

Ph.D. 10893

NEAR INFRA-RED EMISSION STUDIES
USING A SISAM SPECTROMETER

by

Richard Paul Tuckett

of

Queens' College



A dissertation submitted in partial fulfilment of the
requirements for the degree of Doctor of Philosophy
of Cambridge University.

August 1978

To my parents

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Molecular spectroscopy is the study of the energy levels of molecules; transitions between levels (i.e. spectra) can give fundamental information about the structure of molecules. The subject has two quite distinct aspects: instrumentation - the development of spectrometers - and spectral analysis - the fitting of observed spectral lines to well-defined sequences, leading to numerical information about the structure of the molecule. This Ph.D. Thesis is concerned with both aspects.

Instrumental modifications

At the outset of my work, I took over a SISAM interferometric spectrometer which had been built in our Department; its sensitivity and stability were inadequate for my proposed research. The first part of the Thesis will describe its mode of operation, and modifications I have made to the spectrometer. A technique involving the rapid oscillation of one of the spectrometer mirrors, with phase sensitive rectification of the detector output, has dramatically improved the sensitivity of the instrument. Two electronic control systems were then introduced into the

spectrometer operation; they completely eliminated the effects of mechanical instability. These modifications have now brought out the full potential of the instrument.

Preliminary results

The following spectra were obtained during the development phase of the instrument; a partial analysis of these band systems will be presented.

(a) $^3\Sigma_u^- (v = 2) \longrightarrow ^3\Pi_g (v = 1)$ 'Y' band system of N_2 at $1.29 \mu m$.

(b) $^1\Delta_g (v = 0) \longrightarrow ^3\Sigma_g^- (v = 0)$ magnetic dipole band of O_2 at $1.27 \mu m$.

The HO_2 free radical

Near infra-red emission bands of HO_2 between 1.43 and $1.51 \mu m$ have been recorded with a now fully functional spectrometer. The second half of the Thesis will describe the analysis of the $^2A' \longrightarrow ^2A''$ band system; this has yielded much new information about the structure of HO_2 . Unexpected phenomena have been observed, the most interesting being the presence of 'forbidden' lines; they arise from a Renner-Teller interaction between vibrational levels of the two electronic states. The $^2A' \longrightarrow ^2A''$ band of the isotopic species DO_2 has also been recorded in order to determine the geometry of HO_2 in these two electronic states. The bond angle decreases slightly from the ground state to the excited state; HO_2 is thus one of the very few molecules violating Walsh's rules.

PREFACE

The work described in this dissertation was carried out in the Department of Physical Chemistry, the University of Cambridge, between October 1975 and August 1978. Except where otherwise indicated, usually by means of a reference, the work is original and not the result of collaboration with others. It has not been, nor is being concurrently, submitted for any degree at any other university.

I would like to take this opportunity of acknowledging some people who have been especially helpful to me in the course of my research. First, I thank my supervisor, Dr. W.J. Jones, who introduced me to the subject of molecular spectroscopy and suggested the research topic to be described; his continual enthusiasm and encouragement were a great help in my darker hours. Secondly, I thank all the technical staff of the Department for their help and advice on numerous problems concerning apparatus; I specifically acknowledge Mr. C.W. Oates who built the SISAM spectrometer. Thirdly, I thank a large number of researchers in this Department (and especially Dr. P.A. Freedman) for many profitable discussions over a wide area. Fourthly, I thank previous members of the research group (and especially Dr. S.M. Till) who were concerned with the design and construction

of the SISAM spectrometer; without their earlier labours, much of the research to be described would not have been possible. Fifthly, I thank Dr. K.E. Machin of Queens' College for many fruitful discussions concerning the mode of operation of the SISAM spectrometer. Finally, I thank Mrs. J. Nicholson for typing this dissertation.

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CHAPTER 1

INTRODUCTION

Molecules can absorb and emit radiation from the ultra-violet to the far infra-red. The radiation is concentrated in a large number of discrete "lines"; each line is at a well-defined wavelength and there is no continuous radiation between the lines. Quantum Theory requires that the energy of a molecule can only take certain discrete values; each value determines one "state" of the molecule. When a molecule changes from one state to another, it emits or absorbs radiation corresponding to one line of its spectrum. Thus molecular spectroscopy is the study of the energy levels of molecules, and the analysis of spectra can give fundamental information about the structure of molecules.

The symmetry properties of the energy levels require that only certain transitions between levels are allowed; these are the spectroscopic "selection rules". The most interesting spectra, however, arise from very weak or even "forbidden" transitions (i.e. those which violate these selection rules), since their very existence can provide deep information about molecular structure. Inevitably, forbidden transitions are much weaker than allowed ones, so their observation needs a very sensitive spectrometer.

In recording any weak spectrum, a spectroscopist is concerned with two fundamental problems - sensitivity and resolution.

The spectrometer must be able to collect as much radiation as possible from the absorbing or emitting source, yet simultaneously reduce random noise (e.g. from the source itself, detectors and amplifiers) to a minimum, so that very weak spectral features are not hidden in the noise. The "signal-to-noise" ratio of an individual spectral line is a measure of how the required information stands out from the background noise; it is thus a measure of the sensitivity of the spectrometer. Resolution is concerned with the fine detail of the spectrum: can the spectrometer resolve two spectral lines whose energy separation is very small? The ability of the spectrometer to resolve the fine structure of a spectrum is crucial to obtaining accurate information about the structure of the molecule.

Once a spectrum has been obtained, the analysis depends on finding patterns in the spectrum, i.e. sequences of lines usually in the presence of many other sequences. Each line is "assigned" to a particular transition between two energy levels of the molecule: a complete fit to all the assigned lines then gives spectroscopic constants for the molecule which can usually be related to its molecular structure.

It is thus seen that the subject of molecular spectroscopy has two quite separate aspects: instrumentation and spectral analysis. This dissertation will be concerned with both aspects.

At this stage, it is perhaps worthwhile to give a brief description of the layout of this Thesis. At the outset of my work I took over a SISAM interferometer which had been developed during the 1970's in the Department of Physical Chemistry at Cambridge. The first half of Chapter 2 will give a brief resume

of some different kinds of optical spectrometer, and will explain why previous members of the research group originally decided to build a SISAM rather than any other kind of spectrometer. The second half of Chapter 2 will describe the mode of operation of the Cambridge SISAM. When I took over this instrument, its sensitivity and stability were inadequate for my proposed research. Chapter 3 will first describe modifications I have made which have dramatically improved its sensitivity, and secondly the development of two electronic control systems which have completely eliminated the effects of mechanical instability. These modifications have meant that, for the first time, the Cambridge SISAM is now working at its full potential. Preliminary results obtained during the development phase of the instrument will be described in Chapter 4.

Having been developed into a fully functional spectrometer, the SISAM was now ready for use in serious spectroscopy. The second half of this Thesis (Chapters 5 - 8) will present a full analysis of the near infra-red emission bands of HO_2 and DO_2 . This has yielded much new fundamental information about the free radical, including its absolute geometry in the ground and the lowest-lying excited electronic states. Finally Chapter 9 will discuss possible work for the future.

CHAPTER 2

OPTICAL SPECTROMETERS

2.1 Introduction

This section will give a brief resumé of some different types of optical spectrometer. The advantages and disadvantages of each will be discussed, so the reasons why our research group decided to build a SISAM spectrometer in the early 1970's should become apparent.

2.1.1 Conventional slit spectrometers

The use of conventional slit spectrometers for infra-red spectroscopy is well known. A typical example of such an instrument is shown in Figure (2.1). The radiation under study is focussed on to an entrance slit S_1 and collimated by an off-axis parabolic mirror M such that a parallel beam of radiation strikes the dispersing element (which in this case is a diffraction grating, although a prism + Littrow mirror could equally well be used). Radiation of a particular wavelength λ_0 (determined by the angle between the incident beam and the grating) is diffracted back almost along its original path such that it is focussed down by M on to the exit slit S_2 and hence to an external detector. By rotating the grating, the angle between the incident beam and the grating changes, the selected wavelength λ_0 changes, and the spectrum is scanned. The advantages of such an instrument are

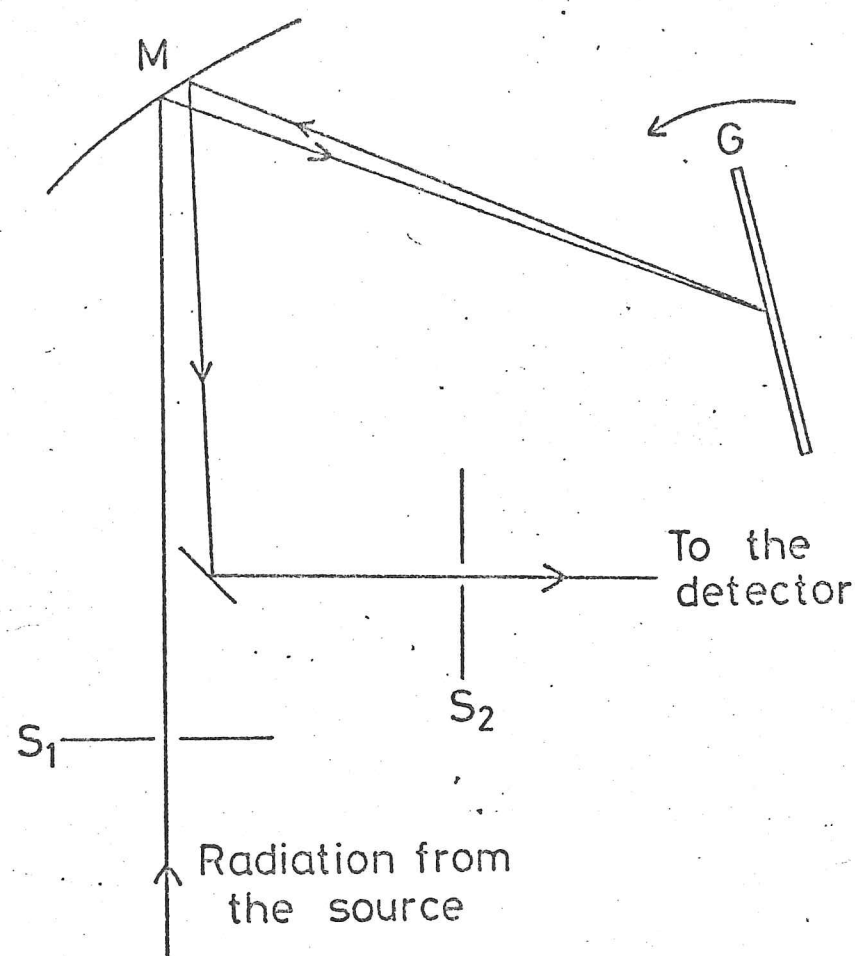


Figure 2.1 : A conventional slit spectrometer. M is an off-axis parabolic mirror, G a diffraction grating. S_1 and S_2 are the entrance and exit apertures respectively.

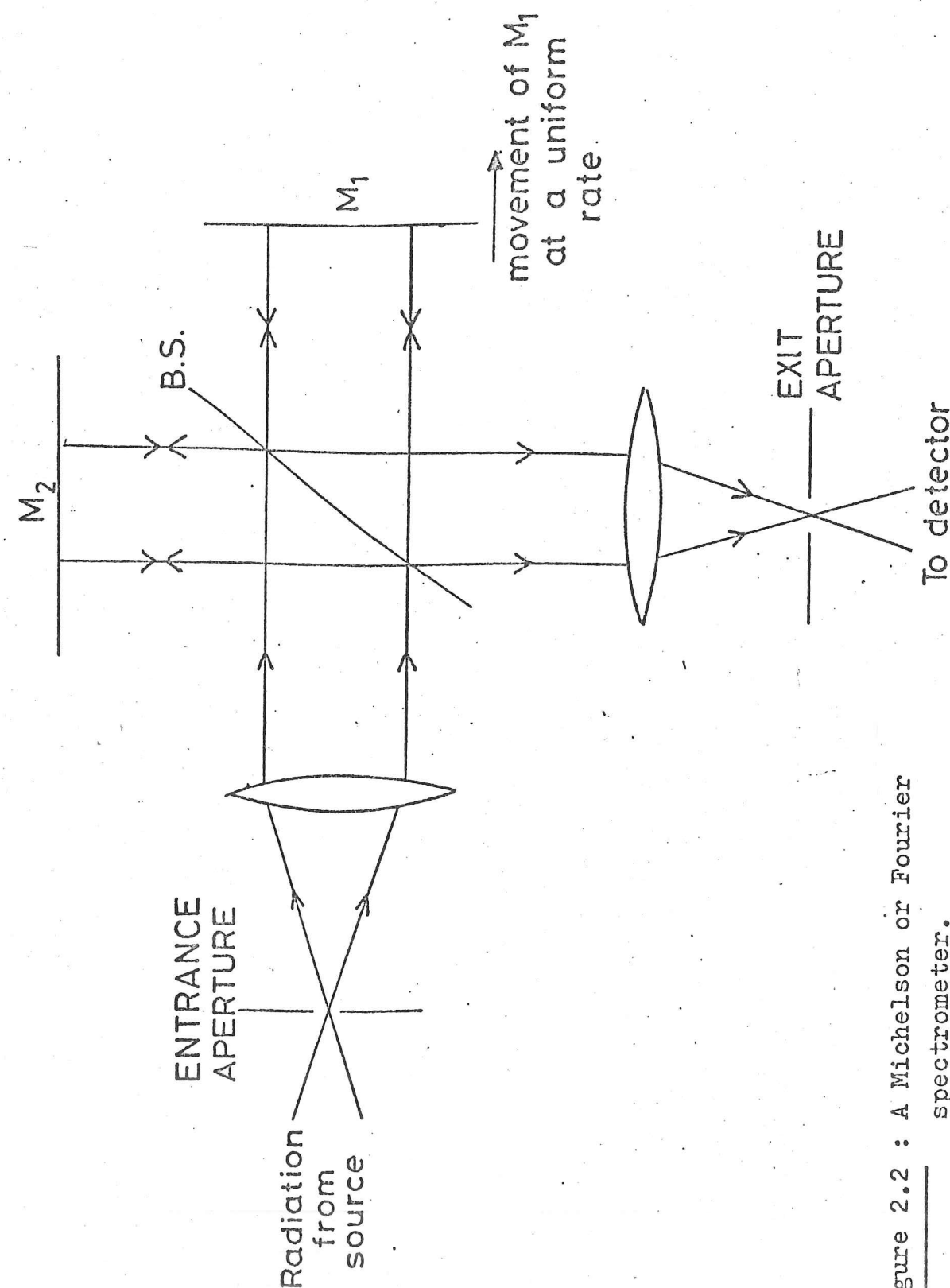


Figure 2.2 : A Michelson or Fourier spectrometer.

its simplicity and its large spectral range. The principle disadvantage can be summarised very easily - The spectral resolution is determined by the width of the exit slit: the narrower the slit, the better the resolution. To obtain improved resolution, therefore, one must sacrifice sensitivity; this, in a nutshell, is the classical drawback of conventional slit spectrometers. Such instruments are therefore only of great use when the source of radiation is very strong.

2.1.2 Interferometric spectrometers

The development of modern interferometric techniques has dramatically changed the situation as far as optical spectrometers are concerned. As we shall see later, the use of interference effects has meant that a high resolution spectrum can be obtained without sacrificing sensitivity by reverting to very narrow entrance and exit slits. The Michelson interferometer falls into this category of instrument. The simplest form of Michelson is shown in Figure (2.2). Collimated radiation from the source strikes a beam splitter B.S. whereby the radiation divides equally into two. The two beams pass on to the plane mirrors M_1 and M_2 , are reflected back along their original paths and recombine at the beam splitter. Assuming zero optical path difference between the two sides of the interferometer, constructive interference occurs and energy is transmitted to the detector. For a path difference of $\frac{1}{2}\lambda$, however, destructive interference occurs and the output intensity from the detector falls to zero. If one mirror (M_1) is therefore moved in a direction perpendicular to

its surface at a constant speed [Figure (2.2)], the intensity of the output beam varies sinusoidally with time. The frequency of this modulated output is inversely proportional to the wavelength of the radiation; in other words radiation of wavelength λ_1 is modulated at a frequency f_1 , radiation of wavelength λ_2 at f_2 where

$$\frac{\lambda_1}{\lambda_2} = \frac{f_2}{f_1} \quad (2.1)$$

For an incident beam of complex spectral content, therefore, each spectral element is modulated at a different frequency. By recording the total detector output intensity against time (which is, of course, equivalent to the displacement of M_2), a Fourier analysis of its composition can be made, and the spectral content of the incident radiation determined.

Such a Fourier spectrometer has two principle advantages:

(a) Information on all the spectral elements is present on the detector for the complete observation time t (which is a variable). Since the total recorded intensity is proportional to t , whilst the random noise from the source is only proportional to $t^{\frac{1}{2}}$, it is thus seen that

$$(\text{signal-to-noise}) \propto (t)^{\frac{1}{2}}$$

Spectrometers enjoying this condition are said to possess the multiplex or Fellgett advantage.

(b) As we shall see later, large entrance and exit apertures

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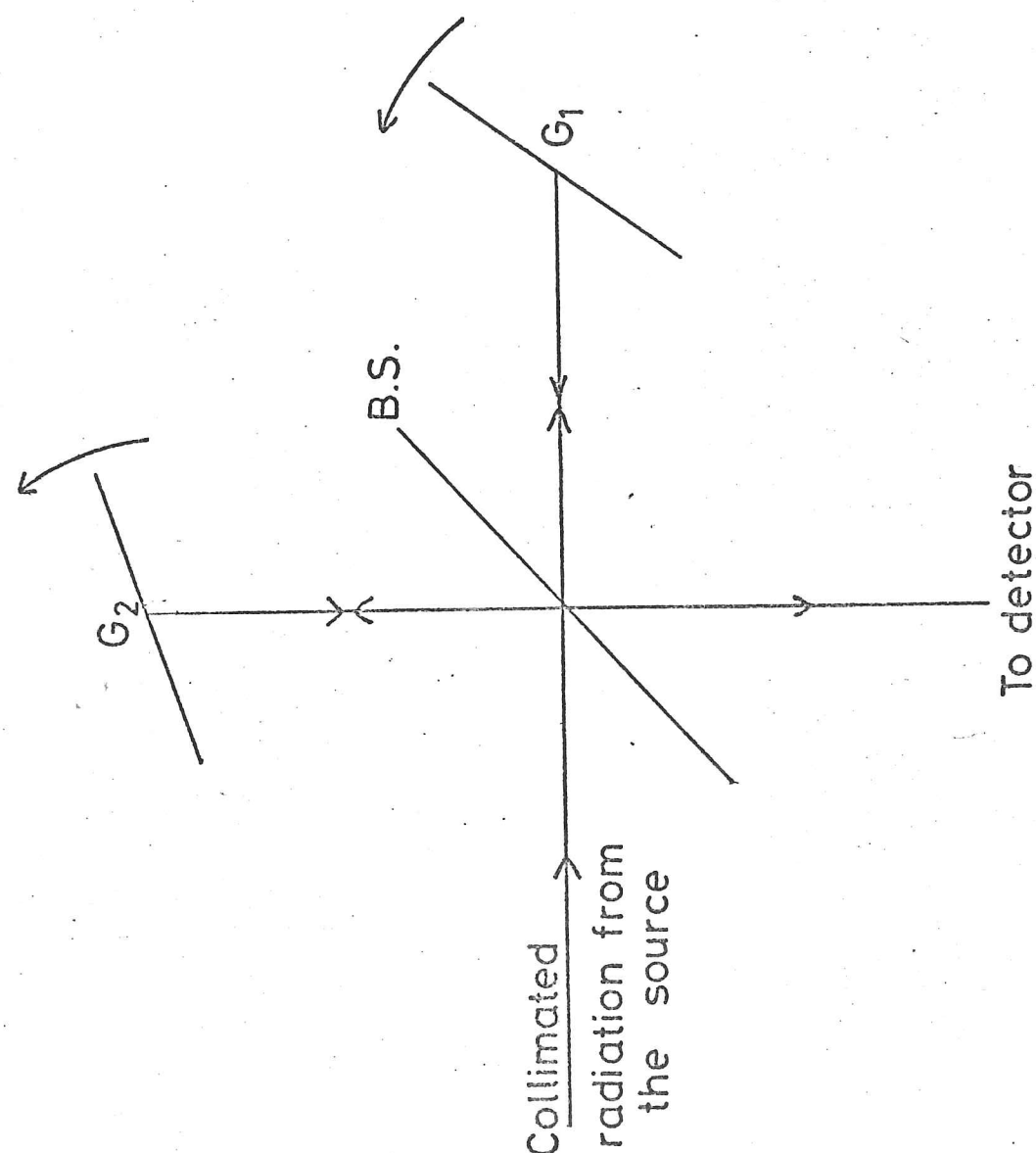


Figure 2.3 : The design of the original SISAM spectrometer.

can be used in this kind of instrument without sacrificing resolution. Such spectrometers are said to enjoy the Jacquinot advantage.

The disadvantages of the Fourier spectrometer should, however, be noted:

(a) It can be shown that the resolution of such an instrument is $1/2D \text{ cm}^{-1}$ where D is the total displacement of M_1 in cm. To obtain a spectral resolution of 0.2 cm^{-1} (which is the present resolution of the Cambridge SISAM spectrometer), therefore, it is necessary to move M_1 by $2\frac{1}{2} \text{ cm}$ at a uniform rate. The mechanical problems associated with this, whilst not insurmountable, are very great indeed.

(b) The instrument has a limited spectral range, and the spectrum is not recorded directly.

(c) The cost of modern digital computers necessary to calculate the Fourier transform make this a very expensive instrument.

The SISAM interferometer (spectromètre interférentiel à sélection par l'amplitude de modulation) falls midway between the conventional slit spectrometer and the Fourier interferometer. The original design for this kind of interferometer is due to the French, and in particular P. Connes, in the late 1950's (1-4). In essence it is very similar to the Fourier interferometer with mirrors M_1 and M_2 of the latter instrument replaced by identical diffraction gratings G_1 and G_2 [Figure (2.3)] in the SISAM.

As before, collimated radiation strikes the beam splitter, splits into two and passes to the two diffraction gratings. Now

only radiation of one particular wavelength returns along its original path; these beams recombine constructively and pass to the detector. If the optical path on one side of the interferometer is now varied uniformly with time, radiation of this wavelength is 100 % modulated. Radiation of all other wavelengths present on the detector (as we shall see later in this Chapter), however, is virtually unmodulated. The SISAM thus differentiates the individual spectral elements by their differing amplitudes of modulated output from the detector (hence explaining the meaning of the initials S.I.S.A.M.), unlike the Fourier instrument which differentiates the individual elements by the different frequencies of modulated outputs. The spectrum is scanned in the SISAM by a synchronous rotation of the two diffraction gratings in the same direction.

The SISAM is thus seen to have properties common to both the conventional slit spectrometer and the Fourier interferometer. It is worth stressing the following points:

(a) Unlike the Fourier instrument, the spectrum is recorded directly in the SISAM, and thus the latter instrument avoids the computational expenses needed for the former.

(b) As we shall see later, the SISAM possesses the Jacquinot advantage, and thus enjoys a considerable gain in signal-to-noise over a slit spectrometer working at the same resolution.

(c) Although the multiplex advantage is lost in the SISAM, its larger spectral range makes it in many ways a much more attractive proposition than the Fourier interferometer.

It was with these reasons in mind that our research group decided to build a SISAM spectrometer for the study of weak

spectral sources from the visible to the infra-red. The fundamental difference in our design from the original French design [Figure (2.3)] is that we have mounted the two diffraction gratings back to back, thus forming a single unit on a common table; in this way, it was hoped that the problems of ensuring a synchronous rotation of the two gratings would be considerably lessened.

Our instrument has already been described in the literature (5,6), and a very full account of its construction has been given by Dr. S.M. Till in her Ph.D. Thesis (7). The rest of this Chapter will give an account of the spectrometer. Whilst not claiming to be original, my description will stress the physical principles of the instrument, but will not present a full mathematical analysis. In this way, it is hoped that this part of my Thesis will complement, rather than copy, Dr. Till's description of the instrument.

2.2 The SISAM spectrometer

A diagram of the Cambridge single-pass * SISAM spectrometer

* The double-pass spectrometer (5,6,7) is preferred for work involving very high resolution; this can only be obtained by sacrificing sensitivity. As my research has been concerned with exceptionally weak emission spectra, the double-pass mode has never been used. It will not be mentioned again in this Thesis.

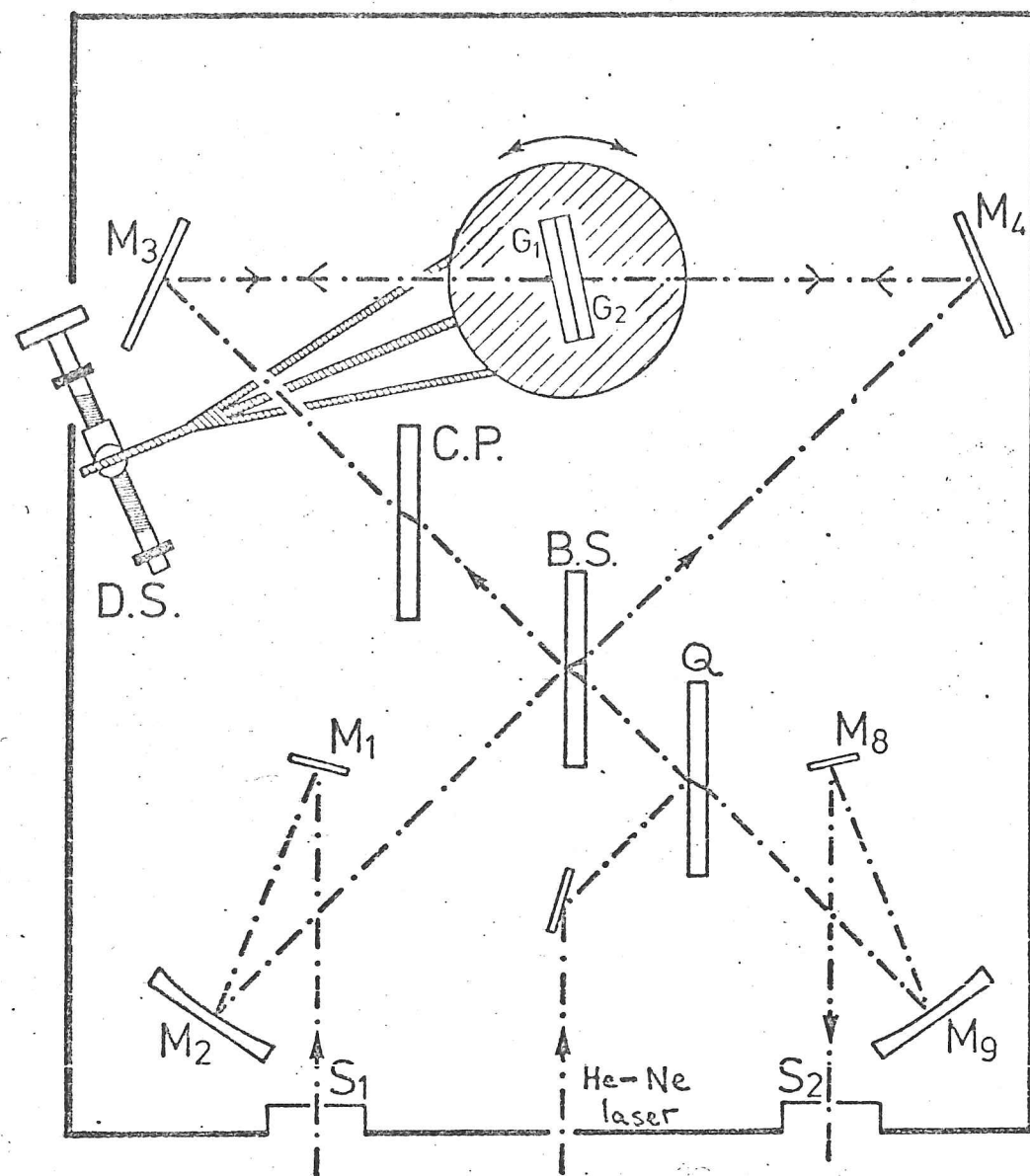


Figure 2.4 : The Cambridge single-pass SISAM spectrometer.

M_1 , M_3 , M_4 and M_8 are plane mirrors, M_2 and M_9 off-axis (18°) parabolic mirrors of 500 mm focal length. B.S. is the beam splitter, C.P. the compensating plate. G_1 and G_2 are two diffraction gratings; D.S. the drive-screw for the grating rotation. S_1 and S_2 are the entrance and exit apertures respectively. A gold spot in the middle of the quartz plate Q reflects a helium-neon laser, used for alignment purposes.

is shown in Figure (2.4). Radiation from the source is focussed on to the entrance aperture S_1 (which is large and circular, as we shall see later) and collected by the collimating element M_2 such that a parallel beam of radiation strikes the beam splitter B.S. This component is, at present, coated on one face for 50 % transmission 50 % reflection in the near infra-red ($1 - 2.5 \mu\text{m}$), so the radiation divides, passes on to plane mirrors M_3 and M_4 and on to two diffraction gratings G_1 and G_2 which are (as mentioned earlier) mounted back to back. Only radiation of one particular wavelength λ_0 (determined by the angle θ between the incident beam and the gratings) will be diffracted back exactly along its original path, such that on recombination of the two beams at the beam splitter their wavefronts are parallel to each other. Hence they recombine constructively and pass out of the spectrometer at the exit aperture S_2 to a suitable detector. By a synchronous rotation of the two gratings, the angle θ steadily changes, the selected wavelength λ_0 changes and the spectrum is scanned. In practice (as we shall see) the mirror M_4 is oscillated to and fro; the detector then gives an alternating output.

2.2.1 Alternating detector output: its importance and consequences

If we can arrange that the detector gives an a.c. rather than a d.c. output, problems of base-line drift in the amplifier following the detector disappear. This can be done in one of two ways:

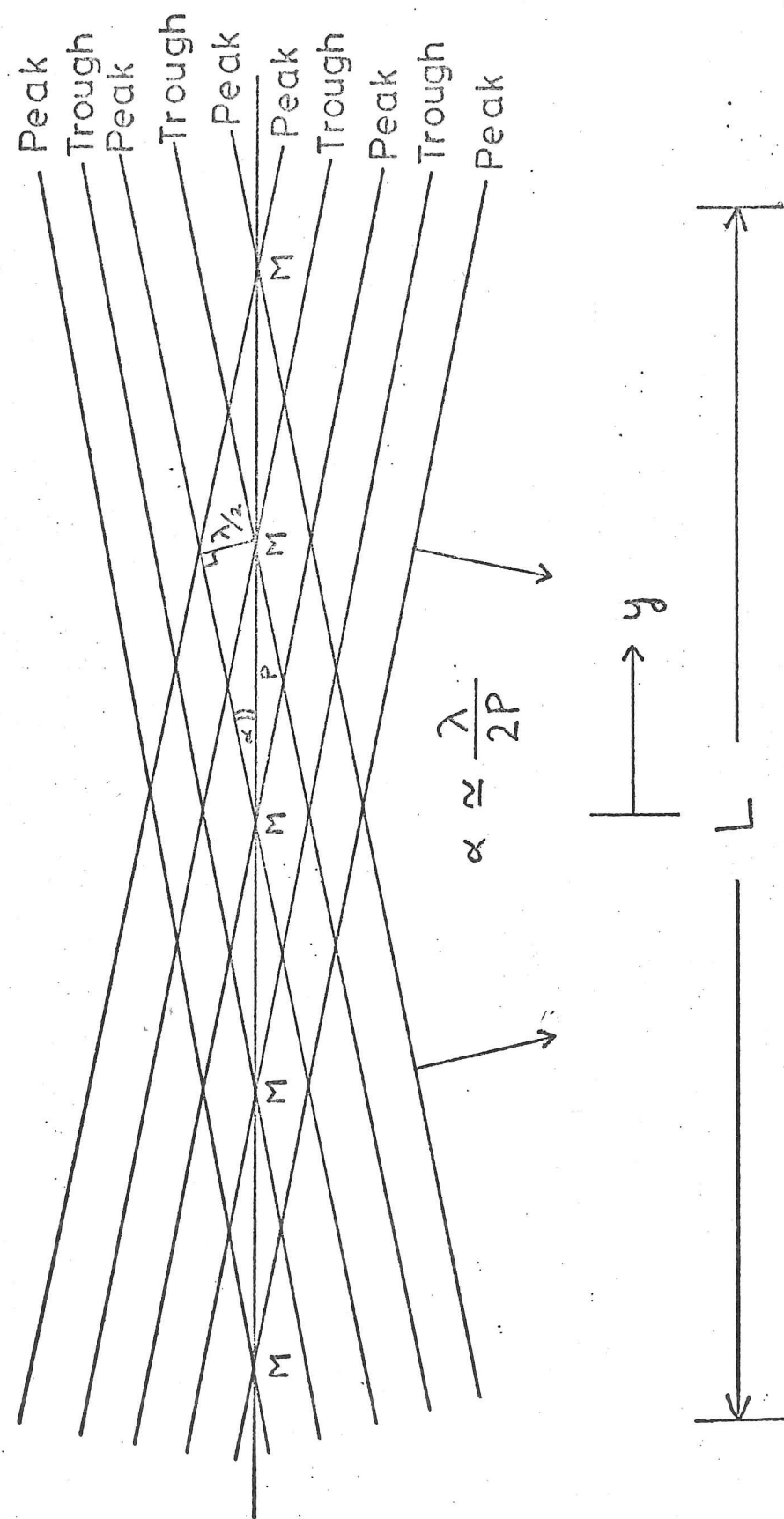


Figure 2.5 : The effect of recombining wavefronts at an angle of 2α . M refers to maxima in the interference fringes formed; P is the separation of successive maxima. L is the width over which the interfering beams extend; i.e. y spans from $-\frac{1}{2}L$ to $+\frac{1}{2}L$.

(a) By chopping the incident radiation before it enters the spectrometer. All the emergent radiation is then modulated, the detector gives an a.c. output, and the instrument behaves as a conventional spectrometer. In other words, the resolution of a spectrum is only a function of the slit width used at the entrance and exit aperture, and improved resolution can only be obtained at the expense of sensitivity. This is, once again, the classical problem of conventional slit spectrometers, and in this mode of operation the SISAM has no advantage over a much simpler slit monochromator working in the same region of the spectrum.

(b) By moving mirror M_4 , a changing path difference is introduced between the two sides of the SISAM interferometer. It is now necessary to explain why this motion differentiates the different spectral elements present on the detector, giving rise to high resolution and a modulated output from the detector for the selected wavelength λ_0 only.

The two beams of the interferometer recombine at the beam splitter and form a transverse set of interference fringes across the width of the combined beam; their spacing is dependent on the angle between the two beams. At the selected wavelength λ_0 , the two beams are exactly parallel, and there is no path difference across the beam width L: the fringe spacing is then infinite. At wavelength $\lambda_0 + d\lambda$ the two beams will be inclined at a small angle 2α to each other [Figure (2.5)], and a path difference of $2\alpha y$ (which is variable across the width of the beam, since y can take values between $-\frac{1}{2}L$ and $+\frac{1}{2}L$) has been introduced between the two beams: the fringes will then be close-spaced [i.e. small P in Figure (2.5)].

The effect of moving M_4 is to sweep the whole fringe system across the beam. If the width of this beam L is small compared with the fringe spacing P , the radiation which passes through it will move through successive maxima and zeros; after this radiation has been focussed on to the exit aperture S_2 and hence on to the detector, this external detector will therefore give an output which is 100 % modulated. If, on the other hand, L is large compared with the fringe spacing [as drawn in Figure (2.5)], several fringes will be contained in the beam. Sideways movement of the fringe system will then cause virtually no change in the amount of radiation passing through the exit aperture; the output from the detector will be almost unmodulated. It is from this property that the high resolution of the SISAM arises: the a.c. signal from the detector is large only when the fringe spacing is large, and this occurs for very small values of α , and therefore a narrow bandwidth about λ_0 .

The modulation of the output from the detector initially falls to zero when the spacing between the interference fringes P is exactly equal to L : in other words, when one fringe exactly is contained in the beam. [It will also be zero when exactly 2, 3, 4 or any integral number of fringes are contained in the beam.] The smallest value of α for which the modulated output is zero therefore occurs when

$$\alpha = \frac{\lambda_0}{2L} \quad (2.2)$$

It can be shown, without too much difficulty, that the amplitude of the modulated output varies with α as a sinc function (5)

[Figure (2.6)], and the α value of $\lambda_0/2L$ clearly corresponds to the Rayleigh criterion for the resolution of the SISAM spectrometer.

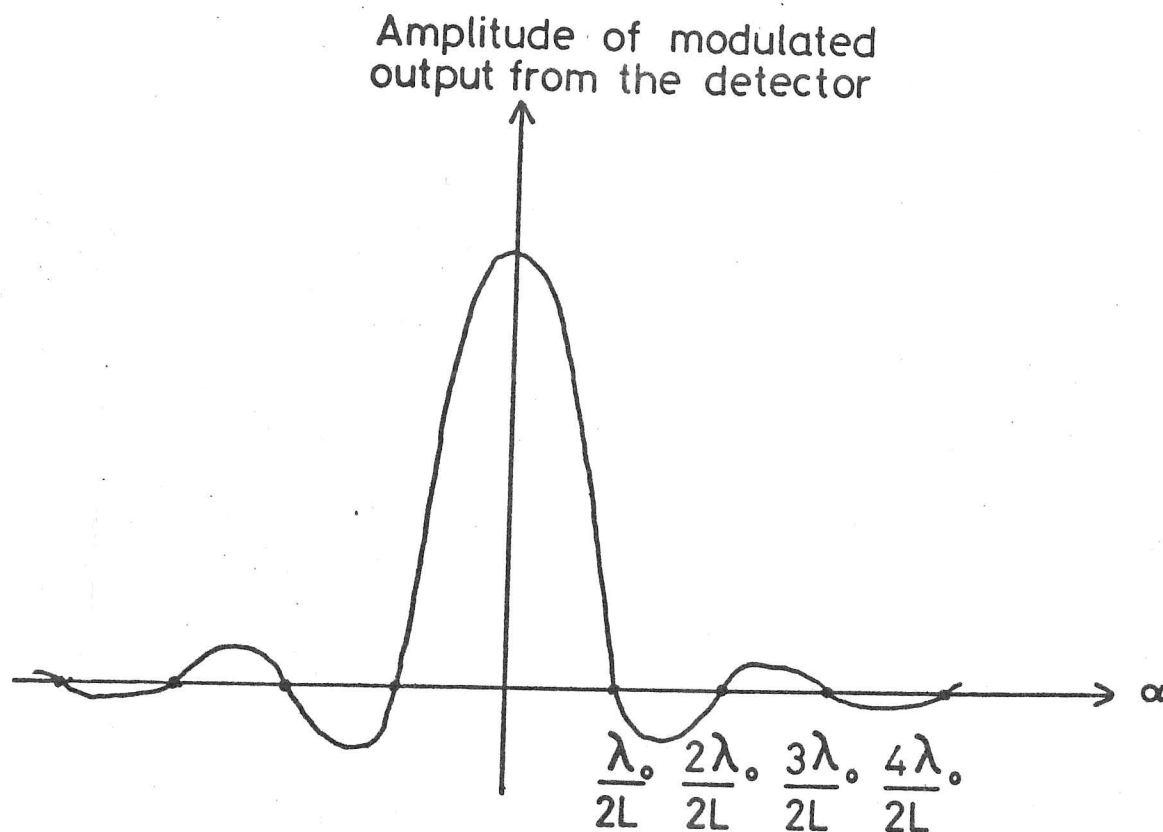


Figure 2.6 : The graph is explained in the text.

