ROTATIONAL ANALYSIS OF SOME VIBRONIC BANDS IN THE $^{1}A' \leftarrow {}^{1}A_{2}$ SYSTEM OF FORMALDEHYDE

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Abstract.

An interferometric method for the resolution and evaluation of the rotational fine structure of the ultra-violet absorption bands of simple polyatomic molecules, initiated by Drs. Poole, Stace and Raynes, has been further developed. In particular, nearly all the time-consuming work in the conversion of fringe measurements into frequencies has been speeded up by electronic computer operations, replacing weeks or months by hours of work. Further, the calibration procedure has been greatly simplified and programmed for an electronic computer. In the calibration of the spectral region 3370 Å to 3640 Å, standard iron lines have been measured to a precision of 0.002 cm^{-1} and better, and the agreement with the international frequencies is of the same order.

Several vibronic bands in the near ultra-violet system of formaldehyde (HCHO and DCDO) have been photographed. Four bands have been examined in detail; the individual frequencies are known to about 0.0035 cm^{-1}, and a practical resolving limit of 0.085 cm^{-1} has been observed. Computer programmes have been written for most stages of the analysis of the bands, including calculations of asymmetric rotor energies and intensities, and least squares fitting of

molecular constants to the observed frequencies; a novel technique has been successfully developed for the assignment of frequencies to their respective sub-branches replacing most of the usual desk procedure by a computer operation. Very accurate rotational and centrifugal distortion constants have been obtained from the analyses, and, in particular, the ground state constants derived from combination differences from three of the bands are probably more accurate than those obtained from the microwave spectrum (by other workers and also, with probably better numerical methods, by the present author).

In the course of this work, a hitherto unsuspected type of perturbation has been identified in the excited state of formaldehyde, between rotational levels of the two members of the inversion doublets. The theory of the interactions involved, (recently published by another worker) has been extended to render it applicable to rotational levels affected by the asymmetry of the molecule. Some other perturbations of possibly a different type have been found and mapped. In addition, the published treatment of centrifugal distortion has been modified, the new treatment being superior when applied to the numerical analysis of actual systems.

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I thank the staff of the University of London Computer Unit both for the use of the computer, and for help in the design and running of the programmes.

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CHAPTER 1

INTRODUCTION

1.1. The structure of vibronic bands.

Early in the history of spectroscopy it was noticed that the spectra of many compounds in the visible and ultra-violet regions of the spectrum consisted of a series of discrete bands, and there existed certain relations between the band centres for some of the simpler molecules. After the development of quantum theory, it has become evident that the bands of a molecule are due to transitions between the discrete vibrational energy levels of two different electronic states, one of which is usually the ground state. The relations between the band centres are due to the more or less regular spacings of sets of these levels. Each set corresponds to successive quanta of one of the normal vibrations of the molecule, the energy levels being given roughly by $(v+\frac{1}{2})h\nu$, where h is Planck's constant (in appropriate units), ν is the fundamental vibrational frequency, and v the quantum number taking all positive integral values including zero. The transitions themselves are governed by various selection rules which limit greatly the number of possible transitions.

Deviations from the harmonic behaviour indicated above are caused by the non-ideality of the chemical bonds of the molecule, by the effects of a non-uniform environment (in the case of solids), or by interactions between different vibrational levels. Such effects may be studied with the aid of so-called medium dispersion instruments, either prism, or coarse grating spectrographs. Analysis of the frequencies obtained from band centres sometimes leads to a unique assignment of the bands to transitions between recognised vibronic levels of the molecule. More often, inconsistencies arise in the analysis which cannot be solved without reference to information from another source.

Such a source for gases and readily vapourisable compounds is found in the rotational fine structure of each of the vibronic bands. Using spectrographs of high resolving power, this structure shows as a large number of closely spaced lines, and is the result of transitions between different rotational levels of the two species involved in the vibronic transition. The energies of the rotational levels are related to the moments of inertia of the molecular species, hence analysis of the fine structure yields information about the geometry of the species. This is often, in itself, a good guide to vibrational assignment. Detailed analysis also yields the true vibrational origins of the bands concerned, and it is this quantity rather than the band centre which should be used in the vibrational analysis. The rotational selection rules are governed by the symmetries of the two combining vibronic levels; their elucidation therefore, is often very useful. Sometimes, the rotational levels of one vibration are perturbed by the levels of a different vibration; this may fix the position of the perturbing level even though actual transitions involving it may not be observed in the spectrum. Finally, the centrifugal distortion constants which emerge for each vibrational level from a detailed analysis, should correlate with force constants derived from the vibrational frequencies. It can be seen therefore, that a thorough rotational analysis of the vibronic bands of a gaseous molecule not only provides information on the molecular dimensions (this is often, of course, the most valuable information), but is an indispensable part of a rigorous vibrational analysis.

Electronic spectra are studied either in absorption or in fluorescence. In the former, the transitions result from an intake of energy by the molecule to excite it from a level in the ground electronic state to a level in an excited electronic state. At low temperatures, most of the molecules are in the vibrationless level, the population of the levels being governed by the Boltzmann distribution law. The absorption bands, then, mainly arise from this one level; this feature simplifies the assignment of such bands. At higher temperatures (depending on the energies of the lowest lying vibrations of the molecule) hot bands appear, originating from higher vibrational levels of the ground state. Unless these bands are specifically of interest, their appearance is best avoided as far as possible by keeping the temperature down.

The fluorescence spectrum is obtained by excitation of the molecules to an electronically excited state by external means, usually a discharge; the spectrum is then observed as transitions from vibrational levels in this state to levels in a lower electronic state, usually the ground state. It is generally much more complex than the absorption spectrum and often suffers from overlapping of neighbouring bands, making rotational analysis difficult.

In the present work, the absorption spectrum of formaldehyde vapour has been studied, and all the bands examined in detail arise from the vibrationless ground state. From these bands we obtain a large amount of information on the rotational energy levels of the vibrationless ground state, after eliminating the vibronically excited state by using combination differences. At the present time, accurate structural information on the ground state is usually obtained from the pure rotational transitions in the microwave region, where frequencies can be measured with very high accuracy. However, in certain cases, and formaldehyde is one of them, the amount of information obtainable from the pure rotational spectrum is somewhat restricted since most of the frequencies lie outside the range covered by present day instrumentation. The ultra-violet spectrum (and possibly also the infra-red spectrum) is then the best source of information, especially if the frequencies are accurately known. Part of this thesis will be concerned with a comparison of the two means of obtaining ground state rotational constants for formaldehyde.

For molecules with several atoms or a few heavy atoms, the principal moments of inertia are relatively large, and the spacing between their rotational levels is correspondingly small. Thus, when studying larger and heavier molecules, it becomes increasingly difficult to resolve the finely spaced rotational structure. It is therefore necessary to employ instruments with very high resolving powers. Such instruments used at the present time are discussed in the next section. As a corollary to their use for high resolution, one is able to measure individual frequencies to high accuracy; indeed, in the present work, a serious limitation on the accuracy of the frequencies obtained lies in the uncertainties in the standard frequencies used for calibration.

1.2. High Resolution Instruments

Two main types of high ~~dispersion~~ resolution instrument are at present in general use, grating spectrographs and the class of instruments known as interferometers. The echelle designed by Harrison (1), which combines some of the properties of both, does not seem to have fulfilled its early promise and does not seem to be used much at the present time. The echelon grating invented by Michelson (2) has also not become widely used due to the great difficulty of its manufacture: in any case its properties restrict its usefulness to a very short frequency range, so that it would be useless for the type of spectrum here considered.

Gratings have been used for many years to resolve molecular spectra due to their relative ease of operation, and the simplicity of determining frequencies from the spectra. Present day ruled gratings have extremely fine rulings, gratings up to 60,000 lines to the inch are now readily available, and can be blazed to deliver most of their output in any desired low order, at a particular wavelength. Since the theoretical resolving power of a grating is given approximately by the product of the number of lines used and the order of the spectrum, high orders are preferable from the point of view of high resolution. However, the efficiency of blazing drops at high orders and the intensity of the spectrum falls sharply. The actual resolving power attainable depends on the quality of the rulings and at high orders, the effects of imperfections become more marked. A high quality grating spectrograph built at Ottawa, employs a 35 ft concave grating ruled with 30,000 lines to the inch and is blazed for the first order at 7000 Å. It has been reported (3) that a resolving power of 400,000 has been obtained when used in the second order at 5000 Å, which is about 80% of the theoretical resolving power. Significant further increase in resolving power is very difficult to acheive even with present day ruling techniques, though claims for higher performance have been made.

Interferometers have been used for many years when very high resolution and high accuracy have been needed in the field of atomic spectra. Wavelength standards are now always determined interferometrically, and the fine structure of atomic lines has been studied at resolving powers of several millions. In these applications however, relatively few lines are examined in the spectral regions concerned and there is little difficulty in determining their frequencies. With molecular spectra, many hundreds of lines occur within a space of 10 Å or so, and the problem becomes complicated by the necessity to sort them from one another, as well as by the need for frequency evaluation over a considerable range. This, and the difficulty of frequency determination compared with grating instruments, has deterred investigators from employing interferometers for molecular studies until quite recently.

Two types of interferometer have proved useful to spectral studies, the etalon introduced by Fabry and Perot in 1897, and the Lummer Plate devised by Lummer in 1901. Both use multiple reflections to produce successive coherent beams differing in phase by virtue of their different numbers of reflections. When brought to a focus, the beams interfere to produce an interference fringe array, the properties of which depend on the wavelength of the radiation. The etalon consists of two plane plates, usually mounted parallel to one another, with an air gap between them (sometimes the instrument is evacuated). The two inner surfaces are coated with some highly reflecting substance but which also allows some transmission of a small percentage of the light. Radiation from an extended source falling on the plates, undergoes multiple reflections before being brought to a focus by a suitable projection lens. The main factor limiting the performance of the etalon is the reflectivity of the inner surfaces. This must be high enough to permit a large number of reflections before the intensity falls to a minimum, but the absorption must be low enough to permit transmission. Since the two factors are related in a complicated way, a compromise must be reached. The compromise is most favourable for thin silver films, in the visible region of the spectrum, but falls off rapidly for this metal below 4000 Å. Although not as good as silver in the visible, aluminium films are superior in the ultra-violet region and are usually employed there. The absorption is still quite high and this has a deleterious effect on the useful resolving power of the instrument. Multilayer dielectric coatings have recently been employed with great success to replace aluminium films in the near ultra-violet.

The Lummer Plate makes use of the high reflectivities of a transparent substance at near the critical angle of (internal) incidence, corresponding to near grazing emergence. A full description of the plate and its properties is given by Tolansky (4), Stace (5), and Haynes(6), and a summary is given in chapter 2 of this thesis. It has been overshadowed in recent years by the etalon; until the present project, probably the last major research undertaken with the Lummer Plate was in 1952 by von Klüber(7). An important property of any interferometer is its free spectral range (the frequency interval between two interference fringes,in adjacent orders, which just overlap). Raynes demonstrated that a free spectral range of about 1 cm^{-1} was desirable in molecular work, and the free spectral range of the Lummer plate employed by him, and used in the present work, was about 1.1 cm^{-1}. The etalon has the advantage over the Lummer plate in that its free spectral range may be altered at will by varying the air gap between the plates. Tolansky has pointed out however, that if the two types of instrument are constructed to have the same free spectral range, then the Lummer plate has the better resolving power due to the superior reflectance/absorption balance of its surfaces, and this advantage increases greatly on moving into the ultra-violet. This comparison, however, was made with the metallised etalon, before the introduction of dielectric coatings.

1.3. Molecular Applications of Interferometers.

Apart from the present project (8), the only reported case of the use of an interferometer to ~~resolve~~ examine the ultra-violet spectra of a molecule is that of Kadesh, Moldenhauer and Winans (9), who employed a Fabry Perot etalon, crossed with a 21 ft grating, to resolve the ultra-violet bands of the diatomic molecule thallous chloride. Although giving little experimental detail, they stated that they were able to measure the frequencies of rotational lines to an accuracy of 0.01 cm^{-1}. Interferometers are now, however, being widely used in the infra-red region.

The use of interferometers in ultra-violet work poses several problems. Firstly, the instrument should be capable of resolving the structure of vibronic bands. As already intimated, interferometers posess a greater potential in this respect than other high dispersion instruments. Then, the frequencies should be determinable over a wide range of frequencies; a typical absorption band may extend over a range of 300 cm^{-1} and a band system may extend over several thousand cm^{-1}. Clearly, to minimise the not inconsiderable labour of calibration of a spectral region, as many bands as possible should be covered with one setting of the optics. The calibration should be adequate to obtain frequencies to high accuracy, of the order 0.001 cm^{-1}, since fringes themselves can be measured to this order of precision. Finally, the problem of overlapping orders must be overcome; this is much more of a problem with molecular spectra than is the case for atomic fine structure studies. In addition, the continuous background employed in absorption must not be allowed to blur out the absorption fringes.

Work has been carried out at University College, London since 1953, which has successfully overcome the problems outlined above. Using an interferometric technique developed by Poole, Stace (5), and Raynes (6) and a method of reduction devised by Poole and Raynes (6), rotational frequencies have been measured in several bands of the near ultra-violet spectrum of formaldehyde to an accuracy (in favourable cases) of about 0.003 cm^{-1}, and better. The problem of overlapping orders has been overcome by making use of channelled spectra, the occurrence of which was first noticed by Gehrke and Reichenheim (10), and which have been used somewhat infrequently since then (7).

Stace found that suitable channelled spectra could be obtained in the 3000 Å region by crossing a quartz Lummer plate of free spectral range about 1.1 cm^{-1}, with a two-prism Littrow spectrograph whose resolving power was of the order 75,000. He photographed the A_2 band of formaldehyde, (3260 Å, the band notation is described on p. 107) and measured some 150 fringes. He found that good resolution was obtained even in the congested central region of the band. Although the theoretical resolving limit of the Lummer plate in the region of the A_2 band is 0.04 cm^{-1}, the closest lines resolved by Stace were about 0.1 cm^{-1} apart; the discrepency was attributed to the natural line width of the lines themselves. He calculated that their Doppler width at 20°C was 0.07 cm^{-1} and that the width due to pressure broadening was 0.013 cm^{-1} at 20 mm pressure. In addition, there was some contribution to the line width from the grain of the photogrphic plate.

Together with the instrumental line width, these effects give a resolving limit of a little over 0.08 cm^{-1} which agrees well with that observed experimentally (in the present work, lines 0.085 cm^{-1} apart have been resolved). He also estimated that the lines themselves could be measured to an accuracy of 0.02 cm^{-1} and concluded that the limiting factor was his inability to control the temperature of the Lummer plate to within the 0.05°C which he considered necessary.

Raynes refined the instrumentation and in particular was able to achieve a degree of temperature control well within this limit. He photographed the formaldehyde spectrum over a much greater range than Stace was able to, from 3286 Å to 3083 Å, and calibrated the region using 15 standard iron lines spread over the range. Although he obtained absorption spectra suitable for measurement of eight bands, B_1, A_2, C_1, E_0, B_2, A_3, F_0 and E_1, he made a detailed investigation on only one of them, the A_2 band. He measured about 4200 fringes in this band, from which he obtained 789 frequencies. For those frequencies for which five or more fringes were measured, 368 of them in all, he made a statistical analysis of the standard errors and found an almost normal distribution with the median at 0.0035 cm^{-1}; he took this figure to give the average accuracy of the frequencies he measured. This claim has since been substantially justified in the rotational analysis of his frequencies, largely accomplished manually by Poole and concluded, with the aid of an electronic computer, by the present author. This work is reported later in this thesis.

1.4. The use of computers in spectroscopy.

The increased availability of high speed electronic computers has, in recent years, greatly increased the scope of spectroscopic investigations over that envisaged some twenty years ago. At two extremes of application, it is now possible both to process large amounts of data (frequency measurements etc.), and to attempt large scale calculations of a, strictly theoretical nature. In the present work, the first type of application has been widely used, while certain theoretical investigations of medium complexity have been programmed. A survey of the uses to which a Ferranti 'Mercury' computer of the University of London Computer Unit, has been put will illustrate the applicability of computing techniques to the experimental side of spectroscopic studies; the theoretical possibilities are too diverse to be discussed here.

The first application of computing techniques to a spectroscopic investigation is in the conversion of measurements into frequencies. In the rotational structure of ultra-violet or infra-red bands, there are usually large numbers of frequencies to be processed, and, although the conversion formula may be quite trivial, the work soon becomes arduous. In the present work, tens of thousands of fringe measurements have had to be processed using a calibration formula that is quite complex. Even so, work which would have involved many months if attempted manually, has needed only a few hours actual computer time. This makes possible the detailed investigation of many more bands of a spectrum where before, selection of the bands more likely to be of interest had to be made. The possibilities of computational errors are, at the same time, greatly reduced.

Once the list of frequencies of any one band has been obtained, they must be analysed. A full scale rotational analysis of a vibronic band of an asymmetric rotor is greatly facilitated using the computer. The procedure found to be highly successful with the bands of the prolate, near-symmetric rotor, formaldehyde, is as follows. After a preliminary rough analysis of the band, approximate values for rotational constants may be obtained. The spectrum may then be computed using these constants and the calculated frequencies compared with the observed spectrum. If the constants are not too poor, it is a simple process to analyse the rest of the band by noting the deviations between the two sets of figures. If the assignments are correct, the deviations should fall on smooth curves when plotted against a suitable coordinate, and any singularities which may occur due to perturbations are readily recognised. When the band has been completely analysed, i.e. when the assignments of the frequencies have been completed, those frequencies that are singly assigned (and are therefore most suitable for numerical analysis) comprise a list of data now used in a programmed least squares procedure to derive refined rotational constants. The two computing operations have been successfully programmed and are discussed at length later in this thesis. Both involve calculations of a fairly complex nature; in particular, both call for the computation of energy levels for an asymmetric rotor involving diagonalisation of matrices which, though relatively simple, can be of order 20 or so. The second process mentioned involves, further, the inversion of a matrix of order up to 25. It would be almost impossible to attempt either of these operations without access to a computer. As an aid to analysis, asymmetric rotor intensities have also been computed and these require operations of similar complexity. A final step in such an investigation, although not attempted in the present work, would be the determination of molecular geometries from the rotational constants derived from the analysis.

As a long term aim there remains the possibility of almost complete automation of rotational analyses in an analogous manner to that already achieved in the field of X-ray crystallography. Several steps in the chain have already been accomplished, of which the present work contributes a part. The first requirement would be the automatic scanning of the spectrum and recording the results in a convenient form for input to the computer, i.e. on paper tape. This has already been accomplished in certain fields, notably in in the far infra-red work developed at the National Physical Laboratory (11), where the output from a continuously operating Michelson interferometer is recorded automatically and processed by Fourier transformation to deliver the rotational frequencies. Similar work is being developed by Jacquinot and co-workers (12) for use in the visible and ultra-violet regions. Complete analysis and constants determination in one continuous process has already been used for simple diatomic molecules. On extending this to more complex molecular spectra, the programme would have to be generalised to a large degree to take account, for example, of all possible perturbations, but since such a process can be performed manually, it must also be possible to programme it for a computer. In the present work it is performed in two stages as discussed earlier, with a relatively trivial intermediate analytical stage, performed manually. A similar technique has been programmed by Broderson and Richardson (13) for the much more simple case of the symmetric rotor. The present work is believed to be the furthest advanced computational treatment of the analysis of the rotational structure of vibronic bands of a slightly asymmetric rotor; it should however be applicable up to quite a high degree of asymmetry.

A survey of the literature on the application of computing techniques to spectroscopic calculations shows that a great deal of duplication has already been made. As an example, there are at least six papers dealing with the computation of reduced energies for a near-symmetric rotor. They all perform essentially the same function and differ only slightly in approach. In fact most of them are concerned with the calculation of coefficients in a series expansion that has only a limited application in any case : for a molecule with an asymmetry parameter b, as small as-0.007 (as is found, for example, for some of the formaldehyde levels), the various series expansions are useless over a large part of the J,K field. Since computers are so readily available now, it would seem obvious to allow the computer to perform the complete calculation in the manner described later in this thesis.

There is a case for some standardisation of programmes of general applicability to spectroscopic problems, as has been partially achieved in the field of X-ray crystallography. The main obstacle to this is the wide variety of computers in use, and the diversity of their programming languages. Some progress is being made in devising a comprehensive language and, if such a language can achieve international acceptance, it should help to keep wasteful duplications to a minimum.

1.5. Rotational analyses of polyatomic molecules

The highly complex nature of the rotational structure of vibronic bands of polyatomic molecules has deterred workers from attempting thorough analyses until quite recently. Indeed, since the first such analysis by Dieke and Kistiakowsky (14) in 1935, of the near ultra-violet transitions of formaldehyde, no work of comparable complexity was reported until the work of Ingold and King (15) and of Innes (16) in 1954, on the 2500 Å system of acetylene. A review of the early work on rotational analyses was given by Sponer and Teller (17) while Robinson (18) has reviewed the field since then and up to quite recently (1960). A brief review of some of the more interesting analyses from the point of view of the present work is given below. A detailed review of the formaldehyde spectrum, which is the subject of the present work, is deferred until chapter 4.

By far the largest number of polyatomic molecules studied have been triatomic molecules. Besides those that are stable under normal conditions, several molecular ions and free radicals have been studied; many of these are isoelectronic with more stable molecules and several interesting correlations have been found (see ref. 18). Since the arrangement of atoms in a molecule is largely determined by the electrons forming the bonds, excitation of an electron from one orbital to another of a different type can have a radical effect on the arrangement of the atoms, and can, indeed, alter the overall shape of the molecule. The first molecule for which this effect was postulated was carbon disulphide (Lieberman (19)) where the molecule was believed to change from a linear structure to a symmetrically bent one on electronic excitation. Since then the phenomenon has proved to be relatively common, at least for the smaller polyatomic molecules. A similar effect was demonstrated for hydrogen cyanide (Herzberg and Innes (20)). The reverse effect, i.e. from bent to linear on excitation, has been demonstrated for the radicals NH_2 (Ramsay (21)) and HCO (Herzberg and Ramsay (21)).

Of the more complicated molecules, with four or more atoms, formaldehyde was the first to be subjected to detailed analysis (14), as detailed above. Subsequent investigations on the spectrum by Brand (23) and Robinson (24) have demonstrated, on purely vibrational arguments, that the molecule changes from a planar structure in the ground state to a pyramidal one in the first excited state; this invalidated certain of Dieke and Kistiakowsky's assumptions in their paper. Rotational analyses of some of the formaldehyde bands by Robinson and di Giorgio (25) and (26) have been referred to, but as yet few details have been given; however, an interesting part of this work is that the transitions to the triplet excited state have been investigated in detail, and this constitues the first analysis of such a state in a polyatomic molecule.

The 2100Å to 2500Å system of acetylene was investigated under medium resolution by Ingold and King (15), and under high resolution by Innes (16). Both concluded that the molecular configuration changed from linear in the ground state to a trans bent structure in the excited state. The interesting molecule propynal, $H\cdot C\vdots C\cdot CHO$, which bears a resemblance to both acetylene and formaldehyde, has recently been studied by Brand, Callomon and Watson (27); in its spectrum, all twelve fundamental vibrations appear and give rise to type A, B, and C bands. Some of the bands are being investigated under high dispersion at the present time (28).

The ammonia spectrum in the vacuum ultra-violet was studied by Benedict (29), who concluded that the excited state was planar. A recent, more detailed analysis by Douglas and Hollas (30) of six perpendicular bands in the region 1400Å to 1689Å has confirmed this conclusion.

Several large molecules with a benzenoid structure have recently been investigated under high resolution. For benzene itself, the true 0-0 band of the 2600Å system is forbidden and does not appear in the vapour spectrum. The false origin of the spectrum, which has one quantum of a planar carbon bending vibration in the excited state, is being studied at the present time by Callomon, Dunn and Mills (31). The large mass of the molecule causes the rotational constants to be small, and therefore ensures that a large number of rotational energy levels are populated (J and K up to 80 and more). Consequently, a band consists of a very large number of transitions, (20,000 or more) restricted to a relatively short frequency range (about

80 cm^{-1}) so that the task of identifying individual transitions becomes impossible. The procedure for analysis is, therefore, (in common with that for the rest of the molecules listed below) one of computing the expected band contour using assumed rotational constants, and comparing this with the observed spectrum. The computation involved has been programmed for an electronic computer by Mills (31); this has been facilitated by the fact that benzene is a symmetric rotor.

A similar approach is being made to the molecules mono- and para di-fluorobenzene by Dunn (32). Since both molecules have quite a high degree of asymmetry, the computation of energy levels and intensities is a much more complicated procedure than for benzene, and can only be done on a computer. Aprogramme written by the present author (described in more detail on page 309 of this thesis) to calculate the frequencies and intensities of the transitions involving J and K $\leqslant$ 40 (the present limit of the programme), and another which computes the frequencies only, up to J and K = 100, have been used in this work. The computed material has been, and is being, sorted manually by Dr. Dunn, to plot the band contours.

The spectrum of naphthalene vapour was studied by Craig, Hollas, Redies and Wait (33), under high resolution and they were ab able to determine the direction of the transition moment by comparison of calculated and observed band contours. As a final example of the rotational analysis of the spectrum of a large molecule, the near ultra-violet spectrum of the molecules pyrazine, pyrimidine and pyridazine have recently been studied by Innes and co-workers (34,35), with a high dispersion instrument.

The technique of analysis used for these last few molecules depends on comparison of the detailed computed band contours with the observed contour. Clearly, the more detail that is resolved in the spectrum, the easier will be the task of fitting a computed spectrum to the structure. Thus, although it may be impossible to resolve individual lines with a high dispersion instrument, no matter how high the resolution, more and more detail should become evident at very high resolving powers. The potentialities of interferometric techniques to this problem are obvious.

1. 6. Aim of the present work.

The success achieved by Stace and Raynes in the resolution of some of the bands in the formaldehyde spectrum has encouraged further work in this field. The instrumentation was set up and used successfully by the two earlier workers and has been taken over by the present author. Apart from a few minor improvements, the main contribution of the present work on the practical side has been the reconstruction of the apparatus on a much more stable base, and its total enclosure with a highly insulating material.

The formaldehyde spectrum has several features which encourage a complete rotational analysis of as many bands as possible to be made. In the first place, some doubt has been cast on the vibrational assignment of some of the bands (36), and rotational analysis is the only means of setting these points. Secondly, since the excited state of the electronic transition has been shown conclusively, (23) and (24), to be pyramidal with a low potential barrier to inversions, it affords the opportunity for study of the effect of such an inversion on the rotational energies of the molecule. Also, since the rotational constants of the ground state cannot be determined adequately from the microwave spectrum (see chapter 4 of this thesis), the ultra-violet spectrum is the best source of this information at the present time. The bands themselves are quite well separated from one another, and the individual frequencies are resolvable with a high resolution instrument, such as that used in the present work. Work has therefore proceeded on some of the bands.

The continued development of the interferometric technique for investigation of molecular spectra is important, since it is in this field that the largest advances in resolution are expected to lie. The Lummer Plate used in the present work has a resolving power comparable with the best of present-day gratings, and therefore represents a first stage in the attainment of very high resolution. Further advance will probably be made with an interferometer of different design from the Lummer Plate, probably with the etalon coated with suitable multi-layer coatings, or perhaps with some new design of interferometer. In the meantime, until such instruments become available, the present and previous work (5) and (6), has shown that the high resolution of, and the high accuracy in measurement attainable with, an interferometer can be applied with great success to the study of molecular absorption spectra.

Finally, the technique of analysis of such spectra, from measurement to extraction of constants, has been almost completely programmed for the computer as outlined in the preceding section.

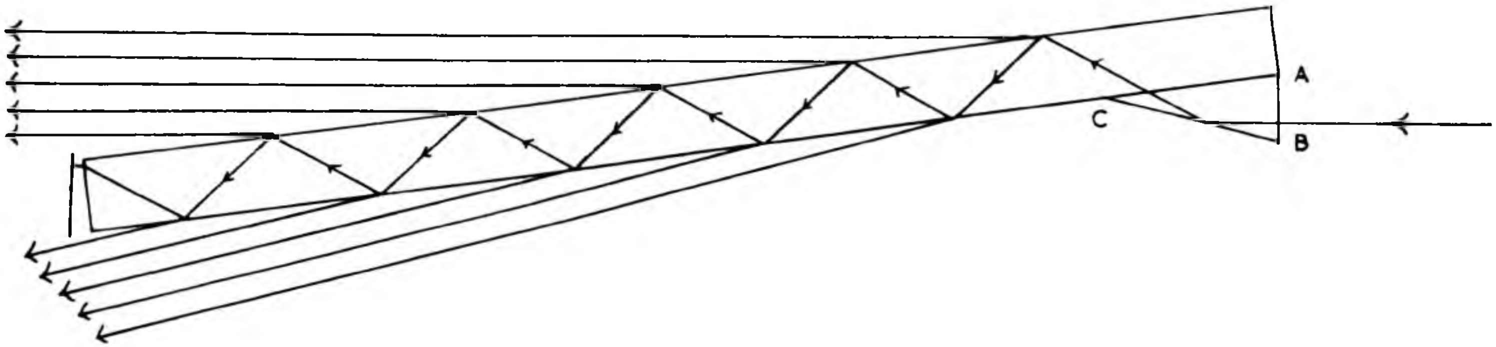
CHAPTER 2

EXPERIMENTAL PROCEDURE

FIGURE 2.1.

SECTION THROUGH THE LUMMER PLATE

SHOWING SUCCESSIVE INTERNAL REFLECTIONS OF A SINGLE INCIDENT LIGHT RAY



2. 1. Introduction.

This chapter is largely a summary of parts 1 and 3 of Raynes' thesis (6), together with an account of some recent improvements to the instrumentation. Raynes discusses in detail, the optical properties of the Lummer plate, and the background to fringe formation. Here, only those aspects are discussed which are relevant to accurate frequency determination in the interferograms which illustrate this chapter.

2. 2. The Lummer Plate Interferometer.

The interferometer is the basis of the experimental technique. It consists of a thin, parallel sided slab of quartz, of dimensions 20cm x 2.7 cm x 3.4 mm, cut with the optic axis in the surface and perpendicular to the long edge. It is mounted in a container fitted with levelling screws, the whole being surrounded by a massive brass housing which is lagged to aid further in temperature stabilisation. High quality quartz windows allow light to enter and leave the interferometer while preventing too much circulation of air round it.

Consider parallel light entering the plate by an optically contacted quartz prism, ABC in the section shown in fig. 2.1. After successive internal reflections, light of one particular frequency can be considered to emerge as a series of parallel coherent ribbons of light, differing in phase due to their different paths through the plate. When brought to a focus these ribbons interfere, and, when the path differences between successive beams is an integral number, n, of wavelengths reinforcement will occur producing an interference fringe; n is termed the order of the fringe. Between adjacent fringes, where destructive interference occurs, the intensity falls to a low (though non-zero) value. The sharpness of the fringe in relation to the regions of low intensity at either side, and also therefore the resolving power obtainable from the instrument, is dependent largely on the number of interfering beams combining to form the fringe, in a way discussed in detail by Tolansky (4), Stace (5) and Raynes (6). The Lummer Plate employed in the present work allows 33 internal reflections before the end of the plate is reached. Since, however, the successive beams arising from these reflections are of gradually diminishing intensity, depending on the reflection coefficient of the quartz to air surfaces, the equivalent number of equal beams used is 28 (these figures relate to the region about 3500Å). Using this figure, Raynes calculated that the resolving limit of the interferometer (on the Rayleigh criterion) at 3500Å, would be about 0.04cm^{-1}, that is the resolving power is of the order 700, 000. The fact that absorption lines of formaldehyde differing by less than about 0.085 cm^{-1} could not be resolved is largely accounted for by their Doppler width and by the effects of pressure broadening. In this respect, formaldehyde

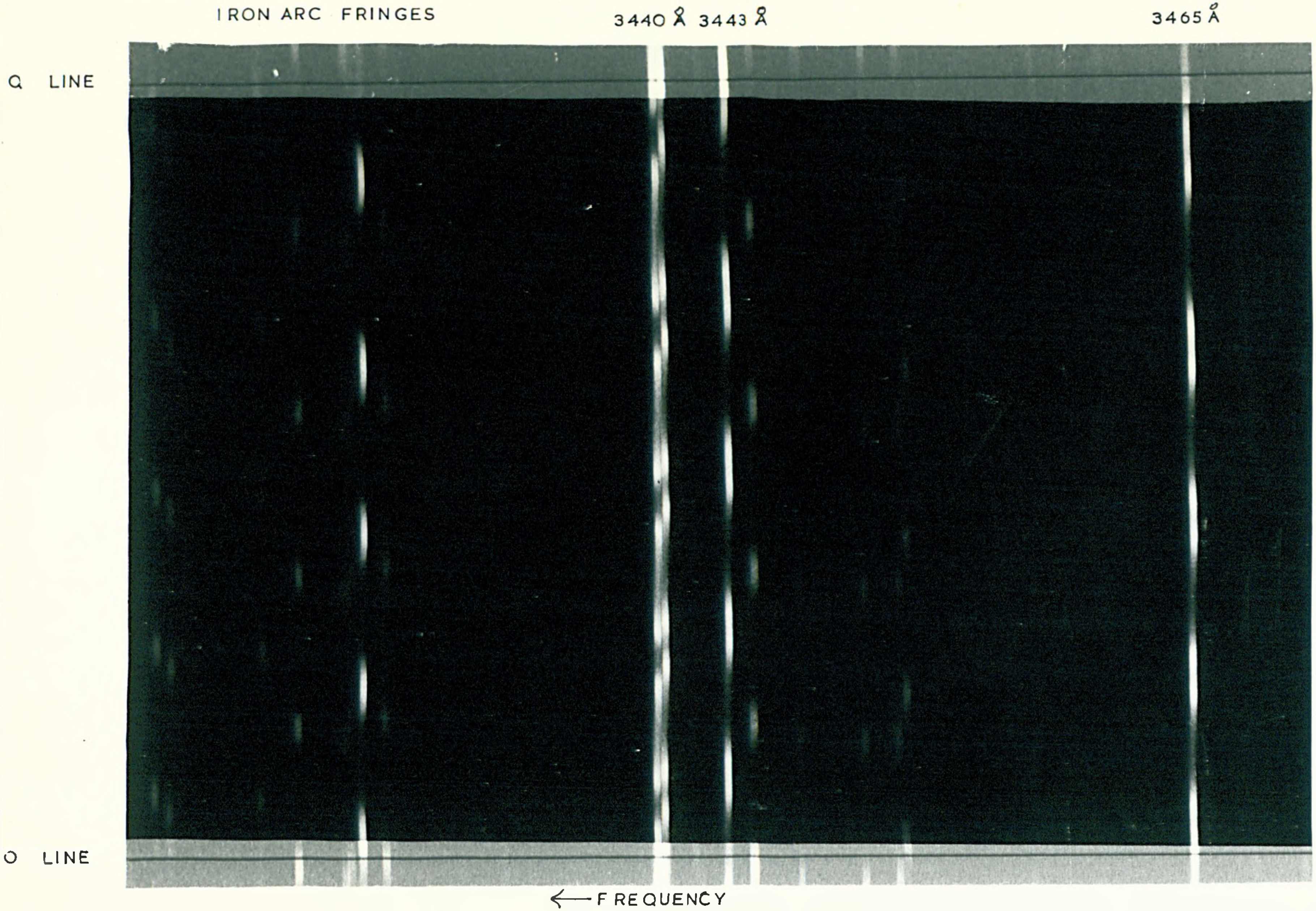


FIGURE 2.2.

is not a good test for the possibilities of the technique.

