07</td>
<td>23.88</td>
<td>1.75</td>
<td>1.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.85</td>
<td>35.36</td>
<td>3.68</td>
<td>2.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.79</td>
<td>39.36</td>
<td>9.80</td>
<td>2.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.50</td>
<td>39.36</td>
<td>3.10</td>
<td>1.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.05</td>
<td>48.93</td>
<td>3.90</td>
<td>2.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53.45</td>
<td>48.93</td>
<td>1.97</td>
<td>2.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53.45</td>
<td>50.95</td>
<td>3.90</td>
<td>1.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Altitude 11.00 km</td>
<td></td>
</tr>
<tr>
<td>25.07</td>
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<td>2.19</td>
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<tr>
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<td>1.14</td>
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<tr>
<td>32.95</td>
<td>35.39</td>
<td>2.46</td>
<td>1.12</td>
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<tr>
<td>38.79</td>
<td>39.36</td>
<td>8.00</td>
<td>3.51</td>
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</tr>
<tr>
<td>41.00</td>
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<tr>
<td>47.05</td>
<td>39.36</td>
<td>6.95</td>
<td>5.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The increase in mixing-ratio with decreasing altitude means that there is a rapid increase in water content as one approaches the tropopause from above; since our measurements yield mean values of $\mu$ averaged over about 5 km altitude, the value of $\mu$ obtained at 11.0 km implies that the true value at this altitude was higher than $4 \times 10^{-6}$ g/g, and probably was nearer $10 \times 10^{-6}$ g/g. This result would be in agreement with the recent comprehensive measurements of McKinnon and Morewood (1970), and with earlier measurements by the British Meteorological Research Flight (Dobson Brewer and Cwilong 1946; Bannon, Frith and Shellard 1952; Murgatroyd, Goldsmith and Hollings 1955; Helliwell MacKenzie and Kerley 1957). Since it appears that the mixing ratio was varying rapidly at 11.0 km, the result obtained at this height should be regarded as only an approximate value, since the technique used here depends on the assumption of a
constant mixing-ratio over the emission path. However, in the case of the 12.2 km result, we were flying at 2.8 km above the tropopause (Table 1) and it can be assumed (McKinnon and Morewood 1970) that the mixing-ratio had probably reached a constant value above this altitude.

(ii) Ozone. An exactly similar procedure has been adopted for O₃, except that the number of O₃ lines which are clearly resolved, and yet close to other lines for comparative purposes, is only three (Fig. 6 and Table 5). Since these lines are only clearly resolved in the observations made at an altitude of 12.2 km, (in fact the two higher frequency lines are only observed at this altitude), the concentration of this gas has only been measured above this level. The integrated areas of the lines chosen have been compared with the areas of adjacent water vapour lines, and the value of μ given in the previous section has been used to obtain the O₃/air mixing ratio. This mixing ratio is used in conjunction with a standard atmosphere (ARDC model, Goody 1964) to give a value of the equivalent path of ozone:

\[ l = 0.35 \pm 0.10 \text{ cm atm} \]

at NTP, and corrected to zenith. In order to arrive at this value the theoretical strengths of the ozone lines have been derived from the work of Gora (1959), and allowance has been made for the fact that the features considered are not single lines but a large number of closely spaced \( \Delta J = 0 \) transitions (since ozone is only slightly asymmetric). For this reason the effective width of the features was greater than for a single line and a value of \( \Delta \sigma_{\text{g}} = 0.15 \text{ cm}^{-1} \) was used for the purposes of the calculation. This approximation and the lack of corroborative experimental measurements mean that the value of \( l \) may contain large systematic errors (± 20 per cent). These are combined with an experimental rms scatter of ± 0.03 cm⁻¹ to give the quoted errors. It is satisfying to note that, within these large quoted errors, the value given here is in reasonable agreement with routine measurements.

(iii) Weak lines. All the lines used in the above analysis are in the ‘strong’ region of the curve of growth (Goody 1964). These lines provide information of the mixing ratio in the nearest 5 – 10 km above the observer (see Section 3(b)). It is possible to utilize other lines which are much weaker, and which can be approximated to the ‘weak’ limit of the Ladenburg-Reiche function (Goody 1964). The difference between these limits for the integrated emission areas can be expressed in terms of the integrated line strengths and the absorber mass \( u \) in the following way

\[ \frac{E_{\text{weak}}}{E_{\text{strong}}} \approx \frac{S_u}{[S_u p]^1} \]

where \( p \) is the ambient atmospheric pressure. It can be seen that in the case of weak lines there is no weighting term due to atmospheric pressure \( (p) \), and so these lines are more sensitive to emission from gas at greater altitudes than are the strong lines.