For convenience later on, it is important to realise that the top of the sinc function corresponds to the point where the change in path difference is only caused by movement of M_4 , and there is no change in path difference across the width of the beam

$$\text{i.e. } \frac{d}{dy} [\text{path difference}] = 0 \quad (2.3)$$

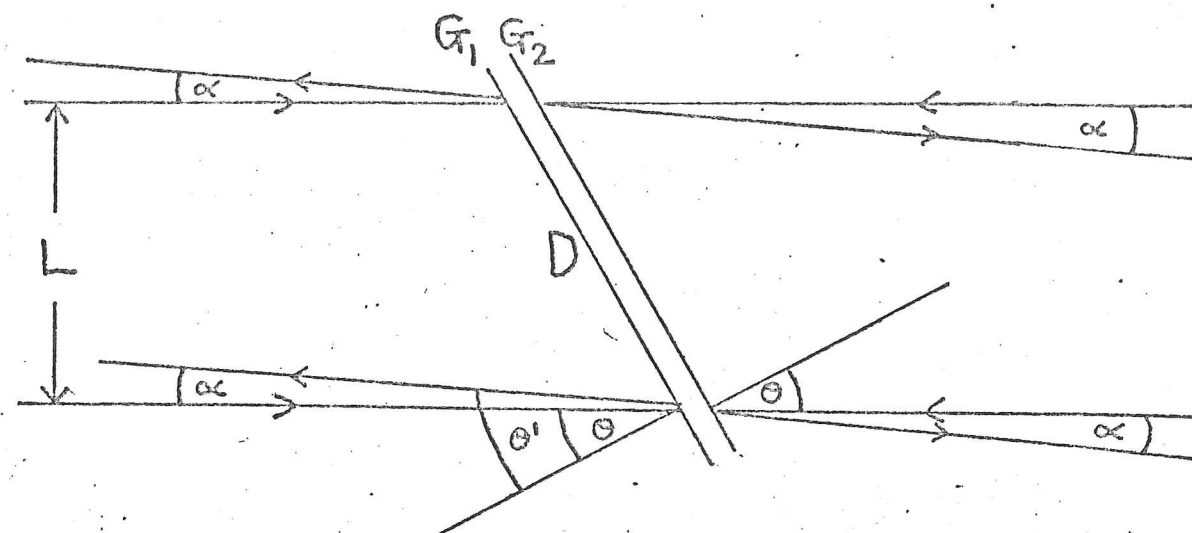


Figure 2.7 : The diffracted beams of radiation from the two gratings. The following symbols are used in the text:

D	width of each grating
N	number of rulings per grating
d	distance between rulings ($d = D/N$)
n	order of radiation incident on the gratings
λ	wavelength of radiation
R	resolving power of a single grating ($R = nN$)
θ	angle of incidence
θ'	angle of diffraction
α	misalignment of the incident and diffracted beams ($\alpha = \theta' - \theta$)
L	width over which the interfering beams, on recombination at the beam splitter, extend ($L = D \cdot \cos \theta$)

When the two beams recombine at the beam splitter with an angular misalignment of 2α , the path difference at any point along the width of the beam is given by

$$\text{P.D.} = 2\alpha y + \left(\text{path difference caused by motion of } M_4 \right)$$

$$\begin{aligned} \frac{d}{dy} (\text{P.D.}) &= 2\alpha \\ &= 0 \quad \text{at the top of the sinc function} \end{aligned}$$

The sinc function therefore has its maximum at $\alpha = 0$ [Figure (2.6)]. This might seem a slightly long-winded argument to explain an obvious result, but the reasons for it will become apparent later in the Chapter.

L represents the width of the smallest optical component in the beam, which in practice is the projected width of the diffraction gratings $D \cdot \cos \theta$ [Figure (2.7)]. By considering the angular dispersion of the gratings, the value of α corresponding to the Rayleigh criterion for resolution [equation (2.2)] can be expressed in terms of an absolute wavenumber resolution, as is shown below.

The diffraction condition for radiation of a general wavelength λ is given by

$$d[\sin \theta + \sin \theta'] = n\lambda \quad (2.4)$$

The angular dispersion is therefore given by

$$d \cdot \cos \theta' = n \frac{d\lambda}{d\theta'}$$

Hence $\delta\theta' \equiv \alpha = \frac{n}{d\cos\theta'} \cdot \delta\lambda$

$$\therefore \alpha = \frac{\sin\theta + \sin\theta'}{\cos\theta'} \cdot \frac{\delta\lambda}{\lambda}$$

$$\simeq 2\tan\theta \cdot \frac{\delta\lambda}{\lambda} \text{ for very small } \alpha$$

$$\therefore \frac{\lambda}{\delta\lambda} = \frac{2\tan\theta}{\alpha} \quad (2.5)$$

As we have seen, the modulation amplitude initially falls to zero when $\alpha = \lambda/2L$. The resolving power of the SISAM is therefore given by

$$\begin{aligned} \frac{\lambda}{\delta\lambda} &= \frac{4L\tan\theta}{\lambda} \\ &= \frac{4D\sin\theta}{\lambda} = \frac{4Nd\sin\theta}{\lambda} \\ &= \frac{4Rd\sin\theta}{n\lambda} \\ &= 2R \text{ when } \theta = \theta' \end{aligned} \quad (2.6)$$

The theoretical resolving power of the SISAM is therefore twice the resolving power of one grating used by itself. The gratings used in our instrument have a resolving power of 38,400 for first order radiation, so in the absence of any other effects

the instrumental resolution at, for example, $1.5 \mu\text{m}$ would be $15,000/76,800 = 0.2 \text{ \AA}^0$ or 0.09 cm^{-1} .

2.2.2 The size of the entrance aperture

It has now been shown why motion of M_4 gives rise to high resolution, and a modulated output from the detector only for a narrow bandwidth about the selected wavelength λ_0 . It has not yet been explained why the SISAM can utilise relatively large circular entrance and exit apertures without losing appreciable resolution. The treatment just given is, in fact, only valid when the SISAM is illuminated by a point source at the centre of the entrance aperture S_1 . The effect of increasing the size of S_1 and S_2 (i.e. increasing the sensitivity of the spectrometer) must now be considered.

One may regard a finite aperture as made up of a large number of individual point sources. As we have seen, the source at the central point of the aperture, A, is collimated by M_2 [Figure (2.8)]; after division at the beam splitter, two parallel beams of radiation strike the gratings G_1 and G_2 at the same angle of incidence θ . Radiation of wavelength λ_0 only is diffracted back exactly along its original path and focussed to a point at the centre of the exit aperture. Changing the path length of one side of the interferometer (by moving M_4) results in a modulated output from the detector, as described by the sinc function in Figure (2.6) which is centred about $\alpha = 0$.

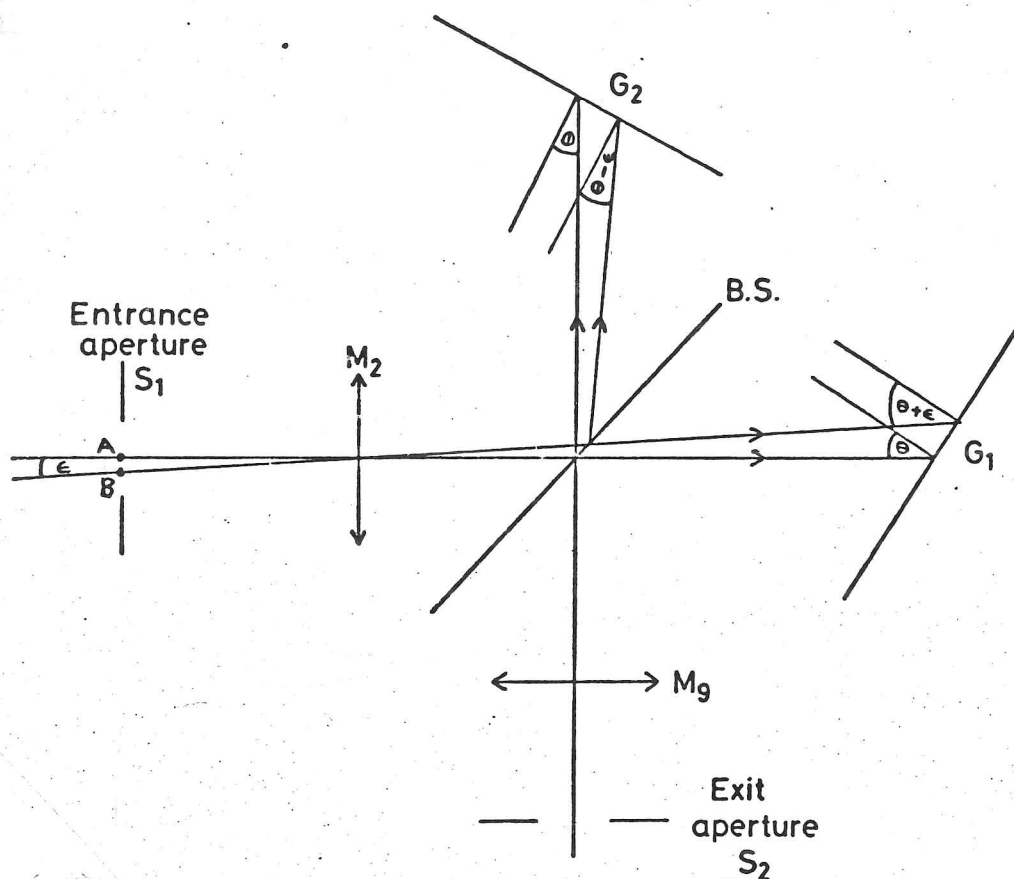


Figure 2.8 : The diagram is explained in the text.

Now consider a point source which is horizontally displaced from A off the optical axis (e.g. B). Radiation from it will also be collimated by M_2 , but after division at the beam splitter the two beams will now strike G_1 and G_2 at slightly different angles of incidence $(\theta + \epsilon)$ and $(\theta - \epsilon)$ respectively

(ϵ corresponding to a misalignment in the horizontal plane). Radiation of wavelength λ_0 is diffracted back, not along its original path, but to first order in ϵ at angles $(\theta - \epsilon)$ and $(\theta + \epsilon)$ respectively. On recombination at the beam splitter, however, there will be no angular misalignment between the two beams, and they will both be focussed to a point horizontally displaced off-axis on the exit aperture S_2 . If, on the other hand, ϵ corresponds to a misalignment in the vertical plane (i.e. B is vertically displaced from A), then the gratings will act as mirrors, so radiation will be reflected back at an angle $-\epsilon$ to the horizontal axis. The two beams will recombine with no angular misalignment, and again are both focussed to a point now vertically displaced off-axis on the exit aperture.

The point being made is that the diffraction gratings, almost by luck, cannot differentiate a misalignment in the horizontal and vertical planes. In other words, to first order the SISAM possesses circular symmetry, even though the presence of gratings ruled in one plane only would seem to contradict this.

We therefore consider a circular annulus of entrance aperture whose radius subtends an angle ϵ at the collimating element M_2 . In Figure 3(b) of reference (5), Till et al showed that such an annulus would introduce an additional path difference between the two sides of the interferometer; its value was shown to be $-2y\epsilon^2 \tan \theta$, and is thus dependent on the distance y from the centre of the recombined beam to any point across its width [see Figure (2.5)]. When the two beams

recombine at the beam splitter with a horizontal angular misalignment of 2α , the path difference at any point across the width of the beam is now given by

$$\text{P.D.} = 2\alpha y - 2y\epsilon^2 \tan \theta + \left(\begin{array}{l} \text{path difference caused} \\ \text{by motion of } M_4 \end{array} \right)$$

Movement of M_4 will result in a modulated output from the detector, but the sinc function will be centred, not about $\alpha = 0$, but about its value such that (see previous argument)

$$\frac{d}{dy} (\text{P.D.}) = 0$$

$$\text{i.e.} \quad 2\alpha - 2\epsilon^2 \tan \theta = 0$$

$$\text{Hence} \quad \alpha = \epsilon^2 \tan \theta \quad (2.7)$$

It is important to appreciate that this value of α is necessarily positive for all values of ϵ .

A full circular entrance aperture is made up of a series of concentric circular annuli, each of different ϵ ; they will all contribute their individual sinc functions to the total modulated amplitude [Figure (2.9)], each sinc function being centred about a value of α which increases as ϵ increases (i.e. as the size of the annulus increases).

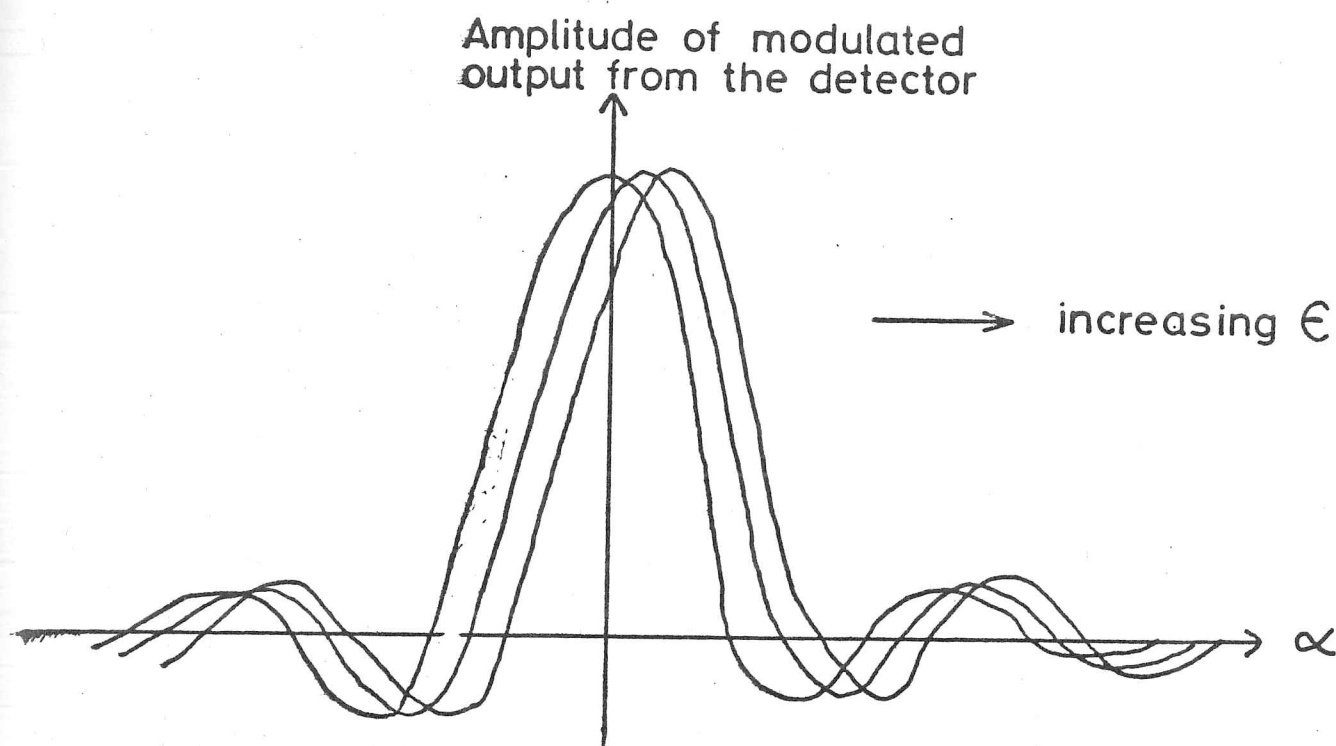


Figure 2.9 : Effect of increasing the size of the entrance aperture on the modulated output. Each circular annulus subtending an angle ϵ at M_2 contributes its sinc function, centred about a value of α which increases as ϵ increases.

The variation of modulated amplitude with α will be the sum of all these individual sinc functions (or, more formally, the convolution of a single sinc function with an aperture function). The following points should be noted:

(a) The amplitude of the modulation will initially fall to zero for a value of α greater than $\lambda_0/2L$. In other words, the resolution is degraded by the presence of more than one circular annulus (assuming the point source A to be a circular annulus subtending an angle $\epsilon = 0$ at M_2).

(b) The amplitudes of the secondary and tertiary maxima will decrease at the expense of the principle maximum.

Thus the instrumental resolution will be dependent on the size of S_1 , or more precisely the solid angle Ω which S_1 subtends at the collimating element M_2 . If S_1 is small, the sinc functions will not extend out far along the x (or α) axis of Figure (2.9), there will be little cancelling of the secondary peaks of the individual sinc functions, so the total modulated amplitude will have comparatively large secondary maxima [Figure 2.10(a)]. Although the lowest value of α for zero modulation will scarcely be degraded from its "one source" value of $\lambda_0/2L$, the small size of S_1 will mean a small light throughput. If, on the other hand, S_1 is too large, the width of the central peak of the total modulated amplitude graph will increase, so resolution is being sacrificed at the expense of sensitivity; in addition, there may be more than one maximum at the top [Figure 2.10(b)].

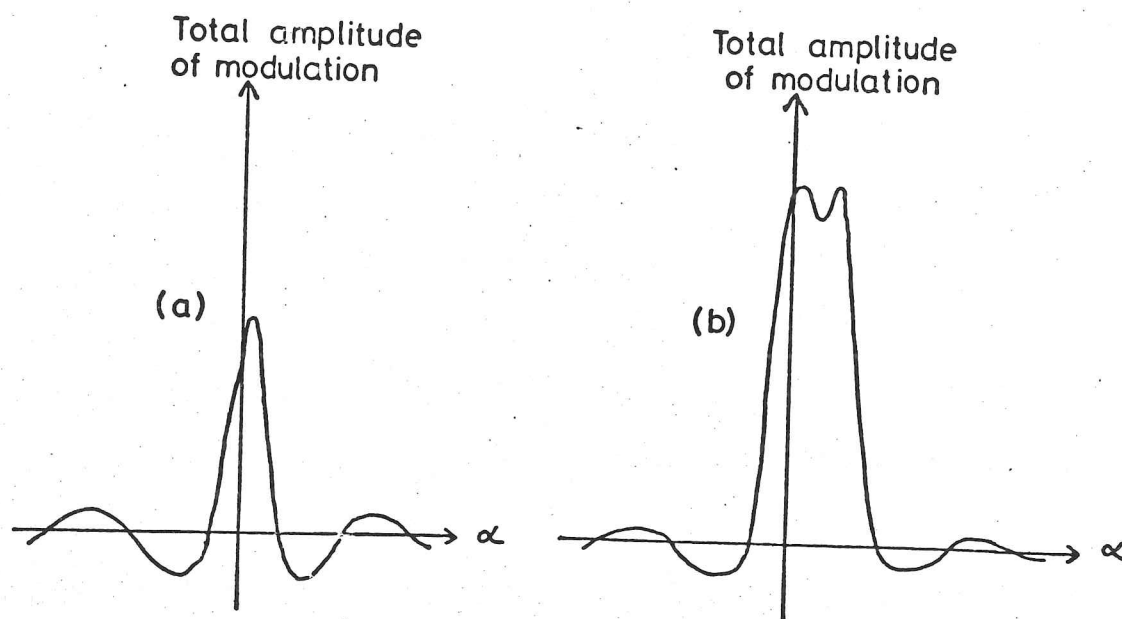


Figure 2.10 : The graphs are explained in the text.

(a) shows the effect of a small entrance aperture, (b) the effect of a large one. Note that the graphs are not symmetrical about $\alpha = 0$.

The best size for the apertures must, therefore, be a compromise between sensitivity and resolution. By performing the integration of all the individual sinc functions arising from all circular annuli over the entrance aperture S_1 and computer-synthesising the resultant lineshape for different values of Ω , Till (7) was able to show that the "best" lineshape compatible with the maximum light throughput was obtained when

$$\Omega = \frac{2\pi}{R} \quad (2.8)$$

"Best" is here defined to mean the greatest resolution for maximum apodization of the secondary maxima. As before, R is the resolving power of a single diffraction grating. In our instrument, with a 500 mm focal length collimating element, it can easily be shown that this value of Ω corresponds to a 7 mm diameter aperture. [It is perhaps a happy coincidence that a circular-shaped aperture is not only the easiest to analyse mathematically, but also the easiest to construct mechanically; it is not necessarily true that a circular aperture will give the best lineshape.] Till also showed that the resultant resolving power was then degraded from $2R$ (for a point source aperture) to $\sim R$; the theoretical resolution of the SISAM at 1.5 μm then becomes $15,000/38,400 = 0.4 \text{ \AA}^0$ or 0.18 cm^{-1} .

What is unclear, however, in both her Thesis (7) and the Royal Society paper (5) is whether it has been appreciated that the convoluted sinc function is no longer centred about $\alpha = 0$ [see Figure (2.10)] - For a finite size of entrance aperture, the maximum in the modulated output no longer occurs at λ_0 (as it does for a point source) but at λ where $\lambda > \lambda_0$. Furthermore, the difference $(\lambda - \lambda_0)$ is dependent on the size of the aperture, since Ω determines the extent to which the individual sinc functions spread out along the (positive) α axis. This final point has recently been demonstrated most elegantly by Ross (8). He has performed the integration of the sinc functions for different values of Ω (as Till did), but has then plotted all

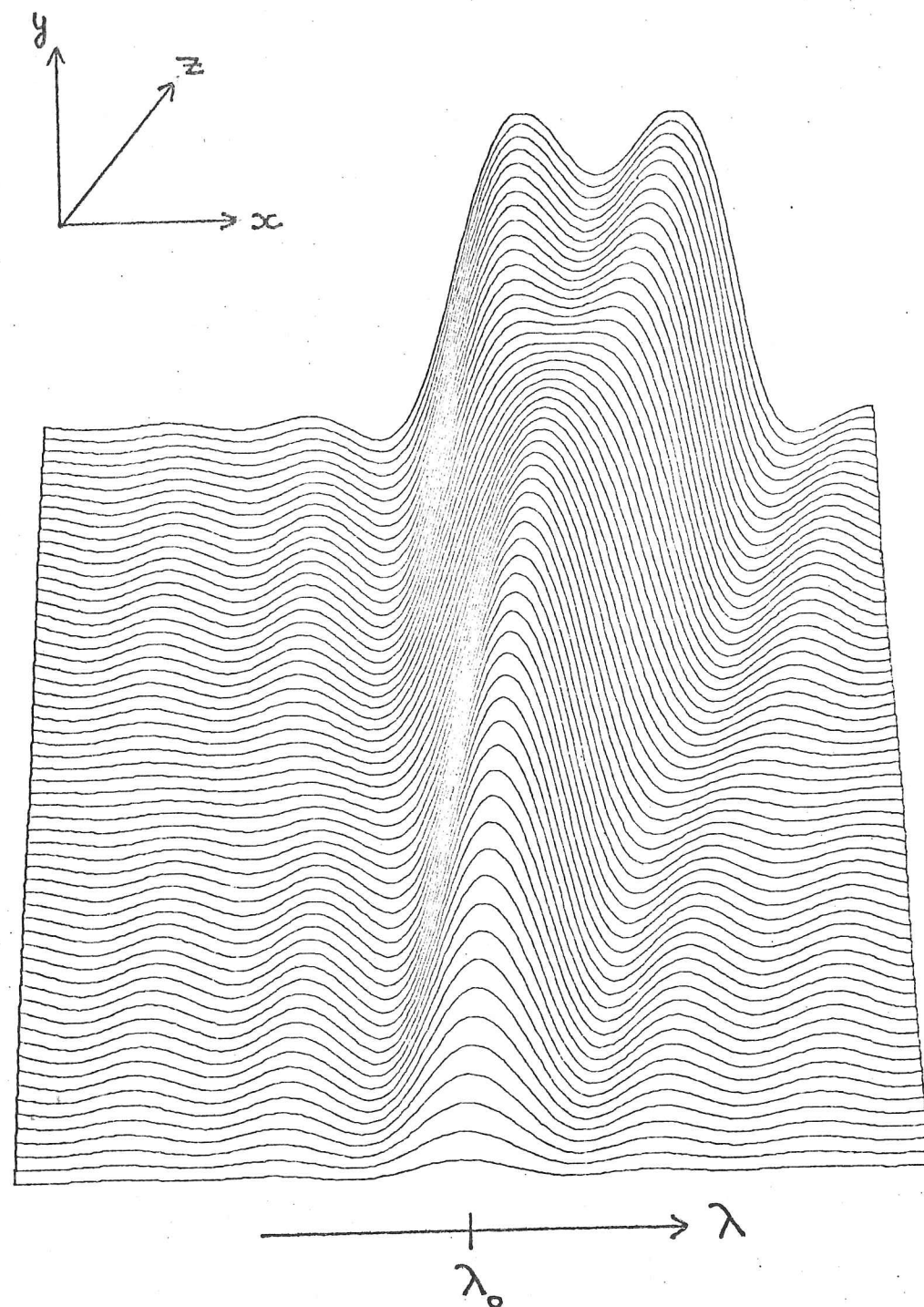


Figure 2.11 : The line contours are explained in the text.

the resultant lineshapes simultaneously in three dimensions [Figure (2.11)]. * In this diagram, the x axis represents α (which is, of course, equivalent to λ), the y axis represents the amplitude of the modulated signal, and the z axis represents increasing Ω ; it is clearly seen that the shift $(\lambda - \lambda_0)$ increases as Ω increases.

The magnitude of this shift can readily be calculated for a 7 mm diameter aperture. The maximum value of ϵ then corresponds to 7×10^{-3} radians, so the sinc function from this outermost annulus will be centred at $\alpha = 49 \times 10^{-6} \tan \theta$ [see equation (2.7)]; the total modulated amplitude will therefore occur at $\alpha = 24.5 \times 10^{-6} \tan \theta$. This value of α can be related to the wavelength shift using equation (2.5)

$$\begin{aligned} \text{i.e.} \quad \lambda - \lambda_0 &= \frac{\alpha \lambda}{2 \tan \theta} \\ &= 12.2 \times 10^{-6} \lambda \end{aligned}$$

So at $1.5 \mu\text{m}$, $(\lambda - \lambda_0) = 0.18 \text{ \AA}$ which is half the instrumental linewidth. To keep this effect in perspective, however, it should be realised that it is unimportant so long as the instrument is calibrated by passing the calibration radiation through the same sized entrance aperture. This in itself, however, is not sufficient - The external optics must ensure that both the unknown near infra-red radiation and the

* I am most grateful to Mr. C.F. Ross for his permission to show this diagram.

calibration radiation actually fill the whole aperture with their respective radiations; only then will the wavelengths of the unknown spectrum and the calibration lines be shifted by the same amount, so there will then be no absolute error in the spectrum being recorded. This point will be mentioned again in the section dealing with calibration (Chapter 3.3.2).

In all the spectra that are to be described later in this Thesis, 7 mm diameter entrance and exit apertures were used. Such large apertures are obviously compatible with my earlier description of the SISAM as a high sensitivity, high resolution spectrometer. This large light throughput of the SISAM represents, in fact, a gain in sensitivity of $\sim 10^3$ over a conventional slit spectrometer working at the same resolution in this near infra-red region of the spectrum, and makes the former instrument such an attractive proposition for the study of very weak spectral sources.

CHAPTER 3

MODIFICATIONS TO THE SISAM SPECTROMETER

3.1 The sensitivity of the SISAM

In the last Chapter it was shown that if the path length on one side of the SISAM interferometer is changed, this motion gives rise to high resolution and a modulated output from the detector. Different ways of introducing this variable path difference between the two sides of the interferometer will now be discussed.

3.1.1 Non-coherent mirror oscillation

The variation in path difference between the two beams can be introduced by applying a voltage to a piezo-electric transducer on which mirror M_4 is mounted. If the distance over which the mirror moves is relatively large (typically between 50 and 100 wavelengths at $1.5 \mu\text{m}$), many interference fringes will be swept across the plane of the recombined beams. The a.c. output from the detector, therefore, has a frequency proportional to the velocity of motion of M_4 . By changing the velocity, this frequency can be suited to the natural frequency response of the detector being used. The output signal is a.c. amplified, then taken to a tunable electronic filter unit. The output from this is rectified with a selectable time constant, and finally taken to a pen recorder.

Two factors, however, make this technique unsatisfactory.

(a) There is a limit to the voltage that can be supplied to the piezo-electric transducer (approx. 3000 volts) without causing irreparable damage to it. As this voltage cannot increase indefinitely, M_4 cannot move continually in the same direction. The voltage has therefore in practice been applied to the transducer as a symmetrical triangular waveform of period 1.4 seconds (5,7). When the voltage on the transducer starts to decrease, M_4 changes direction. * Varying the peak-to-trough voltage, while keeping the period constant, changes the speed at which the interference fringes sweep across the plane of the recombined beams, and hence the frequency of the modulated output.

Using this non-coherent oscillation technique, it is most unfortunate that, every 0.7 seconds, the mirror must change direction. When this happens random phase changes are introduced which produce periodic intensity fluctuations in the modulated signal, adding to the noise seen by the detector.

Discontinuities, corresponding to the turning points of the mirror,

* It is perhaps worth noting that in the Fourier spectrometer (Chapter 2.1.2) the path length on one side of the interferometer must change uniformly in one direction only by $\sim 10,000$ wavelengths in order to obtain a comparable resolution of 0.2 cm^{-1} at $1.5 \text{ }\mu\text{m}$. This must involve a very sophisticated mechanism for driving the moving mirror. In the SISAM the necessary change in path length is very small in comparison, so it can be achieved by a much simpler method (e.g. applying a voltage to a piezo-electric transducer supporting the moving mirror). This was yet another reason for constructing a SISAM rather than a Fourier interferometer.

will then be apparent in the rectified output as a signal at intervals of 0.7 seconds superimposed on the main signal. This "mirror noise" is proportional to the intensity of the radiation, so contributes to the apparent noise level of absorption spectra but not to the background noise of discrete line emission spectra. Nevertheless, noise will be apparent on actual emission lines.

(b) The required frequency selectivity is achieved by a tunable electronic filter unit in the detection circuit. Such filters can never compete with phase sensitive detectors in filtering out noise of unwanted frequencies.

I have therefore introduced a different method of oscillating M_4 . This technique, called "coherent modulation", was first used in one of the French SISAM spectrometers in 1972 (9); its theory is described in the next section.

3.1.2 Coherent mirror oscillation

In this technique, mirror M_4 is oscillated at a relatively high frequency (typically 70 Hz) with amplitude adjusted so that the optical path on its side of the interferometer changes by exactly $\frac{1}{2}\lambda$. In effect, the radiation focussed on to the exit aperture is then oscillating between the maximum and minimum of an interference fringe. No phase change now occurs when the mirror changes direction, and there is no "mirror noise". This factor alone increases the effective signal-to-noise by a factor of approximately 2. The use of a $\frac{1}{2}\lambda$ path difference

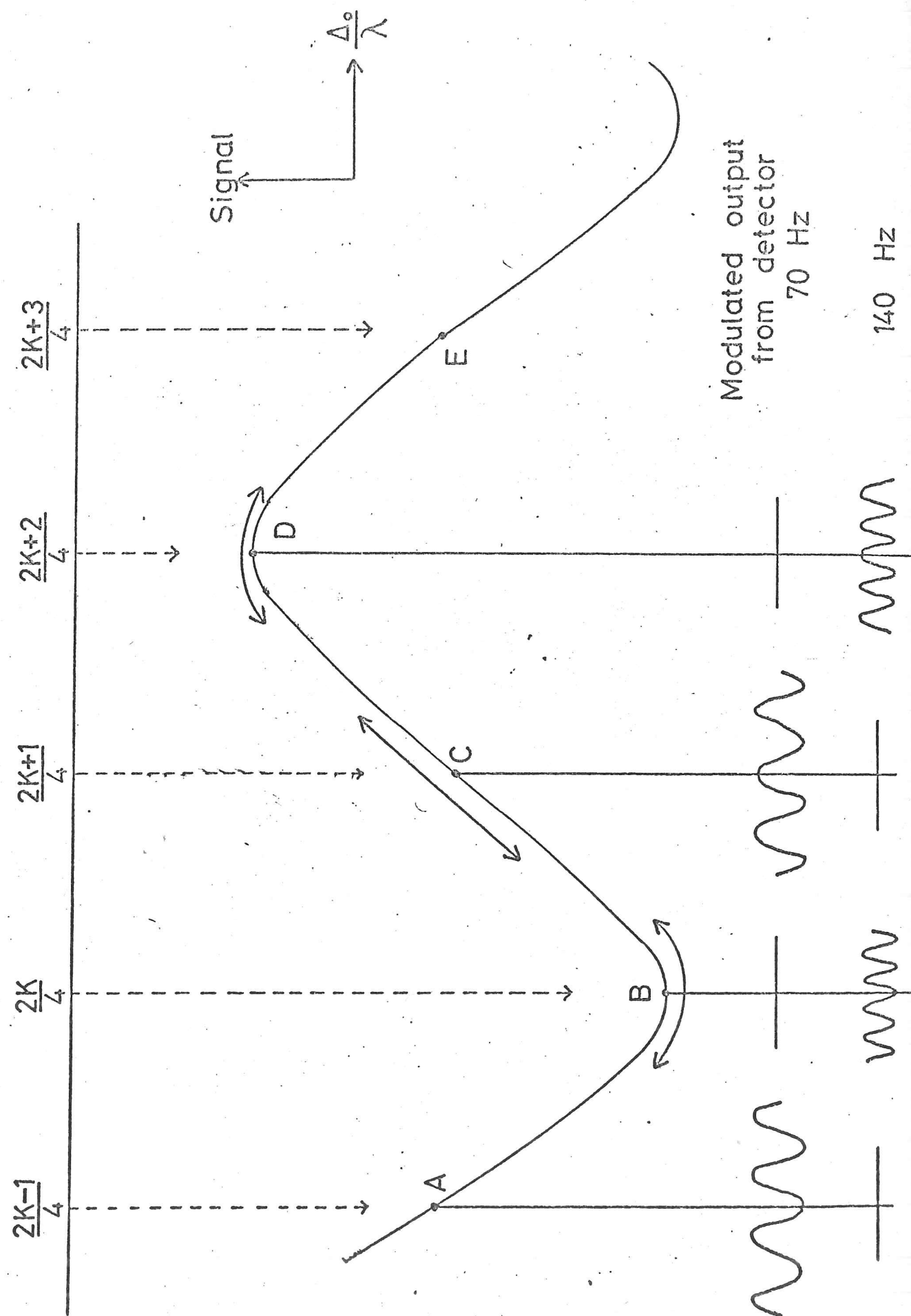


Figure 3.1 : The diagram is explained in the text.

also means that the output of the detector is at the frequency of the mirror oscillation. The voltage driving the piezo-electric transducer can therefore provide a reference signal to a phase sensitive rectification system fed from the detector; this further increases the signal-to-noise by a factor of approximately 3-5. The net gain in signal-to-noise (i.e. in the sensitivity of the spectrometer) is therefore approximately 6-10.*

The introduction of coherent modulation, however, produced problems unforeseen when using non-coherent modulation. When the optical path difference Δ_0 between the two sides of the interferometer obeys the condition

$$\Delta_0 = (2K + 1) \frac{\lambda}{4} \quad (3.1)$$

where K is an integer, a sinusoidal mirror modulation about this mean position [Point C of Figure (3.1)] generates a modulated output from the detector at 70 Hz only, provided the amplitude of modulation is less than $\frac{1}{2}\lambda$,

$$\text{i.e.} \quad 2K \cdot \frac{\lambda}{4} \leq \Delta_0 \leq (2K + 2) \cdot \frac{\lambda}{4} \quad (3.2)$$

As the gratings rotate, λ deviates from condition (3.1), the amplitude of the 70 Hz signal decreases, and a signal arises at

* In the light of recent experiments, the value of 2-3 given in reference (6) is now considered to be a conservative estimate.

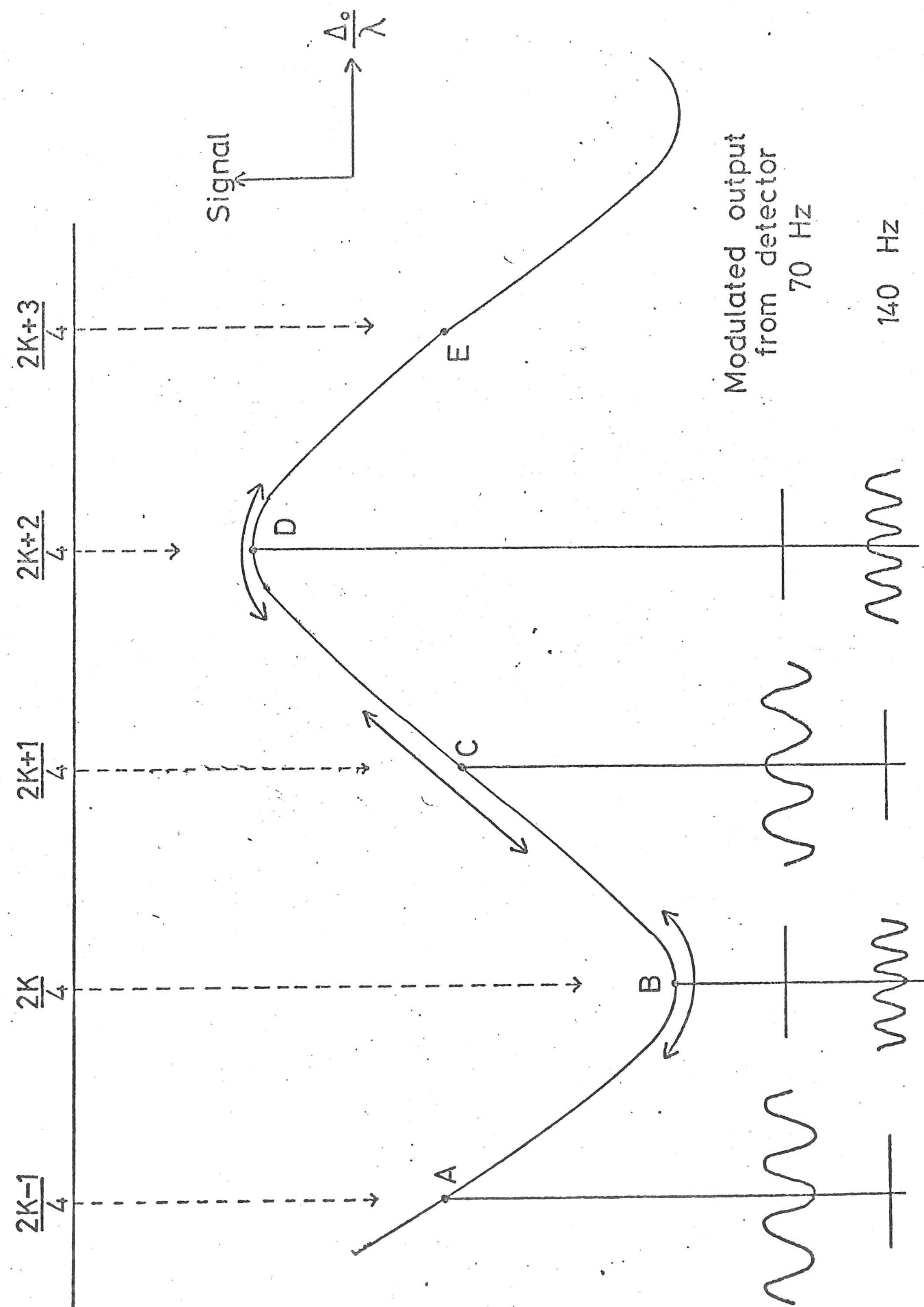


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140 Hz; when $\Delta_o = 2K \cdot \frac{\lambda'}{4}$ where $\lambda' > \lambda$, the detector only gives a modulated output at 140 Hz (Point B). . Thus, for a fixed optical path difference Δ_o , the 70 Hz signal goes through successive maxima and zeros as the gratings rotate:

for $\Delta_o = 10$ mm (a matter of little consequence, incidentally, in non-coherent mirror oscillation) with the instrument operating at $1.5 \mu\text{m}$, the 70 Hz signal would decrease from a maximum to zero for a wavelength change of only $0.00006 \mu\text{m}$. Clearly a spectrum could not be recorded with a signal which fluctuates so rapidly as the spectrum is scanned.