In order to separate the fringe arrays of different frequencies, the system is focused on the slit of a secondary instrument whose dispersion is in the horizontal direction; in the present instance, this is the two-prism Littrow spectrograph described by Stace (5). The fringe systems of two very close frequencies are then dispersed vertically by the interferometer and horizontally, to a smaller extent, by the Littrow. The situation is shown in fig. 2.2, which is a print from a spectrum of the iron arc in the region of 3445 Å. The Littrow dispersion is of the order 0.02 mm $/\mathrm{cm}^{-1}$ on the plate (note the print is an enlargement of some 16 x linear magnification), while the interferometer has a dispersion of about 17 $\mathrm{mm}/\mathrm{cm}^{-1}$. Shown on the print are two very closely spaced doublets at 3440 Å. The two members of each doublet are separated by about 1/40 Å $(\sim \cdot 2\,\mathrm{cm}^{-1})$ while the spacing between the doublets is about 1/2 Å $(\sim 4\,\mathrm{cm}^{-1})$. Clearly the horizontal ~~resolution~~ separation between the two doublets could be improved by decreasing the slit width used; in the case of fig. 2.2, this was 50 μ. Such improvement is effected down to slit widths of the order of 10 μ ; lower than this, the effects of diffraction ~~round the slit edges~~ vitiate any further improvement. Prints similar to fig. 2.2 are used for measurement of the iron fringes where wide fringes are desirable. However, in an absorption band, some 500 to 600 frequencies may be present in the ~~area~~ range covered by fig. 2.2, so there, a slit width of 10 μ is used. Now, at these small slit widths, and when the resolving power of the Littrow is

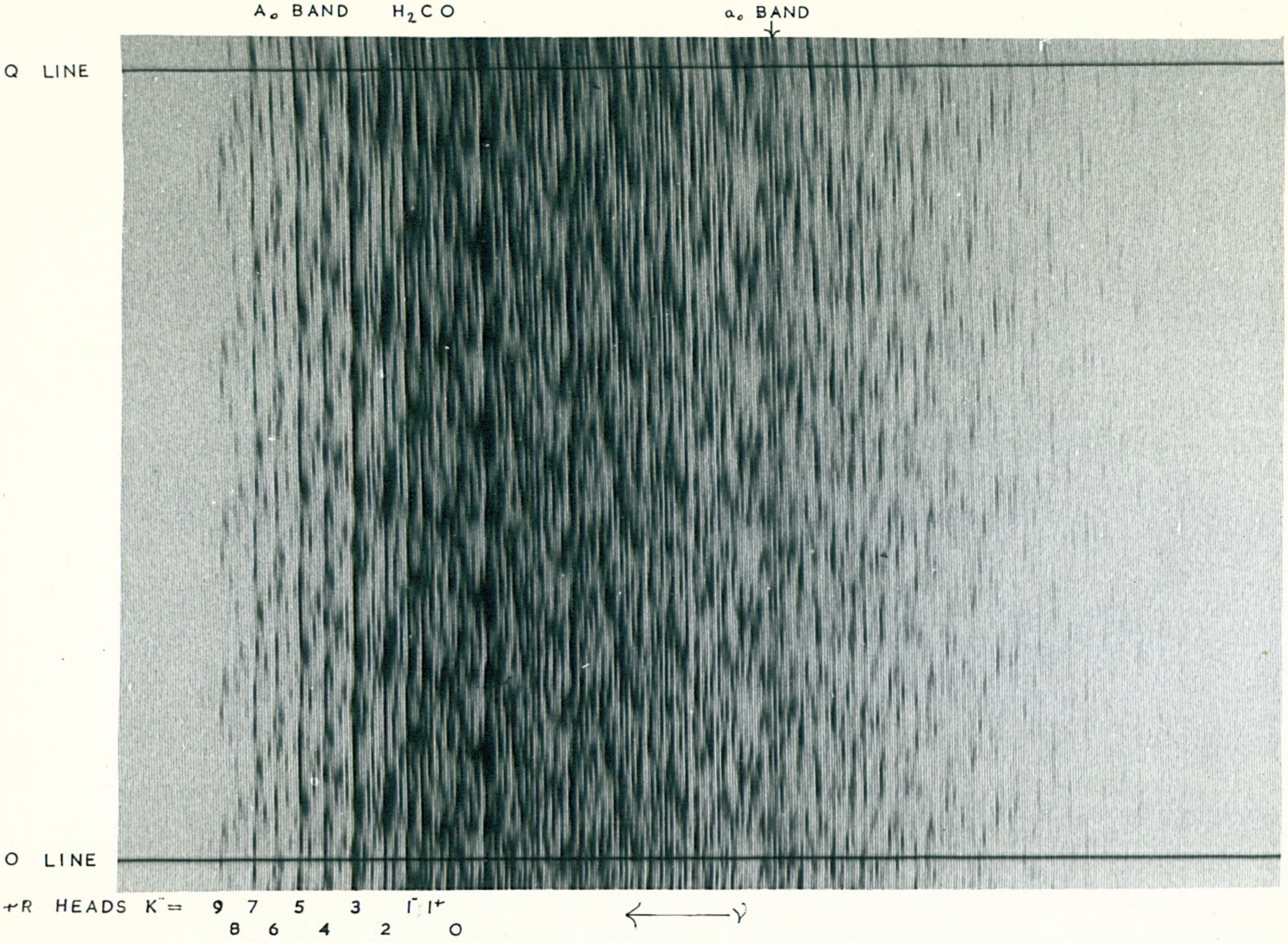

A_0 BAND H_2CO
a_0 BAND
Q LINE
O LINE
$\leftarrow$R HEADS $K'' =$ 9 7 5 3 1^- 1^+
8 6 4 2 0
$\leftarrow \nu$

FIGURE 2.3.

sufficiently large to separate fringes lying beside one another in successive orders, continuous radiation will produce a series of near vertical stripes, or channels, separated by unilluminated lines. Each channel represents a continuous frequency spectrum associated with a particular order of interference, while one channel is separated from the next by the free spectral range of the interferometer, in this case at 3500 Å, about 1.13 cm^{-1}. The channels are seen as the background to fig. 2.3 (which is also a 16 x linear enlargement from a plate). An absorbing substance placed in the optical train results in a series of holes in the continuous channels, and appear in a positive print, such as fig. 2.3, as grey fringes in white channels. The technique thus succeeds in completely separating the neighbouring orders of a complex band.

2.3 The Littrow Spectrograph.

The quality of the prints used for measurement depends to a great extent on the optical quality of the Littrow spectrograph. Its design is indicated in the diagram, fig. 2.5. The dispersion system consists of a Cornu prism in series with the normal Littrow prism, the optics being traversed twice. The resolving power obtained in this way, about 75,000, allows resolution of successive orders making possible the formation of channels. Light entering at the slit is deflected along the spectrograph by the total internal reflection prism, and is collimated by a quartz lens into the prism system. The slit width of 10 μ used in the

3500Å region, allows use of the full aperture of the lens to be made, here f/30, by diffraction ~~round~~ at the slit.~~edges.~~ Such a condition is important when the maximum possible resolution of the instrument is required, as is the case here. The dispersed light emerging from the prism system is brought to a focus at the camera by the quartz lens now used as camera lens. The plates are bent in the camera so that they take up as far as possible, the curvature in the focal field of the camera lens. In fact, some six to eight cms. of the spectrum can be brought to a sensible focus. The optics were designed to minimise lens aberrations and to prevent multiple image formation due to the polarising properties of the crystal quartz optics. In this connection, the inter-prism angle has been calibrated, and is set to the optimum value for the wavelength range under consideration. The other adjustments of the spectrograph: prism-table orientation, focusing, and camera tilt, are all adjusted photographically. In this way optimum adjustment can be obtained; in fact the focusing can be adjusted to well within the standards of the manufacturer of the original Littrow spectrograph.

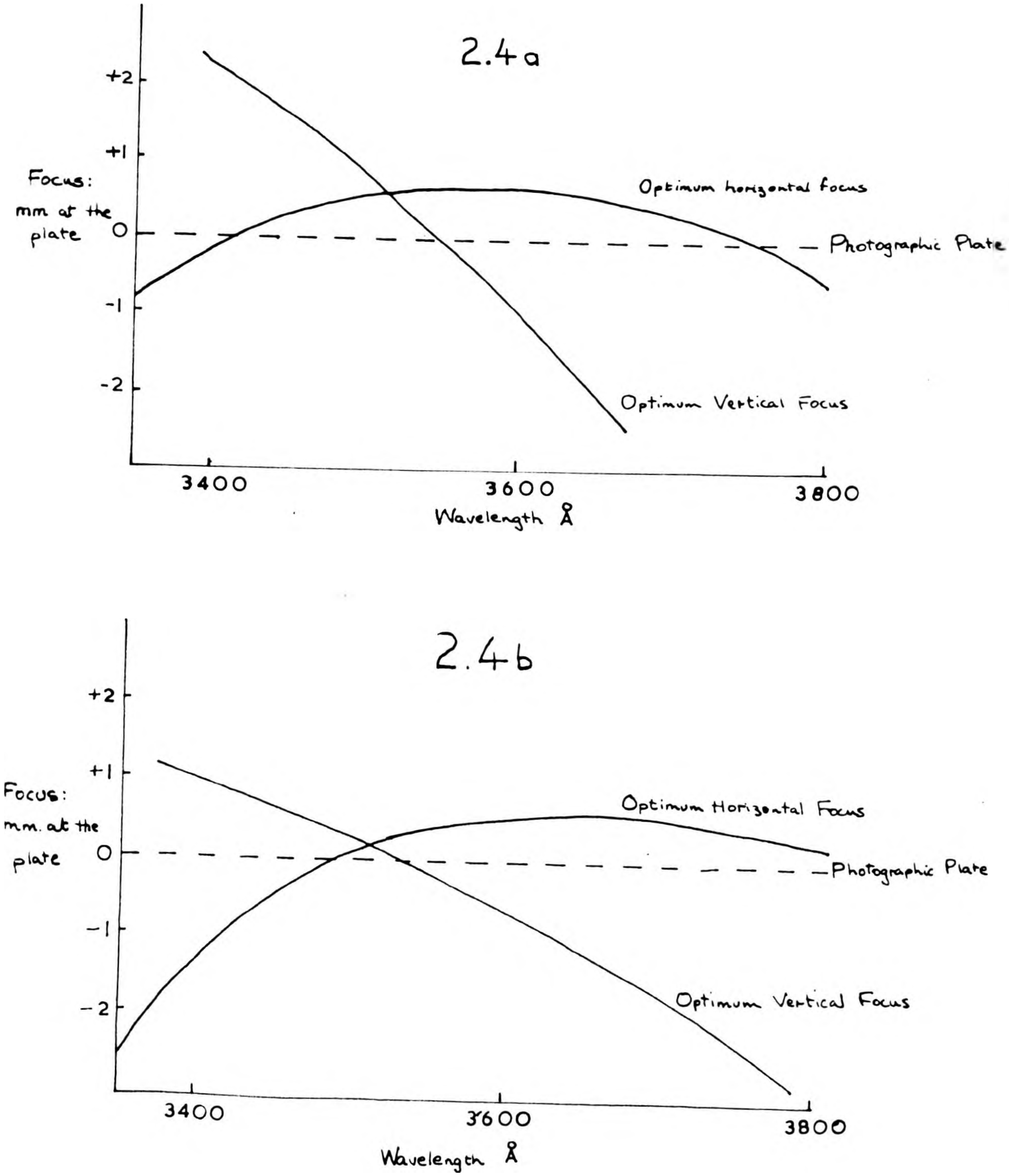
In order to minimise the effect of flaws, in the optics, the prisms and quartz lens have been examined in all possible positions, so to determine the best optical path through them. Since a band of some 20mm. vertical height is used through the prisms, and the prisms themselves have a usable height of 50mm., there are about five positions, differing in vertical height by about 5mm., through which the optical train might pass. A graticule consisting of a series of fine horizontal lines ruled on a piece of perspex, was placed as close as possible to the slit and used to examine the quality of the vertically focused image, while channels were used to study the horizontally focused image.

In the first place, certain aberrations could be seen which were directly attributable to the particular path through the optics, that is they moved up and down with the path. The position of optimum quality was determined by permutation of all possible variables; the vertical height, rotation of the quartz lens, and finally, inversion of the Cornu prism and its replacement by a similar prism. The optimum was found with the optical path traversing the middle of the prism system. This result might have been expected since in this position, the optical path is passing through the lens in a path as nearly symmetrical, geometrically, as is possible in such a train. However, a less symmetrical path might well have been found to be the best since the optics were worked to the best possible quality in the visible. (green light is used for testing) thus ignoring inhomogeneities significant in the ultra-violet but not in the visible. The effect of different orientations of the quartz lens was found to be of minor importance, though two optimum positions were found differing by π.

A second discovery arising from this work was that the system had different horizontal and vertical focus positions. By taking a focusing traverse, the best horizontal and vertical focus positions across the plate could be mapped with, the result shown diagrammatically in fig. 2.4a. The ordinate here corresponds to

FIGURE 2.4

FOCAL FIELDS OF THE LITTROW LENS



the setting of the focusing screw. In previous work, the spectrum was focused and the camera retilted until the optimum horizontal focus position was obtained, the broken line in fig. 2.4a. It was noted by Raynes that his two reference lines, the O and Q lines seen in figs. 2.2 and 2.3, were focused much better at one end of the plate than at the other. This effect is now explicable by the two distinct types of focus. In subsequent work, the camera has been tilted to give a better compromise, shown as the broken line in fig. 2.4b. This results in slightly better focused O and Q lines, while not seriously affecting the quality of the channels.

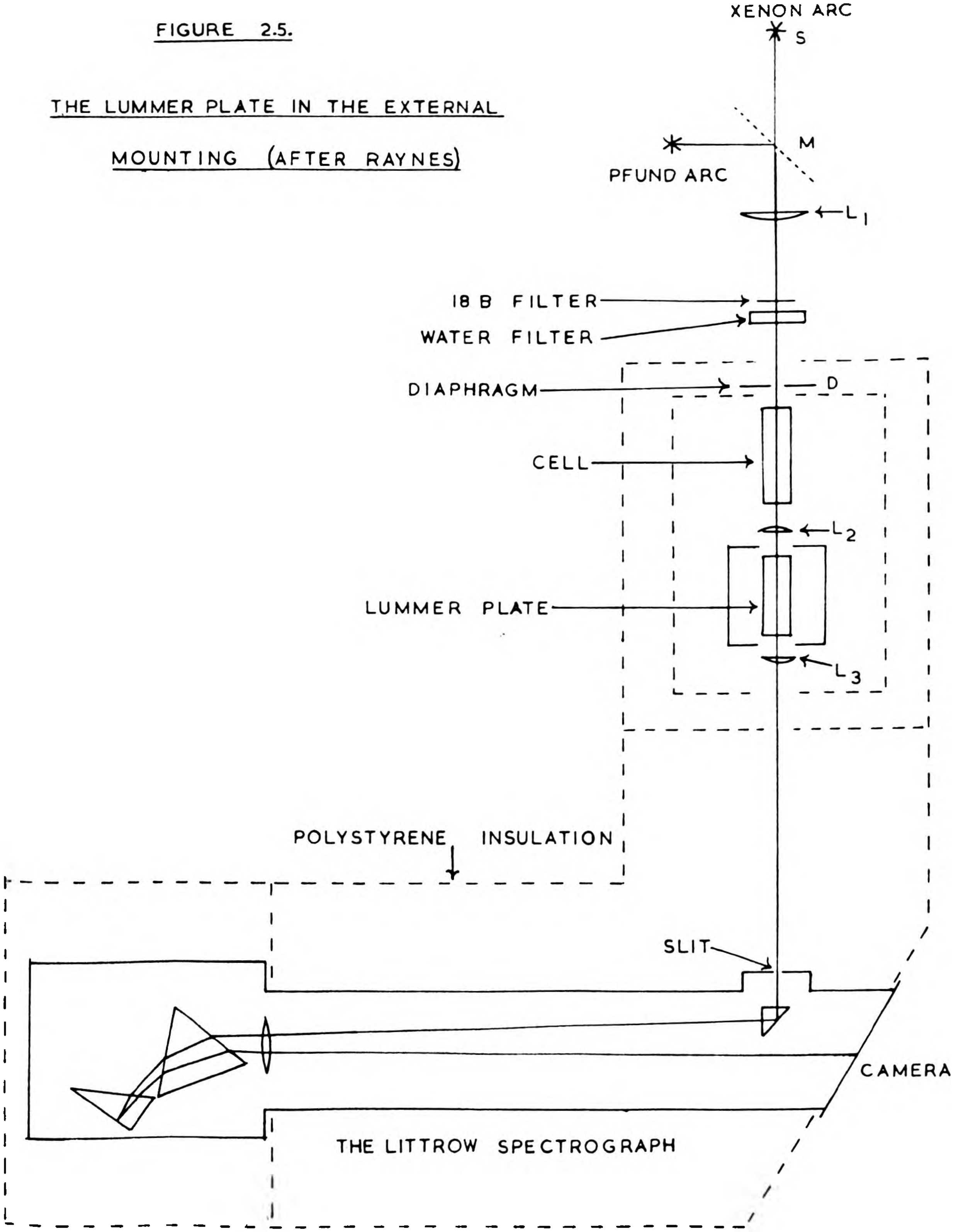
2.4 The External Optics.

The experimental arrangement of Lummer plate, auxiliary spectrograph, source and lenses is similar to that described by Tolansky (4) and called by him, "the external parallel beam mounting". A diagram is shown in fig. 2.5. The source S is focused on a diaphragm, D, with horizontal jaws, by means of a plano-convex quartz lens. In the earlier part of this work, the light source used was a 350 watt, 2 atmosphere xenon arc and was started with a tesla coil. Recently, a 500 watt, 4 atmosphere lamp has been used giving a corresponding increase in light output. A high frequency starter has been incorporated in the circuit for use with this high pressure lamp. The quartz lens L_4 is positioned so that an image of the source, enlarged 1.5 times, is obtained on the diaphragm jaws. The jaws are open (vertically) from 1 to 2 mm. so that only

light

FIGURE 2.5.

THE LUMMER PLATE IN THE EXTERNAL MOUNTING (AFTER RAYNES)



from the relatively stable central portion of the arc is used. A water filter and a Kodak 18B filter are usually used between the source lens and the diaphragm, the first to remove infra-red light and the second to remove visible from the light entering the Lummer plate.

The light is then collimated by a quartz-flourite achromat, L_2, so that parallel light enters the Lummer plate housing. On leaving, the coherent beams are focused on the Littrow slit by a fused silica-lithium fluoride projection lens, L_3, also an achromat.

Three diaphragms are used on the Littrow slit for various purposes. One allows a continuous range of slit lengths to be employed and is used when many spectra are required on the same plate; in particular, for the alignment operations such as focusing, etc.. The second has a vertical slot which coincides with the slit, across which are stretched horizontally, two very fine quartz fibres, some 8 mm apart. They are mounted as close as possible to the slit and when photographed, they produce the shadows across the plate which are used as reference lines (called the O and Q lines), seen in figs. 2.2. and 2.3. The third diaphragm holds a perspex graticule which consists of a strip on which several finely ruled lines have been ruled. It has been mentioned earlier in connection with the determination of vertical focus; an account of its more important use is, however, deferred until the next chapter.

Until recently, the Littrow, and the optical benches holding the external optics including the Lummer plate, were mounted on separate wooden tables. Inevitably, these moved from time to time and the movement disturbed a critical line-up, sometimes during the exposure of an important plate. The apparatus has just been rebuilt* in a much more stable condition. The external optical bench (previously there were two) has been bolted firmly to the Littrow spectrograph, preventing relative movement in both the vertical and longitudinal directions. These two arms are mounted in three places on three concrete blocks, the latter being held firmly together by angle iron. The external optical bench contains all the external optics as far as the source lens; the whole optical train is thus held rigidly in position. A framework has been built round the apparatus and has been so designed that it is completely independent of the critical part of the apparatus which is therefore isolated and protected from mechanical shocks. The framework has been covered with a ½ inch layer of polystyrene foam, so that the whole apparatus is insulated from small fluctuations in the temperature of the surroundings. The region around the Lummer plate housing has been doubly insulated since it is here that strict temperature control is most important.

* This part of the work has been done in conjunction with Mr. D. C. Lindsey.

2.5. Lining up the Apparatus.

Realignment of the optical components should be carried out before a critical series of spectra is taken so that optimum conditions may be obtained; in particular, so that maximum light from the source is obtained in the spectrograph to keep exposure times to the minimum. A major realignment has recently been undertaken*; the general principle governing such a procedure will be given now although it is, to some extent, an empirical procedure.

The Littrow must first be adjusted so that green light is obtained in the centre of the camera field when the slit is illuminated by white light. By placing a small light bulb at this position in the camera, a cone of green light emerges from the slit. The external optical bench may then be aligned along the axis of this beam with the aid of the projection lens, while a final adjustment may be made by altering the orientation of the total internal reflection prism behind the slit of the Littrow, so that the projection lens is symmetrically illuminated. With the interferometer removed, the collimator and source lens may be aligned without much difficulty. The green light is brought to a focus by the source lens and it is a simple matter

*This part of the work has been done in conjunction with Mr. D.C. Lindsey.

to place the central region of the source at this focus. On striking the xenon arc, the Littrow slit should now be illuminated symmetrically although the height may not be correct due to the absence of the Lummer plate. Insertion of the interferometer into its correct position in the optical train should have no lateral effect on the illumination of the slit; if it has, the plate is not correctly aligned along the optical axis. Shadows produced along the plate by vertical masks at the sides of the source lens, should run symmetrically down sides of the plate; if they do not, the plate should be tilted sideways. These operations completed, the limit of adjustments possible with visible light has been reached, the rest must be done photographically.

The spectrograph should now be adjusted so that near ultra-violet light at about 3500Å can be photographed; it is for this region that most is known at present about the optimum plate quality to be aimed for. After adjustment of the inter-prism angle, and the prism table orientation (these two adjustments are calibrated, sufficiently accurately), a rough estimate of the correct camera tilt is made from previous knowledge, and a focusing traverse is undertaken, first at widely spaced intervals then at small intervals. With the 5" x 4" plates used at present, sixteen iron arc spectra may be photographed one below the other. Inspection gives a curve of optimum horizontal focus such as the one in fig. 2.4a. In previous work, the camera was tilted until this curve took up the symmetrical position with respect to the photographic plate shown in fig. 2.4a. In view of the work mentioned earlier which demonstrated the differential horizontal and vertical focusing, the camera is now tilted so that the focus curve takes up the position shown in fig. 2.4b. In this way the best compromise is reached. Finally, the Littrow slit should be aligned vertically by photographing iron arc spectra with a long slit so that successive spectra just touch one another, and then making any adjustment necessary. This done, the spectrograph is in optimum adjustment for the wavelength region chosen.

The components of the external optics should be checked to make sure that they are at their correct distances apart, (these distances between the source and the diaphragm are wavelength-sensitive since the source lens is a non-achromat).

The diaphragm plays an important part in the production of suitable spectra on the plate; its action is described fully by Raynes (6), after Tolansky (4). In essence, it serves to prevent light of unwanted wavelength from reaching the spectrograph, and to ensure the separation of the extraordinary and ordinary rays by the Lummer plate. (This separation occurs in consequence of the different refractive indices of quartz for the O and E rays, and the direction of the optic axis in the Lummer plate. The E-ray spectrum is always used since for the resolution is better.) The light which enters the spectrograph consists of the E-ray light of the wavelengths under observation, some 200 Å to 300 Å in width, and a similar band of O-ray light whose long wavelength limit lies just below the short wavelength limit of the E-ray band. No light of other wavelengths enters the spectrograph so that stray light is kept to a minimum (in fact it just arises by scattering of the unwanted O-ray spectrum from the body and walls of the Littrow, and is then further reduced by suitably sited baffles).

The jaws of the diaphragm therefore determine the precise limits of the E and O-rays and must be adjusted up or down until the required E-ray wavelengths enter the spectrograph. This will probably necessitate the vertical repositioning of the source until the correct central portion of the arc passes through the diaphragm. After a final horizontal traverse of the arc to establish its correct position for maximum intensity, the optical system should be ready to produce channelled spectra.

A final adjustment which might prove necessary after a major realignment is the tilt of the Lummer plate. The tilt from horizontal should not exceed about 1°, to avoid loss of resolving power, nor be less than about 1°, to prevent undue loss of light. The adopted compromise angle which has proved very satisfactory is about 1.5°; this is then the angle of emergence of beams in the direction of the centre of the

Littrow slit. In consequence of the non-linear (quadratic) vertical distribution of fringes, the tilt also affects the number of fringes of any one frequency appearing between the O and Q lines; it has been found convenient to allow four to five orders in the OQ range, and the positions of the quartz fibres have been chosen to achieve this for the adopted tilt mentioned. Consequently, the tilt adjustment is complete when about 4½ orders are recorded in the OQ range.

2.6 Temperature and pressure control.

Raynes (6, p. 117) gives the first comprehensive treatment of the effect of temperature and pressure variations on the fringes obtained from a Lummer plate. He shows that a significant fringe shift~~s~~, equivalent to about 0.002 cm^{-1}, will result from a temperature change of 0.01 $^{\circ}$C, or from a pressure change of 0.3 mm Hg. Since exposure times of several minutes are usually used, such changes are quite possible unless stringent precautions are taken; especially since light sources producing a large amount of heat are used not far from the Lummer plate.

To deal with temperature effects, the whole apparatus has been thermally insulated, as described earlier in this chapter, and the room containing it is thermostatted to about ± 0.1°C. It has not been found practicable to thermostat the room during the summer months, except possibly at an uncomfortably high temperature; in consequence, critical runs are made only outside this period. While a series of important plates is being taken, the xenon arc is run continuously for 24 hours prior to commencement, and left running until the series is terminated. The temperature of the Lummer plate is followed in two ways. A calibrated germanium resistor is contained in a brass block attached to the Lummer plate mounting. The resistance of the germanium is determined by means of a bridge, the current through the resistor being kept as low as possible to avoid self-heating. Such measurement is adequate to indicate temperature fluctuations, although, since there is no direct contact between the plate and the resistor, there is an inevitable time lag. No attempt is made to use any observed temperature drift to correct the fringe positions; instead the observed fringe shifts themselves (only partly due to temperature drift) are used to make corrections, in a way to be described later.

Significant fringe shifts can also occur due to pressure variations. Of course, such variation could not be controlled without drastic redesign of the apparatus. A critical series of plates is therefore commenced only after advice from the Government Meteorological Office that the pressure is steady, or drifting only slowly, that fluctuations in excess of a few tenths of a millimetre are unlikely, and that the conditions are likely to remain favourable over several days. Barometer readings are taken throughout the run, and the recorded pressure behaviour throughout is examined afterwards.

With these precautions, very few plates need to be rejected because of fringe shifts between the beginning and end of the exposure of the plate. Shifts between plates, in the course of the few days necessary, are dealt with as described later.

2.7. Manipulation of formaldehyde.

The formaldehyde used in the present work is the same sample as that prepared and used by Raynes. The pure paraformaldehyde in its storage bulb is warmed, and the gas evolved fills the absorption cell by way of the linking vacuum line. After use, the gas is recondensed in the storage bulb, by cooling the latter with liquid nitrogen; repolymerisation rapidly follows. In this way there is sensibly no wastage of formaldehyde and a small sample may be used many hundreds of times. The pressure inside the absorption cell is measured sufficiently accurately, by means of a spoon guage used as a null instrument, the pressure being read on a mercury column in the usual way. Recently, the vacuum line has been duplicated so that normal formaldehyde or deuterated formaldehydes may be studied in rapid succession, without danger of contamination. So far the dideuterated form has been studied in this way; it was purified from a commercial sample by distillation through a CO_2 cooled trap into its final container.

Two absorption cells have been employed in the present work. One, described by Raynes, is 17 cm long made of thick wall pyrex glass and has silica windows at both ends, attached with araldite. It is designed to be readily removable from the vacuum line so that polymerised formaldehyde, which accumulates after a time on the windows, may be removed by warming. This cell is mounted between the collimator lens and the diaphragm. A second absorption cell of similar design but 60 cms in length, has recently been used in order to obtain stronger absorption from the longer path length of formaldehyde, without employing unduly large pressures. When in use, it is situated between the Littrow slit and the projection lens. Although one might expect some disturbance of the coherent beams emerging from the interferometer when using such relatively imperfect optical components in this part of the light path, no serious effects have been observed. In future, however, it would be better to redesign the optics between the source and the diaphragm so that longer path length cells or even multiple reflection cells may be employed in this less critical region.

2. 8. Details of a run.

As will be explained in the next chapter, an absorption spectrum must be associated with a calibration spectrum, which is then carried over to the absorption spectra by calibration check spectra, also explained in the next chapter. For efficiency then, the several absorption spectra required in a given region are taken associated with a single calibration spectrum. In order that fringe shifts from calibration may be kept as small as possible, (to facilitate correction for them), the whole series of plates should be taken in as short a time as possible; in fact, all the spectra may be taken within a few days.

Before commencement, the apparatus should be lined up in the chosen spectral region as described in a previous section. The region will have been chosen to include, in focus, as many as possible of the absorption bands of interest. When satisfactory weather conditions have been forecast, and the xenon arc and room lights have been running for about 24 hours, (as already described), the series of exposures is started. Throughout the course of exposures, the temperature of the Lummer plate housing is taken from the germanium resistance readings. In addition, a check is also kept on the temperature of the immediate surroundings of the Lummer plate housing with a mercury thermometer graduated in 1/20 °C intervals. Pressure measurements are taken from a barometer sited close to the room containing the spectrograph.

There are two main types of plates taken in the course of a run, the absorption plates and the calibration plates. Both are taken with the quartz fibre diaphragm in position over the slit, and this must not be disturbed during exposure of a plate. It has been found desirable to clean the slit after each plate, since the occurrence of a dust streak on a spectrum can lead to subjective errors in measurements over a wide region around it (about one order wide).

The Calibration Plate.

Although only a single plate is used in the calibration procedure, several are taken to ensure that one, at least, is perfect. The iron arc is placed in the position marked in fig. 2.5 so that, with the mirror M in position, it effectively replaces the xenon arc. Exposures are taken with a slit width of 50μ to produce the wide fringes of fig. 2.2. The quartz fibre shadows are produced by a superimposed short exposure of the xenon arc with a 150μ slit. Each plate can contain four spectra of different exposure times so that a sufficient number of iron lines are available at densities suitable for calibration measurements.

The Absorption Plate.

Four spectra are taken on an absorption plate. The first and last are iron spectra taken exactly as were those used for the calibration plate. Their exposure should be sufficient to ensure recording a reasonable number of lines of suitable intensity. These two spectra are those referred to as check spectra, and their use is dealt with at length in chapter 3.

The second and third spectra are absorption spectra. The series of plates should contain a range of absorption pressures to ensure adequate recording of frequencies of widely different intensities. A maximum of 25mm pressure is usually allowed; pressures greater than this tend to hasten polymerisation in the cell, although a pressure of 60 mm has been employed for a special purpose, in part of the present work. Spectra crossed by lines due to dust on the slit, are rejected for the reason given above.

In the latest run undertaken, the series of absorption plates has been duplicated for dideutero-formaldehyde; in all some 20 absorption plates were taken before a satisfactory set was obtained covering all the desired pressures of both CH_2O and CD_2O.

Special Plates.

In addition to the main plates of a series described above, two extra plates must be taken for special purposes which will emerge in chapter 3. The first is a spectrum of the iron arc, taken with a narrow (10 μ) slit, and superimposed on a weak background of a channeled absorption spectrum. When the two isotopic species are being investigated, spectra should be taken corresponding to each. They are used to identify the iron lines with particular channels, and then to identify these channels on pure absorption spectra.

