THE ATMOSPHERIC INFRARED CONTINUUM

by

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Abstract

This thesis is an account of two major experiments to study the atmospheric infrared continuum in the region 4 to 21 μ , using a high resolution (1.0 cm^{-1} at 20 μ) grating spectrometer with Golay cell detector and Nernst source.

Using open horizontal atmosphere paths of 10, 200 and 400 m, extinction coefficients were measured in 7 windows between 14.0 and 20.9 μ . An extremely high correlation was found with the amount of water vapour in the path; aerosol seemed to have very little effect except under extremely hazy or foggy conditions. The absorption coefficients increased with the partial pressure of water vapour, suggesting a self-to-foreign broadening factor much greater than the value of 6 observed for line centres. However, because of the strong correlation between vapour pressure and temperature in the open air, it proved difficult to distinguish between temperature dependence and self broadening, so the investigation was transferred to the laboratory.

Using a 15.5 m multiple reflection cell giving path lengths in the range 100 - 400 m, with temperature and humidity control, the inferences of the open air experiment were confirmed and extended to include the region 4 - 12 μ . Unexpectedly high absorption was observed in this latter region.

(ii)

These results inspired a reexamination of all available previous work, from which it was concluded that the extinction arises from two separate effects with different frequency and temperature dependence. They are i) a foreign-broadened component, roughly proportional to the foreign gas pressure and probably positively temperature dependent (0.5 to 1% per °C); and ii) a self-broadened component roughly proportional to partial vapour pressure and with a strong negative temperature dependence (2% per °C at 30°C).

On the basis of several assumed line shapes, the accumulated wings of lines in the 50 μ rotation band were computed at several points in the range 12 - 40 μ : the Lorentz shape gave a very good fit ($\pm 10\%$) to the foreign-broadened component, but none gave a satisfactory fit to the self-broadened component.*

The 15 μ CO₂ band was found to give no detectable absorption (< 1% for 43 atm - cm of CO₂, the equivalent of 1.4 km of air at sea level) outside the range 12.7 to 17.8 μ .

The horizontal path experiment has already been reported in a joint paper with F. Saledy and P. A. Sheppard, entitled 'On the Atmospheric Infrared Continuum', J.O.S.A. 53, 466 (1963); a copy is attached to this thesis.

During this research a further paper, on the related topic of terrestrial heat balance, entitled 'Heat-balance measurements from an earth satellite - an analysis of possibilities' was published in Quart. J. Roy. Met. Soc., 87, 231 (1961); a copy is attached.

CONTENTS

CHAPTER IINTRODUCTORY SURVEY

		Page
1.1	Introduction	1
1.2	Theoretical background	3
1.2.1	Definitions and units	3
1.2.2.	Line shape	4
1.2.2.1	Introduction	4
1.2.2.2	Impact or interruption theories	6
1.2.2.3	Statistical theory	9
1.3	Aim of the investigation	9
1.4	Previous work	10

CHAPTER 2HORIZONTAL PATH EXPERIMENT - OPEN AIR

2.1	Introduction	13
2.2	Design of experiment	13
2.3	Apparatus	15
2.3.1.	Source	15
2.3.2.	Optical system	15
2.3.3.	Spectrometer	17
2.3.4.	Detector system	18
2.3.5.	Filters	19
2.4	Performance of the system	19
2.4.1	Typical spectra	19
2.4.2	Calibration	19

		Page
2.4.3	Resolution	20
2.4.4	Stray radiation	20
2.4.5	Linearity of detector system	21
2.4.6	Stability of system	22
2.5	Experimental technique	22
2.5.1	Choice of method	22
2.5.2	Measurement of $\beta_{17} - \beta_4$	24
2.5.3	Measurement of $\beta_{14} - \beta_4$	29
2.5.4	Measurement of $\beta_i - \beta_4$ for Windows 14, 15, 16, 18, 19 and 20	29
2.5.5	Measurement of water vapour	29
2.5.6	CO ₂ absorption in the region 1300 - 478 cm ⁻¹	30
2.5.7	Extinction by aerosol	30
2.6	Results	35
2.6.1	Windows 17 and 19	35
2.6.2	Windows 18 and 20	38
2.6.3	Windows 14, 15 and 16	39
2.7	Discussion	41
2.8	Conclusion	43

CHAPTER 3

THE LABORATORY EXPERIMENT

3.1	Design requirements	45
3.2	Apparatus	47
3.2.1	Cell construction	47
3.2.2	Temperature and humidity control	47
3.2.3	Temperature and humidity measurement	49
3.2.3.1	Dry-bulb temperature	49
3.2.3.2	Wet-bulb depression	50
3.2.3.3	Comparison with Assmann psychrometer	52
3.2.4	Optical system	52

3.2.5	Spectrometer, source and detection system	Page 56
3.3	Performance of the system	57
3.3.1	Calibration, resolution and linearity	57
3.3.2	Transmittance of polyethylene window	57
3.3.3	Variation of mirror reflectivity with humidity	58
3.3.4	Scattering from mirrors and window	60
3.3.5	Stray radiation	61
3.3.6	Aerosol absorption	61
3.3.7	Ozone and carbon dioxide absorption	62
3.4	Experimental technique	62
3.4.1	Choice of method	62
3.4.2	Measurement of $k_{17} - k_4$	62
3.4.3	Measurement of $k_{18} - k_{17}$, $k_{19} - k_{17}$, $k_{20} - k_{17}$	64
3.4.4	Absolute measurement of k_8 , k_{11} and k_{13}	64
3.4.5	Absolute measurements in window near 4μ	65
3.5	Results and discussion	65
3.5.1	$17 - 21 \mu$ region	65
3.5.1.1	Window 17	65
3.5.1.2	Windows 18, 19 and 20	69
3.5.1.3	Systematic differences between London and Ascot results	71
3.5.1.4	Summary of results	72
3.5.1.5	Discussion and comparison with previous work	73
3.5.2	$7 - 12 \mu$ region and 4μ windows	77
3.5.2.1	Windows 8, 11, 13 and 4	77
3.5.2.2	4μ windows	79
3.5.2.3	Discussion and comparison with previous work	79
3.5.3	Summary of all results	85
3.6	Comparison between theory and observation	85
3.7	Conclusion	89

Addendum	Page 93
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APPENDICES

2.1	Observational data for Windows 14, 17 and 19 (Ascot)	94
2.2	Observational data for Windows 15, 16, 18 and 20 (Ascot)	99
3.1	Observational data for Windows 17, 18, 19 and 20 (London)	100
3.2	Observational data for Windows 4, 8, 11 and 13 (London)	102
References		104
Acknowledgements		107

LIST OF FIGURES

Fig. Number	Title	Facing Page
1.1	Schematic picture of interaction at collision	5
2.1	External Optical system at Ascot	16
2.2	Arrangement of spectrometer	18
2.3	Filter characteristics	19
2.4	Location of windows	19
2.5	Effect of stray radiation	21
2.6	Variation of source output with current	22
2.7	Typical continuum run for Window 17	25
2.8	CO ₂ absorption between 10 μ and 21 μ	30
2.9	Atmospheric aerosol distributions	31
2.10	Extinction coefficients in Windows 17 and 19	36

Fig. Number	Title	Facing Page
2.11	Absorption coefficients in Windows 18 and 20	39
2.12	Extinction coefficients in Windows 14, 15 and 16.	39
3.1	Layout of 15.5 m multiple reflection cell	47
3.2	Distribution of temperature and vapour pressure in cell	48
3.3	Effect of diffusion through walls of cell	48
3.4	Diagram of electrical temperature sensors	50
3.5	Circuit diagram of electrical thermometers	51
3.6	Difference between electrical and Assmann humidities	52
3.7	Optical system (London)	53
3.8	Perspective view of optical path for 12 transits of cell	54
3.9	Typical run for Window 17	65
3.10	Extinction in Window 17	66
3.11	Absorption coefficient in Window 17 as a function of vapour pressure and temperature	67
3.12	Extinction in Window 18	69
3.13	Extinction in Window 19	70
3.14	Extinction in Window 20	70
3.15	Summary of results in the 17 - 21 μ region	72
3.16	Comparison between present work and the results of Bolle	74
3.17	Laboratory measurements of Palmer	74
3.18 } 3.19 }	Absorption coefficients derived from Palmer	75
3.20	Extinction in Window 8 and its temperature dependence	77
3.21	Extinction in Window 11 and its temperature dependence	78
3.22	Extinction in Window 13 and its temperature dependence	78
3.23	Extinction in Window 4 and its temperature dependence	78

Fig. Number	Title	Facing Page
3.24	Extinction in 4 μ windows	79
3.25	Extinction of solar radiation in the region 871 - 908 cm^{-1} (from Roach and Goody, 1958)	80
3.26	Effect of diurnal evaporation on solar intensity measurements	80
3.27	Variation of absorption coefficient with time of day and precipitable water in the zenith (Bolle, 1963)	82
3.28	Variation of absorption coefficients with time of day, visual opacity and zenith precipitable water (Dave 1963)	83
3.29	Extinction at 3.97 μ and 9.1 μ (Taylor and Yates, 1957)	84
3.30	Self- and foreign-broadened absorption coefficients, 8 - 40 μ	85
3.31	Contribution of rotation lines to continuum at $\nu = 800, 559.4$ and 261 cm^{-1}	86
3.32	Comparison between observation and theory	88
3.31 } 3.32 }	Amended versions of the above	93

LIST OF PLATES

1.	External optical system at Ascot	15
2.	Magnesium oxide reststrahlen filter and chopper attenuators	19
3.	Temperature sensing head	49

1.1. Introduction

The existence of a continuous absorption throughout the atmospheric infrared window between 8 and 13 microns has been known for a long time, Elsasser (1938) probably being the first to draw attention to it. It has been observed many times since by all workers in the study of atmospheric radiation, both in transmission observations using the sun and artificial sources, and in emission studies from ground and space observatories. Only recently has serious effort been concentrated on the systematic study of the nature of the continuum, most of the earlier work having been directed to the easier practical problem of absorption by spectral lines and bands.

With the development of new infrared techniques, the range of application in the atmosphere has increased correspondingly. Nearly always the continuum casts a veil over the clear picture which must eventually be extracted from combined line and continuum effects, so that accurate knowledge of the continuum has become very desirable to clarify the picture. The following examples may be quoted:-

- i) The estimation of the distribution of atmospheric ozone from surface observations of the 9.6μ band in emission.
- ii) Study of the solar, lunar and planetary surfaces throughout the infrared and microwave spectrum.

Both of these have been pursued for several years from ground observations and the results have always been subject to some uncertainty regarding the manner of correction for the continuum.

iii) Since the advent of artificial earth satellites, several infrared emission experiments have been proposed, or in some cases already been carried out, to determine the earth's surface temperature distribution, cloud top height, ozone and carbon dioxide distribution, and temperature structure in the upper atmosphere. All of these, except possibly the last, require correction to some extent for the continuum.

Much discussion has centred on the question of the origin of the continuum absorption; there is no doubt that it is largely due to water vapour, but the role of aerosol is less certain. That it is necessary to appeal to something other than water vapour appears to be due to the fact that measurements of continuum absorption by different workers do not seem to be consistent when compared on the basis of the existing picture of the water vapour continuum alone. Whilst it is not disputed that aerosol absorption in the $8 - 13\mu$ region can be significant under extremely hazy conditions, the evidence for a definite correlation between extinction and aerosol concentration under more typical conditions is very questionable, and one of the results of this research suggests that the apparent discrepancies may arise through forcing the data to fit an inadequate model of the continuum.

Meteorologically, the continuum, because of its complete spectral coverage, is surprisingly effective in cooling the atmosphere by radiation. Möller (1942) calculated a cooling rate of about 1°C per day under representative conditions in the lowest two kilometres of the atmosphere.

In addition to the above, the continuum is of interest in its own right, yielding information about the shape of the extreme wings of spectral lines in the water vapour bands. No theory specifically intended to treat line wings more than a few wavenumbers from the line centre has yet been presented, and one of the objects of this research is to discover in what respects the observed continuum differs from that to be expected on the basis of the various line shapes which have been proposed.

1.2. Theoretical Background

The following is not intended to be a logical presentation of the theory of molecular spectroscopy, this being fully treated in several standard references. Only the relevant results are given here as a basis for discussion.

1.2.1. Definitions and Units

Many systems of units are in use in quantitative spectroscopy, and that adopted in this thesis is as follows:-

- 1) Wavelengths are denoted by λ , expressed in microns, and wavenumber ($= \frac{1}{\lambda}$) by ν , expressed in cm^{-1}
- 2) Absorption coefficient. This term invariably means the mass extinction coefficient, k , defined by the relation

$$\frac{dI}{dm} = -kI$$

where dI is the change in intensity of a beam of radiation of intensity I passing through a path containing a mass dm of absorber expressed in g cm^{-2} , so that k is expressed in

$\text{g}^{-1} \text{cm.}^2$ To avoid introducing subscripts except where essential, it is understood that monochromatic radiation is implied in the above definition.

- 3) Line intensity. This is defined as the integrated absorption coefficient over the line by the relation

$$S = \int_0^{\infty} k_{\nu} d\nu$$

and is expressed in units of $\text{g}^{-1} \text{cm.}$ in this thesis.

1.2.2. Line Shape

1.2.2.1. Introduction

A transition between two molecular energy levels gives rise to emission or absorption of a photon which is of well defined wavelength, with, however, a small but definite spread. Three distinct mechanisms (natural, Doppler and collision broadening) are responsible for the spread, and they produce characteristic line profiles and half-width.

Natural broadening, representing the lowest possible limit to the spread, is attributed in classical terms to radiative damping of an isolated stationary oscillator; the resulting line width (10^{-5} to 10^{-11} cm^{-1}) is negligible compared with that due to the other two mechanisms.

Doppler broadening arises from relative motion of the absorbing and emitting molecule, and though it becomes important in the upper atmosphere, it is negligible in comparison with collision broadening under typical tropospheric conditions. A typical Doppler half-width would be $3 \times 10^{-4} \text{ cm}^{-1}$

Fig 1.1. Schematic picture of interaction at collision.

A molecule is emitting a wavetrain as a result of a transition between E_2 and E_1 at time t_0 . Two interactions are illustrated: at t_1 a weak interaction, and at t_2 a strong interaction.

Collision broadening has received much attention and several theories have been advanced, each making different assumptions about the interaction at collisions. The relevant theories will be discussed with the aid of Fig.1.1, which serves to fix our ideas. Two energy levels E_1 and E_2 of an isolated molecule are shown as a function of time. When a second molecule approaches sufficiently closely, such as at t_1 and t_2 , the energy levels are temporarily shifted (usually by different amounts), the molecule in effect assuming different moments of inertia and dipole moment owing to the distortion produced by the foreign force field. Fig. 1.1 is intended to illustrate two collisions, one much closer than the other, though the duration of the encounter has been greatly exaggerated, this being in reality only about 10^{-3} or 10^{-4} of the mean time between collisions. Assume that the molecule begins to emit a photon at t_0 as the result of a transition from E_2 to E_1 ; this process continues for a time which is usually long compared with the interval between collisions, so that during the interval illustrated the emitted wavetrain may be considered to have constant amplitude (upper wavetrain in Fig. 1.1.). Near the times t_1 and t_2 , there will be a temporary shift of the wavenumber of the photon from

$$\nu_0 = \frac{E_2 - E_1}{hc} \text{ to } \nu = \nu_0 + \frac{(E_2 - E_1)}{hc} .$$

Line broadening theories seek to describe the probability distribution of the shift $\nu - \nu_0$, and fall into one of several classes outlined below. They all assume that the interaction produces frequency modulation so that the phase of the oscillation is changing continuously during the

encounter. Use is made of the following terms:-

1)	Strong interaction.	Total phase change during collision large ($> 2\pi$)
2)	Weak interaction.	Total phase change during collision small ($\ll 2\pi$)
3)	Adiabatic interaction.	No transition induced by collision
4)	Non-adiabatic interaction.	Transition induced by collision.
5)	Resonance.	A non-adiabatic interaction in which a transition of nearly the same magnitude but of opposite sign is induced in both molecules.

1.2.2.2. Impact or interruption theories.

The molecule is assumed to radiate monochromatically at all times except that at collisions there is an instantaneous change of phase, as illustrated in the lower wavetrain of Fig.1. This represents a strong adiabatic interaction. The precise nature of the perturbation during the collision is immaterial in this theory and is justified by the relatively very small proportion of the time spent in collision. The resulting line profile of absorption coefficient k is given by

$$k_{\nu} = k_{\nu_0} \frac{\alpha^2}{(\nu - \nu_0)^2 + \alpha^2} \quad 1.$$

where the line half-width $(\alpha) = \frac{1}{2\pi \bar{\tau} c}$ with c = velocity of light and $\bar{\tau}$ = the mean time between collisions. The same profile results from Anderson's (1949) analysis of non-adiabatic resonant interactions, though here the line-width is

formulated in quantum mechanical terms.

Eq.1 is the Lorentz profile, well known in many problems involving damped oscillation. From the definition of line intensity we find

$$S = \int_0^{\infty} k_{\nu} d\nu = k_{\nu_0} \pi \alpha$$

so that from Eq.1

$$k_{\nu} = \frac{S \alpha}{\pi ([\nu - \nu_0]^2 + \alpha^2)} \quad 2.$$

Eq2. presents a contradiction with the Debye formulation for static polarisation for a line with $\nu_0 = 0$, which suggests that a modification is required for this, the microwave region. An assumption in the Lorentz derivation is that $\nu - \nu_0 \gg \alpha$; when this is no longer the case, then a slightly different profile results

$$k_{\nu} = \frac{S \alpha}{\pi} \frac{\nu}{\nu_0} \left[\frac{1}{(\nu - \nu_0)^2 + \alpha^2} - \frac{1}{(\nu + \nu_0)^2 + \alpha^2} \right] \quad 3.$$

However a further important factor as $\nu_0 \rightarrow 0$ in the derivation of Eq. 3 is the assumption made regarding the velocity and displacement of the oscillator immediately after the collision. Eq. 3 is derived from a random distribution, whereas a Maxwell distribution would be more appropriate, assuming that the collisions set up a thermal equilibrium. Then there results

$$k_{\nu} = \frac{S \alpha}{\pi} \left(\frac{\nu}{\nu_0} \right)^2 \left[\frac{1}{(\nu - \nu_0)^2 + \alpha^2} + \frac{1}{(\nu + \nu_0)^2 + \alpha^2} \right] \quad 4.$$

* p. 93
See also Addendum

Eq. 4 is the Van Vleck and Weisskopf (1945) profile and experimental evidence suggests that it gives a good approximation in the microwave region. It should be pointed out however that it cannot hold throughout the spectrum since Eq. 4 tends to the constant value $\frac{S\alpha}{\pi\nu_0}$ as $\nu \rightarrow \infty$, implying infinite line intensity. Against the derivation it might be argued that the duration of the interactions is too small to establish thermal equilibrium and that the distribution of velocities and displacements is more nearly random than Maxwellian. This argues for Eq. 3 rather than Eq. 4.

In any event, the line wings would be expected to be stronger than the value obtained from Eq. 2. using the value of $\bar{\tau}$ as defined there. This is because τ has a wide spread among individual molecules and a different type of mean is required for the central and wing regions. From Eq. 2. we see that $k_{\nu_0} = \frac{S}{\pi\alpha} = 2Sc\tau$ so that here the mean time between collisions is the correct interpretation of $\bar{\tau}$.

In the wings, on the other hand, $k_{\nu} = \frac{S\alpha}{\pi(\nu-\nu_0)^2} = \frac{S}{2\pi^2c(\nu-\nu_0)^2} \frac{1}{\tau}$ so that we are now concerned with $\overline{\left(\frac{1}{\tau}\right)}$. For any distribution of τ , $\overline{\left(\frac{1}{\tau}\right)} > \frac{1}{\bar{\tau}}$ and computation for billiard-ball type collisions indicate that the wing absorption predicted by Eq. 2 should be multiplied by 1.146 (Goody 1964, p.107).

Near line centres, both Eq. 4 and Eq. 3 reduce to Eq. 2, so that studies involving line absorption will be insensitive to the choice of profile.

1.2.2.3. Statistical theory

Here the perturbation of the oscillator during weak interactions is accounted for by Lindholm (1945) on the basis of an assumed molecular force field, resulting in an asymmetric line profile with a shifted centre. The theory was developed for transitions far from resonance, e.g. optical spectra, and it is not surprising that experimental data do not fit the Lindholm profile in the extreme wings of infrared lines. No further consideration will be given to this theory.

1.3. Aim of the present investigation

Experimental measurements of line profile are hampered by inadequate resolution to observe the central regions in detail, since spectrometer slit widths are usually at least ten times the line half-width. Indirect methods involving the study of absorption by whole lines or bands are usually resorted to, and some uncertainty must always remain because the small variation in such absorption resulting from different profiles is indistinguishable from that due to uncertainty in the line intensity or half-widths.

A more direct way for investigating line wings is to measure the continuum absorption in the $8 - 20\mu$ region away from the influence of lines, and to compare the results with those computed from accumulated line wings of the different profiles mentioned above. The influence relative to the rotation band of the much weaker 6.3μ vibration-rotation band, for which absolute computation of line intensity is not possible, may be neglected in the $16 - 20\mu$ region,

but might influence the $8 - 12\mu$ region. The $12 - 16\mu$ region is inaccessible unless elaborate precautions are taken to exclude carbon dioxide from the apparatus.

By observing the temperature dependence, a further indication as to the origin of the continuum may be possible, since the very high line intensities near the band centre have a negative temperature dependence, whilst the others are positively temperature dependent.

1. 4. Previous Work

The first spectrometric measurements of atmospheric absorption were made in the $8 - 12\mu$ solar spectrum by Adel (1939) using a rock salt prism giving resolution certainly no better than 10 cm^{-1} , which is insufficient to separate line and continuum absorption. This might account for his result at 900 cm^{-1} being about double the more recent values. This work is of little more than historical interest. The next measurements were made by Gebbie et al (1951) using a horizontal path of about 2 km over water; they observed the transmission in the $2.2 - 11.5\mu$ region relative to that at 0.61μ . The low resolution made it impossible to untangle selective and continuum absorption, and access to the raw data would be necessary to reinterpret it in the light of recent findings. Anthony (1952) employed a solar absorption technique from Table Mountain, California, and obtained a few results (the only published data to date) for 19.0, 17.6, 12.8, 12.0, 11.5, 10.5, 9.0 and 8.0μ ; the circumstances of the observations and instrumental details are not available. Palmer (1957 b, c) published a series of spectra for the $20 - 40\mu$ region with

resolution $2.5 - 5 \text{ cm}^{-1}$, taken under controlled laboratory conditions with different total and partial pressures of air and water vapour; this work provides a valuable source of data which is analysed in Chapter 3. Yates and Taylor (1960) carried out an experiment over horizontal atmospheric paths of 0.3, 5.5 and 16.25 km under different atmospheric conditions; little of this data was published and no analysis in terms of the continuum has appeared. Roach and Goody (1958) using resolution of 7 cm^{-1} in the $8 - 12 \mu$ window, observed solar intensity as a function of zenith angle from observatories in London and Ascot. Some correction for selective absorption was necessary, with attendant uncertainty, but there remained no doubt that the London results indicated much stronger absorption than those taken at Ascot. Roach attributed this to aerosol absorption in the excessively polluted London atmosphere. Vigroux (1959) observed the zenith angle dependence of solar radiation at 1041 cm^{-1} from Arosa (1800 m in the Swiss Alps) and deduced the continuum absorption coefficient; this determination can be presumed free of aerosol effects. Saiedy carried out very careful observations of solar intensity at Ascot in several windows between 790 cm^{-1} and 1202 cm^{-1} using resolution of 2 cm^{-1} . The results, published in Bignell, Saiedy and Sheppard (1963) (hereafter referred to as B.S.S. (1963)), confirmed an overwhelming correlation between absorption and water vapour, with only slight evidence of aerosol extinction. There was some evidence of a temperature effect, but its interpretation was not clear. Dave, Sheppard and Walshaw (1963), working with the same spectrometer as in the present research, observed

emission in three windows near 10μ : the results showed considerable scatter, some of which was attributed to aerosol absorption, with an added tendency for higher absorption in the summer months. Whilst the mean value of Dave at 898 cm^{-1} was 10% higher than that of Saiedy at 901 cm^{-1} , his value at 996.5 cm^{-1} , even under the haziest conditions, was 15 per cent lower than Saiedy's, which is difficult to explain on the grounds of aerosol absorption.

Taking an overall look at the results of the previous work listed above, it was concluded that there were differences which could not be explained by errors of observation. Nor did it seem reasonable on the basis of some rough calculations that aerosol absorption could become significant in the $8 - 20\mu$ region before the visibility had become so poor that the haze could not fail to be noticed. It was felt that the differences were arising rather from the use of an incomplete description of continuum absorption. The aim of the present work was to discover in which respects this description was lacking, rather than merely to measure the absorption coefficient in a previously unexplored region. The latter would only have the doubtful merit of adding another discrepant determination to an already long list without pointing the way to a unified picture.

2.1. Introduction

Earlier work on the atmospheric water vapour continuum cited in Chapter I concentrated mainly on the 8 - 13 μ window, and most workers have used the atmosphere to provide the necessary long path to give sufficient absorption of the solar beam, or, alternatively, sufficient emission to give a precise measurement.

Between 13 and 17 μ , CO₂ absorption precludes the use of these techniques. Beyond 17 μ , whilst relatively free of absorption by other gases, the absorption by water vapour is so strong that under typical conditions very little solar energy reaches sea level, and atmospheric emission almost equals the black body intensity, so that neither technique is applicable at sea level. At the time of the inception of the present work, the only published continuum measurements in the 17 - 20 μ region were those of Anthony (1952) by a solar method from a mountain site. This region of the spectrum offered the best opportunity of obtaining reliable continuum measurements with relatively short paths which could be monitored accurately.

2.2 Design of Experiment

At the outset, two distinct courses of action were possible - either a laboratory study or an open atmospheric experiment. The former, undoubtedly the more attractive, presented several problems whose solutions were not immediately apparent. Moreover, the then simple picture of continuum absorption outlined in Chapter I suggested that

the open atmosphere experiment would provide the required answers. A major consideration supporting this view was that a horizontal path could be used, avoiding much uncertainty introduced by the slant atmospheric paths used by most previous workers. The decision was therefore made in favour of the horizontal path experiment.

The path length required was determined from the following considerations. The transmittance T of a path containing $m \text{ g cm}^{-2}$ of precipitable water is given by $T = e^{-km}$ where k is the mass absorption coefficient, so that $k = -\frac{1}{m} \log_e T$. The fractional error in the determination of k resulting from errors in m and T is then given by

$$\frac{\Delta k}{k} = -\frac{1}{\log_e T} \frac{\Delta T}{T} + \frac{\Delta m}{m} \quad 2.1$$

The transmittance is measured as the ratio of two signals S_1 and S_2 , i.e. $T = \frac{S_1}{S_2}$, so that for random errors of equal magnitude in S_1 and S_2 ,

$\frac{\Delta T}{T} = \sqrt{2} \frac{\Delta S_2}{S_2} \frac{1+T}{T}$. We then see from Eq 2.1 that to minimise $\frac{\Delta k}{k}$ we must minimise $\frac{1+T}{T \log_e T}$. This gives $T \approx 0.28$ or $k_m = 1.3$.

The range of k to be measured (1 to $4 \text{ g}^{-1} \text{ cm}^2$) and the natural variability of atmospheric water vapour density (say 5 to 15 g m^{-3}) mean that some compromise must be reached. Path lengths of 200 m and 400 m enable near optimum conditions to be obtained for the whole range of absorption coefficient expected.

To get some idea of the accuracy possible, we see from Eq 1

that at best (with $T = 0.28$) $\frac{\Delta R}{R} = 3 \Delta T$, neglecting any error in m . An optimistic value for ΔT would be 0.01, implying a signal to noise ratio of the order of 100 : 1, which is a fairly realistic target to aim for. We would then be able to measure k to 3 per cent.

A rough order of magnitude calculation was made to see if a signal to noise ratio of 100:1 was feasible with the available equipment when used at a resolution of 1 to 2 cm^{-1} . Using a Nernst filament at 1500°K and Golay detector, it was confirmed that there would be some margin for imperfect optics even after allowing for reasonable losses in other sections of the path.

2.3. Apparatus

The equipment to be described was set up at the Imperial College Field Station at Ascot, about 40 km WSW of central London. This site gives reasonable freedom from the excessive pollution experienced nearer London.

2.3.1 Source

A B.T.H. Nernst filament of length 2.5 cm and 0.25 cm diameter was supplied from a constant voltage transformer through series barretter tubes for stabilisation. The Nernst was operated in a shield to minimise the effects of draughts.

2.3.2 Optical System

Fig. 2.1 and Plate 1 show the external optical system. The

Plate 1. External optical system at Ascot.

Fig 2.1. External Optical System at Ascot

- (a) The Nernst filament N is shielded from draughts and is mounted just outside the focus of paraboloid M_1 ($f = 305$ cm, diameter 63 cm) so as to give an image on M_2 , which is a spherical mirror of either 200 m radius, 50 cm diameter, mounted at 200 m distance, or of 100 m radius, 25 cm diameter mounted at 100 m distance. In each case the centre of curvature of M_2 is midway between those of M_1 and M_2 , so that M_1 is imaged on M_3 . All mirrors are front - surface aluminised. The chopper (C) frequency is 10 c/s.

- (b) Layout of long path optics.

M_1 , M_{2a} , M_{2b} are mounted in a straight line. M_{2a} is supported on a tall kinematic mount to facilitate its removal from the beam to M_{2b} .

parabolic $f/5$ projector mirror M_1 focussed an image of the Nernst on M_2 , one of two spherical mirrors located 100 m or 200 m away over a ploughed field. M_2 was adjusted so that its centre of curvature lay midway between M_1 and M_3 , the latter being identical to M_1 . All radiation leaving M_1 therefore returned to M_3 . Matching into the $f/10$ spectrometer was then achieved by M_5 and M_6 , M_4 turning the beam through 90° . All concave mirrors were used axially, so that a very sharp image was formed on the entrance slit.

For reasons which will become apparent in § 2.4^{5.2, p. 26,}~~4.1~~ the geometry of the 200 m and 400 m paths had to be as similar as possible. This was achieved by mounting M_1 , M_{2a} and M_{2b} in a straight line; M_{2a} was supported on a tall kinematic mount so that when not required it could be removed bodily from the beam, allowing the beam to carry on to M_{2b} . Focussing was effected by a micrometer adjustment on the Nernst mounting, and by a slide mechanism on the modified gun mounting used to support M_3 . Adjustment of M_{2a} and M_{2b} proved to be very critical and was facilitated by three small plane mirrors mounted around the circumference of M_3 , aligned with their normals passing near M_{2a} and M_{2b} ; with the latter incorrectly adjusted, one of the three plane mirrors could be seen brightly illuminated when viewed from M_2 , and the appropriate correction could readily be made. In this way, M_1 could be imaged on M_3 to within 1 cm.

2.3.3 Spectrometer

p. 18

The spectrometer shown in Fig 2.2 was basically that designed

Fig 2.2. Arrangement of spectrometer.

- D Golay detector
- F_1 Terylene filter, 12μ thick
- F_2 Double reststrahlen magnesium oxide filter for $\lambda > 13\mu$,
or aluminised mirrors for $\lambda < 13\mu$.
- F_3 Bloomed indium antimonide filter
- G Merton replica grating $15\text{cm} \times 15\text{cm}$, 473 lines/cm
- M_1 Ebert mirror (2 identical spherical mirrors)
- M_2 Flat mirror
- M_3 Condenser mirror
- S_1 Entrance slit (outside wall of laboratory)
- S_2 Exit slit

by Goody (1957) for emission studies. It was equipped for this experiment with a 15 cm square Merton replica grating of 473 lines/cm blazed for 20μ in the first order. Using $f/10$ Ebert optics of focal length 150 cm, large slits 2.5 cm long and up to 0.4 cm wide gave good energy gathering power whilst retaining high resolution. A kinematic mount for a reststrahlen magnesium oxide filter was placed just after the exit slit, and the condenser mirror gave an 8 to 1 reduction in order to accommodate the image on the sensitive area (0.3 cm diameter) of the Unicam Golay detector. Spectral scanning at various speeds was effected by a mains - driven synchronous motor and change gears, with provision for manual operation.