The 140 Hz component could, however, be used to generate a correction signal to change the mean length of the piezo-electric transducer supporting M_4 such that condition (3.1) is continually obeyed; the magnitude and phase of this component [Figure (3.1)] is directly related to the error in condition (3.1). As an absorption spectrum is scanned, the optical path difference Δ_o will then change smoothly and continuously:

$$\text{i.e.} \quad \frac{d\Delta_o}{d\lambda} = \frac{2K + 1}{4} = \frac{\Delta_o}{\lambda} \quad (3.3)$$

The optical path difference is therefore "locked" on to a given fringe, so that K is constant. As the necessary rate of change of Δ_o with λ is proportional to the permanent optical path difference in the spectrometer, it is perhaps not surprising that, for the most satisfactory operation of this control loop, it was necessary to reduce this permanent path difference as much as possible. This was accomplished by monitoring, without

engaging the "feedback loop", the separation of the fringes obtained from an incandescent lamp as a function of wavelength. With Δ_0 reduced to about 0.1 mm, the feedback loop functions most satisfactorily: the 140 Hz signal is kept to a minimum, the signal generated at 70 Hz is therefore maximised and can be recorded by phase sensitive detection. In effect, this feedback loop has achieved a longitudinal stabilisation of the SISAM spectrometer.

When scanning a discrete line emission spectrum, the situation is somewhat different. Radiation is then only present on the detector for certain well-defined wavelengths, corresponding to the discrete emission lines. Between these wavelengths there is no signal to effect the change in Δ_0 ; the feedback loop therefore only tries to lock at each emission line, so only a partial and intermittent longitudinal stabilisation can be achieved. If the line has a wavelength near to

$$\lambda = \frac{4\Delta_0}{2K + 1}$$

the correction required will be small; if the emission is strong, a correspondingly strong correction signal is available. The feedback loop locks readily, and the true intensity of the emission line is recorded. [The exceptionally strong argon and neon emission lines shown in Figure 5 of reference (6) provide a good example of this.] If, on the other hand, the wavelength is near to

$$\lambda' = \frac{4\Delta_0}{2K' + 2}$$

a large correction will be needed; if, in addition, the emission line is weak, an adequate correction signal may just not be available. The system may then only achieve a partial correction to Δ_0 , or may fail to lock at all. The line will then be recorded with reduced (perhaps even zero) intensity. In feedback loop terminology, the "loop gain" is too low.

3.2 The stability of the SISAM

Experiments on very weak emission spectra clearly showed that coherent modulation had dramatically improved the sensitivity of the SISAM spectrometer. [The $B' \ ^3\Sigma_u^-(v=2) \rightarrow B \ ^3\Pi_g(v=1)$ band in N_2 (whose spectrum is described in Chapter 4) was recorded at this stage in the development of the instrument.] Nevertheless, two important problems still had to be solved.

(a) Some very weak emission lines would never appear in a spectrum, because there would not be enough signal to lock on to the nearest fringe.

(b) The mechanical stability of the instrument remained unsatisfactory. An extended emission spectrum could not be scanned without frequent manual adjustment. This involved stopping the grating rotation and resetting the vertical alignment of the instrument, which is critical to 10 seconds of arc. [If the misalignment is greater than this, the beam within the instrument is crossed by horizontal interference

fringes, and the sensitivity is reduced.] The vertical mismatch of the wavefronts can be corrected by changing the tilt about a horizontal axis of mirror M_3 [Figure (2.4)]. In order to facilitate resetting this alignment, it was decided to mount M_3 on another piezo-electric transducer; the vertical alignment is then reset by changing the d.c. voltage applied to this transducer, which changes the tilt of M_3 about its optical centre.

As we shall see, the solution to the first problem leads on to a natural way of solving the second.

3.2.1 The first feedback loop

To overcome problem (a), the spectrometer must be locked continuously to a fringe, whilst simultaneously scanning a weak emission spectrum; in other words, we must lock the system as if recording an absorption spectrum, yet scan an emission spectrum. This can be done in the following manner.

Continuum radiation from an incandescent lamp is masked outside the spectrometer in such a way that, on passing through the spectrometer, it illuminates only the top 5 % of the diffraction gratings. This continuum radiation follows the same optical path through the spectrometer as the weak emission radiation until the two types are separated just before the collimating mirror M_9 . The emission radiation passes through the exit aperture to the external detector as before; the continuum radiation is focussed on to an uncooled lead sulphide

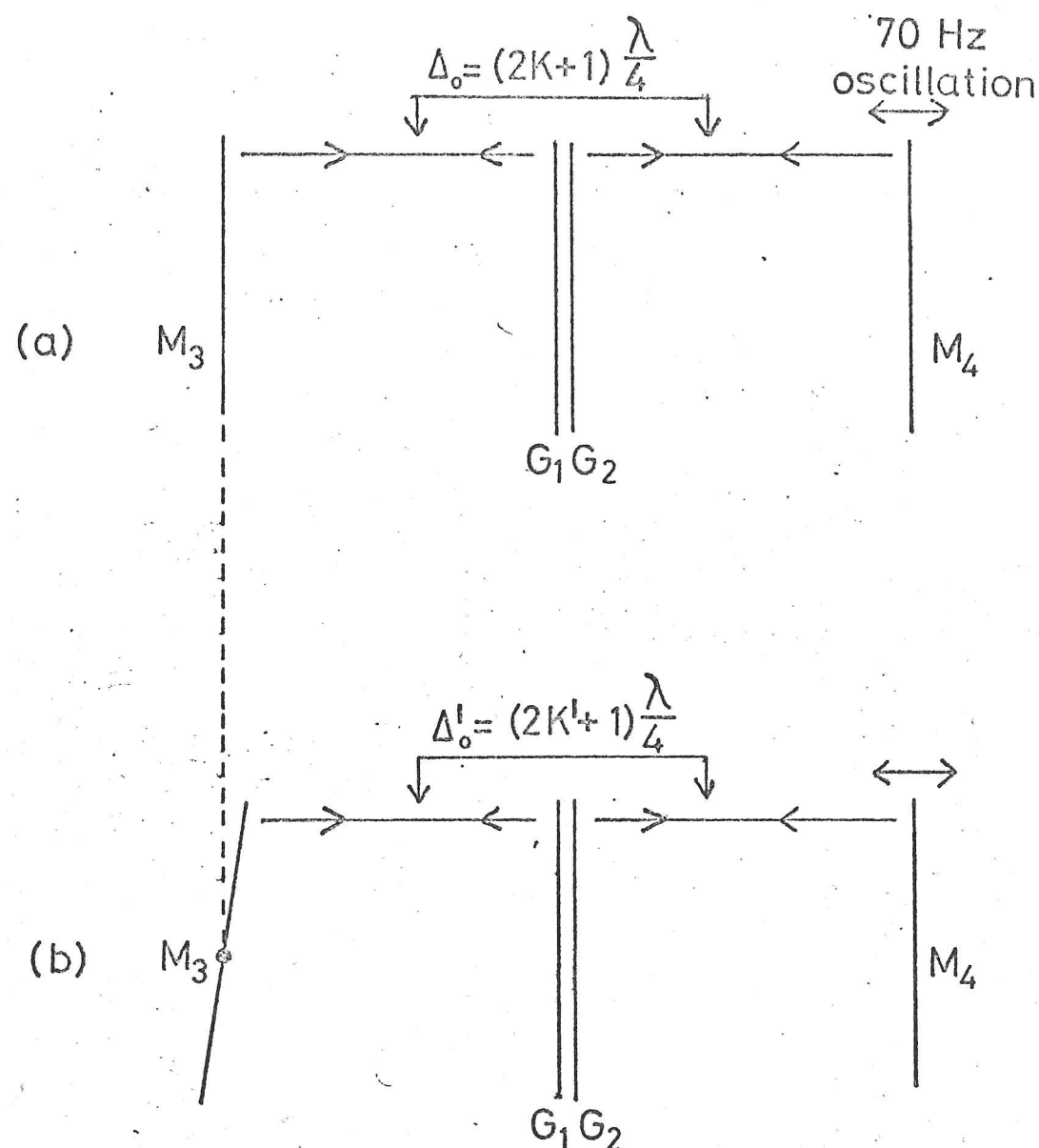


Figure 3.2 : A horizontal view of the most crucial part of the spectrometer. In (a) Δ_0 at the top of the gratings is locked on to the correct fringe, and the instrument is in vertical alignment. In (b) Δ_0 , now different, is locked on to another fringe. The wavefronts from radiation filling the bulk 95 % of gratings will, however, obviously be misaligned.

detector mounted inside the SISAM. Thus, when the optical path difference at the top of the diffraction gratings departs from condition (3.1), the PbS detector gives an output modulated at 140 Hz. This output can be fed to a phase sensitive detector whose reference signal is provided by electronic frequency-doubling of the output of the original 70 Hz oscillator. The output of the p.s.d. forms a correcting signal which, when amplified and applied to M_4 , ensures that condition (3.1) is obeyed. As the gratings rotate and the emission spectrum (filling the remaining 95 % of the gratings) is scanned, the optical path difference at the top of the spectrometer is therefore locked on to a fixed fringe; longitudinal stabilisation has now been achieved at the top of the interferometer.

The solution is not quite as simple as this, however, because the path difference at the top of the spectrometer can lock on to any one of a large number of fringes, each corresponding to a different Δ_0 . Only one locking-point will correspond to zero vertical misalignment between the two beams. The reason for this may not be obvious, but is schematically explained in Figure (3.2).

This unique fringe can only be found by initially passing continuum radiation on to the bulk 95 % of the gratings, and hence on to the external detector; this then sees radiation integrated over the complete optical height of the instrument, so that its modulated output reaches a maximum as the two recombining wavefronts are adjusted into vertical alignment (by changing the d.c. voltage applied to M_3). Δ_0 at the top

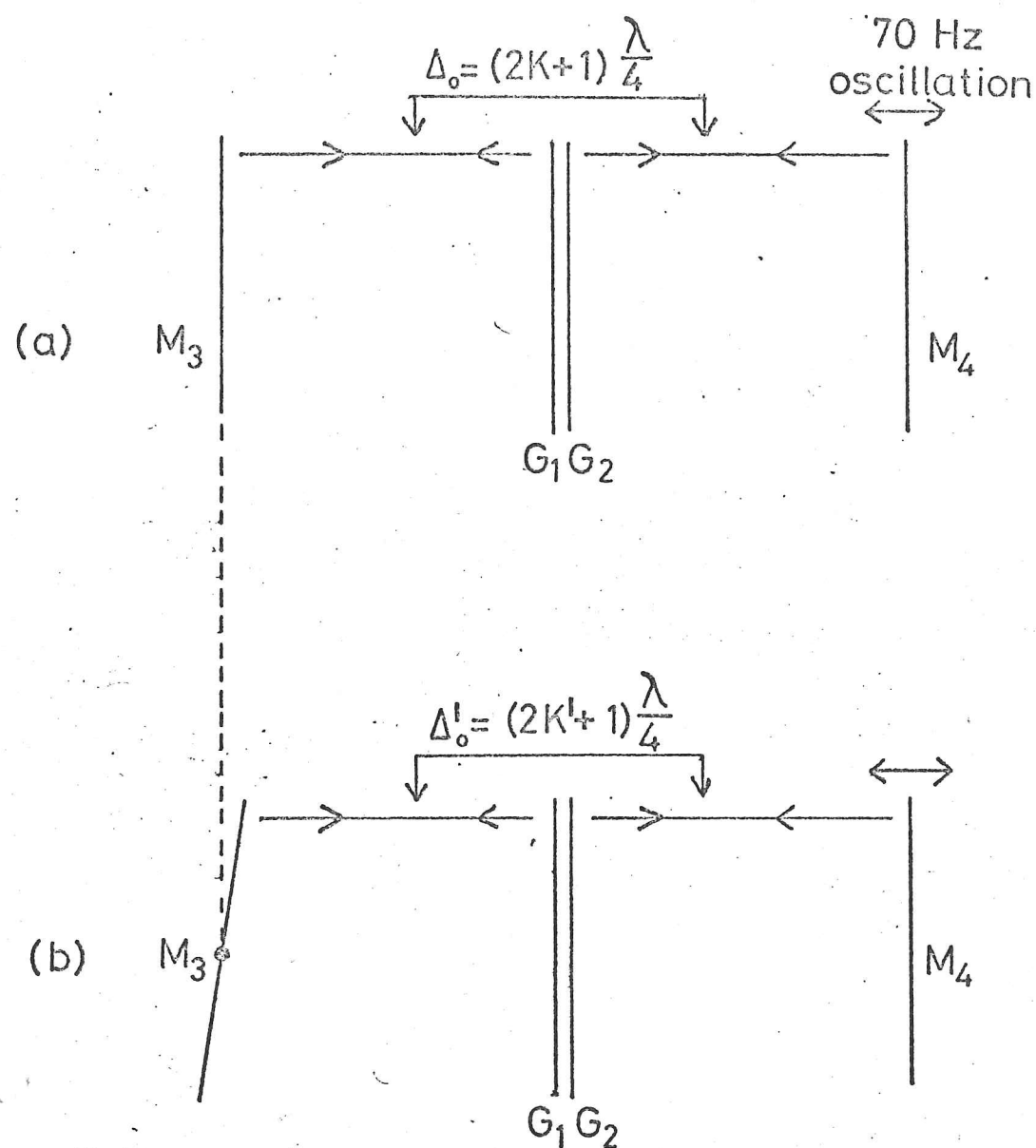


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of the spectrometer is then locked on to the correct fringe; the continuum radiation falling on the external detector is replaced by the unknown emission radiation, and the spectrum is scanned.

Although some quite satisfactory emission spectra were obtained by this method, the instrument was still far from perfect. The reason for this was the ever-present mechanical instability (almost inevitable in an interferometer of this kind). The necessary angle of tilt of M_3 , once set, should not, in principle, need to be changed as the gratings rotate; more often than not, this was found not to be true. What is needed, therefore, is a means of automatically holding the interferometer in vertical alignment as the gratings rotate, and as the emission spectrum is scanned.

3.2.2 The second feedback loop

The solution to this problem becomes obvious, once it has been appreciated that a correct vertical alignment of the two wavefronts is only another description for equality of optical path at top and bottom of the interferometer. The vertical alignment can be stabilised, therefore, by locking the optical path difference, not only at the top, but also at the bottom of the diffraction gratings to the condition

$$\Delta_0 = (2K + 1) \frac{\lambda}{4}$$

If top and bottom of the spectrometer are locked on to fringes with the same value of K , then the two wavefronts of the

unknown emission radiation (filling the central section of the gratings) are necessarily in vertical alignment. A second feedback loop now suggests itself as a natural, almost an inevitable, consequence of the first.

The continuum radiation is masked externally so that it now illuminates both top and bottom 5 % of the gratings (leaving the central 90 % clear for the emission radiation). The bottom beam is focussed on to a second, identical lead sulphide detector mounted inside the SISAM near the first. When the optical path difference at the bottom of the spectrometer varies from the above condition, the bottom PbS detector also gives an output at 140 Hz. This error signal is a.c. amplified, then phase sensitive rectified to give a d.c. correction signal; it is necessary to d.c. amplify this signal (the Y amplifier of an old 1950 Cossor cathode ray oscilloscope is used for this purpose) before applying it to the piezo-electric element which tilts mirror M_3 . The optical path difference at top and bottom of the spectrometer are now each locked to a fringe, and longitudinal stabilisation has been achieved at top and bottom of the SISAM.

To ensure that they are locked to fringes with the same, as distinct from different, value of K , it is necessary (as before) initially to pass continuum radiation on to the central region of the gratings. The external detector then gives a maximum modulated output at 70 Hz when the two recombining wavefronts are in vertical alignment. Once the initial value of the d.c. voltage applied to M_3 has been set, the two feedback loops are engaged, the central continuum radiation is replaced

by the unknown emission, and the spectrum is scanned. The external detector now only gives a modulated output at 70 Hz; the signal is a.c. amplified, phase sensitive rectified, and the output taken to one pen of a two-pen chart recorder.

Quite apart from stabilising the spectrometer completely, these feedback loops can give rise to an additional bonus. By placing the faces of a suitable Fabry-Pérot etalon at right-angles to the continuum radiation, etalon fringes are generated as the gratings rotate. Any emission spectrum can, therefore, be calibrated by recording these fringes on the other pen of the chart recorder. In practice, the etalon was placed in the external optics so as to intercept only part of the beam of radiation which illuminated the top of the diffraction gratings; the continuum radiation modulated at 70 Hz (the 140 Hz component having been minimised by the first feedback loop) could then be taken to the tunable electronic filter unit (another phase sensitive detector being neither necessary nor available), and the etalon fringes resulting as the gratings rotated recorded on the other pen. It is, of course, necessary to calibrate the etalon being used - i.e. to determine $2\mu d$ as a function of λ , where μd is the optical thickness of the etalon. This was done by recording well-determined emission lines from an iron-neon hollow cathode lamp against the etalon fringes (for a full description of this method of calibration, see Till's Thesis (7)). Once this is accomplished, any emission spectrum can, if desired, be calibrated against these fringes.

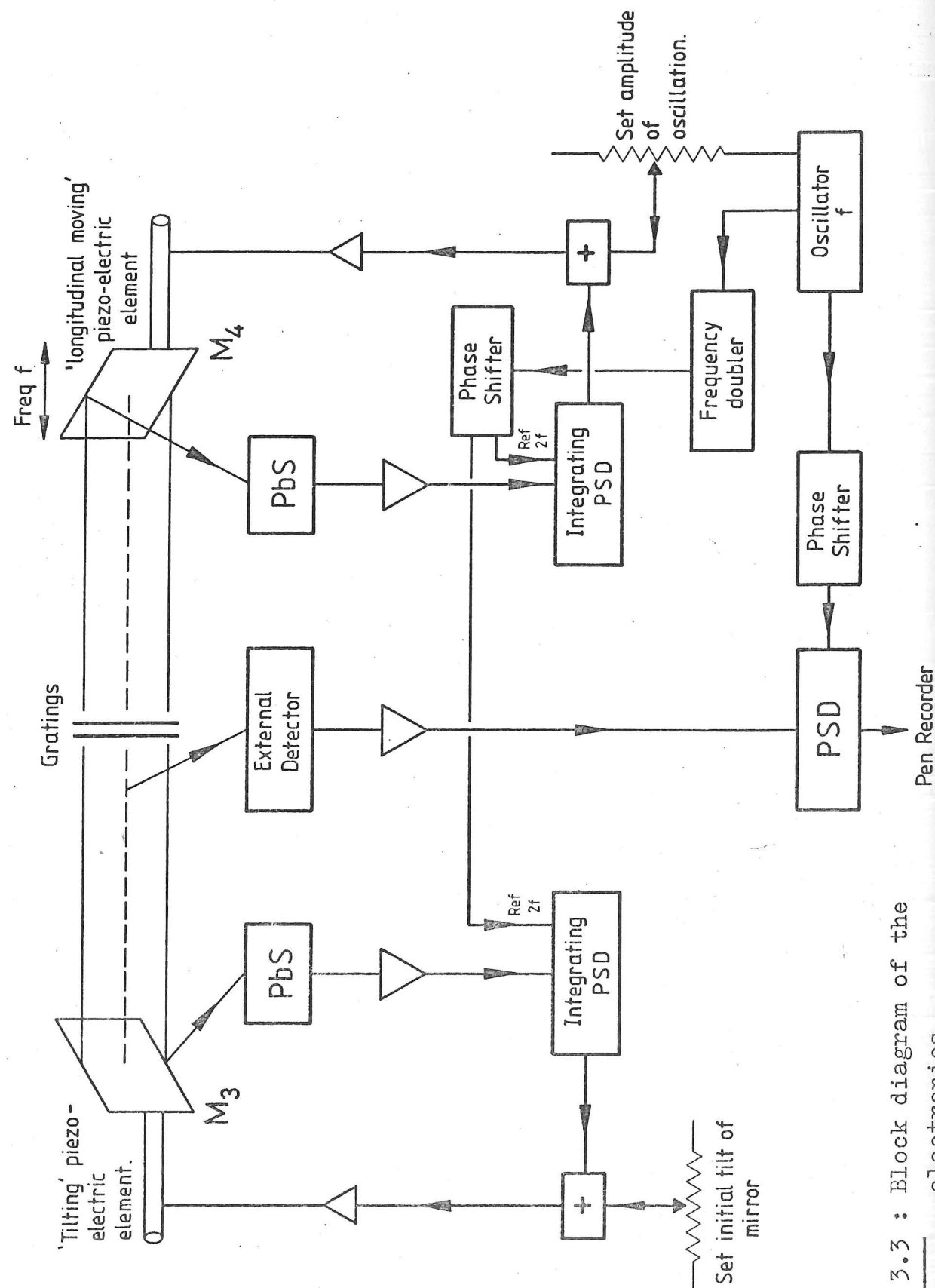


Figure 3.3 : Block diagram of the electronics.

3.3 Operation of the double-loop feedback system

In this Chapter, we have seen how a new mirror oscillation technique has increased the sensitivity of the SISAM spectrometer. Based on this technique, a double-loop feedback system has been developed which has completely eliminated the effects of mechanical instability inherent in the instrument. This section will be concerned with how these feedback loops are, in practice, operated.

3.3.1 The electronics

A block diagram of the electronics is shown in Figure (3.3). The diagram is probably self-explanatory except for a few points:

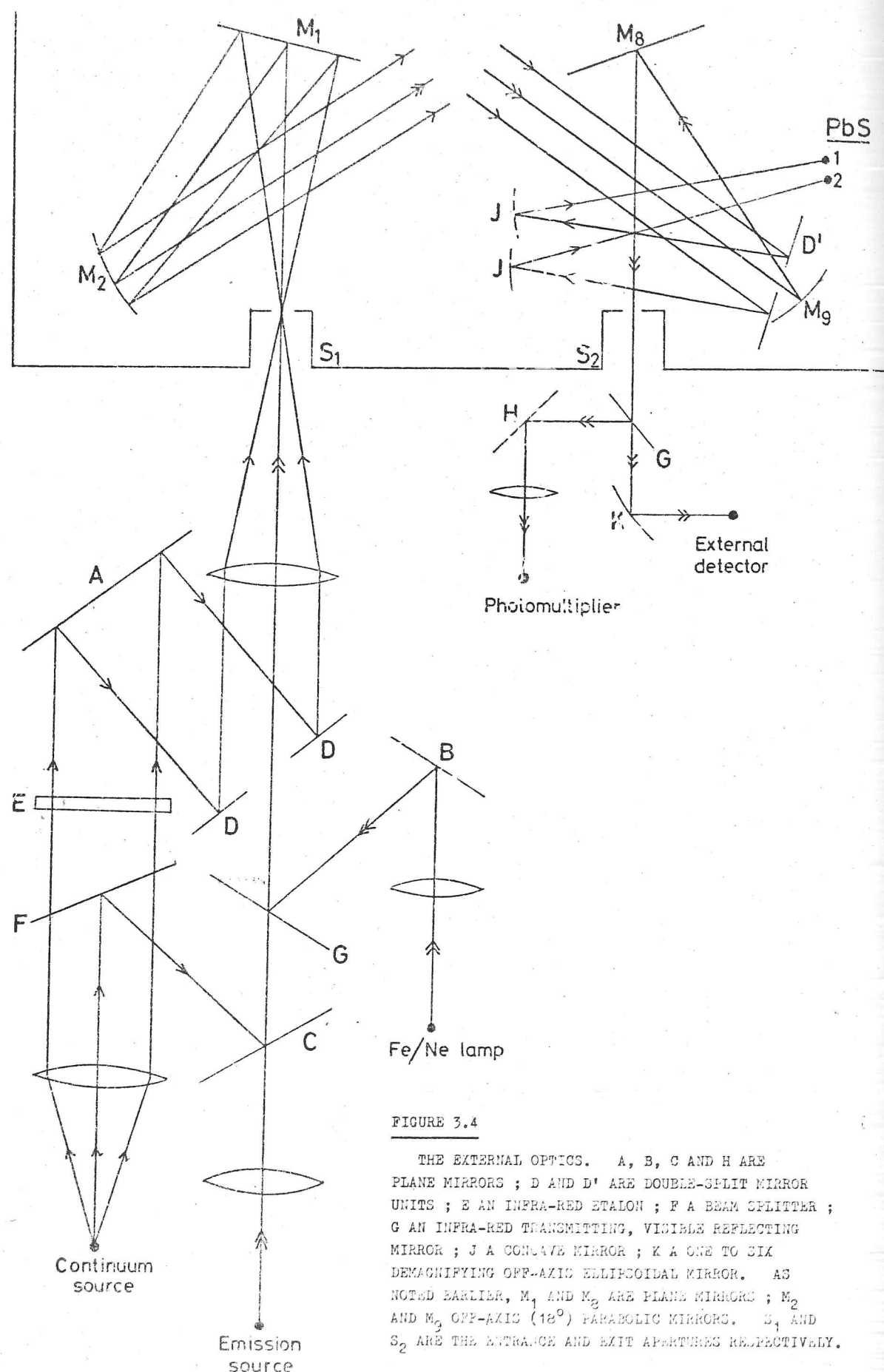
(a) Frequencies f and $2f$ obviously refer to 70 and 140 Hz in the text. Recently, however, M_4 has been oscillated more slowly (at 42 Hz with the error signals phase sensitive rectified at 84 Hz). This was done purely to increase the sensitivity of our best available detector for weak emission radiation in the $1.2 - 1.6 \mu\text{m}$ region (a liquid nitrogen cooled intrinsic germanium detector, time constant ~ 5 msecs). The sensitivity of the lead sulphide detectors then decreases (these photocells being most sensitive at ~ 800 Hz), but so long as they give enough modulated output to operate the feedback loops, this is unimportant.

(b) To avoid interaction between the two loops, it is necessary to apply one correction signal much faster than the other. Typical time constants used are 300 msecs for the first loop, 3 secs for the second.

(c) The oscillator supplies a fixed frequency a.c. voltage to the piezo-electric element supporting M_4 . This voltage is controlled by a ten-turn potentiometer, so the amplitude of movement of M_4 can be adjusted to the required amount.

It is interesting to note that such an oscillator and feedback loop system was used recently in this laboratory to stabilise a single-mode CO_2 laser (10), stabilisation being achieved on the peak of the gain profile. By applying an a.c. voltage to a piezo-electric transducer supporting one of the laser mirrors, the length of the cavity was oscillated at a fast frequency f . When the mean length started to wander (due to changes in temperature, pressure and discharge conditions) from its value for maximum gain, a modulated signal arose at f ; by adjusting the cavity length back to its correct value (i.e. achieving longitudinal stabilisation of the laser), the feedback loop then minimised this signal, and automatically maximised the output at $2f$.

The stabilisation of the SISAM spectrometer and of the single-mode laser have, therefore, much in common. The only fundamental difference is that two path differences in the SISAM are each locked to the side of an interference fringe (maximising the signal at f), whereas the cavity length of the laser is locked to the top of the gain profile, (maximising the signal at $2f$). In principle, there is no reason why the SISAM should not be locked to the top of the interference fringe [point D of Figure (3.1)]. The reason why we have locked to the side is now explained.



The lower frequency limit that can be applied to M_4 is set by inadequacies of transformers in the oscillator (~ 42 Hz), the upper limit by the mechanical response of M_4 (~ 250 Hz). So if the detector for the emission radiation is slow (e.g. the intrinsic germanium detector), it is preferable to lock on to the side of an interference fringe and detect at f (the lower limit of the oscillator obviously being used). If, on the other hand, the detector is fast (e.g. a cooled lead sulphide detector), it may prove advantageous to lock at the top of the fringe, thereby detecting the signal at $2f$ (f now being set to the upper limit of the oscillator).

3.3.2 The external optics

Figure (3.4) shows the external optics necessary to pass continuum radiation through the spectrometer in the manner previously described. A 100 Watt quartz-iodine bulb (whose peak in the black body curve occurs at $\sim 1.4 \mu\text{m}$) acts as the source of continuum radiation. After collimation, parallel radiation from it strikes the plane mirror A and passes to a double-split mirror unit D. The bulk of the radiation passes through the gap in the split mirror (whose size can be controlled in the vertical plane), so only two horizontal strips of radiation (one at the top, one at the bottom) are focussed on to the entrance aperture of the SISAM. Thus, after collimation by M_2 , these two strips of radiation pass through the spectrometer, and illuminate the complete width of the top

and bottom 5 % of the gratings. After diffraction and recombination at the beam splitter, the two beams pass towards the exit aperture; they now strike a second double-split mirror assembly D' (situated just in front of M_9), pass on to two concave mirrors J, and are finally focussed down to two identical lead sulphide detectors mounted inside the spectrometer. * Their outputs are then used to achieve longitudinal stabilisation at top and bottom of the interferometer.

As noted earlier (Chapter 3.2.2), it is initially necessary to ensure that top and bottom are locked to the same optical path difference Δ_0 [i.e. fringes with the same value of K in equation (3.1)]. This is performed by inserting a beam splitter F and a plane mirror C in the external optics [Figure (3.4)], and hence passing continuum radiation also on to the central 90 % of the gratings and on to the external detector. Once the vertical alignment of the instrument (i.e. the initial tilt of M_3) has been set, the two feedback loops are engaged; F and C are then removed from the external optics, so now the unknown emission radiation fills the central section of the gratings and passes to the external detector [see Figure (3.4)].

It was also noted in Chapter 3.2.2 that any emission spectrum can, if desired, be calibrated by recording fringes from a Fabry-Pérot etalon simultaneously with the emission

*

I would like to take this opportunity of thanking Mr. A. Cooke for his help in constructing the double-split mirror units D and D' and the double concave mirror unit J in the Research Students' Workshop of our Department.

spectrum. The etalon E [Figure (3.4)] is so positioned that it only intercepts part of the continuum radiation which illuminates the top of the diffraction gratings. In order to calibrate the etalon, it is necessary to record the fringes against well-determined emission lines from, for example, an iron-neon hollow cathode lamp [Figure (3.4)]; these visible radiation lines are detected by a photomultiplier tube situated outside the spectrometer. Care was taken to ensure that all three types of radiation (unknown emission, continuum and visible calibration lines) filled the complete area of the entrance aperture S_1 , otherwise an absolute error would be introduced in the calibration (see Chapter 2.2.2).

3.3.3 The moving mirrors

In order to achieve the desired stability of the spectrometer, the optical path difference at top and bottom of the SISAM must be set electronically to a very high degree of precision, ideally better than $\lambda/20$; this corresponds to 0.000075 mm at 1.5 μm . These path differences are set by the voltages applied to the two piezo-electric transducers on which mirrors M_3 and M_4 are mounted, so the mechanical movement of these two components must follow the voltages applied to a very high degree of accuracy. The mount for the modulating mirror M_4 has been described by Till ⁽⁷⁾ and is shown in Plate I, whilst the newly constructed mount for the d.c.

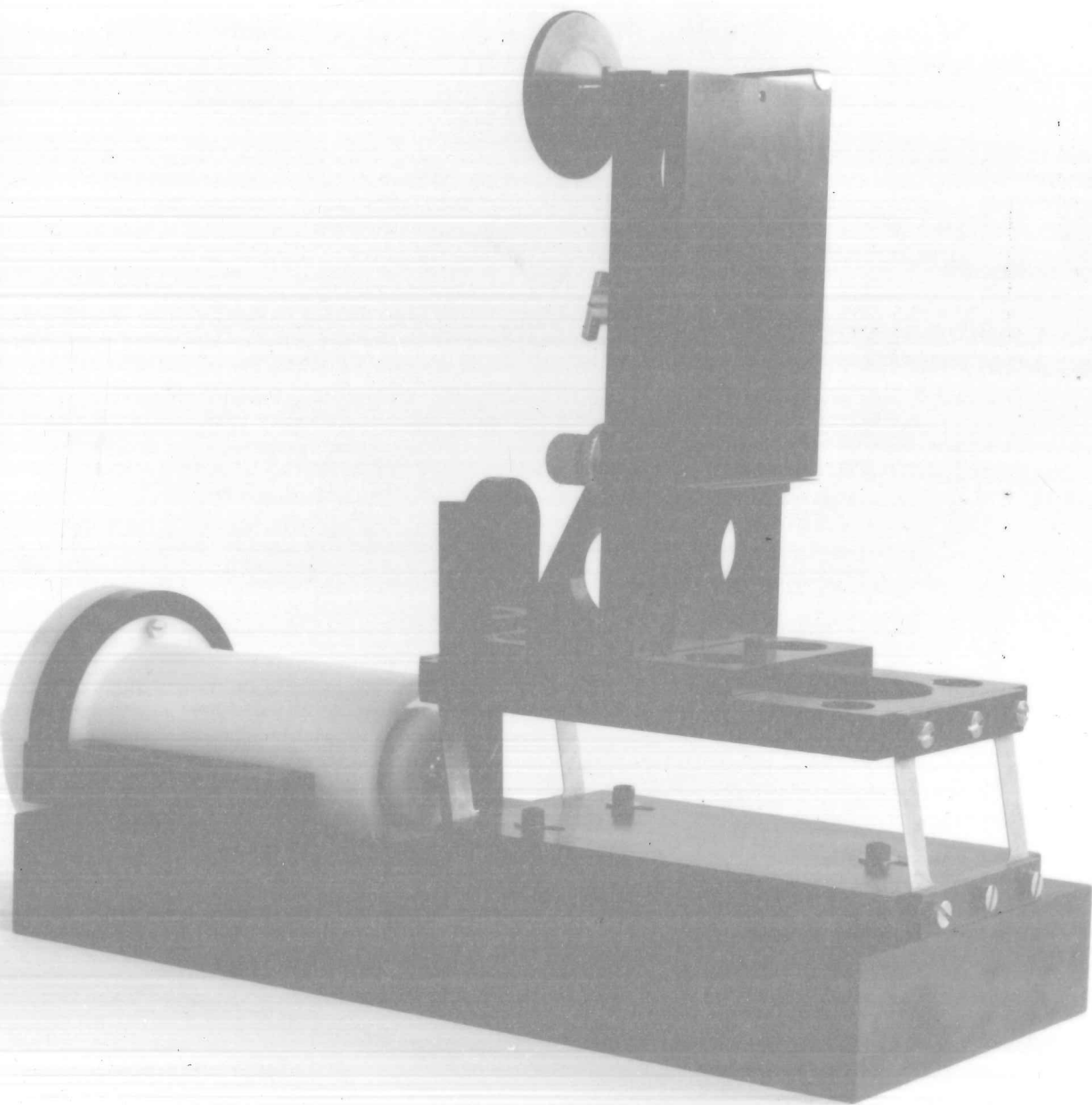
controlled tilting mirror M_3 is shown in Plate II. The complexity of their designs is perhaps the best indication of the care that had to be put into their construction. *

A photograph of the final layout of the spectrometer is shown in Plate III, whilst Plate IV shows the complex nature of the electronics.

* At this stage it is perhaps appropriate to mention once again the work of Mr. C.W. (Charlie) Oates. He was responsible for the design and construction of nearly all the mechanical components of the SISAM. In my mind there is no doubt that without his skill and experience a fully functional spectrometer would never have been achieved; his contribution to the successful stabilisation of the spectrometer cannot be praised too highly.