The second plate is taken with a perspex graticule over the Littrow slit, which in this case is very wide, 150 μ. The graticule is illuminated by continuous radiation through the Lummer plate so that for this spectrum, which is now crossed by graticule lines, the same parts of the Littrow optics are used as for the absorption spectra. An iron arc *line* spectrum (i.e. not taken through the Lummer plate) is superimposed to identify the wavelengths photographed. Prints taken from this plate should show the graticule lines as black against a white background; to achieve this over the whole frequency range of the plate two or three spectra with different exposures are taken on the same plate.

The spectra described above are all taken on plates coated with a special emulsion: Kodak Experimental Type V 1036. This emulsion has grain characteristics of Kodak Type III emulsion but is specially treated to reduce reciprocity failure for the exposure times required. This increases its effective speed to compare with that of the Type II emulsion. In the initial lining up, type II a-O plates were used for the less critical work.

2.9. Enlargement and measurement of prints

For measurement, the plates taken as described above, are enlarged some 25 times. The enlarger was built by previous workers and is described in detail by Raynes (6, p.171). The plate carrier is capable of wide adjustment which is carried out to minimise, as far as possible, the combined optical distortions described in chapter 3. Prints not required for measurement are taken on Kodak Double Weight, Glossy Bromide Paper and glazed in a drier after processing. All the prints from which measurements are to be made are photographed on Kodak Bromide Foil Card, which shows no detectable distortion after processing in the recommended manner.

The prints are measured as required, on a measuring board described by Raynes (6, p.173). The vernier can be read to 0.02 mm, i.e. to about 1/10000 of the OQ distance, corresponding to about 0.0005 cm^{-1}, but it is considered that the reading is significant, as representing a setting on a reasonably good absorption peak, to about four times this amount.

CHAPTER 3

CALIBRATION AND DETERMINATION OF FREQUENCIES

3.1. Introduction.

A spectrum taken using the technique discussed in Chapter 2, consists of an interference fringe array with dispersion in two almost perpendicular directions. Consider the print from an absorption spectrum of formaldehyde, fig. 2.3.(opp. p.39). The horizontal dispersion of the Littrow serves to separate the spectra of successive orders into channels, as explained before. The interferometric dispersion is in the vertical direction; the two quartz fibre lines, the O-line and the Q-line, serve to cut off a convenient portion of the fringe array for measurement and evaluation, and they also establish a coordinate domain along the channels, the properties of which are made use of below. As will be explained, the frequency summation is carried out along the O-line (the inner of the two fibre lines on the fringe array).

It can be seen that we cannot calibrate such a two-dimensional spectrum by superposition of a standard frequency spectrum such as an iron arc spectrum, as in more conventional one-dimensional techniques, since the two sets of fringes would obscure one another and render accurate measurement of both impossible. For this reason a given spectral region is calibrated separately on a calibration plate, the conditions of temperature, pressure and optical alignment during the exposure of this plate being chosen as standard conditions.

Subsequent absorption spectra are then locally calibrated against this standard plate, by determining any shifts in the iron fringes due to non-standard conditions. Ideally the shifts should be small, amounting to not more than one-tenth of an order, otherwise slight complications arise in their incorporation in the procedure for averaging frequencies from different plates. From data given by Raynes (6, p.137), shifts of this magnitude would arise from a temperature difference of 0.5°C. or from a pressure difference of 15 mm. mercury. That part of the shift due to temperature and pressure variations could be determined from accurate observations of these quantities and subsequent calculation as outlined by Raynes. However, since shifts occurred which were attributable to mechanical movement of the optical train, Raynes had to adjust the calculated shifts by making use of the local calibration check spectra, two of which bracketed each absorption spectrum. In the present work it has been found just as reliable and also speedier to determine the shifts empirically from the check spectra and this procedure is outlined in detail below. Consequently the measurements of temperature and pressure need now be made much less stringently than was found necessary by Raynes; they now serve merely to indicate their constancy or otherwise during the exposure of each plate.

The technique of calibration, both in theory and in practice, is given in some detail below since it differs in several important respects from that given by Raynes. In particular, the use of an electronic computer has removed the need for most of the manual calculation undertaken by Raynes, and has made possible a small improvement to his frequency evaluation procedure.

In the following sections of this chapter, the procedures for calibration and frequency determination are described; the frequencies and other material used for illustration are taken from a project begun in December 1961.

3.2. The Calibration Spectrum.

The standard frequency spectrum employed in this work is the iron arc spectrum from an international Pfund iron arc. The advantages and disadvantages of its use have been discussed fully by Raynes (6, p. 187). The adoption by the International Astronomical Union (37) in 1955, of a large number of iron lines as secondary standards, means that several standard lines may be chosen in a given spectral region to effect a calibration. For instance in the spectral range 3370Å to 3640 Å, one of the ranges used in the present work, there are some 21 of these frequencies which have been found suitable for use. In Raynes' work, the iron lines measured by Meggers and Humphreys, (38) were used, but as their list does not extend beyond 3400 Å, it is of no use in the present region.

In one part of the above mentioned range, however, from 3506Å to 3603Å, none of the secondary standards is suitable; those listed are either too weak or are too close to near-neighbours. In order to avoid leaving this serious gap in the calibration range, four non-standard frequencies, taken from an earlier list compiled by Kayser and Konen (39) have been employed. Since to some extent, their use here may be regarded as their re-evaluation relative to a scale mainly determined by the 21 secondary standards, the presence of any serious errors in the used values would, in due course, emerge.

The easy reproducibility of the iron arc spectrum with relatively simple equipment would make it ideal for use as a standard spectrum were it not for the breadth of the lines themselves, and the consequent uncertainty in their measurement. The lines have a half-width of about 0.25 cm^{-1} and in the present work, a single determination of the position of a fringe peak is subject to an error of the main frequency of the order 0.006 cm^{-1}. Since several such measurements are made (from 3 to 15 were made for each frequency in the work listed in table 3.3 p.76), the standard error of the mean frequency can be of the order 0.002 cm^{-1}. Significant further reduction cannot be obtained without a large increase in the number of observations. Greater accuracy in calibration is desirable since absorption frequencies can be determined, in many cases, with a standard error of 0.001 cm^{-1}. Improved sources and accurate frequencies are thus required, but the position in this respect has not changed since a review of this subject was written by Raynes (6, p.196).

The criteria, then, for choosing an iron line for use in the calibration of a given spectral region are:

a) The line should be of accurately known frequency and should be preferably, a secondary standard.

b) It should be of such an intensity that fringes of an intensity suitable for measurement are produced within a reasonable exposure time. With the present experimental arrangement, a maximum of eight minutes has been allowed; longer exposures would increase dangers of temperature and pressure fluctuations during a set of exposures.

c) Finally, it should be free from near neighbours producing visual interference with its measurement.

As intimated above, 25 lines in the region 3370 Å to 3640 Å have been found suitable for calibration, and they are listed in table 3.3. The wavelengths are those listed by the I.A.U. except for those marked with an asterisk, which, as stated before, were obtained elsewhere. The frequencies were determined using Kayser's "Tabelle" (40) together with the Edlen correction (41).

3.3. Measurement and calibration

Prior to measurement of the calibration fringes, we must first determine the order of interference to which each belongs. To this end we make use of the iron arc spectrum in channels (with absorption) mentioned in section 2.8. In this spectrum, the iron fringes appear in channels, each of which is associated with a particular order, and differs in order from its neighbour by unity. If we allocate the number zero to some reference channel and number the channels consecutively, it is a simple matter to determine the order difference of each iron fringe from the zero channel. The latter is chosen so that the first iron calibration fringe lies in a channel at least one removed from the zero channel; all the iron fringes then occur in channels numbered positively.

Since measurements are made on prints enlarged 25 times from the original plates, certain distortions are inevitable in the final image due to the optical aberrations in the enlarger system. (Mechanical distortions in the processed prints are eliminated by using Kodak Aluminium Foil Card for all prints from which measurements are taken.) Such distortions should be constant from print to print since the enlarger settings are not disturbed, as far as possible. Distortions also occur which are attributable to imperfections in the Littrow optics; these, however, are wavelength-sensitive and vary when different regions of the spectrum are printed.

To correct fringe measurements for these two types of distortion, a perspex graticule, with some 40 closely-spaced horizontal lines ruled in it, is placed over the Littrow slit. Plates photographed in the usual way show these graticule lines, of which 23 occur in the region of interest. Comparison of measurements of these lines (converted to fractional distances x, as described below) with measurements of the original graticule give the corrections, from print to slit, to be applied to fringe measurements. Such a comparison is usually made over the whole used area of a print so that a contour map of the corrections can be plotted.

Associated with each print from which fringe measurements are taken a graticule is printed. Comparison of the contour maps from different wavelength regions show that differences occur, but that these differences are only slightly larger than the uncertainty in their measurement; this is estimated to be about 0.04 mm on a print. The variation is not ignorred, however, a separate graticule print being taken and measured for each wavelength region. The corrections themselves range from -0.02 mm to 0.12 mm, which correspond to wavenumber corrections of from -0.0005 to +0.0030 cm^{-1}.

For calibration then, prints are made containing all the useful fringes of the chosen iron lines from the four exposures on the calibration plate. In general, measurable fringes are obtained from two or three of the spectra, and, since just over four orders of each frequency occur between the quartz fibre lines, some eight to twelve are usable for each frequency.

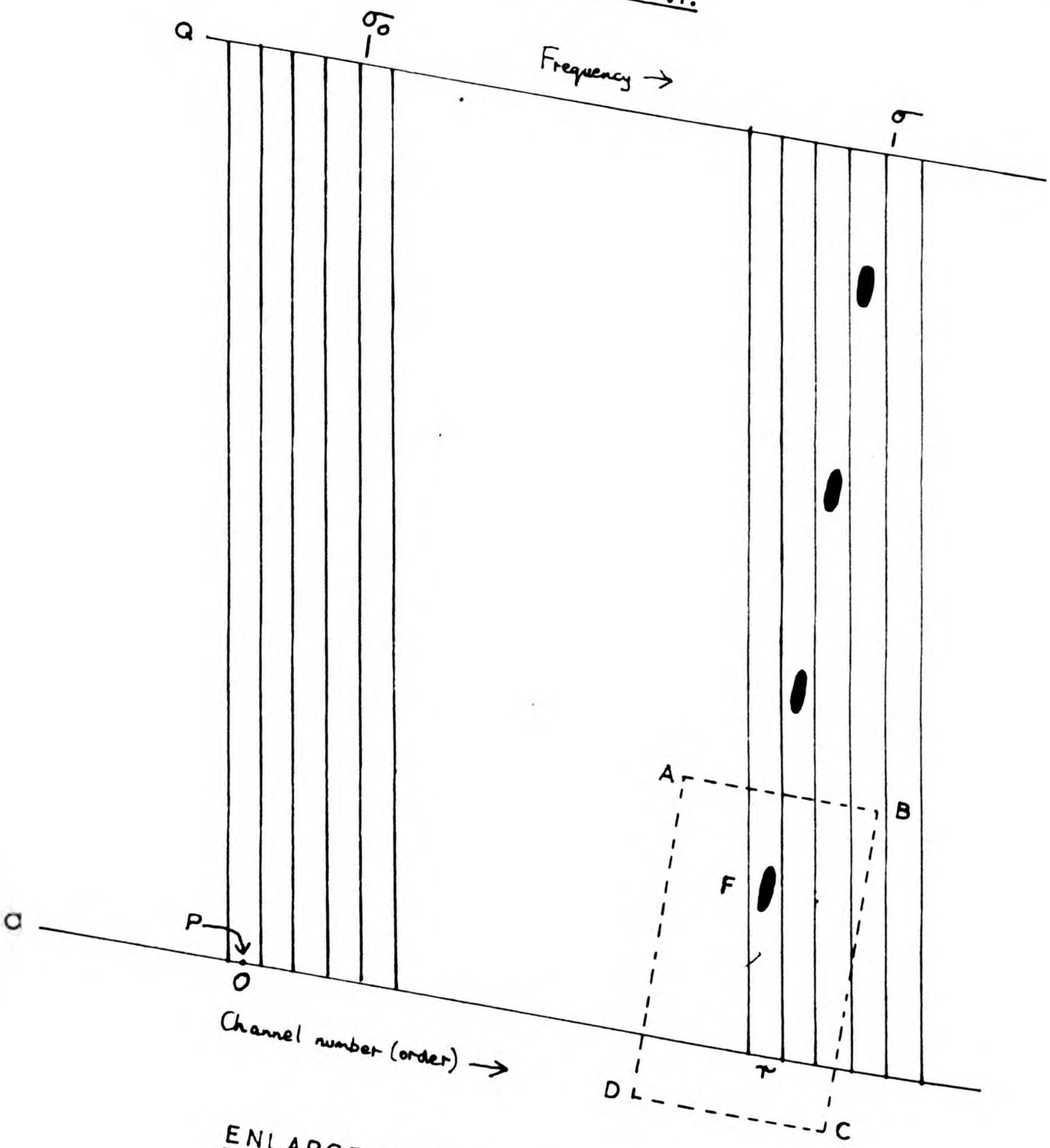
3.4. Frequency evaluation

Raynes has described in detail the procedure for frequency determination. The following is a summary of the algebra required, in practice, for the calibration of a given spectral region, and the subsequent evaluation of unknown frequencies in it; the treatment differs slightly from that given by Raynes, the present one being more amenable to automatic computation.

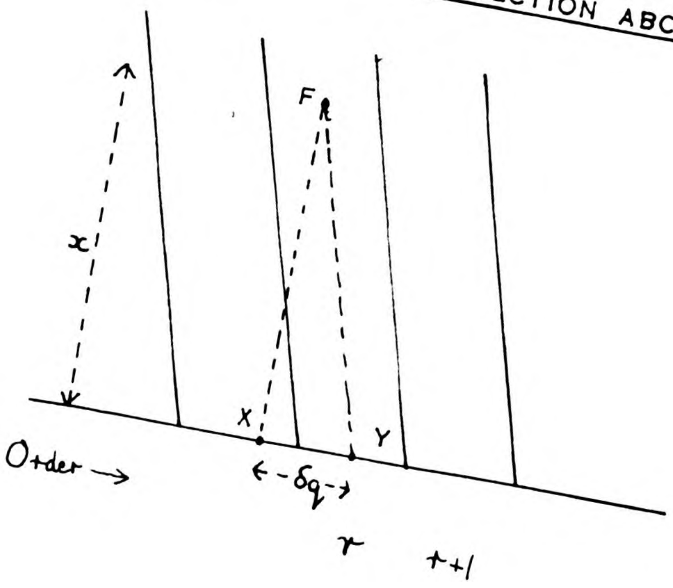
A single frequency produces an interference pattern which has a more or less sharply defined maximum, "a fringe", wherever the path difference between the interfering beams contains an integral number, n, of wavelengths, n being the order of interference. The instrumentation used here produces four or five such fringes between the two reference lines, the O- and Q-lines. Between adjacent maxima, the order is non-integral and so destructive interference occurs, producing a low (though non-zero) intensity. The order where the fringe array of the given frequency crosses the O-line, in general a non-integral quantity, is an important concept in the frequency evaluation procedure since this is essentially a summation along the O-line.

An unknown frequency, σ , is determined as the difference between it and the frequency of some reference point in the spectrum, the latter being termed the fiducial frequency σ_0 .

FIGURE 3.1.



ENLARGEMENT OF SECTION ABCD



The reference point used by Raynes was the first fringe peak of the first calibration frequency. The fiducial frequency was therefore the standard frequency of this line and the fringe measurements of the line had, at least initially, to be accepted as correct.

The new reference point is taken as the point where the channel numbered zero crosses the O-line. The fiducial frequency σ_0, is then the frequency which would produce a fringe peak at this point even though no fringe may be physically observed there. σ_0 is one of the calibration constants to be determined and is dependent on the particular setting of the optics. It is however, a constant for each set of spectra.

Consider now the diagram fig. 3.1 opposite. The fringe F belongs either to one of the standard frequencies or to some unknown absorption frequency, σ. Inspection shows that it lies in some channel, r, and measurement (hereafter regarded as already corrected by the graticule procedure) gives its fractional distance, x, between the O- and Q-lines. The two coordinates, r and x, are uniquely associated with the frequency difference between F and the fiducial point; it is shown below that this frequency difference is expressible as a function of r and x, together with the calibration constants defined below.

The frequency of the fringe F, then, is given by:

$$\sigma = \sigma_0 + \Delta\sigma \qquad 3.0$$

We express the frequency difference $\Delta\sigma$, in terms of the order difference between the fringe and the fiducial point, Δn, in the form:

$$\Delta\sigma = c_0\Delta n + c_1\Delta n^2 + c_2\Delta n^3 + c_3\Delta n^4 \qquad 3.1$$

The constants c_i describe the free spectral range and its variation along the spectrum. Raynes showed that four terms sufficed to give σ to better than 0.0001 cm^{-1} over a range of 2000 cm^{-1}.

Δn is expressed in two parts. The first is the order difference between the fiducial point P, and the base of the channel containing the fringe, F ; this is simply the channel number r. The second part, δq, is the difference in order between the fringe and a point X, defined by the intersection of the 0-line with the continuous diffraction pattern of the frequency for which F represents a region of maximum intensity. The order at X is termed the order at the 0-line of the fringe, and is the quantity mentioned earlier in this section. Thus Δn is given by:

$$\Delta n = r - \delta q \qquad 3.2$$

δq is expressed in terms of x by the formula :

$$\delta q = A x (Q + x) \qquad 3.3$$

Whence :

$$\Delta n = r - A x (Q + x) \qquad 3.4$$

Q is a geometrical constant for the whole spectral region while A varies continuously, but slowly, over the spectrum. The variation is expressed most conveniently in terms of Δn by :

$$A = a_0 + a_1\triangle n + a_2\triangle n^2 \qquad 3.5$$

The five equations 3.1 to 3.5 were derived by Raynes from considerations of the geometrical properties of the optical system. Indeed, first approximations to the 9 calibration constants* involved were derived by Raynes from known optical dimensions of the system, to be refined later by manual fitting to the calibration measurements. In the present method, the calibration constants, listed in table 3.1, are regarded as a purely empirical means of effecting the calibration. This is done by simultaneous solution of a set of normal equations in the nine unknowns, compiled from the fringe data.

Combining equations 3.0, 3.1, 3.4 and 3.5, eliminating $\triangle n$, we obtain an expression for the frequency of a fringe in terms of the calibration constants and of r and x. If we symbolise the constants by $z_1, z_2, \ldots z_9$ (they are identified in table 3.1 (73)) for purposes of explanation, we can write the frequency expression in the form :

$$\sigma = f\,(\, z_i,\, r,\, x\,) \qquad 3.6$$

The detailed form of equation 3.6 is quite simple to derive but,

---

* In Raynes treatment, σ_0 did not occur as a calibration constant; instead, a different quantity, δ_{qf} was used. The change has been made for computational convenience; it has the added advantage that it does not involve the arbitrary adoption of any of the calibration frequencies as exact.

as it is rather lengthy and is of no immediate interest here, it is not given explicitly.

In the expression, some of the constants z_i occur in powers greater than unity so that equation 3.6 cannot be used as it stands, as the equation of condition for least squares solution. Instead, the standard differential technique is used whereby normal equations are set up and solved for small corrections to initially approximate constants.

Partial differentiation of equation 3.6 with respect to each of the z_i gives:

$$\delta\sigma = \sum_{i=1}^{9} \alpha_i \, \delta z_i \qquad 3.7$$

where the δz_i are differential quantities associated with the z_i, and the α_i are their coefficients, themselves functions of the original z_i, and of r and x. A finite $\delta\sigma$ implies that the α_i are approximate since they are derived from approximations to the z_i. Iteration of the solution procedure will refine the z_i and therefore the α_i. Eventually $\delta\sigma$ should approach zero and the z_i approach the final, best values.

In practice, $\delta\sigma$ is identified with the difference between the known frequency of a line, σ_{cal}, and the frequency, σ', calculated using current approximations to the calibration constants. Thus the erratum, ϵ, on the right hand side of an equation of condition is given by:

$$\epsilon = \sigma_{cal} - \sigma' \qquad 3.8.$$

Table 3.1

Calibration constants and coefficients

First define the following quantities:

$$X = x\,(Q + x)$$
$$h = \left[c_0 + 2c_1\Delta n + 3c_2\Delta n^2 + 4c_3\Delta n^3\right]$$
$$d = \left[1 + x(A_1 + 2A_2\Delta n)\right]^{-1}$$

Calibration constants	Input value	Differential	Coefficient αi
σ_0	z_0	δz_0	1
c_0	z_1	δz_1	Δn
c_1	z_2	δz_2	Δn^2
c_2	z_3	δz_3	Δn^3
c_3	z_4	δz_4	Δn^4
a_0	z_5	δz_5	$-h\ X\ d$
a_1	z_6	δz_6	$-h\ X\ d\Delta n$
a_2	z_7	δz_7	$-h\ X\ d\Delta n^2$
Q	z_8	δz_8	$-h\ A\ x\ d$

The coefficients α_i, of the variables δz_i, are listed in table 3.1. Normal equations are set up in the usual way using each fringe measurement once to form an equation of condition. In the calibration recently undertaken, more than 200 such equations were used. The solutions to the normal equations, δz_i, are added to the previous z_i to give refined values for the next iteration.

The above procedure has been programmed (see Appendix 2) for the Mercury digital computer. The programme, entitled L.P. Polynomial, NPL.30, inputs initial approximate constants and the standard frequencies together with their fringe measurements; sets up the equations of condition, and solves the normal equations to produce refined constants. Iteration may be carried out as far as desired, but up to five are normally allowed for; in practice three or four have been found sufficient.

For the first iteration, the approximate constants may be obtained from the geometrical properties of the fringe system as outlined by Raynes. However, it has been found recently that quite crude initial approximations may be employed without invalidating or lengthening the solution procedure.

The results of one such run are shown in table 3.2. The second column shows the initial approximations used. Succeeding columns show the result of refinement, while the last gives the standard error of each constant. The latter is a by-product of the solution procedure. Three refinements only are given, the fourth

TABLE 3.2

REFINEMENT OF CALIBRATION CONSTANTS

	INITIAL	REF 1	REF 2	REF 3	S.E.
σ_0(27450.0+)	0.7	0.808	0.807	0.807	0.003
C_0(1.1+)	0	0.0266206	0.0266402	0.0266408	1.4,-5
C_1(1,-6x)	-5	-4.7973	-4.8214	-4.8231	3.0,-3
C_2(1,-11x)	0	-4.036	-2.341	-2.109	2.2,-11
C_3(1,-15x)	0	-1.50	-5.75	-6.07	5.3,-15
A_0 -	1.1	0.94940	0.95414	0.95417	6.8,-3
A_1(1,-5x)	4	4.1778	4.1868	4.1836	2.1,-6
A_2(1,-9x)	0	-3.16	-3.12	-3.10	1.0,-9
D -	3.7	3.6199	3.6167	3.6166	3.2,-2

TABLE 3.4

CORRELATION COEFFICIENTS

	σ_0	C_0	C_1	C_2	C_3	A_0	A_1	A_2	D
σ_0	1	-0.43	0.23	-0.17	0.15	-0.26	-0.61	0.46	0.37
C_0		1	-0.94	0.88	-0.85	-0.08	0.29	-0.30	0.05
C_1			1	-0.99	0.97	-0.00	-0.04	-0.05	0.00
C_2				1	-0.99	0.02	-0.03	0.03	-0.01
C_3					1	-0.01	0.03	-0.02	0.01
A_0						1	-0.13	0.18	-0.99
A_1							1	-0.96	0.02
A_2								1	-0.09
D									1

TABLE 3.3
RECALCULATED FREQUENCIES

WAVELENGTH	FREQUENCY	REF.1	REF.2	REF.3	NO.	S.E.
3370.7852	29658.158	-0.012	0.001	0.001	12	0.001
3399.3356	29429.438	-0.011	0.002	0.002	16	0.003
3401.5200	29409.072	-0.016	-0.005	-0.005	7	0.002
3407.4611	29390.186	-0.009	0.002	0.002	8	0.002
3413.1339	29338.945	-0.010	0.001	0.001	15	0.001
3396.9774	29290.184	-0.009	0.002	0.002	4	0.001
3417.8428	29249.831	-0.012	0.001	0.001	12	0.002
3424.2861	29194.795	-0.006	0.005	0.005	11	0.002
3427.1213	29170.642	-0.015	-0.007	-0.007	4	0.004
3428.1948	29161.506	-0.012	-0.002	-0.002	12	0.002
3445.1508	29017.988	-0.006	0.003	0.003	11	0.001
3447.2797	29000.068	-0.012	-0.002	-0.002	8	0.002
3450.3304	28974.429	-0.012	-0.001	-0.001	8	0.002
3483.0090	28702.591	-0.010	-0.002	-0.002	3	0.002
3485.3418	28683.380	-0.011	0.000	0.000	8	0.001
3495.2879	28601.763	-0.009	0.003	0.003	8	0.002
3500.5675	28558.627	-0.021	-0.008	-0.008	4	0.008
3506.5004	28510.307	-0.018	-0.007	-0.007	8	0.003
*3527.796	28338.309	-0.014	-0.004	-0.004	8	0.002
*3536.557	28263.009	0.002	0.011	0.011	8	0.004
*3542.080	28223.933	-0.014	-0.003	-0.003	8	0.002
*3545.642	28195.580	-0.007	0.005	0.005	8	0.002
3603.2068	27745.140	-0.013	-0.004	-0.005	8	0.002
3638.2998	27477.533	-0.008	0.001	0.001	8	0.002
3640.3918	27461.741	-0.009	0.001	0.000	8	0.002

and fifth are omitted for space reasons, but they show no significant deviations from column 5. The corresponding fit to the calibration frequencies is shown for each iteration in table 3.3. The first column is the listed wavelength (37 and 39), while the second is the Edlen-corrected frequency. The next three columns show the result of successive refinement, each column being the difference between the standard frequency and the frequency calculated from the corresponding constants of table 3.2. It is obvious that a very satisfactory fit is obtained even after only two iterations. Further iteration does not alter the errata even though small changes do occur in the calibration constants. The reason is that each set of constants is a self-consistent set, and a small alteration to one of the members may be compensated by corresponding changes to the other eight. This is well illustrated in the table 3.4, showing the correlation coefficients between each pair of the constants. High correlation, greater than say 0.95, indicates those pairs of constants which may be adjusted with mutual compensation.

The last two columns of table 3.3 give the number of fringes used for each frequency, and the standard error of the mean frequency calculated from all its relevant fringe measurements. It is from this table that the claim of accuracy of 0.002 cm^{-1} in the determination of iron frequencies was made earlier in the chapter. Since the number of frequencies greatly exceeds the number of calibration constants, the last column does not represent solely the random uncertainties in the present measurements, but the effect of those uncertainties together with the random uncertainties of the standard frequencies themselves.

3.5. Determination of Absorption Frequencies.

a) Local Calibration.

In order to calibrate an absorption spectrum we must first determine the fringe shifts due to temperature, pressure and mechanical deviations from standard. The two iron check spectra which bracket the absorption spectra are used for this. Measurements on the iron lines in those spectra are taken, and the x values obtained are converted to δq's using equation 3.3 of the preceding section.

Comparison between the check spectra on one plate indicates whether or not any significant change in conditions occurred between the two exposures since the resulting shifts would lead to uncertainties in the absorption frequencies. If for any plate, shifts corresponding to 0.002 or more are observed, that plate is rejected; such rejection is however rarely necessary.

For accepted plates, the mean δq for each check frequency, δq_{check}, is taken to correspond to the conditions of the absorption spectrum. The mean δq_{check} are then compared with those δq_{cal}. of the corresponding lines of the calibration spectrum. The differences ϵ_i, are fitted graphically to a first order equation of the type:

$$\epsilon_i = b_o + b_1 \Delta n_i \qquad 3.9.$$

A quadratic term included by Raynes has been found unnecessary since the effects of its omission are negligible (of the order 0.001 cm^{-1}). The Δn_i are order differences as defined in the preceding section. The two coefficients b_o and b_1, suffice to correct any measured δq in the absorption spectra to calibration conditions; they are referred to as the 'b' coefficients.

The local calibration procedure above can be used for quite large departures from calibration conditions although such a case seldom arises. In a special case in the course of this work, however, it was found necessary to correct absorption measurements to the calibration conditions of a plate taken 18 months earlier, during which time adjustments of the apparatus had been frequently carried out. The procedure successfully accounted for shifts amounting to 0.6 of an order (equivalent to 0.7 cm^{-1}).

ii) Measurement and Computation.

Since in any one band of a molecule like formaldehyde, there are many thousands of fringes to be measured and processed, all the operations involved must be carried out to a rigid pattern so that the total labour involved is minimised. To some extent this pattern is governed by the requirements of the computer programmes used to process the data. These are explained in some detail in the appendix; their requirements are outlined below.

After choosing the band to be investigated, enlargements of it are made from spectra of suitable intensity. Usually three or four different pressures of absorbing gas are needed; the highest pressures (or longest path lengths) are used to bring out the weak lines in the wings of the band, the lowest pressures to resolve the strong band centres. The channels are then numbered with the aid of the channeled iron arc spectra, used previously in the calibration procedure. These spectra contain weak absorption so that the two types of spectra may be correlated.

The fringes are measured on each enlargement, channel by channel, beginning with the channel with the highest number, that is from high to low frequency. The measurements are recorded for each channel together with symbolic information on intensity and, if the fringe appears to be an unresolved doublet or is interfered with by another fringe or by some photographic disturbance, this is also noted. On any one plate, the intensities are estimated to belong to any of eight categories from very weak to very strong. Later, the estimates on several plates (generally differing on account of different absorption pressures) are correlated to a single numerical scale from 0 to 9.

The fringe measurements for a given channel from every plate used are <u>all</u> recorded together. A band of the type under consideration in the present work, extends over about 350 channels (400 cm^{-1}) and in it from 5000 to 10000 fringes are measured. When complete, the fringe data together with the calibration constants and 'b' coefficients appropriate to the individual plates, are transferred to punched tape ready for input to the computer. The programme used, entitled "Ordered frequencies, HMU.4.", reads in all the measurements from every plate in the first channel. As each fringe measurement is read, its frequency, intensity and the other information mentioned above are stored in a place of the computer store which identifies the plate number from which it comes. Since the same frequency occurs in four or five adjacent channels, some 80% of the material calculated for the current channel must be retained in the store of the computer, awaiting the data of succeeding channels. The rest, together with the appropriate material retained from previous channels, is then output in order of decreasing frequency, one frequency to each line on the teleprinted output. Besides the frequency, three items of information which serve to identify the source of the estimation are also output, these being the plate number, the channel and the x value. Finally, the estimated intensity is output.

The completed list of 5,000 to 10,000 frequencies is then examined in detail. The frequencies may be marked off into groups, each group containing all the estimates of one frequency. Most groups present no problems, all the estimates being close to some central value, and being well separated from neighbouring groups. An estimate of the intensity is then made for each group from the individual estimates of the group. Occasionally, a group contains frequencies spread closely but over a wide range, so that they cannot all be estimates of a single frequency. This occurs when two or more frequencies lie very close together and are measured on some plates as one frequency, on others as more than one. In such cases, some arbitrary selection and rejection of frequencies must be made, so that two or more individual frequencies stand out; a record is kept that this has been done and appears eventually on the final frequency list. Such frequencies are regarded as approximate and are subject to review.

Several errors inevitably stand out of the frequency list. They are of the three types listed below.

1) A frequency with an anomolous intensity occurs within a group, i.e. a very weak frequency, of strength 0, 1 or 2, in a group of otherwise strong frequencies, say 8 or 9, or vice-versa. This is often due to an incorrect transcription of the strength somewhere on the route between observation and final printing, and may be checked by reference back to the original print, making use of the identification material mentioned above.

Nothing further need be done about these frequencies other than ignoring their intensity when assessing the intensity of the group. They may, however, belong instead to category 2.

2) Incorrect transcription of an actual measurement to tape (or incorrect measurement) will result in an odd frequency appearing once only in the list. It may be of type 1, but more often it stands by itself. Reference back to the print usually confirms its error. Single frequencies may, of course, be due to only one actual observation of the frequency; these, however, should be of low intensity, 0 or 1, but may belong to category 3.

3) Single frequencies of very low intensity are sometimes due to mistaken measurement of a spurious mark on the print. This may be checked with reference to the print and the frequency rejected if necessary.

When completely sorted and checked, a steering data tape is made, to select the individual groups (with rejection of the unwanted frequencies), together with the estimate of the intensity on the final correlated scale. This tape, and one of the tapes containing the full frequency list (there are of course several such tapes), are input to the computer using a programme entitled "Mean frequencies and standard errors, HR1.6". In the output of this programme, each line contains the mean frequency of a group, its intensity, and its standard

TABLE 3.5

OPERATION	TIME ON MANUAL WORK	TIME ON COMPUTER
Taking the series of plates	1-2 weeks	--
Enlargement of calibration spectra and absorption spectra for one band	100 enlargements 30 hours	--
Main calibration: measurement & taping	1-2 weeks	15 mins. for 5 iterations.
Local calibration: measurement and taping	1 day per plate	a few minutes
Measurement of 5,000 to 10,000 absorption fringes in one band from 3 or 4 plates and preparation of data. tapes.	2-4 weeks	60 - 80 mins.
Conversion of long frequency list to mean frequencies.	2-3 days	15 minutes.

error. Where only one or two frequencies are present in a group, the standard error cannot, of course, be determined; instead the letters F, or FF are printed. The resulting lists are shown in Appendix 3, but, of course, without the assignments given there.