2.3.4 Detector System

The standard Unicam Golay detector system was employed using 10 c/s chopping frequency. The signal was recorded on a 15 mV Honeywell Brown potentiometer recorder giving a chart width of 28 cm. All power supplies were derived from a constant voltage transformer. The overall time constant of the system was about 1 sec, and although this could have been increased to give a less noisy record, it was considered preferable to retain the 'lively' record and perform the smoothing where necessary by eye.

The chopper unit, mounted outside the laboratory, was shielded from daylight to prevent fluctuation of the zero reading which otherwise occurred when the illumination varied. Even so, significant fluctuations of both the zero reading and the sensitivity of the system

Fig 2.3. Filter characteristics.

- a Cut-on for bloomed indium antimonide. Beyond 8μ the transmittance decreases slowly to about 50% at 20μ .
- b Transmittance of terylene film, 12μ thick.
- c Cut-on for double reststrahlen magnesium oxide. Beyond 14μ the transmittance remains at about 60%.

Fig 2.4. Location of windows.

- A Spectrum over a horizontal path of 200m, with 0.250 g cm^{-2} of water vapour in the path.
- B Solar spectrum ; $\sim 3 \text{ g cm}^{-2}$ water vapour in slant path.

necessitated frequent zero and calibration signals.

2.3.5. Filters

Separation of orders was achieved with a variety of filters, whose characteristics are shown in Fig 2.3. A permanent bloomed indium antimonide filter mounted over the Gelay window removed all radiation of $\lambda < 7.3\mu$. A double reststrahlen magnesium oxide filter, shown in Plate 2, was mounted kinematically behind the exit slit cutting off nearly all radiation of $\lambda < 13.3\mu$. This filter could be replaced by an identically mounted pair of aluminised mirrors when working in the $7 - 13\mu$ region. A terylene filter mounted after the exit slit was used for a special purpose described in § 2.^{5.2}~~4.3~~ (p.24)

2.4. Performance of the System

2.4.1. Typical Spectra

Fig 2.4 shows a spectrum over a path of 216 m with 0.250 g cm^{-2} of precipitable water. Much of the fine detail can not be shown. A solar spectrum is also shown for comparison, demonstrating the great opacity of the atmosphere at these wavelengths. The windows selected for measurement are shown by numbers 14 to 20 and are listed in Table 2.4,^{p.40} the numbering continuing a sequence beginning in the $8 - 13\mu$ region.

2.4.2 Calibration

The spectrometer was calibrated by reference to several

Plate 2. Magnesium oxide reststrahlen filter and chopper attenuators.

isolated single lines throughout the spectrum, identified from the solar atlas of Migeotte et al (1956, 1957).

2.4.3. Resolution

The resolution achieved came very close to the theoretical value, as inferred from a comparison of the observed central absorption of a line of known intensity and half-width and that computed on the assumption of a triangular slit function. Typical working resolution ranged from 1.9 cm^{-1} at 17μ to 1.2 cm^{-1} at 21μ , these figures representing the full width of the triangular slit function at half height. It was the practice to work with constant slit width.

2.4.4 Stray radiation

A conclusive test of stray radiation is difficult to realise, apart from broad tests of the separation of different order spectra. The best test is offered by an absorber with a narrow opaque band in a transparent region: if the signal drops to zero in the band, then stray must be absent. A few such tests were possible, e.g. the three opaque terylene bands in the $8 - 10\mu$ region, the 15μ CO_2 Q branch, and a few strong water vapour lines beyond 18μ , which were black under high resolution. No stray was found at any of these points, so it is reasonable to assume that none should occur in the window regions.

However, it is instructive to consider the consequences of stray radiation on the results. Suppose that when the spectrometer is set to observe wavenumber ν_1 , it actually passes in addition

Fig 2.5. Effect of stray radiation.

Extinction for $k=1 \text{ g}^{-1} \text{ cm}^2$ with 10% of stray radiation of $k=0$ and $k=2 \text{ g}^{-1} \text{ cm}^2$.

some stray radiation of wavenumber ν_2 amounting to a fraction τ_2 of that incident on the entrance slit. If the intensities are I_1 and I_2 at the source then after transmission through a path containing $m \text{ g cm}^{-2}$ of absorber having mass absorption coefficients k_1 and k_2 respectively, the apparent transmittance will be given by

$$T = \frac{I_1 e^{-k_1 m} + \tau_2 I_2 e^{-k_2 m}}{I_1 + \tau_2 I_2}$$

With $\frac{\tau_2 I_2}{I_1} \ll 1$ there follows

$$-\log_e T = k_1 m + \frac{\tau_2 I_2}{I_1} [1 - e^{-(k_2 - k_1)m}]$$

and
$$-\frac{d \log_e T}{dm} = k_1 + \frac{\tau_2 I_2}{I_1} (k_2 - k_1) e^{-(k_2 - k_1)m}$$

so that the slope of the $-\log_e T$ vs m plot always decreases with m , regardless of the sign of $k_2 - k_1$. Consequently, when data near $m = 0$ are lacking the best straight line through the observations always has a positive intercept. However, the curvature and intercept resulting from a small proportion (10%) of stray are too small to be detected. Fig 2.5 shows the effect of 10 % stray radiation for $k_2 - k_1 = 1$ and $-1 \text{ g}^{-1} \text{ cm}^2$, with $k_1 = 1 \text{ g}^{-1} \text{ cm}^2$. These points will be referred to again in § 2.8^{h.44} and § 3.5^{3.5, h.61} in the discussion of the results, which exhibit a negative intercept and curvature the other way.

2.4.5 Linearity of the detector system

The linearity of the detecting system was checked periodically

Fig 2.6. Variation of $\frac{S_4}{S_{17}}$, $\frac{S_8}{S_{11}}$ and $\frac{S_{11}}{S_{13}}$ with Nernst current.

by use of a set of high speed chopper attenuators of accurately measured geometrical transmittance. These have been described by Saiedy (1959) and two of them are shown in Plate 2. ^{p. 19} At no time was any significant departure (i.e. 0.5%) from linearity observed over the full range of ^{used} signal/in the experiment.

2.4.6. Stability of the System

An appreciable fluctuation of the overall sensitivity and zero reading of the system was observed. Part at least originated somewhere in the detector system, and it is likely that the long path optics suffered slow drifts. Probably the largest effect was the variation of water vapour in the path. Also to be considered was the possible variation of source output with variation in the power supply and ventilation: the effect of the former and indirectly of the latter was investigated by varying the current supply to the Nernst, and Fig 2.6 shows the results for windows 4 and 17 (and also for windows 8, 11, 13, to be considered in Chapter 3) over a wide range of current - certainly far more than would occur under working conditions. The important point to note is that $\frac{I_4}{I_{17}}$ changes by only 2 % over the whole range.

2.5. Experimental Technique

2.5.1. Choice of method

Examination of the stability of the system indicated that little reliance could be placed on any technique involving the comparison of

signals obtained with time separations greater than a few minutes. This consideration ruled out the commonly adopted procedure of recording complete spectra from which window intensities are read off at the peaks between lines. Instead, it would be necessary to make observations at carefully selected wavelengths with the grating stationary, interpolating frequent calibration signals and zero levels.

An absolute method of measuring extinction involves in principle measuring the intensity before and after passing through the absorbing path. This would be possible if, for example, we could perfect a long and a short path giving identical illumination of the aperture of the spectrometer and with identical reflection losses. In such a large apparatus, exposed at times to unfavourable conditions, these demands were ^{si}considered unattainable. Recourse to a relative method was indicated, in which geometrical effects were eliminated by comparing signals at two wavelengths.

Consider the ratio $y_{i,r} = \frac{S_i}{S_r}$ of the two signals s_i and s_r in two windows i and r . Let S_i and S_r be the signals which would be obtained if there were no absorption in the atmospheric path. Then

$$y_{i,r} = \frac{S_i e^{-\beta_i l}}{S_r e^{-\beta_r l}} = S_{i,r} e^{-(\beta_i - \beta_r)l} = S_{i,r} e^{-\beta_{i,r} l} \quad (2.2)$$

where β is the extinction coefficient per unit length of path and l is the path length.

By observing $y_{i,r}$ for two values of l , assuming constant $S_{i,r}$, we can determine β_{i-r} . A very short path suggests itself for one value of l , whilst either of the long paths provide the other value. This method was in fact used in a preliminary set of observations, but for reasons which will be given in § 2.5.2 this was later changed so that the 400 m and 200 m paths were used to provide the two required values.

2.5.2. Measurement of β_{17-4} .

In order to establish an absolute value for β_i it is necessary to choose a window r for which β_r is known. Saiedy has measured continuum absorption coefficients in the $8 - 12\mu$ region using the sun as source, and the results are published in B.S.S. (1963). In this region the absorption coefficients are an order of magnitude smaller than those between 17 and 20μ , so that even if k_r were not known, little error would result from assuming $\beta_r = 0$ in Eq. 2 above.

One difficulty in choosing a reference window near 10μ was that it was then impossible to observe the $17 - 20\mu$ region without changing the filtering arrangements, thus risking disturbance of the set-up. However, a fortuitous combination of circumstances suggested a very simple solution. It was noticed that terylene film 12μ thick has an opaque band at a frequency exactly double that of window 17 (559.4 cm^{-1}). It was therefore a straightforward matter to compare the signal in window 17 with that at $\nu = 1118.8 \text{ cm}^{-1}$ (referred to as window 4 hereafter) by setting the grating for window 17 in the first

Fig 2.7. Typical run for window 17.

order, making use of the second-order spectrum^{of}/window 4. Signals were obtained with and without the terylene filter, an auxiliary sector attenuator of transmittance K being used in the latter case to bring the signals to approximate equality. A typical run is illustrated in Fig 2.7. Let the ratio of these two signals be y . with the terylene filter, only the first-order spectrum of window 17 was transmitted; without it the much more intense second-order spectrum of window 4 was also transmitted. Higher-order spectra were eliminated by the indium antimonide filter.

Let

F_i be the transmittance of the terylene filter in window i ;

S_i , the signal which would be obtained in window i in the absence of absorption along the atmospheric path;

β_i , the extinction coefficient per unit length in window i ; and

l , the path length (l_2 and l_1 are used to denote different path lengths).

Then Lambert's law gives

$$y = \frac{F_{17} S_{17} e^{-\beta_{17} l} + F_4 S_4 e^{-\beta_4 l}}{K [S_{17} e^{-\beta_{17} l} + S_4 e^{-\beta_4 l}]} \quad 2.3$$

For terylene film of 12μ thickness, $F_4 = 0$ and Eq. 2.3 can be written

$$\beta_{17-4} = \log_e S_{17,4} + \log_e \left(\frac{F_{17}}{Ky} - 1 \right) \quad 2.4$$

where $S_{17,4} = S_{17}/S_4$. Thus, given F_{17} , observations of y for two values of l provide β_{17-4} provided $S_{17,4}$ is the same for both determinations of y . We then have

$$\beta_{17-4} L = \log_e \left(\frac{\frac{F_{17}}{K y_2} - 1}{\frac{F_{17}}{K y_1} - 1} \right) = \log_e \frac{y_2}{y_1} \left(\frac{1 - \frac{K}{F_{17}} y_2}{1 - \frac{K}{F_{17}} y_1} \right) \quad 2.5$$

where $L = l_2 - l_1$

With $F_{17} = 0.55$, $K = 0.069$ and $y \sim 1$, the computation of β_{17-4} from Eq 2.5 is very insensitive to the value of $\frac{K}{F_{17}}$, a 20 % error giving less than 1 % error in β_{17-4} . The value of F_{17} was in fact measured for every pair of observations of y by taking the ratio of the signals obtained with and without the filter, the second-order spectrum of Window 4 being eliminated in both by a second fixed terylene filter.

The condition of constancy of $S_{17,4}$ requires care for achievement. Its value depends on the relative magnitude in windows 4 and 17 of (i) the intensity I of radiation emitted by the source; (ii) the product, R , of the reflectances of all the mirrors in the system; (iii) the response of the detecting system, including the grating and filters.

Regarding (i), it was found that I_4/I_{17} was greater by 5 to 10 % at the center than at the edge of the filament. It was therefore necessary to focus and align the image very carefully to ensure that the same part of the source was used in each pair of observations. The variation of I_4/I_{17} with filament temperature was less than 2% over the range $1500^\circ - 2000^\circ\text{K}$, which was certainly much greater than

the temperature variations induced by draughts, (see ^{11.21} § 2.4.6).

Regarding (ii) there was some slight doubt about the constancy of the reflectance of the mirrors with change in humidity, owing to a possible growth of hygroscopic nuclei on the mirror surfaces. Evidence was difficult to obtain, but tests were possible on occasions with near-saturation, when a heater near M_2 could be switched on to lower the relative humidity quickly (all other mirrors were kept in heated enclosures). No significant change of $\gamma_{17,4}$ was observed. The effect was however of no consequence since each pair of observations was made in the minimum interval (about 5 min) to effect the necessary changes, so as to keep changes in humidity to a minimum. It was necessary moreover to assume that R_{17}/R_4 was the same at any one time for each of the mirrors used for M_2 ; which is reasonable because the mirrors were aluminized at the same time and were subsequently kept under similar conditions.

Regarding (iii) the transmission of the terylene filter was found to be uniform over its whole surface, but that of the indium antimonide was somewhat nonuniform, possibly because of variations in the antireflection coating. The efficiency of the grating was also non-uniform and it was therefore essential to ensure identity of position and distribution of illumination in the beams derived from the external optical systems - by accurate alignment and focu^sing, and the introduction of a stop on M_6 to cover the images of obstructions in the beam.

In the course of the experiment, several changes were made in order to improve the reproducibility of $S_{17,4}$. The experimental method and optical layout described in § 2.5.1^{n.22} and § 2.3.2^{n.15} was the final form. It superseded a version in which it was possible to obtain a short path of 10 m as well as paths of 200 and 400 m, but this involved the off-axis use of spherical mirrors, giving considerable distortion. In this earlier method, the values of l used for a pair of observations were $l_2 = 10$ m and $l_1 = 200$ or 400 m. Some systematic error was, however, possible: firstly, from the use of four mirrors not common to both beams (though with the same total number of reflections), with the possibility that different relative reflectances R_{17}/R_4 were involved; secondly, from uncertainty in fulfilling condition (iii) above owing to distortion and different beam geometry. These uncertainties were much reduced in the final method since only one mirror was not common to both beams, and with axial optics it was possible to ensure that both beams were identical.

There was reasonable agreement, however, between the results derived from both methods, indicating that the ^S uncertainties present in the earlier method were not serious. It is probable that $S_{17,4}$ was reproduced to better than 1% in each pair of observations in the final method. Support for this view is afforded by the fact that noticeable deliberate misalignments produced no systematic change in y .

2.5.3 Measurement of β_{14-4}

Employing first-order spectra in both cases, the ratio $\alpha_{14,4}$ ($= \frac{S_{14}}{S_4}$) of the signals in windows 14 and 4 was measured. We then have

$$\alpha_{14,4} = \frac{S_{14}}{S_4} \exp -(\beta_{14} - \beta_4) l .$$

Then from observations over two paths, subject to the experimental precautions stated previously, a value of $\beta_{14} - \beta_4$ may be found.

2.5.4 Measurement of $\beta_i - \beta_4$

A double reststrahlen magnesium oxide filter was mounted kinematically behind the exit slit, cutting off almost entirely all radiation of $\lambda < 13\mu$. This filter was readily interchangeable with a pair of identically mounted aluminized mirrors, used for $\lambda < 13\mu$. The ratios $\alpha_{i,17}$ of the signals for each of the Windows 15, 16, 18, 19 and 20 to that for Window 17 were determined for two path lengths, and β_{i-17} may be found as in § 2.5.3. With simultaneous measurements of β_{17-4} we finally obtain β_{i-4} .

2.5.5 Measurement of Water Vapour

The depth of precipitable water in the path was obtained from readings of an Assmann psychrometer exposed at the mean height (~ 1 m) of the beam, occasional checks being made with a second psychrometer for uniformity along the path.

Fig 2-8. CO₂ absorption 10-21 μ . Circled points: observed transmission of a 43-cm cell of pure CO₂ at 1000mb. Continuous lines: calculated transmission, assuming Lorentz wings (neglecting minor bands, whose positions and strengths (g^{-1}cm) are shown on the abscissa) The positions of windows 6-20 are shown.

2.5.6. CO₂ ABSORPTION IN THE REGION 1300 - 478 cm⁻¹.

Before discussing the results on the water-vapor continuum out to 21μ , it is appropriate to consider the possibility of this continuum being overlaid by that from carbon dioxide and aerosol. Regarding the former, a 43-cm cell of pure CO₂, with windows of polythene, was inserted in the beam, giving a "depth" of 0.082 g cm⁻², the equivalent of 1.4 km of air at sea level. The transmissions on either side of the ν_2 band are shown in Fig 2.8, and are compared with those to be expected if the wings of the CO₂ lines have Lorentz shape, taking the ν_2 band intensity to be 1.22×10^5 g⁻¹ cm and the mean line half-width 0.064 cm⁻¹ at 1 atm and 298°K (Kaplan and Eggers, 1956). We see that the observed absorption is considerably less than from Lorentz wings until quite close to the band center, the absorption due to line centers of the weaker bands indicated in Fig. 2.8 being first apparent. Kaplan (1953) and Benedict (1955) have argued for a decrease faster than Lorentz in the CO₂ wings, and they suggest a wing profile which is consistent with the negligible absorption observed in the present work outside the range 790 to 560 cm⁻¹. Only Windows 14, 15 and 16 were found to be affected by CO₂ absorption, this being attributed to nearby lines, and is therefore analyzed accordingly.

2.5.7 EXTINCTION BY AEROSOL.

During the experiment, it was suspected that the extinction was greater under very hazy conditions, and it was therefore necessary to allow for aerosol attenuation in the analysis. No direct measurements

Fig 2-9. Typical aerosol distributions.

A Turbulent marine air.

B' Coastal air.

C Continental air.

(From Deirmendjian, Ann. Geophys., 15, p. 222).

of particle concentration and size were made, but local visibility data were available and it is of interest to inquire to what extent these could be used to infer the opacity due to aerosol in the 10 - 20 μ region. Deirmendjian (1959, 1960) has computed extinction coefficients from 0.625 to 14 μ for a number of realistic aerosol distributions, illustrated in Fig 2.9. Values for 0.625, 8.6, 10.0, 12.0 and 14.0 μ are reproduced in Table 2.1.

Table 2.1

Extinction coefficient for different aerosol distributions

HAZE MODEL	$\beta_{0.625\mu}$	$\frac{\beta_{0.625}}{\beta_{8.6}}$	$\frac{\beta_{0.625}}{\beta_{10.0}}$	$\frac{\beta_{0.625}}{\beta_{12.0}}$	$\frac{\beta_{0.625}}{\beta_{14.0}}$
A (2 μ)	0.245	23	29	6.2	6.7
B (2 μ)	0.127	38	42	14	-
C (2 μ)	0.0822	33	38	12	7.6
A (4.48 μ)	0.328	4.3	11	4.5	3.7
B (4.48 μ)	0.136	16	27	11	-
C (4.48 μ)	0.0864	19	29	10	6.3

The tabulated quantities are the computed values of β in the expression $T = e^{-\beta L}$ where T is the transmittance for a path length L km. The haze models are illustrated in Fig 2.9; the number in brackets is the radius of the largest particle. For absorption and scattering by water spheres. (After Deirmendjian (1960)).

It can be seen that the ratios of the extinction coefficient at 0.625 μ to those at 10.0, 12.0, 14.0 μ are approximately 30, 11 and 7 respectively, for all distributions except A (4.48 μ) (which has

many large particles), suggesting that the distribution is not very important and that the extinction in the region $8 - 14 \mu$ may be taken to be proportional to that at 0.625μ .

The above computations may be extended to 20μ using a series expansion of the Mie theory for small droplets given by Penndorf (1952) (small droplets in this context would be less than about 2μ radius).

The extinction efficiencies K_s and K_a for scattering and absorption (defined as the ratio of the extinction cross-section to the geometrical area) are given by

$$K_s = \frac{8}{3} \alpha^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \left\{ 1 + \frac{6}{5|m^2 + 2|^2} \left[(n^2 + k^2)^2 - 4 \right] \alpha^2 - \frac{8nk}{|m^2 + 2|^2} \alpha^3 \right\} \quad 2.6$$

$$K_a = \frac{24nk\alpha}{|m^2 + 2|^2} + \frac{4nk\alpha^3}{15} \left\{ 1 + \frac{25}{|2m^2 + 3|^2} + \frac{18}{|m^2 + 2|^4} \left[7(n^2 + k^2)^2 + 4(n^2 - k^2 - 5) \right] \right\} \quad 2.7$$

where $m = n - ik$ = complex refractive index

$$\alpha = \frac{2\pi r}{\lambda} \quad \text{with } r = \text{radius of droplet and } \lambda = \text{wavelength.}$$

The values calculated from these formulae have been found by Penndorf to agree with those computed from the full theory for $\alpha < 0.8$, $k \leq 1$ and $1.25 < n < 1.75$.

Using the absorption coefficients given by Plyler and Acquista (1954) and the refractive index data from Dorsey (1940, p.185)

for 18 and 20 μ , K_a and K_s were calculated for selected wavelengths in the 8 - 20 μ region, giving some overlap with the computations of Deirmendjian for comparison. The results are given in Table 2.2.

Table 2.2

Absorption and scattering efficiencies for small droplets

$\lambda(\mu)$	n	k	K_a	K_s/K_a	$\frac{K_a(\lambda)}{K_a(14\mu)}$
8.94	1.27	0.050	.0819 R + .0125 R ³	.242 R ³	.22
10.0	1.212	0.061	.0915 R + .0089 R ³	.092 R ³	.25 (.25)
11.0	1.190	0.13	.182 R + .0133 R ³	.0267 R ³	.50
12.0	1.165	0.2058	.269 R + .0150 R ³	.0144 R ³	.73 (.81)
14.0	1.309	0.3582	.367 R + .0289 R ³	.0261 R ³	1
18.0	1.43	0.48	.349 R + .0238 R ³	.0165 R ³	.95
20.0	1.480	0.360	.228 R + .0130 R ³	.0150 R ³	.62

K_a and K_s are the ratios of the absorption and scattering cross-sections to the geometrical area, computed from Eqs. 2.7 and 2.6. n and k are the real and imaginary parts of the complex refractive index. Valid for $R < 2$ where R is the droplet radius expressed in microns. The values in brackets for 10.0 and 12.0 μ are taken from Deirmendjian (1960).

The value of n for 10, 11, and 12 μ is just outside the range giving high accuracy, but the error should not exceed 20%. In all cases the fraction of the total extinction attributable to scattering is small for droplets up to 1μ radius, and decreases as the cube of the

radius, so that scattering is entirely negligible for all except the largest droplets. We note that $\frac{K_a(10)}{K_a(14)}$ and $\frac{K_a(12)}{K_a(14)}$ calculated from Eq. 2.7 are in reasonable agreement with Deirmendjians values of $\frac{\beta(10)}{\beta(14)}$ and $\frac{\beta(12)}{\beta(14)}$ respectively. The computations of Table 2.2 may now be used with reasonable confidence to extend Table 2.1 to 20μ , using the normalising wavelength of 14μ , with the result that $K_{18\mu} = 0.2 K_{0.625\mu}$ and $K_{20\mu} = 0.09 K_{0.625\mu}$.

The final step in the argument is to assume that the visual extinction coefficient β_{vis} is proportional to $\beta_{0.625\mu}$. Whilst this is not likely to be very accurate, we are only concerned here with a factor of 2 or so. We may then write

$$\beta_{a,i} = D_i \beta_{vis} \quad \text{where } \beta_{a,i} = \text{aerosol extinction coefficient in window } i$$

$$D_i = \text{constant}$$

For the purpose of the discussion (§ 2.5.1, p.37) of observations in windows 17 and 19 relative to window 4, we note from the above that if we assume $\beta_{vis} = \beta_{0.625\mu}$, then $D_{19} = 0.09$, $D_{17} = 0.13$ and $D_4 = 0.05$.

β_{vis} was estimated from the visual range V by $\beta_{vis} = \frac{3.9}{V}$ (Middleton 1952, p.105). Owing to the difficulty of estimating visual ranges V_A greater than 2 km on the site at Ascot, the data V_L from London Airport, 16 km to the north-east, were used on these occasions (the great majority, in fact) and adjusted if necessary for any

difference of relative humidity between the two sites by the working expression

$$V_A = V_L \frac{100 - H_L}{100 - H_A}$$

where H_L , H_A are the relative humidities (%) at London Airport and Ascot respectively.

This procedure is satisfactory if the nucleus spectrum is the same at the two sites, any difference in visual range then being a function of the respective relative humidities. The form of the above rough correction was suggested by an examination of the theoretical and observed variation of visual range with relative humidity (Wright, 1940).

Some idea of the order of magnitude of aerosol absorption to be expected at 18μ under hazy conditions may readily be calculated. Suppose $V = 5$ km. Then $\beta_{18\mu} = 0.13 \times \frac{3.9}{5}$ per km = 0.10 per km. Over a 400 m path, the transmittance would then be $e^{-0.4 \times 0.10} = 0.960$, or 4% absorption. The absorption due to water vapour, on the other hand, would be between 30% and 50%, depending on the humidity, indicating that aerosol absorption is relatively unimportant.

2.6. Results

2.6.1. Windows 17 and 19

The regression equation relating the observed extinction to vapour content and visibility ($\S$ 2.5.7) may be written

Fig 2.10. Observed extinction coefficients for windows 17 and 19 as a function of water vapour in the path.

$$\beta_{i-4} = k_{i-4} \frac{m}{L} + \frac{3.9}{V} D_{i-4} , \quad 2.8$$

where k is the mass absorption coefficient, $i = 17$ or 19 , m is the mass of water vapour per cm^2 in the path and $L = \ell_2 - \ell_1$ (see § 2.5.2). ^{1.28}

It will be assumed that the variation of the half-width α and intensity S of absorption lines with temperature and pressure may be written

$$\begin{aligned} \alpha(p, T) &= \alpha(p_0, T_0) \frac{p}{p_0} \left(\frac{T_0}{T} \right)^{\frac{1}{2}} , \\ S(T) &= S(T_0) [1 + \epsilon(T - T_0)] , \end{aligned}$$

where $P = p + ae$, p and e being the partial pressures of dry air and water vapour, respectively, a is the ratio of self- to air-broadening, and p_0 , T_0 are standard values of pressure (1000 mb) and temperature (0°C).

Then Eq. 2.8 can be written, to good approximation;

$$\frac{L \beta_{i-4}}{m_p} \left(\frac{T}{T_0} \right)^{\frac{1}{2}} = k_{i-4}(p_0, T_0) \left[1 + \epsilon(T - T_0) + \frac{ae}{p} \right] + \frac{3.9 D_{i-4} L}{V m_p} , \quad 2.9$$

where $m_p = m \frac{p}{p_0}$.

Figure 2.10 shows observations of $L \beta_{i-4} \left(\frac{T}{T_0} \right)^{\frac{1}{2}}$ as a function of m_p for windows 17 and 19. Each point is the result of a pair of observations; the open circles result from $\ell_2 = 414$ m, $\ell_1 = 216$ m; the full circles from $\ell_2 = 414$ m, $\ell_1 = 10$ m. The data are tabulated in Appendix 2.1. ^{1.94} A strong correlation is evident, but the

observations for each window fall distinctly into two groups according as $L = 400$ or 200 m, and the best straight lines through each set of points have significant negative intercepts. For both windows the extinction is apparently greater at a given value of m_p for the shorter path for which the vapour density must be double that on the longer path, so that self-broadening suggests itself as an explanation. However, points of low m_p on all lines were obtained under cold, dry conditions and those of high m_p under warm, humid conditions, so that it is equally possible that a positive temperature dependence of absorption is partly or wholly responsible for the difference in extinction coefficient. A sufficient number of observations ranging as widely as possible over these variables was therefore necessary to discriminate between these effects by multiple regression analysis.

With 224 sets of observations for window 17, and 71 for window 19, such an analysis was possible, and the results are given in Table 2.3. ^(p.38) For both windows it appears that ϵ is not significantly different from zero.

The correlations with aerosol are weak but significant, and the observed values of $D_{17} - 4$ and $D_{19} - 4$, 0.02 and 0.03, respectively, may be compared with 0.06 and 0.04 expected from the reasoning of ^{p.34} 2.5.7; better agreement could hardly be expected in view of the uncertainties involved.

The correlation with vapour pressure is highly significant. The values of 26 and 38 for a for windows 17

and 19, respectively, are remarkably high compared with the figure between 5 and 10 which has been found for the central parts of lines (Palmer 1960); Benedict has suggested, however, that the wings are subject to greater self-broadening than are line centres. Although only about half of the total variance can be accounted for, and this almost entirely by the correlation with vapour pressure, we have fair confidence in ascribing the negative intercepts to self-broadening. If this inference is verified it will be of the utmost importance in the analysis of remote radiation measurements which involve correction for the water-vapour continuum.

Table 2.3

Results of the regression analysis for Windows 17 and 19

Window i	λ (μ)	ν (cm^{-1})	$k_{i-4}(p_0, e_0, T_0)$ ($\text{g}^{-1} \text{cm}^2$)	a	ϵ ($^{\circ}\text{C}^{-1}$)	D_{i-4}	No. of obs.
17	17.88	559.4	1.22 ± 0.13	26 ± 4	0.0006 ± 0.001	0.022 ± 0.005	224
19	20.12	497.0	2.09 ± 0.16	38 ± 6	-0.001 ± 0.001	0.034 ± 0.008	71

Results of a least squares fit of the observations to the relation

$$k_{i-4}(p, e, T) = k_{i-4}(p_0, e_0, T_0) \left[\frac{p+ae}{p_0} \right] [1 + \epsilon(T-T_0)]$$

where p , e are the partial pressures of dry air and water vapour, respectively ($p_0 = 1000 \text{ mb}$, $e_0 = 0 \text{ mb}$), and $T_0 = 0^{\circ}\text{C}$. D_{i-4} represents the aerosol contribution (see § 2.5.7).

~~p.34~~

2.6.2 Windows 18 and 20

With insufficient observations to permit a multiple-regression analysis, it seems reasonable in the light of the

Fig 2-11. Absorption coefficients in windows 18 and 20 as a function of vapour pressure.

Fig 2.12. Observed extinction coefficients for windows 14, 15 and 16.

Full circles: 400m path. Open circles: 200m path. Points denoted by 'C' represent the estimated CO_2 contribution, from measurements with a cell of CO_2

results for Windows 17 and 19 to assume that the temperature and aerosol terms may be ignored in Eq. 2.9. Plots of k_{i-4} ($= \frac{\beta_{i-4}}{m_p}$) against vapour pressure e are shown in Fig. 2.11, where a tendency for k_{i-4} to increase with e is again apparent. For neither window is the sample large enough to allocate a value of a , though for window 18 it is of the order of 30. ^{p.19} Observational data are tabulated in Appendix 2.2.

Mean values of k_{18} and k_{20} corresponding to the mean vapour pressure of 15 mb are given in Table 2.4 ^{p.40} with corresponding values for Windows 17 and 19 for comparison. Use has been made here of the value $k_4 = 0.08 \text{ g}^{-1} \text{ cm}^2$, interpolated from Saiedy (B.S.S., 1963).