PLATE I

The modulating mirror M_4



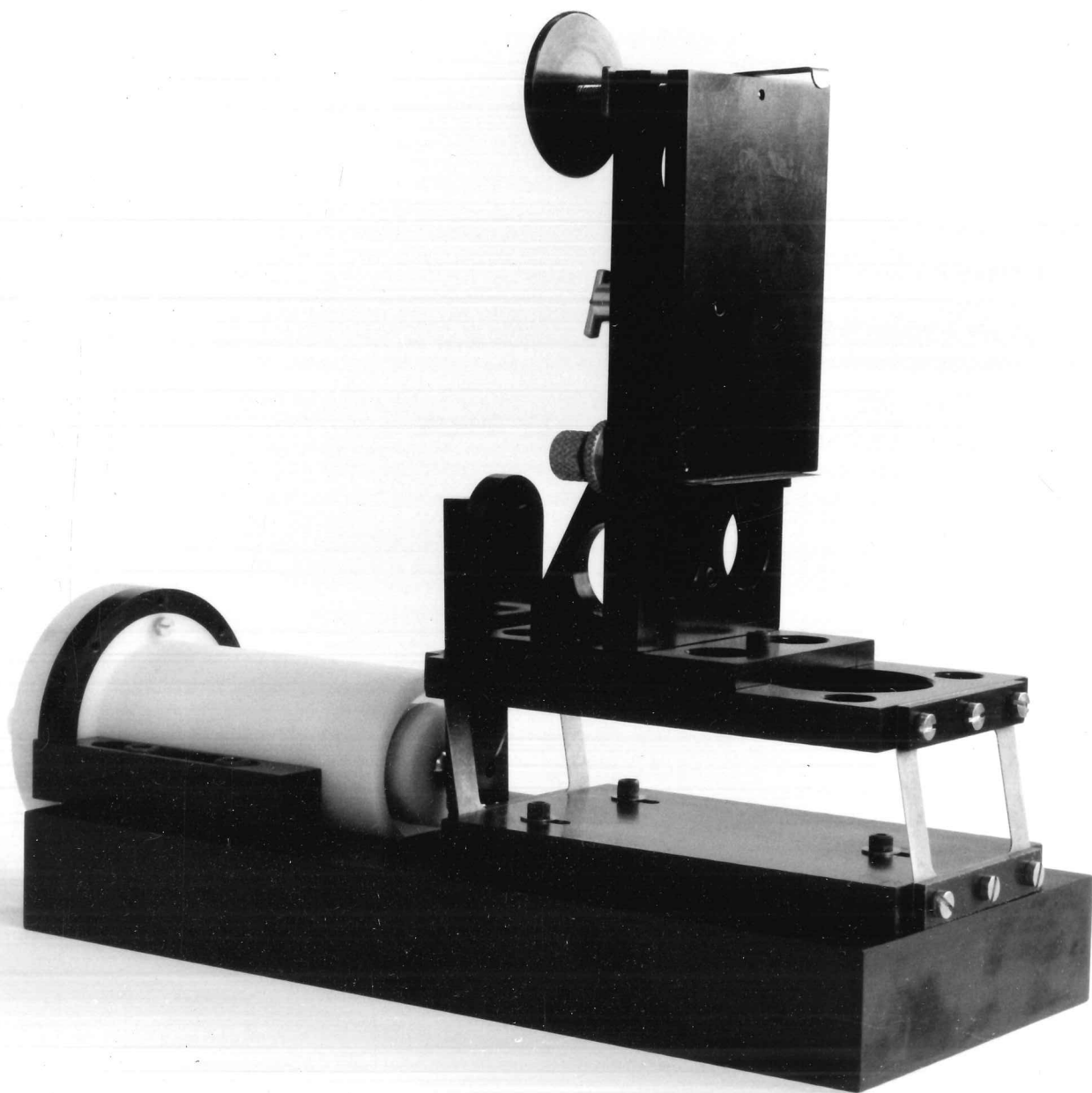


PLATE II

The d.c. controlled tilting mirror M_3

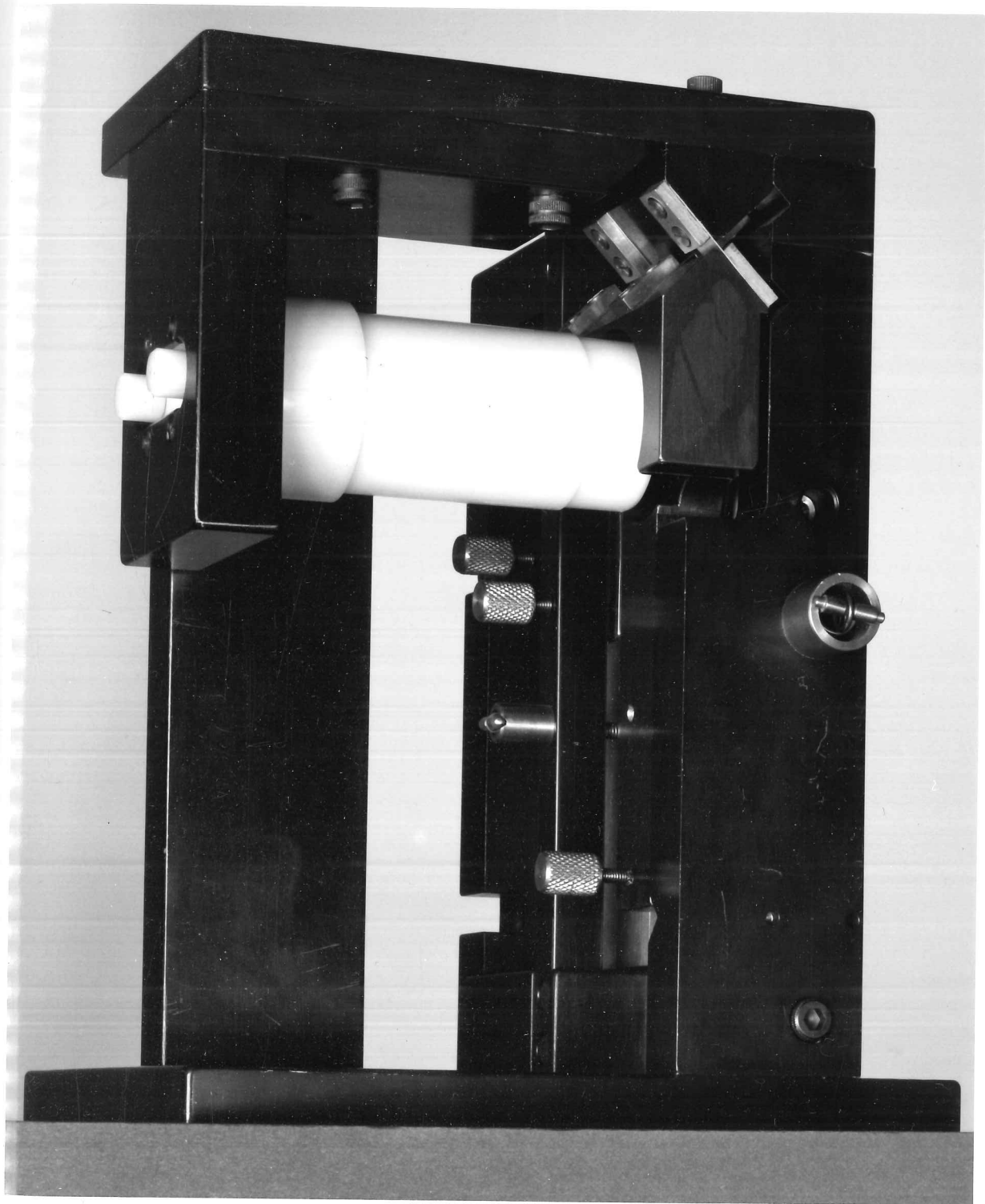


PLATE III

The SISAM spectrometer

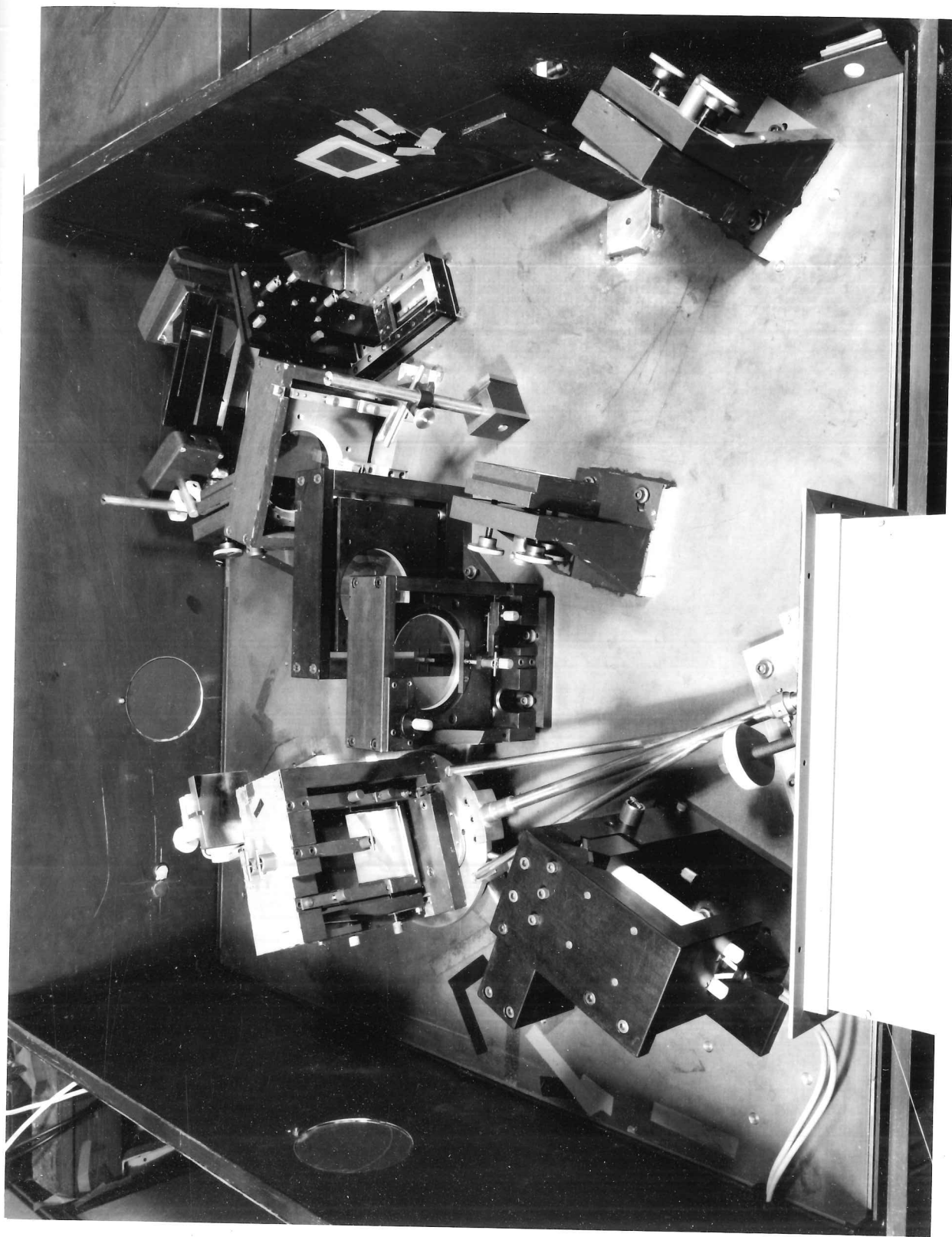
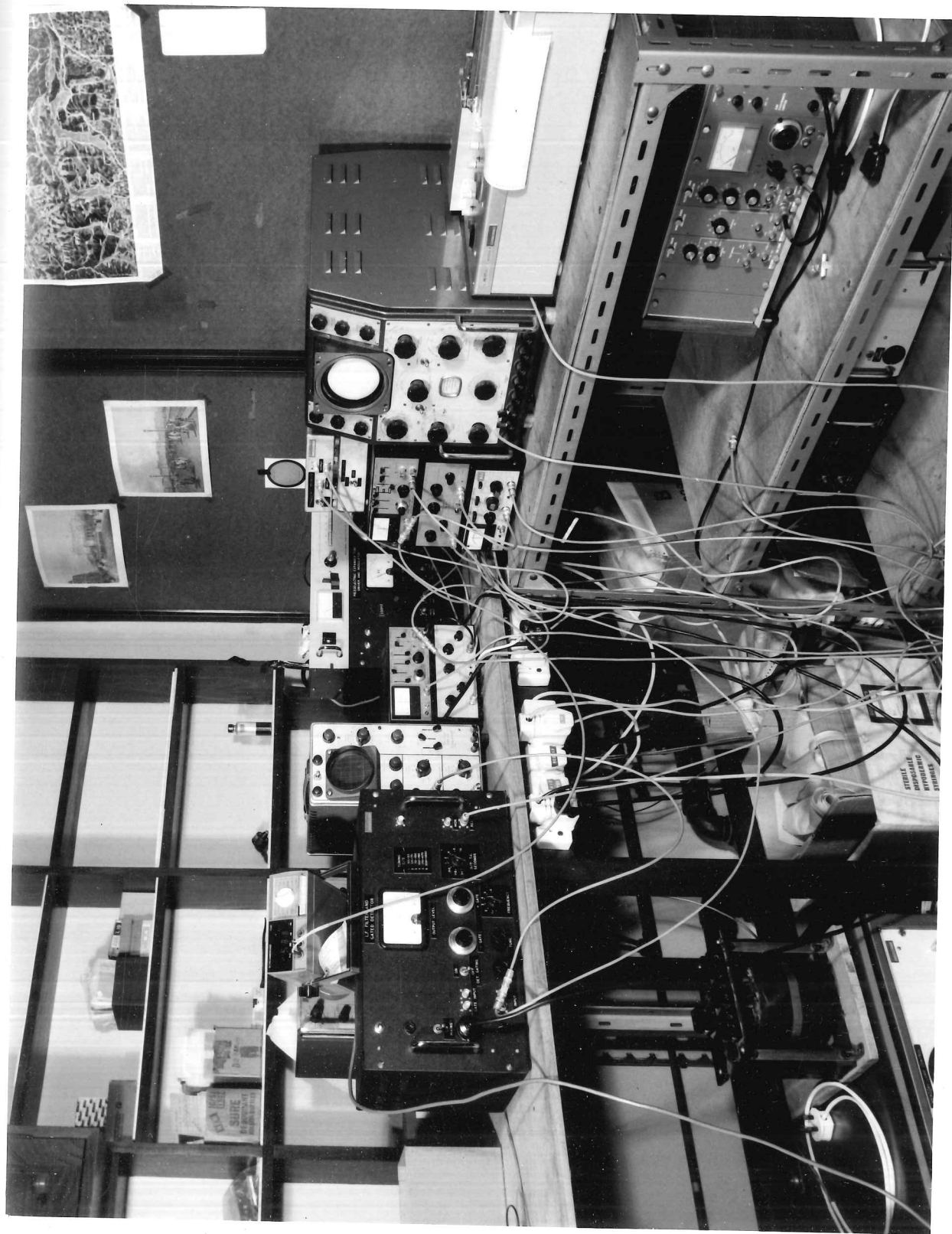


PLATE IV

The electronics



CHAPTER 4

PRELIMINARY RESULTS

4.1 The B' $^3\Sigma_u^-$ ($v = 2$) $\rightarrow$ B $^3\Pi_g$ ($v = 1$) band of N₂
at 1.29 μ m

Chapter 3.1 described a coherent modulation and feedback loop technique which it was hoped would improve the sensitivity of the SISAM spectrometer. Once this was developed, therefore, it was necessary to record a weak emission spectrum to see what improvement had been achieved. A vibrational band of the $^3\Sigma_u^- \rightarrow ^3\Pi_g$ system of nitrogen (sometimes known as the "Y" band system) was chosen for the following reasons:

(a) Little information was available on the highly excited $^3\Sigma_u^-$ electronic state, whilst the lower state of the transition was well characterised, as it is the upper electronic state of the well-known B $^3\Pi_g \rightarrow$ A $^3\Sigma_u^+$ first positive band system of N₂. It was therefore hoped that the spectrum would not be too hard to analyse, yet yield new spectroscopic constants for the $^3\Sigma_u^-$ state.

(b) The $^3\Sigma_u^-$ state can easily be populated in a simple discharge flow system, so the experimental set-up did not need to be very complicated for such a preliminary investigation.

(c) The $v' = 2 \rightarrow v'' = 1$ band at 1.29 μ m was chosen for analysis, since this band, unlike many of the other vibronic bands, is relatively free of overlapping from first positive bands.

The ${}^3\Sigma_u^-$ state of N_2 was excited by a microwave discharge through flowing nitrogen gas at a pressure of 0.5 Torr. The discharged region was then focussed on to the entrance aperture of the SISAM. The spectrum was recorded with a cooled PbS detector mounted outside the spectrometer, calibration being achieved by simultaneously recording visible lines from the Fe/Ne hollow cathode lamp.

The spectrum was initially recorded using the old non-coherent modulation technique. The modifications described in Chapter 3.1 were then carried out, and the same spectrum was recorded using coherent modulation, the signal now being phase sensitive rectified. The improvement in signal-to-noise was seen to be approximately 5-10, and a region of this improved spectrum is shown in Figure (4.1). It was clear that coherent modulation had dramatically improved the sensitivity of the SISAM.

It is important, however, to appreciate the deficiencies of this spectrum:

(a) The total spectrum had to be recorded in several stages, since the optical alignment of the SISAM could never be maintained for the time necessary to record the complete spectrum (~ 2 hours).

(b) The spectrum would never reproduce exactly from day to day, due to the inadequacies of the locking mechanism for such a weak emission spectrum (see Chapter 3.1.2).

In order to reset the alignment of the SISAM, the grating rotation was stopped, the lid of the box in which the SISAM was

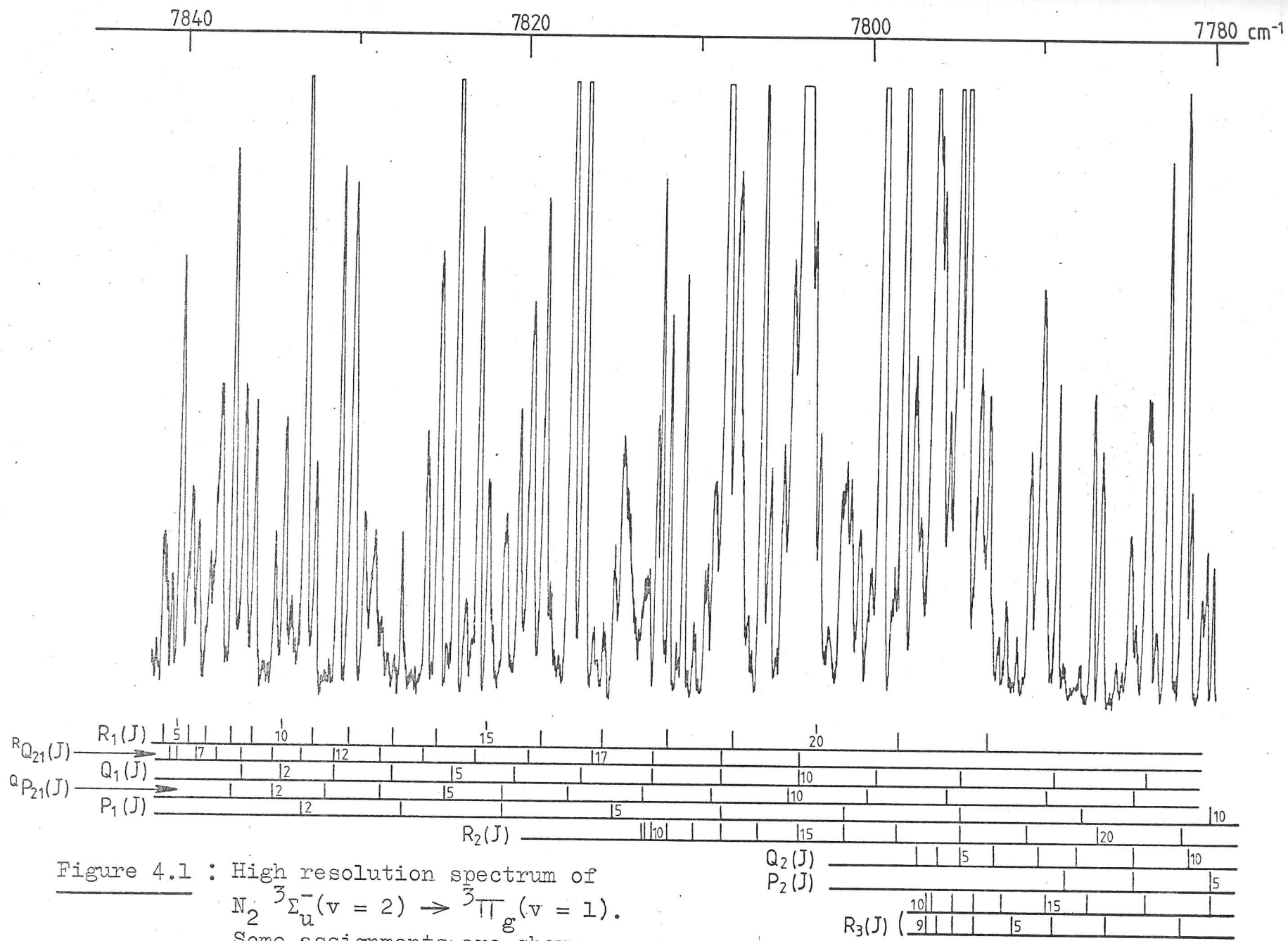


Figure 4.1 : High resolution spectrum of
 $\text{N}_2 \ 3\Sigma_u^-(v=2) \rightarrow 3\Pi_g(v=1)$.
 Some assignments are shown.

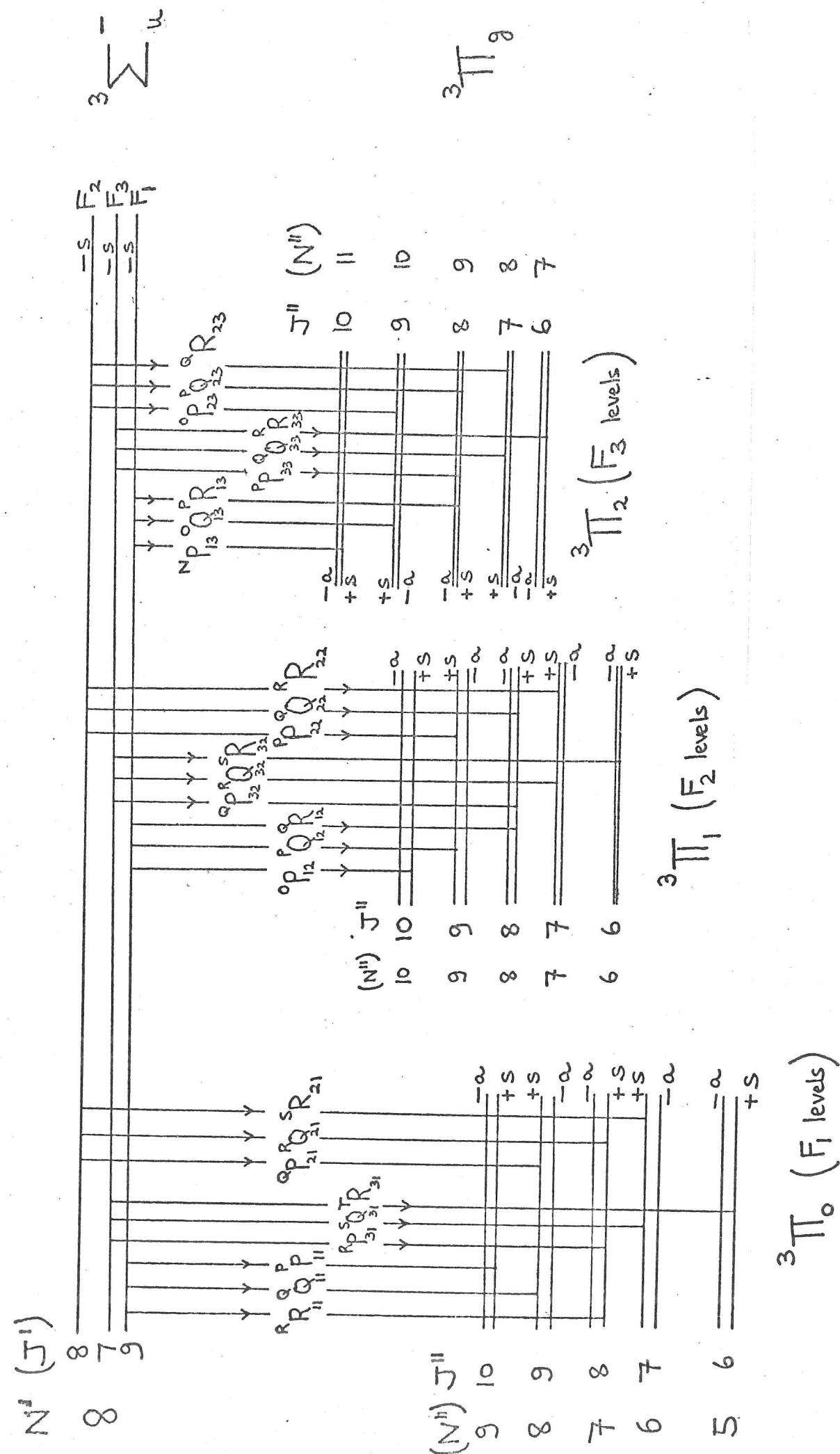


Figure 4.2 : The origin of the 27 branches of a $3\Sigma^- \rightarrow 3\Pi_g$ transition. The notation used is $\Delta N \Delta J_F''$.

mounted was removed, the tilt of M_3 was manually altered to its new value, the lid was replaced, and the grating rotation was restarted - a cumbersome process. . It was at this stage that it was decided to remount M_3 on a piezo-electric transducer so that the vertical alignment could be reset from outside the spectrometer; it was not appreciated at the time how this new component could be used in a feedback loop. As is obvious from Plate II, its design and construction took some time; whilst waiting for it to be built, I decided to make a partial analysis of the Y band spectrum, realising however the inadequacies inherent in it.

The analysis was considerably aided by the fact that Carroll and Rubalcava (11), in 1960, photographically recorded and analysed the $v' = 5 \rightarrow v'' = 1$ band of this same system; spectroscopic constants were therefore available for our common lower level $3\Pi_g (v = 1)$. Formulae and symmetries of the energy levels of both $3\Sigma^-$ and $3\Pi_g$ states have been given by Herzberg (12), and it can readily be shown that a transition between them will have 27 possible branches [Figure (4.2)], comprised of 9 main branches ($\Delta N = \Delta J$) and 18 weaker satellite branches ($\Delta N \neq \Delta J$). In the $v' = 2 \rightarrow v'' = 1$ analysis, I was able to assign ~250 lines in 19 of these branches. Their analysis yielded constants for $3\Pi_g (v = 1)$ which agreed well with Carroll et al's data for this state, and constants for $3\Sigma^- (v = 2)$ entirely compatible with their results for $v' = 5$ of this state. These molecular constants are shown in Table (4.1).

Table (4.1)

Molecular constants for $N_2 \quad {}^3\Sigma_u^-(v=2) \rightarrow {}^3\Pi_g(v=1)$

B'	=	$1.4307 \pm .0010$	} ${}^3\Sigma_u^-(v=2)$
D'	=	$5.9 \pm 1.1 \times 10^{-6}$	
λ'	=	$0.63 \quad 2$	
γ'	=	$-0.005 \quad 2$	
B''	=	$1.6081 \pm .0008$	} ${}^3\Pi_g(v=1)$
D''	=	$2.8 \pm 1.3 \times 10^{-6}$	
A''	=	$42.05 \pm .10$	
ν^{00}	=	$7799.41 \pm .12$	

1. All constants in cm^{-1} ; the uncertainties represent one standard error of the fit
2. These spin-splitting constants of the ${}^3\Sigma_u^-$ state were constrained to Carroll's values for $v' = 5$ of this state
3. B is a rotational constant, D a distortion constant, A a spin-orbit coupling constant, ν^{00} the band origin

This work therefore served a most useful purpose. It showed that coherent modulation had brought about a large increase in sensitivity of the SISAM spectrometer, yet it highlighted the inadequacies still present in it. Once the d.c. controlled tilting mirror mount for M_3 had been built, the next few months were therefore spent constructing the double-loop stabilisation system described in Chapter 3.2.

4.2 The $^1\Delta_g(v=0) \rightarrow ^3\Sigma_g^-(v=0)$ band of O_2 at 1.27 μm

Having developed the two electronic feedback loops, a spectrum was needed to test the stability of the modified spectrometer. I decided to record the forbidden transition in molecular oxygen $^1\Delta_g(v=0) \rightarrow ^3\Sigma_g^-(v=0)$ at 1.27 μm . This is a spin-forbidden, magnetic dipole band, so is exceptionally weak. It has previously been studied at high resolution in absorption by Herzberg and Herzberg⁽¹³⁾ using an enormous absorbing path. A high resolution spectrum in emission has, however, never been published: I recorded this spectrum in emission.

The excited species was formed in the afterglow of a microwave discharge in oxygen at a pressure of 3 Torr. The radiation was collected inside a 5 litre internally gold-coated integrating sphere, downstream of the discharge; the emission was observed through a window in the sphere and focussed on to the entrance aperture of the SISAM. The external detector now being used was the intrinsic germanium detector, and the spectrum

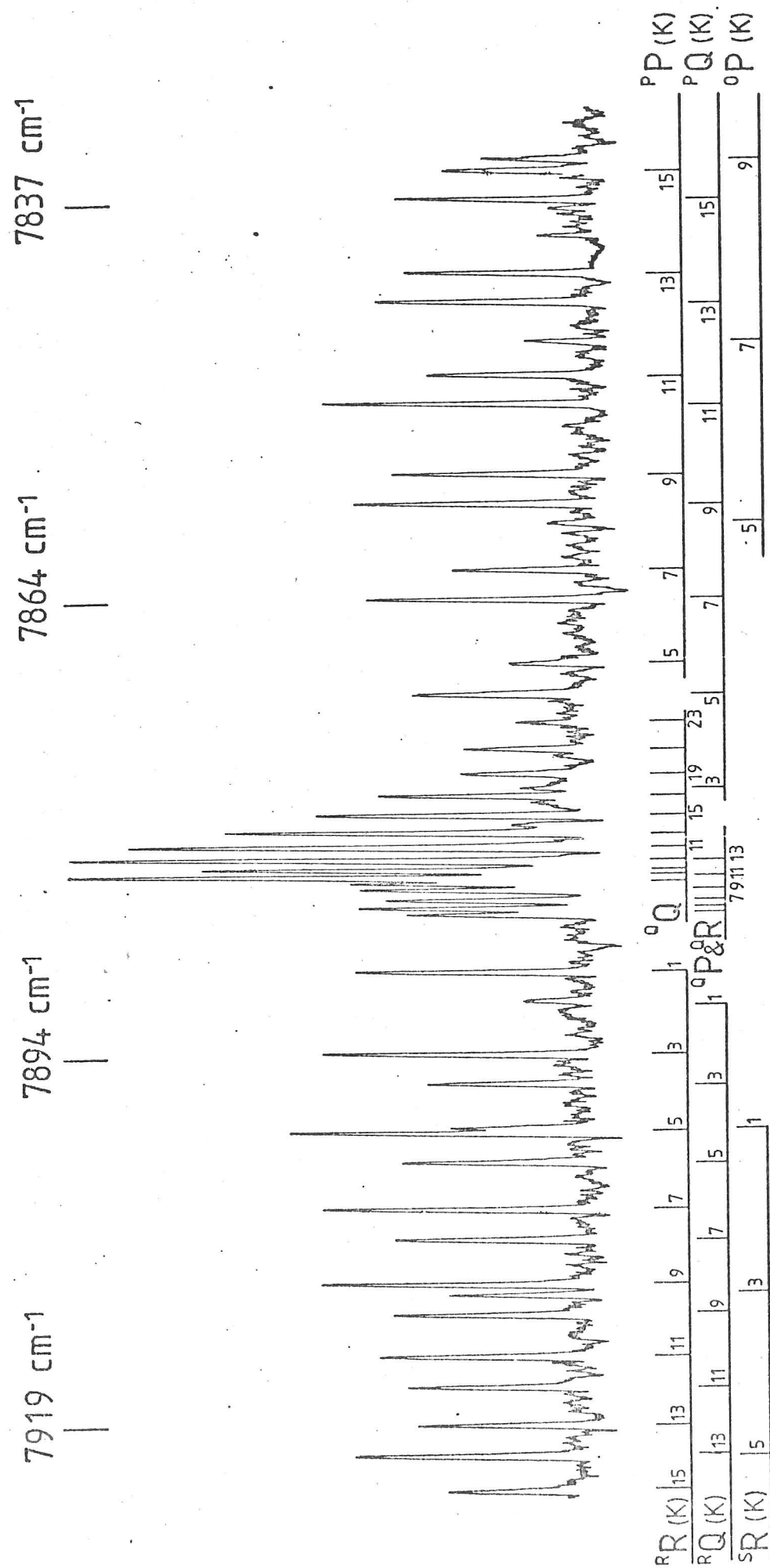


Figure 4.3 : High resolution spectrum of $O_2 \ ^1\Delta_g(v=0) \rightarrow \ ^3\Sigma_g^-(v=0)$.

was calibrated by the combination of Fe/Ne visible lines + etalon fringes (see Chapter 3.2.2).

The spectrum is shown in Figure (4.3), and it is worth noting the following points:

- (a) the spectrum shows a good signal-to-noise.
- (b) The resolution of the spectrum is excellent, being 90 - 95 % of the theoretical value.
- (c) Most important, the spectrum would reproduce exactly on different scans; this spectrum was, in fact, recorded eight times over a period of four days to check this point. The two feedback loops had obviously achieved the desired stability of the SISAM spectrometer.

It can easily be shown that a $^1\Delta_g \rightarrow ^3\Sigma_g^-$ transition has only nine branches [Figure (4.4)]; as the density of lines in the spectrum is therefore relatively low, their assignment proved to be a simple process [Figure (4.3)]. This spectrum was in fact analysed by the Herzbergs in 1947, who obtained very accurate molecular constants for the two states; my spectrum was therefore analysed only to ensure that the molecular constants obtained agreed with theirs. The constants from my analysis are shown in Table (4.2), and the agreement with the Herzbergs' data is most satisfactory.

This work showed that the SISAM spectrometer was now operating stably and with near theoretical performance. It also implied that the development phase of the instrument was complete, and that it was now ready for use in serious spectroscopy. The second half of this Thesis (Chapters 5-8) will present an analysis of the near infra-red emission bands of HO_2 and DO_2 which were recorded with the now fully functional spectrometer.

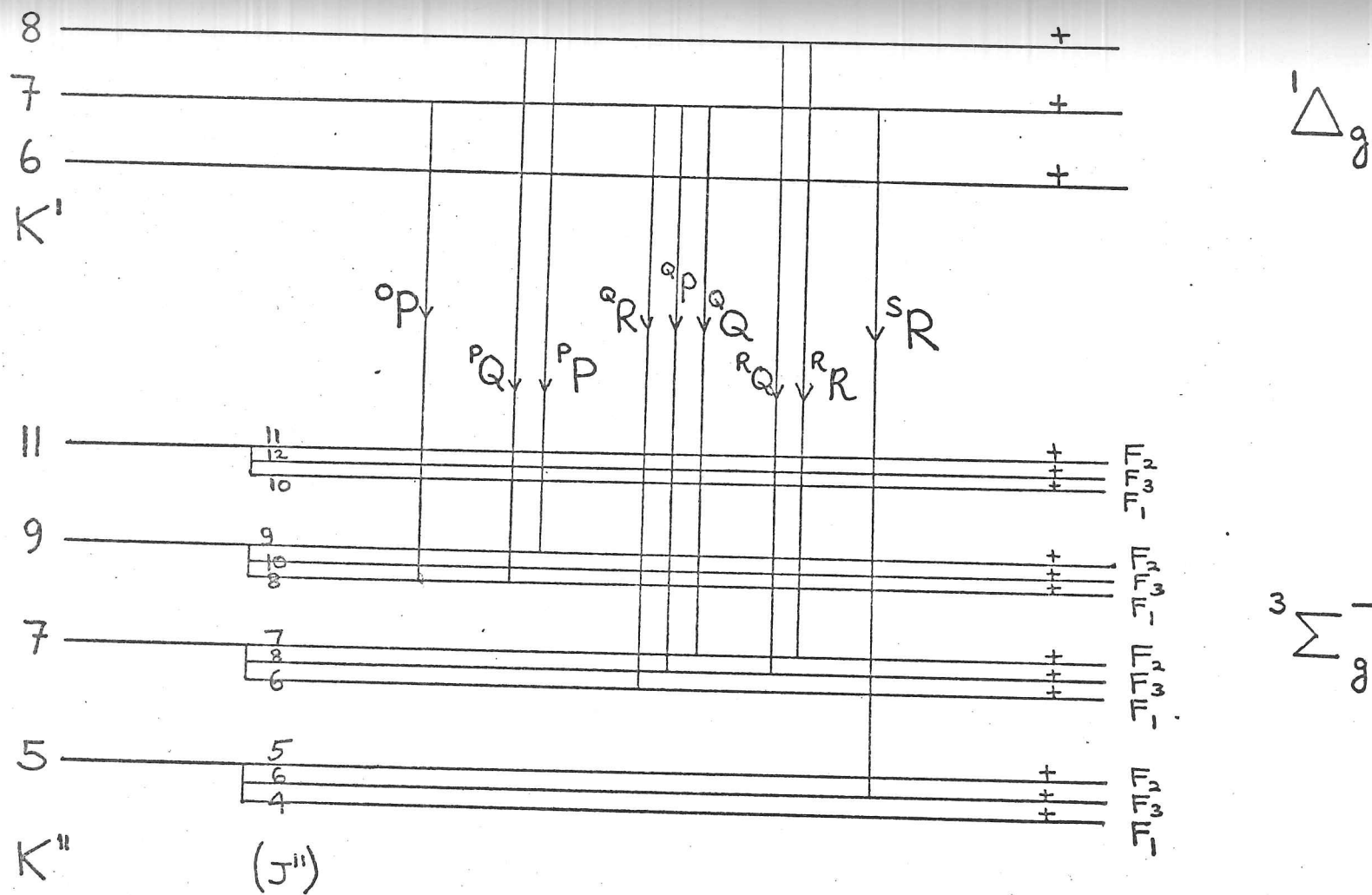


Figure 4.4 : The origin of the 9 branches of a $1\Delta_g \rightarrow 3\Sigma_g^-$ transition. The notation used is Δ_{AJ}^K .

Table (4.2)

Molecular constants for $O_2 \ ^1\Delta_g(v=0) \rightarrow \ ^3\Sigma_g^-(v=0)$

B'	$=$	$1.4174 \pm .0017$	}	$\ ^1\Delta_g(v=0)$
D'	$=$	$1.8 \pm 4.0 \times 10^{-6}$		
B''	$=$	$1.4365 \pm .0015$	}	$\ ^3\Sigma_g^-(v=0)$
D''	$=$	$2.1 \pm 3.8 \times 10^{-6}$		
λ''	$=$	$1.97 \pm .02$		
γ''	$=$	$-0.008 \pm .002$		
ν^{00}	$=$	$7882.32 \pm .04$		

1. All figures in cm^{-1} ; the uncertainties represent one standard error of the fit
2. The large errors in the distortion constants are not surprising for the following reason. Since the afterglow source is rotationally "cold", the branches do not extend out far in K, and only lines of large K (in fact $K > 18$) help to fix the distortion constants. As the number of these lines is few, the distortion constants are not well-determined.

CHAPTER 5

THE NEAR INFRA-RED EMISSION BANDS OF HO_2 5.1 Introduction

The HO_2 free radical has been the source of much speculation and interest over the last two decades. Early identifications of the radical were made by Foner and Hudson in 1962 using mass spectrometric techniques (14), and by Milligan and Jacox in 1963 who observed its vibrational spectra in an argon matrix (15). Notwithstanding much effort, the next ten years produced little new information on the radical; the arrival in the mid-seventies of new spectroscopic techniques, however, transformed this situation. Environmentalists were also becoming especially interested in HO_2 as its reactions with other molecules in the stratosphere were thought to be an important factor for ozone depletion. Since then, the number of people working on HO_2 has increased steadily, so that it is now one of the most frequently discussed free radicals.

The development of highly sensitive laser magnetic resonance (LMR) techniques was mainly responsible for this upsurge in interest. Spectroscopic observation of HO_2 had been hindered by its instability, the general weakness of its emission and absorption spectra, and the difficult regions of the electro-magnetic spectrum where transitions occur. In 1974, however, Radford, Evenson and Howard were able to

observe far infra-red transitions between rotational levels of the electronic ground state ⁽¹⁶⁾, spectroscopically labelled $^2A''$. The subsequent analysis of the LMR spectra, a classic piece of work, yielded accurate molecular constants for the lowest vibrational level, $^2A''(000)$ ⁽¹⁷⁾. These results were improved by Saito ⁽¹⁸⁾ in a very recent microwave study.

The molecule will, of course, possess several excited electronic states. The lowest-lying of these has been the cause of much interest; Walsh's rules ⁽¹⁹⁾, for example, predict an A'' ground state which is strongly bent, and an A' first excited state closer to linearity than the ground state. Transitions between these two electronic states occur, perhaps surprisingly, at relatively low energy in the near infra-red. Four years ago, Becker, Fink, Langen and Schurath ⁽²⁰⁾ reported near infra-red emission from the $O/O_2(^1\Delta_g)/C_2H_4$ reaction system between 1.2 and 2.1 μm , the strongest band at 1.43 μm being assigned to $HO_2\ ^2A'(000) \rightarrow ^2A''(000)$. At the same time, Hunziker and Wendt ⁽²¹⁾ recorded some of these bands in absorption, using mercury-photosensitized decomposition of H_2 in the presence of O_2 to generate ground state HO_2 . Both these studies, however, were at low resolution, and little spectroscopic information was obtained on the upper electronic state, except its existence and position.

As has been described earlier in the dissertation, the SISAM spectrometer developed in Cambridge provides a very sensitive instrument for work in the 1-2 μm region. An initial high resolution spectrum of the $^2A' \rightarrow ^2A''$ emission band of HO_2

at 1.43 μm was obtained here three years ago (22). The signal-to-noise ratio of individual peaks, however, was not high, the hotband assignment was uncertain, and a high resolution spectrum of the ${}^2\text{A}''(200) \rightarrow {}^2\text{A}''(000)$ overtone band at 1.51 μm was not obtained. The modifications to the SISAM spectrometer have dramatically improved its performance, and greatly superior spectra of the emission bands of HO_2 [and for the first time DO_2 (Chapter 8)] between 1.43 and 1.51 μm have been obtained.

5.2 Experimental conditions

Excited state HO_2 was formed in a flow system by the reaction of the products of a microwave discharge in O_2 with C_2H_4 , NH_3 or CH_3OH . The emission was observed through a window of a 5 litre internally gold-coated integrating sphere, downstream of the mixing point of the gases; the radiation was then focussed on to the entrance aperture of the SISAM spectrometer. By chopping the emission radiation before it entered the SISAM, the total integrated intensity over a wide wavelength range was measured, and low resolution spectra could be recorded. Experimental conditions (e.g. gas pressures) were altered to maximise the chopped signal at 1.43 μm before reverting to use the SISAM in its conventional mode as a high resolution interferometer. High resolution spectra were obtained with 7 mm diameter entrance and exit apertures (see Chapter 2.2.2); the resolution of the SISAM

was then $\approx 0.2 \text{ cm}^{-1}$. The emission radiation was detected by the highly sensitive, cooled R.C.A. intrinsic germanium detector (N.E.P. $\approx 5 \times 10^{-14} \text{ W.Hz}^{-1/2}$ at $1.45 \text{ }\mu\text{m}$) mounted outside the spectrometer.

The gases were taken from standard B.O.C. cylinders without further purification, their flows being controlled by Edwards needle valves. In the reaction of discharged O_2 with C_2H_4 the maximum chopped signal at $1.43 \text{ }\mu\text{m}$ was obtained when the gases were mixed outside the integrating sphere at a total pressure of $\sim 1.5 \text{ Torr}$. With this contact-to-observation time of $\sim 20 \text{ msec}$, emission is observed not only from $\text{HO}_2^2\text{A}'$ but also from vibrationally excited OH in its ground electronic state. The individual OH lines were strong and well-determined (23), so they could be used as an internal calibration of the complete HO_2 spectrum. It should be noted that OH emission falls off rapidly with contact-to-observation time, so the intensity of these OH lines are weaker than in the earlier spectrum of Freedman and Jones (22) when the gases were mixed inside the sphere.

5.3 Theory

This section gives a brief account of the theory of asymmetric top molecules. A general theory is presented first. Expressions are then given for the rotational energy levels of a near-prolate asymmetric top molecule, such as HO_2 .

The spin-splitting of these levels is discussed, and the rotational selection rules are given for the transitions observed in HO_2 . This background knowledge is essential before attempting an analysis of the near infra-red emission bands of HO_2 .