These two computing operations might have been combined to produce the final mean frequency list from the original fringe data. It would, however, be extremely difficult to programme the computer to reject the spurious fringes that inevitably occur. The intermediate reassessment with reference back to the original print is, at present, an essential feature of accurate working. If the number of spurious measurements could be reduced considerably, as it may be if a projected plan for semi-automatic measurement materialises, combination of the two stages would result in a significant reduction in the time needed to process a band.

An estimation of the time involved in the various operations outlined in this chapter is given in table 3.5. The times quoted in column 2 assume continuous working for eight hours per day on the relevant project. An increase of up to double the time quoted might be allowed for the measurement of fringes since continuous working is difficult to maintain.

CHAPTER 4

THE FORMALDEHYDE SPECTRUM

4.1. Introduction.

As intimated earlier, the formaldehyde spectrum offers good possibilities for the near-complete elucidation of the rotational, vibrational and electronic motions of the molecule. The spectrum has already been studied in considerable detail by many investigators in most regions of the spectrum. The pure rotational spectrum, which affords inertial constants for the vibrationless ground state, has been investigated fully in the microwave region and several isotopic species have been included in the analysis. The vibration-rotation spectrum has been studied at length in the near infra-red region, while some work has also been done on it using Raman techniques. Finally, the electronic spectrum has been studied, both in absorption and in emission, over a wide frequency range in the near and far ultra-violet.

This chapter is concerned with a review of the spectrum in all these regions and in particular with those points of special relevance to the present work. A detailed account of the theoretical aspects of the rotation of molecules will be given in the next chapter; in the present chapter it will be assumed that concepts of molecular spectra, especially of rotational fine structure, are familiar.

4.2. The Pure Rotational Spectrum.

The investigation of the pure rotational spectrum has been concerned exclusively with the vibration-less level of of the electronic ground state, although there are possibilities of studying excited vibrational levels (see ref. 44 p. 2273). Since the dipole moment of the molecule lies entirely along the principal axis of least moment of inertia, the rotational selection rules allow only parallel transitions, of the type $\triangle J = 0, \pm 1$ and $\triangle K = 0$. The very high rotational constants of formaldehyde cause all but one of the transitions for which $\triangle J = \pm 1$ to lie outside the microwave region. Such lines have not yet been investigated in the far infra-red region, and almost the only transitions available for analysis are of the type $\triangle J = 0$, and $\triangle K = 0$. Since formaldehyde is a slightly asymmetric rotor, many transitions between the K-doublets fall in the microwave region. To date, 33 such lines have been identified for the normally isotopically constituted molecule, together with the single transition $J = 0, K = 0 \longrightarrow J = 1, K = 0$. For the isotopic species D_2CO, HDCO, $H_2C^{13}O$ and H_2CO^{18}, 18, 26, 12 and 3 lines respectively have been identified and measured.

Since the frequency of only (at most) one line with $\triangle J = \pm 1$ is available for each isotopic species, the variation of rotational energy with the quantum number J is not well defined. This is a great limiting factor on the extraction of rotational constants, especially the centrifugal distortion constants, from the microwave frequencies. Only slightly less serious is the total absence of lines for which

Table 4.1.

Rotational constants (in Mc/s) for HCHO
(microwave frequencies)

	L.&S.(42)	Erl.(43)	Oka (44)	Present wk.
$(B+C)/2$	-	-	36,419.22	(36419.22)
$A-(B+C)/2$	245,687	245,686	245,610	245,425
b	-0.009829	-0.009826	-0.009837	-0.009846

Table 4.2.

Group tables for C_{2v} and C_s symmetries (85)

C_{2v}	I	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	R_y
B_2	1	-1	-1	1	R_x

C_s	I	$\sigma(xz)$	
A'	1	1	R_x
A"	1	-1	R_y, R_z

$\Delta K = \pm 1$, since without these, the rotational constant $A - \frac{B + C}{2}$ is then determined only by differences between K-doublets. Only for the asymmetry parameter b, does this spectrum provide sufficient information for its unambiguous evaluation.

The spectrum was first studied in detail by Lawrance and Strandberg (42) who measured and identified 18 lines of H_2CO. They obtained the rotational constants listed in table 4.1, but their distortion constants related to a distortion formula was not now of interest. Erlandson (43) redetermined the constats from 10 of the frequencies with the aid of an electronic computer, and employed the six-constant distortion formula of Kivelson and Wilson (see section 5.3). For reasons soon to become apparent, this distortion formula is also not of immediate interest for the formaldehyde spectrum.

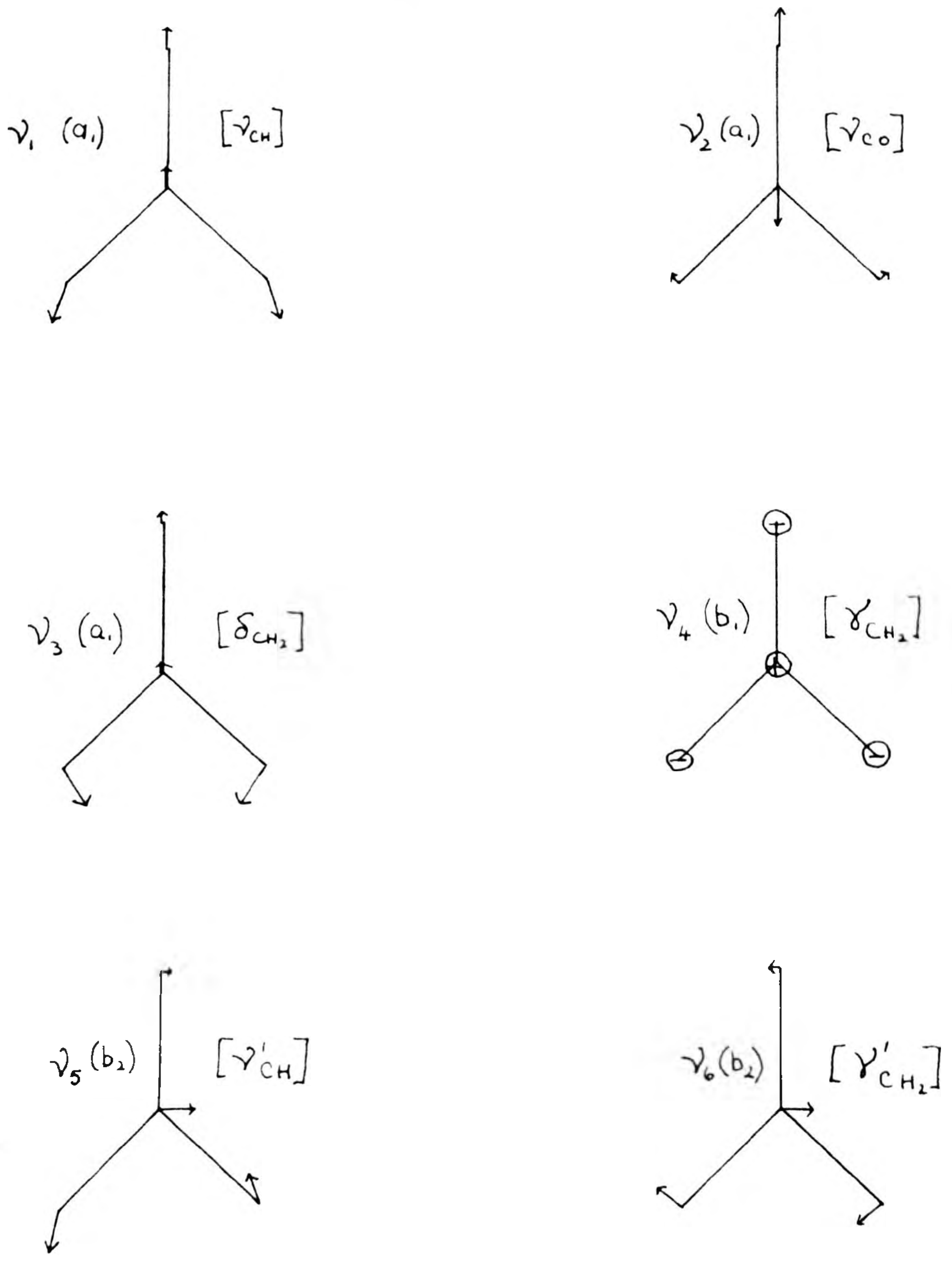
In a very detailed treatment of the microwave spectrum of formaldehyde, Oka et al. (44, 45, 46) used the frequencies obtained by Lawrance and Strandberg, together with others determined in the intervening years (for references to this work see ref. 44), and also measured and identified many new lines, especially for the isotopic molecules. These workers realised that in the first order treatment of centrifugal distortion of Kivelson and Wilson, for a planar molecule there were only four independent distortion constants. Oka therefore decided to use the distortion formulation in terms of the more fundamental quantities $\tau_{\alpha\beta\gamma\delta}$, since there were only four such constants, independent and non-zero. On computing the coefficients of the τ's for each of the observed frequencies, he decided that over the range of frequencies used, there was not sufficient variation in the coefficients to allow direct solution for the τ's. He therefore calculated the centrifugal distortion correction for each frequency using τ's independently computed from the force constants of the molecule (to which they are relatively simply related). Subtracting these corrections from the observed frequencies, he solved for the remaining two rotational constants using a least squares procedure. He then varied one only of the τ's, arbitrarilly selected, until an optimum fit to the frequency data was obtained. In view of this somewhat irregular treatment by Oka, the microwave frequencies have now been re-examined in the light of recent information, obtained in the present work from the ultra-violet spectrum, and an account of this work is given in chapter 8. The rotational constants obtained by Oka and by the present author, from the same set of frequencies, are listed in table 4.1 p89. A full comparison of these two investigations is deferred until chapter 8 of this thesis, but it may be mentioned here that a much better fit to the microwave frequencies has been obtained in the present work than was obtained by Oka.

Valuable information on the pure rotational spectrum could be obtained from the far infra-red region, say from 2 cm^{-1} to 100 cm^{-1}. Although the experimental difficulties are great

FIGURE 4.1.

NORMAL VIBRATIONS FOR PLANAR (C_{2v}) FORMALDEHYDE

[SEE REF (85)]



NOTE: THE DESIGNATIONS IN SQUARE BRACKETS ARE USED TO IDENTIFY THE C_s VIBRATIONS OF THE PYRAMIDAL EXCITED STATE in this region, significant advances in technique have recently been made (see for example ref. 11).

4.3 The vibration-rotation spectrum.

Transitions between the vibrationless state and the excited vibrational states in the ground electronic state of formaldehyde occur in the infra-red region of the spectrum. The molecule has six normal vibrations and these are illustrated in fig. 4.1 opposite; the convention used is that recently recommended (85). Blau and Nielsen (47) have studied the spectrum in detail (earlier work is cited in their paper). They found that all six of the vibrations were excited in the spectrum and they carried out a partial rotational analysis of each of the bands. The three totally symmetric vibrations, ν_1, ν_2, and ν_3 give rise to parallel, type A bands; that is the vibrations induce an electric moment along the A axis of the molecule. The rotational selection rules for such bands are $\Delta J = 0, \pm 1$ and $\Delta K = 0$. The two B_2 vibrations, ν_6 and ν_5 give rise to type B bands, while the single B_1 vibration ν_4, gives rise to a type C band. For these perpendicular bands, the selection rules are $\Delta J = \pm 1$ and $\Delta K = \pm 1$.

The infra-red bands mentioned above have provided good examples of the two main types of vibrational perturbation found in molecules. The first type, termed Fermi resonance (48 p. 215) occurs by mixing of the eigenfunctions of two vibrations which have the same symmetry. The perturbation is largest when the two vibrations are close to degeneracy; the levels are pushed further apart and the intensities of the transitions tend to equalise. The combination level $\nu_2 + \nu_6$ of formaldehyde, which has B_2 symmetry and lies at 3003.3 cm^{-1}, is close to the fundamental level ν_5 and also has the same symmetry. The fact that the intensity of the combination band is abnormally great and that its frequency lies higher than might be expected from the sum of the constituent vibrations (2993 cm^{-1}) is directly attributable to Fermi resonance (47).

The second type of perturbation occurs when vibrational eigenfunctions of different symmetries become mixed by the rotation of the molecule; this type of perturbation is known as a Coriolis interaction (48 p. 467). The condition for perturbation to occur is that the product of the symmetry species of the two vibrations should contain the species of a rotation. Reference to the $C_{2}v$ group table in table 4.2, p 89. shows that the product of the ν_4 and ν_6 vibrations has a symmetry, A_2, which is the same as that for rotation about the z axis. Since the two levels lie close to one another, a strong perturbation is to be expected. This is found in the spectrum (47) and analysis of the two bands is greatly complicated by this factor. Indeed, the assignment of the two bands was in some doubt until a recent more thorough

Table 4.3.

Vibrational frequencies for the electronic ground state of formaldehyde.

	HCHO		HCDO		DCDO	
	I.R.(47)	Raman(49)	I.R.(49)	Raman(49)	I.R.(50)	U.V.(23)
ν_1	2766.4	2781.6±5	2844.1	2846.2	2055.8	
ν_2	1746.1	1742±3	2120.7	2120.3	1700	1704.1
ν_3	1500.6	1500 ±3	1723.4	1723.2	1105.7	
ν_4	1163.5		1074		938	934.7
ν_5	2843.4	2866±10	1400.0	1397.4	2159.7	
ν_6	1247.4		1041		990	

Table 4.4.

Electronic transitions in formaldehyde (after Sidman (52))

TRANSITION	ENERGY (ev)	Inte~~s~~nsity for absorption from the ground state
$^1A_1$	0	-
$^3A_2$, $n_p \rightarrow \pi_2$	3.2	v. weak ($< 10^{-5}$)
$^1A_2$, $n_p \rightarrow \pi_2$	4.3	0.006
$^1B_1$, $n_p \rightarrow \sigma_2$	7.1	0.02
$^1A_1$, $\pi_1 \rightarrow \pi_2$	8.0	Strong
Rydberg	> 8	Strong

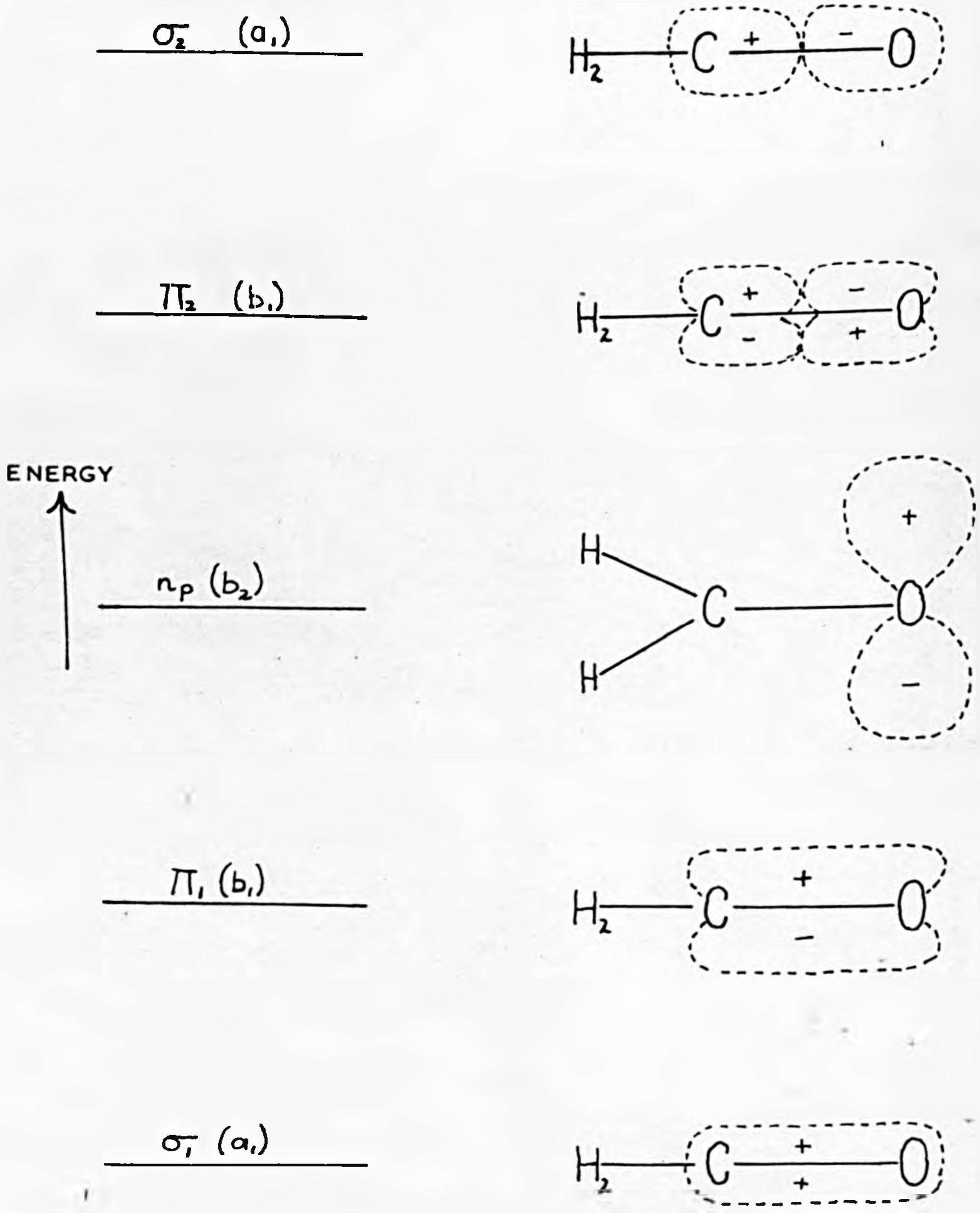
examination of them was undertaken by Innes (49), who, in fact, confirmed the findings of Blau and Nielsen. In their paper, Blau and Nielsen show that the rotational energy levels are dependent in a complicated manner on the quantum number K (roughly linear). Observed Coriolis interactions between ν_3 and ν_6, and between ν_3 and ν_4 (47), should be largely dependent on the quantum number J (the symmetry products, B_2 and B_1 contain the rotational species R_x, and R_y, respectively) but since the vibrations are some distance apart, a much smaller perturbation than the main one above, is to be expected.

The infra-red spectrum of the molecule HDCO was investigated in detail by Davidson, Stoicheff and Bernstein (49). They also found all six fundamental vibrations in the spectrum together with a few overtone and combination levels; the fundamental vibrations are listed in table 4.3. In this spectrum also, the effects of Coriolis and Fermi perturbations are evident; indeed, since the molecule has only two symmetry species (see the group table for C_s symmetry in table 4.2), the possibilities for such perturbations, compared with the more symmetrical molecule HCHO, are greatly increased.

The fully deuterated species DCDO, was last investigated in 1938 by Ebers and Nielsen (50) with a relatively low dispersion instrument, and the vibrational frequencies they

FIGURE 4.2.

MOLECULAR ORBITALS FOR FORMALDEHYDE (AFTER SIDMAN (52))



obtained are listed in table 4.3. No more recent work has been reported.

The vibration/rotation spectrum of the two species HCHO and HCDO have been investigated using the Raman method by Davidson Stoicheff and Bernstein (49), the bands being excited by the mercury 4358Å line. The vibrational frequencies found by them are listed in table 4.3; it can be seen that the agreement with the infra-red frequencies is satisfactory, especially in view of the difficulties in the measurement of the Raman frequencies of HCHO reported by Davidson et al.

4.4 The Electronic Spectrum.

The ultra violet band systems of formaldehyde have been investigated more thoroughly perhaps than the systems of any other comparable molecule. Several electronic transitions have been identified and quite thorough vibrational analyses have been made on one or two. In addition, several vibronic bands have been photographed under high dispersion and partial or complete rotational analyses have been reported.

The electronic transitions have been surveyed theoretically by Pople and Sidman (51), and by Sidman (52). The diagram opposite, (fig. 4.2), shows the occupied molecular orbitals of highest energy, and the lowest unoccupied orbitals, all of which are involved in the electronic transitions studied; the observed transitions are shown in table 4.4. The plain σ bond between the carbon and oxygen is totally symmetric (A_1)

to the operations of the group C_{2v}, while the π bond, π_1 has symmetry B_2. The n_p orbital which is non-bonding and is strictly a p atomic orbital localised on the oxygen atom, and is the highest occupied orbital. The lower lying electronic transitions arise by excitation of an electron from one of these orbitals to either the π_2 or σ_2 anti-bonding orbitals. The first such transition will be from the n_p non-bonding orbital to the π_2 anti-bonding orbital. This transition ($n_p \rightarrow \pi^*$) is well known in molecules containing a carbonyl group, and occurs at from 3000Å to 4000Å, the exact location depending on the electronegativity of the groups attached to the carbon atom. The excited state can be either singlet or triplet, depending on whether the spins of the two unpaired electrons are aligned parallel or anti-parallel to one another. The transition to the singlet state is forbidden on symmetry grounds ($A_2 \leftarrow A_1$) but Pople and Sidman (51) describe a mechanism by which intensity can be induced by a vibrational/electronic interaction. According to those authors, the B_1 vibration ν_4 should be chiefly responsible for the intensity and give rise to vibronic type B bands. This is in substantial agreement with the observed spectrum where the strong bands are all B type, and the strongest form a progression in the excited state fundamental ν_2, with as origin, the excited state vibration ν_4. They state also that the CH_2 bending vibration, ν_6 should also contribute to the intensity of the electronic transition, producing type C bands, but with an intensity some 100 times less than the B bands. In fact there are indications that type C.bands do occur in the band system (see later in this chapter for details) but whether or not they fit into the picture of Pople and Sidman, is not yet apparent. Parallel, type A bands have also been identified in the band system (23) and (24), and Sidman (52) accounts for their intensity by either a rotational/vibrational perturbation or by a magnetic dipole transition mechanism. A recent rotational analysis of one of these bands by Innes (53), indicates the latter of these two possibilities.

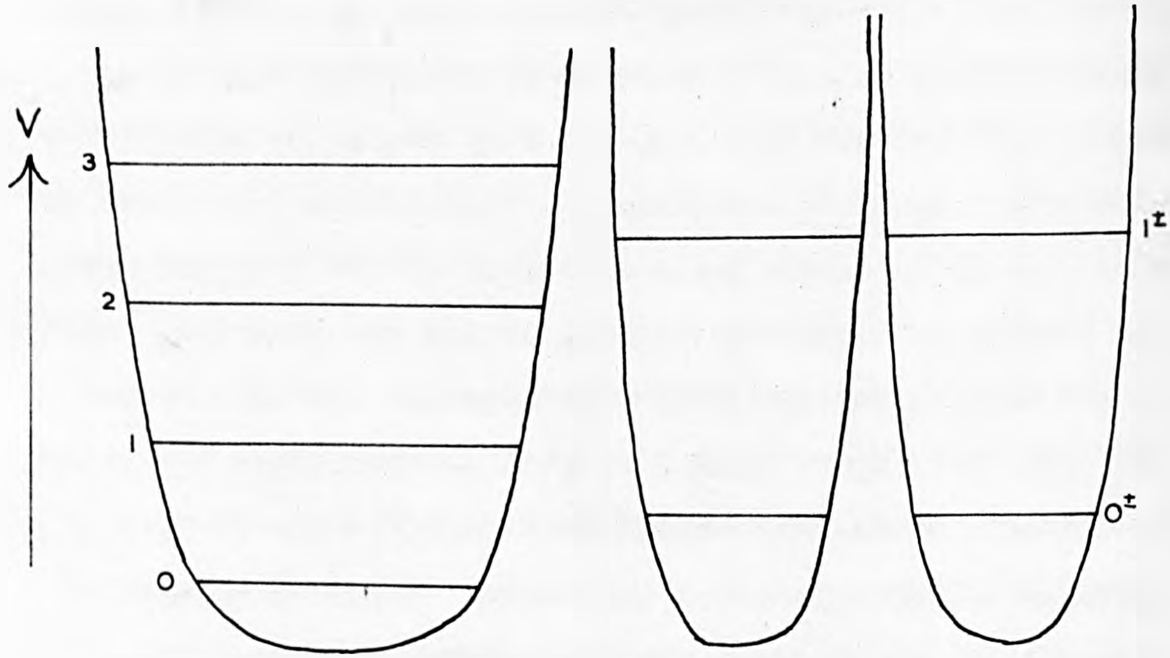
The electronic transition to the triplet state is both symmetry - and multiplicity-forbidden. Sidman (52) suggests that intensity for this transition may be borrowed from other, multiplicity-allowed transitions by a spin-orbit coupling mechanism; the transition which Sidman suggests is responsible is the strong π_1 to π_2 transition at 8.0 ev. The band system is, however, very weak; the total intensity of the singlet-triplet band system being some hundreds of times weaker than the singlet-singlet system. Robinson and di Giorgio(25) and (26) have described rotational analyses of some of the bands, but as yet few details have been reported.

The electronic transitions $n_p \rightarrow \sigma_2$, $(^1B_2)$ and $\pi_1 \rightarrow \pi_2$

FIGURE 4.3.

TRANSITION FROM A PLANAR TO A PYRAMIDAL MOLECULE

POTENTIAL CURVES FOR THE CH_2 OUT-OF-PLANE VIBRATION

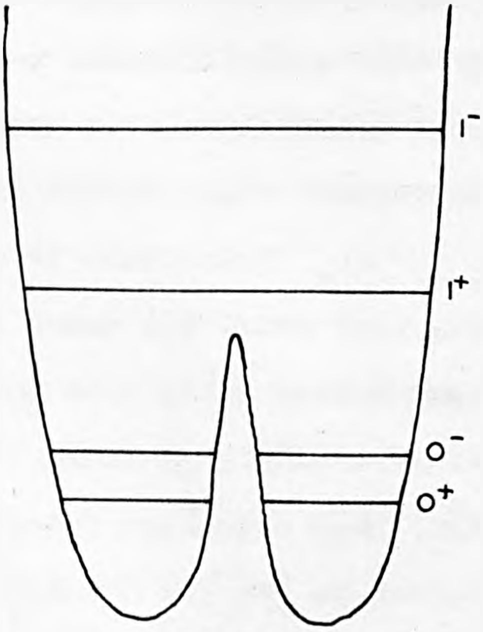


CASE 1

Planar molecule
e.g. HCHO ground state

CASE 3

Stable pyramidal molecule
e.g. AsH_2D



CASE 2

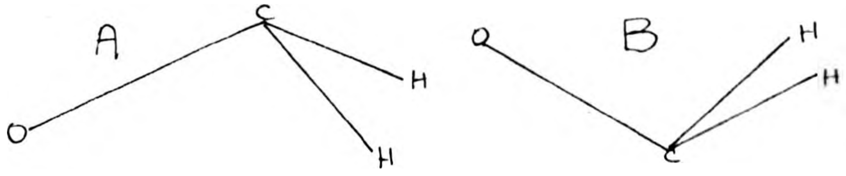
Pyramidal molecule with low barrier to inversion
eg. HCHO 1st. excited state.

have been reported in the far ultra violet while Rydberg transitions have been identified in the vacuum ultra-violet. Since this work is very incomplete and is not relevant to the present work, no more details will be given here.

4.5. The $^1A_2 \leftarrow {}^1A_1$ Transition.

There has been a great deal of experimental work done on the near ultra-violet system of formaldehyde. If we now neglect the singlet-triplet system, which has no direct bearing on the present work, the system has been traced in absorption from 3950 Å to 2600 Å and the fluorescence spectrum has been identified from 6000 Å to 3400 Å.

Walsh (54) suggested that the excitation of an electron from the n_p orbital to the antibonding π_2 orbital, might mean that the normal planar configuration of the ground state would no longer be stable in the excited state. In fact a pyramidal configuration was postulated with a low barrier to inversion; that is the molecule could change from configuration A and B.



The diagram opposite, fig. 4.3, shows potential curves for the out of plane vibration, ν_4 of a planar molecule, a pyramidal molecule with a low barrier to inversion, and a stable pyramidal molecule. In the first case, the molecule oscillates about a planar configuration and the vibrational energy levels are at roughly equal spacings, decreasing regularly perhaps, towards higher energy, due to anharmonicity. If we now introduce a small potential barrier at the planar configuration, as in case 2, then successive pairs of energy levels tend to approach one another, the more so where the effect of the barrier is felt most. We then have a set of levels, unevenly spaced at low vibrational quantum numbers, but tending towards case 1 at higher quantum numbers. Finally, if the barrier at the planar configuration is infinitely large, we have two isolated structures where the energy levels are again almost evenly spaced, but with (all other things being equal) roughly double the spacing of case 1. For convenience, the four lowest lying levels of case 2 are denoted 0^+, 0^-, 1^+ and 1^- and the spacing between the first pair is termed the inversion splitting. In the case of the ammonia molecule, the classic case of such an effect, the inversion splitting is about 1 cm^{-1}. For the $^1A_2$ state of formaldehyde, however, the splitting is about 125 cm^{-1}, which indicates a lower potential barrier than for ammonia. Walsh realised that this cleared up an anomaly between the absorption and fluorescence systems of formaldehyde; this was that the apparent origin of the former spectrum lay some 120 cm^{-1}

Table 4.5

Selection rules for vibronic transition $C_{2v} \rightarrow C_s$.

(after Brand (23))

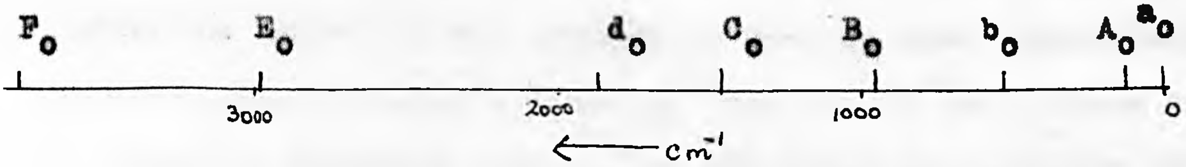
K odd (⊥)		K even (∥)	
c-axis	b-axis	a-axis	forbidden
$A_1 \leftrightarrow A'(-)$	$A_1 \leftrightarrow A''(-)$	$A_1 \leftrightarrow A'(+)$	$A_1 \leftrightarrow A''(+)$
$A_2 \leftrightarrow A''(-)$	$A_2 \leftrightarrow A'(-)$	$A_2 \leftrightarrow A''(+)$	$A_2 \leftrightarrow A'(+)$
$B_1 \leftrightarrow A''(+)$	$B_1 \leftrightarrow A'(+)$	$B_1 \leftrightarrow A''(-)$	$B_1 \leftrightarrow A'(-)$
$B_2 \leftrightarrow A'(+)$	$B_2 \leftrightarrow A''(+)$	$B_2 \leftrightarrow A'(-)$	$B_2 \leftrightarrow A''(-)$

The symbols (+) and (−) distinguish between vibronic sub-levels arising from the inversion doubling.

FIGURE 4.4

Origins of ν_2 progressions for HCHO

(after Brand (23))



higher in energy than the origin of the latter spectrum. It is now apparent, (see the table of selection rules shown in table 4.5) that the first transition of the absorption spectrum is from the ground vibration level to the 0^- level, whereas in fluorescence, the molecule can be in the 0^+ level before radiating energy and falling to the ground state. Walsh also noticed that the strongest fluorescence bands occurred between the lowest levels of the excited state and levels of the ground state where several quanta of the ν_4 vibration were excited, that is, in which the ground state spends much of its time in a markedly non-planar configuration. This would be the condition for maximum intensity according to the Franck-Condon principle, viz. that there should be a minimal change in nuclear configuration in the transition.

Brand (23) has given a full account of his medium dispersion work on formaldehyde and the isotopic species HCDO and DCDO. From these results, it is clear that Walsh's conclusions are substantially correct. In absorption for HCHO, vibronic transitions to the 0^+, 0^-, 1^+ and 1^- levels were identified and Brand interpreted the relative energies of the levels in terms of a potential barrier at the planar configuration of some 720 cm^{-1}. Most of the fluorescence lines involve ground state levels with excited quanta of the ν_4 vibration and Brand could identify the effects of Coriolis interactions with levels involving ν_6, as was described above in connection with the infra-red spectrum. Work reported by Robinson (24), although less extensive than that of Brand, led to the same conclusions.

4.6. Details of the absorption system.

The first detailed investigation of the absorption system of formaldehyde in the near ultra-violet was by Henri and Schou (55) who classified 40 or so bands between 3700 Å and 2600 Å by the periodic variations in intensity of the bands along the spectrum. They measured about 60 lines in each of six bands using an instrument with a resolution limit of 1 cm^{-1}. Dieke and Kistiakowsy (14) in their classic paper reported a high resolution investigation of six bands (A_o, A_1, A_2, B_o, B_1 and C_o, using Brand's notation described below) and gave rotational constants obtained from their analysis. Limitations of the theory at the time of their investigation, in particular the change of shape on excitation mentioned above, and the inadequate treatment of contrifugal distortion then available, have meant that many of their conclusions have had to be rescinded in the light of present day knowledge.

