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Spectroscopic observations of middle atmosphere composition

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The principal advantages and disadvantages of spectroscopic techniques as a means of deducing the composition of the middle atmosphere are reviewed. A brief general survey is given, which includes methods using natural or artificial radiation sources, used in remote-sensing or local sampling configurations, and at spectral wavelengths ranging from the ultraviolet to the microwave. Limitations of space dictate an emphasis on the infrared methods using natural radiation sources employed by most workers in this field.

Composition results obtained by using spectroscopic techniques have often had an important effect on the development of our understanding of the middle atmosphere, and an attempt is made to describe some of the more important measurements of recent years, and the significance of the new results they have produced. This discussion of new results is brought up to date with a description of a recent balloon-borne infrared experiment.

1. INTRODUCTION

The application of spectroscopy to atmospheric studies is a subject with a very long and distinguished history (see, for example, Adel 1949 and references contained therein), so that its use to determine atmospheric composition is not new. The application of spectroscopic methods to study the composition of the middle atmosphere (loosely defined as the layer between 10 and 150 km altitude) is, however, more recent, requiring as it did the development of high altitude balloons and rockets, and more recently spacecraft.

Middle atmosphere spectroscopy, in common with several other disciplines, received a healthy boost during the last decade with the realization that conditions in the middle atmosphere may not be as stable with time as had been imagined and, indeed, might even be susceptible to human influence, albeit unintentional, with possibly detrimental environmental consequences. Spectroscopy is an extremely powerful tool for detecting and monitoring composition even at very low concentrations and, in view of the potential problems, it has been widely used to improve our knowledge, and hopefully our understanding, of the middle atmosphere. The present paper contains a brief description of why and how spectroscopy has been used for this purpose.

We shall first consider (§ 2) the range of instruments and techniques at our disposal for atmospheric spectroscopy; this will orient the readers' thoughts in preparation for later, unqualified, references to a variety of apparatus. Then some consideration will be given, in § 3, to the advantages and disadvantages of spectroscopic methods, and the former will be illustrated by some of the leading work selected from recent years. Finally, in § 4, a description of a recent balloon experiment, which carried several infrared spectrometers into the stratosphere, will be described.

2. TECHNIQUES AND INSTRUMENTS

A wide variety of instruments and techniques are available to the modern atmospheric spectroscopist, and it is necessary to undertake a brief review of these at this stage.

Table 1 lists some representative instrumental types that have been, or are being, used. These instruments have been employed on a variety of observation platforms, at sea level, on aircraft, balloons, rockets and orbiting spacecraft, and in a variety of observational geometries, looking up, down and sideways depending on the requirements of the experiment.

TABLE 1. A SELECTION OF INSTRUMENT TYPES

filter radiometer/photometer
grating spectrometer
grille spectrometer
gas correlation radiometer
correlation radiometer
Michelson interferometer
Fabry–Perôt interferometer
microwave spectrometer
i.r. heterodyne spectrometer

The filter radiometer or photometer operates, as is well known, through the use of a simple spectral selection device to isolate a relatively broad spectral range which includes an absorption band of the atmospheric constituent to be measured (see Low & Rieke 1974). Spectral selection may be effected by using the absorption properties of solid-state filters, multilayer interference filters, or other devices. Generally, in such devices, spectral scanning is not attempted.

The grating spectrometer (Schroeder 1974) is perhaps the best known device of those listed in table 1, and effects spectral selection by utilizing the diffraction properties of a ruled grating. A grating may produce a large number of different ‘orders’ of diffraction and care must be taken in the design of a grating spectrometer to include filters that select only those orders which are required. Spectral scanning can quite easily be implemented by rotation of the grating or, less often, of the input and output slits.

The grille spectrometer, devised by Girard (1963), is essentially a modified grating spectrometer, but deserves special mention because it has been extensively employed to make stratospheric measurements (see below). The input and exit slits of a conventional spectrometer are replaced by an array of slits (a ‘grille’) which is designed carefully to preserve an acceptable instrumental profile. In this way the energy ‘throughput’ or ‘étendue’ of the spectrometer may be increased: such an increase in efficiency is usually important in atmospheric studies where observation time is at a premium.

The use of gas correlation radiometers (Smith & Pigeon 1964) rests upon the novel idea of using, within the instrument, a sample of the gas to be detected in the atmosphere, in order to achieve spectral selection with, in the absence of Doppler shifts of the atmospheric lines, perfect spectral matching, and with the possibility of achieving very high spectral resolution. A number of variations of such a device may be imagined (including ones based on the Michelson interferometer – see Harries & Chamberlain 1976), but the most widely used in atmospheric studies have been the selective chopper radiometer (s.c.r.) and pressure modulator radiometers (p.m.r.) developed by Houghton and coworkers at Oxford; these devices achieve modulation in a spectral line by variation of the pressure of a sample of gas or, equivalently, by switching

between cells containing samples at different pressures. A review of these devices is given by Houghton & Taylor (1973).