2.6.3. Windows 14, 15 and 16

^{p.30} CO_2 absorbs significantly in these windows (see Fig. 2.8), and Eq. 2.9 must now be written (neglecting aerosol and temperature terms)

$$\beta_{i-4} = R_{i-4}(\mu_0) \frac{m_p}{L} \left[1 + \frac{ae}{\mu} \right] + C_i,$$

where C_i is the CO_2 contribution in Window i ($C_4 = 0$). Figures 2.12 (a) and (b) show $\beta_{i-4}L$ against m_p for Windows 16 and 15. We see that the best straight lines do not intercept at the values C_i inferred by scaling the laboratory CO_2 absorption measurements ($\S$ 2.5.6) ^{p.30} to the mass in the horizontal path (regular band absorption assumed). Indeed, graphs of $\beta_{i-4} - C_i$ against m_p for these windows would have identical features to those for Windows 17 and 19 (Fig. 2.10) ^{p.36} discussed in $\S$ 2.6.1, ^{p.37}

and it seems likely that the interpretation would be the same. Mean values of k_i , corresponding to the mean vapour pressure of 15 mb, are given in Table 2.4, assuming $k_{14} = 0.08 \text{ g}^{-1} \text{ cm}^2$.

Table 2.4

Details of windows measured and observed absorption coefficients

Window, i	λ (μ)	ν (cm^{-1})	RESOLUTION (cm^{-1})	$k_i(\mu_0, e)$ $\text{g}^{-1} \text{cm}^2$ *	$\Delta k_i(\mu_0, T_0)$ $\text{g}^{-1} \text{cm}^2$	No. of obs.
4	8.94	1118.8	3.5	0.08 *	0	...
14	13.96	716	2.8	0.6 ± 0.2	0	131
15	16.38	610.5	2.2	0.8 ± 0.1	0.13, +0.7	15
16	17.02	587.4	1.9	1.4 ± 0.1	0.42, +1.3	15
17	17.88	559.4	1.7	1.7 ± 0.1	0.23, +1.0	224
18	18.83	531.2	1.6	1.8 ± 0.1	0.44, +1.1	15
19	20.12	497.0	1.3	3.0 ± 0.1	0.78, +1.2	71
20	20.88	478.9	1.2	3.6 ± 0.1	1.3, +1.7	6

$k_i(p_0, e)$ is the mass absorption coefficient for partial air pressure of 1000 mb and water vapour pressure of 15 mb. $\Delta k_i(p_0, T_0)$ is the contribution to k_i from wings of lines within 10 cm^{-1} computed for $p_0 = 1000 \text{ mb}$ and $T_0 = 14^\circ \text{C}$; the computed temperature coefficient ($\% ^\circ \text{C}^{-1}$) of Δk_i is also shown.

* By interpolation from Saiedy (Bignell, Saiedy and Sheppard, 1963).

(1.39)

Figure 2.12(c) shows the observations for Window 14; in this case absorption by CO_2 is much greater and the scatter is increased by the diurnal and daily variations in the concentration of atmospheric CO_2 . Only a rough estimate of k_{14-4} may be obtained

from the slope of the regression line, and the value of k_{14} is entered in Table 2.4, assuming $k_4 = 0.08 \text{ g}^{-1} \text{ cm}^2$. Observational data for windows 14, 15 and 16 are tabulated in Appendices 2.1 and 2.2.

All results are collected in Table 2.4, and in so far as a vapour pressure dependence has been inferred, they correspond to the mean pressure of the series of observations, i.e. about 15 mb. An estimate of the contribution due to lines within 10 cm^{-1} is included in Table 2.4, computed for the Lorentz line shape (see Chapter 3, § 3.6).

2.7. Discussion .

The only previous work available for comparison with the present results appears to be that of Anthony (1952), Palmer (1957 b) and Yates and Taylor (1960).

Anthony (1952) measured continuum absorption coefficients at 17.6μ and 19.0μ from Table Mountain, California (6000 ft), by a solar method, but the results (0.87 and $0.98 \text{ g}^{-1} \text{ cm}^2$) are not readily comparable with the present work (1.5 and $2.0 \text{ g}^{-1} \text{ cm}^2$) since the circumstances of the observations were not reported. However, it is reasonable to assume that the partial water vapour pressure at the mountain station would not have been higher than about 10 mb, so that if the self-broadening effect inferred from the present work is correct, then one would indeed expect Anthony's results to be lower, though the self-broadening term would have to be about twice as large

as that found in ^{p.37} § 2.6.1 to account for the discrepancy noted above.

Palmer (1957 b,c) carried out an extensive laboratory experiment in a multiple traversal cell 33 m long, giving a total path length of 196 m. He adopted the procedure of recording transmission spectra from 20 - 40 μ for different partial water vapour pressures in the range 0.16 mb to 10 mb, pressure-broadened with nitrogen in the range 0 - 800 mb, at room temperature ($\sim 20^\circ\text{C}$). From the published dimensions of the grating spectrometer (Palmer, 1957a), the calculated resolution at 30, 25 and 20 μ was 2.2, 3.5 and 5.0 cm^{-1} respectively, this being the full width of the triangular slit function at half-height. It is unfortunate that no critical analysis of the results has appeared, so that one is forced to make the best of the published spectra, which undoubtedly lack a great deal of the original detail and in which the thickness of the line represents 2% in transmission. The only window common to Palmer's and the present work is window 20 (478.8 cm^{-1}) in which the resolution achieved by the former (5 cm^{-1}) is very much lower than that used in the latter (1.2 cm^{-1}). Palmer was unable to exclude two rather strong lines at 481.8 cm^{-1} ^{and 476.4 cm^{-1}} , so it is not surprising that his result for the absorption coefficient is rather higher than the value obtained from the present work ($5 \text{ g}^{-1} \text{ cm}^2$ as against $4 \text{ g}^{-1} \text{ cm}^2$).

The full potential of Palmer's work was not realised at the field stage of the present study, but a full analysis became possible in the light of the further work described in Chapter 3,

and this is discussed in § 3.5.1.5.^{p.73}

Yates and Taylor (1960) measured the transmittance over open horizontal atmospheric paths of 0.3, 5.5 and 16.25 km over Chesapeake Bay and another path of 27.7 km at an altitude of about 3 km between Mauna Lao and Mauna Kea in the Hawaiian Islands. They used carbon arc sources and prism spectrometer giving resolution of about 3 cm^{-1} at 10μ . The transmittance of one of the long paths was determined from the ratio of the long path signal to that from the 0.3 km path, allowance for the different beam geometry being made by an independent absolute determination of the transmittance at 0.55μ by a transmissometer. The results from a single run in the $15 - 21 \mu$ region are included in Fig 3.30,^{p.85} where reasonable agreement with the present work is seen. This may, however, be fortuitous, since the general level of scatter in Yates and Taylor's work is very large, exemplified by their observations at 9.1μ and 3.97μ for which several runs were made (see § 3.5.2.3^{p.84} and Fig 3.29^{p.84} for fuller discussion). Whilst some scatter is to be expected on account of aerosol absorption, this can only lead to values greater than the pure water vapour contribution, and it is not clear how to explain those results falling below this level, which has been fairly reliably estimated at $0.06 \text{ g}^{-1} \text{ cm}^2$ for $\lambda = 9.1 \mu$ by Roach and Goody (1958), Vigroux (1959) and Saiedy (B.S.S., (1963)).

2.8 Conclusion

In view of the consequences of a large self-broadened

contribution to the continuum, much attention was devoted to the question of the reality of this effect. Recalling that the inference arose from the interpretation of the negative intercepts in Fig 2.10^{p.36}, an exhaustive investigation was carried out to establish that this was not of instrumental origin, arising for example from the effects of non-linearity, stray radiation, or error in humidity measurement. All these possibilities were finally ruled out: indeed, stray radiation could only have produced a positive intercept (^{p.21} § 2.4.4). Further, independent, evidence of a systematic effect leading to the negative intercepts was afforded by the work of Saiedy (B.S.S., (1963)), who obtained qualitatively the same effect at $\nu = 832 \text{ cm}^{-1}$ and 901 cm^{-1} by a solar method.

Whilst the above analysis suggested that self broadening may account for the observations, the evidence could hardly be regarded as conclusive, and an obligation was felt to confirm (or otherwise) this feature of the results. There appeared to be no alternative to a controlled laboratory experiment if the uncertainties and frustrations of an open atmospheric experiment were to be avoided: an account of the laboratory experiment follows in Chapter 3.

The Laboratory Experiment3.1 Design requirements

The implications of the results of the horizontal path experiment concerning self broadening were considered sufficiently far-reaching to require confirmation from a laboratory experiment in which humidity and temperature could be controlled. The factors considered in the design of this new experiment were as follows:-

- (i) Sufficient path length to cause at least 50 % absorption without resorting to high temperatures or high water vapour partial pressures was essential. This is because the temperature and self broadening effects are uncertain and extrapolation to the conditions more typical of the atmosphere would be unreliable. From § 2.2^{p.14} we see that a path length of about 500 m would be required.
- (ii) The humidity and temperature should be reasonably uniform throughout the path, with provision for accurate measurement. Some means of mixing appeared essential.
- (iii) Aerosol absorption should be kept to a minimum. This did not appear to present any difficulty in principle, since a closed cell could be used, and the relative humidity could be kept low (<60 %) ensuring that hygroscopic nuclei are at least very small.

- (iv) Although facilities for working under reduced pressure would be valuable, it was decided that the programme could be carried out at atmospheric pressure throughout. This would cut down the constructional work enormously.
- (v) The spectral resolution must be at least as good as 1.5 cm^{-1} in the $16 - 20 \mu$ region with 100 : 1 signal to noise ratio. Using a Nernst filament at 1500°K and a Golay cell we saw in § 2.2^{h.15} that this is possible with the available spectrometer.

A multiple reflection cell of the type described by White (1942) was selected as offering the best way of achieving a long path in a small space, which, by use of collimated beams, makes the most economical use of energy. From an energy standpoint, a few transits of a long cell is preferable to many transits of a short cell, because reflection losses may become appreciable in the latter case (about 50% at 20μ for 30 reflections), quite apart from the fact that aberrations and scattering by mirrors cause further loss of energy. On the other hand, a very long cell increases the problems with temperature and humidity control and, moreover, requires larger mirrors to achieve the same aperture ratio. The main consideration in the final design of the cell was the very rapid increase in the cost of mirrors as the diameter surpasses 30 cm. The solution adopted was to build the longest possible cell using 30 cm mirrors, the upper limit being set by the attendant increase in image size,

Fig 3-1. Layout of cell (excluding optics). Not to scale.

A Assmann psychrometers.

C Cooling fins, filled with solid CO_2 when required.

F_1, F_2 Large axial flow fans (45 cm diameter) for circulating air.

F_3, F_4, F_5 Small fans (15 cm diameter) for mixing air.

F_6 Extractor fan for ventilating temperature sensors.

H Heaters.

S Steam generator.

T_1, T_2, T_3, T_4 Nickel resistance thermometers (dry) and thermocouples (wet bulb depression).

W Walls, expanded polystyrene 5 cm thick, with inner seal of .0015 inch polyethylene and outer seal of aluminium foil.

giving image-overlapping; this length turns out to be about 15 m.

3.2. Apparatus

3.2.1. Cell construction

Calculation using manufacturers' data indicated that sufficient heat insulation would be afforded by 2 inch walls of expanded polystyrene, and that sufficient sealing against water vapour diffusion should be provided by an inner lining of polyethylene sheet 0.0015 inch thick. Lack of convenient laboratory space meant that the cell had to be constructed outside the laboratory which housed all the measuring equipment. To provide protection against the weather, the outside of the cell was sealed with metal foil and finally roofed over. The layout of the cell and associated equipment is shown diagrammatically in Fig 3.1.

It was decided that the optical path in the spectrometer and auxiliary optics need not be maintained at the same temperature and humidity as that in the cell, the experimental technique allowing of the elimination of the absorption in the laboratory path. Sealing of the opening between the cell and laboratory was effected with a window of polyethylene 35μ thick.

3.2.2. Temperature and humidity control

To ensure thorough mixing a closed circuit system was considered necessary. The air was extracted from one end of the cell

Fig 3.2. Typical temperature and vapour pressure distributions in the cell (outside values 0°C and 5 mb).

Fig 3.3. Effect of diffusion through walls of cell.

and returned to the other, passing through a heat exchanger on the way. Three small fans at intervals along the cell reinforced the mixing near the temperature sensors. The time taken for one complete circuit of the cell was about 2 minutes. Heaters in the cell and heat exchanger permitted an excess of 40°C over the outside temperature to be maintained; provision for cooling below ambient temperature was included, but the capacity of the heat sink turned out to be inadequate, sufficient only to absorb the heat generated by the circulating fans. Fortunately, it turned out to be unnecessary to work at low temperature.

Water vapour was introduced by boiling a small flask of water with a 700 W immersion heater, situated towards the 'upstream' end of the cell. Diffusion was usually relied upon to restore the humidity to the ambient level, but for runs conducted below ambient humidity a rapid extraction could be effected by cooling the aluminium top-plate of the heat exchanger with dry ice.

The degree of control over both temperature and humidity did not come up to expectation. Gradients of temperature and vapour density were observed, indicating a much greater loss of heat and vapour by diffusion than was expected. Typical distributions along the cell are shown in Fig 3.2, whilst Fig 3.3 shows the decrease of vapour pressure with time after switching off the steam generator. The experimental technique was designed to exploit the latter unforeseen behaviour, and is described in § 3.4.2^{p. 63}. Much better uniformity of temperature ($\pm 1^{\circ}\text{C}$) was later attained by use

of suitably placed additional heaters in the cell.

3.2.3 Temperature and humidity measurement .

With a very large number of temperature measurements envisaged, remote reading thermometers were essential. The choice of technique for humidity measurement needed careful consideration: unquestionably the best method would have been dewpoint hygrometry. However, owing to the lack of a suitable remote reading instrument, this was reluctantly rejected, and the psychrometer method was again adopted.

3.2.3.1. Dry bulb temperature .

Dry bulb temperature was measured with nickel resistance thermometers mounted at four points in the cell (Fig 3.1) ^(p.47) and the wet bulb depression was measured at the same points with constantan-manganin thermocouples connected differentially. Both sensors were fully ventilated with air drawn over them through hoses by an extractor fan in the cell. A diagram of the sensors is shown in Fig 3.4 ^(p.50) and the sensing head is illustrated in Plate 3.

The dry sensor consisted of a 25 ohm coil of 40 S W G annealed nickel wire. This was made by winding the wire on a glass tube 2 cm in diameter and setting it in a very thin film of perspex cement. When dry, the coil was removed from the tube so that it would not be subject to strain effects (earlier coils wound on

Fig 3-4. Electrical temperature sensors.
(actual size)

- N Nickel resistance thermometer.
- D Welded manganin-constantan dry junction, 22 SWG.
- W Manganin-constantan wet junction, 48 SWG, sealed in 22 SWG stainless steel tube, with tissue wick.
- M Manganin wires.
- C Constantan wires.
- P Polyethylene tube.

rigid formers proved very unreliable). After cycling the coils many times between freezing point and 70°C , they were calibrated over the range $0 - 40^{\circ}\text{C}$. They were found to retain their calibration to $\pm 0.02^{\circ}\text{C}$ over a period of a month. It was considered advantageous to be able to read the temperature directly from a decade resistance box in a Wheatstone bridge circuit, and this was readily achieved by adjusting the resistance of the coil so that it increased by $0.100\ \text{ohm}$ per $^{\circ}\text{C}$. No attempt was made to linearise the resistance - temperature characteristic, but by arranging for the indication to be correct at 20°C and 40°C , only a small correction was required at other temperatures ($+ 0.25^{\circ}\text{C}$ at 30°C , $- 0.4^{\circ}\text{C}$ at 10°C). All connections from the nickel coil to the bridge were made with 20 S W G manganin wire; electrical details are given in Fig 3.5. ^{p.51}

3.2.3.2. Wet bulb depression .

Fig 3.4 shows the construction of the thermocouple head. Physically, the exposed surfaces of the dry and wet junctions were of the same dimensions, but the wet junction was made of 48 S W G enamelled wires in order to allow of sealing in 22 S W G stainless steel tube, the latter having the same dimensions as the dry junction. The wet junction was kept moist by a wick of two layers of Kleenex tissue paper rolled tightly round the stainless steel tube, dipping into distilled water supplied through a polyethylene tube from a reservoir. The exposed length of wick leading up to the junction was 2 cm, sufficient to reduce conduction errors to an acceptable level.

Fig. 3.5. Circuit diagram of electrical thermometers.

	Resistance values (ohms)	Function
R ₁	3690	Balance of standardisation circuit
R ₂	20	Damping G ₂
R ₃	1300	} Potential divider for standardisation circuit.
R ₄	3	
R ₅	300	Dropping resistor
R ₆	2.5	} Sensitivity and damping for G ₁ .
R ₇	6.9	
R ₈	300	
R ₉ , R ₁₀ , R ₁₁ ,		To equalise resistance of thermocouple circuits.
R ₁₂		To give mean value of wet bulb depression.
R ₁₃ , R ₁₄ , R ₁₅ , R ₁₆		To make up resistance to 42.000 ohms. at 20°C to obtain digital indication.
R ₁₇	1000	} Wheatstone bridge ratio arms.
R ₁₈	10	
R ₁₉	4000.0	to 4500.0 for temperatures 0 to 50°C.
R ₂₀	20	Damping for G ₃ .
R ₂₁ , R ₂₂ , R ₂₃ , R ₂₄		Nickel resistance thermometers, 25.000 ohms at 20°C.
B ₁		Mallory cell, 4.0 V.
B ₂		Weston standard cell, 1.0186 V.
B ₃		Lead acid accumulator, 2 V.
G ₁		Tinsley mirror galvanometer.
G ₂ , G ₃		Cambridge galvanometers.
W, D		Wet and dry thermojunctions.

Standardisation of G₁.

- 1) S₄ to 'STANDARD'.
- 2) Close S₁
- 3) Close S₂
- 4) Balance G₂ with B₁
- 5) Read G₁
- 6) Open S₂
- 7) Open S₁

Fig 3.6. Difference between electrical and Assmann humidities.

- Position No. 1.
- x Position No. 3.

The e.m.f. generated by the thermocouple was measured by a wall mounted Tinsley mirror galvanometer. The sensitivity was arranged so that the wet bulb depression could be read directly in $^{\circ}\text{C}$, subject to small corrections for non-linearity in the galvanometer scale and for the variation of the thermoelectric efficiency with temperature. A standardisation circuit (see Fig 3.5) (p.5a) permitted day-to-day checks of the galvanometer circuit, and in fact no change of sensitivity was found throughout the programme.

3.2.3.3. Comparison with Assmann psychrometer.

Periodic comparisons were made between the vapour pressures derived from the electrical thermometers and electrically aspirated Assmann psychrometers mounted close to heads 1 and 3. (see Fig 3.1). (p.47) The results of all comparisons are shown in Fig 3.6, and those of an individual run are included in Fig 3.3. (p.48) It is thought that the greatest uncertainty in the experiment lies in the humidity measurements. Although the greatest care was taken, it can be seen that discrepancies of 1 mb in vapour pressure were not uncommon. No systematic trend in the residuals could be found, and it was concluded that the differences were real. However, such differences do not affect the main conclusions of the experiment, though reservations are prudent in some cases.

3.2.4. Optical system

(p.53) Fig 3.7 shows the optical system in plan, and Fig 3.8 shows (p.54) in perspective the path of radiation in the cell. The design and layout

Fig 3-8. Perspective view of optical path for 12 transits of cell (not to scale).

N Nernst filament, 0.25 x 2 cm.

S Entrance slit jaws.

$C_6, C_7, C_8, C_9, C_{10}$ Centres of curvature of $M_6, M_7, M_8, M_9, M_{10}$.

Path of rays:

$N - M_1 - M_2 - M_3 - M_4 - M_5 - M_6 - M_7 - M_8 - M_9 - M_8 - M_7 - M_6 - M_5 - M_4 - M_3 - S$.

I_1
 I_2
 I_3
 I_4
 I_5
 I_6

Fig. 3.7. Diagram of optical system (London) (not to scale)

- S Nernst source, 0.25 cm x 2.5 cm.
- C. Chopper, 10 c/s.
- G Merton replica grating 15 cm x 15 cm, 473 or 985 lines/cm.
- F₁ Polystyrene or terylene filter.
- F₂ Double reststrahlen magnesium oxide filter for $\lambda > 13\mu$ or aluminised mirrors for $\lambda < 13\mu$
- F₃ Bloomed indium antimonide filter.
- D Golay detector.
- W Polyethylene window, 30 μ thick.

<u>Mirrors.</u>	<u>Diameter</u>	<u>Radius of</u>	<u>Separation</u>
	(cm)	Curvature	(cm)
		(cm)	
(Source)	-	-	
M ₁	15	92	88
M ₂	0.5 x 1.5	∞	112
M ₃	15 x 15	∞	206
M ₄	30	361.1	541
M ₅	33.6	∞	967.6
M _{6,10}	10, semicircular	1545	1535.7
M ₇	30	1540.7	1540.7
M ₈	30	1542.3	1546.0
M ₉	30	1546	

Laboratory + spectrometer path = 1324 + 730 = 2086 cm.

Possible cell path lengths (m): 115.5, 177.2, 239.0, 300.7, 362.4,
424.2, 485.9, 547.6.

of the optics was dictated mainly by the shape and size of the laboratory space available, the latter not permitting the use of the simpler version described by White (1942). The tolerances on the radii and on the figure of the mirrors for satisfactory performance are not severe, these subjects being fully discussed by White. The mirrors used in the present work were figured to $\frac{1}{2}$ - wavelength in the visible, with radii equal to within 2 cm in 1550 cm, though a tolerance 10 times greater would have been acceptable.

The essential details of the system are given in the legends to Fig 3.7 and 3.8, and only the following need special comment.

(i) M_1 and M_4 are used off-axis. The off-axis angle is kept to a minimum by allowing the smallest possible clearance between the beam from M_1 to M_2 and the mounts for the source and chopper, and between M_3 and the two beams passing it.

(ii) M_4 is the image of M_4 in M_5 . M_6 and M_{10} , the two halves of a centrally divided circular mirror, are adjusted with their centres of curvature coincident, mid-way between M_4 and M_7 . M_7 is fixed with its centre of curvature at the centre of M_8 , and M_8 with its centre of curvature mid-way between M_7 and M_9 .

(iii) M_9 is mounted on a turntable whose rotation moves C_9 along a horizontal line through the centre of M_8 . The adjustment is made remotely using a Selsyn transmitter and receiver.

(iv) Since M_{10} is imaged on the entrance slit of the spectrometer via M_5 , M_4 and M_3 , the slit will only be illuminated when M_9 is adjusted to one of the discrete settings that give an image on M_{10} . The settings are such that the separation of C_9 and C_7 is $\frac{x}{n}$, where $n = 1, 2, 3$. and x is shown in Fig 3.8; the number of traversals of the cell is then $4(n+1)$. Fig 3.8 illustrates the case of $n = 2$

All mirrors were mounted on sturdy platforms each consisting of 4 slabs of concrete 2 ft square and 2 in thick, separated by rubber spacers which were found to remove all traces of vibration. The platforms for the cell mirrors had to be isolated mechanically from the cell structure, because it was found that some vibration was being transmitted. This was achieved by leaving 2 in clearance between the concrete slabs and the polystyrene floor of the cell, making good the seal with 2 sheets of thin polyethylene.

The initial setting up presented no problems and is summarised below:

- (i) Set M_7 and M_9 at their correct distances from M_8 , i.e. with their centres of curvature on M_8 . This could be done to ± 0.5 cm using the Foucault knife edge technique (e.g. Strong, 1940, p.69)
- (ii) Adjust M_7 and M_9 so that their axes pass through the centre of M_8 (M_8 is then imaged back on itself by M_7 and M_9)

- (iii) Adjust M_8 so that its axis passes midway between M_7 and M_9 (M_7 is then imaged on M_9)
- (iv) M_6 and M_{10} set with centres of curvature coincident, just off edge of M_7 .
- (v) M_5 adjusted so that M_4 imaged on M_7 , via M_5 and M_6 , M_{10} .

Once the initial adjustments had been made as above, routine checking was facilitated by three small lamps and screens set up as follows:

- (i) Lamp and screen just off edge of M_7 ; image formed by M_6 , M_8 and M_{10} (all three are on one mounting), checking M_6, M_8, M_{10}
- (ii) Lamp just off edge of M_4 ; image formed on same screen as used in (i) via M_5 , M_6 and M_{10} , thus checking the alignment of M_5 .
- (iii) Lamp off edge of M_8 , screen diametrically opposite; images formed by M_7 and M_9 , thus checking both.

By noting the positions of the images after the initial alignment, a routine check could be made in 2 min. In fact, the mountings turned out to be so stable that no correction was required during 1 year.

3.2.5. Spectrometer, source and detection system

p.17

The spectrometer, described in Chapter 2 (§ 2.3.3), was the

same instrument as used in the Ascot experiment, having been made more compact. The source, chopper, detector, amplifier and recorder again were all as described in § 2.3^{p.15}, run from a stabilised power supply.

3.3 Performance of the system

Before attempting any absorption measurements, it was necessary to complete an exhaustive series of tests to confirm that all parts of the system were behaving as expected, and to investigate several potential sources of error. They are dealt with in order below.

3.3.1 Calibration, resolution and linearity

The spectrometer was calibrated using 4 isolated water vapour lines, taking the observed wavelengths of Migeotte et al (1956, 1957). Then linearity was tested as described in § 2.4.5^{p.21}; no significant departure from linearity was detected. Owing to improved illumination of the aperture of the spectrometer and a new Golay cell with higher signal-to-noise ratio, the resolution attainable was improved by about 40 % as compared with the Ascot experiment.

3.3.2. Transmittance of polyethylene window

Since the experimental technique involved the measurement of the transmittance of the cell as a function of humidity, it was absolutely essential to be sure that the polyethylene cell window was not affected by changes in humidity. This might conceivably

happen if hygroscopic nuclei adhere to the window, whose radii would then vary with the relative humidity, or through adsorption of water molecules by the window.

To test this possibility, a short cell with polyethylene windows was placed in the beam in front of M_4 , giving four transits through each window. The humidity in the short cell was raised, monitoring the signal at $\nu = 559.4 \text{ cm}^{-1}$. No change in signal was detected until actual condensation appeared on the windows, suggesting that any effect caused by the two transits through the main cell window should be negligible, especially since saturation was never approached in the main cell (relative humidities were nearly always below 60%).

During the course of the main experiment, a run was made without the polyethylene cell window, sealing being effected in this case by a metal sheet which was removed only briefly when making a measurement of transmittance. This run gave the same result as all the others, indicating that the transmittance of the window did not vary detectably with humidity.

3.3.3 Variation of reflectivity of mirrors with humidity

For the same reasons given in § 3.3.2, the mirror reflectivity might vary with humidity, and this required careful investigation. Three tests were devised, all showing that no significant change of reflectivity occurred on raising the humidity to the highest levels used in the experiment.

The first test was to flood M_8 with dry air from a cylinder, having previously brought the humidity to a high level. With the cell adjusted for 24 transits (12 reflections off M_8), the signals at $\nu = 559.4 \text{ cm}^{-1}$ and 1118.8 cm^{-1} were monitored. No detectable change ($< \frac{1}{2} \%$) was observed.

For the second test, an air tight partition was inserted in the cell 1.5 m in front of M_7 and M_9 . The humidity in the longer section, containing M_5 , M_6 , M_8 and M_{10} was now brought to a high level (vapour pressure, e , = 27 mb), leaving the short section containing M_7 and M_9 much drier ($e = 6 \text{ mb}$). Having achieved uniform mixing in the two sections of the cell, the fans were switched off and the partition was suddenly withdrawn. With the cell set for 24 transits, the signals at $\nu = 559.4 \text{ cm}^{-1}$ and 1118.8 cm^{-1} were then recorded continuously, together with humidity measurements at sensing head number 4 (Fig 3.1) ^(A.47) to show the progress of the mixing between the two sections. If the reflectivity of M_7 and M_9 decreased with increasing humidity then a decrease of signal would have been expected as the mixing progressed. On the contrary, an increase of signal occurred. The cause of this effect was later traced to self-broadening and subsequent results explained exactly the increase of signal observed, suggesting that no change occurred in the mirrors.

In the final test, the partition was again used, but the steam generator was moved into the short section containing M_7 and M_9 . The signal was now monitored as mixing progressed from initial values

of $e = 27$ mb in the short section and $e = 6$ mb in the long section. An increase of signal would now be expected if there were any increase in the reflectivity of M_7 and M_9 . In fact, the signal remained constant, which was again consistent with no change ($< 2\%$) in the overall reflectivity (12 reflections).

It was finally concluded that the reflectivity of the mirrors was independent of the humidity in the cell.

3.3.4. Scattering from mirrors and window

It will be seen that M_4 and M_5 are used by both the beams entering and leaving the cell. There is therefore the possibility of backscattering of radiation from the ingoing beam into the emerging one. The same might happen at the polyethylene window.

If either of these occurred, the signal should not drop to zero when a shutter is inserted after M_5 . In fact, the signal did disappear completely in this test, confirming that there were no scattering problems at M_4, M_5 or the window.

A related source of error in a multiple traversal system is the possibility of scattering from one beam into another. An immediate test of this is to check that the signal drops to zero for settings of M_9 between the discreet positions giving an image on M_{10} . This was in fact found to be the case, unless the images were so close as to cause two to fall on M_{10} at the same time.

3.3.5 Stray radiation

It is always difficult to be sure that stray radiation has been eliminated in the spectrometer. The usual tests involve filters having opaque absorption bands, checking that the signal drops to zero on inserting the filter. This test is satisfactory for stray radiation of greatly different wavelength, but always leaves some doubt^{in respect} of wavelengths in the immediate neighbourhood of the one required. The tests applied were as follows:

- (i) Glass plate - Zero signal, showing no stray visible radiation.
- (ii) Terylene filter (narrow opaque band at 9.0μ) - Zero signal at 9.0μ , showing pure spectrum at 9.0μ
- (iii) 15μ CO_2 band. Zero signal at centre of Q branch, showing pure spectrum at 15.0μ .
- (iv) Several strong water vapour lines between 17 and 20μ .
Line centres were fully absorbed under high resolution, showing pure spectrum at these points.

These satisfactory results were taken to indicate that stray radiation was of negligible proportions.

3.3.6 Aerosol absorption

In a closed cell it is possible in principle to remove aerosol by filtering. However, measurements using polluted air drawn from the outside were found to give the same results as those made with clean

air which had been allowed to settle over a long period in the cell. It should be remembered that the relative humidity in the cell was rarely allowed to rise above 60%, so that hygroscopic nuclei should have remained very small. In the circumstances, it was considered that aerosol absorption would be negligible.

3.3.7 Ozone and carbon dioxide absorption

The use of many electric motors led to the generation of ozone in the cell, and probably also N_2O and CO_2 . As a result, it was only possible to work in windows well away from absorption bands of these gases, i.e. windows 4, 8, 11, 13, 17, 18, 19, 20 (see § 2.4.1^{1.19}).

3.4. Experimental technique

3.4.1. Choice of Method

With the facilities to control the humidity, an absolute method of measuring absorption coefficients looked attractive, observing the signal in each window as a function of humidity. However, the long-term stability of the detector system referred to in § 2.4.6^{1.22} proved to be inadequate and a relative method was again selected. The techniques used were broadly similar to those in the Ascot experiment, with some improvements.

3.4.2. Measurement of $k_{17} - k_4$

With the grating set to observe window 17 in the first order,

the second order spectrum of window 4 was removed by a terylene filter of thickness 12μ . Without moving the grating, window 4 was now observed by changing the terylene filter for a polystyrene one, thickness 200μ . The latter is opaque in window 17 whilst transmitting window 4. The signals S_{17} and S_4 were made roughly equal by adding polyethylene sheets totalling about 75μ thickness to the polystyrene filter. Defining $y_{17,4}$ as S_{17}/S_4 , we have

$$y_{17,4} = A_{17,4} \exp \{-(R_{17} - R_4)m\} \quad 3.1$$

where $A_{17,4}$ is a constant involving the relative reflectivities and transmissivities of the mirrors, grating and filters in Windows 17 and 14,

and m is the mass of water vapour per unit area of path, so that a plot of $y_{17,4}$ against m would give $k_{17} - k_4$.

A run was usually carried out in the following manner. An initial observation of $y_{17,4}$ was made with the humidity at the ambient value and the temperature set roughly at the desired value (a long period, of order 3 hours, was required for the temperature to reach a steady value). The humidity was then raised rapidly to a high level and readings of $y_{17,4}$, with simultaneous humidities, were taken periodically as the humidity returned slowly towards the ambient value by diffusion loss. This took a further 3 or 4 hours, during which time the air in the cell was circulated continuously. The final observation was compared with the first, and agreement within experimental error was invariably found.