5.3.1 General theory of asymmetric top molecules

An asymmetric top molecule is one with three different principal moments of inertia. By convention these are arranged in the order $I_a < I_b < I_c$ where a, b and c refer to the inertial axes of the molecule. Symmetric top molecules have two moments of inertia similar and are thus of two types: prolate ($I_a < I_b = I_c$, a-axis unique) and oblate ($I_a = I_b < I_c$, c-axis unique). Any asymmetric top can be regarded as an intermediate between these two limiting forms of symmetric top. The degree of asymmetry in an asymmetric top molecule can usefully be described by an asymmetry parameter b where

$$b = \frac{C-B}{2[A-\frac{1}{2}(B+C)]} \quad (5.1)$$

and the rotational constants A, B and C are defined by

$$A = \frac{h}{8\pi^2 c I_a}, \quad B = \frac{h}{8\pi^2 c I_b}, \quad C = \frac{h}{8\pi^2 c I_c} \quad (5.2)$$

b can take values between 0 (limiting prolate top) and -1

(limiting oblate top). For all molecules, symmetric or asymmetric, the quantum number N defining the total orbital angular momentum (excluding electron spin) is "good"; it therefore defines the rotational energy levels of the molecule. Strictly, the quantum number K , the projection of N along the symmetry axis, is only meaningful (and "good") for a symmetric top molecule. Nevertheless, the energy levels of an asymmetric top may be labelled as $N_{K_p K_o}$ where K_p and K_o are the values of K in the prolate and oblate top limits. Thus 2_{12} represents an asymmetric rotor level; $N = 2$, the projection of N along the top axis being 1 in the prolate and 2 in the oblate limit.

The symmetry properties of such asymmetric rotor levels are determined by their behaviour with respect to a C_2 rotation about the three principal inertial axes a , b and c . Since one rotation is equivalent to the other two carried out successively, it is sufficient to determine the behaviour with respect to two of them; C_2^a and C_2^c are chosen since a and c are the unique axes in the prolate and oblate top limits.

The symmetry of a particular symmetric rotor level $N_{K_p K_o}$ must be independent of asymmetry. Consider, therefore, a C_2^a rotation in the limiting prolate top: the rotational wavefunction will be symmetric [even, e] if K_p is even, and anti-symmetric [odd, o] if K_p is odd. Similarly, considering a C_2^c rotation in the limiting oblate top, the wavefunction will be even, e if K_o is even, and odd, o if K_o is odd. Thus the level 2_{12} has oe symmetry, 4_{04} ee symmetry, and 5_{15} oo symmetry (the first label referring to C_2^a , the second to C_2^c).

5.3.2 The HO_2 free radical

The hydro peroxy radical, HO_2 , [whose ground state structure is shown in Figure (5.1)] is a near-prolate asymmetric top molecule, i.e. $I_b \simeq I_c$. The molecule has only two symmetry elements, the identity and a plane of symmetry; it therefore belongs to the C_s point group. The directions of the a, b and c inertial axes are fixed by the geometry of the molecule. There are six ways in which these can be identified with the molecule-fixed x, y and z axes (24); a III^R representation is used [$x \equiv a$, $y \equiv b$, $z \equiv c$], z being the unique out-of-plane axis [Figure (5.1)].

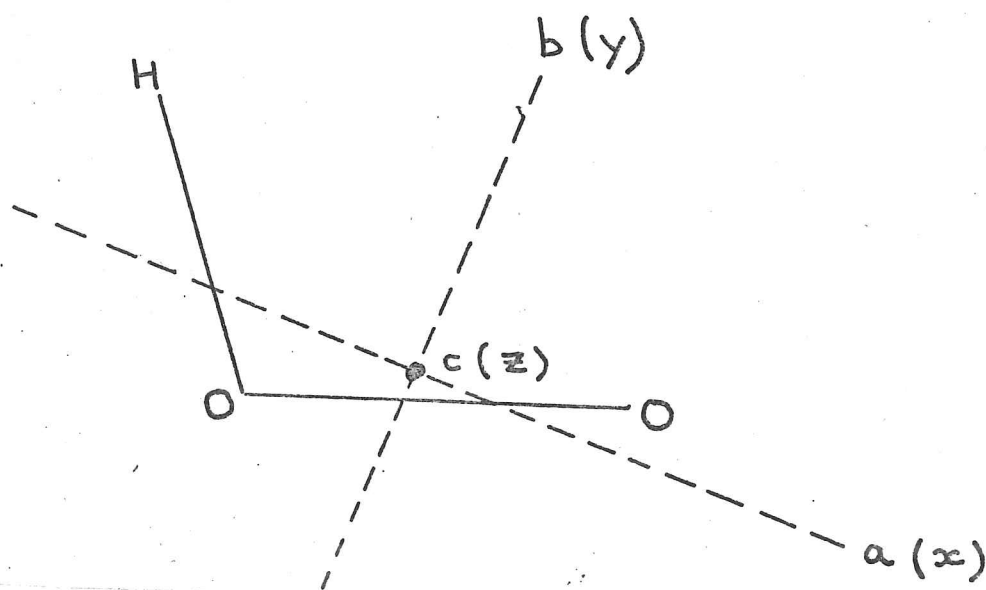


Figure 5.1 : The structure of ground state HO_2 :
 $r(\text{H-O}) = 0.98 \text{ \AA}$, $r(\text{O-O}) = 1.34 \text{ \AA}$,
 $\angle \text{HOO} = 104^\circ$ [Beers and Howard (25)].
 the c inertial axis is into the plane of the paper.

The group character table for a molecule of the C_s point group, z axis unique, is shown below:-

C_s	E	σ_h	
A'	1	1	x, y, R_z
A''	1	-1	z, R_x , R_y

5.3.2.1 The rotational energy levels

The asymmetry parameter b is only $\sim -10^{-3}$ in both the ${}^2A''$ and ${}^2A'$ electronic states of HO_2 . Because of this very low degree of asymmetry it is possible to assume K_p (or K as it will henceforth be labelled) is a reasonably good quantum number, and hence introduce Polo's formulae (26) for the rotational energy levels of a slightly asymmetric top molecule. These equations take the form:-

$$\begin{aligned}
 F(N,K) = & \bar{B}N(N+1) + (A-\bar{B}) \left[1 - \frac{3b^2}{8} \right] K^2 \\
 & + \Delta B_{\text{eff}}^K N(N+1) + \Delta D_{\text{eff}}^K N^2(N+1)^2 \\
 & - D_K K^4 - D_{NK} N(N+1)K^2 - D_N N^2(N+1)^2
 \end{aligned} \tag{5.3}$$

where $\bar{B} = \frac{1}{2}(B+C)$ and D_K , D_{NK} and D_N are the three distortion constants appropriate for a non-rigid symmetric top. This equation represents, therefore, the energy levels of a

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where $\bar{B} = \frac{1}{2}(B+C)$ and D_K , D_{NK} and D_N are the three distortion constants appropriate for a non-rigid symmetric top. This equation represents, therefore, the energy levels of a

symmetric top molecule (with B replaced by $\bar{B}$) plus additional terms introduced by slight molecular asymmetry. The coefficients ΔB_{eff}^K and ΔD_{eff}^K are functions of K and b, taking approximate values (26,27):

$$\begin{aligned}
 \Delta B_{\text{eff}}^K &= 0 \quad \text{for } K = 0 \quad \text{and } K \geq 2 \\
 &= \pm \frac{1}{2} b (A - \bar{B}) \quad \text{for } K = 1 \\
 \Delta D_{\text{eff}}^K &= -\frac{1}{8} b^2 (A - \bar{B}) \quad \text{for } K = 0 \\
 &= -\frac{1}{32} b^2 (A - \bar{B}) \quad \text{for } K = 1 \\
 &= +\frac{1}{48} (2\frac{1}{3}) b^2 (A - \bar{B}) \quad \text{for } K = 2 \\
 &= 0 \quad \text{for } K \geq 3
 \end{aligned} \tag{5.4}$$

Thus the molecular asymmetry splits the two-fold degeneracy of the $K = 1$ and 2 levels [Figure (5.2)]; the splitting in the $K = 1$ sub-bands increases rapidly with N, the splitting of $K = 2$ only becoming resolvable with the SISAM spectrometer at $N \geq 15$. For a molecule of such low asymmetry all rotational levels of $K \geq 3$ are unsplit.

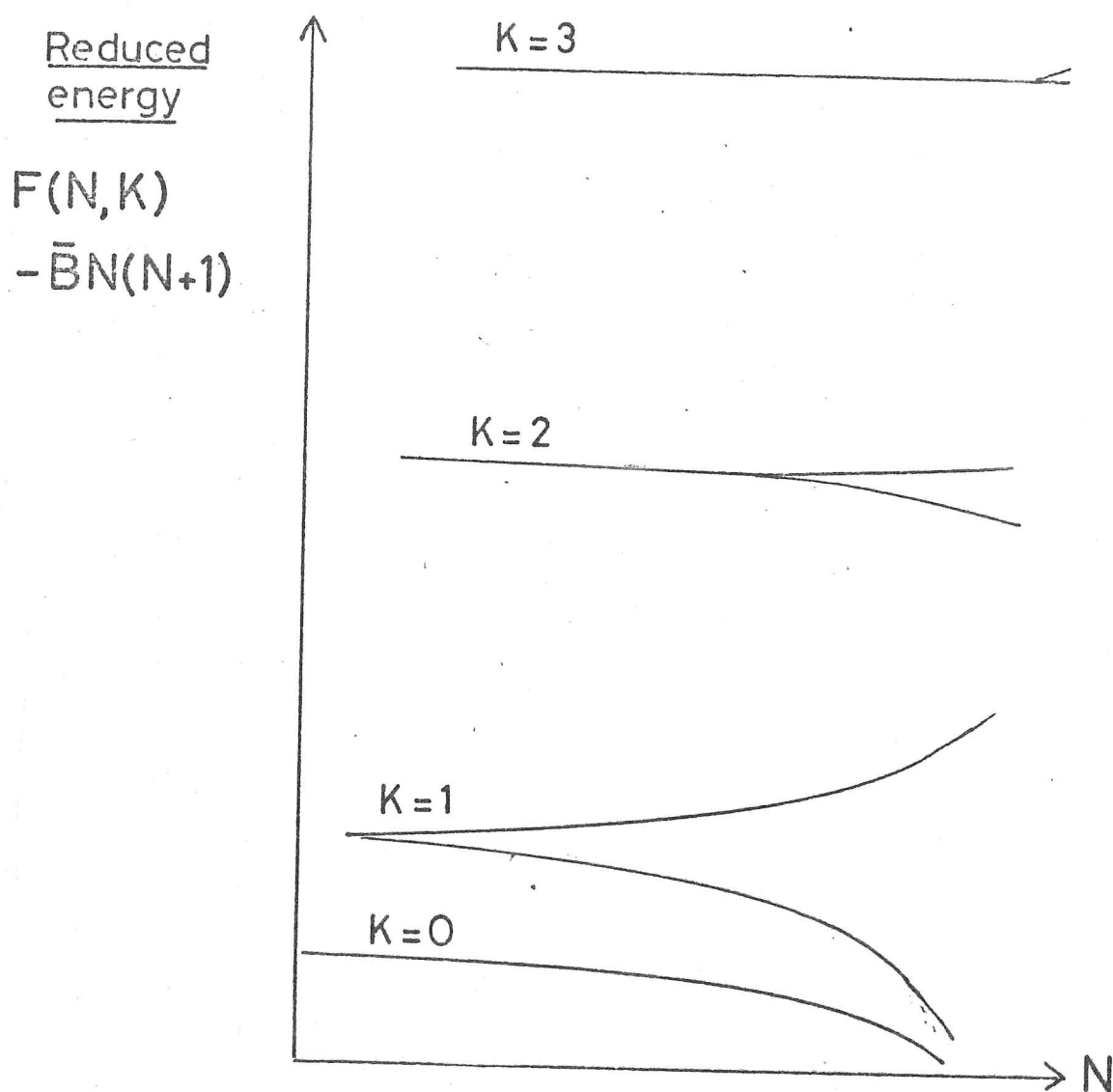


Figure 5.2 : Rotational energy of a slightly asymmetric top molecule as a function of N . The term $\bar{B}N(N+1)$ has been subtracted from the energy, i.e. the deviations of the curves from horizontal lines represent the deviations from the levels of the symmetric top. Distortion terms have been neglected.

5.3.2.2 Rotational selection rules

The main electronic band of HO_2 ${}^2\text{A}'(000) \rightarrow {}^2\text{A}''(000)$ observed at $1.43 \mu\text{m}$ is a C-type transition with non-zero transition dipole moment perpendicular to the plane of the molecule,

$$\text{i.e.} \quad \langle \text{A}' | \mu_z | \text{A}'' \rangle \neq 0 \quad (5.5)$$

where $\langle \text{A}' |$ and $| \text{A}'' \rangle$ are electronic wavefunctions of the upper and lower states. The rotational selection rules for such a transition are obtained by evaluating non-zero matrix elements of

$$\langle r' | \cos \alpha_z | r'' \rangle \quad (5.6)$$

where $\cos \alpha_z$ is the cosine of the angle between the z molecule-fixed axis and some space-fixed axis; $\langle r' |$ and $| r'' \rangle$ represent rotational wavefunctions for the upper and lower states. Symmetry arguments are then used to determine the general C-type selection rules

$$ee \leftrightarrow oe \quad \text{and} \quad oo \leftrightarrow eo \quad (5.7)$$

These correspond to $\Delta K = \pm 1$ for a near-prolate asymmetric top (e.g. HO_2) when K is a reasonably good quantum number. The usual selection rules on N (i.e. $\Delta N = 0, \pm 1$) for electric dipole transitions of a rotating body also apply to asymmetric

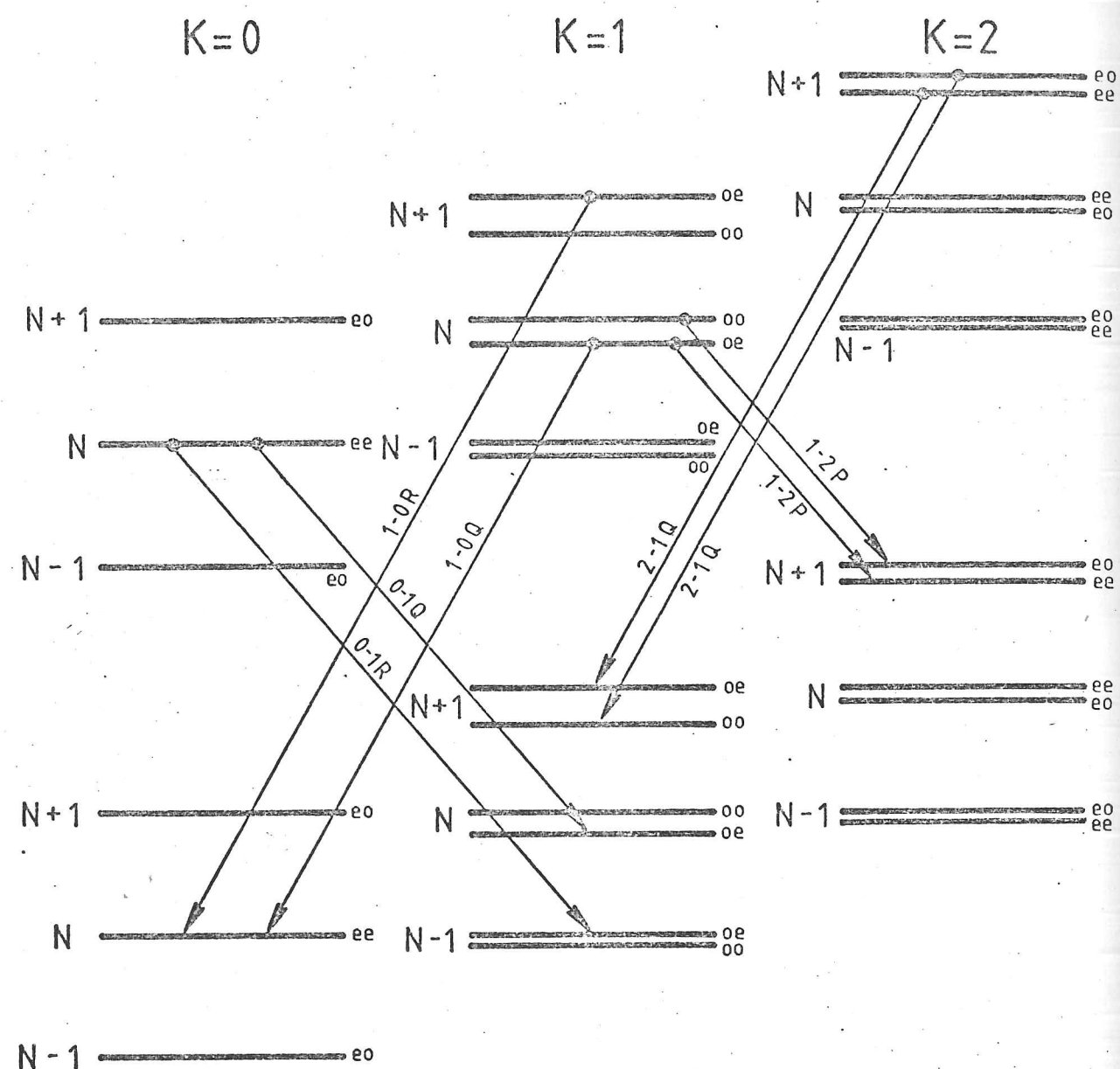


Figure 5.3 : Examples of C-type transitions for an asymmetric top molecule. The rotational quantum number N is assumed to be even, spin-splitting has been ignored, and the diagram is not drawn to scale.

rotors. It will be convenient later on to label C-type transitions as oe transitions, because they link levels where K_p differs by an odd (o) number and K_o differs by an even (e) number; examples of such transitions are shown in Figure (5.3).

All three modes of vibration of HO_2 are symmetric with respect to ~~reflection~~ in the molecular plane, and hence have A' symmetry under the operations of the C_s point group. All vibrational levels in the $^2A'$ electronic state of HO_2 will therefore have A' vibronic symmetry, all levels in $^2A''$ having A'' vibronic symmetry. Hence vibrational hotbands $^2A'(v_1v_2v_3) \rightarrow ^2A''(v_1v_2v_3)$ will be C-type transitions with the same rotational selection rules as above.

The O-H stretching vibrational overtone, $^2A''(200) \rightarrow ^2A''(000)$, which is observed at $1.51 \mu\text{m}$, is restricted to the plane of the molecule and generates an alternating dipole with components along the a and b inertial axes. This overtone will therefore give rise to an A/B - hybrid band with rotational selection rules:

$$\text{A-type} \quad ee \leftrightarrow eo \quad \text{and} \quad oo \leftrightarrow oe$$

$$\Delta K = 0$$

$$\Delta N = 0, \pm 1 [\Delta N \neq 0 \text{ for } K' = 0 \leftrightarrow K'' = 0]$$

$$\text{B-type} \quad ee \leftrightarrow oo \quad \text{and} \quad eo \leftrightarrow oe$$

$$\Delta K = \pm 1$$

$$\Delta N = 0, \pm 1$$

(5.8)

A-type transitions will be labelled eo transitions, B-type oo transitions for similar reasons as before.

5.3.2.3 General method of analysis of the spectra

Using Polo's formulae and these rotational selection rules, it was possible to analyse some observed sub-bands in the HO_2 spectra independently, and hence obtain effective rotational constants which could easily be related to the true rotational constants. Consider, for example, a $K' = 1 \rightarrow K'' = 0$ Q branch (henceforth labelled 1-0 Q) inside the ${}^2\text{A}' \rightarrow {}^2\text{A}''$ electronic band. Transitions can only originate from the lower asymmetry doublet of $K' = 1$ [Figure (5.3)], with line frequencies given by

$$\begin{aligned} \nu = [\nu^{00} + A' - \bar{B}'] + \frac{1}{4}[B' + 3C' - 2B'' - 2C'']N(N+1) \\ + [D_N'' - D_N' + \frac{b''^2}{8} (A'' - \bar{B}'')]N^2(N+1)^2 \end{aligned} \quad (5.9)$$

A fit of the assigned lines to the expression $\nu = \nu^0 + XN(N+1) + Y N^2(N+1)^2$ gave effective constants ν^0 , X and Y which could easily be related to the true molecular constants.

For a $K' = 0 \rightarrow K'' = 1$ Q branch (or 0-1 Q) inside the same electronic band, transitions can only terminate on the lower asymmetry doublet of $K'' = 1$, with line frequencies given by

$$\begin{aligned} \nu = [\nu^{00} - A'' + \bar{B}''] + \frac{1}{4}[2B' + 2C' - B'' - 3C'']N(N+1) \\ + [D_N'' - D_N' - \frac{b'^2}{8} (A' - \bar{B}')]N^2(N+1)^2 \end{aligned} \quad (5.10)$$

so that a similar fit to a quadratic in $N(N+1)$ gave different coefficients v^0 , X and Y which could again easily be related to the true molecular constants.

5.3.2.4 Spin-splitting of the rotational levels

As both upper and lower electronic states of HO_2 are doublet states ($\tilde{S} = \frac{1}{2}$), each asymmetric rotor level $N_{K_p K_o}$ is split into two by the interaction of rotational angular momentum with electronic spin angular momentum, phenomenologically labelled $\tilde{N.S.}$. The spin-splitting parameter δ is defined by

$$2\delta = F_1(N_{K_p K_o}, J = N + \frac{1}{2}) - F_2(N_{K_p K_o}, J = N - \frac{1}{2}) \quad (5.11)$$

where F_1 and F_2 represent standard diatomic notation for the two spin components of given N in a doublet state (28). Hougen et al (17) showed how δ could be related to the three principal components of the spin-rotation interaction tensor $\tilde{\epsilon}$.

Allowing for $\Delta K = 0$ interactions only, they obtained

$$\delta = \frac{N+1}{2} \left[\frac{1}{2}(\epsilon_{bb} + \epsilon_{cc}) - \frac{1}{4}(\epsilon_{bb} - \epsilon_{cc})(-1)^{N-K_o} \delta_{K_p,1} + \frac{\epsilon_{11} K_p^2}{N(N+1)} - \left(\frac{\epsilon_{11}^2}{2(B+C)} \right) \left(\frac{K_p^2}{N(N+1)} \right) \left(1 - \frac{K_p^2 (N^2 + N + 1)}{N^2 (N+1)^2} \right) \right] \quad (5.12)$$

where $\epsilon_{11} = \epsilon_{aa} - \frac{1}{2}(\epsilon_{bb} + \epsilon_{cc})$ and $\delta_{K_p,1}$ is the Kronecker delta symbol. Since $\epsilon_{aa} \gg \epsilon_{bb}$ and ϵ_{cc} , it is seen that δ

increases approximately as K_p^2 , but decreases with increasing N . Their ground state values for ϵ_{aa} , ϵ_{bb} and ϵ_{cc} were invaluable when assigning spin-split doublets in the electronic spectrum.

CHAPTER 6

ANALYSIS OF THE SPECTRA

6.1 Analysis of the ${}^2A'(000) \rightarrow {}^2A''(000)$ band of HO_2

The analysis of the high resolution spectrum shown in Figure (6.1) proved to be a non-trivial process. The assignments of the observed lines are given in Appendix 1 at the end of the Thesis. The analysis was aided by two factors:-

(a) The availability of ground state constants (17,18).

An assignment could always be checked by forming an appropriate ground state combination difference and predicting the position of another line originating from a common upper level.

(b) The earlier work of Freedman and Jones (22) which gave a useful start to the analysis.

The most distinctive feature of the spectrum was a very strong sequence of lines, origin at 7049 cm^{-1} , which was assigned to the 1-0 Q branch; these transitions originate from the lower asymmetry component of $K' = 1$. Only Q(5) and Q(6) were noticeably broadened due to spin-splitting. The 0-1 Q branch is less obviously seen in the spectrum, but has its origin at 7010 cm^{-1} ; now lines $N = 4-8$ show spin-split doublets, and 9 and 10 are noticeably broadened. These observations indicate that the spin-splittings of the upper electronic state are smaller than those of ${}^2A''(000)$, a result which was confirmed by an analysis of the $2 \rightarrow 1$ sub-band.

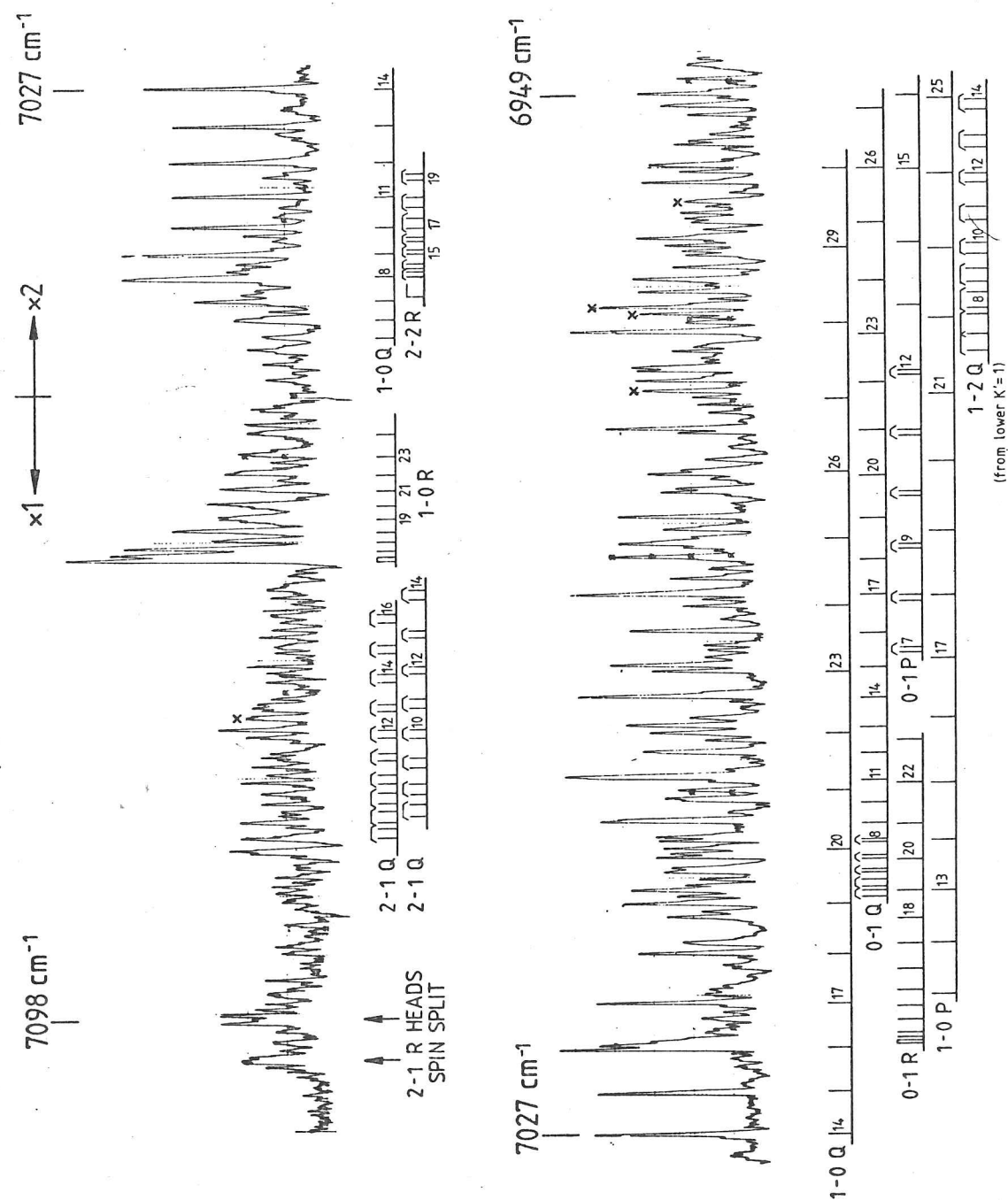


Figure 6.1 : High resolution spectrum of HO_2 $2A' \rightarrow 2A''$.

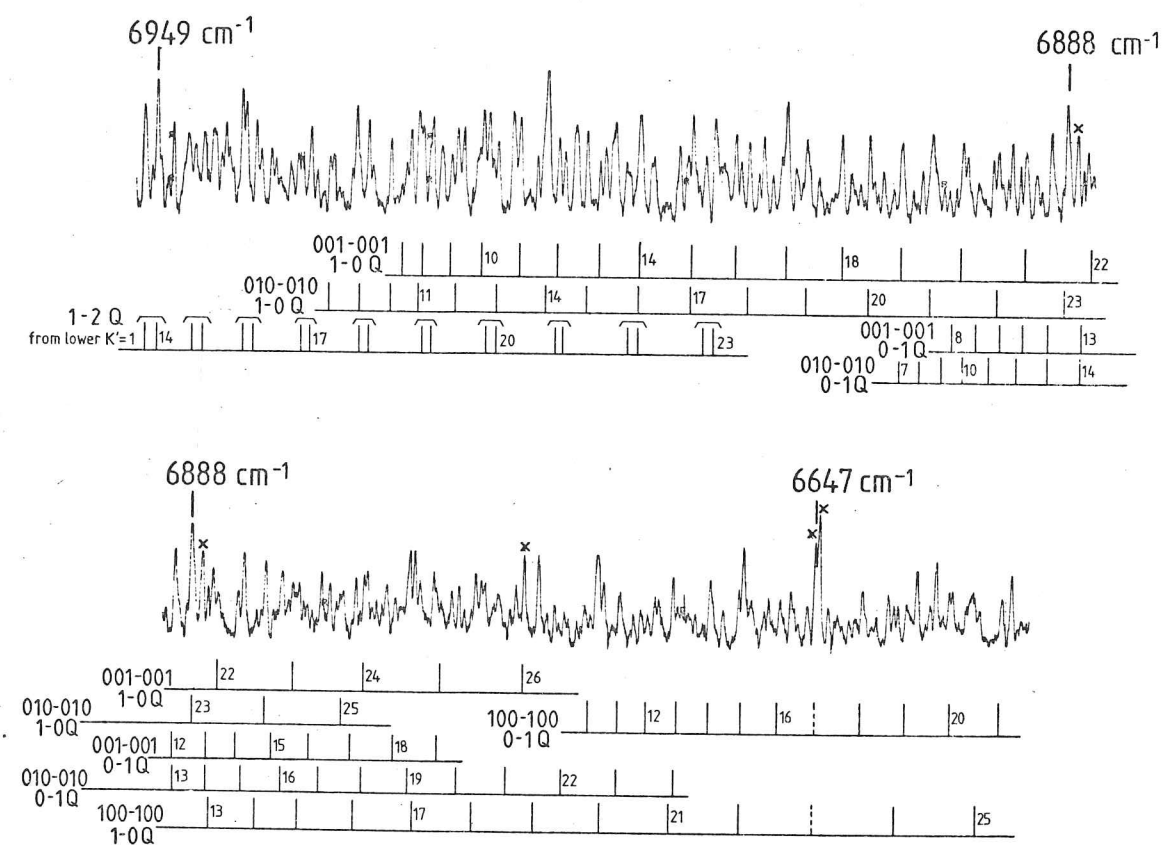


Figure 6.1 : High resolution spectrum of HO_2 $2A' \rightarrow 2A''$ continued. Some assignments are shown. Lines marked x are due to OH emission.

Using ground state combination differences it was possible to assign the 0-1 P and 0-1 R branches, the former showing spin-split doublets up to $N = 12$, the latter having an obvious band head at 7020 cm^{-1} . A complete P and R assignment was also possible for the $1 \rightarrow 0$ sub-band, the 1-0 R head being especially clear in the spectrum at 7063 cm^{-1} . [P and R transitions originate from the upper asymmetry component of $K' = 1$ in the $1 \rightarrow 0$ sub-band, and terminate on the upper component of $K'' = 1$ in the $0 \rightarrow 1$ sub-band (Figure (5.3)).] Assuming that the appropriate Hönl-London factors for a symmetric top can be applied to this near-prolate molecule, then 1-0 R and 1-0 P lines should have half the intensity of the corresponding 1-0 Q lines at large N (29). In practice the ratio of intensities is much lower: in other words, emission from the upper asymmetry component of $K' = 1$ is much weaker than from the lower component - a totally unexpected result.

Combining the 1-0 Q(N) assignments with suitable ground state combination differences, it was possible to assign the 1-2 Q branch, these transitions starting on the lower asymmetry component of $K' = 1$ and terminating on the upper component of $K'' = 2$; each transition is an observed doublet due to the relatively large spin-splitting of $K'' = 2$ in $2A''(000)$ (17). Some $1 \rightarrow 2$ P and R branch spin-doublets could also be assigned, these transitions starting on the lower asymmetry component of $K' = 1$ now terminating on the lower component of $K'' = 2$ (to obey the C-type selection rules $ee \leftrightarrow oe$ and $oo \leftrightarrow eo$).

Similarly, combining the 1-0 P(N) and R(N) assignments with suitable ground state combination differences, P, Q and R lines originating from the upper asymmetry component of $K' = 1$ could be assigned in the $1 \rightarrow 2$ sub-band. The Q lines terminate on the lower asymmetry component of $K'' = 2$, the P and R lines on the upper component. Again every transition is an observed doublet due to the spin-splitting of $K'' = 2$ in ${}^2A''(000)$.

From these assignments it was not possible to determine the sign of the spin-splittings δ , as defined by equation (5.11), in the ${}^2A''$ state. Assuming it to be negative, however (17), the three principal components of the spin-rotation interaction tensor, as defined by equation (5.12), could be determined. The values of $|2\delta|$ for a particular N of $K'' = 2$ were averaged to give $|2\delta|_{\text{obs}}$ with a weighting factor equal to the number of points averaged [Table (6.1)]. The observed splittings in $K'' = 1$ are also shown in the table. A standard weighted least-squares fit of this data to equation (5.12) gave

$$\left. \begin{aligned} \epsilon_{aa} &= -1.58 \pm .02 \text{ cm}^{-1} \\ \frac{1}{2}(\epsilon_{bb} + \epsilon_{cc}) &= -0.0075 \pm .0012 \text{ cm}^{-1} \\ \frac{1}{2}(\epsilon_{bb} - \epsilon_{cc}) &= -0.030 \pm .007 \text{ cm}^{-1} \end{aligned} \right\} \text{ for } {}^2A''(000) \quad (6.1)$$

These values agree very favourably with the more accurate LMR results of (17)

Table (6.1)

Observed spin-splittings of $\text{HO}_2^2\text{A}''(000)$. The $K_p = 2$ values were averaged for each N (see text). The $K_p = 1$ values with $N-K_o = 0$ come from the 0-1 Q(N) splittings, those with $N-K_o = 1$ from the 0-1 P(N) splittings. All figures in cm^{-1} .

N	K_p	K_o	Statistical Weight	$ 2\delta _{\text{obs}}$	obs. - calc.
6	2	av	2	1.497	- .015
7	2		3	1.313	- .028
8	2		3	1.122	+ .017
9	2		4	0.991	+ .037
10	2		4	0.986	- .046
11	2		4	0.870	.000
12	2		4	0.832	- .020
13	2		4	0.743	+ .021
14	2		4	0.812	- .087
15	2		4	0.640	+ .051
16	2		4	0.680	- .017
17	2		4	0.584	+ .055
18	2		4	0.591	+ .027
19	2		4	0.659	- .058
20	2		1	0.605	- .019
21	2		2	0.542	+ .031
4	1	4	2	0.360	+ .137
5	1	5	2	0.330	+ .052
6	1	6	2	0.297	+ .006
7	1	7	2	0.296	- .052
8	1	8	2	0.267	- .069
7	1	6	1	0.398	- .032
8	1	7	1	0.383	- .048
9	1	8	1	0.309	+ .004
10	1	9	1	0.264	+ .033
11	1	10	1	0.308	- .023
12	1	11	1	0.249	+ .027

RMS deviation of fit = 0.050 cm^{-1}

$$\begin{aligned}
\epsilon_{aa} &= -1.630 \pm .008 \text{ cm}^{-1} \\
\frac{1}{2}(\epsilon_{bb} + \epsilon_{cc}) &= -0.0072 \pm .0006 \text{ cm}^{-1} \\
\frac{1}{2}(\epsilon_{bb} - \epsilon_{cc}) &= -0.009 \pm .002 \text{ cm}^{-1}
\end{aligned}
\tag{6.2}$$

As the $K' = 2 \rightarrow K'' = 1$ sub-band occurs to high frequency of the intense transitions, the spectrum is relatively "clean" in this region. It is thus seen that emission from $K' = 2$ of ${}^2A'(000)$ is considerably weaker than would be expected for a Boltzmann population of the rotational energy levels. It was, however, possible to make a complete analysis of this sub-band, giving information about the spin-rotation tensor $\tilde{\epsilon}$ of ${}^2A'(000)$. Two Q branches were assigned, split by asymmetry, each transition being an observed doublet due to spin-splitting of $K' = 2$ in ${}^2A'(000)$. Using ground state combination differences the N numberings of these branches were shown to be correct by predicting the positions of the two 2-1 P and R branches; the R heads are clearly seen in the spectrum around 7100 cm^{-1} , both spin-split, their observed positions being less than half a linewidth from their predicted positions. A fairly complete 2-1 P branch assignment was also possible.

As the ground state spin-splittings were known (17), their small contribution to the observed spin-split doublets in the 2-1 sub-band could be evaluated; absolute upper state spin-splittings inside $K' = 2$ could therefore be determined [listed in Table (6.2)]. The sign of these splittings is again unknown, but to obtain a non-imaginary solution for ϵ_{aa} in ${}^2A'(000)$ the negative sign has to be taken. The data can

Table (6.2)

Absolute spin-splittings of $\text{HO}_2^2\text{A}'(000)$. The value for each N is the average of the two 2-1 Q(N) splittings less the ground state contribution [see text]. All figures in cm^{-1} .

N	K_p	K_o	$ 2\delta _{\text{obs}}$	obs. - calc.
7	2	av	0.737	+ .107
8	2		0.812	- .060
9	2		0.728	- .047
10	2		0.592	+ .034
11	2		0.621	- .038
12	2		0.576	- .029
13	2		0.514	+ .004
14	2		0.522	- .028
15	2		0.454	+ .020
16	2		0.528	- .070
17	2		0.489	- .045
18	2		0.391	+ .041
19	2		0.330	+ .093

RMS deviation of fit = 0.059 cm^{-1}

then be fitted to equation (5.12) to give two components of $\tilde{\epsilon}$ in HO_2 $^2\text{A}'(000)$

$$\begin{aligned}\epsilon_{aa} &= -1.09 \pm .04 \quad \text{or} \quad +5.06 \pm .04 \text{ cm}^{-1} \\ \frac{1}{2}(\epsilon_{bb} + \epsilon_{cc}) &= -0.006 \pm .002 \text{ cm}^{-1}\end{aligned}\quad (6.3)$$

For bent XH_2 molecules in doublet electronic states, Dixon (30) has shown that the predominant contribution to ϵ_{aa} is not a first order effect coupling electronic spin ($\tilde{S}$) with orbital rotation ($\tilde{N}$), but a second order effect coupling electronic spin ($\tilde{S}$) with electronic orbital angular momentum. Second order perturbation theory readily shows that the sign of ϵ_{aa} in an excited electronic state should be opposite to its sign in the ground state, its magnitude often being larger. In his study of the $\text{A}^2\text{A}' \leftarrow \text{X}^2\text{A}''$ absorption spectrum of HNF (which is isoelectronic to HO_2), Woodman (31) used this theory to obtain ϵ_{aa} values of -0.27 cm^{-1} for $\text{X}^2\text{A}''$ and $+0.67 \text{ cm}^{-1}$ for $\text{A}^2\text{A}'$. The large positive value for $\epsilon_{aa} = 5.06 \pm .04 \text{ cm}^{-1}$ is therefore taken for HO_2 $^2\text{A}'(000)$. It should be noted that this large positive value is not in contradiction to the experimental observation that the observed spin-splittings of HO_2 $^2\text{A}'$ are appreciably less than those of the $^2\text{A}''$ ground state, which has a smaller but negative value for ϵ_{aa} [see equation (5.12)].

A few transitions in the 2-3 Q branch could be assigned. This branch is unsplit by asymmetry, but every transition is again a doublet caused predominantly by the large spin-splitting of $^2\text{A}''(000)$ $K'' = 3$.