A correlation radiometer (Barringer & Davies 1973) differs from the latter device in having a *synthetic* version of the spectrum (or interferogram) of the required constituent contained or stored (often electronically) within the instrument. In this case, of course, one avoids the sometimes difficult problem of containing a real sample of a gas; on the other hand a correlation radiometer can never achieve perfect matching with the real spectrum because of imperfections in knowledge, nor, in practice, very high spectral resolution.

The Michelson interferometer and the techniques of Fourier transform spectroscopy (Schnopper & Thompson 1974) have been widely used since the mid-1950s when the Multiplex (or Fellgett) and Étendue (or Jacquinot) advantages were discovered. Because of these advantages, Fourier spectrometers are very efficient instruments for studying weak sources, although care does need to be exercised when designing an experiment that conditions are suitable for the advantages to be effective. Thus, the Multiplex advantage exists only as long as detector noise predominates over other noise terms – in certain circumstances a Multiplex disadvantage can occur (e.g. if noise in the incoming signal dominates). Furthermore, the Étendue advantage is based upon the circular symmetry of the device, due to the absence of slits; however, in certain configurations a slit-like field of view may be necessary (e.g. in limb-sounding – see below), which can more easily be matched to a grating spectrometer slit than the circular field of a Michelson. These points are made to illustrate the fact that the Michelson interferometer may not be the panacea for all weak-source measurement problems. When used properly, however, as we shall see below, it becomes a very powerful, wide spectral bandwidth, high resolution spectrometer.

Fabry–Perôt interferometry (Roesler 1974) is another area of classical spectroscopy that has been applied to atmospheric studies. The Fabry–Perôt is, of course, a plane-parallel interference filter, using a pair of highly reflecting plates and multiple beam interference to limit spectral transmission to certain well-defined frequencies. Energy throughput is good because of the absence of slits; in some cases very high spectral resolution is possible.

Microwave atmospheric spectroscopy has recently been reviewed by Waters (1976). Using monochromatic, tunable (and relatively powerful) local oscillator sources, heterodyne and superheterodyne methods have advanced considerably in the years since 1945. The advantages of such techniques are very high spectral resolution and radiometric sensitivity, coupled with low atmosphere scattering because of the long wavelengths, and measurements of middle atmosphere composition have been made from the ground, aircraft and balloons. Previously the instrumentation required has been extremely heavy and large, but modern microwave spectrometers are light enough to be used on such airborne platforms. Plans are being made for systems that can be operated on orbital spacecraft, and considerable progress can be expected in this field in future years.

Finally, table 1 mentions infrared heterodyne spectroscopy. The development of this method has been hampered until recent years by the lack of suitable local oscillators (lasers) and non-linear mixing elements. Menzies (1976), in a recent review, has shown, however, that many problems have been overcome and that very high spectral resolution infrared heterodyne radiometers can now be developed for atmospheric studies.

To be able to briefly review current activities in atmospheric spectroscopy that use the above mentioned instruments and techniques, table 2 has been compiled. This lists a number of

groups active in this field, the instrumental types and techniques used and the types of observational platforms that have been employed. Abbreviations used in the table are identified in the key that follows it. Table 2 is without doubt incomplete but represents a reasonably broad sample of current activity.

The types of instruments have been identified in table 1 and the preceding text, of course. Other points that should be brought out in considering table 2 are:

(i) The use of two distinct remote sensing methods, i.e. solar occultation and atmospheric emission. The former permits much better signal:noise ratios than the latter, though limiting observations (when used in a limb sounding configuration, as is usual) to local sunrise and sunset. Emission measurements can of course be made at all local times and, indeed, in, any direction.

TABLE 2. ATMOSPHERIC SPECTROSCOPY: A SELECTION OF GROUPS/TECHNIQUES

<i>group</i>	<i>country</i>	<i>technique</i>	<i>platform</i>
Ackerman/Girard <i>et al.</i>	Belgium, France	grille spectrometer/i.r. solar occ.	balloon, aircraft
Anderson <i>et al.</i>	U.S.A.	resonance fluorescence/local measurement	balloon, rocket
Evans <i>et al.</i>	Canada	g.s./M.i./u.v. and i.r. solar occ. and atmospheric emission	balloon, rocket
Farmer <i>et al.</i>	U.S.A.	M.i./solar occ.	balloon, aircraft
Gille <i>et al.</i>	U.S.A.	filter radiometer/atmospheric emission	balloon, satellite
Harries <i>et al.</i>	U.K.	f.i.r. M.i./cryogenic g.s./atmospheric emission	balloon, aircraft
Heath/Kreuger	U.S.A.	u.v. spectrometer/solar trans. and back-scatter	satellite
Houghton <i>et al.</i>	U.K.	s.c.r./p.m.r./atmospheric emission	balloon, satellite, aircraft
Menzies <i>et al.</i>	U.S.A.	i.r. laser heterodyne solar occ.	balloon, aircraft
Murcay <i>et al.</i>	U.S.A.	g.s. (cooled and uncooled)/solar occ./atmospheric emission	balloon, aircraft
Patel	U.S.A.	Laser absorption using spin-flip Raman laser/local measurement	balloon
Offerman <i>et al.</i>	West Germany	cryogenic g.s./atmospheric emission	rocket
Stair <i>et al.</i>	U.S.A.	g.s./cryogenic M.i./atmospheric emission	rocket
Waters	U.S.A.	microwave spectrometer/atmospheric emission	balloon, aircraft, ground balloon
Zander	Belgium	g.s./solar occ.	balloon