3.4.3. Measurement of $k_{18} - k_{17}$, $k_{19} - k_{17}$, $k_{20} - k_{17}$.

With second order spectra removed by a double reststrahlen magnesium oxide filter, the signals in windows 18, 19 and 20 were compared in turn with that in window 17, rough equality of signal being achieved initially by suitable combinations of polyethylene filters. Then the value of $k_{17} - k_i$ was determined as in § 3.4.2, ^{p. 62} using

$$y_{17,i} = A_{17,i} \exp \{ -(k_{17} - k_i) m \}.$$

3.4.4. Absolute measurements of k_4 , k_8 and k_{13} .

A few observations of the change of signal S_i in windows 8, 11 and 13 with humidity were obtained in an attempt to establish absolute values here. To minimise the effects of drifts in the detector system or optics, the measurement was carried out as quickly as possible by introducing steam at the maximum rate, recording the signal continuously. At the end of the run the whole system was checked for drifts by noting the signal after quickly returning the humidity to its original value by opening the cell to the atmosphere. A complete run took 20 min, and about 20% were rejected because the signal did not return to its original level. We then use

$$S_i = \text{const } e^{-k_i m}.$$

The measurements of S_4 taken in the runs for $k_{17} - 4$ were also examined for variation with m . Although these runs often took several

hours, the drift was nearly always small enough to permit their use to give an absolute value of k_4 .

3.4.5. Absolute measurements in windows near 4μ

The absorption in four windows ($\nu = 2687, 2613, 2502$ and 2403 cm^{-1}) near 4μ was measured as described in § 3.4.4, the indium antimonide filter having been replaced by indium arsenide, which cuts on at 3.3μ .

3.5. Results and discussion

3.5.1 $17 - 21\mu$ region

3.5.1.1. Window 17

This measurement, being the simplest to make and involving the movement of only one filter, is regarded as providing a 'standard window' with which others in the $18 - 21\mu$ region may be compared.

A typical run is illustrated in Fig 3.9, together with the results. From Eq. 3.1 we have

$$\log_e y_{17,4} = \log_e A_{17,4} - (k_{17} - k_4) m.$$

A strong curvature in the plot is at once apparent, consistent with a very large degree of self-broadening. Under these circumstances $k_{17} - k_4$ can not be determined from the slope of the curve, but must instead be evaluated point by point, for which a value of $\log_e A_{17,4}$ is required. The only way to measure $A_{17,4}$ is to observe $y_{17,4}$ with

Fig 3-10. Extinction in window 17 for different temperatures.
The origin of the upper eight runs is displaced as shown.

the cell completely dried out; this was attempted on three occasions by freezing the water vapour onto the inside walls of the heat exchanger (area $\sim 1\text{m}^2$), which was surrounded for this purpose with dry ice. Unfortunately, the vapour pressure could not be reduced below 3 mb because at this stage the capacity of this means of extraction was only just keeping up with diffusion from outside (vapour pressure ~ 10 mb). It was felt, however, that the curves obtained from these low humidity runs could be extrapolated to $m = 0$ with confidence to give a value of $\log_e A_{17,4}$; it was noted moreover that its value did not vary detectably over the period of the investigation and has therefore been assumed to have had the same value in those runs (the large majority) in which the vapour pressure was not taken below 10 mb.

A further complication became apparent when runs were carried out at different temperatures. Fig 3.10 shows the results of 11 runs at temperatures between 21°C and 45°C , showing a strong negative temperature dependence, at least at vapour pressures above about 15 mb, (all the results have been scaled to a path length of 402 m to facilitate comparison with the Ascot results presented in Chapter 2). The extrapolated portion of each curve is shown as a broken line, the intercept on the abscissa having been inferred as described above. Values of $k_{17} - k_4$ are next evaluated from

$$k_{17,4} = -\frac{1}{m} \left[\log_e y_{17,4} - \log_e A_{17,4} \right]$$

Fig 3-11. Absorption coefficients in window 17 relative to window 4 as a function of vapour pressure and temperature.

and all the results are shown in Fig 3.11 as a function of vapour pressure. The data are tabulated in Appendix 3.1. Apart from the obvious increase of k_{17-4} with e , the negative temperature dependence is very marked at the higher vapour pressures, but seems to become smaller, or even to disappear, near $e = 10$ mb. This suggests that the absorption coefficient k is composed of two parts; k_s due to self broadening with a negative temperature dependence and k_f due to foreign broadening with positive temperature dependence. There will therefore be a vapour pressure below which the total absorption coefficient increases with temperature, but thereafter the negatively dependent self-broadening term becomes predominant. Unfortunately, with path lengths of 400 m or less, the level of scatter in observations with $e < 10$ mb is too great to permit any conclusion regarding the temperature dependence there.

The form of the functions relating k , e and T can not be deduced from the results but rough values for the parameters in an assumed linear relation can be found. Considering the temperature dependence first, we can assume

$$k(p, e, T_1) = k_f(p, T_1) + k_s(e, T_0) [1 + \alpha(T_1 - T_0)]$$

from which

$$\begin{aligned} \left(\frac{\partial k}{\partial e} \right)_{\substack{T=T_1 \\ e=e_1}} &= [1 + \alpha(T_1 - T_0)] \left(\frac{\partial k_s}{\partial e} \right)_{\substack{T=T_0 \\ e=e_1}} \\ &= [1 + \alpha(T_1 - T_0)] \left(\frac{\partial k}{\partial e} \right)_{\substack{T=T_0 \\ e=e_1}} \quad \text{since } k_f \neq f(e) \end{aligned}$$

so that a plot of $\frac{\partial R}{\partial e}$ as a function of T will give α . The results, shown in Fig 3.11, from runs for which $\frac{\partial R}{\partial e}$ may be evaluated between $e = 20$ and 30 mb, indicate a negative temperature dependence of about 2% per $^{\circ}\text{C}$ at 30°C .

The vapour pressure dependence seems to be significantly non-linear, but this feature is very sensitive to the value adopted for $k_{17,4}$, and a reasonable error here could account for the non-linearity in Fig 3.11. Accordingly it is felt that the observations do not warrant examination beyond first order terms. The best straight line through observations taken at $T = 30^{\circ}\text{C}$ gives $k_{17-4} = 1 + 0.033 e \text{ g}^{-1} \text{ cm}^2$, where e is in millibars, so that the results can be represented roughly by the expression

$$k_{17-4}(T, e) \approx 1.0 f(p, T) + 0.033 e [1 - 0.02(T - 30)] \text{ g}^{-1} \text{ cm}^2$$

in the range $0 < e < 35$ mb

$20 < T < 45^{\circ}\text{C}$.

$f(p, T)$ is an undetermined function of dry air pressure p and temperature, but it is to be expected on theoretical grounds to be linear in p . Furthermore, the apparent disappearance of the temperature dependence of k_{17-4} near $e = 10$ mb could be explained if $f(p, T)$ increases by 0.5% to 1% per $^{\circ}\text{C}$.

Fig 3.12. Extinction in window 18 and comparison with Ascot results.

(p.67)

Fig 3.11 also shows all the results of the Ascot experiment. They are on average $0.35 \text{ g}^{-1} \text{ cm}^2$ higher than the London results; this may be due to the isolation of a 'cleaner' window in the London experiment - a point discussed further in § 3.5.1.3^(p.71). The Ascot results show no systematic temperature dependence in Fig 3.11^(p.67), although on the basis of the London results one would not expect much at these vapour pressures, and in any case it would be masked by the large scatter. The vapour pressure dependence, on the other hand, is in good agreement with the London results.

3.5.1.2. Windows 18, 19 and 20

As in the case of window 17, it is necessary to measure $A_{17,i}$ by extrapolation of low humidity runs, and to assume that it remained the same in the other runs.

(a) Window 18

All the observations for window 18 are shown in Fig 3.12. The regression between β_{18-17} and m seems to be linear, but with a suggestion of a negative intercept which indicates a slight upward curvature arising from a self broadened contribution. Fig 3.12 also shows values of k_{18-17} as a function of e , and the data are tabulated in Appendix 3.1^(p.100). It is interesting to note that the self-broadened contribution is a smaller fraction of the whole than in the case of k_{17-4} ; this suggests that the self-broadened line shape is fundamentally different from the foreign-broadened one.

Fig 3.13. Extinction in window 19, and comparison with Ascot results.

Fig 3.14. Extinction in window 20.

There is evidence of a positive temperature dependence (about 1% per °C) over the whole range of e , and this fits in with the picture inferred for $k_{17} - 4$ since in this case the negatively dependent part is relatively small.

The Ascot results are also shown in Fig 3.12. They are about $0.35 \text{ g}^{-1} \text{ cm}^2$ lower than the London ones - a discrepancy which is discussed further in § 3.5.1.3.

(b) Window 19.

Fig 3.13 shows all the results for $\beta_{19} - 17$ as a function of m . The curvature is more obvious than in the case of window 18, implying a larger self-broadened contribution. The resulting values of $k_{19} - 17$ as a function of e are also shown in Fig 3.13 and the data are tabulated in Appendix 3.1. Although scatter masks any temperature dependence at low vapour pressures ($e < 15 \text{ mb}$), it should be noted that for $e > 15 \text{ mb}$, $k_{19} - 17$ tends to be higher for lower temperatures.

The Ascot results are also shown in Fig 3.13 with mean London values for comparison; the former are seen to be about $0.3 \text{ g}^{-1} \text{ cm}^2$ lower than the latter - a difference similar to that observed for window 18, to be discussed in § 3.5.1.3.

(c) Window 20

Fig 3.14 shows all the results for $\beta_{20} - 17$ as a function of

m, together with the resulting values of k_{20-17} as a function of e . They again show a distinct self-broadened contribution, and although the accuracy does not warrant a quantitative statement about the temperature dependence, it seems to be negative for large e (> 15 mb) and positive for small e (< 10 mb). All the data are tabulated in Appendix 3.1.^{p.165}

The Ascot results are also shown in Fig 3.14.^(p.70) They are about $0.3 \text{ g}^{-1} \text{ cm}^2$ lower than the London ones, and this point is discussed in the next section. Although the Ascot sample is small, the observations taken at higher e show the negative temperature dependence exhibited by the London results.

3.5.1.3 Systematic differences between Ascot and London results

We have seen that k_{17-4} is about $0.35 \text{ g}^{-1} \text{ cm}^2$ lower, and k_{18-17} , k_{19-17} and k_{20-17} are about $0.3 \text{ g}^{-1} \text{ cm}^2$ higher in the London observations than in the Ascot ones. One explanation of all these features might be that window 17 as isolated in the London experiment was in fact more transparent than at Ascot. This is indeed possible, because the resolution in London (1.2 cm^{-1}) was better than that at Ascot (1.7 cm^{-1}), the former being sufficient to exclude two weak water vapour lines at $\nu = 560.42 \text{ cm}^{-1}$ and 560.89 cm^{-1} which were partly included in the Ascot window (the smaller image on the entrance slit in the London experiment precluded the use of the lower resolution to check the measurement under the same conditions).

Fig 3.15. Summary of results as a function of vapour pressure and temperature.

Thin lines : observed values from the laboratory experiment
(the dashed lines have been extrapolated smoothly).

Thick lines : Ascot results.

However, assuming a triangular slit function, it was estimated graphically that these lines could have accounted for no more than $0.1 \text{ g}^{-1} \text{ cm}^2$ of the above discrepancy.

It should also be pointed out that the lower London result for $k_{17} = 4$ (but not the higher ones for windows 18, 19 and 20) could be explained by anomalously high absorption in window 4. The results presented in § 3.5.2^{2.1, 78} do indeed indicate much greater absorption here than would be expected from previous work in this region, though this may be due to a much increased self-broadened contribution at the higher vapour pressures (30 mb) necessary in a short path experiment, compared with the long path low vapour pressure (<10 mb) conditions in all previous work.

It is thought to be most unlikely that the differences can be attributed to aerosol absorption because if this had been significant the results would not have been so exactly reproducible owing to inevitable variation of the aerosol concentrations.

3.5.1.4. Summary of results

The results for the $17 - 21 \mu$ region are summarised in Fig 3.15. The intention is to show the qualitative aspects of the results and not too much weight is attached to the apparent curvature or the derived value of the temperature dependence. The evidence on the latter is rather scanty for low e , and a longer path length is required to settle this point. The dotted parts of the curves are extrapolated

as smooth curves from the regions of higher e where scatter is much less. There is good agreement between the Ascot and London results except for the discrepancy in the case of window 17, which has already been discussed.

3.5.1.5. Discussion and previous work

There has been little previous work on the atmospheric continuum beyond 17μ , and only that of Anthony (1952) and Bolle et al (1963) seems to have been directed specifically to the determination of absorption coefficients. Both investigations were carried out in the open atmosphere, employing, moreover, a slant path, so that variation of the temperature and vapour pressure along the path render the interpretation rather uncertain in the light of the present results.

Anthony (1952) deduced continuum absorption coefficients from the variation of solar intensity with zenith angle during the day and obtained a value of $1.0 \text{ g}^{-1} \text{ cm}^2$ at 19μ , compared with values between 1.2 and $2.0 \text{ g}^{-1} \text{ cm}^2$ in the present work. This observation was made from Table Mountain, California, but temperatures, humidities and instrumental details were not reported (though the vapour pressure was probably below 10 mb), so that whilst ^{the} departure is in the direction expected, it is not possible to make a quantitative test.

Bolle (1963, 1964) reported the results of some very careful emission studies made under widely different conditions in different

Fig 3-16. Comparison between present work and that of Bolle.

Bolle (lines):

- I Beer Sheva; $T \sim 290^\circ\text{K}$, $e \sim 15\text{mb}$; 32.0°N , 34.9°E ; 280m.
- II S. Agata; $T \sim 286^\circ\text{K}$, $e \sim 15\text{mb}$; 40.6°N , 14.2°E ; 455m.
- III Jungfrauoch; $T \sim 256^\circ\text{K}$, $e < 3\text{mb}$; 46.5°N , 8.0°E ; 3570m.
- IV Munich; $T \sim 261^\circ\text{K}$, $e < 3\text{mb}$; 48.2°N , 11.6°E ; 530m.

Present work (points):

- x $T \sim 290^\circ\text{K}$, $e = 15\text{mb}$.
- o $T \sim 260^\circ\text{K}$, $e = 0$.

Fig 3.17. Laboratory measurements of Palmer (1957b,c)

(a) Pure water vapour

(b) Water vapour-nitrogen mixture ($p_{N_2}=800\text{mb}$)

parts of the world, listed in the legend to Fig. 3.16. He used a high resolution grating spectrometer similar in performance to that used in the present work. He devised an ingenious method of analysis in which isolines of continuum emission were calculated for several values of the absorption coefficient, using humidities and temperatures determined in most cases by a simultaneous radio-sonde ascent on the site. With the isolines plotted on the observed emission spectrum it was a simple matter to read off window absorption coefficients by inspection.

The results are shown in Fig 3.16, from which it may be seen that values determined at Beer Sheva and S. Agata are nearly double those measured at Jungfraujoch and Munich. Bolle interpreted this as a positive temperature dependence; however, the difference observed is also ~~consistent~~ consistent with a large self-broadening effect, the high temperature observations being associated with high partial vapour pressure (~ 20 mb at the surface, with a mean of about 15 mb along the slant path) and the low temperature ones with low partial vapour pressure (< 3 mb). Values inferred from the present work (Fig 3.15) ^(p.72) for the approximate conditions encountered by Bolle are included in Fig 3.16 and show surprisingly good agreement.

The laboratory experiment of Palmer (1957 b,c), described in § ^{p.42} 2.7 will now be considered in detail. Fig 3.17a shows the extinction due to pure water vapour (i.e. no foreign broadening) for windows at $\nu = 261, 295, 310, 319, 367, 412$ and 480 cm^{-1} , and Fig 3.17(b)

Fig 3-18.

Fig 3-19.

Absorption coefficients derived from Palmer (1957 b,c).

Fig 3-18. Pure water vapour, pressure e mb.

Fig 3-19. Constant vapour pressure (2.7 mb), variable nitrogen pressure.

The origin is displaced for each curve, and the resolution (cm^{-1}) is shown in brackets (full width at half-height).

shows the corresponding results when nitrogen at 800 mb pressure was added. All lines show an upward curvature (as indeed they must in Fig 3.17 ^(p.74) (a)), indicating significant self-broadening. However, it is apparent that these results ~~can~~ not be accounted for in terms of a self - to - foreign broadening factor of about 6, because the ratio of the extinctions in Figs 3.17 ^(p.74) a and b for the same value of e (mb) would then be $\frac{6e}{800+6e}$, which is about $\frac{1}{28}$ for $e = 5$ mb, compared with the observed values of $\frac{1}{4}$ and $\frac{1}{5}$ respectively for the windows at $\nu = 480$ and 412 cm^{-1} . On further inspection it becomes apparent that the self and foreign contributions have a different frequency dependence, suggesting that they arise in fundamentally different ways, and that it is not appropriate to think in terms of a constant self-broadening factor.

Fig 3.18 shows values of the self-broadened absorption coefficients as a function of vapour pressure, derived from the data plotted in Fig 3.17a. ^(p.74) It can be seen that within the limits of reasonable experimental error they increase linearly with vapour pressure; the regression coefficients are tabulated in Table 3.1. ^(p.76)

Fig 3.19 shows average values of the absorption coefficient as a function of nitrogen pressure, derived from 6 runs at constant water vapour pressures between 0.16 and 10 mb, with a mean of 2.7 mb. Again the values show an almost linear increase with pressure, but with a definite suggestion of a decrease in slope at the higher pressures. This might be due to failure to exclude the effects of

Table 3.1Self - and foreign - broadened absorption coefficients(derived from Palmer, 1957 b,c)

ν , cm^{-1}	261	270	295	310	319	367	412	480
k_s , $\text{g}^{-1} \text{cm}^2 \text{atm}^{-1}$	1050	1050	910	840	650	250	180	150
k_f , "	85	85	76	64	53	13	5.0	2 - 5
k_s/k_f	12.4	12.4	12.0	13.1	13.4	19.2	36	50

nearby lines because of inadequate resolution. Indeed, in one window ($\nu = 319 \text{ cm}^{-1}$) measurements were made with two gratings giving resolutions of 3.8 and 2.0 cm^{-1} , and the absorption coefficients resulting from the latter are smaller by about 20 %. However, except in the case of $\nu = 480 \text{ cm}^{-1}$, it is thought that the effect of nearby lines is small since the windows were selected only if no major lines were listed within 5 cm^{-1} in ^{Benedict and} Kaplan's tables (1963). The ^(p.75) regression coefficients from Fig 3.19 are tabulated in Table 3.1.

Compared with the present work, Palmer's results at $\nu = 480 \text{ cm}^{-1}$ are about 2.5 and 1.6 times larger for self - and foreign - broadening respectively: this is probably due to much lower resolution (5 cm^{-1} compared with 1.2 cm^{-1}) so that two lines are included in Palmer's case.

In conclusion, Palmer's work provides excellent confirmation

Fig 3-20. Extinction in window 8 (901 cm^{-1}) and its temperature dependence.

- (a) Absolute measurements of signal, S_8 , as a function of m . Six runs at different temperatures are shown, with the slopes (g^{-1}cm^2) in brackets.
- (b) Slopes (g^{-1}cm^2) as a function of temperature.

of a strong self - broadening effect which agrees roughly with the present work at 20μ and extends at least to 40μ .

3.5.2. 7-12 μ region and 4 μ windows

3.5.2.1 Windows 8, 11, 13 and 4.

Fig 3.20 (a) shows the variation of signal in window 8 with m for 6 runs. The long time taken to dry the cell below $e = 10$ mb ruled out measurements at low vapour pressures. Observations were made only at the highest and lowest humidities, except on one run when very frequent humidity measurements were made. This latter run is seen to give a very curved plot, suggesting strong self - broadening. It was hoped to obtain more runs in this way but a breakdown in the detector prevented further work before the end of the investigation.

The remarkable feature of these results is that the absorption is much greater than expected on the basis of all previous work in this region. In the absence of the run with many closely spaced observations, there would be no alternative but to connect the points by a straight line, giving absorption coefficients of order $0.4 \text{ g}^{-1} \text{ cm}^2$, about four times the usually accepted result. However, the detailed run suggests a strong curvature, and it is possible that the curves in Fig 3.20 (a) approach the abscissa in such a way that the absorption coefficient is indeed much lower at low vapour pressure (all previous measurements except one have been made with

Fig 3-21. Extinction in window II (832 cm^{-1}) and its temperature dependence.

(a) Absolute measurements of signal, S_{II} , as a function of m . Eight runs at different temperatures are shown, with the slopes (g^{-1}cm^2) in brackets.

(b) Slopes (g^{-1}cm^2) as a function of temperature.

Fig 3.22. Extinction in window 13 (790 cm^{-1}) and its temperature dependence.

- (a) Absolute measurements of signal, S_{13} , as a function of m . Twelve runs at different temperatures are shown, with the slopes (g^{-1}cm^2) in brackets.
- (b) Slopes (g^{-1}cm^2) as a function of temperature.

Fig 3-23. Extinction in window 4 (1118.8 cm^{-1}) and its temperature dependence.

(a) Absolute measurements of signal, S_4 , as a function of m . Twelve runs at different temperatures are shown, with the slopes (g^{-1}cm^2) in brackets.

(b) Slopes (g^{-1}cm^2) as a function of temperature.

$e < 10$ mb). Assuming this to be the case, we can find the value of the intercept which gives agreement with previous work, i.e. $k_8 \approx 0.1 \text{ g}^{-1} \text{ cm}^2$ at $e = 10$ mb, and then estimate the magnitude of the self - broadened component. This works out to be $0.010 \text{ g}^{-1} \text{ cm}^2 \text{ mb}^{-1}$, or $10 \text{ g}^{-1} \text{ cm}^2 \text{ atm}^{-1}$.

The slope of straight lines drawn through runs made between roughly the same vapour pressures shows slight evidence of a negative temperature dependence (Fig 3.20 ^{p.77} (b)). This is consistent with the picture of the self - broadened contribution inferred for the $18 - 21 \mu$ region ($\S 3.5.1$ ^{p.65}).

The reality of the unexpectedly high absorption was doubted for a considerable time, and exhaustive tests were made to try to find another explanation. The results were the same with or without the polyethylene cell window; the mirror reflectivities did not vary with humidity ($\S 3.3.3$ ^{p.58}); two different gratings gave the same results, suggesting that stray radiation from a poor grating was unlikely to be the cause.

Figs 3.21, 3.22 and 3.23 show similar presentations for windows 11, 13 and 4 respectively. They all show the same unexpectedly high absorption, again with a suggestion of a negative temperature dependence. The self - broadened contribution was estimated as for window 8, resulting in the values 13, 17 and $12 \text{ g}^{-1} \text{ cm}^2 \text{ atm}^{-1}$ for windows 11, 13 and 4 respectively.

Fig 3.24. Extinction in 4μ window.

All the observational data are given in Appendix 3.2.

p. 102

3.5.2.2. 4 μ windows

Fig 3.24 shows the results of one run in four windows near 4 μ . The slopes of the lines are about half of those for window 11, so that considerable absorption is indicated here. If it is assumed that this absorption is largely due to self - broadening, the absorption coefficient may be estimated as 6 g⁻¹ cm² atm⁻¹ in the 4 μ region.

3.5.2.3. Discussion and comparison with previous work

The major problem posed by the results in this section is that the absorption in the 8 - 12 μ window is apparently much greater than that usually accepted. One possible explanation suggests itself immediately. If the strong self-broadening effect observed in the 17 - 21 μ region extends to 4 μ , then the present work at vapour pressure near 30 mb would give much higher results than the values deduced from observations carried out mostly below 15 mb. The previous measurements were therefore examined for evidence of systematic variation with vapour pressure.

Roach and Goody (1958) determined continuum absorption coefficients in several wide bands of the 8 - 12 μ window by observing the variation of solar intensity with solar zenith angle. Some of his observations were made from central London and some from Ascot; the results from the former were about double those from the

Fig 3-25. Extinction of solar radiation in the region $871-908 \text{ cm}^{-1}$.
(Roach and Goody, 1958)

●	} Ascot	■	} London
●		Very hazy	
○	Exceptionally clear	□	Very clear

The upper and lower numbers to the right of the London points are the surface vapour pressures (mb) for 0600 and 1800 hrs, respectively, at London Airport.

Fig 3-26. Effect of diurnal evaporation on solar intensity.

- A. Mean of 4 whole-day observations of solar microwave intensity (Bastin et al, 1964)
- B. Calculated variation of solar- 10μ intensity, assuming a 10% increase, by evaporation, of precipitable water during the day.
- C. No evaporation.

latter, and Roach attributed this to aerosol absorption. The evidence for this view is not convincing because inspection of the visibility data and current weather situations suggests that some of the London observations were probably made under clearer conditions than some of the Ascot ones. Again, of the London results, the highest was obtained on the clearest day, and the lowest on the haziest day (see Fig 3.25, showing results for a typical region, $871 - 908 \text{ cm}^{-1}$). Similarly, of the Ascot results, those taken on particularly hazy days are no higher than the average.

It is possibly significant that all of the London observations were made in the afternoon and all except two of the Ascot ones in the morning, and moreover, the vapour pressures were on average higher in the former case. It seems possible that a systematic difference may arise between morning and afternoon observations, which is best explained by reference to Fig 3.26. Consider the variation of solar intensity during a uniformly clear day on which the amount of precipitable water remains constant. Early in the morning, with large zenith angle (Z), the intensity is relatively low but increasing as the sun rises; the plot of $\log I_z$ against $\sec Z$ will be a straight line, ^C~~AB~~. At local noon I_z reaches a maximum, and thereafter returns along the same line as the sun sinks.

However, the assumption of constant water vapour is hardly likely to be valid, especially since these observations must of necessity be made on the type of day when evaporation from the ground

is favoured. An examination of the humidity data for London Airport on the days of Roach's London observations showed that the surface vapour pressure increased on average by 18 % between 0600 and 1800 hrs, the largest increase being 42 %. It is unfortunate that radio - sonde ascents are not timed favourably to observe the diurnal evaporation, the midnight - to - midnight difference probably having as much to do with large scale transport as with evaporation from the ground.

Let us suppose that on a typical sunny day the evaporation amounts to 0.2 cm, which seems reasonable and is about 10 % of that already present in the vertical path. Then the morning and afternoon curves in Fig 3.26 ^(p.30) become separated, so that the afternoon slope is steeper than the morning one. If in addition one assumes that there is a self - broadening effect proportional to the partial vapour pressure, the separation is even greater. Assuming that most of the evaporation occurs during the middle part of the day, a rough idea of the separation may be obtained; this is shown in Fig 3.26, ^{curve B, p.80} It can be seen that an increase of only 10 % in precipitable water during the day results in about 40 % difference between the slopes of the morning and afternoon curves. On occasion the difference may be much more.

Since Roach took the midday radiosonde ascent, his morning results (Ascot) would be expected to be below the correct value, and conversely for the afternoon ones (London).

The work of Bastin et al (1964) provides good evidence of

Fig 3-27. Variation of apparent absorption coefficient with time of day and zenith precipitable water.

(Derived from emission measurements in 14 windows between 8.1 and 12.9μ made by Bolle (1963) from S. Agata).

The ratio of the values at any hour to the mean for all observations is shown on the ordinate. A measure of the vapour pressure is obtained from the precipitable water, W , in the zenith and is indicated as follows :—

- $W > 2.3 \text{ g cm}^{-2}$
- $2.3 > W > 2.0 \text{ g cm}^{-2}$
- $W < 2.0 \text{ g cm}^{-2}$

Very hazy conditions are indicated by a cross.

the diurnal increase of precipitable water. They observed the variation of solar microwave radiation as a function of solar zenith angle from central London, and although their sample is rather small, the difference between morning and afternoon observations is ^{curve A, p.80} unmistakable (see Fig 3.26).

Saiedy (B.S.S., (1963)), using the same technique as Roach and Goody (1958), but observing only in the mornings from Ascot, obtained results in the $8 - 12\mu$ window throughout the year. Though it was not recognized by Saiedy, the summer results were higher than the winter ones and this is not inconsistent with the self - broadening hypothesis inferred from the present work.

The emission studies of Bolle (1963, 1964), discussed in ^{p.73} § 3.5.1.5, raise some interesting questions. Measurements from Jungfraujoch in the $8 - 12\mu$ region gave results up to five times greater than those from S. Agata, where the vapour pressure was much higher. This could arise if there were some emission from something other than water vapour, since the effect becomes very large as the amount of water vapour decreases. On examination, it is found that the S. Agata results seem to be correlated with the time of day, being maximum at about local noon when they are about double the values in the early morning and in the evening (Fig 3.27). The question arises as to whether this is due to scattering of solar radiation by aerosol or molecules, or to increased self - broadened absorption coefficients in the middle of the day following the diurnal evaporation cycle. The

Fig 3.28. Variation of apparent absorption coefficient with time of day, visual opacity and precipitable water in the zenith. (From the emission measurements of Dave et al (1963) at Ascot in a window at $\nu=897.9 \text{ cm}^{-1}$).

- (a) An index of the aerosol content is obtained from surface visibility data.
- (b) An index of the vapour pressure is obtained from the precipitable water, W , in the zenith.

former seems rather unlikely, because three results obtained on particularly hazy days (excluding fog) are no higher than the average; on the other hand there is a tendency for the results to be higher on days with more water vapour in the zenith, which gives a rough measure of the mean vapour pressure in the atmosphere.

Dave et al (1963), with the spectrometer used in the present work, measured the water vapour continuum in four windows between 897.9 cm^{-1} and 1159.0 cm^{-1} . Dave concluded that aerosol played a significant role in continuum emission, since the latter appeared to be greater under hazy conditions. In a search for other possible correlations, the results for $\gamma = 897.9 \text{ cm}^{-1}$ were plotted as a function of time of day, with vapour pressure and haziness as parameters (Figs 3.28 (a) and (b)). The pressure - corrected mass of vapour in the zenith was taken as a rough index of the vapour pressure, and the visibility data from the site and from London Airport (16 km to the north-east) were used to assess the aerosol content in a scale ranging from 1 for clear to 4 for very hazy. Whilst it is true that four of the six highest results occur under very hazy conditions, the rest are uniformly scattered. The alternative interpretation in terms of vapour pressure seems to be at least as good, the higher results at a given hour tending to occur at higher vapour pressures, with an added tendency for the afternoon results to be higher. This latter effect is similar to that found in the results of Roach and Goody (1958) and Bolle et al (1963), and could be explained by an increase

Fig 3-29. Extinction at 3.97μ and 9.1μ (Taylor and Yates, 1957).

Horizontal paths of 5.5 km (circles) and 16.25 km (triangles) over Chesapeake Bay, and of 27.7 km (squares) between Mauna Lao and Mauna Kea (10000 ft approx) in the Hawaiian Islands.

Data :-

Path length	km	5.5	16.25	5.5	16.25	5.5	16.25	16.25	27.7	27.7
Ppt. water	$g\ cm^{-2}$	2.2	6.7	4.2	15.1	9.4	27.7	37	20	8-13
Rel. Hum.	%	66	41	51	53	73	82	50	100	41
Vapour press.	mb	5.1	5.6	10.4	12.8	23.8	23.5	26.0	9.4	4-6
Temperature	$^{\circ}C$	3	12	18	20	26	23	31	6	0
$-\log_e T(9.1\mu)$		.04	.732	.186	.545	.211	2.12	—	1.273	1.205
$-\log_e T(3.97\mu)$		.342	.618	.104	.478	.116	.693	.356	.655	.755
$-\log_e T(vis)$		.915	1.23	.358	.840	1.20	2.30	3.91	1.35	—

of humidity by evaporation between the 1100 Z radio-sonde ascent and the afternoon observations.