The absorption spectrum was analysed by Brand (23) although recent work has cast doubt on some of his interpretations. The main feature of the band system is the appearence of progressions in an upper state fundamental frequency of 1200 cm^{-1}. Since this frequency must be totally symmetric and is sensibly unchanged on isotopic substitution for hydrogen, it has been assigned to the carbonyl stretching vibration ν_2. Origins of the progressions occur as shown in fig. 4.4, p.104, taken from Brand (23)

The progression starting from A_0 begins with the 0^- level and the successive quanta of ν_2 are indicated in the subscripts of A_0, A_1, A_2 etc. The weak parallel progression a_1, begins with the 0^+ level; however, although the member a_0 is observable as a weak band overlapped by the much stronger A_0 band, a detailed investigation of the A_2 band in the present work has given no indication of lines assignable to the a_2 band; Brand's observation of this band might possibly be an accidental accumulation of lines belonging entirely to the A_2 band. The origins of the progressions b_0 and B_0 have been assigned to the 1^+ and 1^- levels respectively. The diagram in fig. 4.3 (case 2), p. 101, has been drawn roughly to scale to show the relative positions of the four lower levels and the height of the potential barrier. Brand assigned the origins of the C, E and F progressions to the excited state frequencies, $\nu_3 + 0^-$, $\nu_1 + 0^-$ and $\nu_1 + 1^-$ respectively. Some recent work by Innes (53) and by the present author (see later in this thesis for details) has suggested that the C progression consists of bands that are C-type. If so, Brand's assignment can no longer be maintained, since bands with vibrations of symmetry A' in the excited state must necessarily be type B. A type C band would require an A'' vibration (see table 4.5) and, bearing in mind the work of Pople and Sidman described earlier, it is possible that the assignment should be the vibration ν_6:

CHAPTER 5

THE ROTATIONAL STRUCTURE OF VIBRONIC BANDS

5.1. Introduction.

The fine structure of a vibronic band arises from transitions between rotational energy levels of two different vibronic species. The rotational selection rules which govern the choice of combining levels and which, together with the individual intensities to be described in section 5.5, govern general appearance of the band are discussed in section 5.6.

Generally, rotation causes distortion of a molecule by stretching of the bonds, with consequent changes in the rotational constants. It is convenient, however, to express the rotational energy not in terms of these varying rotational constants, but as the sum of several parts, the main part being the rotational energy of a rigid rotor with the geometry of the non-rotating and therefore undisturbed molecule; this is the rigid rotor approximation. The effects of distortion are then contained in a second part, the contrifugal distortion correction. In addition, the presence of other vibronic levels close to one of the levels of the band, can cause perturbations to the rotational levels and can give rise to quite significant energy shifts, which may then be included as a third part. Further, each of these parts is expressible, in various ways, as the sum of a number of terms; the rigid rotor approximation, the centrifugal distortion correction, and the effects of perturbations (the latter expressly in relation to formaldehyde) are dealt with in the next three sections.

5.2. The rigid rotor.

The quantum mechanical treatment of the rigid asymmetric rotor has been reviewed in detail by van Winter (56) and full reference to earlier work is given there. The only problem at the present time is the numerical determination of energy levels, and this can involve a large amount of tedious calculation. The availability of electronic computers has now made the task almost trivial and several authors have programmed the calculation in various ways. Much of the present section will be concerned with the method devised in the present work for use particularly with rotational levels in electronic spectra, since here certain special features render the more standard procedures rather inefficient.

A brief summary of the theory of the rigid rotor is necessary to understand the origin of the secular equations from which the energy levels are derived. The energy of a rotating body may be expressed as:

$$W = \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z} \qquad 5.1$$

where the P_g^2 (g = x, y, z) are angular momenta, and the I_g are moments of inertia about the principal axes, x, y, and z, of the rotor. The principal axes are defined so that the matrix of components of inertia about some general set of axes, x', y' and z', with the origin at the centre of mass of the molecule, becomes diagonal. That is, we define the general element of the moment of inertia matrix, I_{uv}, about the axes u,v as :

$$I_{uv} = \tfrac{1}{2} \sum_i m_i \, r_{iu} \, r_{iv} \qquad 5.2$$

where m_i is the mass of the ith atom of the molecule, and r_{iu} and r_{iv} are the perpendicular distances from the two axes u and v. When the general matrix 5.3 is diagonal, the diagonal elements are the principal moments of inertia of the molecule.

$$\begin{vmatrix} I_{x'x'} & -I_{x'y'} & -I_{x'z'} \\ -I_{y'x'} & I_{y'y'} & -I_{y'z'} \\ -I_{z'x'} & -I_{z'y'} & I_{z'z'} \end{vmatrix} \qquad 5.3$$

When considering the energy of a rotor, it is convenient to define three quantities A, B and C, inversely proportional to the principal moments of inertia I_a, I_b and I_c, and termed the <u>inertial constants</u>.

$$A = \frac{h}{8\pi^2 I_a} \,, \quad B = \frac{h}{8\pi^2 I_b} \,, \quad C = \frac{h}{8\pi^2 I_c} \qquad 5.4$$

where we identify the axes a, b and c in such a way that $I_c \geq I_b \geq I_a$. (Note that the axes x, y and z are identified with the principal axes by other considerations. Thus for a planar C_{2v} molecule such as formaldehyde, the z axis is taken as the symmetry axis and the x axis is taken to be perpendicular to the molecular plane. These conventions are taken from a recent report on notation for molecular spectra (85).) We see then that $A \geqslant B \geqslant C$.

In general, A, B and C are all different; this is the general case of the asymmetric rotor. If, however, we consider the two extreme cases where $B = A$ or where $B = C$, we then have a symmetric rotor with in the first case oblate symmetry and in the second case prolate symmetry. One of these conditions prevails whenever the molecule has a 3-fold or higher axis of symmetry; and for small molecules, this is quite often the case. For formaldehyde, B is quite close in magnitude to C and both are considerably smaller than A. Such a condition is close to the limiting prolate symmetric rotor; formaldehyde may be referred to as a prolate near-symmetric rotor. The procedure described below was designed as especially convenient for such a case, but with slight modifications, it should be applicable over the whole range of asymmetry.

In order to derive an expression for the energy, it is convenient to have a parameter which measures the degree of asymmetry. For the present case, the parameter b, introduced by Wang (57), has been found most convenient; it is defined by :

$$b = \frac{C - B}{2A - B - C} \qquad 5.5$$

When $C=B$ (i.e. in the prolate symmetric rotor), $b = 0$, while when $B=A$, $b = -1$; b is thus always negative. This parameter is especially convenient for a prolate near-symmetric rotor, and when desirable it may be symbolised by b_{prolate}. In other parts of the asymmetry range, other parameters are more convenient. Thus for asymmetries close to the oblate limit, an expression different from, but closely related to 5.5, is used, and the asymmetry parameter is also symbolised by b, or b_{oblate}. (see Townes and Schawlow (63) p.84); in the oblate limit, this b becomes zero. In the region of high asymmetry, a parameter κ defined by King, Hainer and Cross (53), has been found most useful while another parameter δ, (see ref.(58)) closely related to κ has been employed by some authors near the prolate symmetric limit. (In the following treatment, b is to be read as $b_{prolate}$.)

If we replace the angular momenta P_g^2 in equation 5.1 by quantum mechanicaloperators in the usual way, and identify A, B and C with the axes x, y and z as already implied, it can be shown that an energy matrix is obtained with elements given by:

$$(J,K \,|\, W_r \,|\, J,K) = \frac{B+C}{2}\,J(J+1) + \left(A - \frac{B+C}{2}\right) K^2 \qquad 5.6$$

and $$(J,K \,|\, W_r \,|\, J,K+2) = -b\, f^{\frac{1}{2}}(J,K+1) \qquad 5.7$$

where $$f(J,n) = \tfrac{1}{4}\Big[J(J+1)-n(n+1)\Big]\Big[J(J+1)-n(n-1)\Big] \qquad 5.8$$

The equations 5.6 and 5.7 define a matrix, infinite in extent, each diagonal element being associated with a particular J,K, the two quantum numbers describing the quantisation of the angular momentum (for an asymmetric rotor, no quantitative significance can be attached to K but it does provide a convenient means for designating a particular energy level, as will emerge below). Since, however, the matrix is diagonal in J, it may be factorised into

J, it may be factorised into sub-matrices, each associated with a particular J, and since K takes all integral values between -J and +J, each sub-matrix is of order 2J+1. We can now write the elements of each sub-matrix, M, after removing the common terms, as follows :

$$(K\,|E(b)|\,K) = K^2 \qquad 5.9$$

$$(K\,|E(b)|\,K+2) = -b\,f^{\frac{1}{2}}\,(J,K+1) \qquad 5.10$$

The latent roots of such a reduced matrix, which we denote by E(b), are obtained by diagonalising the secular determinant $|M - \lambda I|$, (where the λ are to be identified with the various roots E(b), and I is the unit matrix) and are used in an energy expression of the form:

$$W(J,K) = \frac{B+C}{2}\,J(J+1) + A-\frac{B+C}{2}\,E(b)_{J,K} \qquad 5.11$$

The E(b) are thus reduced energies. For convenience in writing, in the rest of this thesis the two compound rotational constants will be symbolised by D and α so that equation 5.11 becomes:

$$W(J,K) = D\,J(J+1) + \alpha\,E(b)_{J,K} \qquad 5.12$$

The subscripts J,K will be dropped in future when it is understood that E(b) refers to a general root of the reduced energy matrix, or to a particular J,K already specified.

We now consider the reduced energy matrix defined by eqns. 5.9 and 5.10. It can be seen that the matrix is of order 2J+1 and has diagonal terms K^2. The remaining non-zero elements all lie on two off-diagonals separated from the main diagonal by zeros. It was found by Wang (57) that the reduced matrix could

Table 5.1

Rigid asymmetric rotor energy matrices

$$E^+ \begin{pmatrix} 0 & 1 & 0 & 0 & \cdot \\ 2b^2f(J,1) & 4 & 1 & 0 & \cdot \\ 0 & b^2f(J,3) & 16 & 1 & \cdot \\ 0 & 0 & b^2f(J,5) & 36 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

$$E^- \begin{pmatrix} 4 & 1 & 0 & 0 & \cdot \\ b^2f(J,3) & 16 & 1 & 0 & \cdot \\ 0 & b^2f(J,5) & 36 & 1 & \cdot \\ 0 & 0 & b^2f(J,7) & 64 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

$$O^+ \begin{pmatrix} 1-bf^{\frac{1}{2}}(J,0) & 1 & 0 & 0 & \cdot \\ b^2f(J,2) & 9 & 1 & 0 & \cdot \\ 0 & b^2f(J,4) & 25 & 1 & \cdot \\ 0 & 0 & b^2f(J,6) & 49 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

$$O^- \begin{pmatrix} 1+bf^{\frac{1}{2}}(J,0) & 1 & 0 & 0 & \cdot \\ b^2f(J,2) & 9 & 1 & 0 & \cdot \\ 0 & b^2\,f(J,4) & 25 & 1 & \cdot \\ 0 & 0 & b^2f(J,6) & 49 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

be factorised still further into four sub-sub-matrices. This factorisation is useful in greatly reducing the labour of diagonalisation. The four matrices are denoted by E^+, E^-, O^+ and O^-, the E matrices having even diagonal elements and the O matrices, odd diagonal elements. Their detailed form is shown in table 5.1. It can be seen that apart from a few elements close to the top left hand corner, the elements show a regular pattern which extends as far as allowed by the condition $K \leqq J$. The effect of the off-diagonal terms is to shift the roots away from the diagonal elements, the magnitude of this shift being dependent on and roughly parallel to the magnitude of the off-diagonal terms (i.e. to the degree of asymmetry), and inversely proportional to the difference between successive diagonal elements. Thus the most perturbed roots are those at the top left hand corner of each matrix. The matrices are such that the roots derived from a + matrix are always higher than the corresponding root in the - matrix; this is the justification for our later reference to roots from a + matrix as U (upper) levels, and those from a - matrix as L (lower) levels.

If we substitute b = 0, that is we consider a prolate symmetric rotor, then all the off-diagonal elements become zero. The latent roots are then simply K^2 and the energy expression 5.11 reduces to the well-known symmetric rotor formula:

$$W(J,K) = B\,J(J+1) + (A-B)\,K^2 \qquad 5.13$$

If we now consider the oblate symmetric rotor, b = -1 (here still expressed by $b_{prolate}$), then diagonalisation of the reduced matrices gives a set of roots also equal to the squares of alternate integers, denoted K_{+1}^2. The relation between the two limiting roots K_{-1}^2 and K_{+1}^2 (K_{-1}^2 is here the prolate root) is then :

$$K_{-1} + K_{+1} = J + \gamma \qquad 5.14$$

where $\gamma = 0$ or 1 for a + or a - matrix respectively. This relation provides a unique means for identification of a root for any degree of asymmetry; thus when it is required to specify a particular root, it can be described as J, K_{-1},K_{+1}.

In order to obtain the rotational energy levels, the reduced energy matrices of table 5.1 must be diagonalised; a wide variety of procedures have been devised to effect this. The matrix may be expanded about some required root in the form of a power series, with the asymmetry parameter as the argument. The coefficients c_i may be obtained either by expressing the secular determinant in the form of a continued fraction (see King, Hainer and Cross (58, p.35)) or by using nth order perturbation theory (which is in fact algebraically equivalent); n is the highest power of the series at which the expansion is to be cut off. The expression used to obtain a root is then :

$$E(b) = \sum_{i=0}^{n} c_i b^i \qquad 5.15$$

The coefficients must be determined for each required root. This has been done for the expansion in terms of b by Townes and Schawlow (63) p.522, for J,K up to 12,12, and extended by Schwendemann (59) for J,K up to 40,40; by Wait and

Barnett (60)[*] for the expansion in terms of δ (J,K up to 100,100); and by King Hainer and Cross (58) for an expansion in terms of κ centred on the region $\kappa = 0$, (J,K up to 12,12). Polo (61) has described a method of expressing the coefficients themselves in the form of a power series and he gives these coefficients for an expansion in terms of his asymmetry parameter ϵ ($\epsilon = b/2$) up to the fifth power. As it stands therefore, Polo's treatment is exactly equivalent to using the Schwendemann coefficients, as far as the latter extend.

The usefulness of most of these expansions is limited to molecules with a low degree of asymmetry (b close to 0) and to levels with low J and high K_{-1} quantum numbers. Outside these cases, the terms in the expansion 5.15 do not converge sufficiently rapidly up to the fifth power of b (the limit of Schwendemann's tables) and indeed they soon begin to diverge. In the present work, in order to try to extend the usefulness of the Schwendemann coefficients, higher terms in the expansion have been computed (up to c_8 for even K_{-1} and to c_7 for odd K_{-1}); even with this extension, over a large part of the J,K field this approach cannot be used even with a molecule of the small asymmetry of formaldehyde ($b \sim -0.01$). For this reason, in the

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[*] An error in this paper, discovered in the course of the present work while attempting to use Wait and Barnetts coefficients, makes these coefficients invalid for the determination of energy levels (see Wait, J. Mol. Spect., 6, p.276)

present work it has been found necessary to reject the series expansion method.

Another approach that has been widely used is to prepare tables of reduced energies over a range of asymmetries, for each individual level. Turner, Hicks and Reitwiesner (62), have prepared such tables (reproduced by Townes and Schawlow (63)) for J,K up to 12,12 at intervals of the asymmetry parameter κ of 0.01, from $\kappa = 0$ to $\kappa = 1$, while Erlandsson (64) has extended them, at intervals of 0.1 for J,K up to 40,40. In use one has to interpolate between the tabulated values and this inevitably introduces some uncertainties which are in fact unacceptably large for the spectrum at present under investigation; we have, however, found these tables very useful in the present work for obtaining initial approximations to the energies, which are then refined iteratively by the computer as described below.

Another procedure has been devised by Golden (65), who made use of the similarity of the reduced energy matrix to the matrix obtained in the solution of Mathieu functions, for which the characteristic roots have been tabulated. Since the Mathieu matrices are infinite in extent, the best correlation between them and the asymmetric rotor matrices occurs when the latter are of high order. i.e. high J; the Golden procedure is thus a useful supplement to the power series procedure, especially where the latter begins to break down due to high J.

Because of the ready availability of an electronic computer for the present work, it was decided to cabulate reduced energies from the original reduced matrices, and not to rely on any of the approximate methods outlined above. Two procedures have been employed, the first when only one root is required from a given matrix, and the second when all roots are required.

Because of the nature of the rotational structure of bands of a prolate, near-symmetric rotor, it is by far the most convenient to compute E(b)'s for a run of increasing J's for each K in turn: since each energy matrix has latent roots of several K's for a single J, it would be inefficient to diagonalise the whole matrix when only one root is required. Therefore, a method has been employed which delivers roots singly; it is referred to by King, Hainer and Cross (58) p.36. If we symbolise the diagonal elements of one of the reduced energy matrices M, by $a_1, \ldots a_n$, the secular determinant $|M - \lambda I|$ may be expanded in the form of a recursion formula :

$$A_p = A_{p-1} (a_p - \lambda) - A_{p-2} b^2 f(J,q) \qquad 5.16$$

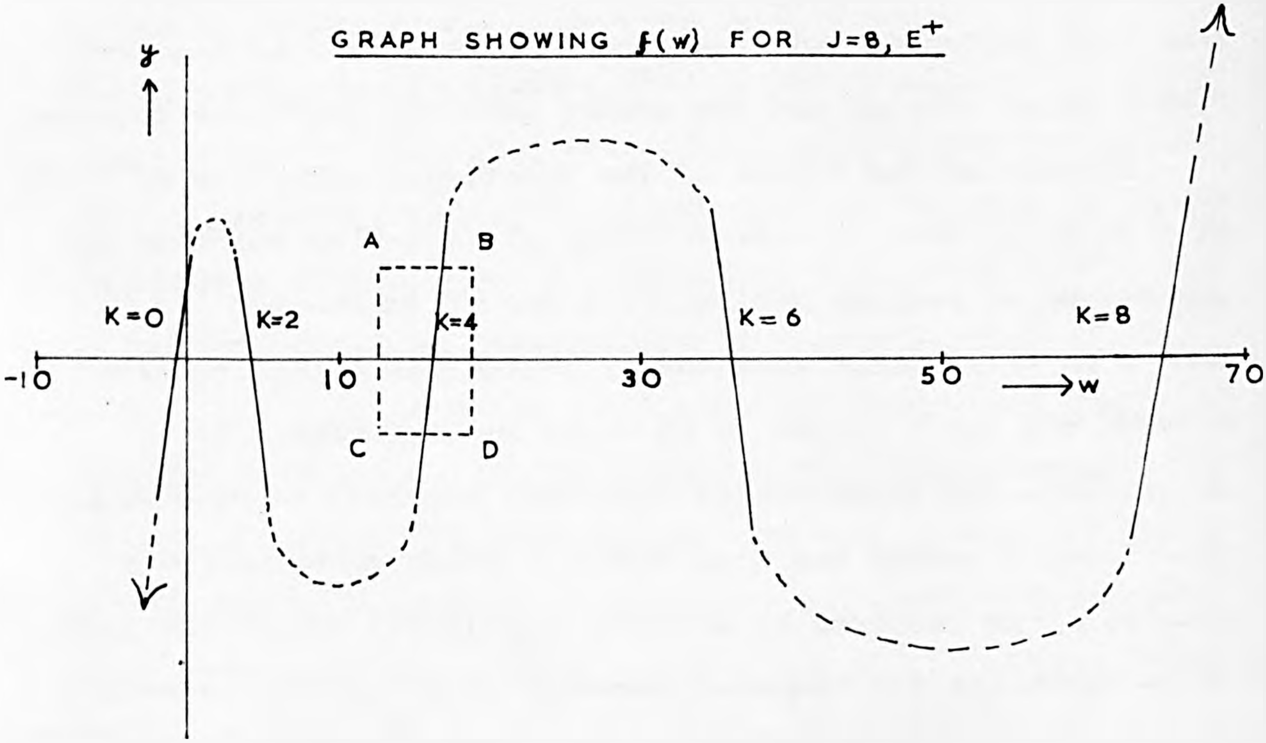
$$p = 1, 2 \ldots n$$

where $A_{-1} = 1$, $A_o = a_1 - \lambda$, and a_n is the last diagonal element. The correct $f(J,q)$ is that one enclosed by the diagonal elements a_p and a_{p-1}. The quantity A_n should be zero when one of the latent roots, λ_i, is substituted. If we substitute instead, an approximation w_1 to one of the λ_i, a non-zero value for A_n will be obtained, say y_1. We can now generalise equation 5.16 in the form :

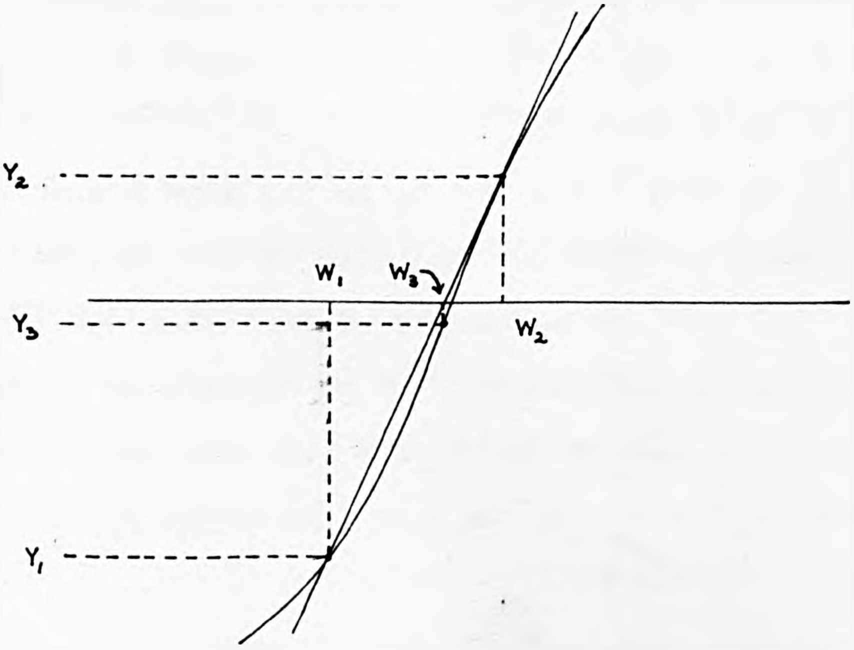
$$y = f(w) \qquad 5.17$$

FIGURE 5.1.

GRAPH SHOWING $f(w)$ FOR $J=8$, E^+



ENLARGEMENT OF SECTION ABCD



The form of this function is oscillatory, and crosses the $y = 0$ axis a total of n times, each intersection corresponding to a root λ_i. The situation is shown diagrammatically in fig. 5.1 for the E^+ matrix of $J = 8$ (the ordinate is not drawn to scale).

If we choose now, a second approximation w_2 to λ_i, an arbitrary (small) distance from w_1, and calculate its corresponding y_2, then it is easy to show by simple coordinate geometry that a better approximation w_3 to λ_i is obtained from the relation :

$$w_3 = \frac{y_2 w_1 - y_1 w_2}{y_2 - y_1} \qquad 5.18$$

This process is known as the method of <u>regula falsi,</u> and may be continued iteratively until the difference between successive approximations is less than some fixed value, ϵ , w_n is then equal to the required root, to an accuracy fixed by ϵ. In practice, ϵ must not be so small that errors of computation due to rounding will cause fluctuations in the w_i greater than ϵ .

This procedure has been programmed as a standard routine, so that it may be incorporated in other programmes; a brief summary of the computing aspects of the routine is given in the Appendix (p.285). For the particular range of asymmetries used in the present work, K^2 is a sufficiently good first approximation w_1 to the root for any J, K with $K \geq 4$; for $K \leqslant 3$, the initial approximation w_1 is set up internally in the routine using an empirical equation of the form:

$$w_1 = K^2 + c_1J^2 + c_2J^2 + c_3J^3 \qquad 5.19$$

for which the coefficients c_i have been computed for each value of K (+ or −) by fitting this cubic equation to approximate values for the roots obtained by interpolation in the reduced energy tables mentioned above (62) and (64).

The second procedure for obtaining reduced energies, when all roots of a given matrix are required, has also been programmed. It is a direct transcription to a computing language of a procedure devised by Bennett, Ross and Wells (74) for use with asymmetric rotor matrices. Its use in the present work is in connection with the computation of asymmetric rotor intensities, and it will be discussed further in the section (5.5) dealing with this topic.

5.3. The non-rigid rotor: centrifugal distortion.

In several papers, Wilson and co-workers (66,67) have developed the theory of centrifugal distortion up to first order, for the general asymmetric rotor. The energy due to distortion, δW, is written in the general form:

$$\delta W = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta \qquad 5.20$$

where the P_α, P_β etc. are angular momentum operators about the principal axes of the molecule; α, β, γ and δ may be any of x, y or z. The τ's are centrifugal distortion constants of the molecule. Of the 81 τ's defined by this equation, many are equal and others are necessarily zero depending onthe symmetry of the molecule.

In the treatment of Kivelson and Wilson (67) the centrifugal energy was determined using a first order perturbation technique. The Hamiltonian for the unperturbed rotational energy was given as equation 5.1 in the previous section; the perturbing Hamiltonian is obtained directly from equation 5.20, in the usual way. Solution of the wave equation to first order gives the expression 5.21 for the energy of a non-rigid rotor.

$$\begin{aligned} W = W_0 &+ A_1 W_0^2 + A_2 W_0 J(J+1) + A_3 J^2(J+1)^2 \\ &+ A_4 J(J+1)(P_z^2)_{av} + A_5 (P_z^4)_{av} \\ &+ A_6 (P_z^2)_{av} W_0 \end{aligned} \qquad 5.21$$

W_0 is the rigid rotor energy, J is the usual quantum number quantising the total angular momentum, and $(P_z^2)_{av}$ is the average or expectation value of the operator $(P_z^{\,2})$; $(P_z^2)_{av}$ is simply $\frac{\partial W_o}{\partial 1/I_{zz}}$, and using the notation of the previous section,

$$(P_z^{\,2})_{av} = \frac{\partial W_o}{\partial A} = \frac{\partial}{\partial A}\left\{D\ J(J+1) + \alpha\, E(b)\right\}$$
$$= E(b) - b\ \frac{E(b)}{b} \qquad 5.22$$

The differential of E(b) with respect to b may be numerically determined as $\frac{E(b+\delta b) - E(b)}{\delta b}$. In the programmed routine for calculation of asymmetric rotor energies, mentioned in the previous section and described in detail in the Appendix p.285, provision is made for calculation of the quantities E(b) and $\frac{\partial E(b)}{\partial b}$ (and incidentally also $\frac{\partial^2 E(b)}{\partial b^2}$) concurrently. The quantity $(P_z^{\,4})_{av}$ in equation 5.21 is more difficult to determine. A route is given by Kivelson and Wilson (67) for its calculation, but for the present work, where low asymmetries are involved, it is given sufficiently well by $(P_z^2)_{av}^{\,2}$.

The six constants A_i are then the centrifugal distortion constants to be determined from the spectrum. In the limiting case of the symmetric rotor, W_o is given by $B\ J(J+1) + (A-B)K^2$ and $(P_z^{\,2})$ becomes K^2. We then have the well-known symmetric rotor formula :

$$W = W_o - D_K\ K^4 - D_{JK}J(J+1)\ K^2 - D_J J^2(J+1)^2 \qquad 5.23$$

where the constants D_K, D_{JK} and D_J are functions of the A_i and the rotational constants, (note here defined with -ve signs).

The present work has shown that equation 5.21, as it stands,

Comparison of distortion formulae. $J = 15, K = 1^{+}$

Table 5.2. (6 A_i)

Constant	Numerical value	Coefficient	Product
A_1	-3.2995^{-5}	94670	-3.124
A_2	7.1136^{-5}	73840	5.253
A_3	-3.9963^{-5}	57600	-2.302
A_4	-1.7793^{-4}	292.56	-0.052
A_5	1.6907^{-4}	1.486	0.000
A_6	1.7179^{-4}	375.06	0.064

Centrifugal distortion = -0.161

Table 5.3. (6 D_i)

Constant	Numerical value	Coefficient	Product
D_E	-6.371^{-4}	3.936	-0.003
D_{EJ}	-4.32^{-5}	476.2	-0.021
D_J	-2.29^{-6}	57600	-0.132
D_4	1.86^{-5}	156.7	-0.003
D_5	2.25^{-7}	18960	-0.004
D_6	1.19^{-7}	6241	0.001

Centrifugal distortion = -0.162

Table 5.4. (4 τ's)

Constant	Numerical value	Coefficient	Product
τ_{xxxx}	-1.3124^{-5}	12105	-0.159
τ_{zzzz}	-2.7627^{-3}	1.423	-0.004
τ_{xxzz}	4.5460^{-6}	262.5	0.001
τ_{xzxz}	-8.2243^{-5}	193.0	-0.016

Centrifugal distortion = -0.178

is not in the arithmetically most convenient form for use in the analysis of a spectrum. In table 5.2, the numerical values for the various terms of that equation are listed separately for a rotational level taken at random (the effect to be discussed is shown by all levels); the constants used are those found experimentally for the ground state of formaldehyde as indicated later, in chapter 8. The total centrifugal distortion is a small quantity, -0.2 cm^{-1}, but is derived as the algebraic sum of terms more than an order of magnitude larger. This indicates that in the formulation as it stands, several terms contain large quantities which later cancel in their sum. The formulation is thus ill-conditioned in the variables A_i. This conclusion is further amplified in practice, as described in section 8.2, since the A_i emerge from a least squares analysis with standard errors of the same magnitude as the constants themselves, and, in addition, the coefficients of correlation between the constants are all over 0.97. This indicates that while one set of constants, computed from the frequency data, may give a good fit to the actual centrifugal distortion, an infinitude of other sets will give a fit, almost as good.

We propose therefore, that a different formulation be used. Substitution in equation 5.21 of the expressions 5.11 for W_o, 5.22 for $(P_z^2)_{av}$ and of $(P_z^2)_{av}^2$ for $(P_z^4)_{av}$, gives an equation in which like terms are collected together and the above behaviour is avoided. (Note that the last substitution above renders the new formulation applicable only to molecules with small asymmetry; the approach should be generally applicable.) The equation we obtain is then :

$$W = W_o + D_E\,E(b)^2 + D_{EJ}\,E(b)J(J+1) + D_J J^2(J+1)^2 + D_4\,E(b)\,E'(b) + D_5\,J(J+1)\,E'(b) + D_6\,(E'(b))^2 \qquad 5.24$$

in which the centrifugal energy is described by way of the six new distortion constants D_i. The first three terms in this equation are analogous to the three terms of the symmetric rotor formula 5.23. The three remaining terms are an order of magnitude smaller than the first three (at least they are in the present work where the asymmetry is small). Table 5.3 shows the magnitude of the six terms of 5.24, determined for the same level as was used for table 5.2. It is immediately obvious that this formulation is superior to that of Kivelson and Wilson for extraction of distortion constants in practice, from a spectrum. The constants obtained, D_i, may readily be converted to the A_i if required.

In order to obtain useful information from the centrifugal distortion constants, such as force constants of the molecule, they must be converted into the τ_i defined by equation 5.18, since these quantities are related more directly to the force constants. Kivelson and Wilson (67) give equations relating the A_i to the six independent τ's that emerge from their first order treatment. Instead of using equation 5.24, we could of course solve directly for the τ's using a distortion relation of the form :

$$W = W_0 + \sum_{i=1}^{6} c_i \tau_i \qquad 5.25$$

This could be done, but since in the case of the pyramidal excited state of formaldehyde, the two sets of constants, D_i and τ_i are equally valid and may be interrelated without too much difficulty, in the case of the excited state the extra work in setting up the coefficients c_i using Kivelson and Wilson's relations, would not be justified.

The situation is, however, different in a planar molecule such as the ground state of formaldehyde. In such a case, of the six τ's, two are necessarily zero as demonstrated by Dowling (68). Clearly, it is more satisfactory here to use equation 5.25 where there are only four non-zero terms, rather than use either of the other two six-constant formulae. This has been done in the present work in order to obtain the final ground state constants for formaldehyde, though computations have also been carried out for both the six D_i and the six A_i. The computation of the four coefficients c_i of the τ_i for each rotational level is a laborious procedure and would only be attempted with the aid of an electronic computer. The route is given in some detail now since it is particularly amenable to automatic computation. A similar procedure has been used by Oka et. al. (44) but in their paper there appear to be certain inconsistencies; these are referred to later.

We first define a matrix R, of order 6 x 6, which relates a vector $\bar{A}$, of the six A_i of equation 5.21, with a vector $\bar{R}$, of six intermediate constants, D_J, D_K, D_{JK}, R_5, R_6 and δ_J,

Table 5.5

U-matrix

	τ_{xxxx}	τ_{zzzz}	τ_{xxzz}	τ_{xzxz}
D_J	$-\frac{1}{32}\ 3\frac{C^4}{B^4} + \frac{2C^2}{B^2} + 3$	$-\frac{3C^4}{32A^4}$	$\frac{1}{16}\ \frac{3C^4}{A^2B^2} + \frac{C^2}{A^2}$	0
D_K	H_o	$H_1 - \frac{1}{4}\ 1 - \frac{C^2}{A^2}$	$H_2 + \frac{1}{4}\ 1 + \frac{C^2}{B^2}$	$\frac{1}{2}$
D_{JK}	$-2H_o$	$-H_1 - H_5 - \frac{1}{4}$	$-H_2 - H_6$	$-\frac{1}{2}$
R_5	$-\frac{1}{32}\ 1 - \frac{C^4}{B^4}$	$\frac{1}{32}\ \frac{C^4}{A^4} - \frac{2C^2}{A^2}$	$\frac{1}{16}\ \frac{C^4}{A^2B^2} - \frac{C^2}{B^2} + 1$	$\frac{1}{8}$
R_6	$\frac{1}{64}\ 1 + \frac{C^4}{B^4} - \frac{2C^2}{B^2}$	$\frac{C^4}{64A^4}$	$\frac{1}{32}\ \frac{C^4}{A^2B^2} - \frac{C^2}{A^2}$	0
δ_J	$-\frac{1}{16}\ 1 - \frac{C^4}{B^4}$	$\frac{C^4}{16A^4}$	$\frac{C^4}{8A^2B^2}$	0

Table 5.6.

H-matrix.