Key to table 2: i.r. infrared u.v. ultraviolet
solar occ. solar occultation f.i.r. far infrared
g.s. grating spectrometer s.c.r. selective chopper radiometer
M.i. Michelson interferometer p.m.r. pressure modulator radiometer

(ii) Mention is made of the resonance fluorescence spectrometer measurements of Anderson and coworkers; this technique is a local sampling method, and as such will be discussed in an accompanying paper by Dr Ehhalt. However, it is mentioned in table 2 as a most interesting application of spectroscopy to atmospheric studies. A description may be found in Anderson *et al.* (1977).

(iii) The development of completely cold spectrometric systems – often of quite high degrees of complexity – is being undertaken in several laboratories. Cryogenically cooled devices may achieve improved sensitivity, when looking at very weak emissions, by removing thermal emission from optical components which otherwise could totally swamp the desired atmospheric signal. Of course, cooled detectors have been used in atmospheric spectrometers for

many years, and so the use of cryogenic liquids and refrigerators themselves is not new; the cooling of a complete spectrometer does, however, present many new problems including the design of satisfactory moving parts, and the interface between the cold spectrometer and the (relatively) warm atmosphere.

(iv) Even though several new and ingenious devices have been developed in recent years, table 2 illustrates the fact that most spectral devices can find application in one type of investigation or another. It is, indeed, important to carry out investigations with many different types of technique in order to increase the quantity of independent information that is available.

3. ADVANTAGES AND DISADVANTAGES

The widespread use of spectroscopy for atmospheric studies clearly indicates that there are strong advantages implicit in the method; but at the same time certain very important disadvantages exist which must be considered. Table 3 shows a summary of some of the more important aspects. A discussion of table 3 follows.

TABLE 3. SPECTROSCOPY OF THE TERRESTRIAL ATMOSPHERE

some advantages:

- large information content;
- high intrinsic sensitivity;
- possible to integrate signals over long paths to increase sensitivity further;
- local contamination reduced by long optical paths;
- remote sensing possible;
- 'discovery' aspect;
- 'archival' aspect;

some disadvantages:

- complex spectrum to unravel;
- atmospheric structure and spectral structure to deconvolve (e.g. inversion problem);
- instruments can be complicated and/or large and/or expensive.

Clearly, the most attractive feature is the very large information content explicitly displayed in the absorption or emission spectrum of an atmospheric molecule or atom. This may be illustrated by figure 1 which shows, in the lowest frame, the spectrum of solar radiation attenuated by the atmosphere as seen at sea level in the spectral range 1–15 μm ; the shading represents regions of absorption and the ordinate is given in units of fractional absorptance (0–100%). The upper frames show spectra of several atmospheric constituents, recorded in the laboratory, and a comparison of these with the solar spectrum immediately shows that this one spectrum contains information on the concentration of each of these constituents, from the intensity of absorption in each case.

When it is remembered that the spectra shown in figure 1 are recorded at relatively low spectral resolution (*ca.* 5 cm^{-1} or so) it will be appreciated that at the higher resolutions currently achievable (0.1–0.001 cm^{-1}) an enormous quantity of information, on a great number of atmospheric constituents, becomes available to us. Connes & Connes (e.g. 1966) have illustrated on many occasions in their study of planetary spectra with Fourier spectroscopy how increased resolving power produces more and more spectral detail and information.

High sensitivity is mentioned in table 3, and, indeed, in the laboratory spectroscopy is often used as an analytical tool for this reason. In the atmosphere high sensitivity means that spectroscopy may be used to detect rather small quantities of specific constituents.

Sensitivity can, of course, be improved upon, as is mentioned in the table, by integrating absorption and emission signals over very long paths. Indeed, most remote sensing applications of atmospheric spectroscopy necessarily involve long atmospheric paths which in some cases may represent effective path lengths of several hundred kilometers.

In the middle atmosphere, of course, the absolute concentrations of many constituents are very low, and it is not difficult to contaminate severely the locality of a balloon-borne sensor, for example with material outgassing from the balloon itself and/or from the instrument. This problem has been met, for example, in many early attempts to measure stratospheric water vapour density. Spectroscopic methods that integrate over long paths are clearly less sensitive to local contamination because of the large integration path outside the contaminated zone.