The only other relevant investigation is that of Taylor and Yates (1957), described in § 2.7. ^{p.43} It seems to be the only published measurement at high vapour pressures (> 20 mb) so that it is more readily comparable with the present work, both at 4μ and near 9μ . Values of $-\log_e(\text{transmittance})$
~~The extinction coefficients~~ derived from the published spectra are plotted as a function of precipitable water in Fig 3.29. Although there is a lot of scatter, the absorption coefficients in both windows show no sign of increasing with vapour pressure, and at 9.1μ the value of $0.07 \text{ g}^{-1} \text{ cm}^2$ is in good agreement with all previous work. The 4μ observations show no correlation with water vapour at all, and evidently the extinction has to be explained otherwise; however, nor is there any correlation with the visual extinction.

Mention should also be made of the $8 - 12\mu$ window observations made by Tiros III. Although there is some uncertainty regarding absolute calibration of the radiometer, it seems that the inferred effective temperatures are considerably lower (5 to 15°K) than the actual temperature, even after allowing for continuum and line emission in the window (see, e.g., Nordberg et al, 1962). This points to a 'dirtier' window than had been expected. The differences between between satellite inferred and actual temperatures are being examined for a correlation with vapour pressure for regions where the relevant conditions are known. This implies restriction to sea surface

Fig 3.30. Observed self- and foreign-broadened continuum absorption coefficients, 8.5-40 μ .

observations with a clear atmosphere to avoid uncertainty regarding the surface emissivity. No results are available yet.

In conclusion, were it not for the results of Taylor and Yates' measurement at high vapour pressure, it would be possible to claim that the work described in § 3.5.2.1^{p.77} and § 3.5.2.2^{p.79} is not inconsistent with previous results, though no positive evidence has been found to support it. A possible explanation of the differences between earlier works has been suggested, but clearly difficulties remain to be resolved.

3.5.3 Summary of all results

All available data for the region $8-40\mu$ have been assembled in Fig 3.30. It falls naturally into two groups, attributed to self - and foreign - broadening. Much of the work in the $8 - 12\mu$ region was conducted at low vapour pressure so that these results correspond largely to foreign - broadening, with, however, a systematic spread arising from the effects of self - broadening described in § 3.5.2.3^{p.79}. The increase in the foreign - broadened component from 1100 cm^{-1} to 1200 cm^{-1} is probably due to the wings of lines in the 6.3μ water vapour band.

3.6. Comparison between observation and theory

The results given in § 3.5.3 are now compared with the values expected on the basis of accumulated wings of the profiles

Fig 3-31. Contribution of rotation lines to continuum
at $\nu=800$, 559.4 and 261 cm^{-1} .

(SEE ALSO ADDENDUM)

Upper section: Lorentz line shape. Lower section: Van Vleck line shape.
Computed for nitrogen-broadened half-width for temperatures of 300°K
(solid lines) and 260°K (dashed lines)

Benedict and discussed in § 1.2.2.2. Using Kaplan's (1963) tables of rotation line intensities and half widths, and $H_2O - H_2O$ line half widths derived from Benedict and Kaplan (1964), the foreign - and self - broadened absorption coefficients were calculated for 7 windows between 800 and 261 cm^{-1} for the Lorentz, full Lorentz and Van Vleck profiles. The calculations were made for temperatures of 300°K and 260°K , and the results are given in Table 3.2. (p.37)

To illustrate the relative contributions of lines in the 50μ band, a selection of the results is plotted for 20 cm^{-1} intervals in Fig 3.31.* The temperature dependence of the contributions changes from negative in the $0 - 260\text{ cm}^{-1}$ region to positive thereafter. For the Lorentz line shape, most of the absorption at 800 cm^{-1} arises from lines in the region $50 - 350\text{ cm}^{-1}$, so that the overall temperature dependence is small (-0.1% per $^\circ\text{C}$ at 300°K): at 559.4 cm^{-1} , about 30% of the total absorption arises from lines within 20 cm^{-1} , largely accounting for the overall temperature dependence of $+0.3\%$ per $^\circ\text{C}$; at 261 cm^{-1} nearly all absorption arises from lines within 20 cm^{-1} , so that the temperature dependence is again very small ($+0.1\%$ per $^\circ\text{C}$).

The full Lorentz shape gives results only slightly higher than ordinary Lorentz in the region $250 - 400\text{ cm}^{-1}$, but then gives progressively larger values until they are twice Lorentz at 800 cm^{-1} .

For the Van Vleck shape the continuum for $\nu > 500\text{ cm}^{-1}$ arises largely from lines between 0 and 100 cm^{-1} , so that here the

* See also Addendum. (p.43)

Table 3.2* Computed absorption coefficients for various line shapes

	Ordinary Lorentz		Full Lorentz		Van Vleck		
ν , cm^{-1}	300	260	300	260	300	260	T, °K
261	62.5	60.4	65.5	64.0	73.5	73.5	
310	59	48	61	50	69	60	
367	12.2	9.4	13.2	10.5	19.9	18.9	NITROGEN
412	4.65	3.54	5.45	4.34	12.5	13.1	BROADENING
478.8	2.60	2.22	3.16	2.92	10.0	11.2	
559.4	0.560	0.500	0.873	0.930	7.93	9.30	
800	0.115	0.121	0.300	0.318	6.81	8.54	
261	364	348	354	344	429	431	
310	322	265	340	285	379	334	
367	67	54	73	60	107	106	
412	26.0	20.5	30.4	25.3	69	75	SELF
478.8	14.4	12.0	17.6	15.4	55	63.7	BROADENING
559.4	3.19	2.94	5.39	5.41	42	53	
800	0.643	0.732	1.68	1.87	37.0	48.1	

The tabulated quantities are mass absorption coefficients, in units of $\text{g}^{-1} \text{cm}^2 \text{atm}^{-1}$.

* See also Addendum. (p. 93)

Fig 3.32. Comparison between observation and theory. (SEE ALSO ADDENDUM)

143

temperature dependence is negative (0.5 % per °C); for $\nu < 500$ cm^{-1} the contribution from lines within 20 cm^{-1} becomes more important so that the temperature dependence is very small near 260 cm^{-1} .

Since all three line profiles are very similar within about 20 cm^{-1} of line centres, the calculated absorption coefficient in the region 260 - 300 cm^{-1} is not sensitive to the choice of line profile, most of the absorption arising from nearby lines.

On average, continuum absorption coefficients computed from $\text{H}_2\text{O} - \text{H}_2\text{O}$ collision half widths are between 5.5 and 6.0 times those for $\text{H}_2\text{O} - \text{N}_2$ collisions.

The computed values for 300°K are shown in Fig 3.32^{*}, together with the observations summarised in § 3.5.3^{p.85} for comparison. Agreement between the observed foreign - broadened contribution and that computed from the Lorentz profile is very good. On the other hand, the self - broadened component is not well represented by any of the computed curves, because although there is quantitative agreement with the Van Vleck curve at 20 μ , the frequency and temperature dependence is not correct.

It is possible that the absorption attributed here to self - broadening of water vapour lines is due instead to a broad band of the molecule $(\text{H}_2\text{O})_2$. Rough calculations suggest that there should be such a band in the far infrared and, moreover, that it should have

* See also Addendum. (p.93)

very wide lines resulting in continuum - like absorption. All evidence suggests that $(\text{H}_2\text{O})_2$, if it occurs in water vapour, forms only a very small fraction under atmospheric conditions ($< 0.2\%$ in saturated vapour at 20°C , Dorsey, 1940, p 56). However, its abundance would be expected to be roughly proportional to vapour pressure and to decrease rather rapidly with temperature, which might explain qualitatively the vapour pressure and temperature dependence of the observed absorption.

3.7. Conclusion

Partly from the present work, and partly from a re-examination of previous work inspired by it, the following picture of continuum extinction in the region from 7μ to 40μ is suggested:

- 1) There seem to be two ~~separate~~ sources of absorption with different frequency and temperature dependence: a) a foreign - broadened component which, at least in the region $20\mu - 40\mu$, is roughly proportional to the foreign gas pressure. Although it was not possible to measure its temperature dependence directly, it seems likely to be positive and of order $0.5\% - 1\%$ per $^\circ\text{C}$. Its magnitude in the region $12\mu - 40\mu$ is roughly what would be expected from accumulated Lorentz line-wings from the 50μ rotation band; b) a self - broadened component, roughly proportional to the partial vapour pressure, with

strong negative temperature dependence ($\sim 2\% ^\circ\text{C}^{-1}$ at 30°C). Its magnitude is not well represented on the basis of any proposed line shape, but the Van Vleck shape together with the half - width for water - water collisions gives the nearest agreement (a factor of 2); however, the frequency dependence is not correct.*

- 2) There is little evidence that aerosol absorption (other than fog) plays any important role, and examination of the positive inferences drawn by previous workers shows that the evidence is equally well (or better) explained on the basis of self broadening together with an inherent systematic error in their technique arising from diurnal evaporation.
- 3) Unexpectedly high absorption (4 times expected) was observed in the relatively transparent $4 - 12\mu$ region. The measurements had to be conducted at high vapour pressure (~ 30 mb), and the results might be reconciled with the previous work at lower pressures (< 10 mb) on the basis of self broadening. However, one previous investigation at vapour pressures up to 25 mb shows no evidence of this, and, moreover, gives essentially the same result as that of all other workers. This point requires further careful investigation.

* See also Addendum. (p. 95)

- 4) The 15μ CO_2 band does not give any detectable continuum outside the range $12.7\mu < \lambda < 17.8\mu$ (transmittance $> 99\%$ for 43 atm - cm of CO_2). This confirms theoretical evidence that CO_2 line - wings cut off more sharply than the Lorentz profile.

The results have important consequences, both theoretically and practically. Regarding the foreign - broadened continuum, the results show very good agreement with computation based on the Lorentz profile thereby giving confidence in its application in extreme line - wings. The self - broadened contribution, however, is not well represented, particularly regarding the frequency and temperature dependence, by any suggested line shape.* There is a possibility that water molecules polymerise, giving a small fraction of $(\text{H}_2\text{O})_2$, and the latter may give rise to a band of very broad lines, resembling a continuum.

The inference of the temperature and composition of the earth and atmosphere from satellite radiation observations requires correction for the water vapour continuum. It is possible that the discrepancies already found from early Tiros observations between actual and inferred temperature may be explained by a proper treatment of the continuum; this has not been attempted in the present work because the results in the $8 - 12\mu$ region are open to doubt, so that further measurements must be awaited.

* See also Addendum (p.93)

Any future experimental work must be very carefully controlled if the parameters of the absorption are to be disentangled - clearly, any open atmosphere measurement is bound to fail. The experiment described in this thesis was not designed with such a complicated picture in mind and consequently the measurements are in some cases pushed to the limit to reach a conclusion.

Fig 3-31. Contribution of rotation lines to continuum at $\nu=800$, 559.4 and 261 cm^{-1} (amended).

Upper section: Lorentz line shape. Lower section: Van Vleck line shape. Computed for nitrogen-broadened half-width for temperatures of 300°K (solid lines) and 260°K (dashed lines)

Fig 3-32. Comparison between observation and theory(amended).

ADDENDUM

p.7 I am indebted to Dr. L. D. Kaplan for pointing out that Eq. 1.4 is only strictly valid when ν and ν_0 are both small, or, alternatively, nearly equal. The general expression, allowing for induced emission, is

$$k(\nu) = \frac{S\alpha}{\pi} \frac{1 - e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu_0}{kT}}} \left(\frac{\nu}{\nu_0} \right) \left[\frac{1}{(\nu - \nu_0)^2 + \alpha^2} + \frac{1}{(\nu + \nu_0)^2 + \alpha^2} \right] \quad 1.4$$

(p.87) The effect of this is to modify the values given in Table 3.2, and those in Figs. 3.31 and 3.32 as shown in the following amended versions

Table 3.2 (amended). Computed continuum for Van Vleck profile.

ν , cm ⁻¹	261	310	367	412	478.8	559.4	800
Self-broadening { 300°K	404	363	92	50	34.9	20.4	12.7
{ 260°K	384	303	83	48	37.0	23.3	14.9
Foreign-broadening { 300°K	69.0	66.4	16.7	9.1	6.3	3.7	2.3
{ 260°K	68.1	54.4	14.6	7.9	6.3	3.9	2.6

The quantities tabulated are the mass absorption coefficients, in g cm² atm⁻¹.

The frequency dependence of the computed values is now much closer to that observed, although the latter are larger than the former by a factor of 2 or 3 for $\nu < 500$ cm⁻¹, and by 1.5 to 2.0 for $\nu > 500$ cm⁻¹.

The temperature dependence is still negative for $\nu > 400$ cm⁻¹, but is reduced in magnitude, being about - 0.4% per °C at $\nu = 800$ cm⁻¹ for self-broadening at 300°K.

APPENDIX 2.1. OBSERVATIONAL DATA FOR WINDOWS 14, 17 AND 19 (ASCOT).

- Y — YEAR :- 0 = 1960 ; 1 = 1961 .
- MM — MONTH ; DD — DAY ; HHHH — TIME, GMT.
- P — OPTICAL PATH :- 1; $L_2 = 404\text{m}$. 2; $L_2 = 414\text{m}$. 3; $L_2 = 206\text{m}$
 $L_1 = 10\text{m}$ $L_1 = 216\text{m}$ $L_1 = 10\text{m}$
- eee — WATER VAPOUR PARTIAL PRESSURE $\times 10$ (mb).
- TT — TEMPERATURE, °C. RR — RELATIVE HUMIDITY, %.
- yyy — MEASURE OF AEROSOL = $\frac{3.9}{V_L} \frac{100 - R_L}{100 - R_A} \frac{L_2 - L_1}{m} \left(\frac{I}{I_0}\right)^{1/2}$ (SEE TEXT).
- mmm — MASS OF WATER VAPOUR IN PATH, g cm^{-2} .
- $\beta\beta\beta$ — $-1000 \log_e$ (TRANSMITTANCE).
- RRR — $100 \times$ MASS ABSORPTION COEFFICIENT.

Y	MM	DD	HHHH	P	eee	TT	RR	yyy	mmm	WINDOW 17		WINDOW 19		WINDOW 14
										$\beta\beta\beta$	RRR	$\beta\beta\beta$	RRR	$\beta\beta\beta$
0	08	16	0905	1	141	17	70	006	420					391
		17	0930	1	141	17	73	014	425					371
		17	1630	1	117	18	56	010	352					646
		18	1030	1	171	19	88	031	545					783
		18	1350	1	167	19	77	018	485					765
		18	2000	3	134	12	97	158	210					398
		19	0900	3	129	15	74	012	202					323
		22	1650	1	189	20	80	011	553					712
		23	2200	1	154	13	99	999	472					712
		25	2300	3	137	12	98	091	218					398
		26	1730	1	152	19	70	008	474					688
		27	1200	1	165	21	67	007	497					666
		27	1410	1	159	20	70	008	497					698
		28	1540	1	156	19	71	009	465					698
		28	1855	3	158	16	86	011	243					411
		29	1618	3	146	19	66	005	226					380
		31	1200	3	143	20	62	014	223					378
0	09	02	1015	3	159	18	80	012	251					399
		08	1730	1	151	18	73	050	435					668
		09	1510	1	162	19	74	021	505					727
		09	1630	1	149	19	69	023	445					698
		10	1810	1	163	20	72	028	505					717
		12	1027	1	162	18	74	047	483					736
		12	1236	3	176	23	62	035	269					409
		13	1650	3	115	19	53	014	179					373
		15	1650	1	108	15	63	013	323					635
		24	1852	1	135	12	96	580	417	678	156	1170	280	690

Y	MM	DD	HHHH	P	eee	TT	RR	yyy	mmm	WINDOW 17		WINDOW 19		WINDOW 14	
										$\beta\beta\beta$	$\mathcal{R}\mathcal{R}\mathcal{R}$	$\beta\beta\beta\beta$	$\mathcal{R}\mathcal{R}\mathcal{R}$	$\beta\beta\beta$	
0	09	25	1744	1	117	16	63	030	353	519	143			624	
	09	27	2212	1	091	09	82	045	289	362	121			591	
	09	29	1655	1	118	14	77	046	374	556	145			619	
	10	11	1242	1	072	10	58	021	221	270	118			542	
		11	1437	1	070	10	56	021	217	252	112			515	
	11	08	1155	1	075	05	88	020	233	364	150			623	
		08	1245	1	075	06	80	126	233	364	150			633	
		09	1452	1	081	09	71	022	252	355	143			566	
			1512	1	082	08	74	024	256	367	140			571	
			1529	1	082	08	76	026	258	381	150			570	
			1615	1	085	07	82	033	266	390	149			564	
			1730	1	081	07	83	038	253	382	153			582	
			1803	1	081	06	85	042	254	374	149			575	
			1817	1	080	06	84	040	251	376	152			577	
			1845	1	077	06	83	039	243	366	152			575	
			1858	1	075	06	83	040	237	372	159			577	
			1925	1	075	05	86	047	238	359	152			569	
			1948	1	075	05	87	052	236	371	158			564	
			2009	1	075	05	87	053	235	373	160			564	
	15		1243	1	092	11	73	021	287	461	159			623	
			1610	1	085	05	95	120	269	430	156			589	
	18		1522	1	098	09	86	037	307	499	159			612	
			1600	1	096	08	87	041	299	477	157			603	
			1645	1	097	07	94	088	304	536	174			653	
	22		1600	1	102	09	88	042	315	525	164			620	
	24		1514	1	090	10	74	017	278	468	166			662	
			1613	1	091	09	77	020	283	487	169			666	
			1635	1	089	10	74	017	270	475	174			656	
	25		1035	1	096	10	77	030	295	482	161			603	
	29		1031	1	100	08	90	032	311	487	154			600	
0	12	01	1435	1	101	11	75	013	313	473	154			589	
			1500	1	100	11	75	013	310	461	152			589	
			1525	1	101	11	76	013	313	472	154			589	
			1530	1	101	11	76	013	313	490	159			598	
			1600	1	102	11	79	015	317	495	159			601	
			1617	1	104	11	81	016	323	496	157			604	
			1637	1	104	11	82	017	324	500	157			603	
		02	1410	1	084	08	79	010	268	405	153			587	
			1451	1	084	08	77	011	266	371	142	0681	254	587	
			1519	1	084	07	82	012	266	381	144	0676	254	591	
			1626	1	081	06	88	018	260	370	143	0676	254	579	
			1701	1	079	05	91	027	252	364	146	0645	248	575	
			1727	1	077	04	91	028	246	361	148	0637	253	575	
			1750	1	077	04	92	031	246	361	148	0630	256	581	
			1805	1	078	05	89	022	250	350	143	0632	257	582	
0	12	02	1805	1	078	05	89	022	250	367	148	0637	255	582	
1	01	12	1430	1	076	07	76	104	241	359	146			591	
			1620	1	079	07	80	120	252	377	146			615	
			1705	3	079	06	82	128	129	220	167			356	
		20	1635	3	078	04	88	170	127	207	146			359	
			1722	1	075	04	92	360	239	360	148			567	
			1740	1	074	05	94	170	237	360	160			564	
	03	09	1457	1	102	12	72	350	321	498	153	0876	273	712	
			1515	1	099	12	72	355	314	510	160	0913	291	730	
			1534	1	101	12	72	351	317	495	154	0922	291	729	
			1629	1	101	11	74	389	317	509	158	0888	280	738	

Y	MM	DD	HHHH	P	eee	TT	RR	yyy	mmm	WINDOW 17		WINDOW 19		WINDOW 14	
										$\beta\beta\beta$	$k k k$	$\beta\beta\beta\beta$	$k k k$	$\beta\beta\beta$	
1	03	09	1643	1	096	11	73	392	305	482	156	0878	288	742	
			1700	1	099	11	76	457	314	492	155	0898	283	758	
			1729	1	096	09	85	430	305	512	165	0917	301	795	
			1739	1	097	09	85	425	310	507	161	0904	292	788	
			1755	1	095	09	84	414	302	528	173	0930	308	801	
			1817	1	093	08	88	550	298	541	179	0955	321	815	
			1840	1	091	07	92	860	293	537	180	0925	316	811	
			1920	1	089	06	95	7999	285	550	190	0917	322	834	
		15	1455	1	072	20	31	022	222	340	154	0590	246	661	
			1520	1	073	20	32	022	223	337	152	0570	256	665	
			1545	1	074	20	33	022	227	337	149	0572	252	677	
			1615	1	075	19	35	021	231	307	133	0540	234	648	
			1640	1	071	18	34	022	218	299	137	0525	241	646	
			1705	1	066	17	33	024	208	307	151	0521	257	654	
			1735	1	064	17	33	024	199	296	143	0491	246	643	
			1800	1	073	14	46	026	230	267	114	0485	211	636	
		17	1505	1	100	14	64	018	310	521	168	0901	291	629	
			1529	1	099	14	64	018	309	504	163	0886	287	634	
			1636	1	094	12	69	020	273	521	177	0882	301	643	
			1756	1	097	10	78	031	301	536	183	0950	316	649	
			1823	1	095	10	77	030	296	500	167	0887	300	625	
			1644	1	074	15	42	018	226	354	161			639	
	05	31	1644	1	074	15	42	018	226	354	161			639	
	06	01	0036	1	077	06	85	070	233	378	164			610	
		02	1141	1	112	16	59	034	342	502	151	0950	278	659	
	03		1329	1	105	16	55	034	320	489	157	0898	281	657	
			1423	1	102	18	51	031	308	477	160	0875	284	672	
			1539	1	107	16	59	035	330	530	165	1000	303	675	
			2325	1	096	07	96	400	303	498	166	0942	311	730	
			0006	1	092	06	95	330	289	478	168	0849	294	763	
			0023	1	088	05	98	910	280	473	170	0887	317	767	
			0150	1	092	06	96	414	290	480	168			734	
			0820	1	113	16	61	036	344	505	151	0929	270	680	
			0858	1	107	17	55	033	330	484	151	0891	270	678	
			0930	1	108	18	53	031	330	495	155	0891	270	690	
			1020	1	107	19	49	030	326	504	160	0925	284	698	
			1029	1	104	19	48	029	318	501	163	0915	288	687	
			1059	1	108	20	47	028	328	517	163	0970	296	696	
			1130	1	111	20	47	028	336	529	163	0918	273	700	
			1203	1	110	20	47	028	334	525	163	0971	291	705	
			1230	1	115	21	45	025	348	547	163	0956	275	710	
			1337	1	113	22	43	025	342	516	157	0985	288	665	
			1525	1	115	20	48	027	348	540	161	1043	300	685	
			1708	1	120	20	51	027	361	598	171	1113	309	679	
	16		1345	1	148	20	64	017	448	811	185				
			1413	1	150	21	61	016	455	803	181				
			1432	1	156	22	60	015	466	819	179				
			1434	1	166	23	60	014	497	795	163				
			1436	1	158	22	60	014	474	764	164				
			1437	1	161	22	59	014	484	795	168				
			1523	1	153	22	58	015	459	794	177				
			1540	1	144	20	61	016	440	772	179				
			1600	1	151	21	61	016	456	800	180				
			1633	1	146	21	60	015	440	779	181				
			1815	1	144	19	65	018	438	769	179				
			1857	1	148	18	70	020	453	810	182				
			1934	1	151	17	77	008	460	839	184				

										WINDOW 17	WINDOW 19		WINDOW 14	
Y	MM	DD	HHH	P	eee	TT	RR	yyy	mmm	BBB	RRR	BBB	RRR	BBB
1	06	16	2013	1	149	16	81	009	457	805	179			
			2033	1	146	16	82	010	451	829	186			
		20	1358	1	106	20	46	040	325	483	151			
			1446	1	107	21	42	036	326	477	149			
			1521	1	105	21	43	037	322	496	156			
			1554	1	104	20	44	039	318	490	156			
			1615	1	103	21	42	037	315	493	159			
			1628	1	105	21	42	036	321	507	160			
			1746	1	107	19	48	040	331	512	157			
			1815	1	107	19	49	022	330	508	156			
			1915	1	106	18	53	023	328	517	160			
			1933	1	113	16	61	027	348	526	152			
			1951	1	117	15	72	035	368	578	161			
			2012	1	115	14	74	039	360	606	170			
			2025	1	115	13	77	044	362	608	169			
	24		1400	1	143	27	41	014	423	747	182			
			1410	1	140	26	41	014	415	723	180			
			1459	1	137	26	41	015	406	698	176			
			1615	1	135	26	39	015	400	681	174			
			1647	1	134	26	40	015	398	699	181			
			1805	1	128	25	40	016	381	650	175			
			1846	1	130	24	42	014	388	661	175			
			1925	1	135	23	48	015	404	694	176			
			1935	1	137	22	50	015	411	737	183			
			1952	1	134	21	51	015	404	722	182			
			2010	1	139	20	59	019	423	744	179			
			2027	1	143	20	62	020	436	771	180			
			2029	1	143	20	63	021	433	791	186			
			2030	1	150	20	66	021	455	813	182			
	27		1436	1	103	21	42	012	312	444	145			
			1510	1	096	19	44	012	293	443	153			
			1520	1	095	20	40	011	291	414	147	0721	248	651
			1557	1	094	18	44	013	285	440	156			
			1627	1	092	18	44	014	279	433	157			
			1743	1	091	19	43	013	277	436	160			
			1801	1	077	19	36	013	237	402	172	0611	258	623
			1837	1	078	18	37	013	239	375	164			
			1914	1	079	17	40	013	242	371	155			
			1929	1	084	16	45	014	257	396	155			
			1948	1	088	15	53	016	272	438	162			
			2010	1	093	13	61	018	289	457	162	0792	274	641
			2022	1	096	13	63	017	300	502	168			
	30		1344	1	122	29	32	020	360	627	180			
			1347	1	121	28	33	020	363	626	178			
			1503	1	119	29	29	019	349	574	170			
			1508	1	123	29	30	019	352	596	175			726
			1541	1	120	27	32	020	354	585	170			
			1635	1	134	27	37	019	397	708	184			736
			1758	1	139	25	44	021	417	753	186			
			1804	1	136	25	43	020	408	728	186			747
			1820	1	141	25	44	021	422	735	179			
			1913	1	150	23	54	023	451	794	180			
			1922	1	149	22	55	024	449	800	185			755
			2044	1	157	20	65	029	477	867	189			804
			2048	1	154	20	65	029	465	831	182			
07	28		1600	2	120	20	48	015	129	192	154			

Y	MM	DD	HH	P	eee	TT	RA	yyy	mm	WINDOW 17		WINDOW 19	
										BBB	RRR	BBB	RRR
1	07	28	1736	2	113	18	54	014	161	249	160		
			1830	2	102	17	51	014	147	229	161		
	08	03	1130	2	100	18	50	006	162	209	133		
			2030	2	131	15	77	013	203	296	150		
	08	08	1410	2	115	19	51	006	165	211	132		
			0940	2	119	17	63	006	181	249	141		
	28		1400	2	168	25	52	010	246	343	145		
			1600	2	165	25	49	011	225	372	173		
	29		1530	2	176	30	43	016	255	359	149		
			1615	2	186	30	44	016	255	390	161		
	30		1430	2	133	26	40	013	195	253	135		
			1913	2	142	18	70	026	207	369	184		
			1950	2	140	16	80	037	214	357	162		
			1130	2	122	22	42	031	153	201	136		
	09	04	1520	2	171	17	90	148	268	459	176		
			2030	2	173	16	95	231	261	457	180		
			2120	2	177	16	96	290	254	535	217		
			1550	2	144	18	73	027	226	371	169		
	09	08	0014	2	099	08	95	160	150	221	149		
	08	28	1530	2	168	25	50	010	248			0741	299
	09	12	1000	2	145	16	85	018	225	336	153		
			1040	2	139	17	71	010	191	300	162		
		13	2130	2	125	14	92	030	244	432	181		
			0910	2	146	15	90	018	224	377	173		
			1033	2	139	17	74	008	207	341	170		
			1355	2	167	20	49	005	168	244	150		
			1543	2	113	18	53	006	164	240	152		
			1621	2	118	18	54	010	147	217	153		
	16		1028	2	167	24	61	007	281	452	169		
			1022	2	190	22	68	009	261	475	187		
	19		1128	2	193	23	67	007	273	505	193		
			1340	2	167	24	63	008	283	501	185		
	20		1630	2	165	16	88	014	245	430	181		
			1550	2	152	18	72	010	225	357	165		
	10	04	0900	2	135	14	91	059	229	375	168		
			1025	2	140	17	80	023	260	417	165		
	05		1037	2	123	17	67	009	193	299	160		
			1358	2	154	18	58	007	197	278	146		
			1553	2	119	16	69	010	190	272	147		
			1409	2	132	17	70	010	208	301	149		
	06		1606	2	131	16	73	011	197	312	163		
			1700	2	099	15	66	010	176	298	175	0536	305
	10		0930	2	171	17	86	011	253	444	180		
			1040	2	168	18	82	009	254	448	182		
	12		1128	2	134	15	80	131	191	342	184		
			1345	2	105	17	56	071	161	212	136	0404	251
			1415	2	107	17	56	071	158	217	141	0385	244
			1526	2	118	16	62	066	160	237	152	0425	266
			1630	2	118	14	75	086	184	257	143	0491	267
			1603	2	103	15	60	049	149	196	136	0392	263
	13		1643	2	107	14	70	059	170	244	148		
			1936	2	113	10	90	125	162	244	154		
			2012	2	110	09	95	235	168	248	150	0455	271
			1152	2	107	14	68	012	154	257	171		
	25		1404	2	104	13	67	013	139	208	153		
	27		1425	2	106	12	75	013	153	229	152		
			1421	2	106	12	75	013	154	233	154		

APPENDIX 2.2. OBSERVATIONAL DATA FOR WINDOWS 15, 16, 18 AND 20 (ASCOT).

FOR EXPLANATION OF SYMBOLS, SEE APPENDIX 2.1.

Y	MM	DD	HHH	P	eee	TT	RR	yyy	mmm	$\beta\beta\beta$ 17-15	$\beta\beta\beta$ 17-16	$\beta\beta\beta$ 18-17	RR 18-17	$\beta\beta\beta$ 20-17	RRR 20-17	$\beta\beta\beta$ 17-4	RRR 17-4
0	08	27	1520	1	127	19	68	008	430	028	074	189	44			661	154
		28	1600	1	158	19	73	009	491	-006	047	202	41			766	156
	09	28	1924	3	158	16	87	011	255	021	029	115	45			439	172
		09	1653	1	163	19	75	019	509	018	079	183	36			794	156
		10	1837	1	171	18	81	041	533	028	057	229	43			804	151
		12	1118	1	170	19	76	051	526	070	084	211	40			768	146
		12	1450	3	179	22	67	040	282	040	034	098	36			406	144
		13	1715	3	122	18	58	027	197	100	042	057	29			248	126
		15	1710	1	106	14	63	013	326	161	087	134	41			456	140
		24	1917	1	129	11	98	900	416	085	055	175	42			649	156
	1	08	28	1530	2	163	25	50	010	016	053	122	49	700	282	360	145
		28	2050	2	143	17	90	055	219					628	287	378	173
		29	1628	2	182	29	43	016	254	-009	055	112	44	693	273	409	161
		30	1512	2	137	26	42	013	198	045	046	085	43	471	278	267	135
		30	1936	2	146	16	79	037	220	029	035	121	55	565	257	356	162
		31	1142	2	108	22	40	031	159	044	066	031	20	359	226	216	136

APPENDIX 3-1 (CONTINUED).