No transitions could be assigned for $K' > 2$, a very surprising phenomenon. This cut-off in emission from the high K levels of HO_2 $^2\text{A}'$ is observed in the three reaction systems $\text{O} + \text{C}_2\text{H}_4$, $\text{O} + \text{NH}_3$ and $\text{O} + \text{CH}_3\text{OH}$ over a wide range of experimental conditions. Possible explanations for this phenomenon will be discussed in Chapter 7.

6.1.1 Evaluation of the rotational constants

The ground state of HO_2 has now been accurately established by LMR (17), microwave (18), and EPR (32) techniques. As has been shown, the LMR constants were of great assistance in assigning the electronic spectrum. [As this work was being completed, the EPR analysis provided even more accurate constants. At my relatively modest resolution, however, the effect of the small changes in the ground state constants made no difference to the analysis.] I could not hope to improve these constants, so little further work was done on this state. To ensure, however, that my analysis was not completely wrong, two kinds of ground state combination difference were formed inside the strong $0 \rightarrow 1$ sub-band

$$\begin{aligned} Q(N) - P(N+1) &= E^U(N+1,1) - E^L(N,1) \\ \text{and } R(N-1) - Q(N) &= E^L(N,1) - E^U(N-1,1) \end{aligned} \quad (6.4)$$

The notation being used here is $E^U(N+1,1)$, for example, represents the absolute energy of the upper asymmetry component of $N'' = N+1$ inside $K'' = 1$. Use of Polo's formulae then

gives

$$Q(N) - P(N+1) = \frac{1}{2}(3B'' + C'')(N+1) + \frac{1}{2}(B'' - C'')N(N+1) \\ - 4(N+1)^3 \left[D_N'' + \frac{b''^2}{32} (A'' - \bar{B}'') \right]$$

and

$$R(N-1) - Q(N) = \frac{1}{2}(3B'' + C'')N - \frac{1}{2}(B'' - C'')N(N+1) \\ - 4N^3 \left[D_N'' + \frac{b''^2}{32} (A'' - \bar{B}'') \right] \quad (6.5)$$

A simultaneous fit of the combination differences to these two equations gave rotational constants for $^2A''(000)$.

$$B'' = 1.118_0 \pm .001_4 \text{ cm}^{-1} \\ C'' = 1.057_0 \pm .001_4 \text{ cm}^{-1} \\ D_N'' = 3.7 \pm 1.5 \times 10^{-6} \text{ cm}^{-1} \quad (6.6)$$

These should be compared with the LMR results of (17)

$$B'' = 1.117_9 \pm .000_5 \text{ cm}^{-1} \\ C'' = 1.056_7 \pm .000_5 \text{ cm}^{-1} \\ D_N'' = 4.2 \pm .8 \times 10^{-6} \text{ cm}^{-1} \quad (6.7)$$

The agreement is seen to be most satisfactory, giving confidence to these assignments; this is of considerable importance since assignments of the higher K sub-bands weigh heavily on those of the lower K sub-bands. At this stage, therefore, no further work was done on the ground state.

The main purpose of this work, however, was to establish accurate molecular constants for the upper electronic state of HO_2 (not, as yet, detected by LMR, microwave or EPR techniques). Two separate methods were used to obtain the rotational constants for $^2\text{A}'(000)$. The first method used the results of fitting lines of the strong 1-0 Q and 0-1 Q branches to a quadratic in $N(N+1)$, as described earlier. [Low N transitions of the latter branch are spin-split: the average position of each doublet was taken for these transitions.] Using the most accurate ground state data ⁽³²⁾, the following constants were obtained

$$A' = 20.39 \pm .05 \text{ cm}^{-1}$$

$$B' = 1.021_2 \pm .001_5 \text{ cm}^{-1}$$

$$C' = 0.969_3 \pm .001_5 \text{ cm}^{-1}$$

$$D_N' = 4.3 \pm 2.0 \times 10^{-6} \text{ cm}^{-1}$$

$$\nu^{00}[^2\text{A}'(000) \rightarrow ^2\text{A}''(000)] = 7029.48 \pm .10 \text{ cm}^{-1} \quad (6.8)$$

This method of analysis determines B' and C' quite accurately; A' , however, is not well-determined as only a small amount of the total data available has been used.

The second method of analysing the upper state, therefore, performs a complete fit on all independent upper state combination differences that can be constructed from the assignments; a full asymmetric rotor fitting program ^{*} was

* I am most grateful to Dr. J.H. Carpenter for the use of this program.

used for this purpose. The average position of all spin-split doublets was taken in forming a combination difference; this approximation would only introduce serious error at very low N values, which were never observed in the spectrum (see, for example, Herzberg (27)). The majority of upper state combination differences formed were inside a common K' level; these helped to fit B' and C' , but gave no information on A' . The only genuine combination differences that could be formed involving a change in K' were those of the form $K' = 2 \Rightarrow K' = 0$ (with $K'' = 1$ as a common lower level). To determine A' precisely, therefore, it was necessary to construct upper state combination differences of the form $K' = 2 \Rightarrow K' = 1$, and $K' = 1 \Rightarrow K' = 0$; these were obtained by combining suitable assignments with well-determined absolute ground state energies (17). [A complete list of all combination differences used in the fit is given in Appendix 2 at the end of the Thesis.] As emission was only observed from $K' \leq 2$, it was necessary to constrain $D_{K'}$ and $D_{NK'}$ to the ground state values (17). The following constants for $\text{HO}_2 \ ^2A'(000)$ were then obtained:

$$\begin{aligned}
 A' &= 20.464_4 \pm .004_4 \text{ cm}^{-1} \\
 B' &= 1.021_8 \pm .000_6 \text{ cm}^{-1} \\
 C' &= 0.969_0 \pm .000_6 \text{ cm}^{-1} \\
 D_N' &= 5.20 \pm .69 \times 10^{-6} \text{ cm}^{-1} \\
 D_{NK'}' &= 1.2 \times 10^{-4} \text{ cm}^{-1} \\
 D_{K'}' &= 4.1 \times 10^{-3} \text{ cm}^{-1}
 \end{aligned}
 \quad \begin{array}{l} \\ \\ \\ \\ \text{constrained} \\ \end{array}
 \quad (6.9)$$

The most interesting result here is the value of A' ; it has changed negligibly from the ground state value of 20.357 cm^{-1} . This should be contrasted with the results obtained in the equivalent $A' \leftrightarrow A''$ electronic transition in similar triatomic molecules; in HCO the A value changes from 24.295 to ∞ ⁽³³⁾, in HNO from 18.479 to 22.164 ⁽³⁴⁾, and in HNF (which is iso-electronic to HO_2) 17.688 to 27.570 ⁽³¹⁾ (the first value referring to the ground electronic state, the second to the excited state, all figures in cm^{-1}). HO_2 appears to be behaving anomalously; this observation is confirmed in the following section.

6.1.2 $\Delta K = 0$ emission

In the analysis of the ${}^2A' \rightarrow {}^2A''$ spectrum of HO_2 , the presence of anomalous, unassigned lines near the band origin was soon apparent. The lines appeared in the region $7043 - 7033 \text{ cm}^{-1}$, and are readily observed as the spectrum is relatively "clean" here. They appeared in the three reaction schemes $\text{O} + \text{C}_2\text{H}_4$, $\text{O} + \text{NH}_3$ and $\text{O} + \text{CH}_3\text{OH}$ (all found to be a good source of HO_2 ${}^2A'$), so there can be little doubt that these lines are due to HO_2 emission, and not due to a different molecule or radical. Unsuccessful attempts were initially made to fit them to high N values of the 1-0 R branch, and high N of the 2-1 Q and P branches.

All the anomalous lines can now be assigned to the R branches of forbidden $\Delta K = 0$ transitions, the main intensity

being observed in the $K' = 2 \rightarrow K'' = 2$ R branch. [Again, no emission could be identified from $K' > 2$.] As the lines of this branch only become split by asymmetry at high N , it is not easy to determine whether these are ee or eo transitions (using the nomenclature defined in Chapter 5.3.2.2); examples of these two types of transition are shown below [Figure (6.2)].

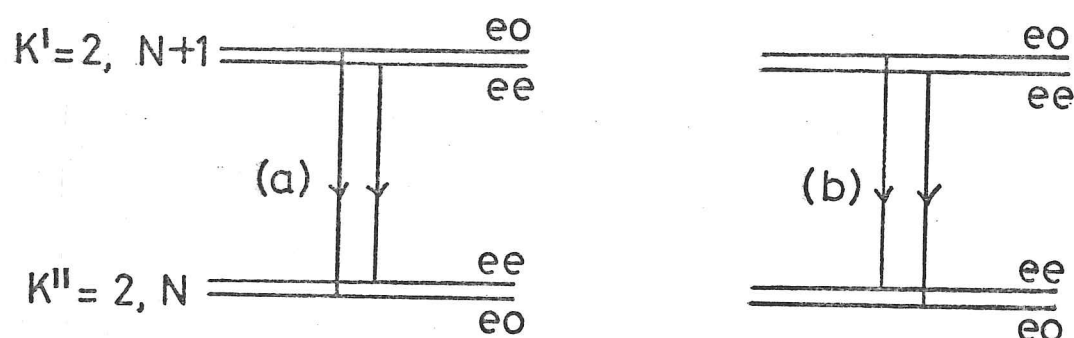


Figure 6.2 : Examples of forbidden transitions in the $2-2$ R(N) branch. (a) shows transitions which are ee in character, (b) shows transitions eo in character. The rotational quantum number N is assumed to be even.

A small clue was obtained by predicting the positions of the forbidden $K' = 1 \rightarrow K'' = 1$ R heads. If the forbidden lines are ee, then they link the upper [lower] asymmetry component of $K' = 1$ $N' = N+1$ with the lower [upper] asymmetry component of $K'' = 1$ $N'' = N$ [Figure (5.3)], so the positions of the predicted heads will be well-separated; broad unassigned lines could be assigned to these two heads at 7046.71 and 7038.46 cm^{-1} . If the lines are eo, then the two 1-1 R heads are both predicted to occur at 7041.35 cm^{-1} ; the nearest observed line already has three assignments. Hence there is slight evidence that these forbidden transitions are ee in character.

The main intensity of these forbidden lines, however, is in the 2-2 sub-band. Each line is spin-split, the observed splitting being small since δ [as defined in equation (5.11)] is negative in both electronic states. [Transitions obeying the selection rule $\Delta J = \Delta N$ therefore link the upper [lower] spin-split component of $K' = 2$ $N' = N+1$ with the upper [lower] spin-split component of $K'' = 2$ $N'' = N$; the spin-splitting observed is thus the difference of the two individual spin-splittings.] Great reliance should not be placed on the magnitude of the observed splittings, however, since many transitions are blended with strong 1-0 Q(N) lines.

The presence of weak forbidden $\Delta K = 0$ bands in a C-type $\Delta K = \pm 1$ electronic transition has been observed in other planar triatomics, notably HCO (33), HNF (31), HSiCl and HSiBr (35). Their presence has been explained by a phenomenon

called "axis-switching" (36), although a better description would probably be axis-tilting. This is predominantly caused by a substantial change in the geometry of the molecule between the two states, and hence a change in the orientation (i.e. a tilting) of the inertial axes of the states involved. (e.g. in the X^2A'' ground state of HCO the bond angle is $\sim 125^\circ$, but the molecule is linear in the A^2A' state). The following points, however, suggest that these forbidden lines in HO_2 are not predominantly caused by an axis-switching mechanism.

(1) The intensities of these $K' = 2 \rightarrow K'' = 2$ lines are much stronger than those observed in similar molecules; to within a factor of ~ 3 , they have the same intensity as the allowed $K' = 2 \rightarrow K'' = 1$ bands.

(2) As my analysis shows that the A rotational constant only changes from 20.357 to 20.464 cm^{-1} , there would not appear to be a large change in molecular geometry between the two electronic states of HO_2 . Hence strong axis-switching lines should not be present. An accurate HOO bond angle in the $^2A'$ state would obviously help clarify this point.

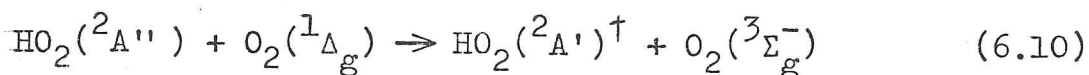
Knowledge of the three principal moments of inertia of a planar triatomic is not sufficient to determine an absolute geometry of the molecule. [Assuming the inertial defect is zero, two moments of inertia predetermine the third, i.e. $I_c = I_a + I_b$: two bond lengths plus one bond angle cannot be uniquely determined from only two independent moments of inertia.] Molecular constants from an isotopic species are needed. The structure of the ground state of HO_2 has been

approximately established by Beers and Howard (25) [Figure (5.1)]; they observed microwave transitions inside $K = 0$ of DO_2 $^2\text{A}''(000)$ and hence established $(B + C)$ for this state. It was to determine the absolute structure of HO_2 $^2\text{A}'$ that I recorded the $^2\text{A}' \rightarrow ^2\text{A}''$ spectrum of DO_2 with the SISAM spectrometer; the analysis is presented in Chapter 8. As suspected, the bond angle of HO_2 $^2\text{A}'$ is effectively unchanged from its ground state value, so axis-switching can be rejected as the principal cause of the $\Delta K = 0$ lines in the HO_2 spectrum.

Other possible explanations for these strong forbidden lines will be discussed in Chapter 7.

6.2 Analysis of the $^2\text{A}'(v_1v_2v_3) \rightarrow ^2\text{A}''(v_1v_2v_3)$ hotbands of HO_2

As a possible form of population of the excited state of HO_2 is by energy transfer from $\text{O}_2(^1\Delta_g)$ to the ground state of HO_2 $^2\text{A}''$ (20)



it is not unreasonable to expect transitions from vibrationally excited $\text{HO}_2(^2\text{A}')^\dagger$. Transitions to the ground electronic state of the type $^2\text{A}'(v_1v_2v_3) \rightarrow ^2\text{A}''(v_1v_2v_3)$ are called sequence "hotbands"; they are C-type transitions with the same rotational selection rules as the mainband (designated 000 - 000). The high resolution spectrum of HO_2 still had unassigned

structure to lower frequency of the mainband; much of it could be assigned to vibrational hotbands.

Two strong sequences of lines were easily found, one with origin 6938 cm^{-1} , the other 6945 cm^{-1} ; when fitted to a quadratic in $N(N+1)$ they gave approximately the same coefficient of $N(N+1)$ as the 1-0 Q branch of the mainband. This coefficient, value -0.1053 cm^{-1} in the mainband, can be equated to $\frac{1}{4}[B' + 3C' - 2B'' - 2C'']$ (or $(\bar{B}' - \bar{B}'') + \frac{1}{4}(C' - B'')$) [equation (5.9)]. Although no rotational constants are known for any excited vibrational state of either electronic state of HO_2 , it was assumed that the value of this coefficient would not change very much in any of the three vibrational hotbands 100-100, 010-010 and 001-001. These two sequences were therefore assigned to 1-0 Q branches of vibrational hotbands [second page of Figure (6.1)]. Likewise, it was assumed that the coefficient of $N(N+1)$ in a 0-1 Q branch fit, $\frac{1}{4}[2B' + 2C' - B'' - 3C'']$ (or $(\bar{B}' - \bar{B}'') - \frac{1}{4}(C'' - B'')$), would not alter appreciably from the mainband value of -0.0770 cm^{-1} . An additional criterion which helped to assign these branches of the hotbands was that the coefficient of $N^2(N+1)^2$ should be positive in a 1-0 Q fit but negative in a 0-1 Q fit [equations (5.9) and (5.10)]. Two 0-1 Q branch sequences, which satisfied the conditions just stated, could be assigned which "paired up" with the 1-0 Q sequences.

The separation of the 1-0 Q and 0-1 Q sub-band origins is $A' - \bar{B}' + A'' - \bar{B}''$ [equations (5.9) and (5.10)]. Assuming $\bar{B}'$ and $\bar{B}''$ are unchanged from their mainband values in any

vibrational level of HO_2 $^2\text{A}'$ and $^2\text{A}''$ respectively (the error introduced by this assumption is less than 1 % in any of the three fundamental modes of vibration of HNO $^1\text{A}''$ (37)), values of $\text{A}' + \text{A}''$ and the band origin are therefore obtained for these two hotband sequences [Table (6.3)]. The values of $\text{A}' + \text{A}''$ should be compared with the mainband value of 40.82 cm^{-1} . In either electronic state of HO_2 the A value is predicted to change little on exciting the O-O stretching vibration (001), to increase on exciting the bending vibration (010) and to decrease on exciting the O-H stretching vibration (100). [In HNO $^1\text{A}''$, A changes by -0.347 cm^{-1} in (001), $+1.896 \text{ cm}^{-1}$ in (010) and -1.453 cm^{-1} in (100) from the (000) value of 22.164 cm^{-1} (37).] Hence the hotband with origin 6916.67 cm^{-1} is assigned to the $^2\text{A}'(001) \rightarrow ^2\text{A}''(001)$ O-O stretching hotband, the one with origin 6924.22 cm^{-1} to the $^2\text{A}'(010) \rightarrow ^2\text{A}''(010)$ bending hotband. Using other workers' values for the vibrational frequencies of HO_2 $^2\text{A}''$ (38,39) [$\nu_1 = 3410$, $\nu_2 = 1390$ and $\nu_3 = 1097.6 \text{ cm}^{-1}$] I therefore obtain

$$\begin{aligned}\nu_2(^2\text{A}') &= 1285 \text{ cm}^{-1} \\ \nu_3(^2\text{A}') &= 984.8 \text{ cm}^{-1}\end{aligned}\tag{6.11}$$

The bending frequency of HO_2 $^2\text{A}'$ has not previously been reported in the literature. The O-O stretching frequency should be contrasted to Hunziker and Wendt's value from absorption spectroscopy of $\nu_3(^2\text{A}') = 925 \text{ cm}^{-1}$ (40); possible reasons for this serious discrepancy will be discussed in Chapter 7.

Table (6.3)

Molecular constants of HO_2 $^2\text{A}'(\nu_1 \nu_2 \nu_3) \rightarrow ^2\text{A}''(\nu_1 \nu_2 \nu_3)$ in cm^{-1}

Parameter	000 - 000	001 - 001	010 - 010	100 - 100
A''	20.357 ²	20.309 ³	----	----
B''	1.1179 ²	1.1072 (42)	1.1223 (27)	1.1198 (30)
C''	1.0565 ²	1.0350 (42)	1.0611 (27)	1.0588 (30)
A'	20.464 (4)	19.74 (22)	----	----
B'	1.0218(6)	1.0055 (42)	1.0253 (27)	1.0460 (30)
C'	0.9690(6)	0.9526 (42)	0.9727 (27)	0.9605 (30)
A'' + A'	(40.821) ⁵	(40.049) ⁵	43.90 (15)	38.96 (23)
Band origin	7029.48	6916.67	6924.22	6887.97
Vib. freq. $^2\text{A}''$	----	1097.6 ³	1390 ⁴	3410 ⁴
Vib. freq. $^2\text{A}'$	----	984.8	1285	3268.5

1. The numbers in parentheses represent
one standard error of the fit

2. Constrained; reference [32]

3. Constrained; reference [39]

4. Constrained; reference [38]

5. For reference only

Using as a first approximation combination differences of the 000-000 mainband for both lower and upper states, it was possible to assign other weaker transitions inside these two hotbands; 1-0 R, 1-0 P, 1-2 Q and 0-1 P lines could be assigned in both the hotbands. Upper state combination differences could therefore be formed inside $K' = 1$ of both ${}^2A'(001)$ and ${}^2A'(010)$; fitting them to the appropriate Polo formulae [by the method previously described for $K'' = 1$ of ${}^2A''(000)$] gave B' and C' for these two states. When these results were combined with the coefficients of $N(N+1)$ in the 1-0 Q and 0-1 Q fits, B'' and C'' were obtained for ${}^2A''(001)$ and ${}^2A''(010)$. All these constants are shown in Table (6.3). The values of B'' and C'' for ${}^2A''(001)$ agree well with the results obtained from a very recent laser magnetic resonance study of the ${}^2A''(000) \rightarrow {}^2A''(001)$ transition (39). Using Johns et al's value of A'' for ${}^2A''(001)$, I therefore obtain $A' = 19.74 \pm 0.22 \text{ cm}^{-1}$ for ${}^2A'(001)$. As in the main electronic band, emission is not observed from the high K levels of ${}^2A'(001)$ and ${}^2A'(010)$, so independent values of A' and A'' could not be determined in the bending hotband.

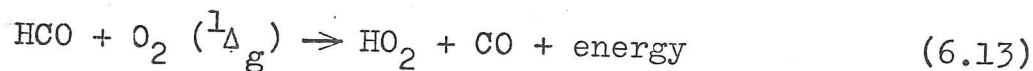
Finally, two more sequences of strong lines were found to even lower energy of the two hotbands already described. When fitted to a quadratic in $N(N+1)$ the line positions satisfied the criteria for 1-0 Q and 0-1 Q branches of another vibrational hotband of HO_2 ${}^2A' \rightarrow {}^2A''$. The separation of the sub-band origins gave an $A' + A''$ value of 38.96 cm^{-1} . This data is

consistent with a ${}^2A'(100) \rightarrow {}^2A''(100)$ O-H stretching hotband, since the A rotational constant in both electronic states is expected to decrease noticeably on exciting the O-H stretch. The band origin of this hotband is 6888 cm^{-1} ; using Paukert and Johnston's value for $\nu_1({}^2A'')$ (38) I therefore obtain

$$\nu_1({}^2A') = 3268.5\text{ cm}^{-1} \quad (6.12)$$

Utilising mainband combination differences for both upper and lower states, it was again possible to assign lines in other branches (1-0 P, 0-1 R and 0-1 P). The data was fitted in the manner described previously for the other two hotbands to give rotational constants for upper and lower states [Table (6.3)].

It is not immediately obvious how the ${}^2A'(100)$ level of HO_2 is populated in the $\text{O} + \text{O}_2({}^1\Delta_g) + \text{C}_2\text{H}_4$ reaction scheme. Energy transfer from $\text{O}_2({}^1\Delta_g)$ to ground state HO_2 [equation (6.10)] would only populate vibronic levels of $\text{HO}_2 \leq 8000\text{ cm}^{-1}$ above the ground state, whereas the ${}^2A'(100)$ level is $\sim 10,300\text{ cm}^{-1}$ above ${}^2A''(000)$. One possibility is the chemiluminescent reaction



This reaction is predicted to be $\sim 30\text{ kcal.mole}^{-1}$ exothermic (41), so vibrational levels of $\text{HO}_2({}^2A')$ up to $15,000\text{ cm}^{-1}$ above ${}^2A''(000)$ could energetically be populated by this mechanism; this would then explain the observed emission from ${}^2A'(100)$.

6.3 Analysis of the ${}^2A''(200) \rightarrow {}^2A''(000)$ overtone band of HO_2

Figure (6.3) shows a spectrum of the HO_2 ${}^2A''(200) \rightarrow {}^2A''(000)$ overtone band which is observed at 1.51 μm . Strongest HO_2 emission was now observed at a very small contact-to-observation time: the products of a microwave discharge in O_2 and C_2H_4 were mixed inside the integrating sphere. Under these conditions emission inside the ground electronic state of OH is very strong; lines of the $v' = 2 \rightarrow v'' = 0$ and $v' = 3 \rightarrow v'' = 1$ bands are clearly seen in the spectrum (marked x). Although these OH lines inevitably conceal information on the weaker HO_2 overtone band, they act as a very useful internal calibration of the HO_2 spectrum. Emission from HO_2 ${}^2A''(200)$ was noticeably reduced when contact-to-observation time was ~ 20 msec, the best condition for the ${}^2A' \rightarrow {}^2A''$ electronic spectrum.

As outlined previously, the overtone band of HO_2 is an A/B-hybrid band, the former having $\Delta K = 0$, the latter $\Delta K = \pm 1$ as their principal selection rules. Because $\bar{B} (= \frac{1}{2}(B + C))$ is not expected to differ appreciably in the two states (both being inside a common electronic state), the Q branches of the $\Delta K = 0$ emission appear as heads, now being assigned up to $K' = 4$. Although many lines are superimposed, the total intensity of each head is relatively weak; this can presumably be attributed to the rapid fall-off with increasing N of the Hönl-London intensity expression, whose value is $\frac{K^2}{N(N+1)}$ in the symmetric top approximation (42). These Q branch sub-band origins could be fitted to the expression

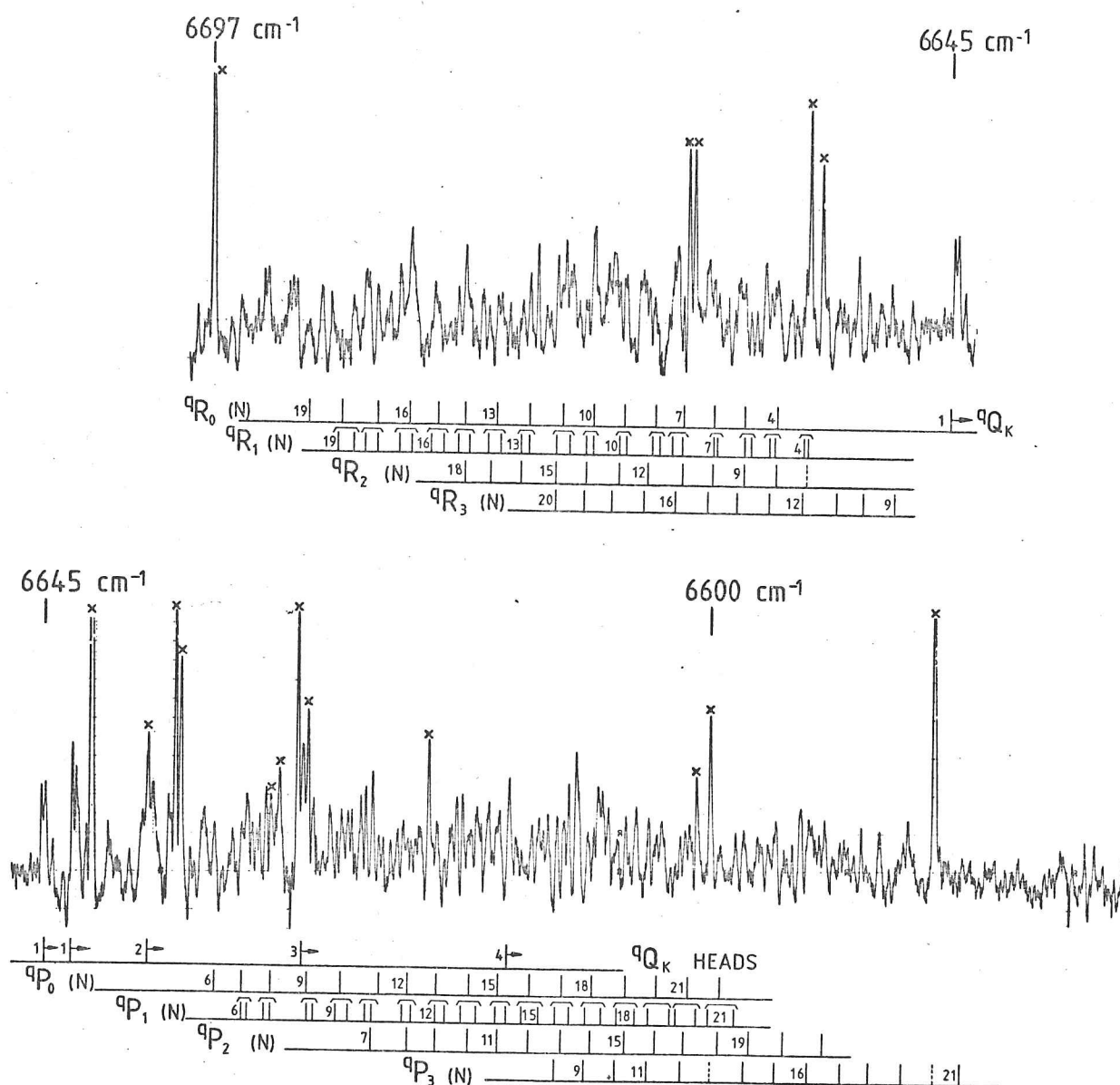


Figure 6.3 : High resolution spectrum of HO_2 $2A''(200) \rightarrow 2A''(000)$. Only A-type $\Delta K = 0$ transitions are shown. Notation used is $\Delta K_{\Delta N_K}(N)$. Lines marked x are due to OH emission.

$$\nu_{\text{sub-band}} = \nu^{00} + [(A' - \bar{B}') - (A'' - \bar{B}'')]K^2 \quad (6.14)$$

to give approximate values for the band origin ν^{00} and $(A' - A'')$. Using the former value, the R branch of the $K' = 0 \rightarrow K'' = 0$ sub-band ${}^qR_0(N)$ was assigned; ground state combination differences then helped to predict the ${}^qP_0(N)$ branch.

Using the approximate value for $(A' - A'')$, lines of the ${}^qR_1(N)$ branches could be assigned. These transitions are asymmetry split, linking the upper [lower] asymmetry component of $K' = 1$ with the upper [lower] component of $K'' = 1$. Ground state combination differences then predicted the two corresponding ${}^qP_1(N)$ branches. R and P branches of the $K' = 2 \rightarrow K'' = 2, 3 \rightarrow 3$ and $4 \rightarrow 4$ sub-bands could similarly be assigned, all lines of these three sub-bands being unsplit by asymmetry. Spin-splitting was not observed in the $\Delta K = 0$ sub-bands, presumably because the two vibronic states, being inside a common ${}^2A''$ electronic state, have very similar spin-splitting constants.

The predominant emission in this overtone band is thus seen to be of the $\Delta K = 0$ A-type; this is in obvious agreement with Hunziker and Wendt's low resolution absorption spectrum of this band (21). A few B-type transitions were, however, observed: lines in the $K' = 0 \rightarrow K'' = 1$ P, Q and R, $1 \rightarrow 0$ Q and $2 \rightarrow 1$ Q branches were assigned. (All these assignments are listed in Appendix 3 at the end of the Thesis.)

In obtaining accurate rotational constants for the upper state, knowledge of the ground state was again a great help.

As the emission is predominantly A-type, the majority of genuine upper state combination differences that can be formed are inside a common K sub-band; such differences will give no information on A' or D_K' . It was therefore necessary to construct combination differences of the form $K' = 1 \Rightarrow K' = 0$, $2 \Rightarrow 1$, $3 \Rightarrow 2$ and $4 \Rightarrow 3$, obtained by combining suitable assignments with absolute ground state energies (17). As emission is now observed up to $K' = 4$, it was possible to float D_K in the fit. The following constants for $\text{HO}_2^2\text{A}''(200)$ were then obtained:

$$A' = 18.212 \pm .011 \quad \text{cm}^{-1}$$

$$B' = 1.1170 \pm .0009 \quad \text{cm}^{-1}$$

$$C' = 1.0566 \pm .0009 \quad \text{cm}^{-1}$$

$$D_K' = 3.2 \pm .6 \times 10^{-3} \quad \text{cm}^{-1}$$

$$D_N' = 5.2 \pm 1.5 \times 10^{-6} \quad \text{cm}^{-1}$$

$$D_{NK}' = 1.2 \times 10^{-4} \quad \text{cm}^{-1} \quad (\text{constrained})$$

$$\nu^{00}[^2\text{A}''(200) \Rightarrow ^2\text{A}''(000)] = 6646.59 \pm .15 \text{ cm}^{-1}$$

(6.15)

CHAPTER 7

DISCUSSION OF THE RESULTS

The analysis of the near infra-red emission bands of HO_2 between 1.43 and 1.51 μm has yielded much new spectroscopic information on the $^2\text{A}'$ and $^2\text{A}''$ electronic states. Expected transitions have been the cause of most of this data. Unexpected phenomena, however, are always the most interesting results to spectroscopists. This analysis has posed three important problems:

(a) the presence of strong forbidden $\Delta K = 0$ lines in the $^2\text{A}' \rightarrow ^2\text{A}''$ C-type transition;

(b) a serious discrepancy in the value of $\nu_3 (^2\text{A}')$ with another result in the literature;

(c) an absence of emission from the high K levels of HO_2 $^2\text{A}'$.

These three points will be considered in turn.

7.1 The forbidden $\Delta K = 0$ lines

Since assigning forbidden $\Delta K = 0$ lines in the $^2\text{A}'(000) \rightarrow ^2\text{A}''(000)$ spectrum of HO_2 at 1.43 μm , it is encouraging to note that Becker et al also report strong

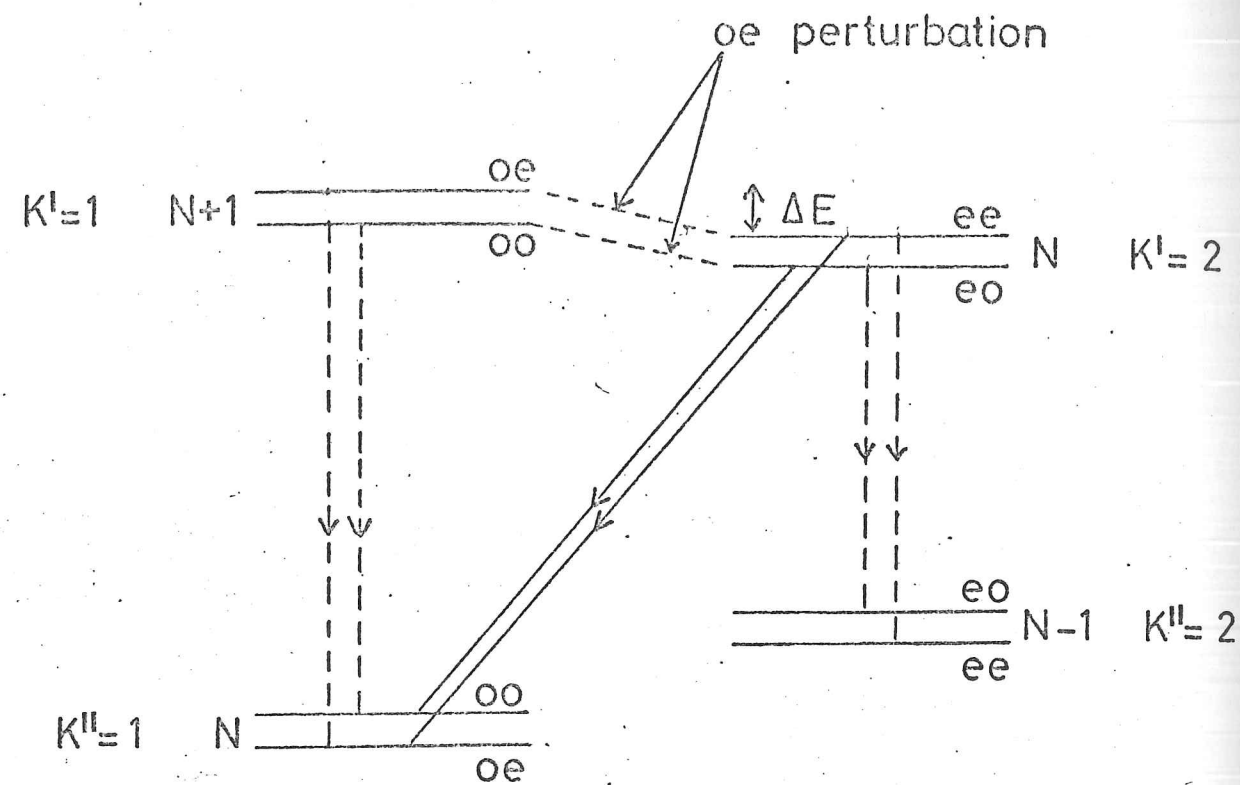


Figure 7.1 : Possible effects due to off-diagonal elements of the spin-rotation tensor on the selection rule on K in HO_2 $2A' \rightarrow 2A''$. Solid lines indicate C-type transitions (oe), the dotted lines forbidden $\Delta K = 0$ transitions (ee) introduced by the perturbation. The rotational quantum number N is assumed to be even, and spin-splitting has been ignored.

$\Delta K = 0$ emission in this same band (43). Since their earlier work (20) they have improved their experimental conditions such that they can now record the HO_2 emission bands at a resolution of 6 cm^{-1} (using a conventional slit monochromator). They found that the majority of their spectrum could be fitted to the expected $\Delta K = \pm 1$ structure of a C-type transition in HO_2 ; they could only computer-simulate intensities near the band centre, however, by assuming that in addition to $\Delta K = \pm 1$ strong $\Delta K = 0$ transitions were also occurring. They could not explain the presence of these forbidden transitions.

Axis-switching is one means of introducing $\Delta K = 0$ transitions into a $\Delta K = \pm 1$ perpendicular band system. This mechanism was considered in the previous Chapter and rejected as the predominant cause. Other possibilities will now be considered.

Although it has been assumed that off-diagonal elements of the spin-rotation tensor are zero, this may not be true for HO_2 $2A'$, since the ϵ_{aa} value, $+5.06 \text{ cm}^{-1}$, is so large in this state. Off-diagonal terms such as ϵ_{ab} and ϵ_{ba} will have matrix elements of $\Delta K = \pm 1$, $\Delta N = 0, \pm 1$, $\Delta J = 0$ in the spin-rotation Hamiltonian; they will, for example, mix $K' = 1$ levels of $2A'(000)$ with $K' = 0$ and 2 levels. By this means intensity is transferred from $\Delta K = \pm 1$ sub-bands to $\Delta K = 0$ and ± 2 . Such an effect would give rise to the observed ee transitions, since a C-type perturbation [oe] is mixed into a C-type transition [oe] to give forbidden ee transitions [Figure (7.1)]. This effect, however, would be very local in K' and N' , since such second-order perturbations would be

strongly dependent on the energy difference ΔE between the two interacting levels; this phenomenon was observed by Saito (18) in his microwave study of the ground state of HO_2 . Although there are some anomalous intensity effects in my $\Delta K = 0$ emission, it is doubtful whether this perturbation would give rise to such strong $\Delta K = 0$ lines as are observed; in addition, it does not explain their marked K dependence, i.e. $K' = 2 \rightarrow K'' = 2$ emission is much stronger than $1 \rightarrow 1$ emission. This mechanism is therefore rejected as the predominant cause of $\Delta K = 0$ emission in HO_2 ${}^2\text{A}'(000) \rightarrow {}^2\text{A}''(000)$.

A third possible explanation of these anomalous lines will now be considered. * Following Walsh's diagram for HAB molecules (19), the ground state of HO_2 is predicted to have electronic configuration

$$(a's_B)^2(a')^2(a')^2(a'')^2(a')^2(a's_A^*)^2(a''^*)^1 \quad {}^2\text{A}''$$

the first excited electronic state having

$$(a's_B)^2(a')^2(a')^2(a'')^2(a')^2(a's_A^*)^1(a''^*)^2 \quad {}^2\text{A}'$$

As both these states correlate with a ${}^2\Pi$ linear configuration

$$(\sigma_B)^2(\sigma)^2(\sigma)^2(\pi)^4(\pi^*)^3$$

* Many of the ideas which are now to be presented are due to Dr. P.A. Freedman, Department of Physical Chemistry, Cambridge. I am indebted to him for many fruitful and stimulating discussions.

a Renner-Teller A-type interaction is likely between vibronic components of the two Renner components ${}^2A'$ and ${}^2A''$.

[Such an interaction is caused by a coupling of electronic orbital angular momentum with rotation of the molecule about the a inertial axis. Two vibronic levels $\langle 1|$ and $|2\rangle$ may interact in this way if

$$\langle 1| \times |2\rangle \text{ contains } R_a \quad (7.1)$$

Using a III^R representation ($a \equiv x$), R_a transforms as A'' in C_s point group, so $\langle A'' | R_a | A' \rangle$ is totally symmetric.] The effect of this perturbation is to couple rotational levels of the same K_p and J but with K_0 differing by unity (i.e. an eo interaction), the interaction term being proportional to $2AK$ (44). (The selection rules given by Mills (44) for a Coriolis coupling of two vibrational levels are exactly the same as for a Renner-Teller coupling of two vibronic levels.)