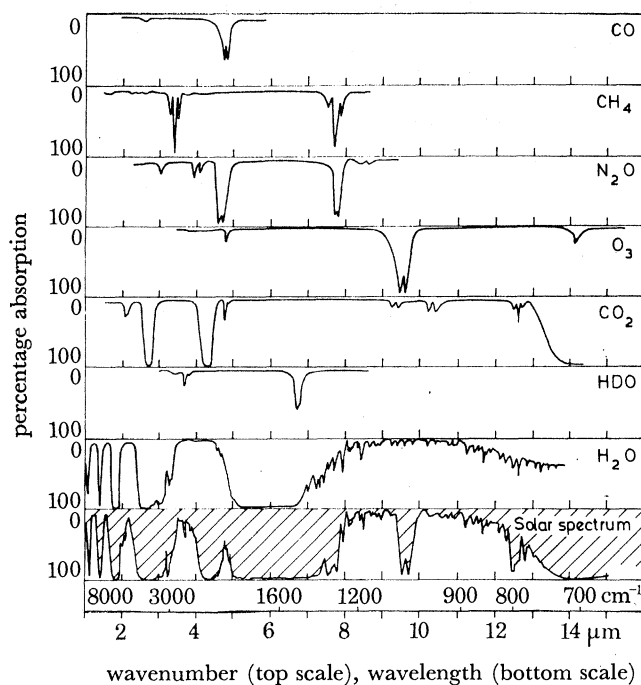


FIGURE 1. Comparison of the transmission of solar radiation through the atmosphere to sea level (bottom curve), compared with the laboratory spectra of atmospheric gases contributing to the atmospheric spectrum. In each curve the abscissa shows wavelength in μm (lower scale) or wavenumber (top scale), and the ordinate is 0–100% absorbance.

A further aspect listed in table 3 may seem rather obvious but should be mentioned because of its importance: a piece of atmosphere quite remote and distant from the sensor can be investigated or 'remotely sensed'. Ingenious methods have been developed, based on the exponential decrease of atmospheric density with height and 'topside' (or down-looking) viewing, which ensure that most of the radiation detected by a spectroscopic sensor at a given wavelength comes from a rather compact, remote parcel of the atmosphere.

Next, table 3 contains what I have called the 'discovery' aspect of atmospheric spectroscopy. This simply stated means that each time an improved measurement of the atmospheric spectrum is made (e.g. at increased spectral resolution, with a better signal:noise ratio, or in a new spectral region) new bands may be discovered, possibly due to unknown constituents. This discovery aspect is not a feature of certain other methods such as chemical sampling,

where an experiment is designed specifically for a given measurement (we should point out, of course, that such methods may have other advantages which make them valuable).

A rather beautiful result which illustrates this aspect was the discovery in the late 1960s of the presence of nitric acid, HNO_3 , in the stratosphere by Murcray and coworkers at the University of Denver. This group was engaged in studies of the absorption spectrum of the stratosphere with the use of a solar-pointing grating spectrometer mounted on a balloon gondola.

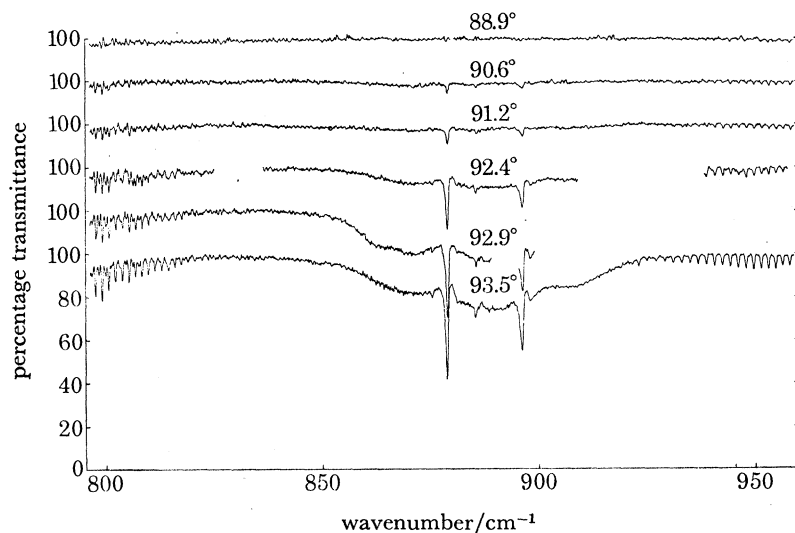


FIGURE 2. Measurements of solar transmission at a number of solar zenith angles (marked on each curve) in the 800–950 cm^{-1} region. Each curve is displaced by 20% for clarity. The observation altitude was 30 km (Murcray *et al.* 1974a).

Measurements were made at large zenith angles, in order to maximize the absorption along a very long atmospheric path, to study the detailed spectroscopy of the 5–20 μm region. When measurements were made with solar zenith angles $> 90^\circ$ (i.e. below the local horizontal, looking through atmospheric layers below the flight level) new absorptions were discovered in the 1325 cm^{-1} (7.55 μm) and later in the 890 cm^{-1} (11.2 μm) regions, which were assigned to the HNO_3 molecule. The observations at 11.2 μm were particularly remarkable since prior to this work this region had been known as one of particularly high transmission (a ‘window’ region). Figure 2 (taken from Murcray *et al.* 1974a) shows a series of spectra around 11.2 μm illustrating the rapid growth of the HNO_3 absorption bands as the zenith angle increases. These data were measured from a balloon floating at *ca.* 30 km, with the solar zenith angles θ_z marked on each trace: it can be seen that for $\theta_z < 90^\circ$, the region is one of very high transmission, but that at $\theta_z > 91^\circ$, HNO_3 absorption increases very rapidly.