101

RUN No.	P	TR	17-4			RRR	18-17			19-17		20-17	
			eee	mmm	ppp		eee	mmm	ppp	RRR	RRR	ppp	RRR
18	5	43	259	712	6087	153							
18	5	41	206	596	0772	130							
18	5	38	118	326	0403	124							
18	5	42	144	403	0483	120							
26	5	27	234	680	1218	181	240	697			1290	185	2255 324
26	5	26	217	630	1095	174	216	629			1145	182	2002 318
26	5	26	205	595	0978	164	203	590			1061	180	1910 324
26	5	26	191	555	0885	159	187	544			0958	176	1700 313
26	5	25	158	459	0651	142	147	430			0696	162	1302 303
26	5	25	143	415	0559	135	130	380			0602	158	1083 285
26	5	24	123	357	0344	096	115	333			0536	161	0962 289
27	4	45	356	972	1900	195	374	1025	1013	99			
27	4	45	308	841	1470	175	321	880	775	88			
27	4	45	274	748	1192	160	282	773	724	94			
27	4	45	236	645	0940	146	242	663	574	87			
27	4	45	209	571	0773	135	213	584	535	92			
27	4	45	160	437	0526	121	163	446	399	89			
27	4	44	108	295	0329	111	106	291	245	84			
28	4	43	359	987	2100	213							
28	4	43	330	907	1773	196							
28	4	43	302	830	1498	181							
28	4	43	277	761	1302	171							
28	4	43	225	619	0927	150							
28	4	43	192	528	0690	131							
28	4	43	140	385	0462	120							
28	4	42	097	267	0300	112							
30	5	33	342	971	2300	237							
30	5	33	310	860	1895	215							
30	5	33	271	770	1487	193	290	826	655	79			
30	5	33	246	699	1238	177	259	737	576	78			
30	5	33	226	642	1082	168	219	624	505	81			
30	5	33	195	554	0877	159	192	547	410	75			
30	5	33	152	432	0587	134	156	445	280	63			
30	5	33	120	341	0391	115	126	359	261	73			
30	5	30	073	208	0249	119	080	229	169	74			
40	5	21					085	252	140	56	0322	128	0608 241
40	5	17					040	120	098	82	0173	144	0302 251
40	5	15					033	100	052	52	0101	101	0212 212
41	6	21	051	151	0137	091	051	151	091	60	0188	124	0334 221
41	6	21	104	308	0359	117	050	148	096	65	0185	124	0332 224
41	6	22	086	255	0285	112	099	293	172	59	0367	125	0682 233
41	6	21	062	184	0191	104	091	270	153	57	0346	128	0624 231
41	6	18	045	133	0145	109	081	239	137	57	0305	128	0578 241
41	6	14	032	095	0081	085	058	172	109	64	0211	123	0403 203
41	6	11	029	088	0094	107	042	126	070	56	0170	135	0299 237
41	6	11	029	088	0101	115	031	094	052	55	0119	127	0203 216
41	6	11	032	095	0096	101	031	095	045	47	0099	104	0217 229
42	5	31	130	371	0428	115	127	364	276	76	0535	147	0927 255
42	5	32	115	329	0373	113	113	323	241	75	0469	145	0833 258
42	5	33	104	297	0333	112	104	296	211	71	0430	145	0760 257
42	5	32	096	274	0324	118	095	271	230	85	0425	157	0742 274
42	5	31	087	249	0272	109	084	241	197	82	0366	152	0642 266
42	5	27	064	183	0210	115	062	180	128	71	0252	140	0448 249
42	5	23	054	155	0185	119	054	159	126	79	0209	131	0398 251
43	5	11	050	153			050	153	100	65	0190	124	0318 208
43	5	20	061	180			061	180	132	73	0225	125	0419 233
43	5	28	078	224			078	224	155	69	0309	138	0550 245
43	5	34	093	263			093	263	215	82	0387	147	0711 270
43	5	39	102	284			102	284	229	81	0438	154	0804 283
43	5	40	049	151			049	151	095	63	0171	113	0309 205

APPENDIX 3.2. OBSERVATIONAL DATA FOR WINDOWS 4, 8, 11 AND 13 (LONDON).

P - PATH LENGTH :-
 2 - 115.5 m.
 3 - 177.2 m.
 4 - 239.0 m.
 5 - 300.7 m.
 6 - 362.4 m.
 7 - 424.2 m.
 8 - 485.9 m.

TT - TEMPERATURE, °C.
 eee - PARTIAL WATER VAPOUR PRESSURE X 10, mb.
 mm - MASS OF WATER VAPOUR IN PATH X 1000
 (SCALED TO A PATH LENGTH OF 402 m), g cm⁻².
 Si - SIGNAL IN WINDOW i. (log_e Si is
 SCALED TO A PATH LENGTH OF 402 m).

WINDOW 4

RUN No.	P	TT	eee	mm	log _e Si	RUN No.	P	TT	eee	mm	log _e Si	RUN No.	P	TT	eee	mm	log _e Si
01	4	31	112	318	121	03	5	38	208	581	196	07	5	27	191	553	301
		32	159	453	179			39	250	698	233			29	231	665	327
		32	182	519	239			39	278	773	263			31	262	748	364
		32	208	595	241			40	313	845	307			33	291	825	441
		32	257	735	320	03	6	30	107	306	088	07	6	28	142	417	131
		33	281	800	385			38	172	481	140			27	192	558	185
		31	132	377	301			38	203	568	173			30	232	665	236
02	3	26	132	370	112			39	250	698	215			31	262	750	303
		37	182	508	161			39	275	767	238			33	293	831	428
		38	243	679	265			40	307	850	302	07	7	23	142	418	133
		39	290	805	341	03	7	30	107	307	070			27	189	545	209
		39	340	945	382			38	169	475	127			30	232	667	231
		38	365	1020	403			38	200	561	165			31	262	751	283
03	2	30	109	310	170			39	244	680	182			33	291	828	328
		38	175	488	241			39	273	760	203	27	4	45	356	972	424
		38	212	592	262			40	304	845	252			45	308	841	387
		39	258	718	288	07	2	21	135	397	125			45	274	748	342
		39	288	797	349			26	189	547	222			45	236	645	265
		40	325	898	383			29	234	672	317			45	209	571	217
03	3	30	107	304	108			29	220	630	343	28	4	43	359	987	340
		38	172	480	204			31	267	759	412			43	330	907	290
		38	207	580	234			33	300	850	501			43	302	830	256
		39	258	716	289	07	3	22	137	404	060			43	277	761	257
		39	287	800	314			26	191	553	186			43	225	619	191
		40	319	885	344			29	235	671	196			43	192	528	163
03	4	30	110	317	112			31	265	757	280			43	140	385	094
		38	170	475	187			33	293	833	314			42	097	267	-038
		38	208	583	227	07	4	22	138	406	118	42	5	31	130	371	322
		39	253	707	314			26	191	554	204			32	115	329	317
		39	283	791	338			29	234	670	247			33	104	297	328
		40	315	875	344			31	265	758	283			32	096	274	277
03	5	30	107	306	102			33	295	838	337			31	087	149	268
		38	170	475	161	07	5	23	140	413	182			27	064	183	175

APPENDIX 3.2 (CONTINUED).

103

WINDOW 8																	
RUN No.	P	T	eee	mmm	log _e Si	RUN No.	P	T	eee	mmm	log _e Si	RUN No.	P	T	eee	mmm	log _e Si
22	5	44	298	818	164	33	7	36	227	640	122	37	5	38	306	856	228
		43	146	400	044			36	237	668	138			38	244	683	173
23	5	23	176	518	099			36	248	699	154			37	142	398	060
		23	103	300	048			36	257	725	168	39	5	40	114	318	044
24	5	33	248	706	172			36	265	747	181			40	151	420	078
		33	107	305	030			37	241	679	213			40	183	510	096
33	7	36	109	307	027			35	122	344	043			40	210	585	114
		36	115	324	035	25	5	37	242	680	163			40	234	650	132
		36	134	378	043			37	122	343	035			40	256	719	151
		36	149	420	052	29	5	25	100	292	044			40	275	765	173
		36	163	460	061			26	205	600	104			40	298	830	191
		36	175	493	072			26	131	383	044			40	317	881	205
		36	189	532	085	31	5	32	270	771	198			40	335	933	226
		36	202	570	098			32	150	429	060			43	300	835	193
		36	215	605	109	37	5	38	115	322	030			41	141	392	027

WINDOW 11																	
RUN No.	P	T	eee	mmm	log _e Si	RUN No.	P	T	eee	mmm	log _e Si	RUN No.	P	T	eee	mmm	log _e Si
13	3	22	117	346	117	15	4	37	305	859	488	32	5	24	173	511	140
		33	290	858	363			36	166	467	267			24	113	334	062
		23	085	251	113			35	166	467	269	37	5	38	115	322	132
15	4	37	140	394	258	22	5	44	298	818	301			38	206	856	370
		37	170	479	321			43	146	400	153			38	244	683	290
		37	206	580	343	23	5	23	176	518	177			37	142	398	168
		37	235	660	388			23	103	303	098	39	5	40	114	318	237
		37	245	689	402	24	5	33	248	706	314			43	300	835	450
		37	260	732	428			33	107	305	156			41	141	392	244
		37	270	760	448	25	5	37	242	680	333	33	7	36	109	307	020
		37	280	788	465			37	122	343	164			37	241	679	219
		37	290	815	479	31	5	32	270	771	328			35	122	344	096
		37	310	872	518			32	150	429	154						

WINDOW 13																	
RUN No.	P	T	eee	mmm	log _e Si	RUN No.	P	T	eee	mmm	log _e Si	RUN No.	P	T	eee	mmm	log _e Si
16	4	35	147	415	309	19	5	22	155	459	137	21	5	26	205	600	271
		36	150	423	305			21	101	299	073			26	131	383	182
		36	162	457	319	20	8	23	193	570	272	31	5	32	270	771	460
		36	180	508	350			22	105	311	135			32	150	429	222
		36	195	550	379	21	8	41	285	793	372	32	5	24	173	511	153
		36	215	604	415			40	253	704	340			24	113	334	053
		36	235	663	450			39	138	386	186	33	7	36	109	307	143
		36	255	720	490			39	141	395	186			37	241	679	378
		36	276	779	529	22	5	44	298	818	352			35	122	344	198
		36	204	857	575			43	146	400	173	37	5	38	306	856	581
		36	323	910	615	23	5	33	176	518	209			38	244	683	472
		37	325	917	615			33	103	303	106			37	142	398	293
		32	119	340	270	24	5	33	248	706	388	39	5	40	114	318	260
19	5	21	100	296	108			33	107	305	196			43	300	835	530
		23	174	515	164	29	5	25	100	292	134			41	141	392	260

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On the Atmospheric Infrared Continuum

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Observations of extinction in the atmospheric continuum at 19 frequencies between 1202 and 479 cm^{-1} have been made by two methods: (I) solar absorption, between 1202 and 790 cm^{-1} ; (II) 200 and 400 m horizontal paths using a Nernst source, between 716 and 479 cm^{-1} . Method I was made absolute by reference to a blackbody; Method II provided extinction coefficients relative to that for 1119 cm^{-1} , given by Method I. In Method I, the water vapor in the path was deduced from the area of the line at 871 cm^{-1} , and some measure of the particulate matter in the path was obtained from the extinction in the visible. In Method II, the horizontal visibility was used for the latter purpose, and observations with a cell of pure CO_2 were made in order to determine the limits of CO_2 absorption.

The following conclusions are drawn from the observations: (1) The results strongly support Elsasser's suggestion that the continuum is mainly due to the accumulated wings of distant lines in the water-vapor bands at 1595 and 200 cm^{-1} . The observed absorption coefficient increases from 0.06 $\text{g}^{-1} \text{cm}^2$ at 1100 cm^{-1} to about 4.1 $\text{g}^{-1} \text{cm}^2$ at 480 cm^{-1} , though nearby lines account for half of the latter. (2) None of the line shapes examined gives a satisfactory representation of the continuum over the whole range studied, though Lorentz shape, in both approximate and exact form, gives qualitative agreement with observation. (3) In the interpretation of the observations reported here, CO_2 absorption may be ignored outside the frequency range 790 to 560 cm^{-1} . It is much more confined than would be the case if the CO_2 line wings had Lorentz structure. (4) The extinction due to particulate matter is small compared with that due to water vapor throughout the range observed, except under very hazy dry conditions. (5) Evidence is presented for a considerable self-broadening effect (about 30 times air broadening), and if correct, this will be of the utmost importance in the analysis of remote terrestrial radiation measurements which involve correction for the water-vapor continuum. This must, however, be confirmed under controlled conditions.

1. INTRODUCTION

THE existence of a continuum (Lambert's law absorption) in the so-called atmospheric window between 8 and 13 μ and beyond, due to the wings of strong lines in the water-vapor bands on either side of the window, was first suggested by Elsasser (1938). Moller (1942) demonstrated its probable meteorological importance in representative conditions by calculating a cooling rate of about 1 $^\circ\text{C}/\text{day}$ for the first two kilometers of the atmosphere, assuming a continuum absorption coefficient β of 0.1 per unit air mass around 10 μ .

Observations on the transmission of infrared radiation through the atmosphere, using low-resolution spectrometry ($\sim 10 \text{ cm}^{-1}$ at 1000 cm^{-1}) (a) over a long horizontal path (Gebbie *et al.*, 1951; Taylor and Yates, 1957), and (b) using the sun as source (Adel, 1939; Anthony, 1952), showed the existence of larger attenuations than would be expected from selective absorption alone, while later, Roach and Goody (1958), from observations on the sun with a resolution of 7 cm^{-1} , estimated a continuum absorption as a function of water vapor in the path from the combined effects of continuum and selective absorption. In the latter work, error in determining the amount of water vapor in the path, lack of data on atmospheric aerosol (already suggested as making a significant contribution to the atmospheric continuum), and the difficulty of separating selective and continuous absorption prevented a firm conclusion on the nature of the continuum.

The present paper describes new measurements made by relatively high-resolution spectrometry in order to

obtain more precise information on the continuum and its origin. Two methods of observation have been used:

Method I: Measurement of continuum extinction between 832 cm^{-1} and 1202 cm^{-1} , using the sun as source and a high-temperature blackbody as reference. The water vapor in the path was determined by simultaneous measurements of the area of a neighboring H_2O rotation line and some indication of the aerosol in the path was obtained, in a part of the series, from the extinction in the visible using the Volz (1959) actinometer.

Method II: Measurement of the continuum extinction between 478.0 and 611.2 cm^{-1} over a horizontal path up to 400 m in length using a Nernst filament source. Observations were also made using a cell of pure CO_2 , 43 cm long, in the path to determine the limits beyond which the continuum is not affected by CO_2 .

The observations were made at Ascot, 40 km to the west of London.

2. METHOD I. BASIS

Let

$k(\nu, \bar{p}, \bar{T})$ be the continuum mass absorption coefficient at frequency ν , effective mean pressure $\bar{p}$, and mean temperature $\bar{T}$;

m, c , the mass of water vapor and carbon dioxide, respectively, in the vertical atmospheric column above unit area;

$\gamma(\nu)$, the extinction coefficient per unit air mass due to aerosol;

N , the air mass (relative to zenith) in line of sight, corrected for earth's curvature and refraction; and

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FIG. 1. Solar spectrum showing the windows used for measurement. Regular N_2O lines may be seen in Window 2. The full spectrum was recorded with an unbloomed indium antimonide filter, while the small section near 1040 cm^{-1} shows the increased resolution achieved with a bloomed filter.

$I_0(\nu)$, $I(\nu)$, the solar intensity at the top and bottom, respectively, of the earth's atmosphere.

Then, assuming no selective absorption,

$$I(\nu) = I_0(\nu) \exp[-N\beta(\nu, \bar{p}, \bar{T})], \quad (2.1)$$

where

$$\beta(\nu, \bar{p}, \bar{T}) = k(\nu, \bar{p}, \bar{T})_{\text{H}_2\text{O}} m + k(\nu, \bar{p}, \bar{T})_{\text{CO}_2} c' + \gamma(\nu). \quad (2.2)$$

Assuming now that the continuum absorption is due to the wings of distant strong lines whose half-width α_i is proportional to the effective pressure, $\bar{p}$ (in the absence of self-broadening, which is assumed to be the case, $\bar{p}$ corresponds to the mean air pressure, defined below), then

$$\beta(\nu, \bar{p}) = k(\nu, p_0)_{\text{H}_2\text{O}} (\bar{p}/p_0) m + k(\nu, p_0)_{\text{CO}_2} c' + \gamma(\nu),$$

or

$$\beta(\nu, \bar{p}) = k(\nu, p_0)_{\text{H}_2\text{O}} m_{\bar{p}} + k(\nu, p_0)_{\text{CO}_2} c' + \gamma(\nu), \quad (2.3)$$

where

$$\bar{p} = \frac{1}{m} \int_0^m p(m') dm';$$

p_0 = standard pressure (taken to be 1000 mbar);

$m_{\bar{p}} = m\bar{p}/p_0$;

c' = mass of CO_2 in the vertical column, scaled for pressure, $= c/2$ for constant mixing ratio.

The temperature dependence of a continuum due to the wings of distant strong lines is not known, but is

likely to be small because line intensities at the center of a band are negatively dependent, and just away from the center are positively dependent, on temperature. As a first approximation, therefore, k is assumed independent of temperature. It then follows from (2.1) and (2.3) that a plot of measured $\beta_{\bar{p}}$ against $m_{\bar{p}}$ will have a slope of $k(\nu, p_0)_{\text{H}_2\text{O}}$ and an intercept of $k(\nu, p_0)_{\text{CO}_2} c' + \bar{\gamma}(\nu)$ provided γ is not correlated with $m_{\bar{p}}$. Differences of γ from its mean value $\bar{\gamma}$ will add scatter to the plot. The questions of temperature dependence, self-broadening, and correlation of γ with $m_{\bar{p}}$ will be taken up again later in the light of the results.

Regarding the determination of $m_{\bar{p}}$, the equivalent width W of a line in the H_2O rotation band, in the square-root region of absorption, is related to $m_{\bar{p}}$ by

$$m_{\bar{p}} = W^2 / (4S_0\alpha_0\bar{\phi}N), \quad (2.4)$$

where S_0 , α_0 = line intensity at T_0 (273°K) and half-width at p_0 , and $\bar{\phi}$ = mean temperature factor $= 1/m \int_0^m \phi(m') dm'$, where ϕ is given by Eq. (4) of Saiedy (1961). The constant $S_0\alpha_0$ for the particular line chosen (871 cm^{-1}) has been measured by Saiedy (1961). $\bar{\phi}$ for this line was found empirically to be related to the surface dew point t_d (°C) by

$$\bar{\phi} = 0.02t_d + 0.90, \quad (2.5)$$

to $\pm 3\%$ in $\bar{\phi}$, provided no sharp inversion was present. In the latter case $\bar{\phi}$ was calculated from the appropriate upper-air sounding.

The square-root law used in (2.4) is valid for the particular line used ($S_0 = 0.444\text{ g}^{-1}\text{ cm}$) from Schwende-

FIG. 2. Typical records of sun and blackbody at 901 cm^{-1} ($11.10\text{ }\mu$). The electrical attenuator, the time, the sector disk number used, and the temperature of blackbody are shown on the record. The rapid increase of solar intensity in the early morning is illustrated.

man and Laurie (1958); $\alpha_0 = 0.047\text{ cm}^{-1}$ from Benedict and Kaplan (1959), provided $N > 1\text{ g cm}^{-2}$, a quantity exceeded throughout the observations reported. The effect of particulate matter, by absorption or scattering, on the equivalent width of a molecular line is negligible since both are slowly varying functions of frequency.

3. METHOD I. OBSERVATIONAL PROCEDURE

The infrared spectrometer (see Saiedy and Goody, 1959), was a small double monochromator using a $7 \times 5\text{ cm}$ Merton replica grating having 1000 lines/cm and blazed for $10\text{ }\mu$ in the first-order spectrum. Higher-order spectra of shorter wavelengths were eliminated by means of an indium antimonide filter with an antireflection coating of lead chloride. A Golay cell detector was used, and the radiation was chopped at 11 cps. A sample solar spectrum in which the resolution is about 0.3 cm^{-1} at 1000 cm^{-1} is shown in Fig. 1. The windows used for measurement are indicated by numbers 1–13 (except Window 4, which was used for Method II), and are listed in Table I.

Absolute measurements of β were made in Windows 11 and 8 which are well away from any absorption lines, and in Window 2 where there are some weak N_2O lines. If the latter are significant they should provide a positive intercept on the β axis of the β, m_p plot.

The value of $I(\nu)$ Eq. (2.1) was determined by comparing the solar intensity at these frequencies with that

of a blackbody at approximately 1300°K , the slitwidth being 2 cm^{-1} . Approximate equality ($\pm 1\text{ dB}$) in signal was achieved by use of an appropriate sector disk (of geometrically determined attenuation) in the solar path, together with a calibrated electrical attenuator. Errors due to nonlinearity in the system were thereby kept to not more than 0.3%. Each solar observation was bracketed between blackbody observations, to allow for slight changes in gain, a representative sequence of observations being shown in Fig. 2.

The value of $I_0(\nu)$ [Eq. (2.1)] at the three frequencies has been determined to better than 1% by Saiedy and Goody (1959) and Saiedy (1960a) and thus $\beta(\nu, \bar{p}, \bar{T})$ can be inferred.

Windows 8 and 11 were examined carefully for any weak absorption lines unreported in the literature, using a slitwidth of 0.4 cm^{-1} and high water vapor ($\sim 25\text{ g cm}^{-2}$) in the path to the sun. A weak unreported line was indeed found at 902.7 cm^{-1} but its intensity, if due to water vapor, is only $0.001\text{ g}^{-1}\text{ cm}$ and its contribution to the continuum using a slitwidth of 2 cm^{-1} could not exceed 0.1%. The effect of other neighboring but more distant lines ($\sim 10\text{ cm}^{-1}$) on these windows, assuming Lorentz line shape, is less than 1%.

In addition to the absolute determination of β for windows 2, 8, and 11, relative values of β were obtained for these and nine other windows (see Table I) between 790 and 1202 cm^{-1} , so as to delineate the frequency

TABLE I. Details of frequencies used in Method I and observed continuum extinction (comparison method).

Window, <i>i</i>	ν (cm^{-1})	Slitwidth (cm^{-1}) and lines in the interval	β_{sel}^a (air mass $^{-1}$)	$k_{\text{H}_2\text{O}}^a$ ($\text{g}^{-1}\text{ cm}^2$)	k_i/k_8	k_{p0} ($\text{g}^{-1}\text{ cm}^2$)	No. of obs, <i>n</i>
1	1202	3.00, N_2O , CH_4	0.007		0.800	0.0740	1
2	1159	2.80, N_2O	0.028		0.650	0.0601	3
3	1128	2.55, N_2O , O_3	0.010		0.643	0.0595	3
5	1095	2.50, O_3	0.010		0.675	0.0625	1
6	986	2.03, CO_2 , O_3	0.016		0.720	0.0666	1
7	962	1.93, CO_2 , H_2O	0.003	0.003	0.741	0.0685	5
8	901	1.70, free			1.000	0.0925	
9	874	1.60, free			1.132	0.105	5
10	846	1.50, free			1.232	0.114	5
11	832	1.43, free			1.288	0.119	7
12	820	1.40, CO_2	0.006		1.285	0.119	5
13	790	1.30, free ^b	b	b	1.704	0.158	3

^a β_{sel} is the computed selective extinction coefficient for N_2O , CO_2 , O_3 , and CH_4 , and $k_{\text{H}_2\text{O}}$ is that for H_2O , for the lines in each window.

^b The contribution from nearby strong CO_2 and H_2O lines may be appreciable. The absorption coefficients k_{p0} are computed from k_i/k_8 (mean of *n* obs taking $k_8 = 0.0925\text{ g}^{-1}\text{ cm}^2$ from Sec. 4).

FIG. 3. Observations of continuum extinction coefficient per unit air mass, $\beta_{\bar{p}}$, for (a) Window 11 (832 cm^{-1}), (b) Window 8 (901 cm^{-1}), and (c) Window 2 (1159 cm^{-1}) as a function of scaled water vapor in the zenith.

dependence of $\beta(\nu)$ more precisely by avoiding error in the absolute measurement of intensities. For this purpose series of observations of relative intensity as a function of air mass were made at several frequencies on suitable clear days, the slope of the regression of $\log$ (relative intensity) against air mass providing β . A constant geometrical slitwidth was used in these observations (see Table I). Since only half the number of windows chosen could be included in one observational day, Window 8 was used as the normalizing point between the two sections of the spectrum to allow for changes in water vapor, etc., from day to day. Blackbody observations at one frequency were used to measure the gain change during a run and the solar signal was kept close to that of the blackbody by means of the sector disks. At frequencies above 960 cm^{-1} all windows (see Table I) contain weak lines of one or other of N_2O , CO_2 , CH_4 , and H_2O and an estimated correction to β was made for their selective absorption based on the solar atlas of Migeotte, Neven, and Swensson (1956-57) and our own high-resolution spectra.

The solar absorption (including equivalent linewidth W) measurements reported here covered the period summer 1958 to summer 1959 and were restricted to clear skies but did not exclude haze. Misty conditions were avoided as signals then fluctuated considerably, sometimes by an order of magnitude. Measurements of extinction at 0.44μ using the Volz actinometer on the sun were introduced in October 1958 to provide some measure of particulate matter in the line of sight.

Saiedy (1961) has estimated the standard error in $m_{\bar{p}}$ from W to be $\pm 8\%$, which is about a third of the error in $m_{\bar{p}}$ obtained from radio sonde humidities from a nearby Meteorological Office station, Crawley.

4. METHOD I. ABSOLUTE VALUES OF CONTINUUM EXTINCTION AND THEIR INTERPRETATION

The results of the absolute measurements of $\beta_{\bar{p}}$ as a function of $m_{\bar{p}}$ for Windows 11, 8, and 2 are given in Fig. 3, (a-c), and the properties of the regressions there shown are listed in Table II. The high correlations

provide good evidence for the source of the continuum being in water vapor, with absorption coefficients k of the amount shown. Since the effect of neighboring lines is small there is a strong presumption that the wings of the lines in the two major H_2O bands are responsible.

The positive intercept (0.042 ± 0.012) on Fig. 3(c) may be attributed to N_2O absorption of 0.028 (air mass) $^{-1}$ in Window 2 (cf. Table I). Regarding the small negative intercepts in Fig. 3(a) and (b), it was assumed in Sec. 2 that k is independent of temperature and self-broadening effects. But a positive temperature coefficient and a self-broadening greater than air-broadening would both cause similar nonlinearity in the relation between $\beta_{\bar{p}}$ and $m_{\bar{p}}$, since high values of $m_{\bar{p}}$ tend to occur with high temperature and high partial pressure of water vapor. Whilst the resulting nonlinearity could not be detected against the scatter in the available observations, with a reasonable magnitude (2% per $^\circ\text{C}$) for the former effect, a straight line fitted to them would then have a negative intercept of about the magnitude which is in fact noticed in Figs. 3(a) and (b); N_2O absorption masks this effect in Fig. 3(c). Equally, a self-broadening to air-broadening ratio of 30 [this high value receives considerable support from the results (Sec. 10) of Method II] would account for the negative intercepts. Apart from this uncertainty in interpretation, Figs. 3(a) and (b) suggest that the contribution of CO_2 to the continuum at these frequencies is very small. Direct evidence is presented later (Sec. 8) that this is indeed so.

TABLE II. Properties of the correlation between $\beta_{\bar{p}}$ and $m_{\bar{p}}$ for Windows 2, 8, and 11.

Window	ν (cm^{-1})	$k_{p_0}^a$ $\text{g}^{-1} \text{cm}^2$	r^b	Intercept on $\beta_{\bar{p}}$ axis (air mass) $^{-1}$	No. of observations
11	832	0.1144 ± 0.0077	0.95	-0.021 ± 0.014	28
8	901	0.0925 ± 0.0061	0.93	-0.015 ± 0.009	35
2	1159	0.0545 ± 0.0098	0.86	$+0.042 \pm 0.012$	12

^a k_{p_0} = the slope of the regression line, i.e., the absorption coefficient (base e) per g of water vapor at pressure p_0 , with standard error.

^b r = correlation coefficient between $\beta_{\bar{p}}$ and $m_{\bar{p}}$.

FIG. 4. Deviation $\Delta\beta_8$ of observed extinction from regression line of β_8 on $m_{\bar{p}}$ against β_{vis} (0.44μ).

Although Fig. 3 implies that the continuum is primarily due to water vapor, the possible contribution of particulate matter to extinction needs examination. For this purpose the departures of observed β_8 from the regression line of Fig. 3(b) ($\equiv \Delta\beta_8$) were correlated with the values of β_{vis} obtained with the Volz actinometer, fitted for this measurement with a narrow band filter centered at 0.44μ . The relation between them is shown in Fig. 4 in which the regression coefficient is 0.07 (this is in good agreement with the value of 0.05 predicted by computations cited in Sec. 9) and the correlation coefficient is 0.78, but these values are seen to depend strongly on one or perhaps two only rather high values of each

variable. (This procedure is equivalent to multivariate analysis of β_8 on $m_{\bar{p}}$ and β_{vis} , provided there is no correlation between $m_{\bar{p}}$ and β_{vis} ; the correlation coefficient between the latter is in fact 0.26 for the 20 pairs of observations and is not significant.)

It is of interest to inquire whether the observed variance in $\beta_{\bar{p}}$ for Windows 8 and 11 can be satisfactorily accounted for by the above correlations and the estimated experimental variance arising from errors in chart measurement, in $m_{\bar{p}}$ and I_0 . (The observations for Window 2 are too few to make the analysis here worthwhile.) Short-circuiting the details (see Saiedy, 1960b), the ratio of observed to expected total variance is found to be 1.27 and 1.75 for Windows 11 and 8, respectively. These values are not unsatisfactory, as they would need to be 2.00 and 1.85, respectively, to be significant at the 5% level.

5. METHOD I. FREQUENCY DEPENDENCE OF CONTINUUM, 790 TO 1202 cm^{-1}

A typical set of regression lines of log (relative intensity) against air mass for the lower frequencies ($\nu \leq 901 \text{ cm}^{-1}$) of Table I is given in Fig. 5. Figure 6 shows all the results of this series of observations in terms of β_i/β_8 against frequency. The experimental error in these ratios is estimated to be about $\pm 4\%$, but for $\nu > 901 \text{ cm}^{-1}$ there may also be systematic error due to selective absorption. In particular, Window 13 is almost certainly affected by neighboring strong lines and the curve of Fig. 6 has accordingly been drawn below the points for this frequency. The mean of seven

FIG. 5. Typical regression lines of log of relative intensity as a function of air mass, 14.5 (1959).

values of β_{11}/β_8 is 1.28 ± 0.05 , which is in reasonable agreement with the value 1.24 ± 0.09 derived from Sec. 4.

We have already referred to the possible evidence for the effect of temperature or self-broadening on the continuum in the discussion of the negative intercepts on Figs. 3(a) and (b). Further evidence is afforded by apparent day-to-day changes in β_i/β_8 which appear to be correlated with the effective mean temperature,

$$\bar{T} = -\frac{1}{m} \int_0^m T(m') dm',$$

computed from nearby radiosonde data. Figure 7 illustrates this for Windows 9, 10, 11, and 12. Although there is little doubt that the ratio increases with temperature, it is questionable whether it is a true temperature effect, for this would imply an unreasonably large difference in temperature coefficient between Window 8 and Windows 9, 10, 11, and 12. Further observations are required before Fig. 7 can be interpreted with confidence.

6. METHOD II. BASIS AND APPARATUS

Method I cannot be applied near sea level in wavelengths beyond 14μ because of the high continuum absorption in that range. This is illustrated by the solar spectrum shown in Fig. 8 taken with 3 g cm^{-2} of precipitable water in the path. Satisfactory measurements of the continuum out to 21μ require only about 0.1 to 0.5 g cm^{-2} of vapor in the path, and were therefore made in a horizontal-path experiment with path lengths of 200 and 400 m which provide the required range of water vapor. A spectrum taken over a path of 200 m is shown in Fig. 8. An absolute determination of absorption is very difficult in this case, and the technique developed provides values of the difference between the absorption coefficients in any two windows. By choosing for one of the latter a window in the very transparent region treated by Method I, a good estimate of the absorption coefficient for the other is possible.

The external optical system is shown in Fig. 9. An image of the power-stabilized Nernst source is formed on the entrance slit of the spectrometer after the radiation has traversed a path of 200 or 400 m, the external optical system ($f/5$) being matched to the spectrometer ($f/10$) by mirrors M_5 and M_6 .

The spectrometer, described by Goody (1957), was equipped for this experiment with a 15-cm-square Merton replica grating of 473 lines/cm blazed for 20μ in the first order. All radiation of $\lambda < 7.3 \mu$ was eliminated by a bloomed filter of indium antimonide, and filters of terylene and (reststrahlen) magnesium oxide were used in various contexts. The transmissions of these filters are indicated qualitatively in Fig. 8.