Consider, therefore, such an interaction between HO_2 ${}^2A''(000)$ and ${}^2A'(000)$. Treating the effect as a simple first-order perturbation, $|{}^2A''(000)\rangle$ will take on some ${}^2A'$ character

$$\text{i.e.} \quad |{}^2A''(000)\rangle + \frac{2AK}{\Delta E} |{}^2A'(000)\rangle \quad (7.2)$$

Similarly $|{}^2A'(000)\rangle$ will take on some ${}^2A''$ character

$$\text{i.e.} \quad |{}^2A'(000)\rangle - \frac{2AK}{\Delta E} |{}^2A''(000)\rangle \quad (7.3)$$

ΔE is the energy difference (defined to be positive) between the interacting levels. There will, of course, be contributions from other vibronic terms. For the moment the problem is being simplified, and it is being assumed that the main contribution to ${}^2A''(000)$ [${}^2A'(000)$] will be from the lowest vibrational level of ${}^2A'$ [${}^2A''$], since this level gives the largest Franck-Condon overlap factor with the 000 [000] level of ${}^2A''$ [${}^2A'$]. The transition dipole moment in the α direction R^α ($\alpha = x, y$ or z) will, therefore, not simply be

$$\langle {}^2A''(000) | \mu_\alpha | {}^2A'(000) \rangle \quad (7.4)$$

but

$$\langle {}^2A''(000) + \frac{2AK}{\Delta E} {}^2A'(000) | \mu_\alpha | {}^2A'(000) - \frac{2AK}{\Delta E} {}^2A''(000) \rangle \quad (7.5)$$

Equation (7.5) could in principle give rise to non-zero transition dipole moments along all three x, y and z axes

$$R^z = \langle {}^2A''(000) | \mu_z | {}^2A'(000) \rangle \quad (7.6)$$

$$R^{x,y} = \frac{2AK}{\Delta E} \left[\langle {}^2A''(000) | \mu_{x,y} | {}^2A''(000) \rangle - \langle {}^2A'(000) | \mu_{x,y} | {}^2A'(000) \rangle \right] \quad (7.7)$$

R^z gives rise to the expected C-type transition with $\Delta K = \pm 1$ as the principal selection rule, $R^{x,y}$ to forbidden A and B-type transitions, $\Delta K = 0$ and ± 1 respectively as their principal selection rules. The first integral on the RHS of equation

(7.7) is, of course, the expectation value of the dipole moment of HO_2 $^2\text{A}''(000)$ along the x [y] axis, the second term being its value in $^2\text{A}'(000)$. Recent theoretical studies (45,46) predict a change in μ_x of ~ 0.3 Debye and approximately zero change in μ_y between these two electronic states of HO_2 ; Buenker and Peyerimhoff (45) also calculate the electronic transition dipole moment, R^Z , to be 0.03 Debye.

This large change in μ_x would then give rise to a transition dipole moment along the x axis, and hence $\Delta K = 0$ emission in the $^2\text{A}' \rightarrow ^2\text{A}''$ band of HO_2 . Since intensity is proportional to (transition dipole moment)², the relative intensities of $\Delta K = 0$ and ± 1 emission can be estimated:

$$\frac{\text{Intensity of } \Delta K = 0}{\text{Intensity of } \Delta K = \pm 1} = \left(\frac{R^x}{R^Z} \right)^2 \sim \left(\frac{2\Delta K}{\Delta E} \right)^2 \left(\frac{0.3}{0.03} \right)^2$$

$$\sim 10^{-2} \quad \text{for } K = 2 \quad (7.8)$$

The following points should be noted:

(a) This mechanism would produce much more intense $\Delta K = 0$ emission than either axis-switching or the off-diagonal elements of $\tilde{\epsilon}$ in $^2\text{A}'(000)$.

(b) The relative amount of $\Delta K = 0$ to $\Delta K = \pm 1$ emission is very sensitive to the values of the theoretical dipole moments

and the transition dipole moment R^Z . *

(c) Since the intensity of $\Delta K = 0$ emission is proportional to K^2 , this mechanism explains the strong K dependence of the observed $\Delta K = 0$ lines.

(d) The ee nature of the observed lines is also explained, since this mechanism mixes an A-type perturbation [eo] into an A-type transition [eo] to give forbidden ee transitions.

Although the neglect of interaction with other vibronic levels will alter the magnitude of the calculated $\Delta K = 0$ transition moment, this mechanism is believed to be the predominant reason for their presence. The other two routes may, of course, contribute to the observed intensity; unfortunately, not enough is known to assess the absolute magnitude of their contribution.

*

In a recent private communication, Dr. H.E. Hunziker has informed me that he has experimentally measured the allowed transition dipole moment R^Z to be half of Peyerimhoff's prediction. He also informs me that his colleagues McClean and Yoshimine ⁽⁴⁷⁾ have done a very high quality configuration interaction calculation for $(\mu_X'' - \mu_X')$, and obtain 0.37 Debye (which is larger than Peyerimhoff's value). Both these factors will, of course, enhance the relative amount of $\Delta K = 0$ to $\Delta K = \pm 1$ emission from the value of 10^{-2} given in equation (7.8); these numbers therefore help to explain my observation that the intensities of the forbidden $K' = 2 \rightarrow K'' = 2$ transitions are almost as strong as the allowed $2 \rightarrow 1$ transitions.

7.2 The discrepancy in ν_3 HO_2 ($^2\text{A}'$)

Knowledge that $\Delta K = 0$ transitions are present in the $^2\text{A}' \rightarrow ^2\text{A}''$ spectrum of HO_2 led to a reconsideration of possible reasons for the discrepancy in the value of ν_3 ($^2\text{A}'$).

As outlined in Chapter 5.1, Hunziker and Wendt have recorded near infra-red absorption bands of HO_2 between 0.5 and 2.2 μm (21,40) with a conventional slit monochromator; superior spectra have since been obtained at a spectral slit-width of 32 $\text{\AA}$ (48). They assigned the strongest bands at 1.43 μm and 1.26 μm to HO_2 $^2\text{A}'(000) \leftarrow ^2\text{A}''(000)$ and $^2\text{A}'(001) \leftarrow ^2\text{A}''(000)$, and measured from the maximum point on one spectrum to the maximum point on the other (48) to obtain a value for ν_3 ($^2\text{A}'$) of 925 cm^{-1} (40). This is in serious disagreement with my value of 984.8 cm^{-1} obtained from the $^2\text{A}'(001) \rightarrow ^2\text{A}''(001)$ hotband [equation (6.11)]. (The relative insensitivity of the germanium detector at low wavelength unfortunately prevented me from recording the 1.26 μm band in emission and checking this value.)

Hunziker and Wendt are clearly seeing absorption from high K levels of $^2\text{A}''(000)$ [Figure 2(a) of reference (21)]; substantial $\Delta K = 0$ transitions might therefore be expected in their 1.43 μm absorption band, since the intensity of these transitions is predicted to be proportional to K^2 [equation (7.8)]. To test this theory, a computer program was written to simulate the $^2\text{A}'(000) \leftarrow ^2\text{A}''(000)$ transition in HO_2 . *

* The original program, written by Dr. P.A. Freedman, was considerably modified for this purpose.

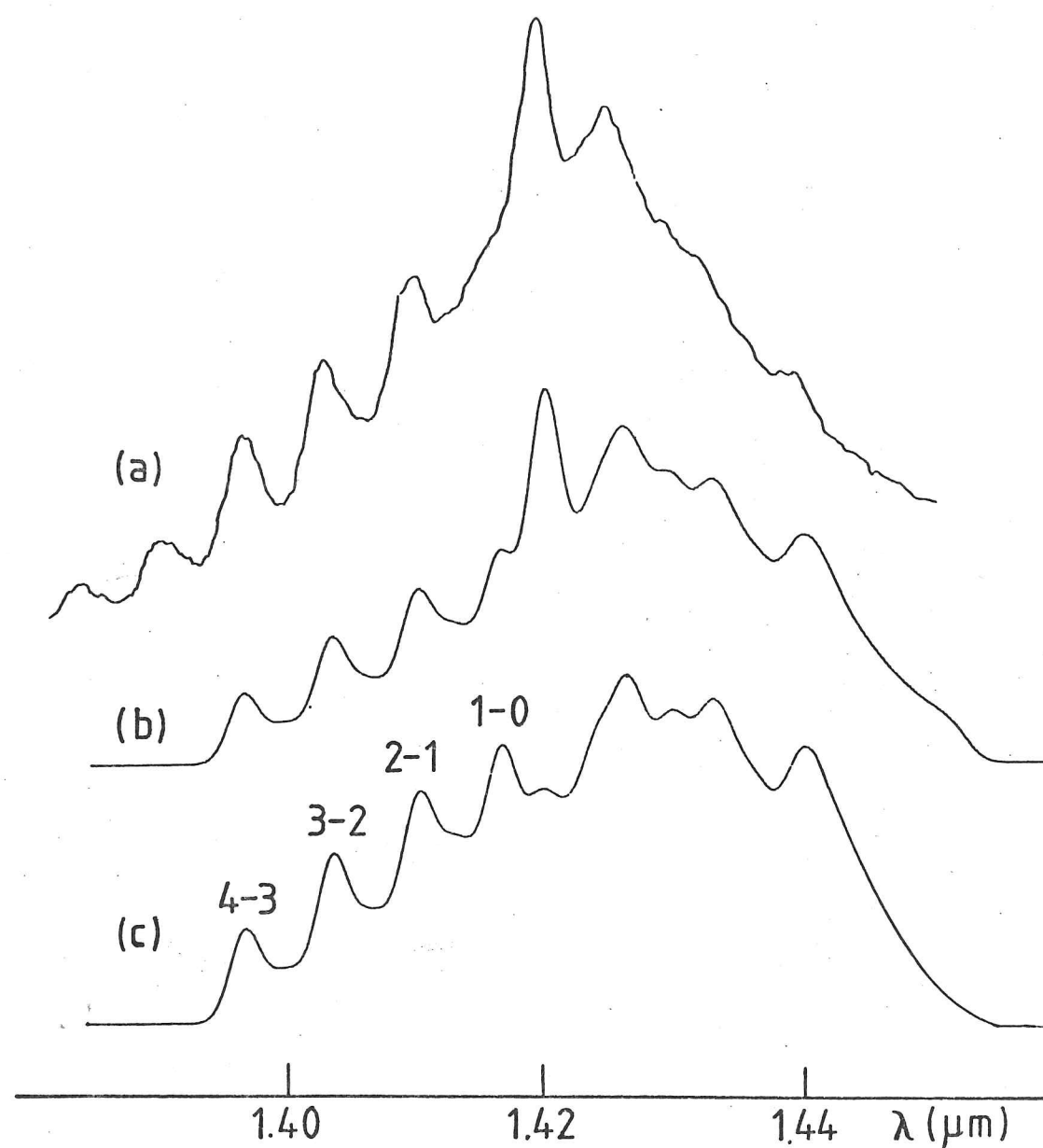


Figure 7.2 : The graphs are explained in the text.
The allowed $\Delta K = +1$ R heads are shown.

The spectrum was calculated using well-determined ground state constants ⁽¹⁷⁾ and upper state constants obtained from my analysis [equation (6.9)]; a Boltzmann population of the energy levels for a temperature of 298 K was assumed. The spectrum was then drawn by a plotting routine for a spectral resolution of 16 cm^{-1} ; this corresponds to the resolution of $32 \text{ \AA}$ at $1.43 \text{ }\mu\text{m}$ at which Hunziker recorded his most recent spectrum ⁽⁴⁸⁾ [Figure 7.2(a)].* If allowance was made for $\Delta K = \pm 1$ transitions only, the simulated spectrum [Figure 7.2(c)] matched Hunziker's observed spectrum very well except for the absence of a strong peak near the band centre. A good agreement was only obtained when, in addition to $\Delta K = \pm 1$, $\Delta K = 0$ transitions were considered, the anomalous peak obviously being due to the $\Delta K = 0$ R heads. The intensity of any $\Delta K = 0$ transition was written in the program as

$$\frac{I_{K N''}}{I_{K N'}} = \xi K^2 \left[S_{\text{HL}} \cdot \text{Boltzmann factor} \right] \quad (7.9)$$

where S_{HL} is the appropriate Hönl-London factor for a parallel band transition. The best simulation [Figure 7.2(b)] with the observed spectrum was obtained for

$$\xi = 0.05 \quad (7.10)$$

Computer simulation of the ${}^2A'(001) \leftarrow {}^2A''(000)$ band at $1.26 \text{ }\mu\text{m}$ yielded agreement with Hunziker's most recent spectrum of this band ⁽⁴⁸⁾ for a much lower value of ξ ,

* I am most grateful to Dr. H.E. Hunziker for his permission to show this spectrum.

i.e. $\Delta K = 0$ is greatly reduced in this band. [This, incidentally, seems to disagree with the recent work of Becker et al (43). Their emission spectrum, however, unlike the absorption one, is overlapped by $O_2 \ ^1\Delta_g \Rightarrow \ ^3\Sigma_g^-$ transitions, so their observation of $\Delta K = 0$ must be less certain.]

This observation that the amount of $\Delta K = 0$ has a strong vibrational dependence could tie in nicely with the suggested vibronic coupling mechanism for the following reason.

Consider the $^2A'(001) \Leftrightarrow ^2A''(000)$ transition at 1.26 μm . Assuming that the main contribution to $^2A''(000)$ [$^2A'(001)$] is from the 000 [001] level of $^2A'$ [$^2A''$], the transition dipole in the α direction will not simply be

$$\langle ^2A''(000) | \mu_\alpha | ^2A'(001) \rangle \quad (7.11)$$

but

$$\langle ^2A''(000) + \frac{2AK}{\Delta E} ^2A'(000) | \mu_\alpha | ^2A'(001) - \frac{2AK}{\Delta E} ^2A''(001) \rangle \quad (7.12)$$

The transition dipole along the x direction (giving rise to $\Delta K = 0$ emission) is therefore

$$R^x = \frac{2AK}{\Delta E} \left[\langle ^2A'(000) | \mu_x | ^2A'(001) \rangle - \langle ^2A''(000) | \mu_x | ^2A''(001) \rangle \right] \quad (7.13)$$

Each integral on the RHS of equation (7.13) is a vibrational transition dipole moment, typically one or two orders of

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Each integral on the RHS of equation (7.13) is a vibrational transition dipole moment, typically one or two orders of

magnitude smaller than the expectation value of a dipole moment (each integral on the RHS of equation (7.7)). This mechanism therefore predicts $\Delta K = 0$ transitions to be much weaker in ${}^2A'(001) \leftarrow {}^2A''(000)$ than in ${}^2A'(000) \leftarrow {}^2A''(000)$.

Again it is appreciated that this is a vastly oversimplified treatment; there will be several vibrational levels of ${}^2A'$ [${}^2A''$] contributing to ${}^2A''(000)$ [${}^2A'(001)$]. If one tries to allow for all such terms, there rapidly become too many unknowns to solve the problem. All that can be said is that it would be very surprising if the amount of $\Delta K = 0$ did not show a marked vibrational dependence.

It is therefore suggested that an accurate value for ν_3 (${}^2A'$) cannot be obtained by measuring the separation of the peak of the 1.43 μm spectrum to the peak of the 1.26 μm spectrum, since $\Delta K = 0$ is considerably disturbing the intensity near the band centre of the former band. If the separation of equivalent $\Delta K = \pm 1$ R heads on Hunziker's spectra is measured instead, values between 965 and 985 cm^{-1} are obtained for ν_3' , results which agree most favourably with my value of 984.8 cm^{-1} . *

* Dr. Hunziker has recently informed me that he is quite happy with this explanation, and he now realises that this part of his initial analysis of these spectra was in error.

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* Dr. Hunziker has recently informed me that he is quite happy with this explanation, and he now realises that this part of his initial analysis of these spectra was in error.

7.3 The absence of emission from the high K levels of $\text{HO}_2^2\text{A}'$

The absence of emission from $K' > 2$ of $\text{HO}_2^2\text{A}'(000)$ is a very surprising phenomenon. There would appear to be three possible explanations: an instrumental cut-off, a failure to populate these levels in the reaction, or their subsequent removal by competing non-radiative processes.

An instrumental cut-off for $\lambda < 1.41 \mu\text{m}$ (due, for example, to a faulty detector) can immediately be rejected, since emission at wavelengths less than $1.41 \mu\text{m}$ is observed from high K levels of DO_2 in the corresponding $^2\text{A}'(000) \rightarrow ^2\text{A}''(000)$ spectrum [see Chapter 8].

For the three different reaction systems $\text{O} + \text{C}_2\text{H}_4$, $\text{O} + \text{NH}_3$ and $\text{O} + \text{CH}_3\text{OH}$ used to generate $\text{HO}_2^2\text{A}'$, this cut-off in emission was always apparent over a wide range of pressures, both in high and low resolution: the cut-off in all chopped spectra for $\lambda < 1.41 \mu\text{m}$ was especially clear. This initially suggested, therefore, that the high K levels were never populated in the reaction. In their recent experiments, however, Becker et al observed emission from many K levels of $\text{HO}_2^2\text{A}'(000)$ in the $\text{O} + \text{O}_2(^1\Delta_g) + \text{C}_2\text{H}_4$ reaction scheme (43). Although our means of producing excited state HO_2 are the same, Becker et al observed their emission ~ 300 msec downstream of the mixing point (49), whereas our emission was observed almost instantaneously after mixing. These observations suggest that the emitting state $^2\text{A}'(000)$ is initially generated in low K levels only; a rotational equilibration

then occurs so that emission is observed from the high K levels at long contact-to-observation times.

A predissociation mechanism for the removal of these high K levels can be discarded for two reasons. First, this process would not account for the difference in the spectra at long and short contact times. Secondly, the energy of HO_2 $^2\text{A}'(000)$ $K' = 3$ ($\sim 7200 \text{ cm}^{-1}$ above $^2\text{A}''(000)$) would have to be near the dissociation energy of the molecule: yet Foner and Hudson ⁽¹⁴⁾ obtain $16,200 \pm 700 \text{ cm}^{-1}$ for the H-OO energy of dissociation, the HO-O dissociation energy being even higher. In other words, the energy of $^2\text{A}'(000)$ $K' = 3$ is well below the dissociation limit of the molecule, so predissociation cannot account for the removal of the high K levels of HO_2 $^2\text{A}'$.

The most satisfactory explanation of these experimental observations assumes another Renner-Teller A-type interaction between high vibrational levels of $^2\text{A}''$ and the initially populated state of $^2\text{A}'$ (assumed to be many vibrational quanta above $^2\text{A}'(000)$). Since the magnitude of the interaction term is proportional to K^2 , the wavefunctions of high K levels of any two interacting vibronic states are mixed to a greater extent than those of low K. At the relatively high energy at which it is assumed that $^2\text{A}'$ is generated, the density of vibrational states of $^2\text{A}''$ is much greater than the density of $^2\text{A}'$ states, so the rate of cascade down the A'' vibrational ladder is much greater than down the A' ladder. The higher K levels of $^2\text{A}'$ thus cross over to $^2\text{A}''$ and are "sucked" down

the ground state ladder much more rapidly than are the low K levels of $^2A'$. Hence only low K levels of the bottom vibrational levels of $^2A'$ are initially populated.

If the $^2A' \rightarrow ^2A''$ emission is therefore observed at short or even zero contact-to-observation times, there is no time for rotational equilibration of the upper state to occur, and emission is not observed from the high K levels of $^2A'$. If, on the other hand, the emission is observed at a long contact time, rotational equilibration now has time to occur; emission is therefore observed from all K levels of $^2A'(000)$, their relative populations only being dependent on the temperature of the source.

CHAPTER 8

ANALYSIS OF THE NEAR INFRA-RED EMISSION BAND OF DO_2 :
DETERMINATION OF THE MOLECULAR GEOMETRY8.1 Introduction

In the last two Chapters, an analysis of the near infra-red emission bands of HO_2 was presented. Besides deriving many new molecular constants of the radical, some unexpected phenomena were observed; strong forbidden $\Delta K = 0$ transitions were present in the ${}^2\text{A}'(000) \rightarrow {}^2\text{A}''(000)$ band. Axis-switching is one means of introducing $\Delta K = 0$ transitions into a $\Delta K = \pm 1$ C-type electronic band system; this mechanism depends, however, on a substantial change in bond angle between the two electronic states. An accurate geometry of HO_2 , besides being very useful information, is needed to clarify this point. Such information can only be obtained using molecular constants of an isotopic species. The ${}^2\text{A}' \rightarrow {}^2\text{A}''$ spectrum of DO_2 was therefore recorded at high resolution with the SISAM spectrometer. This Chapter presents the analysis and results.

8.2 Experimental conditions

The experimental conditions were very similar to those used in the HO_2 work. Excited state DO_2 was formed in the

discharge flow system by the reaction of $O/O_2(^1\Delta_g)$ with CD_3OD at a total pressure of 3.5 Torr. [Unlike the relatively cheap cost of C_2H_4 and NH_3 , C_2D_4 and ND_3 are prohibitively expensive: it was not therefore feasible to form DO_2 by their reactions with discharged O_2 .] The gases were mixed inside the integrating sphere, so contact-to-observation time was effectively zero.

As there is no overlapping from OD emission between 1.4 and 1.5 μm , an alternative calibration of the DO_2 spectrum had to be found. This was performed by recording visible lines from the Fe/Ne hollow cathode lamp and infra-red etalon fringes simultaneously with the emission spectrum. A fuller description of this method of calibration can be found in Chapter 3.3.2.

8.3 Analysis of the $^2A'(000) \rightarrow ^2A''(000)$ band of DO_2

The high resolution spectrum of this band is shown in Figure (8.1); the assignments are given in Appendix 4 at the end of the Thesis. Although the spectrum is very similar in outline and appearance to that in HO_2 , two factors made the DO_2 analysis, in many ways, more difficult.

(a) Ground state constants were not available. Beers and Howard (25) have recently observed a few microwave transitions inside $K = 0$ of DO_2 $^2A''(000)$, and hence established $(B + C)$ for this state; this, however, was the only available starting information on DO_2 .

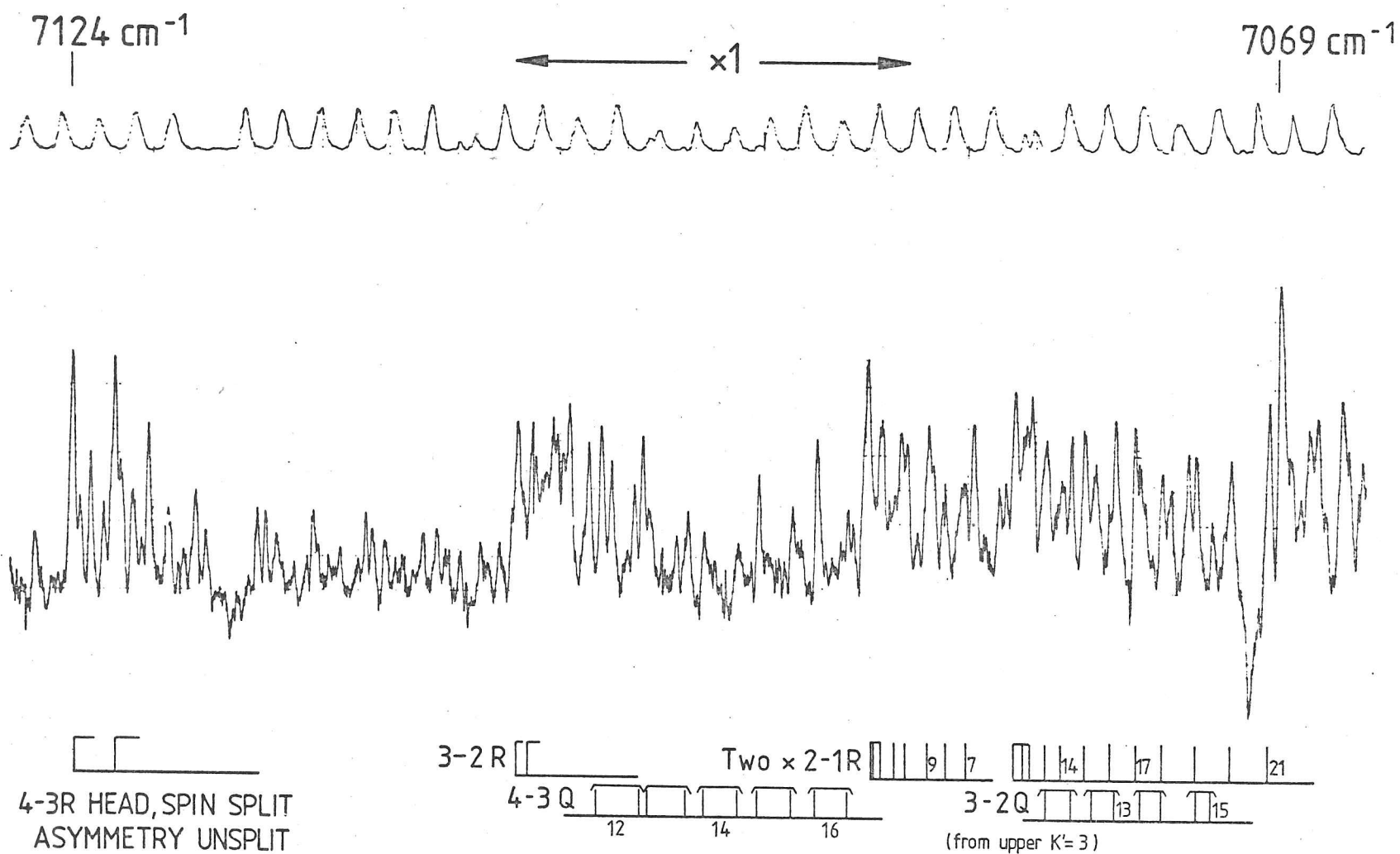


Figure 8.1 : High resolution spectrum of DO_2 $2\text{A}'(000) \rightarrow 2\text{A}''(000)$: region of the high K levels.
Some assignments are shown.

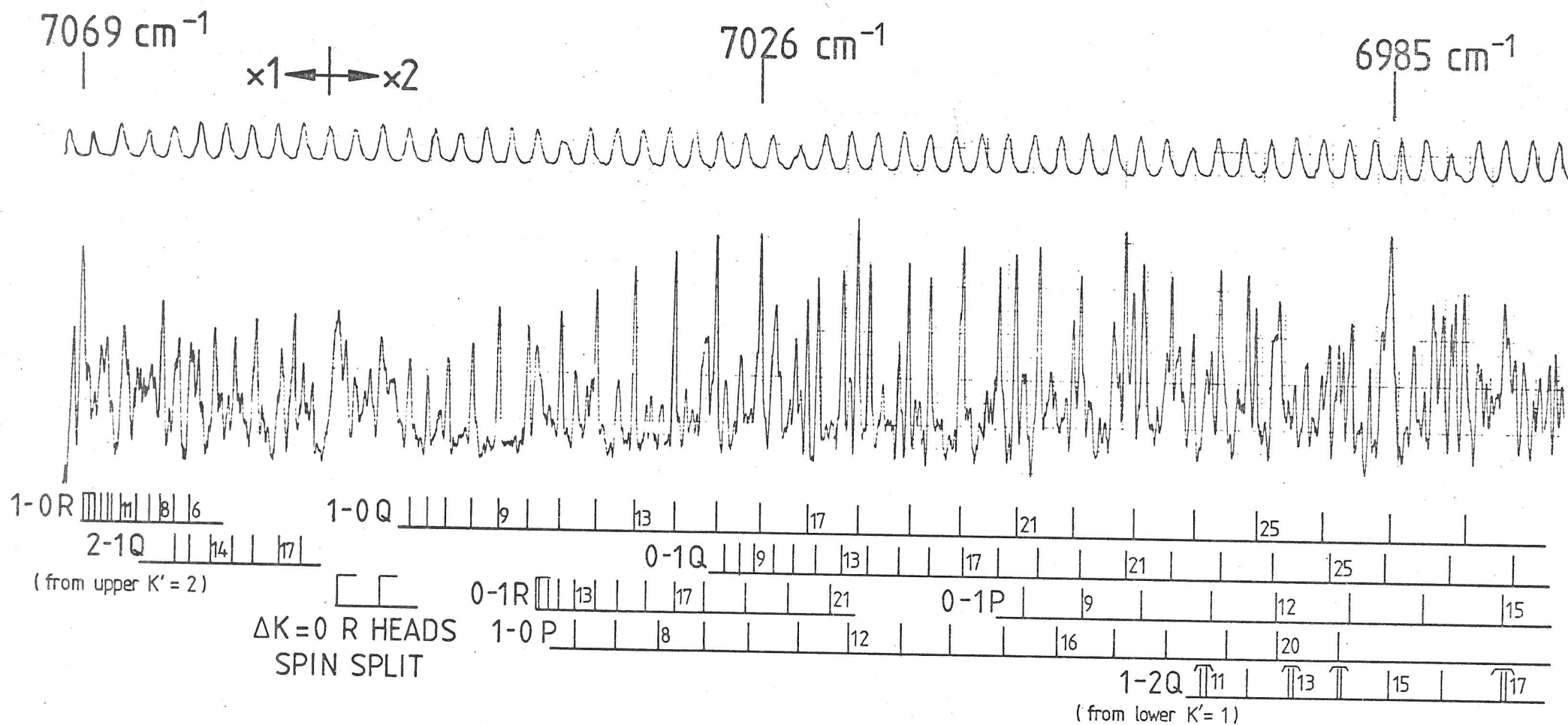


Figure 8.1 : continued. DO_2 $2\text{A}'(000) \rightarrow 2\text{A}''(000)$:
the central region of the band. Some
assignments are shown. The etalon fringes
calibrate the spectrum (see text).

(b) As DO_2 has greater asymmetry than HO_2 in both electronic states, great care has to be taken when using Polo's formulae for the rotational energy levels of DO_2 . In particular, they introduce serious error at low K and high N , the quantum numbers where, in fact, the strongest transitions are observed. When evaluating trial energy levels of the molecule, therefore, a full diagonalisation procedure was employed.

The two strong series of lines, assigned to the $K' = 1 \rightarrow K'' = 0$ Q and $0 \rightarrow 1$ Q branches, were readily observed in the spectrum. Establishing the rotational numbering of each branch was, however, much more difficult: P and R branch lines had to be found. Not surprisingly, this involved a certain amount of trial and error: some rotational constants were assumed, and the energies of the P and R lines evaluated for a particular rotational numbering of the Q branch. The positions of the observed 1-0 and 0-1 R heads at 7069.5 and 7040.0 cm^{-1} helped to determine the final numberings of these two Q branches.

Once this was established, the assignment of the high frequency region of the spectrum (i.e. the region of the high K levels) proved to be comparatively simple. The R heads of the 4-3, 3-2 and 2-1 sub-bands are readily seen; the first two are spin-split and unsplit by asymmetry, whereas the 2-1 heads are spin-unsplit (unlike HO_2) but noticeably split by asymmetry. Lines in the 4-3 Q, 3-2 Q and 2-1 Q branches could also be assigned. All such transitions helped to establish accurate molecular constants for the upper state.

The $\Delta K = -1$ transitions occur in the central region of the band, so their assignments were more difficult due to the severe problems of blending. Some assignments could, however, be made in the 1-2 and 2-3 sub-bands. Assuming, initially, that the ground state ϵ_{aa} was approximately half its value in HO_2 , some of the lines of the 1-2 Q and all the lines of the 2-3 Q branches were assigned as spin-split doublets. (The predicted splitting of the 1-2 lines is only slightly greater than the instrumental resolution at high N; bearing in mind the high density of lines, it is perhaps not surprising that only some of the splittings in this branch are resolved.) All such transitions helped to establish accurate ground state constants.

As in HO_2 , forbidden $\Delta K = 0$ transitions are observed in the spectrum of DO_2 ; the R heads are especially clear around 7051 cm^{-1} . Their mere presence does not, of course, suggest a particular mechanism for their existence. The observed heads do, however, show a pronounced spin-splitting [Figure (8.1)] which is compatible with the expected splitting of a $K' = 4 \rightarrow K'' = 4$ transition (see next section); that is, the DO_2 $\Delta K = 0$ transitions, like HO_2 , are showing a strong K dependence. We will return to this point later in the Chapter.

8.3.1 Evaluation of spin-splitting constants

The spin-split doublets observed in DO_2 have contributions from the ground and excited state splittings. In evaluating

ground state constants, the observation that the $2 \rightarrow 1$ sub-band is not spin-split is of considerable importance, since it strongly suggests that the absolute splitting of $K' \leq 2$ is less than the instrumental resolution. To this degree of approximation, therefore, the observed splittings of the $1 \rightarrow 2$ and $2 \rightarrow 3$ Q branches and the ground state splittings of $K'' = 2$ and $K'' = 3$ are synonymous. These splittings could then be fitted to equation (5.12) to yield ground state spin-splitting constants [Table (8.1)].

The upper state constants could be evaluated from the observed splittings of the $4 \rightarrow 3$ and $3 \rightarrow 2$ sub-bands. As the ground state contribution could now be evaluated, it was soon apparent that the magnitude of the observed splittings was greater than the magnitude of the ground state contribution. In other words, the sign of δ [equation (5.11)] is different in the two electronic states; the observed splitting is therefore the sum, as distinct from the difference (as in HO_2), of the two individual splittings. Absolute upper state splittings, both magnitude and sign, could now be evaluated; fitting them to the appropriate formula yielded upper state spin-splitting constants [Table (8.1)].

It should be noted, not only that the signs of ϵ_{aa} in the two electronic states are again different, but also that their magnitudes are approximately half their magnitudes in HO_2 . This is good evidence to support the theory that the main contribution to ϵ_{aa} arises from a second order mixing of electronic states, mainly by spin-orbit coupling (30);

Table (8.1)

Molecular constants for DO_2 in cm^{-1}

Parameter	$^2A''(000)$	$^2A'(000)$
A	11.166 (4)	11.147 (7)
B	1.0564 (3)	0.9700 (3)
C	0.9616 (3)	0.8873 (3)
D_K	$2.1 \times 10^{-3} \quad ^2$	$7.3 (5) \times 10^{-3}$
D_{NK}	$1.2 \times 10^{-4} \quad ^2$	$1.2 \times 10^{-4} \quad ^2$
D_N	$3.5 \times 10^{-6} \quad ^2$	$3.5 \times 10^{-6} \quad ^2$
ϵ_{aa}	-0.87 (6)	+2.46 (7)
$\frac{1}{2} (\epsilon_{bb} + \epsilon_{cc})$	-0.006 ³	-0.006 ³
ν^{00}	7041.10 (10)	

1. The numbers in parentheses represent one standard error of the fit.
2. Parameter constrained to this value.
3. Parameter constrained to this value from reference [25].

such a mechanism would predict ϵ_{aa} to be proportional to the A rotational constant, whose value in DO_2 is approximately half its value in HO_2 .

8.3.2 Evaluation of the rotational constants

As mentioned earlier, the ground state of DO_2 has not yet been accurately established by other techniques (e.g. LMR, microwave or EPR), although this situation will probably be remedied in the very near future. In the absence of such information, the ideal way to fit the electronic spectrum would be to perform a simultaneous two-state fit to all the assignments. Knowing, however, that other groups would almost certainly soon establish the ground state much more accurately than I could hope for at my resolution, I decided that the time spent in writing a two-state fitting program would not justify the end product. Each state of DO_2 was therefore fitted independently.

Combination differences inside the ground state were constructed. Those inside a common K sub-band (i.e. those involving a change in N) will help to fit B, C and D_N , whereas those involving a change in K will fit A and D_K . As few combination differences could be formed which involved a change in N at high N, D_N was not well-determined when its value was floated; it was therefore constrained in the final fit to a sensible value (slightly less than the well-determined HO_2 value (32)). Likewise, it was necessary to

constrain D_K and D_{NK} , since not enough confident assignments at high K values could be found. The results of the final fit are shown in Table (8.1). These constants will, no doubt, be improved before long by other workers; they were quite satisfactory, however, for determining an accurate geometry for the ground state of HO_2 .

To fit the upper state, combination differences inside this state were similarly formed. In order to use the information available from the high K level transitions, constructed as well as genuine combination differences were used in this fit; the former were obtained by combining suitable assignments with ground state energies evaluated from the ground state fit. [I realise that this method of analysis is slightly unsatisfactory, since any error in the ground state constants is being carried into the upper state fit; I feel it is justified to proceed in this manner, however, since transitions from high K' levels (which could otherwise not be used in a genuine upper state fit) will help to determine A' and D_K' with great accuracy.] The results of this upper state fit are likewise shown in Table (8.1).

It should be noted that, as in HO_2 , the A rotational constant is effectively unchanged between the two electronic states of DO_2 : this again suggests a small change in bond angle between the two states.

8.4 Determination of the molecular geometry of HO₂

As rotational constants (and hence moments of inertia) are now known for both states of HO₂ and DO₂, an accurate geometry can be determined for each state. Gordy and Cook (50) showed how the moments of inertia of a bent XYZ molecule could be related to the geometric parameters. Due to the effects of zero point energy, slightly different geometries will be obtained if different combinations of rotational constants are used. For each electronic state, only the A and B constants of HO₂ and DO₂ (i.e. four variables) have been used to fit the geometry (two bond lengths and a bond angle), since any Coriolis coupling between vibrational levels of a common electronic state will be C-type and hence perturb the C rotational constant; a non-linear least squares fitting program was written for this purpose. The results obtained are shown in Table (8.2).

It is seen that, not only is the change in bond angle between the two electronic states small (as suspected), but also that it actually decreases from ground to excited state. This is in sharp contrast to the A' $\leftrightarrow$ A'' transition in similar triatomics (e.g. HCO (33), HNO (34) and HNF (31)) where the excited state bond angle is always greater than the ground state. In addition, HO₂ would seem to be one of the very few molecules violating Walsh's simple, but generally effective rules (19). It is interesting to note that this very small change in bond angle is compatible with Hunziker's observation (40) that no progression is observed in

Table (8.2)

Molecular geometry of HO₂

Parameter	² A'' (000)	² A' (000)
r _{O-H}	0.9754 (21)	0.9654 (11)
r _{O-O}	1.3291 (6)	1.3933 (3)
θ	104.02 (24)	102.69 (12)

1. Bond lengths in Angstrom units, bond angles in degrees.
The numbers in parentheses represent one standard error of the fit.

absorption from the ground state of HO_2 to the $^2\text{A}'(0\nu_2 0)$ levels; the relatively large change in O-O bond length [Table (8.2)], however, would presumably explain the strong progression to the $^2\text{A}'(00\nu_3)$ ladder (40).

8.5 Concluding remarks

The most interesting phenomenon observed in this HO_2 and DO_2 work is undoubtedly the presence of forbidden $\Delta K = 0$ transitions. As the change in bond angle between the two electronic states is so small, axis-switching is rejected as the predominant mechanism for their presence; a vibronic coupling mechanism, described in detail in Chapter 7, is favoured instead. A similar kind of coupling has been observed by Jungen et al (51) in the near ultra-violet absorption spectrum of CS_2^* ; interaction between the two Renner components of the excited state (also showing a K^2 dependence) results in transitions being observed from the ground state to both components, even though one transition would be forbidden in the absence of such an interaction. To the best of my knowledge, however, HO_2 is the first example of forbidden transitions being observed between the two Renner components due to Renner-Teller interaction. The

* I would like to thank Dr. Ch. Jungen for drawing my attention to this work.

relatively small separation of the two electronic states (only 7000 cm^{-1}) is undoubtedly a factor contributing to their existence. It is interesting to speculate whether such transitions would be observed in similar free radicals, were they to emit in this region.

CHAPTER 9

CONCLUSIONS AND FUTURE WORK

This Thesis has been concerned with the two quite separate aspects of molecular spectroscopy. The first few Chapters were concerned with instrumentation, or more specifically the development of a high sensitivity, high resolution SISAM spectrometer; the second half of the Thesis has reported results obtained with it on the HO_2 and DO_2 free radicals. These spectra have emphasised that the SISAM is now working at its full potential. The question must be asked - To what use will this potential be put in the future?