Table 3 also mentions the ‘archival’ aspect of atmospheric spectroscopy: thus it has been found in recent experience that high resolution atmospheric spectra recorded previously may be re-examined later either to search for new constituent absorptions or to reanalyse the raw data when improved spectral data or analysis techniques become available.

The most serious drawbacks to the method are, of course, the complexity of the spectrum and the difficulty of extracting unambiguous data from it. Thus a molecular vibration or rotation spectrum is usually extremely complicated and great care and attention needs to be paid to correct assignment of the observed spectral features to the constituent responsible.

A rather beautiful example of spectral analysis is shown in figure 3, again taken from the work of Professor Murcray and his group at Denver University (Murcray *et al.* 1974*b*). The top frame of figure 3 shows an atmospheric transmission spectrum measured by using a grating spectrometer, with the Sun as a source, from an aircraft at an altitude of about 15 km. The lower frames show how theoretical calculations of the transmission spectra of H₂O, CH₄ and NO₂ have been combined (multiplied together) to produce a synthetic spectrum that very

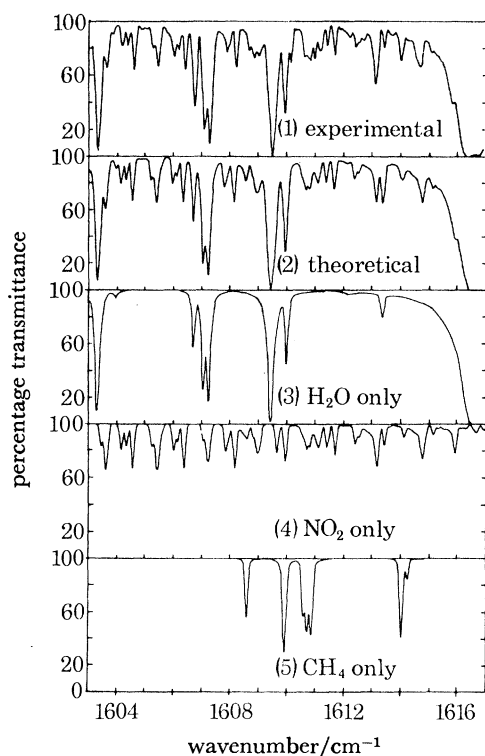


FIGURE 3

FIGURE 3. The atmospheric transmission spectrum measured from an aircraft experiment at *ca.* 15 km altitude is shown in the top frame: the second frame shows a calculated spectrum constructed from the spectra calculated for H₂O (third frame), NO₂ (fourth frame) and CH₄ (fifth frame). The calculated spectra clearly demonstrate that features in the 1604–1606 cm⁻¹ and 1611–1614 cm⁻¹ regions are due to NO₂ (Murcray *et al.* 1974*b*).

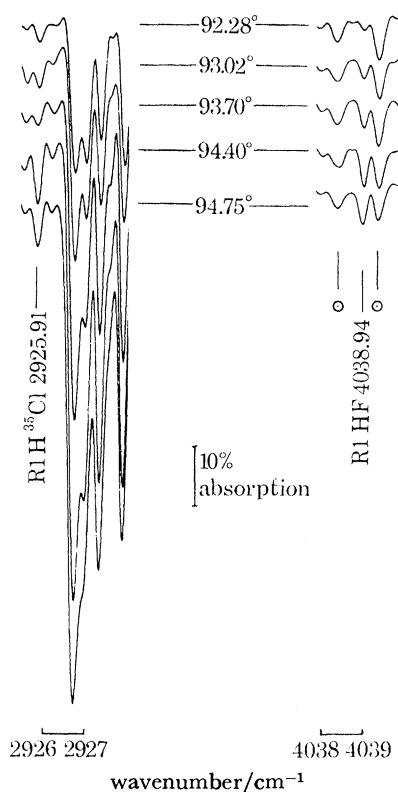


FIGURE 4

FIGURE 4. Atmospheric transmission measurements made from a balloon at *ca.* 35 km altitude using a Michelson interferometer, in the 2900 cm⁻¹ region and 4000 cm⁻¹ region. Absorption features due to HF, HCl and solar CO (o) are marked (Farmer *et al.* 1977).

closely matches the experimental result. In this case the aim of the exercise was to demonstrate unambiguously the absorption features due to NO₂, and as can be seen by a close inspection of the 1604–1606 cm⁻¹ and 1611–1614 cm⁻¹ regions in particular, this exercise was very successful. In fact, when faced with the analysis of a very complex line spectrum this process of building up a matching synthetic spectrum species-by-species is the most satisfactory and convincing way of completing such analysis.