A constant geometrical slitwidth was chosen to provide a signal to noise ratio better than 100:1 at all wavelengths except the longest, the resolution achieved being 2.2 cm^{-1} at 600 cm^{-1} and 1.2 cm^{-1} at 480 cm^{-1}

FIG. 6. Variation of continuum extinction coefficient with frequency relative to extinction at 901 cm^{-1} .

(Table IV, Sec. 10B). Stray radiation was shown to be negligible by the complete absence of signal at several line centers under high resolution. By the use of sector attenuators of accurately measured transmittance for the control of input, the Golay detector and voltage-stabilized amplifier system was found to be linear to better than 0.5% over the range of input used.

The windows chosen for measurement are identified on Fig. 8 by numbers 14–20, and are listed in Table IV. Window 4 was used for comparison purposes and was chosen for its high transparency, freedom from lines, and so that it fell in an opaque band of the terylene filter at a frequency exactly double that of one of the other windows.

7. OBSERVATIONAL PROCEDURE

Three techniques were employed in the determination of the extinction coefficients. The first gives values of $\beta_{17}-\beta_4$, from which β_{17} may be inferred with little uncertainty since $\beta_{17}/\beta_4 \approx 15$. The second gives values of $\beta_{14}-\beta_4$, and the third $\beta_i-\beta_{17}$, from which $\beta_i-\beta_4$ is inferred using $\beta_{17}-\beta_4$ already determined. The three techniques are now described in order. The notation β_{i-} is used to denote $\beta_i-\beta_r$.

FIG. 7. Effect of temperature on β_i/β_8 for Windows 9, 10, 11, and 12.

FIG. 8. Method II. Location of windows and filter characteristics. (a) Cut-on for bloomed indium antimonide. Beyond 8μ the transmission decreases slowly to about 50% at 20μ . (b) Transmission of terylene film, 12μ thick. (c) Cut-on for double reststrahlen magnesium oxide. Beyond 14μ transmission remains at about 60%. (d) Spectrum over horizontal path of 200 m, with 0.250 g cm^{-2} of water vapor in the path. Nernst source and filters (c) and (a). (e) Solar spectrum; 3 g cm^{-2} water vapor in slant path. Filters (c) and (a).

A. Measurement of β_{17-4}

With the grating set to $\nu_{17} = 559.4\text{ cm}^{-1}$ in the first order, signals are obtained with and without the terylene filter, an auxiliary sector attenuator of transmission K being used in the latter case to bring the signals to approximate equality. Let the ratio of these two signals be y . When the terylene filter is used, only the first-order spectrum (Window 17) is transmitted; without it the much more intense second-order spectrum of Window 4 is also transmitted. Higher-order spectra are eliminated by the indium antimonide filter.

Let

F_i be the transmittance of the terylene filter in window i ;

S_i , the signal which would be obtained in window i

in the absence of absorption along the atmospheric path;

β_i , the extinction coefficient per unit length in window i ; and

l , the path length (l_2 and l_1 are used to denote different path lengths).

Then Lambert's law gives

$$y = \frac{F_{17}S_{17} \exp(-\beta_{17}l) + F_4S_4 \exp(-\beta_4l)}{K[S_{17} \exp(-\beta_{17}l) + S_4 \exp(-\beta_4l)]} \quad (7.1)$$

For terylene film of 12μ thickness, $F_4 = 0$ and Eq. (7.1) can be written

$$\beta_{17-4}l = \ln S_{17-4} + \ln[(F_{17}/Ky) - 1], \quad (7.2)$$

FIG. 9. External optics of horizontal path experiment. The Nernst filament N is shielded from draughts and is mounted just outside the focus of paraboloid M_1 ($f=305$ cm, diam 63 cm) so as to give an image on M_2 , which is a spherical mirror of either 200 m radius, 50 cm diameter, mounted at 200 m distance, or of 100 m radius, 25 cm diameter, mounted at 100 m distance. In each case the center of curvature of M_2 is midway between those of M_1 and M_3 , so that M_1 is imaged on M_3 . All mirrors are front-surface aluminized. The chopper (C) frequency is 10 cps.

where $S_{17,4} = S_{17}/S_4$. Thus, given F_{17} , observations of y for two values of l provide β_{17-4} provided $S_{17,4}$ is the same for both determinations of y . The value of F_{17} is in fact measured for every pair of observations of y by taking the ratio of the signals obtained with and without the filter, the second-order spectrum of Window 4 being eliminated in both by a second fixed terylene filter.

The condition of constancy of $S_{17,4}$ requires care for achievement. Its value depends on the relative magnitude in wavelengths 4 and 17 of (i) the intensity I of radiation emitted by the source; (ii) the product, R , of the reflectances of all the mirrors in the system; (iii) the response of the detecting system, including the grating and filters.

Regarding (i), it was found that I_4/I_{17} was greater by 5 to 10% at the center than at the edge of the filament. It was therefore necessary to focus and align the image very carefully to ensure that the same part of the source was used in each pair of observations. The variation of I_4/I_{17} with filament temperature was less than 2% over the range 1500°–2000°K, which was certainly much greater than the temperature variations induced by draughts.

Regarding (ii), evidence (unconfirmed) was obtained that for the complete system of mirrors (13 reflections), R_{17}/R_4 decreased by about 10% for a change of relative humidity from 50 to 90%, as inferred from a change of intercept, $\ln S$ in Eq. (7.2). The effect is however of no consequence since each pair of observations was made in the minimum interval (about 5 min) to effect the necessary changes, so as to keep changes in humidity to a minimum. It was necessary moreover to assume that R_{17}/R_4 was the same at any one time for each of the mirrors used for M_2 ; which is reasonable because the mirrors were aluminized at the same time and were subsequently kept under similar conditions.

Regarding (iii), the transmission of the terylene filter was found to be uniform over its whole surface, but that of the indium antimonide was somewhat nonuniform, possibly because of variations in the antireflection coating. The efficiency of the grating was also non-uniform and it was therefore essential to ensure identity of position and distribution of illumination in the beams derived from the external optical systems—by accurate alignment and focusing, and the introduction of a stop on M_6 to cover the images of obstructions in the beam.

In the course of the experiment, several changes were made in order to improve the reproducibility of $S_{17,4}$. The experimental method and optical layout described in Sec. 6 was the final form. It superseded a version in which it was possible to obtain a short path of 10 m as well as paths of 200 and 400 m, but this involved the off-axis use of spherical mirrors, giving considerable distortion. In this earlier method, the values of l used for a pair of observations were $l_2 = 10$ m and $l_1 = 200$ or 400 m. Some systematic error was, however, possible: firstly, from the use of four mirrors not common to both beams (though with the same total number of reflections), with the possibility that different relative reflectances R_{17}/R_4 were involved; secondly, from uncertainty in fulfilling condition (iii) above owing to distortion and different beam geometry. These uncertainties were much reduced in the final method since only one mirror was not common to both beams, and with axial optics it was possible to ensure that both beams were identical.

There was reasonable agreement, however, between the results derived from both methods, indicating that the uncertainties present in the earlier method were not serious. It is probable that $S_{17,4}$ was reproduced to better than 1% in each pair of observations in the final method. Support for this view is afforded by the fact

FIG. 10. Circled points: observed transmission of a 43-cm cell of pure CO_2 at atmospheric pressure. Continuous lines: calculated transmission, assuming Lorentz wings [neglecting minor bands, whose positions and strengths ($\text{g}^{-1} \text{cm}$) are shown on the abscissa]. The positions of Windows 6-20 are shown.

that noticeable deliberate misalignments produced no systematic change in y .

B. Measurement of $\beta_{14} - \beta_4$

The ratio $x_{14,4}$ of the signals obtained in Windows 14 and 4 was measured, whence

$$x_{14,4} = (S_{14}/S_4) \exp - (\beta_{14} - \beta_4)l.$$

Then from observations over two paths, subject to the experimental precautions stated previously, a value of $\beta_{14} - \beta_4$ may be found.

C. Measurement of $\beta_i - \beta_{17}$

A double reststrahlen magnesium oxide filter was mounted kinematically behind the exit slit, cutting off almost entirely all radiation of $\lambda < 13 \mu$. This filter was readily interchangeable with a pair of identically mounted aluminized mirrors used in Secs. (A) and (B). The ratios $x_{i,17}$ of the signals for each of the Windows 15-20 to that for Window 17 were determined for two path lengths, and β_{i-17} may be found as in (b).

D. Measurement of Water Vapor

The depth of precipitable water in the path was obtained from readings of an Assmann psychrometer exposed at the mean height ($\sim 1 \text{ m}$) of the beam, occasional checks being made with a second psychrometer for uniformity along the path.

8. CO_2 ABSORPTION IN THE REGION $1300\text{--}478 \text{ cm}^{-1}$

Before discussing the results on the water-vapor continuum out to 21μ , it is appropriate to consider the possibility of this continuum's being overlaid by that from carbon dioxide and aerosol. Regarding the former, a 43-cm cell of pure CO_2 , with windows of polythene, was inserted in the beam, giving a "depth" of 0.082 g cm^{-2} , the equivalent of 1.4 km of air at sea level. The

transmissions on either side of the ν_2 band are shown in Fig. 10, and are compared with those to be expected if the wings of the CO_2 lines have Lorentz shape, taking the ν_2 band intensity to be $1.22 \times 10^5 \text{ g}^{-1} \text{ cm}$ and the mean line half-width 0.064 cm^{-1} at 1 atm and 298°K (Kaplan and Eggers, 1956). We see that the observed absorption is considerably less than from Lorentz wings until quite close to the band center, the absorption due to line centers of the weaker bands indicated in Fig. 10 being first apparent. Kaplan (1953) and Benedict (1955) have argued for a decrease faster than Lorentz in the CO_2 wings, and they suggest a wing profile which is consistent with the negligible absorption observed in the present work outside the range 790 to 560 cm^{-1} . Only Windows 14, 15, and 16 were found to be affected by CO_2 absorption, this being attributed to nearby lines, and is therefore analyzed accordingly.

9. EXTINCTION BY AEROSOL

During the experiment, it was noted that the extinction was greater under very hazy conditions, and it was therefore necessary to allow for aerosol attenuation in the analysis. No direct measurements of particle concentration and size were made, but local visibility data were available and it is of interest to inquire to what extent these could be used to infer the opacity due to aerosol in the $10\text{--}20\text{-}\mu$ region. Deirmendjian (1959, 1960) has computed extinction coefficients from 0.625 to 14μ for a number of realistic aerosol distributions; the ratios of the extinction coefficient at 0.625μ to those at 10.0 , 12.0 , and 14.0μ are approximately 30, 11, and 7, respectively, for all distributions except when there are many large particles, suggesting that the distribution is not very important. In the region beyond 14μ , computations from the Mie theory are greatly simplified for droplets up to $1\text{-}\mu$ radius by an expansion given by Van de Hulst (1957, p. 270). Using this and the absorption coefficients given by Plyler and Acquista (1954) and

refractive index data from Dorsey (1940, p. 185) for 18 and 20 μ , we find that $\beta_{0.625\mu}/\beta_{18\mu} \approx 9$ and $\beta_{0.625\mu}/\beta_{20\mu} \approx 11$, both ratios being insensitive to the aerosol distribution. It is concluded that the aerosol contribution, $\Delta\beta$, to the extinction in the region 10–20 μ , is proportional to that at 0.625 μ within a factor of 2 for all likely aerosol distributions. With the further, more doubtful, assumption that the visual extinction coefficient β_{vis} [computed from the visibility V , by $\beta_{vis} = 3.9/V$ (Middleton, 1952, p. 105)] is proportional to $\beta_{0.625\mu}$, we may define a constant D_i by $\Delta\beta_i = D_i\beta_{vis}$, and hence

$$\Delta\beta_{i-r} \equiv \Delta(\beta_i - \beta_r) = D_{i-r}\beta_{vis} = (3.9/V)D_{i-r},$$

where $D_{i-r} = D_i - D_r$. For the purposes of the discussion (Sec. 10A) of observations in Windows 17 and 19 relative to Window 4, and of those in Window 8, Sec. (4), we note from the above that if we assume $\beta_{vis} = \beta_{0.625\mu}$, then $D_{19} = 0.09$, $D_{17} = 0.11$ and by interpolation of the computations of Deirmendjian (1960), $D_4 = 0.05$ and $D_8 = 0.05$.

10. METHOD II. RESULTS

Values of absorption coefficients derived from early observations showed much more scatter than could be accounted for by errors of observation, in the elucidation of which effort was concentrated on the measurement of β_{17-4} and β_{19-4} (chosen for their freedom from CO_2 absorption and for adequate signal). The interpretation of the observations for these windows will be discussed first, since the conclusions throw light on the interpretation of the smaller samples of data for the other windows.

A. Windows 17 and 19

Figure 11 shows the observations of extinction coefficients for Windows 17 and 19 as a function of the mass m_p of water vapor in the path. A strong correlation is evident, but the observations for each window fall distinctly into two groups according as $l_2 - l_1 = 400$ or 200 m, and the best straight lines through each set of points have significant negative intercepts. For both windows the extinction is apparently greater at a given value of m_p for the shorter path for which the vapor density must be double that on the longer path, so that self-broadening suggests itself as an explanation. However, points of low m_p on all lines were obtained under cold, dry conditions and those of high m_p under warm, humid conditions, so that it is equally possible that a positive temperature dependence of absorption is partly or wholly responsible for the difference in extinction coefficient. A sufficient number of observations ranging as widely as possible over these variables was therefore necessary to discriminate between these effects by multiple regression analysis.

The regression equation relating the observed extinction in Windows 17 and 19 to vapor content and visibility (Sec. 9) may be written

$$\beta_{i-4} = k_{i-4}m + (3.9/V)D_{i-4}, \quad (10.1)$$

FIG. 11. Observed extinction coefficients $\beta_i - \beta_4$ for Windows 17 and 19 as a function of water vapor in the path ($m_p = m/p/p_0$).

where k is the mass absorption coefficient for water vapor, $i = 17$ or 19, and m is the mass of water vapor per unit length of path per cm^2 .

It will be assumed that the variation of the half-width α and intensity S of absorption lines with temperature and pressure may be written

$$\alpha(P, T) = \alpha(p_0, T_0)(P/p_0)(T_0/T)^{\frac{1}{2}},$$

$$S(T) = S(T_0)[1 + \epsilon(T - T_0)],$$

where $P = p + ae$, p and e being the partial pressures of dry air and water vapor, respectively, a is the ratio of self- to air-broadening, and p_0 , T_0 are standard values of pressure (1000 mbar) and temperature (0°C). Then Eq. (10.1) can be written, to good approximation,

$$\frac{\beta_{i-4}}{m_p} \left(\frac{T}{T_0} \right)^{\frac{1}{2}} = k_{i-4}(p_0, T_0) \left[1 + \epsilon(T - T_0) + \frac{ae}{p} \right] + \frac{3.9D_{i-4}}{Vm_p}, \quad (10.2)$$

where $m_p = m(p/p_0)$.

With 224 sets of observations for Window 17, and 71 for Window 19, a multiple-regression analysis was pos-

TABLE III.^a Results of the regression analysis for Windows 17 and 19.

Window, <i>i</i>	λ (μ)	ν (cm^{-1})	$k_{i-4}(p_0, e_0, T_0)$ ($\text{g}^{-1} \text{cm}^2$)	a	ϵ ($^{\circ}\text{C}^{-1}$)	D_{i-4}	No. of obs
17	17.88	559.4	1.22 ± 0.13	26 ± 4	0.0006 ± 0.001	0.022 ± 0.005	224
19	20.12	497.0	2.09 ± 0.16	38 ± 6	-0.001 ± 0.001	0.034 ± 0.008	71

^a Results of a least-squares fit of the observations to the relation

$$k_{i-4}(p, e, T) = k_{i-4}(p_0, e_0, T_0) [(p + ae)/p_0][1 + \epsilon(T - T_0)],$$

where p , e are the partial pressures of dry air and water vapor, respectively ($p_0 = 1000$ mbar, $e_0 = 0$ mbar), and $T_0 = 0^{\circ}\text{C}$. D_{i-4} represents the aerosol contribution (see Sec. 9).

sible, and the results are given in Table III. For both windows it appears that ϵ is not significantly different from zero, which lends support to the assumption tentatively made in Sec. 2. The correlations with aerosol are weak but significant, and the observed values of D_{17-4} and D_{19-4} , 0.02 and 0.03, respectively, may be compared with 0.06 and 0.04 expected from the reasoning of Sec. 9; better agreement could hardly be expected in view of the uncertainties involved.

The correlation with vapor pressure is highly significant. The values of 26 and 38 for a for windows 17 and 19, respectively, are remarkably high compared with the figure between 5 and 10 which has been found for the central parts of lines (Palmer 1960); Benedict has suggested, however, that the wings are subject to greater self-broadening than are line centers. Although only about half of the total variance can be accounted for, and this almost entirely by the correlation with vapor pressure, we have fair confidence in ascribing the negative intercepts to self-broadening. If this inference is verified it will be of the utmost importance in the analysis of remote radiation measurements which involve correction for the water-vapor continuum.

B. Windows 18 and 20

With insufficient observations to permit a multiple-regression analysis, it seems reasonable in the light of the results for Windows 17 and 19 to assume that the temperature and aerosol terms may be ignored in Eq. (10.2). Plots of β/m_p against vapor pressure e are shown in Fig. 12, where a tendency for the absorption to in-

crease with e is again apparent. For neither window is the sample large enough to allocate a value of a , though for Window 18 it is of the order of 30.

Mean values of k_{18} and k_{20} corresponding to the mean vapor pressure of 12 mbar are given in Table IV, with corresponding values for Windows 17 and 19 for comparison.

C. Windows 14, 15, and 16

CO_2 absorbs significantly in these windows (see Fig. 10), and Eq. (10.2) must now be written (neglecting aerosol and temperature terms)

$$\beta_{i-4} = k_{i-4}(p_0)m_p[1 + (ae/p)] + c_i,$$

where c_i is the CO_2 contribution in window i ($C_4 = 0$). Figures 13(a) and (b) show β_{i-4} against m_p for Windows 16 and 15. We see that the best straight lines do not pass through the intercepts c_i inferred by scaling the CO_2 absorption measurements (Sec. 8) to the mass in the path according to the law appropriate to a regular band. Indeed, graphs of $\beta_{i-4} - c_i$ against m_p for these windows would have identical features to those for Windows 17 and 19 (Fig. 11) discussed in Sec. 10A, and it seems likely that the interpretation is the same. Mean

TABLE IV. Frequencies used in Method II and observed absorption coefficients.

Window, <i>i</i>	λ (μ)	ν (cm^{-1})	Reso- lution (cm^{-1})	$k_i(p_0, e)^a$ ($\text{g}^{-1} \text{cm}^2$)	$\Delta k_i(p_0, T_0)^b$ ($\text{g}^{-1} \text{cm}^2$)	No. of obs
4	8.94	1118.8	3.5	0.08 ^c	0	...
14	13.96	716	2.8	0.6 ± 0.2	0	15
15	16.38	610.5	2.2	0.8 ± 0.1	0.13, +0.7	15
16	17.02	587.4	1.9	1.4 ± 0.1	0.42, +1.3	15
17	17.88	559.4	1.7	1.7 ± 0.1	0.23, +1.0	224
18	18.83	531.2	1.6	1.9 ± 0.1	0.44, +1.1	15
19	20.12	497.0	1.3	3.0 ± 0.1	0.78, +1.2	71
20	20.88	478.9	1.2	2.1 ± 0.1	1.3, +1.7	6

^a $k_i(p_0, e)$ is the mass absorption coefficient for partial air pressure of 1000 mbar and water-vapor pressure of 12 mbar (see Sec. 10B).

^b Δk_i is the contribution to k_i from wings of nearby water-vapor lines for $p_0 = 1000$ mbar and $T_0 = 14^{\circ}\text{C}$; the computed temperature coefficient ($\% ^{\circ}\text{C}^{-1}$) of Δk_i is also shown.

^c By interpolation from Method I.

FIG. 12. Absorption coefficients for Windows 18 and 20 as a function of vapor pressure. It has been assumed that temperature dependence and aerosol absorption are negligible.

FIG. 13. Observed extinction coefficients for Windows 14, 15, and 16. Full circles: 400 m path. Open circles: 200 m path. Points denoted by 'C'₁₆ and 'C'₁₅ represent the estimated CO₂ contribution, from measurements with a cell of CO₂.

values of k_i , corresponding to the mean vapor pressure of 12 mbar, are given in Table IV, assuming $k_p = 0.05 \text{ g cm}^{-2}$.

Figure 13(c) shows the observations for Window 14; in this case absorption by CO₂ is much greater and the scatter is increased by the diurnal and daily variations in the concentration of atmospheric CO₂. Only a rough estimate of k_{14-4} may be obtained from the slope of the regression line and this is also entered in Table IV.

11. DISCUSSION OF RESULTS AND FORM OF THE CONTINUUM

The results (Methods I and II) reported in this paper for the region 1200–800 cm⁻¹ are on the average 20% less than those obtained by Roach and Goody (1958) by a solar method at the same site but with lower resolution, and agree with the result of Vigroux (1959) taken at Arosa at 1041 cm⁻¹, and are some 30% larger than those of Anthony (1952) taken at Table Mountain, California, also by a solar method. Anthony also observed the continuum at 17.6 and 19.0 μ, but the results (0.87 and 0.98 g⁻¹ cm²) are not readily comparable with the present work since the circumstances of the observation were not reported.

It is significant that the results from Method II for Windows 17 to 20 are similar in character to those for Windows 8 and 11 from Method I, in that plots of β against $m_p l$ [Figs. 3(a) and (b)] have negative intercepts, and it was noted in Sec. 4 that temperature dependence or self-broadening could produce this effect. Method II provides evidence that the latter is responsible in the region $\nu < 600 \text{ cm}^{-1}$, and it is suggested that the same is true for $\nu > 600 \text{ cm}^{-1}$, though confirmation is clearly needed from experiments carried out under controlled conditions. The negative intercepts in Figs. 3(a) and (b) provide a value of a of order 30, which agrees with that determined independently from Method II, and it is possible that the differences between the present and previous results may also thereby be explained.

We now attempt to relate the observed features of the continuum to the properties of the water-vapor bands

(CO₂ may be neglected, Sec. 8), and to determine which of the line shapes variously suggested in the literature best fits the data, realizing however that wing forms so far from line centers can hardly be expected to be given by existing theories.

The line strengths and half-widths of the water-vapor rotation band have been computed by Schwendeman and Laurie (1958) and Benedict and Kaplan (1959), respectively, and observational support has been given to these computations (Saiedy 1960). The contribution to the continuum at 1000 mbar from this band, assuming the Lorentz line shape, was kindly computed for us by L. D. Kaplan from

$$k(\nu) = (1/\pi) \sum S_i \alpha_i / (\nu - \nu_i)^2,$$

and the results can be represented to within 1% or 2% in the region 1200–800 cm⁻¹ by

$$k(\nu, p_0) = 4.1 \times 10^4 / (\nu - 200)^2 \text{ g}^{-1} \text{ cm}^2, \quad (11.1)$$

which is equivalent to a single strong line at 200 cm⁻¹.

The absolute line intensities in the ν_2 vibration-rotation band are not yet available, but the necessary data were extracted from an analysis by Cowling (1950) of earlier work and from the high-resolution spectra of Nielsen (1941). It was found that $k(\nu, p_0)$ due to the ν_2 band can be represented to within 2% or 3% for $\nu < 1200 \text{ cm}^{-1}$ by

$$k(\nu, p_0) = 3.7 \times 10^3 / (\nu - 1550)^2 \text{ g}^{-1} \text{ cm}^2. \quad (11.2)$$

In comparing the observations with the sum of Eqs. (11.1) and (11.2), it must be remembered that if the hypothesis regarding self-broadening is correct, then the observations do not correspond to an effective pressure p_0 , but to about $1.18 p_0$ in the case of Method I with $a \approx 30$ and $e \approx 6$ mbar, and to $1.36 p_0$ in the case of Method II with $e \approx 12$ mbar. Thus, the observations of Method I reanalyzed in the manner of Sec. 10B give $k(901, p_0) = 0.064 \text{ g}^{-1} \text{ cm}^2$.

Figure 14 shows (a) the values of $k(\nu)$, as observed, in the region 1202–479 cm⁻¹; (b) values corrected to p_0 according to the self-broadening hypothesis; (c) values

FIG. 14. Comparison between observed and calculated continuum for different line shapes. (1) Lorentz shape; (2) complete Lorentz; (3) Lindholm; (4) Van Vleck and Weisskopf.

predicted by Eqs. (11.1) and (11.2) (Curve 1). Agreement between (a) and (c) is not unsatisfactory [better, indeed, than that between (b) and (c)] in the region 1200–800 cm^{-1} , but the discrepancy increases rapidly for $\nu < 800 \text{ cm}^{-1}$. Better agreement might be expected here if the contribution from nearby lines were subtracted from the observed values. The strengths and half-widths of all lines in the region 1180–423 cm^{-1} were computed from the references cited earlier in this connection and their contribution, Δk , to the continuum in Windows 14 to 20, assuming Lorentz line-shape, is given in Table IV. We see that neighboring lines are particularly important in Windows 18, 19, and 20, but even after allowing for their effect, a discrepancy of a factor of 3 remains between (c) and (b) at 500 cm^{-1} . Although it may be argued that the effective band center must be moved nearer for this region, the shift required (to $\nu = 340 \text{ cm}^{-1}$) is far greater than can be accounted for by the profile of the rotation band, for which a shift to $\nu = 235 \text{ cm}^{-1}$ would be appropriate. It seems unlikely that the continuum can be represented over a wide region by any simple formula.

Benedict (1961) has suggested that the near wings (up to a few tens of wavenumbers) are stronger and the far wings weaker than Lorentz, and this would be consistent with the observations reported here. Much more precise observations of the absolute absorption coefficients and their temperature coefficients are required before a definite conclusion can be reached. Such observations are now being attempted by one of us.

For comparison with the prediction from the Lorentz

shape, Fig. 14 also shows the continuum computed on the basis of other line shapes, which are:

Curve 2: the full Lorentz expression (Van Vleck and Weisskopf, 1945):

$$k(\nu) = \sum \frac{S\alpha}{\pi} \frac{\nu}{\nu_0} \left[\frac{1}{(\nu - \nu_0)^2 + \alpha^2} - \frac{1}{(\nu + \nu_0)^2 + \alpha^2} \right]$$

Curve 3: the asymmetric Lindholm line shape (Plass and Warner, 1952):

$$k(\nu) = 0.933 \sum \frac{S\alpha}{\pi} M^{-1} (\nu_0 - \nu)^{-1/3} \quad \text{for } \nu < \nu_0,$$

$$k(\nu) = 0.638 \sum \frac{S\alpha}{\pi} M^{-1} (\nu - \nu_0)^{-7/3} \quad \text{for } \nu > \nu_0,$$

where $M \approx 3 \text{ cm}^{-1}$.

Curve 4: the line shape for the microwave and far-infrared region (Van Vleck and Weisskopf, 1945):

$$k(\nu) = \sum \frac{S\alpha}{\pi} \frac{\nu^2}{\nu_0} \left[\frac{1}{(\nu - \nu_0)^2 + \alpha^2} + \frac{1}{(\nu + \nu_0)^2 + \alpha^2} \right]$$

We see that Curve 2 gives better agreement with the observations for $\nu < 700 \text{ cm}^{-1}$, but is too large by at least a factor of 2 in the region 1200–800 cm^{-1} , whilst Curves 3 and 4 do not even give qualitative agreement.

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Heat-balance measurements from an earth satellite –
an analysis of some possibilities

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SUMMARY

A detailed discussion of the basic 'black' and 'white' sphere experiment designed by Suomi, and successfully launched in more elaborate form in Explorer VII in October 1959, is presented. It is concluded that this experiment is in almost every respect well suited for making heat-balance measurements from a simple unstabilized satellite, but that it suffers from the serious disadvantage of any such system that the sampling rate is inadequate for giving the daily or short-term heat balance of any region of the earth. Other main conclusions are: the magnitude of the possible error incurred by employing a spherical detector to measure the vertical intensity of a diffuse, anisotropic radiation stream is estimated to be a few per cent only; corrections for heat transfer by conduction and radiation to the spheres from the main body of the satellite can be reduced to negligible proportions, but heating due to high velocity impacts with gas molecules may be considerable for low orbits ($0.16 \text{ cal cm}^{-2} \text{ min}^{-1}$ at 200 km); the time constant of the detector is shown to be not less than about two minutes; the sensitivity is of the order of 1°K per $0.01 \text{ cal cm}^{-2} \text{ min}^{-1}$; the prospects of checking the calibration of the equipment in flight seem reasonable.

1. INTRODUCTION

The importance of heat-balance measurements has been discussed in a paper by Suomi (1958) in which he describes apparatus for making the necessary observations from an earth satellite. Up to the date of writing, this appears to be the only satellite experiment proposed for heat-balance studies, although several writers mention the opportunities afforded by earth satellites (Kelly 1955; Widger and Touart 1957; Wexler 1960). The temperature variation of a satellite vehicle as a function of the radiative field is discussed by Gast (1956).

The instrumentation of a simple satellite must fulfil some very important requirements; the following are essential: simplicity, robustness, low weight and low power consumption. If the satellite is not attitude-controlled, a further very desirable property of a radiation instrument is that it should give the same response for all orientations and should not be influenced by spinning motions. The apparatus described by Suomi satisfies all of the above requirements. It consists essentially of two spherical detectors whose surfaces have different relative absorptivities in the visible and infra-red wavebands. By measuring the temperatures of the spheres it is possible to deduce the intensities of the long and short-wave radiation streams at the satellite, so that information on the heat balance of the earth-atmosphere system can be inferred. A recent article (National Academy of Sciences, Washington; I.G.Y. Bulletin No. 29) refers to a more elaborate array of sensing elements mounted on Explorer VII, consisting of four spheres and two hemispheres, but the principles of operation are not given.

The present study shows that while the technique described by Suomi is admirably adapted to an unstabilized satellite, there are certain difficulties in sampling and in the interpretation of the data. These difficulties are discussed in the following sections and summarized in § 7.

The following symbols are used :

A	$\frac{R}{R+h}$
B	$2 \left(\frac{1 - \sqrt{1 - A^2}}{A^2} \right)$
$B(\lambda, T)$	Planck function
C_L	long-wave anisotropy factor
C_s	short-wave anisotropy factor
e_L	long-wave absorptivity of a surface ($\lambda > 4 \mu$)
e_L'	total hemispherical emissivity of a surface
e	short-wave absorptivity of a surface ($\lambda < 4 \mu$)
F_L	outward vertical flux per unit area of long wave radiation from earth and atmosphere
F_N	outward vertical flux per unit area of net radiation
F_s	outward vertical flux per unit area of direct solar radiation, i.e., F_s is negative
F_{ss}	outward vertical flux per unit area of scattered solar radiation from earth and atmosphere
h	height of satellite above earth's surface
H	thermal capacity of sphere
i	inclination of satellite orbit to the earth's equator
k	$\frac{e_L}{e_s} \quad k' = \frac{e_L'}{e_s}$
R	radius of earth
$r(p)$	water vapour mixing ratio as function of pressure
S	solar constant at the outer limit of the earth's atmosphere ($2 \text{ cal cm}^{-2} \text{ min}^{-1}$)
$T(p)$	temperature of atmosphere as function of pressure
x	$BC_s F_{ss} + S$
y	$BC_L F_L$
Z	solar zenith angle
α	semi-angle subtended by earth at the satellite $= \sin^{-1} A$
σ	Stefan's constant $= 5.73 \times 10^{-5} \text{ erg cm}^{-2} \text{ sec}^{-1} \text{ }^\circ\text{K}^{-4}$
ψ θ	$\left. \begin{array}{l} \\ \end{array} \right\}$ directional coordinates (see Fig. 1)

Other symbols are defined where they occur.