The region of the near infra-red where the SISAM is now operating ($1 - 2.5 \mu\text{m}$) could prove a very rewarding one for the study of high-lying electronic states of simple molecules and radicals. The density of electronic states is greater the higher the excitation of the molecule, and hence the number of possible transitions to other states only $4,000 - 10,000 \text{ cm}^{-1}$ away is larger. [It is perhaps worth mentioning that HO_2 and O_2 are relatively rare species, in that their lowest-lying electronic state is only $7,000 - 8,000 \text{ cm}^{-1}$ above the ground state.] Emission from these highly excited states will only be observed from the discharged region itself, since electronic relaxation tends to be fast. Comprehensive spectra have, in fact, recently been obtained

of transitions between Rydberg states of NO, the source being a 3 kV, 100 mA d.c. discharge in flowing NO gas; analyses of these spectra are now in progress. It is perhaps unfortunate that NO was initially chosen, since many of its Rydberg states have already been characterised by Miescher and his co-workers (52), but such spectra could be pointing a way to the future; it is hoped to commence a study of these states of the isoelectronic species O_2^+ (using a hollow cathode discharge in flowing oxygen) very soon.

Having exhausted the near infra-red, it will then be a natural progression to extend the range of the spectrometer to the infra-red proper. [Extending the other way into the visible would probably not be so rewarding, since then the SISAM would be competing with the whole field of photographic plates which are especially sensitive in this region.] This will involve changing the beam splitter and the diffraction gratings so that they can operate at longer wavelength. Components which will work up to 6 μm have in fact been obtained and tested, and are quite literally waiting to be put into the spectrometer. It should then be possible to detect very weak vibrational transitions in interesting free radicals (e.g. HO_2 , HCO , HNO , HSO). Relatively little work has been done on the study of vibration-rotation spectra of short-lived species in the 2.5 - 5 μm region, so the potential of this instrument could be very great.

It is quite possible that the combination of high sensitivity and high resolution, together with its large spectral range, may make the SISAM spectrometer one of the

most useful tools for the study of simple molecules and radicals.

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APPENDICES

1. Assignments of $\text{HO}_2 \ ^2\text{A}' \rightarrow \ ^2\text{A}''$
2. Upper state combination differences
inside $\text{HO}_2 \ ^2\text{A}'(000)$
3. Assignments of $\text{HO}_2 \ ^2\text{A}''(200) \rightarrow \ ^2\text{A}''(000)$
4. Assignments of $\text{DO}_2 \ ^2\text{A}'(000) \rightarrow \ ^2\text{A}''(000)$

(Figures for all assignments in cm^{-1})

APPENDIX 1

Assignments of HO_2 $^2\text{A}' \rightarrow ^2\text{A}''$

H02 ELECTRONIC BAND 000-000

J	KP	KO	J	KP	KO	NU(CM-1)
4	0	4	4	1	4	7008.975
						7008.515
5	0	5	5	1	5	7008.129
						7007.699
6	0	6	6	1	6	7007.121
						7006.824
7	0	7	7	1	7	7006.053
						7005.757
8	0	8	8	1	8	7004.779
						7004.512
9	0	9	9	1	9	7003.298
						7001.581
10	0	10	10	1	10	6999.924
						6999.924
11	0	11	11	1	11	6998.09
						6996.080
12	0	12	12	1	12	6993.924
						6991.548
13	0	13	13	1	13	6989.012
						6986.272
14	0	14	14	1	14	6983.475
						6980.49
15	0	15	15	1	15	6977.302
						6970.380
16	0	16	16	1	16	6966.749
						6962.874
17	0	17	17	1	17	6958.698
						6954.425
18	0	18	18	1	18	6950.114
						6945.432
19	0	19	19	1	19	7020.523
						7020.226
20	0	20	20	1	20	7019.958
						7019.704
21	0	21	21	1	21	7019.273
						7019.035
22	0	22	22	1	22	7018.201
						7017.294
23	0	23	23	1	23	7016.059
						7014.409
24	0	24	24	1	24	7012.507
						7010.518
25	0	25	25	1	25	7008.515
						7006.053
26	0	26	26	1	26	7003.298
						7000.338
27	0	27	27	1	27	6997.188
						6993.673
28	0	28	28	1	28	6989.867
						6980.486
29	0	29	29	1	29	6977.302
						6966.053
30	0	30	30	1	30	6954.425
						6945.432
31	0	31	31	1	31	7020.523
						7020.226
32	0	32	32	1	32	7019.958
						7019.704
33	0	33	33	1	33	7019.273
						7019.035
34	0	34	34	1	34	7018.201
						7017.294
35	0	35	35	1	35	7016.059
						7014.409
36	0	36	36	1	36	7012.507
						7010.518
37	0	37	37	1	37	7008.515
						7006.053
38	0	38	38	1	38	7003.298
						7000.338
39	0	39	39	1	39	6997.188
						6993.673
40	0	40	40	1	40	6989.867
						6980.486
41	0	41	41	1	41	6977.302
						6966.053
42	0	42	42	1	42	6954.425
						6945.432
43	0	43	43	1	43	7020.523
						7020.226
44	0	44	44	1	44	7019.958
						7019.704
45	0	45	45	1	45	7019.273
						7019.035
46	0	46	46	1	46	7018.201
						7017.294
47	0	47	47	1	47	7016.059
						7014.409
48	0	48	48	1	48	7012.507
						7010.518
49	0	49	49	1	49	7008.515
						7006.053
50	0	50	50	1	50	7003.298
						7000.338
51	0	51	51	1	51	6997.188
						6993.673
52	0	52	52	1	52	6989.867
						6980.486
53	0	53	53	1	53	6977.302
						6966.053
54	0	54	54	1	54	6954.425
						6945.432
55	0	55	55	1	55	7020.523
						7020.226
56	0	56	56	1	56	7019.958
						7019.704
57	0	57	57	1	57	7019.273
						7019.035
58	0	58	58	1	58	7018.201
						7017.294
59	0	59	59	1	59	7016.059
						7014.409
60	0	60	60	1	60	7012.507
						7010.518
61	0	61	61	1	61	7008.515
						7006.053
62	0	62	62	1	62	7003.298
						7000.338
63	0	63	63	1	63	6997.188
						6993.673
64	0	64	64	1	64	6989.867
						6980.486
65	0	65	65	1	65	6977.302
						6966.053
66	0	66	66	1	66	6954.425
						6945.432
67	0	67	67	1	67	7020.523
						7020.226
68	0	68	68	1	68	7019.958
						7019.704
69	0	69	69	1	69	7019.273
						7019.035
70	0	70	70	1	70	7018.201
						7017.294
71	0	71	71	1	71	7016.059
						7014.409
72	0	72	72	1	72	7012.507
						7010.518
73	0	73	73	1	73	7008.515
						7006.053
74	0	74	74	1	74	7003.298
						7000.338
75	0	75	75	1	75	6997.188
						6993.673
76	0	76	76	1	76	6989.867
						6980.486
77	0	77	77	1	77	6977.302
						6966.053
78	0	78	78	1	78	6954.425
						6945.432
79	0	79	79	1	79	7020.523
						7020.226
80	0	80	80	1	80	7019.958
						7019.704
81	0	81	81	1	81	7019.273
						7019.035
82	0	82	82	1	82	7018.201
						7017.294
83	0	83	83	1	83	7016.059
						7014.409
84	0	84	84	1	84	7012.507
						7010.518
85	0	85	85	1	85	7008.515
						7006.053
86	0	86	86	1	86	7003.298
						7000.338
87	0	87	87	1	87	6997.188
						6993.673
88	0	88	88	1	88	6989.867
						6980.486
89	0	89	89	1	89	6977.302
						6966.053
90	0	90	90	1	90	6954.425
						6945.432
91	0	91	91	1	91	7020.523
						7020.226
92	0	92	92	1	92	7019.958
						7019.704
93	0	93	93	1	93	7019.273
						7019.035
94	0	94	94	1	94	7018.201
						7017.294
95	0	95	95	1	95	7016.059
						7014.409
96	0	96	96	1	96	7012.507
						7010.518
97	0	97	97	1	97	7008.515
						7006.053
98	0	98	98	1	98	7003.298
						7000.338
99	0	99	99	1	99	6997.188
						6993.673
100	0	100	100	1	100	6989.867
						6980.486

27	1	26	26	0	26	7049.563
6	1	5	7	0	7	7040.427
7	1	6	8	0	8	7027.202
8	1	7	9	0	9	7023.891
9	1	8	10	0	10	7020.226
10	1	9	11	0	11	7016.416
11	1	10	12	0	12	7012.507
12	1	11	13	0	13	7008.515
13	1	12	14	0	14	7004.512
14	1	13	15	0	15	7000.027
15	1	14	16	0	16	6995.534
16	1	15	17	0	17	6991.003
17	1	16	18	0	18	6986.272
18	1	17	19	0	19	6981.416
19	1	18	20	0	20	6976.289
20	1	19	21	0	21	6971.127
21	1	20	22	0	22	6965.740
22	1	21	23	0	23	6960.405
23	1	22	24	0	24	6954.948
24	1	23	25	0	25	6949.227
25	1	24	26	0	26	6943.486
26	1	25	27	0	27	6937.596
27	1	26	28	0	28	6931.588
6	1	6	6	2	4	6968.198
7	1	7	7	2	5	6966.749
8	1	8	8	2	6	6965.418
9	1	9	9	2	7	6964.935
10	1	10	10	2	8	6963.795
11	1	11	11	2	9	6962.874
12	1	12	12	2	10	6961.939
13	1	13	13	2	11	6960.873
14	1	14	14	2	12	6959.821
15	1	15	15	2	13	6958.406
16	1	16	16	2	14	6957.501
17	1	17	17	2	15	6956.766
18	1	18	18	2	16	6955.949
19	1	19	19	2	17	6955.225
20	1	20	20	2	18	6954.495
21	1	21	21	2	19	6953.754
22	1	22	22	2	20	6953.008
23	1	23	23	2	21	6952.268
24	1	24	24	2	22	6951.528
25	1	25	25	2	23	6950.788
26	1	26	26	2	24	6950.048
27	1	27	27	2	25	6949.308
28	1	28	28	2	26	6948.568
29	1	29	29	2	27	6947.828
30	1	30	30	2	28	6947.088
31	1	31	31	2		

										HO2 100-100 HOTBAND																			
										J KP KO J KP KO NU(CM-1)																			
10	2	8	10	1	10	7080.822				J	KP	KO	J	KP	KO	NU(CM-1)	20	1	20	20	0	20	6901.337						
						7079.942				10	0	10	10	1	10	6861.677	21	1	21	21	0	21	6897.116						
						7079.350				11	0	11	11	1	11	6859.869	22	1	22	22	0	22	6892.715						
11	2	9	11	1	11	7078.227				12	0	12	12	1	12	6858.048	23	1	23	23	0	23	6888.107						
						7077.696				13	0	13	13	1	13	6856.072	24	1	24	24	0	24	6883.235						
12	2	10	12	1	12	7076.422				14	0	14	14	1	14	6853.943	25	1	25	25	0	25	6877.987						
						7075.830				15	0	15	15	1	15	6851.759	13	1	12	12	0	12	6959.223						
13	2	11	13	1	13	7074.345				16	0	16	16	1	16	6849.239	14	1	13	13	0	13	6959.223						
						7073.860				17	0	17	17	1	17	6846.777	15	1	14	14	0	14	6958.698						
14	2	12	14	1	14	7072.190				18	0	18	18	1	18	6844.065	16	1	15	15	0	15	6958.698						
						7071.755				19	0	19	19	1	19	6841.228	17	1	16	16	0	16	6957.503						
15	2	13	15	1	15	7069.939				20	0	20	20	1	20	6838.100	18	1	17	17	0	17	6957.501						
						7069.485				21	0	21	21	1	21	6834.737	19	1	18	18	0	18	6956.495						
16	2	14	16	1	16	7067.594				22	0	22	22	1	22	6831.504	20	1	19	19	0	19	6955.562						
						7067.080				23	0	23	23	1	23	6827.645	21	1	20	20	0	20	6954.425						
17	2	15	17	1	17	7065.070				24	0	24	24	1	24	6823.903	10	1	9	11	0	11	6912.657						
						7064.708				25	0	25	25	1	25	6820.138	11	1	10	12	0	12	6908.735						
21	2	19	21	1	21	7053.339				10	0	10	9	1	8	6880.389	12	1	11	13	0	13	6904.676						
						7053.113				11	0	11	10	1	9	6880.091	13	1	12	14	0	14	6900.422						
22	2	20	22	1	22	7050.030				12	0	12	11	1	10	6879.750	14	1	13	15	0	15	6896.330						
						7049.819				14	0	14	13	1	12	6878.413	15	1	14	16	0	16	6891.800						
23	2	21	23	1	23	7046.709				15	0	15	14	1	13	6877.447	16	1	15	17	0	17	6886.966						
						7046.393				16	0	16	15	1	14	6876.126	17	1	16	18	0	18	6882.167						
24	2	22	24	1	24	7043.466				17	0	17	16	1	15	6874.664	18	1	17	19	0	19	6877.447						
						7043.016				18	0	18	17	1	16	6873.018	11	1	11	11	2	9	6848.325						
9	2	7	8	1	7	7098.593				20	0	20	19	1	18	6869.007							6847.565						
						7097.982				21	0	21	20	1	19	6866.642	12	1	12	12	2	10	6845.597						
10	2	8	9	1	8	7098.593				22	0	22	21	1	20	6864.123							6844.810						
						7097.982				23	0	23	22	1	21	6861.296	13	1	13	13	2	11	6843.166						
11	2	9	10	1	9	7098.303				24	0	24	23	1	22	6858.048							6842.365						
						7097.982				10	0	10	11	1	10	6834.191	14	1	14	14	2	12	6839.573						
12	2	10	11	1	10	7097.982				11	0	11	12	1	11	6829.392							6838.689						
						7097.555				12	0	12	13	1	12	6824.600	15	1	15	15	2	13	6836.867						
13	2	11	12	1	11	7097.555				13	0	13	14	1	13	6819.678							6836.208						
						7097.066				14	0	14	15	1	14	6814.333	16	1	16	16	2	14	6832.889						
14	2	12	13	1	12	7096.425				15	0	15	16	1	15	6809.399							6832.245						
						7095.937				16	0	16	17	1	16	6803.517	17	1	17	17	2	15	6828.945						
15	2	13	14	1	13	7095.525				11	1	11	11	0	11	6892.073							6828.134						
						7095.220				12	1	12	12	0	12	6889.504													
16	2	14	15	1	14	7094.274				13	1	13	13	0	13	6886.695													
						7093.939				14	1	14	14	0	14	6883.818													
17	2	15	16	1	15	7093.039				15	1	15	15	0	15	6880.674	J	KP	KO	J	KP	KO	NU(CM-1)						
						7092.628				16	1	16	16	0	16	6877.192	8	0	8	8	1	8	6895.515						
18	2	16	17	1	16	7091.789				17	1	17	17	0	17	6873.359	9	0	9	9	1	9	6894.029						
						7091.439				18	1	18	18	0	18	6869.389	10	0	10	10	1	10	6892.458						
7	2	5	8	1	7	7064.708				19	1	19	19	0	19	6865.156	11	0	11	11	1	11	6890.845						
						7063.998				20	1	20	20	0	20	6860.815	12	0	12	12	1	12	6889.033						
9	2	7	10	1	9	7056.742				21	1	21	21	0	21	6856.439	13	0	13	13	1	13	6886.966						
						7056.004				22	1	22	22	0	22	6851.759	14	0	14	14	1	14	6885.086						
10	2	8	11	1	10	7052.406				23	1	23	23	0	23	6846.777	15	0	15	15	1	15	6882.690						
						7051.774				24	1	24	24	0	24	6841.692	16	0	16	16	1	16	6880.091						
11	2	9	12	1	11	7047.82				25	1	25	25	0	25	6836.208	17	0	17	17	1	17	6877.447						
						7047.264				26	1	26	26	0	26	6830.525	18	0	18	18	1	18	6874.664						
12	2	10	13	1	12	7043.016				10	1	9	11	0	11	6873.359	19	0	19	19	1	19	6871.628						
						7042.551				12	1	11	13	0	13	6856.156	8	0	8	9	1	8	6873.713						
13	2	11	14	1	13	7038.085				13	1	12	14	0	14	6861.296	9	0	9	10	1	9	6869.389						
						7037.367				14	1	13	15	0	15	6856.848	10	0	10	11	1	10	6865.156						
14	2	12	15	1	14	7032.833				15	1	14	16	0	16	6852.027	11	0	11	12	1	11	6860.307						
						7032.534				17	1	16	18	0	18	6842.365	12	0	12	13	1	12	6855.847						
15	2	13	16	1	15	7027.47				18	1	17	19	0	19	6837.133	13	0	13	14	1	13	6850.830						
						7026.918				19	1	18	20	0	20	6831.700	14	0	14	15	1	14	6845.779						
16	2	14	17	1	16	7021.968				20	1	19	21	0	21	6826.598	15	0	15	16	1	15	6840.449						
						7021.402				21	1	20	22	0	22	6821.016	7	1	7	7	0	7	6933.049						
17	2	15	18	1	17	7016.059											8	1	8	8	0	8	6931.299						
						7015.717											9	1	9	9	0	9	6929.376						
8	2		8	3		6928.509				J	KP	KO	J	KP	KO	NU(CM-1)	10	1	10	10	0	10	6927.233						
						6926.588				7	0	7	7	1	7	6899.162	11	1	11	11	0	11	6924.740						
9	2		9	3		6926.588				8	0	8	8	1	8	6897.817	12	1	12	12	0	12	6922.143						
						6924.740				9	0	9	9	1	9	6896.330	13	1	13	13	0	13	6919.362						
10	2		10	3		6924.740				10	0	10	10	1	10	6894.772	14	1	14	14	0	14	6916.655						
						6922.922				11	0	11	11	1	11	6893.058	15	1	15	15	0	15	6913.447						
11	2		11	3		6922.922				12	0	12	12	1	12	6891.202	16	1	16	16	0	16	6910.286						
						6921.048				13	0	13	13	1	13	6889.176	17	1	17	17	0	17	6906.855						
12	2		12	3		6920.918				14	0	14	14	1	14	6886.966	18	1	18	18	0	18	6903.171						
						6918.944				15	0	15	15	1	15	6884.658	19	1	19	19	0	19	6899.162						
13	2		13	3		6918.325				16	0	16	16	1	16	6882.167	20	1	20	20	0								

APPENDIX 2

Upper state combination differences inside $\text{HO}_2^2\text{A}'(000)$.

The final 39 are constructed rather than genuine
combination differences (see text).

N_{K_p, K_o}	N_{K_p, K_o}	$\Delta_2 F'$	obs. - calc.	N_{K_p, K_o}	N_{K_p, K_o}	$\Delta_2 F'$	obs. - calc.
$12_{0,12}$	$10_{0,10}$	45.706	+0.078	$15_{1,15}$	$14_{1,13}$	23.864	+0.030
$13_{0,13}$	$11_{0,11}$	49.646	+0.026	$16_{1,16}$	$15_{1,14}$	24.989	-0.000
$14_{0,14}$	$12_{0,12}$	53.514	-0.049	$17_{1,17}$	$16_{1,15}$	26.023	-0.066
$15_{0,15}$	$13_{0,13}$	57.473	-0.026	$18_{1,18}$	$17_{1,16}$	27.052	-0.082
$16_{0,16}$	$14_{0,14}$	61.634	+0.205	$19_{1,19}$	$18_{1,17}$	28.108	-0.016
$17_{0,17}$	$15_{0,15}$	65.415	+0.064	$20_{1,20}$	$19_{1,18}$	29.068	+0.009
$18_{0,18}$	$16_{0,16}$	69.268	+0.002	$21_{1,21}$	$20_{1,19}$	29.862	-0.077
$19_{0,19}$	$17_{0,17}$	73.168	-0.005	$22_{1,22}$	$21_{1,20}$	30.916	+0.152
$20_{0,20}$	$18_{0,18}$	77.216	+0.144	$23_{1,23}$	$22_{1,21}$	31.615	+0.081
$22_{0,22}$	$20_{0,20}$	84.973	+0.130	$24_{1,24}$	$23_{1,22}$	32.221	-0.029
$23_{0,23}$	$21_{0,21}$	88.702	-0.013	$25_{1,25}$	$24_{1,23}$	33.116	+0.205
$24_{0,24}$	$22_{0,22}$	92.512	-0.065	$26_{1,26}$	$25_{1,24}$	33.552	+0.034
$25_{0,25}$	$23_{0,23}$	96.557	+0.129	$27_{1,27}$	$26_{1,25}$	34.503	-0.065
$26_{0,26}$	$24_{0,24}$	100.120	-0.150	$28_{1,28}$	$27_{1,26}$	34.503	-0.065
$15_{1,14}$	$14_{1,14}$	35.482	+0.128	$14_{1,14}$	$13_{1,12}$	22.657	+0.032
$16_{1,15}$	$15_{1,15}$	38.491	-0.013	$15_{1,15}$	$14_{1,13}$	23.837	+0.003
$17_{1,16}$	$16_{1,16}$	41.361	+0.016	$16_{1,16}$	$15_{1,14}$	25.032	+0.043
$18_{1,17}$	$17_{1,17}$	44.224	-0.010	$17_{1,17}$	$16_{1,15}$	26.222	+0.133
$19_{1,18}$	$18_{1,18}$	47.172	-0.002	$18_{1,18}$	$17_{1,16}$	27.168	+0.034
$20_{1,19}$	$19_{1,19}$	49.962	-0.200	$19_{1,19}$	$18_{1,17}$	27.935	-0.189
$21_{1,20}$	$20_{1,20}$	53.058	-0.142	$9_{1,8}$	$8_{1,8}$	20.033	-0.004
$22_{1,21}$	$21_{1,21}$	56.326	+0.040	$10_{1,9}$	$9_{1,9}$	22.621	+0.099
$23_{1,22}$	$22_{1,22}$	59.483	+0.063	$11_{1,10}$	$10_{1,10}$	24.998	-0.061
$24_{1,23}$	$23_{1,23}$	62.629	+0.028	$12_{1,11}$	$11_{1,11}$	27.661	+0.014
$25_{1,24}$	$24_{1,24}$	65.943	+0.113	$13_{1,12}$	$12_{1,12}$	30.396	+0.111
$26_{1,25}$	$25_{1,25}$	69.040	-0.066	$14_{1,13}$	$13_{1,13}$	32.843	-0.132
$27_{1,26}$	$26_{1,26}$	72.525	+0.097	$15_{1,14}$	$14_{1,14}$	35.723	+0.009
$7_{1,7}$	$6_{1,5}$	12.589	-0.043	$16_{1,15}$	$15_{1,15}$	38.503	-0.001
$8_{1,8}$	$7_{1,6}$	14.105	-0.117	$17_{1,16}$	$16_{1,16}$	41.341	-0.0004
$11_{1,11}$	$10_{1,9}$	18.600	-0.068	$18_{1,17}$	$17_{1,17}$	44.435	+0.200
$12_{1,12}$	$11_{1,10}$	20.027	-0.015	$15_{1,14}$	$14_{1,14}$	35.475	-0.239
$13_{1,13}$	$12_{1,11}$	21.329	-0.032	$16_{1,15}$	$15_{1,15}$	38.371	-0.133
$14_{1,14}$	$13_{1,12}$	22.406	-0.219	$17_{1,16}$	$16_{1,16}$	41.541	+0.196

N_{K_p, K_o}	N_{K_p, K_o}	$\Delta_2 F'$	obs. - calc.	N_{K_p, K_o}	N_{K_p, K_o}	$\Delta_2 F'$	obs. - calc.
18 _{1,17}	17 _{1,17}	44.255	+0.021	8 _{2,7}	7 _{2,5}	16.029	+0.135
19 _{1,18}	18 _{1,18}	47.108	-0.066	10 _{2,9}	9 _{2,7}	19.753	-0.087
20 _{1,19}	19 _{1,19}	50.164	+0.002	11 _{2,10}	10 _{2,8}	21.732	-0.072
7 _{1,7}	6 _{1,5}	12.707	+0.075	12 _{2,11}	11 _{2,9}	23.766	+0.005
8 _{1,8}	7 _{1,6}	14.156	-0.066	13 _{2,12}	12 _{2,10}	25.658	-0.051
9 _{1,9}	8 _{1,7}	15.883	+0.075	14 _{2,13}	13 _{2,11}	27.646	-0.001
10 _{1,10}	9 _{1,8}	17.340	+0.099	16 _{2,15}	15 _{2,13}	31.221	-0.265
11 _{1,10}	10 _{1,9}	18.676	+0.008	17 _{2,16}	16 _{2,14}	33.273	-0.111
12 _{1,12}	11 _{1,10}	19.992	-0.050	18 _{2,17}	17 _{2,15}	35.299	+0.035
13 _{1,13}	12 _{1,11}	21.399	+0.038	7 _{2,5}	7 _{0,7}	77.765	-0.044
14 _{1,14}	13 _{1,12}	22.454	-0.171	8 _{2,6}	8 _{0,8}	77.976	+0.158
15 _{1,15}	14 _{1,13}	23.823	-0.011	9 _{2,7}	9 _{0,9}	77.978	+0.144
16 _{1,16}	15 _{1,14}	24.933	-0.056	10 _{2,8}	10 _{0,10}	78.065	+0.208
18 _{1,18}	17 _{1,16}	27.217	+0.083	11 _{2,9}	11 _{0,11}	78.037	+0.147
12 _{2,11}	11 _{2,9}	23.802	+0.041	12 _{2,10}	12 _{0,12}	78.022	+0.028
13 _{2,12}	12 _{2,10}	25.637	-0.072	14 _{2,12}	14 _{0,14}	78.050	-0.021
14 _{2,13}	13 _{2,11}	27.661	+0.014	15 _{2,13}	15 _{0,15}	78.164	-0.003
15 _{2,14}	14 _{2,12}	29.499	-0.074	16 _{2,14}	16 _{0,16}	78.325	+0.040
16 _{2,15}	15 _{2,13}	31.287	-0.199	17 _{2,15}	17 _{0,17}	78.617	+0.188
8 _{2,6}	7 _{2,6}	15.980	+0.050	21 _{2,19}	21 _{0,21}	79.299	-0.026
10 _{2,8}	9 _{2,8}	19.874	-0.055	22 _{2,20}	22 _{0,22}	79.545	-0.101
12 _{2,10}	11 _{2,10}	23.961	+0.015	23 _{2,21}	23 _{0,23}	79.802	-0.211
13 _{2,11}	12 _{2,11}	25.994	-0.020	24 _{2,22}	24 _{0,24}	80.307	-0.124
14 _{2,12}	13 _{2,12}	27.937	-0.052	7 _{2,6}	6 _{0,6}	91.750	+0.031
15 _{2,13}	14 _{2,13}	29.859	-0.165	8 _{2,7}	7 _{0,7}	93.818	+0.115
17 _{2,15}	16 _{2,15}	34.336	+0.208	9 _{2,8}	8 _{0,8}	95.733	+0.045
9 _{2,7}	8 _{2,7}	17.905	-0.023	10 _{2,9}	9 _{0,9}	97.605	-0.069
10 _{2,8}	9 _{2,8}	19.939	+0.010	11 _{2,10}	10 _{0,10}	99.727	+0.066
11 _{2,9}	10 _{2,9}	22.016	+0.081	12 _{2,11}	11 _{0,11}	101.710	+0.059
12 _{2,10}	11 _{2,10}	23.961	+0.015	13 _{2,12}	12 _{0,12}	103.754	+0.110
13 _{2,11}	12 _{2,11}	26.092	+0.128	14 _{2,13}	13 _{0,13}	105.551	-0.090
14 _{2,12}	13 _{2,12}	27.740	-0.249	16 _{2,15}	15 _{0,15}	109.421	-0.231
15 _{2,13}	14 _{2,13}	30.000	-0.024	17 _{2,16}	16 _{0,16}	111.719	+0.050
17 _{2,15}	16 _{2,15}	34.418	+0.290	18 _{2,17}	17 _{0,17}	113.837	+0.144

N_{K_p, K_o}	N_{K_p, K_o}	$\Delta_2 F'$	obs. - calc.
19 _{2,18}	18 _{0,18}	115.800	+0.072
20 _{2,19}	19 _{0,19}	117.654	-0.120
21 _{2,20}	20 _{0,20}	119.947	+0.115
22 _{2,21}	21 _{0,21}	121.862	-0.043
23 _{2,22}	22 _{0,22}	123.802	-0.191
24 _{2,23}	23 _{0,23}	125.874	-0.224
5 _{1,5}	5 _{0,5}	19.040	-0.028
6 _{1,6}	6 _{0,6}	18.871	-0.040
7 _{1,7}	7 _{0,7}	18.692	-0.037
8 _{1,8}	8 _{0,8}	18.480	-0.043
9 _{1,9}	9 _{0,9}	18.292	-0.001
10 _{1,10}	10 _{0,10}	18.158	+0.118
11 _{1,11}	11 _{0,11}	17.869	+0.104
12 _{1,12}	12 _{0,12}	17.469	+0.001
13 _{1,13}	13 _{0,13}	17.149	-0.003
14 _{1,14}	14 _{0,14}	16.760	-0.055
15 _{1,15}	15 _{0,15}	16.507	+0.046
16 _{1,16}	16 _{0,16}	16.096	+0.006
17 _{1,17}	17 _{0,17}	15.773	+0.069
18 _{1,18}	18 _{0,18}	15.316	+0.014
19 _{1,19}	19 _{0,19}	14.962	+0.074
20 _{1,20}	20 _{0,20}	14.453	-0.010
21 _{1,21}	21 _{0,21}	13.938	-0.089
22 _{1,22}	22 _{0,22}	13.635	+0.052
23 _{1,23}	23 _{0,23}	13.117	-0.015
24 _{1,24}	24 _{0,24}	12.629	-0.047
25 _{1,25}	25 _{0,25}	12.464	+0.248
26 _{1,26}	26 _{0,26}	11.912	+0.159
27 _{1,27}	27 _{0,27}	11.259	-0.031
28 _{1,28}	28 _{0,28}	10.882	+0.054
30 _{1,30}	30 _{0,30}	9.754	-0.159

N_{K_p, K_o}	N_{K_p, K_o}	$\Delta_2 F'$	obs. - calc.
9 _{2,8}	9 _{1,8}	57.138	+0.010
10 _{2,9}	10 _{1,9}	56.763	-0.096
11 _{2,10}	11 _{1,10}	56.598	+0.036
12 _{2,11}	12 _{1,11}	56.244	+0.004
13 _{2,12}	13 _{1,12}	55.999	+0.108
14 _{2,13}	14 _{1,13}	55.254	-0.261
16 _{2,15}	16 _{1,15}	54.456	-0.231
17 _{2,16}	17 _{1,16}	54.112	-0.122
18 _{2,17}	18 _{1,17}	53.590	-0.165
19 _{2,18}	19 _{1,18}	53.380	+0.128
21 _{2,20}	21 _{1,20}	52.386	+0.120
22 _{2,21}	22 _{1,21}	51.712	+0.120
23 _{2,22}	23 _{1,22}	50.995	+0.004
24 _{2,23}	24 _{1,23}	50.037	-0.228

RMS deviation of fit
= 0.111 cm⁻¹

APPENDIX 3

Assignments of HO_2 $^2\text{A}''(200) \Rightarrow ^2\text{A}''(000)$

KP KO J KP KO NU (

[illegible]

APPENDIX 4

Assignments of DO_2 $^2\text{A}'(000) \Rightarrow ^2\text{A}''(000)$

ASSIGNMENTS OF DO_2 $2A'$ (000) $\rightarrow$ $2A''$ (000)

7	0	7	7	1	7	7027.867	11	1	10	10	0	10	7065.871	19	2	17	18	1	17	7074.725
8	0	8	8	1	8	7026.897	12	1	11	11	0	11	7066.688	20	2	18	19	1	18	7073.225
9	0	9	9	1	9	7025.882	14	1	13	13	0	13	7067.852	21	2	19	20	1	19	7071.665
10	0	10	10	1	10	7024.659	15	1	14	14	0	14	7068.154	22	2	20	21	1	20	7069.985
11	0	11	11	1	11	7023.391	16	1	15	15	0	15	7068.593	8	2	7	8	1	7	7064.255
12	0	12	12	1	12	7021.961	17	1	16	16	0	16	7069.047	9	2	8	9	1	8	7062.400
13	0	13	13	1	13	7020.337	18	1	17	17	0	17	7069.486	10	2	9	10	1	9	7060.420
14	0	14	14	1	14	7018.654	19	1	18	18	0	18	7069.486	11	2	10	11	1	10	7057.766
15	0	15	15	1	15	7016.690	20	1	19	19	0	19	7069.486	12	2	11	12	1	11	7055.732
16	0	16	16	1	16	7014.742	5	1	4	6	0	6	7037.482	13	2	12	13	1	12	7052.871
17	0	17	17	1	17	7012.602	6	1	5	7	0	7	7034.772	14	2	13	14	1	13	7050.057
18	0	18	18	1	18	7010.315	7	1	6	8	0	8	7031.931	15	2	14	15	1	14	7047.066
19	0	19	19	1	19	7007.762	8	1	7	9	0	9	7029.166	16	2	15	16	1	15	7043.882
20	0	20	20	1	20	7005.108	9	1	8	10	0	10	7026.255	18	2	17	18	1	17	7036.419
21	0	21	21	1	21	7002.235	10	1	9	11	0	11	7023.004	19	2	18	19	1	18	7032.962
22	0	22	22	1	22	6999.304	11	1	10	12	0	12	7019.845	20	2	19	20	1	19	7028.718
23	0	23	23	1	23	6996.199	12	1	11	13	0	13	7016.690	8	2	7	7	1	7	7083.407
24	0	24	24	1	24	6992.699	13	1	12	14	0	14	7013.434	9	2	8	8	1	8	7084.456
25	0	25	25	1	25	6989.129	14	1	13	15	0	15	7010.018	10	2	9	9	1	9	7085.079
26	0	26	26	1	26	6985.129	15	1	14	16	0	16	7006.709	11	2	10	10	1	10	7086.053
27	0	27	27	1	27	6981.281	16	1	15	17	0	17	7002.960	12	2	11	11	1	11	7086.616
28	0	28	28	1	28	6977.180	17	1	16	18	0	18	6999.556	13	2	12	12	1	12	7087.209
8	0	8	7	1	6	7040.029	18	1	17	19	0	19	6995.786	14	2	13	13	1	13	7087.209
9	0	9	8	1	7	7040.029	19	1	18	20	0	20	6992.330	15	2	14	14	1	14	7087.833
10	0	10	9	1	8	7040.029	20	1	19	21	0	21	6988.525	16	2	15	15	1	15	7087.833
11	0	11	10	1	9	7039.804	6	1	6	6	2	4	7006.709	17	2	16	16	1	16	7087.833
12	0	12	11	1	10	7039.175	10	1	10	10	2	6	7005.983	12	2	10	12	3	10	6979.031
13	0	13	12	1	11	7038.485	8	1	8	8	2	6	7003.495							6978.311
14	0	14	13	1	12	7037.482							7002.960	13	2	11	13	3	11	6977.180
15	0	15	14	1	13	7036.194	11	1	11	11	2	9	6997.411							6976.358
16	0	16	15	1	14	7034.772							6996.983	14	2	12	14	3	12	6974.959
17	0	17	16	1	15	7032.962	12	1	12	12	2	10	6994.382							6974.112
18	0	18	17	1	16	7031.168	13	1	13	13	2	11	6991.725	15	2	13	15	3	13	6972.983
19	0	19	18	1	17	7029.047							6991.327							6972.323
20	0	20	19	1	18	7026.539	14	1	14	14	2	12	6988.525	16	2	14	16	3	14	6970.579
21	0	21	20	1	19	7023.719							6988.230							6970.080
22	0	22	21	1	20	7020.590	15	1	15	15	2	13	6985.224	17	2	15	17	3	15	6967.634
23	0	23	22	1	21	7017.731	16	1	16	16	2	14	6981.840							6967.210
24	0	24	23	1	22	7013.924	17	1	17	17	2	15	6977.871	18	2	16	18	3	16	6965.234
7	0	7	8	1	7	7008.786							6977.636							6964.927
8	0	8	9	1	8	7004.916	18	1	18	18	2	16	6973.540	11	2	10	11	3	8	6980.075
9	0	9	10	1	9	7001.095	19	1	19	19	2	17	6969.055							6979.031
10	0	10	11	1	10	6996.702							6968.835	12	2	11	12	3	9	6978.649
11	0	11	12	1	11	6992.507	20	1	20	20	2	18	6964.357							6977.871
12	0	12	13	1	12	6987.876							6964.093	15	2	14	15	3	12	6971.458
13	0	13	14	1	13	6982.987	21	1	21	21	2	19	6959.257							6970.754
14	0	14	15	1	14	6977.871	22	1	22	22	2	20	6953.786	16	2	15	16	3	13	6968.835
15	0	15	16	1	15	6972.660	23	1	23	23	2	21	6948.427							6968.191
16	0	16	17	1	16	6967.210	6	1	5	6	2	5	7008.608	12	3	10	12	2	10	7079.154
17	0	17	18	1	17	6961.258							7007.970							7078.137
18	0	18	19	1	18	6955.463	8	1	7	8	2	7	7006.709	13	3	11	13	2	11	7076.787
19	0	19	20	1	19	6949.053							7006.235							7075.923
20	0	20	21	1	20	6942.497	10	1	9	10	2	9	7004.382	14	3	12	14	2	12	7074.331
21	0	21	22	1	21	6935.680							7003.819							7073.574
22	0	22	23	1	22	6928.863	11	1	10	11	2	10	7002.960	12	3	9	12	2	11	7079.852
23	0	23	24	1	23	6921.802							7002.575							7078.744
24	0	24	25	1	24	6914.139	15	1	14	15	2	14	6996.983	13	3	10	13	2	12	7077.697
25	0	25	26	1	25	6906.466							6996.702							7076.787
6	1	6	6	0	6	7047.066	16	1	15	16	2	15	6995.003	14	3	11	14	2	13	7075.696
7	1	7	7	0	7	7045.730							6994.678							7074.725
8	1	8	8	0	8	7044.123	17	1	16	17	2	16	6992.699	15	3	12	15	2	14	7073.225
9	1	9	9	0	9	7042.473	18	1	17	18	2	17	6990.574							7072.498
10	1	10	10	0	10	7040.569	19	1	18	19	2	18	6988.525	12	4		12	3		7099.788
11	1	11	11	0	11	7038.485							6988.230							7097.925
12	1	12	12	0	12	7036.194	20	1	19	20	2	19	6985.725	13	4		13	3		7097.650
13	1	13	13	0	13	7033.755	11	2	9	11	1	11	7064.798							7095.880
14	1	14	14	0	14	7031.168	12	2	10	12	1	12	7063.379	14	4		14	3		7095.132
15	1	15	15	0	15	7028.524	13	2	11	13	1	13	7062.246							7093.637
16	1	16	16	0	16	7025.703	14	2	12	14	1	14	7060.873	15	4		15	3		7092.677
17	1	17	17	0	17	7022.646	15	2	13	15	1	15	7059.575							7091.198
18	1	18	18	0	18	7019.428	16	2	14	16	1	16	7058.203	16	4		16	3		7090.086
19	1	19	19	0	19	7016.125	17	2	15	17	1	17	7056.530							7088.731
20	1	20	20	0	20	7012.750	18	2	16	18	1	18	7055.144	11	4		10	3		7123.714
21	1	21	21	0	21	7009.261	19	2	17	19	1	19	7053.533							7121.775
22	1	22	22	0	22	7005.553	20	2	18	20	1	20	7051.757	12	4		11	3		7123.714
23	1	23	23	0	23	7001.731	9	2	7	8	1	7	7081.219							7121.775
24	1	24	24	0	24	6997.899	10	2	8	9	1	8	7081.219	13	4		12	3		7123.714
25	1	25	25	0	25	6993.851	11	2	9	10	1	9	7081.219							7121.775
26	1	26	26	0	26	6989.616	12	2	10	11	1	10	7080.703	14	4		13	3		7123.406
27	1	27	27	0	27	6985.224	13	2	11	12	1	11	7080.475							

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