This aspect of atmospheric spectroscopy is so close to the heart of the whole topic that it merits further example. Figure 4 shows a result due to Farmer & Raper (1977). This shows a

series of atmospheric transmission spectra in the 2900 and 4000 cm^{-1} regions measured by using a rapid-scan Michelson interferometer looking at the Sun from a balloon platform at about 35 km. The simultaneous detection of HCl and HF is observed quite clearly along the line of sight. In this short wavelength infrared region care must be taken to separate absorption features arising within the Earth's atmosphere from those occurring within the solar atmosphere – the spectral features labelled \odot in figure 4 are indeed due to absorption by solar CO.

The problem of deconvolving spectral and spatial structure, also mentioned in table 3, has received considerable attention over the past 20 years. It is a very complicated matter, since the atmospheric structure itself along the line of sight (i.e. the variation of pressure, mixing ratio and temperature) may be highly variable. Furthermore, at wavelengths where the atmosphere is optically thin, photons are received over great distances in the atmosphere, while at optically thick wavelengths photons from great distances are completely absorbed before reaching the observer and so the local atmosphere dominates the signal detected.

The problem may be regarded as an application of information theory, and one of the mistakes it is easy to make is to try to extract too much information from a deconvolution (more commonly called 'inversion' or 'retrieval') exercise, considering the limitations in the real data being used as input. The more advanced methods being used to analyse satellite remote sensing measurements generally provide some extra information to the measurement, in one way or another, in order to constrain the number of possible concentration (or temperature) profiles that may give rise to a measured radiance profile. Valuable reviews of this subject may be found in Rodgers (1976) and Twomey (1977).

An interesting development has been the limb-sounding method (Gille & House 1971) in which the vertical resolution of an atmospheric profile is determined geometrically by scanning the limb (horizon) of the atmosphere with an instrument possessing a narrow vertical field of view. This contrasts with the vertical sounding method originally suggested by Kaplan (1959), which depends on using a variety of optical depths (i.e. different wavelengths across a chosen absorption band) to probe different levels of the atmosphere.

The final point in table 3 is introduced to indicate to the reader not experienced in atmospheric spectroscopy that atmospheric spectrometers may in some cases be large, heavy and complicated and expensive to fly. Indeed, experiments weighing more than 1 ton have been flown on balloons. This is not a general rule, however, and atmospheric spectrometers can range in weight from a few kilograms upwards.

4. A RECENT BALLOON-BORNE SPECTROMETER EXPERIMENT

At the National Physical Laboratory we have exploited the large information content of the infrared spectrum (particularly the far infrared at wavelengths beyond 100 μm) to explore the possibility of studying many middle atmosphere gases at once. In the far infrared, the pure rotation bands of a large number of atmospheric spectra are overlaid, not separated by differing vibrational fundamental frequencies as in the shorter wave infrared. Measurements have been made from aircraft and balloons of the atmospheric emission spectrum at these very long wavelengths by using Michelson interferometers and Fourier transform techniques.

An example spectrum is shown in figure 5 (Harries *et al.* 1976). Only a small range of the measured spectrum is shown. Atmospheric emission is shown increasing upwards, and the 34–39 cm^{-1} region ($\lambda = 294\text{--}256 \mu\text{m}$) is displayed. The spectrum was measured by using a

liquid helium-cooled InSb detector at an altitude of about 37 km, a zenith angle of about 93° , and a spectral resolution of about 0.05 cm^{-1} . Features can be seen due to H_2^{16}O , H_2^{18}O , $^{16}\text{O}_2$, $^{16}\text{O}_3$ and NO_2 . Elsewhere in the spectrum, lines due to other species, such as HNO_3 , occur.

Figure 6 shows profiles of H_2O , NO_2 and HNO_3 calculated from a series of spectra like that shown in figure 5. These profiles were obtained during local daylight, on 20 September 1974, and were measured simultaneously. It is this last point which provides the basic philosophy for our current activities, that is to provide measurements of as many (related) middle atmosphere constituents as possible at the same place and the same time. In this way we hope to avoid the difficulties of combining data measured at different places and different times which may contain important differences due to spatial, temporal and seasonal (i.e. long term temporal) variations.