	D_J	D_K	D_{JK}	R_5	R_6	δ_J
A_1	0	0	0	0	$\frac{16}{(B-C)^2}$	0
A_2	0	0	0	0	$-\frac{16(B+C)}{(B-C)^2}$	$-\frac{4}{(B-C)}$
A_3	-1	0	0	0	$2+\frac{16\ BC}{(B-C)^2}$	$\frac{2(B+C)}{(B-C)}$
A_4	0	0	-1	$\frac{4(B+C)}{(b-C)}$	$16\ \frac{(A^2-BC)}{(B-C)^2}-\frac{4}{b^2}$	$-\frac{2}{b}$
A_5	0	-1	0	$\frac{4}{b}$	$\frac{4}{b^2}-2$	0
A_6	0	0	0	$\frac{8}{(B-C)}$	$\frac{16}{b(B-C)}$	0

This last set of constants was used by Nielsen (69) in his centrifugal distortion treatment, but they are here used only as intermediaries. The elements of H may be determined by inspection from the equations numbered 35 in Kivelson and Wilson's paper (67). The relation may be written symbolically as:

$$\bar{A} = H . \bar{R}$$

A second matrix U, of order 6 x 4, relates the vector $\bar{R}$ with a vector $\bar{T}$, of the four τ's of table 5.4. Its elements are obtained from equations 36 of the reference just cited. This relation may be written:

$$\bar{R} = U . \bar{T}$$

If now we symbolise equation 5.21 by

$$W = W_o + \bar{D} . \bar{A}$$

$$W = W_o + \bar{D} . H . U . \bar{T}$$

($\bar{D}$ is of course the vector of the coefficients of the A_i). The vector $\bar{C}$ of the coefficients of the τ's therefore given by:

$$\bar{C} = \bar{D} . H . U \qquad 5.26$$

$\bar{C}$ is obtained by multiplication of the three matrices symbolised in 5.26. The elements of the two matrices H and U are given in tables 5.5 and 5.6. Since they are functions only of the rotational constants of the molecule, they need only be calculated once for a series of energy levels, and then multiplied to give a compound matrix X = H . U. The $\bar{C}$ vector for each level is then obtainedby pre-multiplication of X by a $\bar{T}$ vector characterising the particular level.

Table 5.4 p.125 gives the individual terms of the formulation in terms of the τ's for the same level as that used in the earlier illustrations; it can be seen that the τ formulation, like the D formulation, does not suffer from the defects of Kivelson and Wilson's formulation.

5.4. Rotational perturbations.

Perturbations of the Fermi and Coriolis types were mentioned earlier (section 4.3) in connection with the excited vibrational levels of the electronic ground state. In the vibronic bands studied in the present work, no evidence of Fermi resonance has yet been discovered, but a modified form of Coriolis interaction is observable in some of the bands. This perturbation, described recently by Lide (70), occurs by rotational mixing of the gyrovibronic wave functions of the two members of an inversion doublet. Some anomalies in the microwave spectrum of dideutero-cyanamide, noticed by Millen, Topping and Lide (71), were accounted for by assuming a perturbation of this type. Lide assumed a pyramidal structure for cyanamide with a linear N!C·N chain at an angle to the NH_2 plane. He expressed the angular momentum produced by the out-of-plane NH_2 motion in terms of a set of axes oscillating with the NH_2 plane; in the quantum mechanical treatment this produced matrix elements connecting two vibrational levels.

Lide's theory should be equally applicable to the $^1A'$ electronic state of formaldehyde which also has a pyramidal structure. The perturbation will be described in detail in relation to formaldehyde since some extension to the published treatment is required for this molecule; in particular, Lide's formulation was intended to be applicable to molecules of the very low asymmetry of cyanamide ($b \sim -0.001$) and is inadequate for describing interactions between rotational levels whose energies are greatly affected by the asymmetry. It is however, capable of development for the more general case, and this has now been carried out after a suggestion by Lide (72).

In the published treatment, a Hamiltonian of the form;

$$H = H_v + H_{sr} + H_1 + H_2 + H_3 \qquad 5.27.$$

is obtained where

H_v is the Hamiltonian for the purely vibrational problem,

H_{sr} is the symmetric rotor Hamiltonian, and

H_1 is the usual asymmetry term.

H_2 and H_3 describe the coupling between rotation and vibration.

Lide then proceeds to choose the eigenfunctions of $H_v + H_{sr}$ as basis functions in the quantum mechanical treatment and treats the remaining terms as a small perturbation. If instead, we now choose as basis functions, the eigenfunctions of $\left| H_v + H_{sr} + H_1 \right|$ whose eigenvalues are readily determinable (see section 5.2), and treat $\left| H_2 + H_3 \right|$ as the perturbing Hamiltonian, we obtain a matrix with elements given by :

$$(J,K,v \left| H_v + H_{sr} + H_1 \right| J,K,v) = W_v + W(J,K) \qquad 5.28$$

$$(J,K,v \left| H_2 + H_3 \right| J,K+1,v') = \left[d+e(2K+1) \right] \left[(J-K)(J+K+1) \right]^{\frac{1}{2}} \qquad 5.29$$

where W_v is the eigenvalue of the vibrational level v,

$W(J,K)$ is the rotational energy of the level, including the effects of asymmetry,

and d and e are abbreviated symbols for Lide's parameters $d_{vv'}$ and $e_{vv'}$.

There are, in addition, elements of the form $\left| JKv \; ; \; J,K+3,v' \right|$ not present in the simpler formulation of Lide, but the effect of these has been shown to be practically insignificant in the present work.

The last two quantities d and e are related in a complicated way to shape and height of the potential barrier which causes the inversion splitting.

The matrix described by equations 5.28 and 5.29 is diagonal in J and so each J may be considered separately. Each of these matrices may be factorised into two sub-matrices, one of which contains the states v even, K even and v odd, K odd, while the second contains v even, K odd and v odd, K even. The first of

Table 5.7

Perturbation matrix (after Lide (72))

$$\begin{pmatrix}
W_v^0 + W_{J,3^-} & \beta_{J,-3} & 0 & 0 & 0 & 0 & 0 \\
\beta_{J,-3} & W_v^1 + W_{J,2^-} & \beta_{J,-2} & 0 & 0 & 0 & 0 \\
0 & \beta_{J,-2} & W_v^0 + W_{J,1^-} & \beta_{J,-1} & 0 & 0 & 0 \\
0 & 0 & \beta_{J,-1} & W_v^1 + W_{J,0^+} & \beta_{J,0} & 0 & 0 \\
0 & 0 & 0 & \beta_{J,0} & W_v^0 + W_{J,1^+} & \beta_{J,1} & 0 \\
0 & 0 & 0 & 0 & \beta_{J,1} & W_v^1 + W_{J,2^+} & \beta_{J,2} \\
0 & 0 & 0 & 0 & 0 & \beta_{J,2} & W_v^0 + W_{J,3^+}
\end{pmatrix}$$

these matrices is given in table 5.7 for the case $J = 3$. W_v^0 and W_v^1 are the vibrational energies of the two inversion levels, say the 0^+ and 0^- levels of $^1A'$ formaldehyde, and their difference is the inversion splitting, I. The remaining terms are given by:

$$W(J,K) = B\,J(J+1) + \alpha E(b)$$

$$\beta_{J,K} = \left[d + e\,(2K+1)\right]^2 \left[J(J+1) - K(K+1)\right]$$

In the last equation, K is taken with a negative or a positive sign according to whether the level is from a − or a + reduced energy matrix (see section 5.2).

It now remains to diagonalise each of these matrices in order to obtain the perturbed energy of each level. To first order, this energy, W', for a level in an upper member of an inversion doublet, is given by the equation:

$$W' = W_0' + \frac{\left[d \pm e\,(2K-1)\right]^2 \left[J(J+1) - K(K-1)\right]}{I + W_0 - W(J,K-1)^p} + \frac{\left[d \pm e\,(2K+1)\right]^2 \left[J(J+1) - K(K+1)\right]}{I + W_0 - W(J,K+1)^p} \qquad 5.30$$

Here K is to be read as $|K|$, W_0 is a rigid rotor energy.
In this equation, W_0' is the unperturbed energy for the level J,K, that is the rotational energy including the effects of centrifugal distortion. The terms with the superscript p represent the appropriate parts of the diagonal elements adjacent to that for the level J,K in the matrix typified by table 5.7 : that is, they are the <u>unperturbed energies</u> of the

perturbing levels. This expression thus gives the total energy of a rotational level J, K, in the upper member of an inversion doublet, as perturbed by the rotational levels J, K±1 of the lower member. There is of course a corresponding perturbation for the lower member by the upper member; the expression for it is obtained simply by changing the sign of I and the appropriate primes in equation 5.30.

Strictly, the energy terms in the denominators of equation 5.30 should represent the actual rotational energies of the perturbing and perturbed levels (i.e. including the effects of centrifugal distortion and the actual perturbation itself - this part would have to be treated iteratively); in the present work, as also in Lide's treatment, the energies of the undistorted, unperturbed levels have been used since, in any case, the expression 5.30 is derived from a first order approximation. The essential difference in this treatment from that of Lide is that the energy terms here include the effects of asymmetry, whereas Lide used the symmetric rotor approximation.

We now consider the individual terms of the perturbation expression in more detail. The numerators contain the quantities d and e which may be regarded with I, as parameters describing the perturbation. The ± signs correspond respectively to the cases of a K^+ and a K^-

perturbed level; thus if the e and d terms are of comparable magnitude, levels J,K^+ and J,K^- will be shifted to a different extent; if these levels were previously degenerate (i.e. for high K, where the effects of asymmetry are small) they will therefore be split by the perturbation. In fact, in the present work for the A_2 band (which has been most fully investigated in this connection) least squares solution for d and e together with the rest of the rotational constants, delivers a value for e which is almost negligible; no significant splitting should occur, and none is observed.

Each denominator contains the parameter I, (the inversion splitting) and the difference between two rotational energies. When this difference becomes numerically equal, but of opposite sign, to I, that is when the two gyrovibronic levels concerned become degenerate, the denominator becomes zero, and the perturbation becomes, at least to first order, infinite. If we keep J constant, and consider levels of increasing K (or vice-versa) then the energies of the perturbed levels increase at a different rate from those of the perturbing levels. As degeneracy is approached, with change of J or K, the magnitude of the perturbation increases sharply, changes sign as degeneracy is passed, and finally decreases slowly.

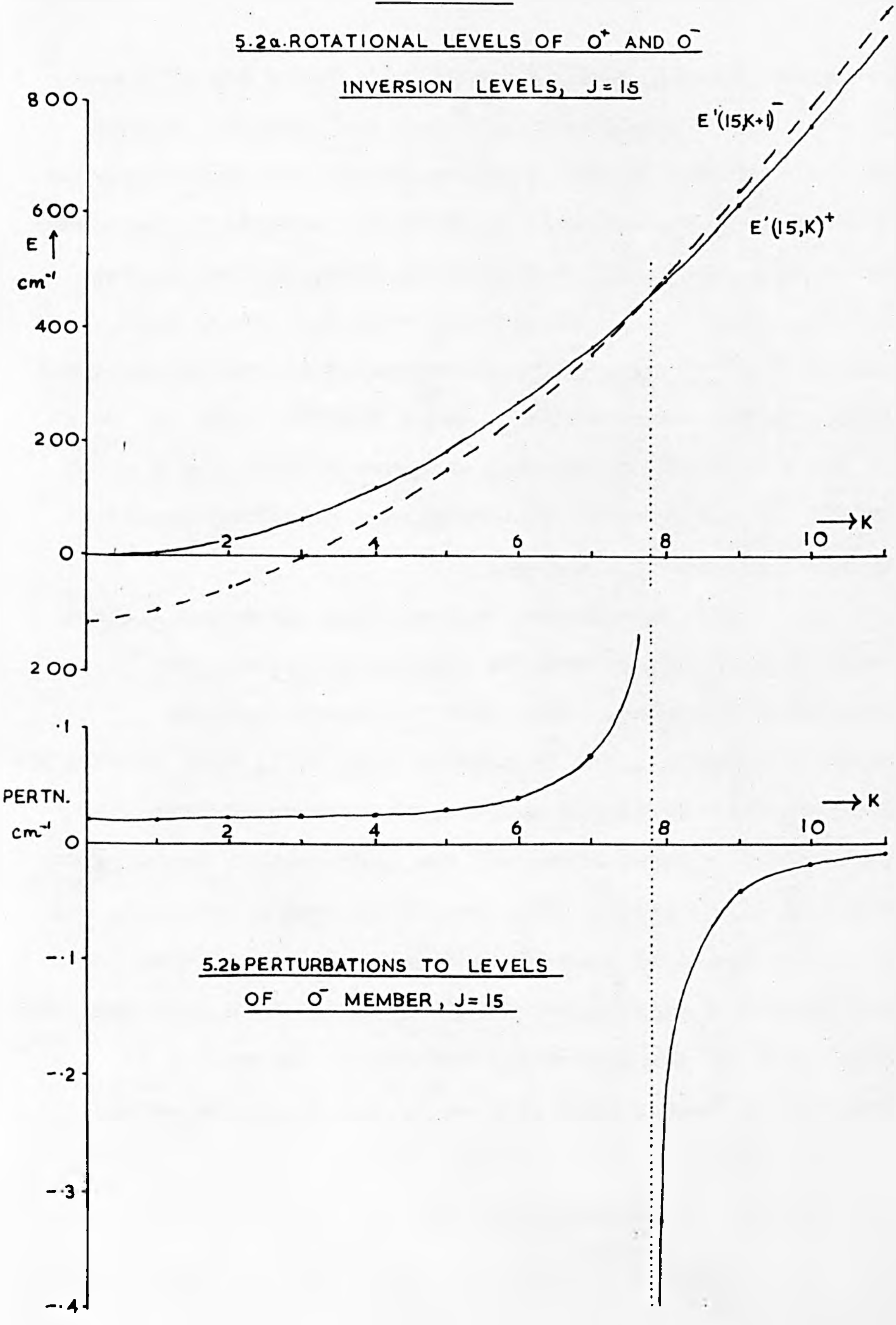


FIGURE 5.2.

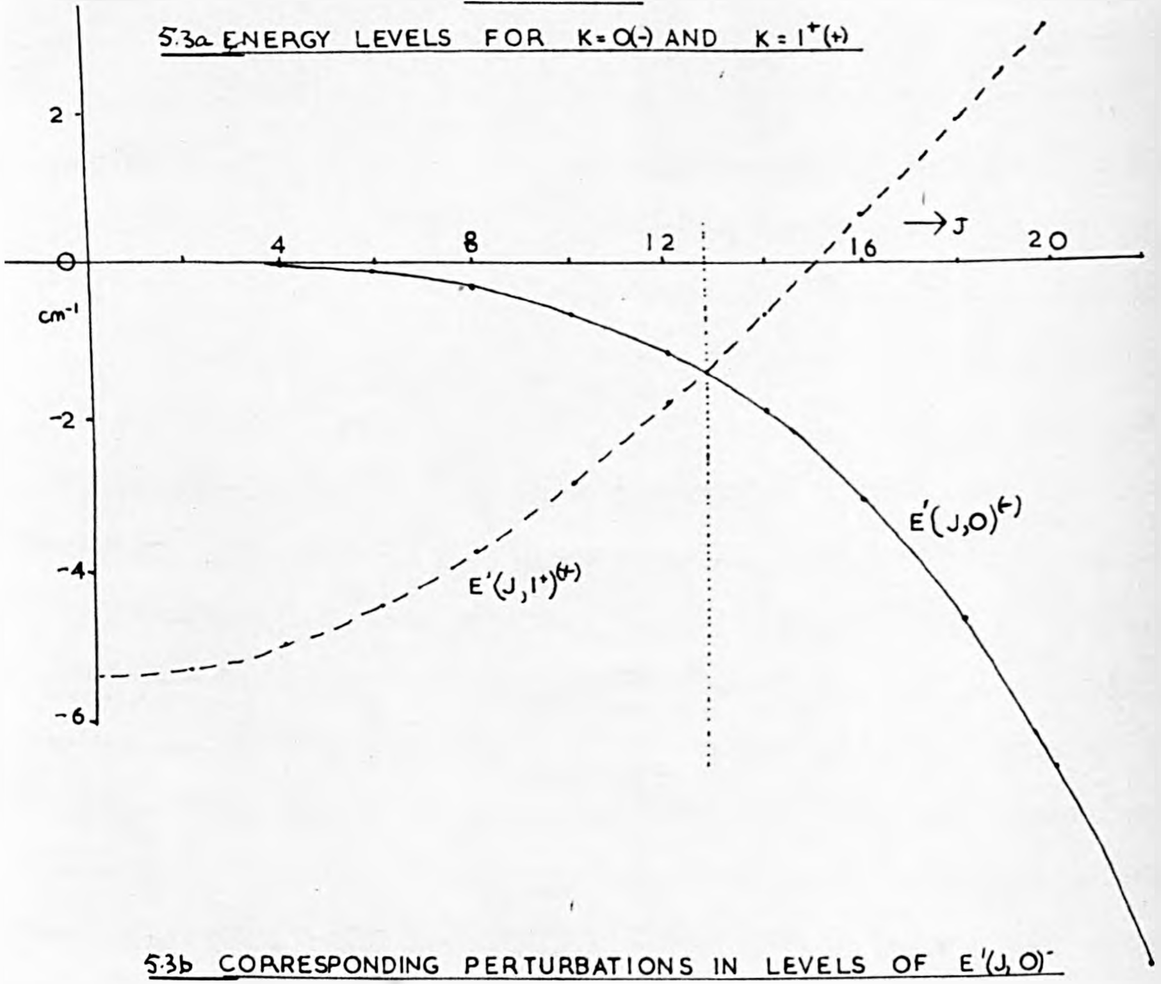
5.2a. ROTATIONAL LEVELS OF 0^+ AND 0^- INVERSION LEVELS, J = 15

5.2b PERTURBATIONS TO LEVELS OF 0^- MEMBER, J = 15

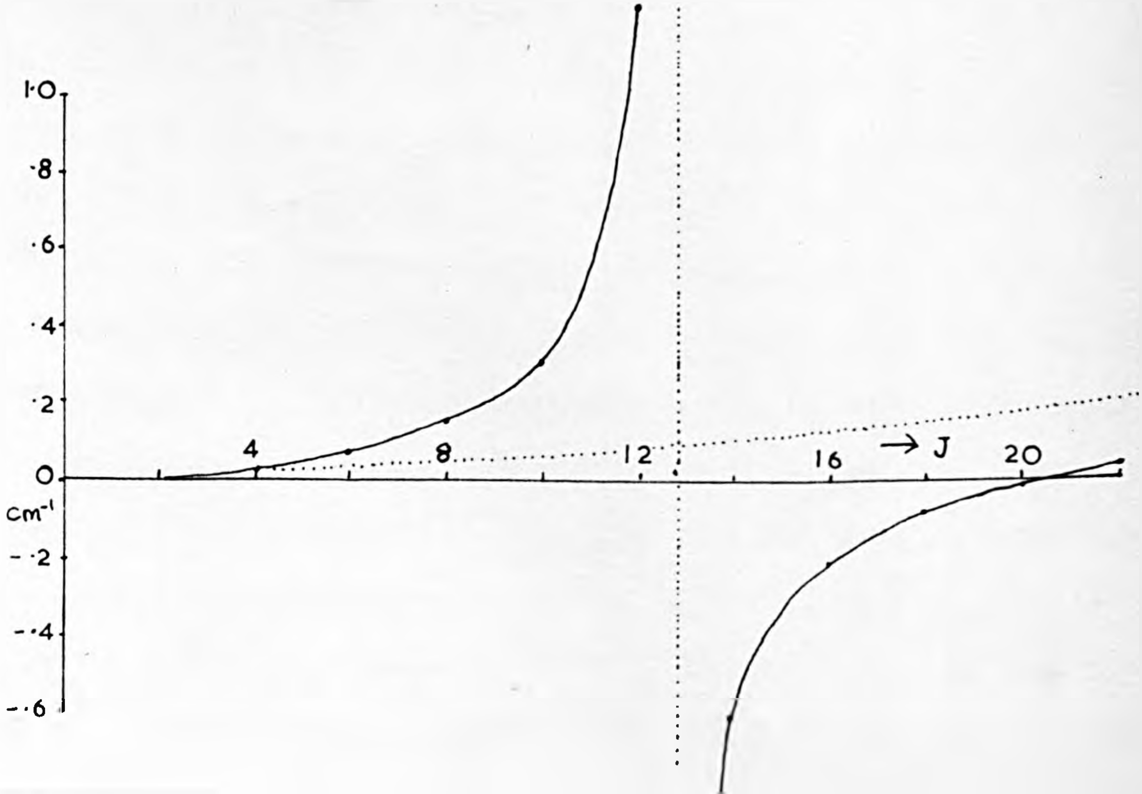
The two possible situations are demonstrated in figs. 5.2 and 5.3. In the first, fig. 5.2a, we have a case similar to that arising in formaldehyde due to the observed inversion splitting of 125 cm^{-1} between the 0^+ and 0^- levels. We will consider initially, only the perturbation arising from rotational levels J,K of the 0^- state by levels J,K+1 of the 0^+ state. The points lying on the full curve correspond to the unperturbed energy levels for the 0^- level, of a constant value of J, and the energies are plotted against their increasing values of K. (For clarity, the asymmetry splitting of the levels at low values of K is not shown since it is not immediately relevant to the present argument. Also, the DJ(J+1) term in the energies has been removed for the same reason.) The points on the dashed curve arise from the 0^+ level and are for the same J as the other curve; these are however plotted against K-1 so that levels which perturb one another according to the symmetry selection rule inherent in Lide's treatment (K perturbed by $K\pm1$) lie on the same ordinate. The curve for perturbation by levels K-1 in the 0^+ state is not shown; in fact it lies below the two curves shown, and since it never crosses the curve of the 0^- levels, that part of the perturbation arising from it it small and regularly increasing with J. Both curves shown are for rigid rotor energies, and the rotational constants used here for purposes of illustration are $\alpha = 7.5$ cm^{-1}, b = -0.007 and I is taken as 125 cm^{-1}; these figures approximate to the actual figures for excited

FIGURE 5.3.

5.3a ENERGY LEVELS FOR K = 0(-) AND K = 1+(+)



5.3b CORRESPONDING PERTURBATIONS IN LEVELS OF E'(J,O)⁻



formaldehyde in its 0^+ and 0^- states. In the actual case however, the rotational constants differ in the two vibronic levels; where known, even approximately, their different values are used in the numerical analysis.

Fig. 5.2b shows the corresponding perturbations in the levels of the 0^- state; in their calculation, d and e have been taken as 0.07 and 0 respectively (again approximately those found in practice for one such perturbation occuring in the A_2 band), and the curves are drawn for $J = 15$. As can be seen, the perturbation can rise to about 0.6 cm^{-1} with the rotational constants mentioned above. In the present work, perturbations of this kind have been found of similar magnitude and the run of the perturbation along K is similar. It is apparent from equation 5.30, that for a perturbation of this type, the effect of increasing J will be to increase the magnitude in a manner roughly proportional to $J(J+1)$.

In fig. 5.3b we have the case of an inversion doublet where the splitting is much smaller than in the previous case; 13 cm^{-1} has been chosen as an example. The full curve shows the energy levels for $K = 0$ of an 0^- level, plotted now against J, while the dashed curve shows the levels for $K = 1^+$ of the 0^+ level, also plotted against J; levels in the same vertical line can then perturb one another. Here again, the energy term $DJ(J+1)$ has been omitted for purposes of clarification; if we assume each vibronic level to have the same value for D, introduction of this term would merely increase the slopes of the two curves without altering the vertical distance between them. In the more general case, small differences in D can occur; inclusion of this term does not materially affect the character of the perturbation but its numerical effect cannot be treated as negligible. The effect of asymmetry at these levels of low K is seen in the two curves as the departure from horizontal straight lines. The rotational constants are again $\alpha = 7.5$ and $b = -0.007$ for both levels.

A crossing point occurs with this situation also, here due entirely to the effects of asymmetry; it was in order to account for such a perturbation observed in the region of low K that Lide's original theory was modified. The perturbations corresponding to fig. 5.3a are shown in the accompanying fig. 5.3b, again taking $d = 0.07$ and $e = 0$. The effect of the second term in equation 5.30 (that is in this case, a perturbation of levels $K = 0$ by $K = 1^-$ in the other state) is always positive but small throughout; it steadily increases with J, whereas the first term, initially predominant, decreases steadily after the near-degeneracy, so that at high J the curve again becomes positive as will be seen in fig. 5.3b.

Formaldehyde does not, of course, have inversion doublets of this low magnitude: the effect of adding a vibration common to both levels would, if anything, be expected to increase rather than decrease the inversion splitting. However, it is quite possible that higher vibrational levels built on a (+) inversion level, accidentally become near-degenerate with other vibrational levels built on a (-) level. Then, if the symmetries of the two sets of perturbations are the same, the two composite levels will perturb one another. Such a perturbation is more like a normal Coriolis perturbation but it is expected that the general form of Lide's theory is substantially applicable to this case. The parameters d and e would not have the significance they have in a straightforward case of a Lide perturbation. Perturbations of qualitatively the same form as fig. 5.3b have been found in some of the vibronic bands of formaldehyde, and their origin, in relation to the above account, is discussed in chapter 7 where the observed bands are described individually.

5.5. Intensities of asymmetric rotor transitions.

In the rotational analysis of vibronic bands, an estimate of the expected intensity of a transition is almost as important as the expected frequency as an aid to the assignment of observed transitions. The calculation of intensities has been described in detail by Cross, Hainer and King (73); a summary is given below, especially with relevance to the use of electronic computers for their calculation.

The integrated intensity of a spectral line, I, is given by:

$$I = \frac{8\pi^3 \nu N \, g_{n''} \, (1 - e^{-h\nu/kt}) \, e^{-E_{n''}/kt}}{3\,h\,c \sum (g_n - e^{-E_{n''}/kt})} \left| \mu_{n'',n'} \right|^2 \qquad 5.31$$

(excited state quantities are primed, ground state quantities are double primed). We now consider each of the terms in 5.29 separately.

1) ν is the true frequency of the transition. The range of wavenumbers in a band of formaldehyde is about 300 cm^{-1} while the actual frequencies themselves are of the order 30,000 cm^{-1}; therefore, only a 1 error is introduced by assuming the factor ν in 5.31 to be constant over a single band. Since in the present work, only relative intensities are of interest and these can only be estimated from the observed spectrum to something like 10% accuracy, this factor is rejected in the present calculations.

2) N is the number of molecules per cc ; this factor is empirically corrected for in assessing spectra from different plates in a manner described earlier in section 3.5.

3) The factor $(1-e^{-h\nu/kt})$ does not differ appreciably from 1 for the rotational frequencies considered, while the sum over states in the denominator is constant.

4) g_n'' is the statistical weight factor of the lower state of the transition described by a set of quantum numbers abbreviated as n". Without going into the well known theory of the effects of the nuclear spins of equivalent nuclei on the population of rotational levels (see Townes and Schawlow (63)

p.102), it is sufficient to state here that for formaldehyde (HCHO), levels with even K have $g_{n''} = 1$ while levels with odd K have $g_{n''} = 3$. The dideuterated form, DCDO, has statistical weight factors 6 and 3 for even and odd K respectively.

5) The Boltzmann factor, $e^{-E_{n''}/kt}$, is readily calculable from the known energy of the lower state level of the transition, $E_{n''}$, and the temperature of the absorbing gas, t.

6) The last factor, $|\mu_{n'', n'}|^2$ is the square of the magnitude of the n'', n' element in the matrix of the transition moment vector μ. It may be expressed in terms of the components along the molecule-fixed axes, (g = a, b and c) and the direction cosines Φ_{Fg}, relating the space-fixed axes (F = X, Y, Z) to the molecule - fixed axes. Since we are interested only in the relative strength of transitions, the magnitude of the transition moment is of no immediate interest. The direction cosines may be factored into J-, K- and M-dependent terms in the fashion,

$$(J'',K'', M''|\Phi_{Fg}| J', K', M') = (J''|\Phi_{Fg}|J').(J''K''|\Phi_{Fg}|J'K').$$
$$\times (J'', M''|\Phi_{Fg}| J'M') \qquad (5.33)$$

in which J, K, and M are the quantum numbers describing the state and which previously were summarised as n. The factors of the dipole matrix elements in a symmetric rotor representation have been reproduced by several authors but

Table 5.8

Factors of the direction cosine matrices

(1) $\left(\Phi_{Fg}\right)_{J'';J'}$		
	$J\rightarrow J+1$	$\left[4(J+1)\sqrt{(2J+1)(2J+3)}\right]^{-1}$
	$J\rightarrow J$	$\left[4J(J+1)\right]^{-1}$
	$J\rightarrow J-1$	$\left[4J\sqrt{(4J^2-1)}\right]^{-1}$
(2) $\left(\Phi_{Fa}\right)_{J''K'';J'K'}$		
	$J\rightarrow J+1$	$2\sqrt{(J+1)^2-K^2}$
	$J\rightarrow J$	$2K$
	$J\rightarrow J-1$	$-2\sqrt{J^2-K^2}$
(3) $\left(\Phi_{Fb}=\pm i\,\Phi_{Fc}\right)_{J'',K'';J'K''\pm1}$		
	$J\rightarrow J+1$	$\mp\sqrt{(J\pm K+1)(J\pm K+2)}$
	$J\rightarrow J$	$\sqrt{(J\mp K)(J\pm K+1)}$
	$J\rightarrow J-1$	$\pm\sqrt{(J\mp K)(J\mp K-1)}$
(4) $\left(\Phi_{Zg}\right)_{J''M'';J'M''}$		
	$J\rightarrow J+1$	$2\sqrt{(J+1)^2-M^2}$
	$J\rightarrow J$	$2M$
	$J\rightarrow J-1$	$-2\sqrt{J^2-M^2}$
(5) $\left(\Phi_{Yg}=\pm i\,\Phi_{Xg}\right)_{J''M'';J'M''\pm1}$		
	$J\rightarrow J+1$	$\mp\sqrt{(J\pm M+1)(J\pm M+2)}$
	$J\rightarrow J$	$\sqrt{(J\mp M)(J\pm M+1)}$
	$J\rightarrow J-1$	$\pm\sqrt{(J\mp M)(J\mp M-1)}$

they are given again in table 5.8 with some extra clarification.

All that is required now is to transform the matrices defined by the elements of table 5.8 into an asymmetric rotor representation. Since all but the J,K factors are invariant to such a transformation, we need only consider at first the elements in rows 2 and 3 of the table. The outline of the procedure given below is followed more or less in the computer programmes HR515 and HR5.25 in the course of this work; (see the Appendix, p.309 for more details).

We first set up the relevant matrix of symmetric rotor direction cosine elements which contains the transition under consideration, say J", K" J', K'. Such a matrix is of order 2J" + 1 x 2J' + 1, but this may be factorised into four sub-matrices in an analogous manner to the factorisation of the reduced energy matrices (see section 5.2); this also provides a convenient means of expressing the selection rules. These selection rules are given in table 5.11, and are explained in more detail in the next section. A typical direction cosine matrix is given in table 5.9 for a b-axis transition between the E^+ levels for J = 10 and the O^- levels for J = 9; the elements are obtained directly from table 5.8. We transform this matrix, M_{Sr} by the relation

$$M_{a.r.} = T_1^{-1} \cdot M_{s.r.} \cdot T_2 \qquad 5.32.$$

Table 5.9

J,K factors of direction cosine matrix for J=10, $E^+ \rightarrow 9, 0^-$

$J' = 9\ (0^-)$

	K' K''	1	3	5	7	9
$J''=10$ (E^+)	0	$\sqrt{180}$	0	0	0	0
	2	$\sqrt{132}$	$\sqrt{56}$	0	0	0
	4	0	$\sqrt{178}$	$\sqrt{34}$	0	0
	6	0	0	$\sqrt{240}$	$\sqrt{12}$	0
	8	0	0	0	$\sqrt{306}$	$\sqrt{2}$
	10	0	0	0	0	$\sqrt{380}$

Table 5.10

$$P = \sum_{F,M'',M'} \left(\Phi_{Fg}\right)^2_{J'':J'} \cdot \left(\Phi_{Fg}\right)^2_{J''M'':J'M'}$$

J''	J+1	J	J-1
P	$\frac{1}{4(J+1)}$	$\frac{3(2J+1)}{4J(J+1)}$	$\frac{1}{4J}$

Table 5.11

Asymmetric rotor selection rules

	$J \rightarrow J\pm1$	$J \rightarrow J$
a axis	$E^+ \longleftrightarrow E^-$ $0^+ \longleftrightarrow 0^-$	$E^+ \longleftrightarrow E^-$ $0^+ \longleftrightarrow 0^-$
b axis	$E^+ \longleftrightarrow 0^-$ $0^+ \longleftrightarrow E^-$	$E^+ \longleftrightarrow 0^+$ $0^- \longleftrightarrow E^-$
c axis	$E^+ \longleftrightarrow 0^+$ $0^- \longleftrightarrow E^-$	$E^+ \longleftrightarrow 0^-$ $0^+ \longleftrightarrow E^-$

where T_1 and T_2 are the matrices which diagonalise the appropriate lower and upper state reduced energy matrices, respectively. These matrices are obtained in the programme by first setting up the reduced energy matrices, diagonalising them by the method of Bennett, Ross and Wells (74), already referred to on p.122, and then calculating the transformation matrices by the method described by Gora (75). The required elements may then be picked out from the matrix and squared. The J"; J' factor of equation 5.33 is obtained directly from table 5.8. The factor involving J",M";J'M' must be summed over all M" and M' since, in the absence of external fields, all the levels described by different M quantum numbers are degenerate. Summation over M" is simply multiplication by the factor 2J + 1 since this is the M-degeneracy of a given J. Summation over all possible M' may be shown to be equivalent to multiplication by 4(J + 1)(2J+3) for the case J → J + 1, by 4J(J + 1) for the case J → J, and by 4J(2J-1) for J → J-1. Also, since X, Y, and Z (the space fixed axes) are all equivalent in the absence of external fields, summation over F involves multiplication by the factor 3. Thus for a given transition J" → J', all the elements J,K:J',K' are to be multiplied by a composite common factor; these factors are given in table 5.10.