2. SPECIFICATION OF THE RADIATION STREAMS

Let us now specify the radiation streams at a point P height h above O on the earth's surface (Fig. 1). The area visible from P is indicated by the closed curve; the radius r of this area (semi-angle at P $= \alpha$) as a function of h is given in Table 1, together with the radii $r_{0.5}$ and $r_{0.75}$ of those areas subtending 50 per cent and 75 per cent respectively of the total solid angle subtended by the earth at P.

TABLE 1. RADII OF VISIBLE AREA AND AREAS SUBTENDING 0.5 AND 0.75 OF TOTAL SOLID ANGLE

h (km)	200	300	400	500	600	700	800	900	1,000
r (km)	1,591	1,912	2,190	2,450	2,670	2,860	3,040	3,200	3,360
$r_{0.5}$ (km)	258	366	465	555	640	723	795	870	930
$r_{0.75}$ (km)	450	615	770	905	1,030	1,135	1,255	1,360	1,457
B	1.608	1.541	1.495	1.458	1.419	1.397	1.371	1.349	1.329

The radiation streams at P are :

- (i) Direct solar radiation denoted by F_s ; very nearly all of this is confined to wavelengths shorter than 4μ
- (ii) Diffuse scattered solar radiation from the earth and atmosphere, denoted by F_{ss} ; like F_s , this is confined to wavelengths shorter than 4μ
- (iii) Diffuse 'thermal' radiation from the earth and atmosphere, denoted by F_L ; very nearly all of this is confined to wavelengths longer than 4μ .

In general (ii) and (iii) will be anisotropic, so it is necessary to specify their intensities as functions of direction. In a system of cylindrical coordinates, let the intensities of (ii) and (iii) in a direction QP be $I_s(\theta, \psi)$ and $I_L(\theta, \psi)$ respectively, where

$$I_s(\theta, \psi) = \int_0^{4\mu} I_\lambda(\theta, \psi) d\lambda \quad I_L(\theta, \psi) = \int_{4\mu}^{\infty} I_\lambda(\theta, \psi) d\lambda$$

Figure 1. The area visible from the satellite at P is indicated by the closed curve. Solar radiation is incident along SP. O is vertically beneath P and the direction PQ is specified by θ, ψ .

The outward vertical fluxes of radiation per unit area for each radiation stream are then given by :

$$\left. \begin{aligned} \text{(i)} \quad F_s &= -S \cos Z \\ \text{(ii)} \quad F_{ss} &= \int_{\psi=0}^{\psi=2\pi} \int_{\theta=0}^{\theta=\alpha} I_s(\theta, \psi) \sin \theta \cos \theta \, d\theta \, d\psi = 2\pi \int_0^\alpha I_s(\theta) \sin \theta \cos \theta \, d\theta \\ \text{(iii)} \quad F_L &= \int_{\psi=0}^{\psi=2\pi} \int_{\theta=0}^{\theta=\alpha} I_L(\theta, \psi) \sin \theta \cos \theta \, d\theta \, d\psi = 2\pi \int_0^\alpha I_L(\theta) \sin \theta \cos \theta \, d\theta \end{aligned} \right\} \quad (1)$$

where $I_s(\theta)$ and $I_L(\theta)$ are the mean intensities around a strip with constant θ .

3. MEASUREMENT OF THE RADIATIVE FLUXES

(a) Introduction

In general, the only direct way of measuring the flux of a diffuse radiation stream across unit area in a given direction is to employ a plane-sensing element placed normal to this direction. But this, for satellite use, would involve the difficult task of satellite stabilization in a terrestrial frame, and the use of an omnidirectional sensor is therefore suggested. It is shown in § 3 (b) that it is then necessary to know the functions $I_s(\theta)$ and $I_L(\theta)$ in order to obtain a correct result. The only truly omnidirectional sensor is an isolated sphere.

(b) Theory of the spherical sensor

Consider a sphere, radius a , situated at P (Fig. 1). We want to find the relation between the flux f incident on the sphere (this determines its temperature, which is to be the measured quantity) and the outward vertical flux per unit area, F , of any radiation stream at P . We have

$$f = \pi a^2 \int_0^\alpha I(\theta) 2\pi \sin \theta \, d\theta$$

which with Eq. (1) gives

$$F = \frac{1}{\pi a^2} \frac{\int_0^\alpha I(\theta) \sin \theta \cos \theta \, d\theta}{\int_0^\alpha I(\theta) \sin \theta \, d\theta}$$

It is convenient to rearrange this by multiplying and dividing by

$$B = \frac{\int_0^\alpha \sin \theta \, d\theta}{\int_0^\alpha \sin \theta \cos \theta \, d\theta} = 2 \frac{1 - \sqrt{1 - A^2}}{A^2}$$

$$\text{Then} \quad F = \frac{1}{\pi a^2 CB} f \quad (2)$$

$$\text{where} \quad C = \frac{\int_0^\alpha \sin \theta \cos \theta \, d\theta \int_0^\alpha I(\theta) \sin \theta \, d\theta}{\int_0^\alpha I(\theta) \sin \theta \cos \theta \, d\theta \int_0^\alpha \sin \theta \, d\theta} \quad (3)$$

For numerical values of B as a function of h , see Table 1.

(c) Effects of anisotropic radiation

For isotropic radiation, $I(\theta) = \text{constant}$ and $C = 1$ from Eq. (3). For all other cases C will be different from unity because a spherical sensor gives equal weight to radiation from all directions, whereas the vertical flux per unit area, F , is a sum over all elements of solid angle weighted by $\cos \theta$. So if $I(\theta)$ is a decreasing function of θ (limb darkened), C will be less than unity to offset the effect of the added weight given to the darker limb regions. Similarly, if the limb is brighter than the central regions, C will be greater than unity.

Figure 2 (a) (b) (c). Fields of anisotropic radiation : (a) for instantaneous response; (b) for slow response. The figures on the left in (a) and (b) show the bright (unshaded) and dark (shaded) areas corresponding to the figures on the right. Typical limb darkening in the infra-red is shown in (c) for $h = 200$ km.

It is of interest to know the limits between which C must lie. The derivation of the function $I(\theta)$ giving a stationary value to C is difficult, but a simple approximation which is particularly appropriate here is a step function, since bright and dark regions will often be separated by sharp boundaries, such as the edges of cloud systems. With this simplification the departure of C from unity will be a maximum (see Fig. 2 (a)) when

$$\left. \begin{aligned} I(\theta) &= \text{constant} (= I) & \text{for } 0 < \theta < \beta \\ I(\theta) &= \text{constant} (= nI) & \text{for } \beta < \theta < \alpha \end{aligned} \right\} \quad (4)$$

where n is a constant and β is to be determined.

The value to be taken for n is the ratio of the maximum and minimum intensities likely to occur over the area visible from the satellite. For long-wave terrestrial radiation n is about 2 or 3, corresponding to the ratio of the total black body intensities at around 280°K and 220°K. For reflected solar radiation n can be as high as 10, corresponding to the albedo ratio of snow or cloud and the oceans. The stationary value C_0 of C is easily determined by inserting Eq. (4) into Eq. (3) and eliminating β by using the condition $(\partial C / \partial \beta)_{C=C_0} = 0$. The result is

$$C_0 = \frac{A^2}{2(1 - \sqrt{1 - A^2})} \frac{1 + \sqrt{n}}{(1 + \sqrt{n}\sqrt{1 - A^2})} \quad (5)$$

Inspection of Eq. (5) yields the following :

- (i) For isotropic radiation $n = 1$ and $C_0 = 1$ for all h
- (ii) As $A \rightarrow 0$ (i.e., $h \rightarrow \infty$) $C_0 \rightarrow 1$ for all n
- (iii) As $A \rightarrow 1$ (i.e., $h \rightarrow 0$) $C_0 \rightarrow (1 + \sqrt{n})/2$

Values of C_0 for $n = 2, 10, \frac{1}{2}$ and $\frac{1}{10}$ as a function of h are given in Table 2.

TABLE 2. VALUES OF C_0 AS A FUNCTION OF HEIGHT AND n

h (km)	200	300	400	500	600	700	800	900	1,000
$n = 10$	1.46	1.40	1.35	1.31	1.29	1.27	1.25	1.24	1.22
2	1.12	1.10	1.09	1.08	1.08	1.07	1.07	1.06	1.06
$\frac{1}{2}$	0.905	0.916	0.921	0.926	0.935	0.937	0.940	0.943	0.948
$\frac{1}{10}$	0.761	0.779	0.794	0.807	0.823	0.828	0.837	0.845	0.855

We see that $(1 - C_0)$ decreases with increasing h , i.e., uncertainties due to anisotropy are smaller for high orbits. It should be emphasized that these values of C_0 correspond to the most unfavourable distributions of radiating matter below the satellite, and would be encountered very rarely. They take the form of a circular bright (or dark) area centred under the satellite surrounded by a dark (or bright) region (see Fig. 2 (a)). For long-wave radiation, with $\frac{1}{2} < n < 2$, we obtain $0.9 < C_L < 1.1$ and for short-wave radiation, with $\frac{1}{10} < n < 10$, we obtain $0.76 < C_s < 1.46$ at a height of 200 km, which is the lowest height at which a satellite has a useful lifetime. These are instantaneous values, and, as the satellite traverses such regions, the form of $I(\theta)$ changes rapidly such that C returns towards unity. Since the time constant of a practicable detector is likely to be of order one minute (see § 3 (g)) we are more interested in the possible extremes in the mean value $\bar{C}$ over about five minutes than in the instantaneous value. If in this time the satellite travels a distance comparable with the instantaneous diameter of its field of view the variation in intensity in the direction of motion is smoothed out and the only contrasts of importance are those perpendicular to the path. From Table 1 we see that this is a fair approximation for low orbits (speed ≈ 8 km sec⁻¹). The configuration of radiating surfaces

giving an extreme value to $\bar{C}$ for this case is a bright (or dark) lane placed centrally under the satellite's orbit in a dark (or bright) region (see Fig. 2 (b)). Approximate calculations show that, for the above values of n , we now have $0.98 < \bar{C}_L < 1.02$ and $0.9 < \bar{C}_s < 1.1$ at a height of 200 km. Thus the smoothing effect of the slow detector is such that we may enter Table 2 with $0.8 < n < 1.2$ for long-wave radiation and $0.5 < n < 2$ for short-wave radiation.

A further cause of anisotropy, in the case of long-wave radiation, is the 'natural' limb darkening due to obliquity of view of an atmosphere in which temperature and composition are height-dependent. Approximate calculations for a typical atmosphere (e.g., Elsasser 1942, p. 27) were made using the Elsasser radiation chart, giving the result shown in Fig. 2 (c) for a height of 200 km. For this distribution we find that $1.01 > \bar{C}_L > 1.005$ for $200 \text{ km} < h < 1,000 \text{ km}$.

Summarizing the above discussion, we can state that in all cases

$$0.98 < \bar{C}_L < 1.02$$

$$0.9 < \bar{C}_s < 1.1$$

Since the special configurations of cloud giving rise to these limiting values will be very rare and the pattern of intensity contrasts will not often be highly organized, $\bar{C}$ will in general be much closer to unity than these limits.

(d) *Equilibrium temperature of the sphere as a function of the radiation field*

Initially we neglect any heat transfer by conduction and radiation from the main body of the satellite and by conduction to the very tenuous atmosphere. From Eq. (2) the long and short-wave fluxes absorbed by the sphere are

$$\left. \begin{aligned} f_L &= \pi a^2 B C_L F_L e_L \\ f_s &= \pi a^2 (B C_s F_{ss} + S) e_s \end{aligned} \right\} \quad (6)$$

where e_L and e_s are the respective absorptivities of the surface defined by

$$e_L = \frac{\int_{4\mu}^{\infty} e_{\lambda} I_{\lambda} d\lambda}{\int_{4\mu}^{\infty} I_{\lambda} d\lambda} \quad e_s = \frac{\int_0^{4\mu} e_{\lambda} I_{\lambda} d\lambda}{\int_0^{4\mu} I_{\lambda} d\lambda}$$

where e_{λ} is the hemispherical spectral emissivity of the surface and I_{λ} is the spectral distribution of the incident radiation stream.

If the effective equilibrium temperature of the sphere is T , then

$$f_L + f_s = 4\pi a^2 \sigma T^4 e_L' \quad (7)$$

where

$$e_L' = \frac{\int_{4\mu}^{\infty} e_{\lambda} B_{(\lambda, T)} d\lambda}{\int_{4\mu}^{\infty} B_{(\lambda, T)} d\lambda}$$

In fact there will be some variation of temperature over the surface of the sphere, depending on the orientation of the spin axis relative to the incident radiation. In the worst case of solar radiation incident along the spin axis the temperature difference between the poles is proportional to $a^2 e_s / Kd$ where K is the thermal conductivity of the shell and d its thickness. For a black painted aluminium sphere 1 cm in diameter and 0.1 mm thick the temperature difference is of the order of 1°C , assuming the paint to be a good conductor.

Eqs. (6) and (7) give

$$B(C_L F_L k + C_s F_{ss}) + S = 4\sigma k' T^4 \quad (8)$$

where

$$k = \frac{e_L}{e_s} \quad k' = \frac{e_L'}{e_s}$$

For the ideal surface material e_λ would be constant out to at least 20μ . Then $e_L = e_L'$ and $k = k'$ to a very close approximation. In practice, e_λ would not be constant, but the difference between e_L and e_L' should not be more than a few per cent since the weighting functions $B_{(\lambda, T)}$ and I_λ are broadly similar, the main difference being that I_λ is relatively large in the $8\text{--}13 \mu$ window region.

(e) Measurement of F_N

The quantity of greatest interest to the meteorologist is the net flux of radiation F_N from the earth-atmosphere system; the earth satellite provides an opportunity of making world-wide measurements for the first time. We now discuss the determination of F_N at the position of the satellite. We have $F_N = F_L + F_{ss} - S \cos Z$, considered as positive in the outward direction. This can be written, using Eq. (8), as

$$F_N = \frac{4\sigma k' T^4}{B} - S \left(\frac{1}{B} + \cos Z \right) + (1 - k) \bar{C}_L F_L - \left(1 - \frac{1}{\bar{C}_L} \right) \bar{C}_L F_L - \left(1 - \frac{1}{\bar{C}_s} \right) \bar{C}_s F_{ss} \quad (9)$$

In this form we separate those terms which can in principle be determined experimentally from those which can not. Since the product $\bar{C}_L F_L$ can be determined (§ 3 (f)), while $\bar{C}_L$ and $\bar{C}_s$ are both unknown, only the last two terms on the right-hand side of Eq. (9) cannot be evaluated, though some indication of their values might be available from synoptic charts of cloud cover. The upper limits of these terms are estimated to be 0.01 and $0.1 \cos Z \text{ cal cm}^{-2} \text{ min}^{-1}$ respectively, since $F_L < 0.5$ and $F_s < \cos Z \text{ cal cm}^{-2} \text{ min}^{-1}$ under the conditions giving rise to extreme values of $\bar{C}_L$ and $\bar{C}_s$.

In most cases these terms will be much smaller than the values given above so that their neglect would not lead to serious error in F_N when F_N is greater than $0.1 S \cos Z$.

A special case of Eq. (9) should be noted: if we choose $k = 1$ and neglect the last two terms, the expression for F_N reduces to

$$F_N = \frac{4\sigma k' T^4}{B} - S \left(\frac{1}{B} + \cos Z \right)$$

So a single sphere can give all the information necessary for measuring F_N (S is to be assumed) without determining the component fluxes separately. However, it may not be possible to obtain a surface with $k = 1$ in which case it would be necessary to determine $\bar{C}_L F_L$ in order to evaluate the third term in Eq. (9); this problem is dealt with in the next section.

(f) Discrimination between and determination of the fluxes

Even if it were possible to obtain F_N without measuring the long and short-wave fluxes separately, it would still be of great interest to measure the latter fluxes. In particular, a measure of F_{ss} would give the albedo of the underlying surface, which in turn is a measure of the cloud amount.

A simple special case arises when the satellite is in the earth's shadow. Eq. (8) then reduces to

$$BC_L F_L = 4\sigma T^4 \frac{k'}{k} = 4\sigma T^4 \frac{e_L'}{e_L} \quad (10)$$

We see that $C_L F_L$ can be determined on the night side of the earth by measuring T only. Further, since $k'/k \approx 1 (= e_L'/e_L)$ to a very good approximation for all surfaces [see § 3 (d)], T will depend only slightly on the coating material of the sphere, especially as $T \propto (k/k')^{1/4}$.

On the sunlit side of the earth we must employ two spheres whose surfaces have different values for k (k_1 and k_2). We then obtain two equations of the form of Eq. (8) which are solved to give

$$BC_L F_L = 4\sigma \frac{k_1' T_1^4 - k_2' T_2^4}{k_1 - k_2} = y \quad (11)$$

$$BC_s F_{ss} + S = 4\sigma \frac{k_1 k_2}{k_2 - k_1} \left(\frac{k_1'}{k_1} T_1^4 - \frac{k_2'}{k_2} T_2^4 \right) = x \quad (12)$$

The relation between the incident fluxes and the equilibrium temperature of a sphere is shown in Fig. 3 for $k_1 = k_1' = 20$ ('white' sphere) and $k_2 = k_2' = 1$ ('black' sphere), 'black' and 'white' referring to properties in the visible. The sensitivity $\Delta T/\Delta F$ is readily assessed from this diagram, which clearly illustrates the decrease of sensitivity with increase of sphere temperature. Typical values of $\Delta T/\Delta F_L$, with $B = 1.5$, are 0.14°K and 0.04°K per $0.001 \text{ cal cm}^{-2} \text{ min}^{-1}$ at $T = 200^\circ\text{K}$, 300°K respectively.

Figure 3. Relation between the incident fluxes and the equilibrium temperatures of black ($k_2 = k_2' = 1$) and white ($k_1 = k_1' = 20$) spheres ($S = 2 \text{ cal cm}^{-2} \text{ min}^{-1}$). Over the night side of the earth both spheres have the same temperature.

A discussion of the errors of the determination of x and y from Eqs. (11) and (12) is given in § 6. It is shown there that the error in x is considerably larger than that in y . This is particularly unfortunate from the point of view of estimating albedo since the relevant part of x (i.e., $BC_s F_{ss}$) is often – with low sun – only a small fraction of S . The consequence is that F_{ss} can be measured only to moderate or poor relative accuracy, especially when it is small, i.e., when the solar zenith angle is large; under these conditions we can estimate the albedo only roughly.

Suomi (1958) refers to an alternative method of measuring F_{ss} over areas where the sun is low. He employs two additional spheres of low long-wave emissivity (Tabor coating, $k = 0.11$) and shielded from sunlight. It is difficult to assess the likely improvement in the precision of the measurement without a knowledge of the geometry of the shields and the effects of obscuration of the scattered radiation and their own long-wave emission, and possible incomplete shielding from the sun as the spin axis of the satellite precesses.

(g) Effect of time constant and local sources of heat

The incident flux of radiation will be a varying quantity, and the time constant of the sphere will lead to a lagging response. The effect on sphere temperature of the heat transfer by radiation and conduction from the main body of the satellite and from the residual atmosphere is also to be considered.

The time constant of a spherical shell of thickness d , density ρ_s at temperature T is $\tau = d\rho_s C/4\sigma T^3 e_L'$ where C is the specific heat of the material. This is the lower limit for τ since the conductivity of the shell and coating has been assumed infinite. For a magnesium shell 0.1 mm thick we find $\tau = 60$ sec at $T = 200^\circ\text{K}$ and 20 sec at $T = 300^\circ\text{K}$. Although it would seem desirable to have a faster response, the advantage is probably rather doubtful since the time averages $\bar{C}_L$ and $\bar{C}_s$ are more uncertain for shorter intervals (see § (3 c)). It is to be noted that in an interval of about 5 minutes the satellite traverses a distance of the same order as its instantaneous diameter of vision on the earth.

The heat transfer to the sphere by conduction and radiation from the main satellite body can be reduced to negligible proportions by separating these bodies sufficiently. Since only very slender supports are required there is in principle no difficulty in obtaining the required separation and the ideal conditions so far considered may almost be realised in practice.

The energy dissipation due to collisions with gas molecules is given by $\frac{1}{2}\pi a^2 \rho V^3$ where ρ is the air density and V is the satellite velocity (large compared with molecular thermal velocities). Assuming this energy to be used in heating the sphere, putting $V = 8$ km sec⁻¹ and using recent satellite data for ρ (King-Hele 1960), we find that this source of heat is equivalent to an increase of 0.15 cal cm⁻² min⁻¹ in the incident radiation stream at $h = 200$ km ($\rho = 4 \times 10^{-13}$ gm cm⁻³) and 0.002 cal cm⁻² min⁻¹ at $h = 400$ km ($\rho = 6 \times 10^{-15}$ gm cm⁻³). Thus, provided perigee height is greater than about 400 km, the effect is negligible.

(h) Reduction of the observations to a standard level

In general, the satellite's orbit will be elliptical and the flux measurements will be made from different heights at different points in the orbit. It is desirable, indeed essential for integral studies, to reduce the observations to a standard level, at height h_0 , say. The flux per unit area at h_0 can be written :

$$F_{h_0} = K \left(\frac{R+h}{R+h_0} \right)^2 F_h$$

where K is a constant at any instant. When the region visible from the satellite is horizontally homogeneous the radiation field below the satellite is radial and $K = 1$, but in all other cases it will differ from unity by an amount depending on the location and intensity of inhomogeneities. It becomes progressively more difficult to estimate K as $h_0 \rightarrow 0$, where the field can be appreciably non-radial, so that it is probably not profitable to reduce the observations to a level lower than perigee height. As an example, in the reduction of an observation made at $h = 1,000$ km to $h_0 = 500$ km, we find $0.5 < K < 2$ for $n = 10$ and $0.8 < K < 1.2$ for $n = 2$.

4. CHOICE OF k

For a two-sphere system we must choose k_1 and k_2 so that the effect of errors in the measured values of T_1 , T_2 , k_1 and k_2 is a minimum. A statistical analysis shows that the errors are minimized by making $k_1 - k_2$ as large as possible, i.e., the surfaces should have the largest possible difference in relative emissivities in the long and short wavebands.

There is a major disadvantage in employing a surface with $k < 1$ since this can only be achieved by making $e_L < 1$ and so increasing the time constant, which at best is already long (> 1 minute). Further, diminishing e_L could lead to undesirably high temperatures, at which conventional thermistor materials cannot be used, e.g., a Tabor coated sphere with $k = 0.11$ attains a temperature of 500°K to 600°K on the day side of the earth.

The practicable upper limit of k depends on how highly reflecting a surface can be made in the solar waveband. Suomi quotes a value of $k = 19$ for lead carbonate white paint for which $e_L = 0.95$ and $e_s = 0.05$; other figures quoted are for black paint ($e_L = e_s = 0.95$) and for the Tabor coating ($e_L = 0.10$, $e_s = 0.90$).

We conclude that the choice of k is mainly determined by technical restrictions, with $k_1 \approx 20$, $k_2 \approx 1$.

5. IN-FLIGHT CALIBRATION

(a) Introduction

Ideally, once the satellite leaves the laboratory the instrumentation should maintain its calibration, i.e., the k 's and the temperature calibrations (temperature *vs* signal parameter) should not change. There is the possibility that both of these conditions could fail, the first owing to surface erosion by micrometeorites or radiation damage (Lagow 1957) and the second owing to the development of minor faults in the electronics, including the temperature measuring elements. There are ways of detecting the occurrence of these defects from the observations and it might be possible to correct for them to a fair degree of accuracy.

(b) Check on temperature calibration

We have already seen from Eq. (10) that both spheres must have nearly the same temperature when on the dark side of the earth. If the observations indicate an abnormal systematic difference of temperature, then a fault must be inferred in the temperature calibration of at least one sphere, which may be located in either measuring element or in a part of the electronic circuits not common to both elements. In the event of a serious change of calibration it would be possible to recalibrate approximately by reversing the sense of the experiment on suitable occasions, e.g., when the satellite is known to be over a substantial area of reasonably homogeneous surface and atmosphere of known constitution ($T(p)$ and $\tau(p)$ from radiosonde data). It would then be possible to compute F_L from radiation charts to fair accuracy (± 10 per cent) and thence determine the temperature of the spheres to $\pm 5^\circ\text{K}$ (from Eq. (10) $\Delta T/T = \frac{1}{4} \Delta F_L/F_L$). This provides a single check to $\pm 5^\circ\text{K}$ at one point on the temperature calibration. By making repeated checks of this kind over different regions of the earth, the accuracy could be improved and the range covered would be about 160°K to 200°K .

(c) Check on surface emissivities

The cooling and warming curves as the satellite enters or leaves the earth's shadow might allow estimates of the emissivities of the surface to be made. At these times there is a large known change ($\pm S$) in the incident radiation and the slope of dT/dt against T^4 is then proportional to e_L' provided that the fluxes arriving from the earth are not also changing. The magnitude of the latter changes is, however, relatively small. With similar reservations, the value of e_s can be inferred directly from the change in the value of dT/dt at the instant of sunrise or sunset. Although the precision of an individual check of this kind is unlikely to be high, it will be possible to perform them about 30 times per day.

It should also be noted that the combination $k_1 k_2/k_1 - k_2$ could be estimated from observations taken when the satellite is in sunshine over the twilight region of the earth, for Eq. (12) then provides, as $F_{ss} \rightarrow 0$,

$$S = 4\sigma \frac{k_1 k_2}{k_1 - k_2} \left(\frac{k_1'}{k_1} T_1^4 - \frac{k_2'}{k_2} T_2^4 \right)$$

in which [see § 3 (d)] k_1'/k_1 , $k_2'/k_2 \approx 1$. Thus the precision in measuring F_{ss} is aided (see, also, § 6 below). This check can be made about 15 times daily, just before entry into the shadow (observations taken just after exit from the shadow will be subject to large lag corrections as the temperatures are then changing rapidly).

6. ERRORS

Errors in the flux determinations due to uncertainties in k_1 and k_2 will be systematic, while those due to uncertainties in T_1 and T_2 will be partly random. For this reason these sources of error are considered separately. Table 3 gives estimated errors in the derived fluxes for uncertainties of ± 5 per cent in k_1 and k_2 ($k_1 = 20$, $k_2 = 1$) and $\pm 1^\circ\text{K}$ in T_1 and T_2 .

It has been assumed for the purpose of this analysis that k_1 and k_2 are known only from laboratory measurements to ± 5 per cent. The resulting relative error in $k_1 k_2 / k_1 - k_2$ is about 10 per cent. As explained in § 5 (c) this factor can be determined from in-flight data. If T_1 and T_2 are measured to $\pm 1^\circ\text{K}$ then it is determined to about ± 3 per cent, which may be better than the accuracy obtainable from laboratory measurements, giving improved precision in the measurement of F_{ss} .

TABLE 3. SUMMARY OF ERRORS DUE TO STATED UNCERTAINTIES IN k AND T (units are $\text{cal cm}^{-2} \text{min}^{-1}$)

Quantity		From error in T $\pm 1^\circ\text{K}$ (Partly random)	From error in k (± 5 per cent) (Systematic)	Anisotropy error	Range of quantity
$BC_s F_{ss}$		·04 to ·08	0 to 0·2	0	0 to 2
$BC_L F_L$	Day	·003 to ·018	0 to 0·2	0	0·2 to 1·0
	Night	·003 to ·018	0	0	0·2 to 0·5
F_N	Day	0 to 0·02	0 to 0·1	$0·1 \cos Z$	0·1 to -1·5
	Night	0 to 0·02	0	0·01	0·2 to 0·3

7. SAMPLING

We now examine the sampling obtainable by a satellite. Figure 4 shows the disposition of the satellite's orbit with respect to the earth's equator and orbit in the most general case. The terminator is the great circle dividing the day and night sides of the earth;

Figure 4. Geometry of a satellite orbit

it rotates slowly in space (at about 1° per day) about the pole of the ecliptic, which is the normal to the plane of the earth's orbit, so that its intersection N_2 with the equator moves in the direction indicated. The satellite's orbit precesses about the earth's axis in the direction shown at a rate of approximately $9 \cos i$ degrees per day (for a low, nearly circular orbit; King-Hele 1960), its inclination i remaining constant. Consider a point X situated on the earth at latitude ϕ ($< i$). Since the rotation of the earth carries X under the orbit twice a day it follows that the satellite, unless otherwise controlled in flight, will, in general, pass close to X only twice daily, when X is near A and B . It is convenient to specify A and B by their local solar times t_1 and t_2 . It is apparent that all places with latitude ϕ will be observed by the satellite at about the same two local times t_1 and t_2 . The effect of the earth's angular motion around the sun and the precession of the satellite's orbit is to cause a slow change in t_1 and t_2 given by

$$\frac{\partial t_1}{\partial t} = \frac{\partial t_2}{\partial t} \approx -4(1 + 9 \cos i) \text{ min day}^{-1} \text{ (for a low, nearly circular orbit)}$$

So the satellite will cross a given latitude circle about 22 min earlier (in local time) each day for $i \approx 60^\circ$. For the special case of $i = 96.5^\circ$ the orbital precession cancels the earth's angular motion and the satellite always crosses a given latitude circle at the same local times.

Since the orbital period is $1\frac{1}{2}$ to 2 hours, we should obtain 12-16 observations around each latitude circle in the course of a day at each of two nearly fixed local times determined initially by the time of launch. Since the useful area observed by the satellite is of order 1,000 km across, a good sample of observations will be provided in longitude, L .

Figure 5. Qualitative nature of the diurnal variation of F_N neglecting diurnal variation of cloud amount.

The problem now arises of how to obtain values of the heat balance as a function of latitude and longitude. A desirable aim is to arrive at a world-wide picture of the net radiation $Q(\phi, L)$ where $Q = \int F_N dt$ taken over a period of a day or at most a few days. Now there is a large diurnal variation in F_N , shown qualitatively in Fig. 5 in which the diurnal variation of cloud is neglected. Clearly, observations of F_N at two points only of this curve, at practically the same local times in all longitudes, do not allow construction of the whole curve. Observations over a week would moreover only cover two sections of the curve each about $2\frac{1}{2}$ hr wide ($i \approx 60^\circ$), making use of the precession of the orbit. Wexler (1960) remarks that a solution to the sampling problem could involve the launching of a number of satellites into 'stationary' orbits of inclination 96.5° so that they are suitably spaced in local time about the earth.

If a high satellite orbit were used, say $h = 3,000$ km, then each place on the earth within the orbital zone would be observable over about 6 hours per day, but at the expense, in the two-sphere experiment, of large spatial smoothing. A high orbit recommends itself,

however, for a restricted-aperture radiometer giving spatial resolution of order say 100 km, but this requires an advanced, altitude-controlled satellite and it would then be necessary to assume (or measure) the form of the angular distribution of intensity of radiation leaving each area in order to obtain fluxes.

8. CONCLUSIONS

We state first the conclusions which are relevant to all satellite measurements of total radiation, no matter how they are made.

(1) Satellite measurements can only give the flux at the position of the satellite, i.e., at a height of 200 km or more. The flux at a lower level can only be inferred with precision under ideal conditions (visible area homogeneous).

(2) The sampling of data obtainable with a single satellite is inadequate for the purposes of world-wide heat balance studies because observations of F_N at a point are made at only two times during the day. Since all points around a given latitude circle are observed at the same two local times the data will be sufficient to give a zonal mean of the net flux at these two times.

The following conclusions relate to the two-sphere experiment described.

(1) The use of an omnidirectional sensing element gives rise to an uncertainty in the determination of the vertical fluxes at the satellite. It is shown that this uncertainty is acceptably small (< 2 per cent for long wave flux and < 10 per cent for short-wave flux) in most situations. The difficulty can only be avoided by using a plane sensing element maintained parallel to the earth's surface at all times.

(2) The experiment described is simple, and the apparatus required could be made very small and light, with small power requirements.

(3) The sensitivity is shown to be sufficient and the errors in the flux determinations are tolerably small in most cases. In the event of the occurrence of a minor defect not causing a complete breakdown of the experiment it should be possible to recalibrate the equipment in flight sufficiently well to make good use of continued observations.

(4) Conduction and radiation errors from the satellite itself can be made acceptably small. Heating by collision with gas molecules cannot be avoided and may be appreciable for low orbits (< 300 km), but is negligible above 400 km.

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