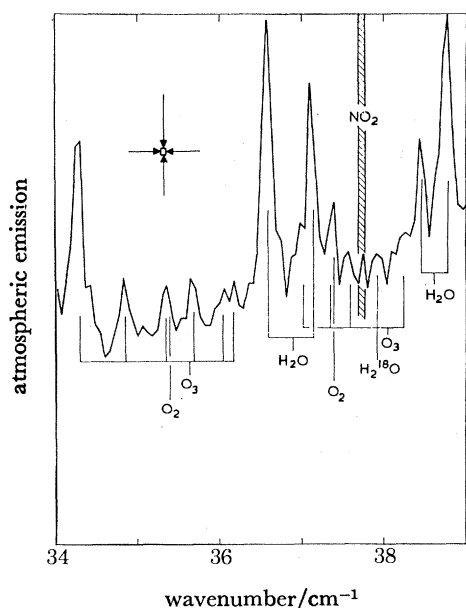


FIGURE 5

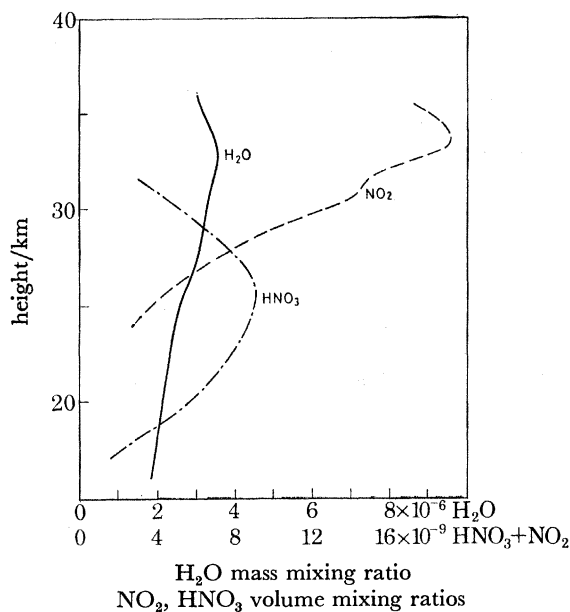


FIGURE 6

FIGURE 5. Atmospheric emission spectrum in the far infrared, measured at *ca.* 37 km altitude and with a zenith angle of 93° . Spectral resolution is 0.05 m^{-1} and atmospheric emission increases upwards. Spectral features due to H_2^{16}O , H_2^{18}O , NO_2 , O_2 and O_3 may be identified.

FIGURE 6. Profiles of H_2O , HNO_3 and NO_2 derived from spectra including that shown in figure 5 measured simultaneously from a balloon experiment floating at 37 km, during the day on 20 September 1974.

Recently, a balloon flight was made of the latest experiment in our programme. Titled **SIBEX** (submillimetre infrared balloon experiment) this experiment is being carried out in collaboration with Dr B. Carli and colleagues at the Institute of Research on Electromagnetic Waves (I.R.O.E.) in Florence, Italy. **SIBEX** comprises two instruments, a liquid nitrogen-cooled grating spectrometer operating in the $8\text{--}20 \mu\text{m}$ region, and a high resolution Michelson interferometer operating in the far infrared (or submillimetre region) between about 100 and $1000 \mu\text{m}$. Both instruments view the same parcel of air and detect atmospheric emission by using the limb-sounding technique.

Table 4 illustrates the measurements made by using **SIBEX**: as can be seen, the combination of the two instruments allows us to measure, simultaneously, the concentrations of a large number of atmospheric species, many of them closely related photochemically.

SIBEX was flown on 17 November 1978 from the National Scientific Balloon Facility at Palestine, Texas, U.S.A., The two instruments operated very well, and the analysis of the results is currently under way in Italy and the U.K.

An example of the raw spectral data obtained using the cooled grating spectrometer has been prepared by Dr S. Pollitt and Mr M. J. Bangham, of the N.P.L. group, and is shown in figure 7. The adjacent sections show spectral scans from two of the three channels in the instrument. The spectra have been annotated to indicate emission features due to a number of constituents; the spectra are complicated by the effects of grating blaze efficiency and transmission edges due to order-sorting filters. Each of these effects is, of course, removed during the calibration process which is currently in progress.

TABLE 4. MIDDLE ATMOSPHERE TRACE CONSTITUENTS TO BE MEASURED BY SIBEX

<i>instrument</i>	<i>spectral region</i>	<i>constituent</i>
far infrared (submillimetre) Michelson interferometer	10–100 cm ⁻¹ (1000–100 μm)	H ₂ O
		O ₃
		HNO ₃
		NO ₂
		N ₂ O
		CO
		HF
		HCl
		NH ₃
		ClO*
		mid infrared cooled grating spectrometer
O ₃		
CF ₂ Cl ₂		
CFCl ₃		
HNO ₃		
CH ₄		
CCl ₄		
ClNO ₃ *		

*, measurement uncertain.