To sum up, the line strength of a transition is obtained by first calculating the JK factor, squaring it and multiplying by the relevant factor from table 5.10.

Finally the Boltzmann and statistical weight factors are computed and multiplied in.

The programme that has been written for this job is designed to be as general as possible. It allows a-, b- and c- axis transitions to be computed for J, K up to 40,40 and allows for the asymmetry parameter of the upper and lower states to differ, while in the calculation of ground state energies(needed for the Boltzmann factor), the rigid rotor approximation is adequate and is therefore used. Also, the corresponding frequencies may be determined at the same time since the relevant material has to be computed for the line strengths; although not directly applicable to the present work, this feature allows band contours to be calculated, and the programme has in fact been used for this purpose by Dunn (32), as mentioned earlier, in section 1.6.

Tables of line strengths have been published ((73), and reproduced by Townes and Schawlow (63) p. 557), but since in these only five asymmetry values are made to cover the entire range from prolate to oblate symmetry, interpolation is both tedious and subject to error. In addition, the tables apply only to transitions involving J, K $\leqslant$ 11.

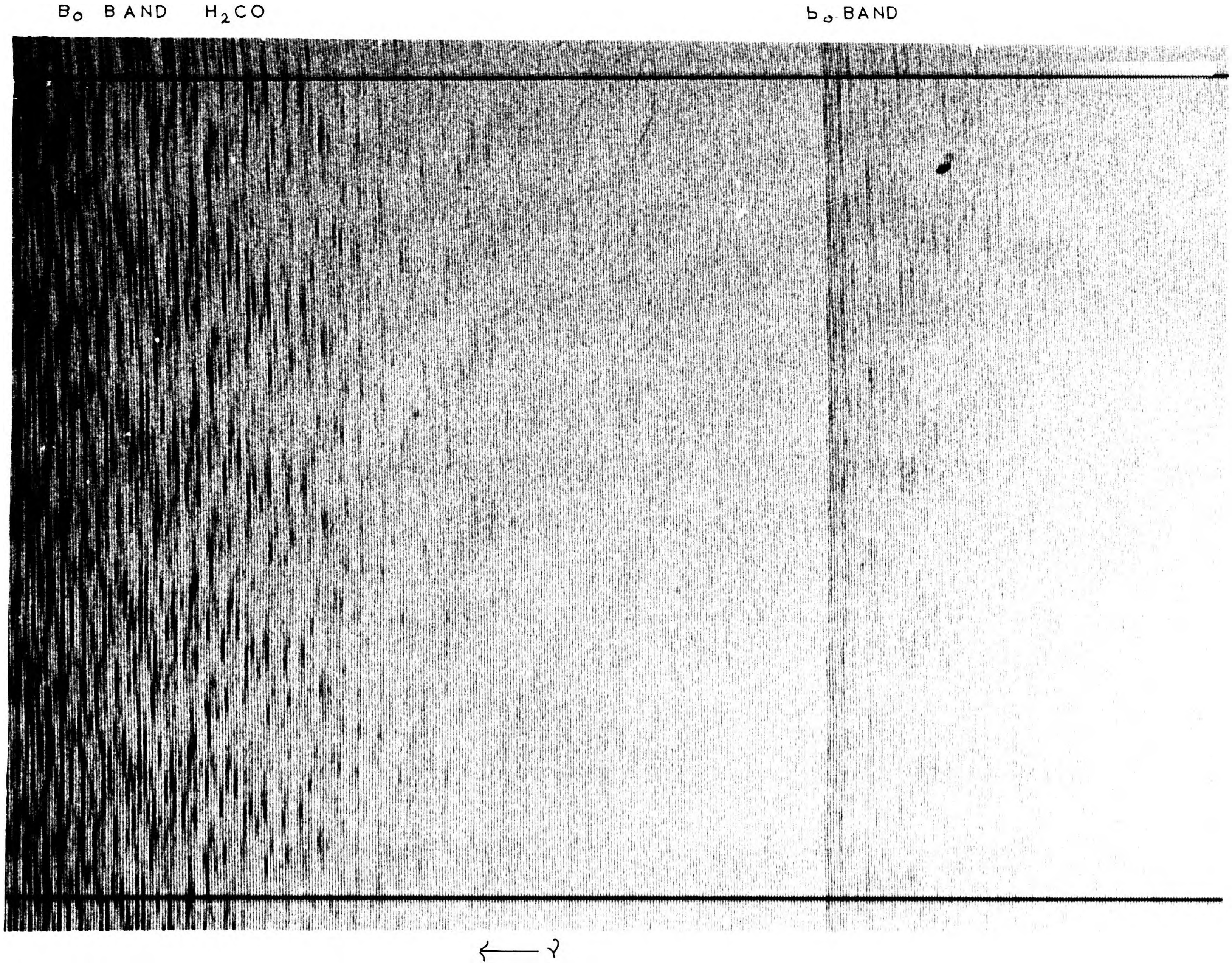


FIGURE 5.4.

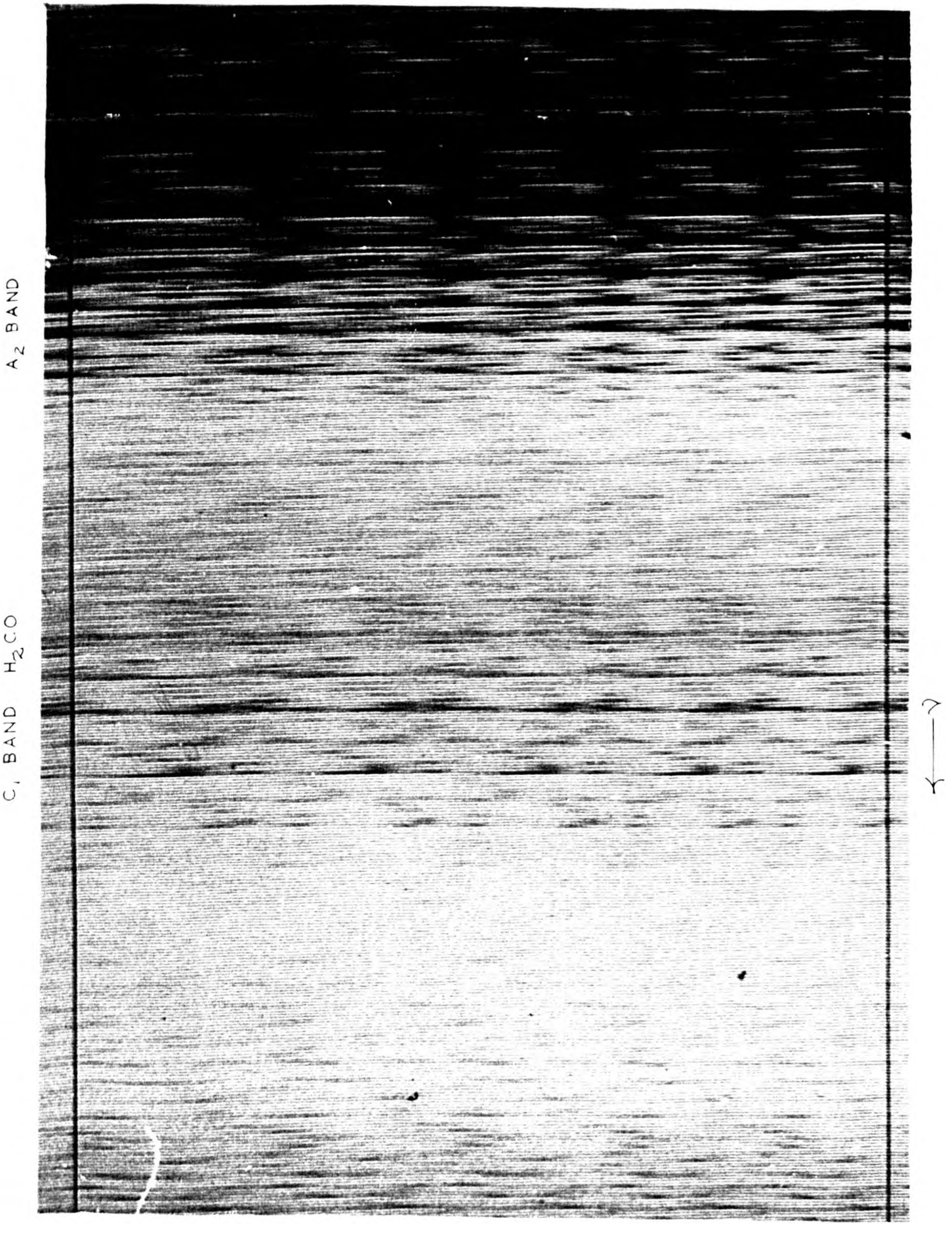
5.6. The structure of vibronic bands of formaldehyde.

The detailed structure of a band is governed by three factors; the energies of the rotational levels (discussed above in sections 5.2 to 5.4), the intensities of the transitions (discussed in section 5.4); and finally the selection rules governing the occurrence of transitions.

The selection rules arise directly from the quantum mechanical treatment and have been given in table 5.11. They depend on the direction of the transition moment of the molecule and are rigidly adhered to. However, since most asymmetric molecules have a low degree of symmetry and indeed the symmetry group often changes on electronic excitation, it is rare for the transition moment to lie wholly along a single axis of the molecule. Also the interaction between rotation or vibration and electronic motions can induce transition moments along any of the axes, and it is therefore quite common for bands of types A, B and C (p. 93) to occur in a spectrum. It is usual to class type A bands separately from types B and C; the former are termed parallel bands ($\Delta K = 0$) while the others are both termed perpendicular ($\Delta K = \pm 1$).

The rotational structure of bands of a prolate near-symmetric rotor is most conveniently analysed into sub-branches, that is, series of lines with a common K'', ΔK and

FIGURE 5.5.



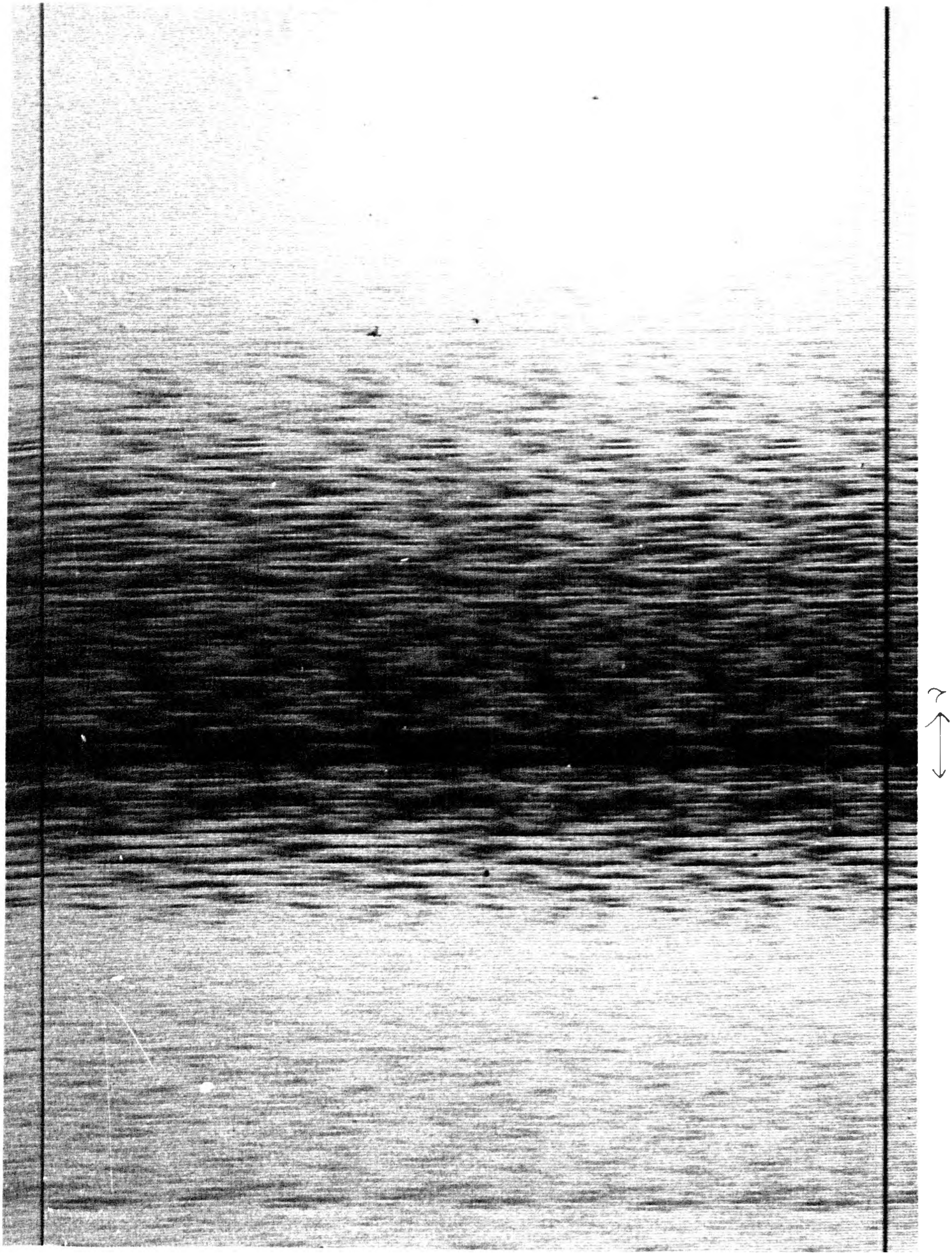
ΔJ but with increasing values for J''. The sub-branches with low K are further analysed into sub-sub-branches, in consequence of the K splitting; hereafter, all sub-sub-branches are discussed as though they were individual sub-branches. Some of these can be picked out from the enlargements of the spectrum simply by inspection, e.g. see fig. 2.3, p. 38.

The parallel bands of formaldehyde have a very condensed structure since the restriction $\Delta K = 0$ causes the origins of sub-branches to fall very close to one another. An example of such a band is shown in fig. 5.4 which is the b_o band of formaldehyde, HCHO. In HCHO, these bands are all very weak compared with the relatively strong type B bands; indeed, fig. 5.4 was obtained from a spectrum with the highest pressure and longest path-length of absotbing gas used in the present work.

A typical type B band is shown in fig. 2.3, p. 38 which is the A_o band of HCHO. The very weak parallel band a_o can just be discerned beneath the structure of the stronger band. The difference between type B and type C bands is not so well marked. The C_1 band of formaldehyde, shown in fig. 5.5, is now believed to be of type C; here, apart from an anomolous intensity effect at low K values, discussed in chapter 7, the general appearence of this band is roughly similar to the usual type B bands. The difference only becomes apparent when the lines affected most by the asymmetry of the molecule are analysed.

The effect of deuteration on the shape of a band is shown in fig. 5.6 which is of the A_o band for DCDO. The much more condensed structure compared with that of the

FIGURE 5.6.



A_0 BAND D_2CO

same band for HCHO, fig. 2.3 p.38, is due to the smaller rotational constants, especially α . In addition, the statistical weight factor in the expression for the intensity of a rotational transition has changed on deuteration from 3 : 1, to 3 : 6 for levels with odd and even K", repectively. This has the effect of making the intensities of the successive rR heads for DCDO bands more regular than in the HCHO bands, where the heads with odd K" stand out from those with even K".

All these effects will be described in detail in chapter 7 , when the bands investigated in the present work will be discussed individually.

We now consider in detail, the rotational structure of type B bands of formaldehyde, since it is with this that much of the rest of this thesis is concerned. (In work conducted by Dr. Poole, immediately prior to the present work, it was demonstrated conclusively that the A_2 band was of type B, in accord with the findings of Dieke and Kistiakowsky (14) and others.) Expressions for the rotational energies of the levels have been discussed earlier in this chapter and the selection rules have also been stated in table 5.11. The selection rules for a b-axis moment may now be stated in a more convenient form as :

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

$$\Delta K_{-1} = \pm 1, \pm 3, \pm 5 \text{ etc.}$$

$$\Delta K_{+1} = \pm 1, \pm 3, \pm 5 \text{ etc.}$$

$$K_{-1} + K_{+1} = J + \gamma \quad \text{(for both levels involved)} \qquad 5.34$$

$$(\gamma = 0, 1)$$

that is the parity of both K_{-1} and K_{+1} must change in a transition. Although the transitions with ΔK greater than ± 1 are made allowed by the asymmetric rotor selection rules, they are here in fact, negligibly weak. The usual notation for describing sub-branches and individual transitions will be followed, that is, sub-branches with $\Delta K_{-1} = -1$ and $+1$ will be described as p and r type branches, while for $\Delta J = -1, 0$ and $+1$, the designation P, Q and R will be used, the two symbols following consecutively. After these two, the letter J (or its numerical value, J'' when we are considering a particular transition) is written followed by the appropriate value for K''. Finally, for sub-branches split by the asymmetry, the letters U or L follow the K'' value, according to whether the ground state level is a U or an L level See p.116; when the transition (or sub-branch) is not split, no symbol is attached. As an example, the b-axis transition denoted by rQ 9 1 U begins and terminates on levels with quantum numbers $9_{1,8}$ and $9_{2,7}$ respectively. (In the lists of assignments given in the appendix, capital letters have had to be used for both of the first two symbols, due to the limitations of the teleprinter; the first letter is to be read as a small letter.) In general, the strongest sub-branches for a given K'' are the rR and pP sub-branches, followed closely by the rQ and pQ sub-branches; the rP and pR sub-branches are considerably weaker. This general rule no longer holds with the branches of low K'' since for these, the asymmetry tends to cause the intensities to follow those for the oblate limit, that is for ΔK_{+1} instead of for ΔK_{-1}).

The fact that the rotational constant D is larger in the ground state than it is in the vibrational levels of the excited state examined so far, causes the rR and pR sub-branches to form heads. This is readily seen in figure 2.3 p.38 where the rR heads are marked from K" = 0 to K" =6; after this, heads are not formed since the low J" values are missing (J" $\geqslant$ K"). The pR heads are much weaker and do not stand out so well. The sub-branches rRJ 2 and rRJ 1 form two heads, due to the splitting of the sub-branches by the asymmetry at the J values involved.

CHAPTER 6

ANALYSIS OF VIBRONIC BANDS

6.1. Preliminary analysis.

The analysis of vibronic bands is often complicated by the fact that the rotational constants of the two combining vibronic levels are widely different. In the absence of any prior information, both ground state and excited state constants for a band must be determined from the ultra-violet spectrum. For some molecules, however, ground state constants are known, to high accuracy, from microwave data, and in any case they are known for several bands when one band has been successfully analysed; the excited state constants, however, must be determined from the U.V. spectrum, and usually this will be done jointly with checking or improvement of the ground state constants.

The visible characteristics of vibronic bands vary very widely, according to the type of band and to the molecular geometry and mechanics, with the result that no single routine procedure is possible for their analysis. Generally, however, some values, even rough, for the more important of the molecular parameters must be found as soon as possible, from such regularities as can be observed in the band frequencies.

Since we are here concerned specifically with formaldehyde, the detailed description of procedure which follows is presented with the formaldehyde bands in mind; moreover, it is written primarily in relation to the semi-automatic procedure for analysis, as developed and used in the present work, which will be described in the subsequent sections of this chapter.

In the preliminary analysis we aim at obtaining a first set of constants, close enough to the correct ones so that the spectrum of a band, calculated from them, does not deviate by more than, say, 1-2 cm^{-1} from the observed spectrum over the currently recognisable ranges of the sub-branches. Sometimes even this preliminary analysis may be obviated if a good enough guess can be obtained from other sources: for example, the members A_0, A_2 and A_3 of the carbonyl progressionof formaldehyde have been analysed fully in the present work; constants of considerable accuracy for the A_1 band can probably be obtained by interpolation in this series. A guide has also been obtained for some of the present bands from the analyses of Dieke and Kistiakowsky (14) mentioned in chapter 4.

The most obvious features of the perpendicular bands of formaldehyde are the well defined rR heads mentioned in section 5.6. Their K-numbering may be determined by counting out from the centre as shown in fig. 2.3, making use of the 1 : 3 intensity alternation for even and odd K, respectively. The J-numbering of each sub-branch may then be determined by comparison of the successive heads. Since K is a component of J and cannot therefore exceed J, the first member of an rR sub-branch has J" = K" and hence each successively higher sub-branch has one member less than the previous one. This fixes the J-numbering to sufficiently high J, eg. to J = 10 or so, for this stage of analysis. If we confine attention at this stage to the rR sub-branches with K" > 3, (the J-numbering is more difficult to ascertain for $K'' < 3$) we can fit a symmetric rotor formula to these sub-branches since the effect of asymmetry is here very small. The symmetric rotor formula for the rR branches is:

$$\sigma(J,K) = \sigma_{00} + D'(J+1)(J+2) + \alpha'(K+1)^2 - D''(J(J+1)) - \alpha''K^2 \qquad 6.1.$$

We could introduce centrifugal distortion terms in K^4, but for the present purpose, this refinement is not really necessary. Since the ground state constants (those marked ") are very well known for the bands considered in the present work, both from the microwave data and from earlier analyses of the ultra-violet spectrum, the only unknowns to be determined from equation 6.1, using the observed data, are D', α' and σ_{00}. When analysing bands of other molecules, for which less prior information is available, this treatment would have to be extended, and in particular we would have to determine approximations for the ground state constants as well.

Determination of a value for the asymmetry parameter b' is rather more difficult. Once the J-numbering has been established for the rR branches with $K'' \geqslant 3$ - a relatively simple task - the numbering of the rR branches with $K'' < 3$, which are the ones most affected by b', may then be attempted. This may be accomplished by an iterative method; this is essentially the computer procedure described later. Using the rotational constants so far obtained and a guess at b', the expected run of the low K branches may be calculated. Observation of the deviations between the observed and calculated values, beginning with the next lower sub-branches with $K'' = 2$, gives a guide for further assignment along the branches and so on. Once the two rR sub-branches for $K'' = 2$ have been assigned (the U and L sub-branches are split after about $J'' = 5$) a better value for b' should be obtainable from the difference between the two curves sincee this difference is dependent almost entirely on the error in b' (as long as the other constants, especially b'', are substantially correct; if not, suitable combination differences can be used to isolate, to a large extent, the effects of errors in either b'' or b'). Wang's approximation formula for the level doublet splitting, in terms of the Schwendemann-type coefficients already referred to (p. 117), is useful in this connection, at least in the region of small splitting of the order 1 or 2 cm^{-1} (see e.g. Townes and Schawlow (63) p. 87). Tables of reduced energies for values of the asymmetry likely to be encountered in the bands of HCHO have been computed to extend this procedure, using the Routine 95, already mentioned in section 5.2. Repetition of the above procedure for the rR sub-branches with $K'' = 1$, will deliver a still more refined value for b' and this should be adequate for the later work.

All this analysis has so far been restricted to sub-branches of the rR type. If necessary, the rQ, pP or pQ may be employed in this part of the work, although their identification is somewhat more difficult. For those of the present bands which have been analysed using the fully developed analytical procedure, the rough constants derived from the rR branches have been found perfectly adequate as starting material for the subsequent work.

In the following sections, the description is essentially in terms of the use of electronic computing methods, though some of it would apply to manual work, in so far as this is practicable.

6.2. Main analysis: part 1 - automatic assignment.

The first automatic computing stage in the analytical procedure is the calculation of the complete spectrum using the best available values for the rotational constants, and the comparison of the calculated frequencies with the list of observed frequencies. For a given sub-branch, the deviations between the two sets (those up to 1 cm^{-1} or so are useful) should fall on a smooth curve when plotted against the quantum number J". It is then usually a simple procedure to pick out the correct assignments, provided the two spectra agree closely enough.

Firstly, then, the input values of the rotational constants are decided on; they are either the initial approximate constants, or at a later stage, already partially refined constants. The energy formula used contains three parts: the purely vibronic term σ_{00}, and the upper and lower state rotational energies. The ground state energy is expressed in terms of the normal rigid rotor formula, already given in equation 5.12, viz.

$$W(J,K) = D\,J(J+1) + \alpha\,E(b)_{J,K} \qquad 6.2.$$

together with the centrifugal distortion correction

$$\delta W = D_E\,E(b)^2 + D_{EJ}\,E(b)J(J+1) + D_J\,J^2(J+1)^2 + D_4\,E(b)E'(b) + D_5J(J+1)E'(b) + D_6\,E'(b)^2 \qquad 6.3.$$

There are therefore nine ground state constants.

The excited state expression duplicates this formula but in addition, allowance has been made for two perturbations of the Lide type (see section 5.3); the formula given as equation 5.30 has been used to describe the perturbation. Besides the three parameters for each perturbation (I, d and c), allowance has been made for the three rotational constants of the perturbing levels (of each perturbation) to be set as different from those of the perturbed levels where they are known or can reasonably be assumed; 12 constants are required, therefore for the two perturbations. Thus provision for 31 constants in all is required, and is made, for the description of the energy levels.

In practice, in the early stages of an analysis, many of the constants will be zero, especially if no information about perturbations has been found from the preliminary analysis. A rough guess at the three most significant excited state distortion constants is required in the early stages; these can simply be the same as the ground state constants.

The programme used for this job is entitled, "U.V. Spectrum and Assignments, HR 4.35", and is described in more detail in the Appendix. In order to avoid duplication of calculated energy levels (each level is required for several frequencies), all of the levels involved in the spectrum are specified by the operator, by way of the ranges of the quantum numbers J, K_{+1} and γ required at the current stage of analysis; these levels are then computed and stored, to be drawn on as required by the selection rules. After this, the list of observed frequencies and associated strengths is read in; this list is simply the output frequency list from programme HR 1.6, mentioned in chapter 3. Finally, the operator must specify each sub-branch required and also its length in J". For economy, all the sub-branches belonging to a given K" are called out at a time so that wasteful internal machine transfers are kept to a minimum. As each frequency is calculated from the stored ground and excited state energies and the vibronic frequency, it is printed out from the computer. The list of observed frequencies is then scanned and those frequencies lying close to the calculated frequency are printed out as their deviations (in thousandths of a cm^{-1}) from the calculated value, together with their estimated strengths. It has been found that about 2000 frequencies from about 90 sub-branches must be computed to

TABLE 6.1

SPECTRUM AND ASSIGNMENTS

RRJ 6 D

J	FREQ.					
6	403.065	131 1	20 3	-534 5	-751 3	
7	403.104	92 1	-19 3	-573 5	-790 3	
8	402.842	354 1	243 3	-311 5	-528 3	-757 1
9	402.279	252 5	35 3	-194 1	-502 3))	
10	401.414	363 3))	-496 3	-683 3		
11	400.247	484 3	-70 0	-462 2		
12	398.777	493 0	-432 2	-689 3		
13	397.002	-409 1				
14	394.923	180 2	-161 on	-373 2		
15	392.538	362 8	153 7	-18 7	-377 6	-733 2
16	389.845	335 6	-309 1	-481 0		
17	386.844	305 1)	149 5)	-276 1		
18	383.533	-260 0	-400 0			
19	379.912	264 1	30 4	-209 2))	-403 4	
20	375.979	336 3	36 1	-104 4	-306 1	
21	371.731	154 1				
22	367.169	76 2	-425 3			
23	362.290	255 5))	-23 4	-317 3))		
24	357.093	449 6)•	198 7)	86 7)	-128 4	-448 5
25	351.576	472 2	94 1))	-128 2)	-238 3)	-490 6))

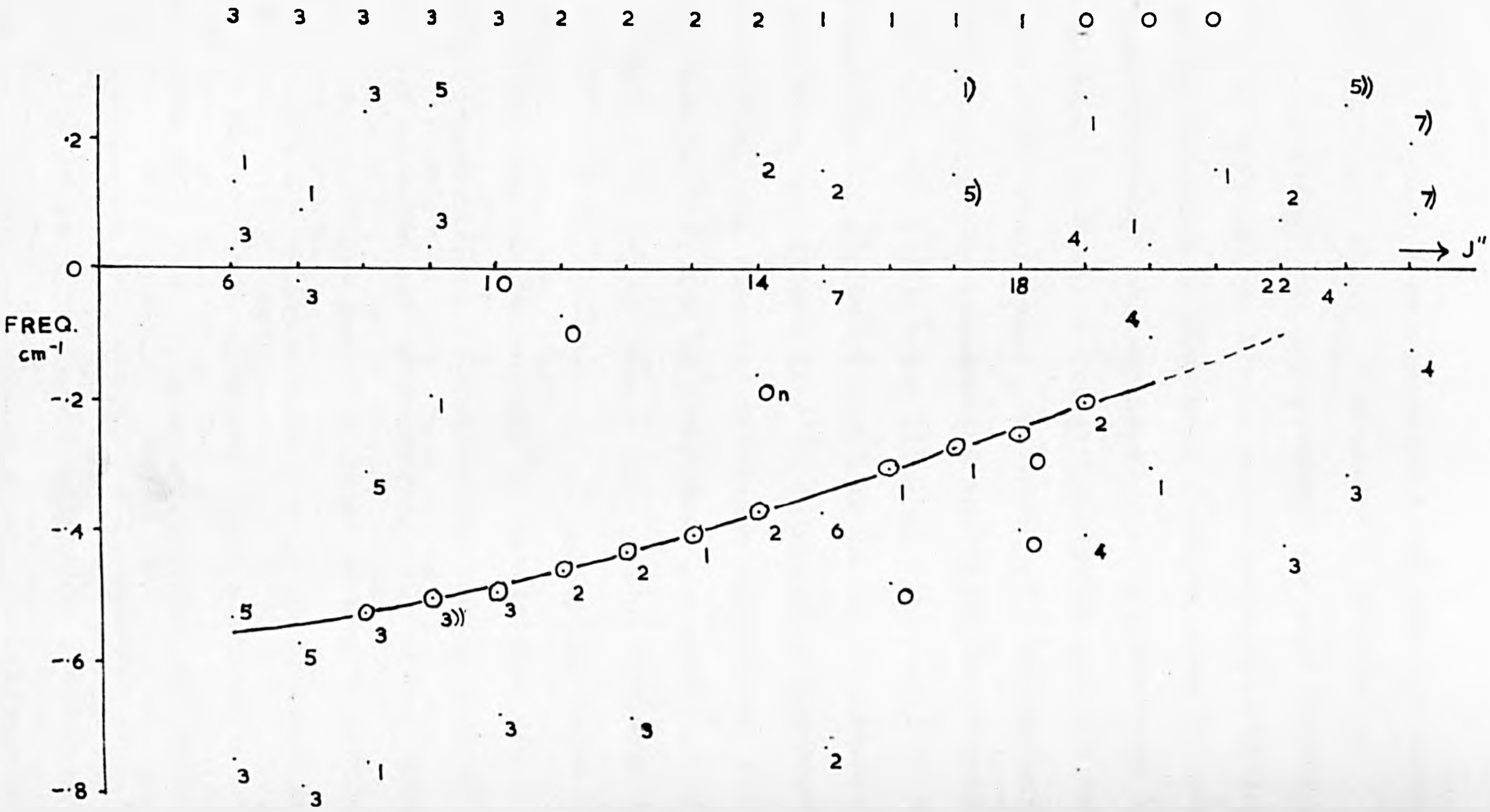
account for all the frequencies of a band.

An example is shown in table 6.1 opposite, exactly as it is output from the computer, for the sub-branch rR J 6, except that the correct assignments (identified graphically as is described later in this section) have been underlined; as can be seen from the magnitudes of the deviations in the table, the constants used for the calculated spectrum are some distance from being correct. Nevertheless, there is no doubt about the well-defined drift and the absence of ambiguity in most of the assignments. In fact, most of the error is due to the distortion terms of the excited state, as has been shown by subsequent calculation on this particular band: for this table these distortion constants had been the initial guessed values. Even so, assignment of the rest of the branches of the spectrum (which also showed drifts of a similar magnitude) was still quite simple.

The development of this programme has saved a large amount of tedious manual calculation. Such manual calculation of the energy levels was undertaken by Dr. Poole in the preliminary analysis of the A_2 band, and what was then accomplished in many weeks work, is now calculated by the computer in less than 30 minutes. Until recently, that part of the work involved in scanning the spectrum and calculating deviations was done manually (the computer just calculating the expected frequencies), requiring several days of tedious calculations of a repetitive nature; it was also highly prone to error

FIGURE 6.1.

ASSIGNMENTS FOR τRJ6 (A_0 BAND)



(often temporary, but with excessively time-delaying consequences).

The next stage in the analysis, that of identifying the correct assignments, is still performed manually, since this type of operation, although not onerous when done manually, would be very difficult to programme. The deviations for each sub-branch are plotted against J'' (or for some purposes against $J''(J+1)$) as shown in fig. 6.1, which is for the sub-branch rRJ 6 considered in table 6.1. The numeral against each point represents the intensity of the line on the visually estimated scale referred to earlier, in section 3.5; the meaning of the attached symbols is given in the Appendix, p.300. It is obvious from the run of frequencies and intensities that the only possible assignments are those on or close to the line given. Those frequencies which at the current stage have not been assigned elsewhere are ringed, the rest being multiple assignments. It can be seen that the points more than a few hundredths of a cm^{-1} away from the line, though within the practical resolving limit of 0.085 cm^{-1} of it (in the figure, 1 mm = 0.01 cm^{-1}), must be multiple assignments; the abnormally high intensity of some of them is further proof of this. It is also seen that the singly assigned points show a smooth run of intensities and the branch fades to an unobservable intensity soon after the intensity 1 has been reached. At the high J end of a sub-branch, lines are sometimes missing from the recorded list due perhaps to the presence of strong near neighbours. When two or more consecutive lines are missing, further assignment can become ambiguous unless a very good set of constants has been used for the computation (in which case the assignments will lie on or close to the zero line).