We have carried out an analysis of the emission of certain weak lines in order to make an estimate of the distribution of water vapour above the aircraft. The distribution obtained using three weak water lines (6₋₃ – 7₁ at 42.6; 7₋₁ – 8₋₅ at 43.2; and 6₋₄ – 7₆ at
48.1 cm⁻¹) combined with the mean value of mixing ratio \( \mu \) obtained using strong lines is found to be in approximate agreement with earlier estimates using a similar analysis in the near infra-red (Houghton 1963) indicating an increase in mixing ratio in the upper stratosphere to about 10 \( \times \) 10⁻⁶ g/g. However, before too great an emphasis is placed on this result certain points concerning the observations must be made. First, the existence of a number of unexplained emission features, especially at low wave-numbers, means that apparently excessive emission of weak lines might be attributed to an additional contribution due to unidentified atmospheric sources. This is also supported by the observation of a large number of weak absorption features in the laboratory due to HDO (Fig. 9 and also Burroughs, Harries and Gebbie 1969). To take the extreme case in the present analysis, it is estimated that at 223°K the strength of the H₂O feature (7⁻₁ — 8⁻₃) at 43.2 cm⁻¹ is increased by about 9 per cent when the presence of additional emission due to two unresolved HDO lines (2₁ — 2⁻₁ and 5⁻₃ — 5⁻₁) (Sloan 1964) is included in the calculation. This correction cannot, of course, allow for the effect of, as yet, unidentified atmospheric emission, and so this result must still be viewed with caution.

A second point concerning the use of weak lines is that, by definition, the signal-to-noise ratio in a measurement of \( E_{\text{H}_2\text{O}} \) is less than that for a corresponding strong line, and consequently the accuracy of any subsequent analysis is limited.

Since the assumption of an isothermal atmosphere cannot be made above about 25 km, a correction for the variation of temperature with altitude must also be made in the weak line study. This has been done in the manner discussed by Bolle (1965), but still we find a value which is a factor of 2 — 3 times in excess of that measured at 12 km.

Despite the reservations expressed above concerning the accuracy of the weak lines study, it is clear that further work will be able to provide information on the vertical distribution of water in the stratosphere, especially if the wave-number range is extended to about 100 cm⁻¹, in order to accommodate more weak H₂O emission lines.

4. Discussion and Conclusions

The results presented above illustrate the fact that high-quality spectra of the submillimetre radiation emitted by the stratosphere are now obtainable. The spectra which have been presented can be very satisfactorily explained in terms of emission lines of H₂O, O₁ and O₂, although some unexplained features do exist that have also been reported by other workers (see Table 2). The most important point which we wish to stress, however, is the use of emission lines due to H₂O and O₂ in the evaluation of the humidity mixing ratio of the stratosphere.

The values we have obtained for the stratospheric humidity mixing ratio are in good agreement with values expected for a dry lower stratosphere; although some early work pointed to the existence of very large concentrations of water vapour in the stratosphere (Barclay, Elliott, Goldsmith and Jelley 1959; Murcroy, Williams and Leslie 1960), other work in the 1940's and 1950's (Dobson et al. 1946; Murgatroyd et al. 1955) and later measurements have indicated that this is not the case, and that, in the lower stratosphere, values of the mixing ratio within the range 2.4 \( \times \) 10⁻⁶ g/g are obtained (Houghton and Seeley 1960; Williamson and Houghton 1965; Neporent, Kiseleva, Makogolenko and Shlyakov 1968; Mastenbrook 1968; Pick and Houghton 1969). More recently, very extensive aircraft measurements of near infra-red solar radiation by McKinnon and Morewood (1970) have given added support to the dry model up to 17 km. The earlier high values have been questioned on the basis of possible contamination with water vapour in the instrumental packages (Gutfnick 1961; Zander 1966). As has been mentioned above, spectroscopic methods such as our own, which do not depend solely upon local measurements are not so susceptible to contamination as hygrometer methods. It should further be noted that in an aircraft the local contamination is negligible save for water vapour in the cabin (Houghton 1966), which in the present results was extremely low (see Section 2).

The good agreement with other values indicates, therefore, that both our experimental results and the new method of analysis which we have used are correct.
Since the value of water vapour mixing ratio is now fairly well accepted in the lower stratosphere the most obvious extension is to use the present system in a balloon study at higher altitudes (about 30 km) above which the mixing ratio is by no means so well measured. It is therefore envisaged that a lightweight Michelson interferometer could be used in conjunction with a fast-response thermal detector (e.g. the TGS pyroelectric detector (Putley 1966)) to make balloon-borne measurements of stratospheric emission. Working between altitudes of 20 and 35 km this system could select an optimum atmospheric path length to make accurate measurements of the mixing ratio in the 10 km above the platform, which would be relatively little affected by local contamination. In this system it will be possible to extend the bandwidth up to about 100 cm\(^{-1}\) (Fig. 4), since no thick polypropy-

![Laboratory absorption spectrum of pure water vapour](image)

**Figure 9.** A laboratory absorption spectrum of pure water vapour, illustrating a higher wave-number region which might be investigated. The positions and strengths of the H\(_2\)O lines are indicated by the bars at the top of the diagram; the positions of O\(_2\) and HDO (indicated by 'D') lines expected in the stratospheric spectrum are also shown.

lene window will be necessary. This will increase the number of water vapour lines available for analysis, and will also include a number of other interesting lines not presently accessible. These include several HDO lines (shown in Fig. 9) and the region around 68 cm\(^{-1}\) where atomic oxygen may possibly emit (Bates 1951; Kockerts and Peetersmans 1970).

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