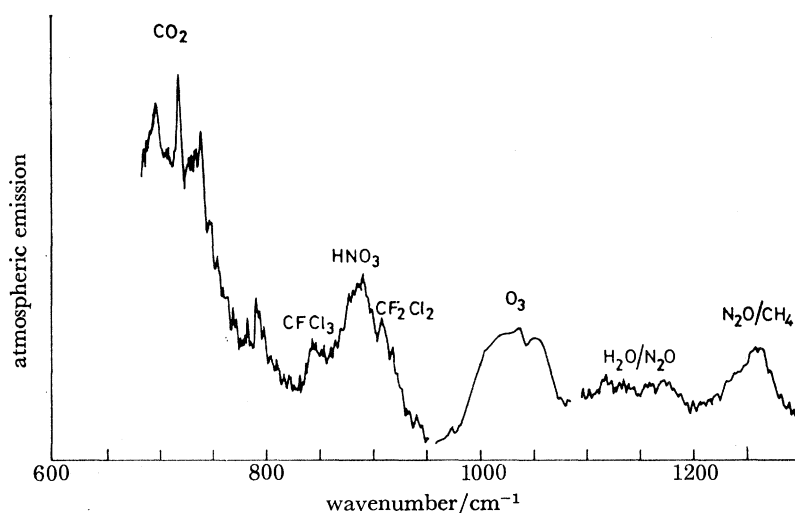


FIGURE 7. Raw spectral data recorded using the cryogenic grating spectrometer on board the SIBEX experiment. The sections of the diagram represent two separate channels of the spectrometer, and in each case the ordinate is signal received at the detectors, and the abscissa is wavenumber. Provisional wavenumber scales and spectral identifications have been superposed.

The far infrared experiment data is still being calibrated and Fourier transformed, and so we can only illustrate the anticipated performance of that device in figure 8. This shows a calculated emission spectrum (Bangham 1978) in the 41–42 cm^{-1} region ($\lambda = 244\text{--}238\ \mu\text{m}$), in which lines due to HF and HCl in the concentrations shown have been added to a spectrum of H_2O , O_2 and O_3 . The calculation was carried out for a limb-sounding experiment carried on a platform outside the atmosphere, and a tangent ray height of 30 km, though the result closely approximates that for a balloon floating above 35 km. The simulated spectral resolution is $0.01\ \text{cm}^{-1}$. The estimated experimental noise level is about the magnitude of the weakest O_3 line, and so, as can be seen, both HF and HCl should be clearly detectable in the spectra obtained from this experiment.

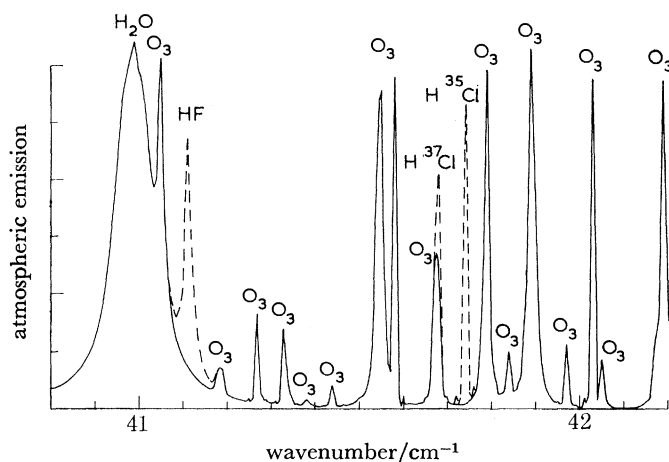


FIGURE 8. A calculated far infrared spectrum of atmospheric emission at high resolution (*ca.* $0.01\ \text{cm}^{-1}$) evaluated for conditions resembling the SIBEX balloon experiment of 17 November 1978. The continuous curve is the emission spectrum due to H_2O , O_2 and O_3 . The broken lines indicate the effect of adding HF and HCl with an assumed constant mixing ratio with height of 1×10^{-9} : the zenith angle is *ca.* 91° .

5. CONCLUSION

This paper has considered the justification for applying spectroscopic techniques to studies of middle atmosphere composition, and has attempted to illustrate the intrinsic power of these techniques.

It should be clear from the several examples quoted that the subject of atmospheric spectroscopy is a very active one with many workers applying a variety of ingeniously devised spectroscopic techniques to measurements of composition.

Clearly there is still a strong need for a considerable improvement in the sensitivity and resolving power of spectroscopic instruments, however. As the amount of information to be extracted from a spectrum increases, so must the amount of detail we can resolve. No one instrument will provide all the answers, of course, but a large potential for improvement would seem to exist in the use of i.r. heterodyne radiometers and in microwave spectrometers, in both cases because of their very high resolving power. Gas correlation spectroscopy is currently making great contributions, and I believe we can expect this principle to be used in a variety of applications in the future. One of the other areas in which there is great excitement, because of the extremely high sensitivities which are possible, is in the development of cryogenically cooled high resolution grating spectrometers and Michelson interferometers.

Another area, though somewhat beyond the range of interest defined by the title of this paper, where spectroscopic techniques might be developed considerably is in the remote sensing of atmospheric winds. Currently spectroscopic methods are being tested, which are based on measurements of the Doppler shifts of spectral lines averaged along a given line-of-sight. Sensitivities need to be improved, and consideration needs to be given to the most appropriate instruments for making such measurements.

Finally, I make a plea for the continued support of laboratory spectroscopy in order to obtain the line parameters which are needed for the analysis of all atmospheric spectroscopic measurements. At present, uncertainties in line parameters often represent the largest source of error in a composition measurement, and a significant fraction of available resources should be diverted to support workers active in this field. We should remember that a measurement of a constituent concentration from the best atmospheric spectrum (which may be very difficult and expensive to produce) is only as accurate as the basic spectroscopic data used in the analysis.

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