Once a sufficient number of branches spread over the spectrum have been analysed, the intensities of the singly assigned frequencies are compared with predicted intensities calculated using programme HR 5.15, referred to in section 5.5. From the correlations, the two intensity scales may be matched and a certain range of theoretical intensity attributed to each unit of the observed scale. The predicted intensities of the lines of each sub-branch may then be read off from graphs of calculated intensities prepared for this purpose. These estimates are shown in fig. 6.1 above the main graph. The agreement between observed and calculated intensities for the singly assigned lines is surprisingly good in view of the crudity of the visual estimation procedure. This calculated scale is of great use both in extending assignments, and in limiting the extent in J, of the assignments for each sub-branch, to those transitions theoretically observable.

When completely assigned, the frequencies are ready for use in the next stage of the work, the determination of molecular parameters, which is the subject of the next section. In preparation for this, the graphs and frequency lists are inspected and a list of <u>singly assigned, undisturbed lines</u> is made out and recorded on tape, together with the spectral designations of the lines, ready for input to the programme next to be used. Usually, out of the total of 900 or so frequencies recorded in a band, some 300 - 400 have the requisite freedom from disturbance. Inclusion of lines other than those, since they must represent less accurately the frequencies of the designated transitions, would necessarily reduce materially the accuracy of any values of molecular parameters obtained (in any case, 350 represents the maximum number of lines which the present computer can accommodate in this programme).

6.3. Main analysis; part 2 - the determination of constants.

The next part of the analytical procedure is to determine the rotational constants from the observed frequencies, once these have been assigned. In earlier work, this part of the investigation has been the most intricate part since each frequency is a function of many variables. A useful technique that is often used when the the procedure is attempted manually is the method of combination differences. There, combinations of frequencies are formed which cancel out some of the variables, reducing the number which have to be solved for. Thus by choosing two frequencies which have a common gyrovibronic ground state and taking their difference, we are left with a frequency expressible in terms of only the excited state constants; a similar procedure may be used to filter out the excited state when solving for the ground state constants. An advantage of this method is that the two vibronic states may be considered separately; but it has the disadvantage that if we limit the combinations to the differences between singly assigned (and therefore undisturbed) frequencies, the amount of data available for use is greatly diminished, since many lines cannot be matched.

A more straightforward method of obtaining constants is to attempt a least squares solution for all the constants simultaneously; then every item of data may be used. The possible drawback in application of such a method is that any singularity occurring in one of the vibronic levels (i.e. a perturbation) which is not completely accounted for by the energy expression for that level, will cause its effects to overflow numerically into the other vibronic level and in fact into the ~~the~~ values obtained for all the constants. In the present work, both methods have been employed for the extraction of constants, the combination difference method being used to obtain the ground state constants only.

(It would, of course, be possible to replace many of the multiply assigned frequencies by values obtained by interpolation on curves such as fig. 6.1, possibly without untoward consequences. However, such interpolated values would be subject to errors certainly not independent of those of other frequencies, so that the essential basis of a least squares treatment, or of any other less searching method, would be absent,)

Only the availability of an electronic computer has made the application of the second method (simultaneous solution for all constants) feasible, since the least squares technique must be able to cope with up to 25 parameters in the energy expression for a frequency; a task of this magnitude would never be attempted manually. Both techniques have been programmed and the programmes have been designed to accommodate a molecule with a degree of asymmetry similar to formaldehyde; extensions of their use to other classes of molecules would require certain (relatively small) modifications. The second (full scale) procedure will be described first since it demonstrates many points common to both.

A straight-forward least squares solution for the variables cannot be undertaken since the energy expression is not linear in many of them. We therefore employ the differential method as was used earlier (Chapter 3) for calibrating the spectrum obtained from the interferometer; that is, instead of solving normal equations for the variables themselves, we solve for corrections to previously adopted or determined approximations for them. Thus, if we symbolise the expression for a ~~for a~~ frequency as

$$\sigma = f\,(x_1,\ x_2\ \ldots\ldots\ldots\ x_n) \qquad 6.4.$$

where the x_i are rotational constants, distortion constants, etc., then the small difference $\delta\sigma$ between an observed frequency σ_{obs} and the frequency σ_{calc}, calculated using approximations x_i' for the actual rotational constants, x_i, is given to first order by partial differentiation of the frequency expression, and this may be symbolised by the linear expression:

$$\delta\sigma = \sum_i c'_i \, \delta x_i = \sigma_{obs} - \sigma_{calc.} \qquad 6.5$$

in which the c_i' are known.

The refined constants, x_i, are given by

$$x_i = x_i' + \delta x_i \qquad 6.6$$

The coefficients c_i' of the δx_i have a quite complicated form when a rigorous differentiation is carried out, and they are described in detail below. Some of them contain the rotational constants themselves, and since initially, these are only known approximately, the coefficients are themselves approximate. We therefore have to iterate the solution procedure in order to obtain final, refined constants. The least squares procedure is well known (see for example Buckingham (76)p.305) and need not be elaborated here. Briefly, equation 6.5 is used as the equation of condition and $\delta\sigma$ now represents the experimental datum, here referred to as the "erratum". If we consider a matrix V of all the coefficients, consisting of m rows and n columns (where m and n are the number of equations of condition and the number of unknowns respectively with $m > n$) and a column vector $\bar{f}$, of order m, consisting of the errata of the equations of condition, then the original equations are represented by $V\bar{x} = \bar{f}$, where $\bar{x}$ is the vector of the solutions x_i. The estimates of the individual frequencies are independent of one another, i.e. their errors are uncorrelated, and we treat the frequency estimates, and therefore the $\delta\sigma$, as all of equal weight*. The best least squares fit to the residuals is given by

$$V'.V\bar{x} = V'.\bar{f}, \quad \text{or} \quad A.\bar{x} = \bar{d} \qquad 6.7$$

where $A = V'.V$ and $\bar{d} = V'.\bar{f}$, — V' being the transpose of the matrix V.

The equations represented by 6.7 are termed the <u>normal equations</u>, and their solution (the $\bar{x}$ vector) gives the best values for the unknowns. If we premultiply each side of equation 6.7 by the inverse of the matrix A, that is A^{-1}, then $\bar{x}$ is given by:

$$\bar{x} = A^{-1}.\bar{d} \qquad 6.8$$

Thus, once the normal equations have been set up, the main task is the determination of the inverse matrix, A^{-1}. There are several numerical techniques for the inversion of matrices, some of which are designed for manual operation and others are more suitable for use with automatic machines. For the present work, the method attributed to Choleski (the " square root method ") (see Appendix 1) has been programmed by Dr. Poole as a standard sub-programme (Appendix 2, p.289)

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* Strictly each equation of condition should be appropriately weighted, most satisfactorily by the reciprocal of the variance of its frequency term. The variances are known from the programme HR 1.6, which combines the information from several fringes of each frequency, and could easily be used in this way - this is probably a worth while modification to the present programme, but has not yet been implemented.

for insertion into other programmes requiring it. Since in the arithmetic of inversion, there is a large amount of destructive cancellation, here accentuated by the fact that the normal equations matrix has elements ranging from 10^{-2} to 10^{10}, each arithmetical step in the inversion procedure must be carried out to a precision greater (far greater for a matrix of large order) than that required in the solutions. The programme has therefore been written making use of the Mercury computer's "Double Length Arithmetic" facilities; this means that each arithmetical step is carried out to an accuracy of about 1 part in 10^{17}.

We now consider the detailed form of the equation of condition, which, as stated earlier, is obtained by differentiation of the frequency expression with respect to each of the x_i in turn. For simplicity, the energy expression may be considered in several parts. Differentiation of the rigid rotor termss(equation 6.2) gives:

$$\delta W = J(J+1) . \delta D + E(b).\delta\alpha + \frac{\partial E(b)}{\partial b}.\delta b \qquad 6.9$$

The introduction of the quantity $\frac{\partial E(b)}{\partial b}$ enables one to solve specifically for δb; it was mentioned earlier in section 5.2 where also the means for its evaluation was given. From this, we have seven parameters contributing to the description of an erratum $\delta\sigma$: three, δD, $\delta\alpha$ and δb, for each vibronic level, and the correction, $\delta\sigma_{oo}$, to the vibronic energy.

Differentiation of the centrifugal distortion terms

Table 6.2.

Coefficients for differentials of molecular constants

(for explanation of symbols see chapter 5)

(E'(b) and E"(b) indicate $dE(b)/db$ and $d^2E(b)/db^2$ repectively)

(1) Rigid rotor terms

δD — $J(J+1)$

$\delta\alpha$ — $E(b)$

δb — $E'(b)\left[\alpha + 2E(b)D_E + J(J+1)D_{EJ} + E'(b)D_4\right] + E''(b)\left[E(b)D_4 + J(J+1)D_5 + 2E'(b)D_6\right]$

(2) Distortion terms

δD_E — $E(b)^2$

δD_{EJ} — $E(b)J(J+1)$

δD_J — $J^2(J+1)^2$

δD_4 — $E'(b).E(b)$

δD_5 — $E'(b).J(J+1)$

δD_6 — $E'(b)^2$

(3) Pure vibronic term

$\delta\sigma_{oo}$ — 1

(4) Perturbation terms

first define the following quantities

$u = 2K-1$ $\qquad v = 2K+1$

$u' = J(J+1)-K(K-1)$ $\qquad v' = J(J+1)-K(K+1)$

$W = (d \pm eu)$ $\qquad X = \left[I + W^{!}_{J,K} - W^{p}_{J,K-1}\right]^{-1}$

$W' = (d \pm ev)$ $\qquad X' = \left[I + W^{!}_{J,K} - W^{p}_{J,K+1}\right]^{-1}$

then:

δI — $-W^2 . X^2 : u' - W'^2 : X'^2 : v'$

δd — $2W : X : u' + 2W' : X' : v'$

δe — $\pm 2W.X.u.u' \pm 2W'.X'.v.v'$

(equation 6.3) is quite straightforward, but besides introducing differentials of each of the six D_i, this introduces a composite term in δb, which must be added to the similar term from equation 6.9. There are now a further 12 constants, six δD_i for each vibronic level. The coefficients for all the differential unknowns are given in table 6.2. Of course, since the excited state and ground state constants enter into the energy expression with positive and negative signs respectively, these signs are included in the coefficients.

The coefficients obtained by differentiating equation 5.30, (the expression for the Lide perturbation) with respect to the I, d and e are also given in table 6.2. Strictly, the expression should also be differentiated with respect to the excited state (and perturbing state) constants D, α and b which enter into the energies in the denominators. However, the additions to the coefficients of these quantities arising from such a differentiation are very small, and the trivial errors arising from their omission are taken up by iteration; the great complication to the coefficients of the rigid rotor constants would therefore not be justified.

We now have an expression for an erratum $\delta\sigma$ in terms of the corrections δx_i to (a) the 18 rotational and distortion constants, (b) the vibronic energy, and (c) the three parameters for each perturbation.

The basic computer programme written for this work is entitled, "Molecular constants from frequency data, MR8.55", and is described in the Appendix, p. 311 . After reading in the approximations to the constants the computer then reads in the frequencies for the particular run (chosen as described in section 6.2). Where the U and L members of a given transition J", K" → J', K' are unresolved, that is where the levels concerned are outside the region of high J and low K where the asymmetry splits the levels, the observed frequency is treated as the mean of the two members, (the coefficients of the equations of condition are also treated as means); this approximation has been shown to be well justified in view of the near symmetrical departure of the terms affected by asymmetry in the region where the departure itself is small. As each frequency is read, the several E (b), E'(b) and E"(b) appropriate to the levels contributing to the frequency, are computed and stored, together with the frequency and identification material for the particular frequency. Then the list is complete, the erratum $\delta\sigma$ for each frequency is calculated using the approximate constants, and subsequently the coefficients for the equations of condition are set up; finally, the normal equations matrix is formed, inverted, and the solutions calculated as summarised in equations 6.7 and 6.8. The refined constants may then be obtained and used in an iterative process to calculate a new normal equations matrix and so on. The programme is designed so that any desired number of iterations may be undertaken; in practice after the second, little further improvement to the constants is made so that three iterations are all that is normally required. The programme allows for two perturbations, each requiring three parameters, so that there is provision for 25 constants (this number is the maximum possible within the limitations of the Mercury computer). However, signals may be added to the data to instruct the computer to omit from the solution procedure as many of the unknowns as desired; thus for example in the early stages of the analysis, when some of the assignments may be tentative, there is little point in using the full six-constant centrifugal distortion formula, the first three terms being sufficient at this stage. Further, in the early stages, there is no point in solving for the ground state constants when these are already know to high accuracy. The programme is written so that if desired, any term may be replaced by some different term; for example on occasions, one of the smaller centrifugal distortion constants of the excited state has been replaced by a term linear in K', in order to look for possible effects of Coriolis perturbations.

6.4. Ground state constants : combination differences.

The combination difference method has so far been used only for obtaining ground state constants, by elimination of the excited state and the vibronic frequency. For a given band, of the 300 or so singly assigned frequencies, some 200 can be paired, each pair having a common excited state rotational level; the remaining 100 either have no matching levels or they match with levels already paired. It has been decided to reject all pairings of the type AB, BC since the frequency differences of each pair are not independent; their inclusion would be permissable, however, if they were suitably weighted, i.e. the simple procedure symbolised in equations 6.7 would have to be modified to allow for correlations between the equations of condition. The modified equation for the best least squares fit is of the form

$$V'.M^{-1}.V.\bar{x} = V'M^{-1}.\bar{f} \qquad 6.10$$

and the normal equations matrix A is then V'.M.V, where M is a matrix of order m x m which contains the correlations of the equations of condition. For a completely uncorrelated set, as in the full-scale treatment of the frequencies mentioned above, the matrix M is a unit matrix, of order m, and equation 6.10 reduces to equation 6.7. Correlations introduce off-diagonal terms in M, which, though easily set up, greatly increase the complexity of the programming.

Because of the smaller number of unknowns to be determined, i.e. only ground state constants, it has been found possible to ~~use~~ programme the formulation of centrifugal distortion in terms of the τ quantities, see section 5.3, and since there are four of these for the planar ground state of formaldehyde, there are altogether seven constants to be determined (including the three rigid rotor constants). A glance at tables 5.5 and 5.6 (pp. 129,130) from which the coefficients of the τ's are derived, will show that these coefficients are quite complex functions of the inertial constants A, B and C, and therefore of the rotational constants D, α and b. Partial differentiation of the full energy expression in terms of the τ's would introduce large complications in the coefficients of δD, $\delta\alpha$ and δb. In order to avoid this, the τ's are set equal to zero after each iteration of the solution procedure, and the solution of the normal equations is therefore in terms of corrections to the three main rotational constants, but in terms of the whole of the distortion constants. This does, of couse, mean that the equation of condition is not exactly valid. However, the errors introduced into the coefficients of the corrections to the three rotational constants are a small percentage of the coefficients themselves, so that as long as the corrections to the constants are small (this condition is amply satisfied since the approximations used for the initial input of these constants are derived from previous solutions in terms of the D_1), no errors are introduced which are not eliminated by the iteration procedure.

The programme used for this work is entitled, "Molecular constants from U.V. combination differences, HR 8.60" and is described in the Appendix, p.315. The data are input by specifying each combining level of the combination, as well as the frequency difference; in this way the complications of selection rules are avoided. Apart from the form of the input data and the complications associated with the coefficients of the τ's described above, the programme follows the same iterative procedure as the programme HR 8.50 described in the previous section. The treatment of an observed frequency which represents the unresolved U and L members of a transition is similar to that described earlier, on p. 179 ; a special feature of the present programme is that combinations are slightly restricted in that any pair consisting of an unresolved doublet and a member of a resolved doublet is excluded.

Two further programmes have been written in terms of the 6-constant distortion formulae D_1 and A_1 repectively, to allow study of the relative merits of the three possible treatments. This comparison has already been mentioned in section 5.3, but it is dealt with at greater length in chapter 8.

The three programmes mentioned above for solution from combination differences may also be used, after trivial alterations, for obtaining molecular constants from microwave frequencies. With them, the microwave spectrum frequencies of formaldehyde reported by Oka et. al. (44) have been reprocessed and this work is reported in chapter 8. Also, molecular constants for the molecule Cl_2O have been determined in conjunction with Dr. D.J. Millen, using microwave frequencies obtained by Dr. R.H. Jackson (78) and (79).

6.5. Excited state constants.

Although the combination difference method has not yet been programmed for obtaining excited state constants, there still remains a means of improving the excited state constants x_i obtained following the complete solution procedure described in section 6.3. The quantities which emerge most accurately from a manual analysis of rotational structure are the differences Δx_i between the excited and ground state constants, e.g. $\Delta D = D' - D''$, since the frequencies of a sub-branch have differences, or second differences, that run roughly parallel to the more important Δx_i. The actual values of the constants themselves are obtained somewhat less accurately from the variation of these differences between the different types of sub-branch, i.e. pP, pQ, pR etc.. Although this feature is disguised in the normal equations of a least squares solution, it must still be contained in them and made use of in the solution procedure. That it is so may be seen from the following example.

In a least squares solution for a total of 22 ground and excited state constants for the A_0 band (see section 7.2), the constants D" and D' emerged with numerical values of 1.21486_7

and 1.06840_4, both with standard errors of 0.00006; the value of ΔD is therefore -0.14646. In order to determine the standard errors of the differential constants Δx_i, we use the equation 6.12 given in the next section. Applying it to the above example we obtain the relation:

$$\sigma_{\Delta D}^2 = \sigma_{D'}^2 + \sigma_{D''}^2 - 2\, r_{D'D''} \cdot \sigma_{D'} \cdot \sigma_{D''} \qquad 6.11$$

where the σ_i are standard errors and $r_{D'D''}$ is the correlation coefficient between D'' and D' (see section 6.6 for an account of these quantities). For the present example, the correlation coefficient is the high one of +0.981. (That it is large and also positive means, in descriptive terms, that any error in the solution value of one of the constants is accompanied by about the same error, in the same direction, as the other one.) We find then, that the standard error of the differential quantity ΔD is 0.00001, some six times lower than the standard error of either of the individual quantities. In practice, a significant effect of this kind is only shown when the correlation coefficient is greater than 0.5; for values less than 0.5, the determined quantities may be considered as uncorrelated.

It can be seen therefore, that the differential quantities Δx_i determined in this way provide a very accurate indication of the change in the rotational constants on vibronic excitation, and they will, no doubt, prove to be of great value in calculating the geometry of the excited state. We can combine these differential constants with the best values obtained from the combination difference procedure for the ground state constants, and obtain in this way 'improved' excited state constants, i.e. $x' = x'' + \triangle x$. However, since some of the data used to obtain the ground state constants were also used to determine the differential quantities, there exists some (unknown) correlation between the two sets of quantities making up the "derived" excited state constants. We cannot, therefore, calculate the true standard errors of these constants. In the following chapter, where the excited state constants derived from analyses of several vibronic bands are described in detail, the "derived" constants are calculated assuming no correlation. For this reason, we retain, as definitive, the constants obtained from the full-scale solution,

It is worth mentioning that a programme used in the early stages did in fact solve directly for the x_i'' and the $\triangle x_i$; the $\sigma_{\triangle x_i}$ found were low, and the correlations between x_i and the corresponding $\triangle x_i$ were also low, as would be expected.

6.6. Correlation coefficients, standard errors and molecular constants.

In this section we will consider some aspects of the rotational constants derived as in the previous sections, including their manipulation to deliver molecular constants more directly useful for further work.

(i) Correlation coefficients and standard errors.

The least squares solution procedure described in the appendix delivers not only the best solutions for the equations of condition but also delivers valuable information about the accuracy of, and the significance to be attached to, the solutions obtained. The standard errors of the solutions obtained from this procedure are to be regarded as a measure of the precision of each variable, considered only as a member of the whole set; that is, if we divorce one from the rest, we must not necessarily expect the numerical value obtained for the solution to be a true estimate of the actual physical quantity (subject to the standard error delivered). Thus, it is desirable in any least squares determination, not only to obtain the set of solutions which gives the best fit to the experimental material but also to obtain their standard errors, and a measure of the correlation between every pair of solutions. In the present work the correlation coefficients, (derived in the manner explained on p.290) are always computed at the same time as the solutions and standard errors. Their significance is dealt with at length in standard statistical text books (see for example Smart (86) Chapter 9); here we make use of them in connection with the calculation of new constants derived from the original solutions, and the manner of using them for this purpose will be described. It must be emphasised, however, that their usefulness does not, by any means, end there.

When we derive a constant from two or more others (for example, in the previous section we obtained the differential constants as differences between the excited and ground state constants,) it is important to know what significance we can attach to the derived quantity. Commonly it is assumed in such cases that the variance (σ^2) of the new quantity is obtained simply as the sum of the variances of the other quantities (for a simple sum or difference relation - it is more complicated when products or other functions are involved); this is, however, correct only when these quantities are uncorrelated. Correlations between them can have a very marked effect on the standard error of the derived quantity: as an example, if the values of D" and D' are treated as uncorrelated, the variance of their difference $\Delta D = D' - D''$, will necessarily be greater than that of either D' or D", whereas if the correlation between them is taken into account, by way of the correlation coefficients actually obtained in the analysis, the variance is several times smaller than that of either D' or D". Thus in one band investigated in the present work (the A_0 band - see section 7.2) the variances of D" and D' are 31.47×10^{-10} and 30.91×10^{-10} respectively, while their correlation coefficient is 0.981. The variance of ΔD obtained using the correlation coefficient is 1.18×10^{-10} while the value apparent from the simpler treatment would be 62.38×10^{-10}; the standard errors differ, therefore, by a factor of 7. This is the justification for employing the technique of section 6.5.

We give in the next paragraph, a general expression for the variance of a function of any number of quantities in terms of their variance and the correlation coefficients between them; it is taken from Smart (86) p.150, with a change of notation to suit the present work. The validity of the expression is based on the assumption that the standard error of each quantity is small, that is, this expression arises from a first order treatment only.

If we define a function Φ of the variables x_1, x_2 etc., in the form $\Phi(x_1, x_2, \ldots)$, then the standard error σ_Φ is given to first order, in terms of the correlation coefficients r_{ij}, by

$$\sigma_\Phi^2 = \left(\sigma_{x_1} \cdot \frac{\partial\Phi}{x_1}\right)^2 + \left(\sigma_{x_2} \cdot \frac{\partial\Phi}{x_2}\right)^2 + \left(\sigma_{x_3} \cdot \frac{\partial\Phi}{x_3}\right)^2 + \text{etc.}$$

$$+ 2r_{12}\,\sigma_{x_1}\sigma_{x_2}\frac{\partial\Phi}{x_1}\cdot\frac{\partial\Phi}{x_2} + 2r_{13}\,\sigma_{x_1}\sigma_{x_3}\frac{\partial\Phi}{x_1}\cdot\frac{\partial\Phi}{x_3}$$

$$+ 2r_{23}\,\sigma_{x_2}\sigma_{x_3}\frac{\partial\Phi}{x_2}\cdot\frac{\partial\Phi}{x_3} + \text{etc.} \qquad 6.12$$

As an example of the use of this formula we will apply it to the derivation of the standard errors of the inertial constants A, B and C from the rotational constants D, α and b. The application to the differential problem mentioned above, follows directly from one of the examples.

The relations between the two sets of constants are :

$$A = D + \alpha$$

$$B = D - \alpha b$$

$$C = D + \alpha b \qquad 6.13$$

Application of equation 6.12 to the first of these gives:

$$\sigma_A^2 = \sigma_D^2 + \sigma_\alpha^2 + 2r_{D\alpha}\sigma_D\,\sigma_\alpha \qquad 6.14$$

Thus, since the standard errors of D and α, and the correlation coefficient $r_{D\alpha}$, are readily derived from the least squares procedure, it is a simple matter to obtain the required standard error. For the difference between two constants (as in the differential problem referred to above), we simply change the sign of the last term in equation 6.14 .

Similarly,

$$\sigma_B^2 = \sigma_D^2 + b^2\sigma_\alpha^2 + \alpha^2\sigma_b^2 - 2br_{D\alpha}\sigma_D\sigma_\alpha - 2\alpha r_{Db}\sigma_D\,\sigma_b + 2\alpha br_{\alpha b}\sigma_\alpha\,\sigma_b \qquad 6.15$$

and,

$$\sigma_C^2 = \sigma_D^2 + b^2\sigma_\alpha^2 + \alpha^2\sigma b^2 + 2br_{D\alpha}\sigma_D\sigma_\alpha + 2\alpha r_{Db}\sigma_D\,\sigma_b + 2\alpha br_{\alpha b}\sigma_\alpha\,\sigma_b \qquad 6.16$$

a numerical application of these equations is given eg. on p 202 .

Finally, it should be added that due regard to correlation must be made whenever we employ such quantities, say in the determination of molecular parameters; this can be done in principle, by expressing the required parameters as functions of the quantities directly obtained in the least squares procedure (so that the required correlation coefficients are known). This aspect appears not to have been previously considered in such work, presumably because of the less powerful methods of obtaining least squares solutions usually employed. It could be that the accuracies quoted in the literature for bond lengths and angles derived from rotational constants might be seriously over- (or under-) estimated if the quantities used to calculate them were highly correlated.

ii) Moments of inertia.

The derivation of inertial constants has just been dealt with in another connection (equations 6.13). The principal moments of inertia are obtained in terms of these constants (expressed in cm^{-1}) by the relations:

$$I_a = \frac{h}{8\pi^2 c A} \quad \text{etc.} \qquad 6.17$$

Convenient units for expressing moments of inertia are amu.Å^2. The constants used for this conversion are given below; they are taken from a list compiled by Cohen, DuMond, Layton and Rollett (Rev. Mod. Phys., **27**, 363 (1955)).

$c = 299793$ km/sec

$h = 6.62517 \times 10^{-27}$ erg.sec

1 amu $= 1.65976 \times 10^{-24}$ gm.

The conversion equations become then:

$$I_a = 16.8632 \times \frac{1}{A} \text{ amu.} \text{Å}^2 \quad \text{etc.} \qquad 6.18$$

(iii) The inertial defect.

The inertial defect Δ , defined by

$$\Delta = I_c - I_b - I_a \qquad 6.19$$

gives an indication of the planarity of a molecule. For a rigid planar molecule, the inertial defect should be zero; that is; for such a molecule there are only two independent moments of inertia. Any actual molecule cannot be rigid however; for a non-rigid molecule having a planar equilibrium configuration, the effect of the zero point vibrations is to give a finite value for Δ . Thus, for the ground state of formaldehyde, Oka and Morino (46) and (84) have calculated the inertial defect expected from the known behavior of the zero point vibrations; the value they obtain, +0.0561 amu.Å^2, is in very good agreement with the value obtained spectroscopically in our work, 0.0576 amu.Å^2. The inertial defects for the excited state levels, obtained in the present work (see chapter 7) are negative and some 4 to 6 times larger; this is in itself a good indication of the non-planar equilibrium structure of the excited state.

(It should be added that Lide (70) has recently drawn attention to the need for caution in the use of Δ as an index to planarity or non-planarity; this is an aspect of his treatment of vibration-rotation interactions not directly concerned with inversion. In the case of formaldehyde, however, the conclusion that the excited states are non-planar does not rest only, or primarilly, on the value of Δ .)

CHAPTER 7.

Results : part 1, the absorption bands.

7.1. Introduction.

The results described in the rest of this thesis are derived from three sets of plates, one set photographed and calibrated by Raynes (6) and referred to from now on as set 1; the two remaining sets, 2 and 3, have been photographed and calibrated in the present work.

Raynes's set of plates was taken in the region 3083 Å to 3286 Å with absorbing paths of formaldehyde of 0.0018, 0.0027, 0.0040 and 0.0056 m-atm, the path length being the maximum permitted by his experimental arrangement, 17cm. The plates give an adequate record of the following formaldehyde bands: B_1, A_2, E_0, B_2, A_3 and E_1, (Brand's notation (23) p. 861) while the weaker bands C_1 and F_0 are present but their intensities are rather too low on the strongest plate to allow an adequate investigation.

The plates of set 2 were taken to extend the intensity of absorption in the same region as the plates of set 1, by employing absorptions of 0.0078, 0.0123 and 0.0134 m-atm, the same path length being used. It can be seen that in the last of these, the pressure of gas used was 60 mm; for this plate, and to a lesser effect for the other two, the high pressure has noticeably increased the width of the fringes by pressure broadening and this has been reflected in the greater difficulty of their measurement. In order to reduce the labour of calibration of this set of plates, the absorption fringes themselves were employed instead of iron emission fringes. Selected lines from sets 1 and 2 were measured from bands spread out over the focused range and their δq's were determined from Raynes's calibration constants. The differences between the δq's of corresponding fringes from both sets were used to calculate the coefficients of the b-correction formula (see section 3.5), which then enabled the fringe measurements of set 2 to be reduced to the calibration conditions extant for set 1. The magnitude of the correction was found to be the high one of 0.6 of an order; the success of the calibration procedure may be judged by inspection of tables A1 and A2 in the Appendix. In the first are given Raynes's frequencies for the A_2 band, while in table A2, some of these frequencies are given as obtained from the plates of set 2; the agreement between common frequencies is excellent. The plates of set 2, with the calibration thus set up, enable the weaker bands of the region to be measured and also bring up the weaker lines in the wings of other bands.

Recently, (November 1961) a full scale run* has been undertaken in the spectral region from 3350 Å to 3650 Å, and the spectra of both HCHO and DCDO have been photographed,

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* This run was carried out with the assistance of Mr. D. C. Lindsey.

with absorptions of between 0.002 and 0.016 m-atm. for both compounds. For the higher absorptions, a 60cm absorption cell was employed between the projection lens and the Littrow slit (see fig. 2.5) and as mentioned earlier, no noticeable deleterious effects have been found due to its use in this critical region of the optical train. This set of plates constitutes set 3 and a full calibration has been executed as described in chapter 3; indeed, the illustrations given there were obtained during this calibration. In the region covered, the bands A_0, B_1, and A_1 for both isotopic species are ~~ready~~ suitable for measurement and analysis. In addition, the weaker bands C_0 and b_0, and for DCDO only, the hot band $\alpha_{1,-1}$ at 28550 cm^{-1} (see Brand (23) p. 863) are all recorded but are probably too weak for a worthwhile analysis to be attempted.

In the succeeding sections, work on the four HCHO bands A_0, A_2, A_3 and C_1 is described in detail. The frequencies for A_0 were obtained from set 3 and these are considered to be the best set of frequencies obtained, from the point of view of precision of the set as a whole; they form the basis for the detailed statistical treatment of errors, reported in section 9.3. The set of frequencies measured by Raynes (6) for the A_2 band from plates of set 1 have been taken over in the present work for the analysis (see also below) but have been supplemented by measurements on set 2 at the high frequency end of the band. The A3 band measurements were made from a combination of prints from sets 1 and 2, while the measurements for the C_1 band come from set 2. All the frequencies obtained are presented in tables A1 to A5 of the appendix.

Prior to the investigation reported later in section 7.3, Raynes's frequencies for the A_2 band were analysed in detail by Mr. Poole and his assignments are those reported in table A1. He also obtained a good set of rotational constants for this band, which formed the basis for their refinement, described in section 7.3. In the course of his analysis, Poole showed conclusively that the A_2 band obeyed b-axis selection rules and he also discovered and mapped the two perturbations which affect the excited state rotational levels of the band. The work of the present author on this band has consisted mainly in refinement of rotational constants including the application of the new formulation of centrifugal distortion developed in this work as described in section 5.3, and an investigation of the perturbation. In addition, Raynes's frequencies were used in the pilot work connected with the programmed analytical procedure, which is now fully developed and has been applied with great success to the frequencies of the A_0 and A_3 bands.

7.2. The A_0 band.

The upper level of the A_0 band is the lowest lying vibrational level of the ${}^1A'$ state of formaldehyde to appear usefully in the absorption spectrum, so that it is this band which has been most extensively investigated by previous workers. The analysis of Dieke and Kistiakowsky (14) produced vary good rigid rotor constants D and α for the excited and ground levels but since they were unable to resolve and analyse the sub-branches with low K, their values for b" and b' could not be regarded as reliable. Further, they could not account adequately for the centrifugal distortion because of the inadequacy of the theory available at the time. Robinson (24) reported having made an analysis of this band from his high dispersion plates and he gives some preliminary rotational constants; however, he does not seem to have followed up this work. Accordingly, the high resolution and great accuracy inherent in the present work has been applied to the band.

The rotational constants obtained for the excited state are likely to be the best available from any of the bands in the absorption system, since (a) the band is much clearer of overlapping bands than many of the others, and (b) the upper level is less likely to be affected by perturbations since the nearest vibrational levels, apart from the 0^+ level, are many hundreds of wavenumbers away.

The frequencies that have been used in the present work were measured from the plates of set 3, and are given in table A5 of the Appendix. The 925 frequencies reported there were derived from over 8500 fringe measurements; it is demonstrated later, in section 9.3, that the median error of measurement of the frequencies is about 0.0035 cm^{-1} and it is considered that this set of frequencies is the most accurate of any obtained in the present work.

The analysis of the band has proved very simple, and by employing the fully developed analytical prodedure described in chapter 6, only a few days work has been required. As can be seen from table A5, there are about 130 lines left unassigned; of these, most are very weak (of strength 0 or 1) and are therefore probably either spurious or are members of sub-branches that have been lost earlier in their run of J. Those that are of greater strength, 2 or 3, lie in the region where the a_o band is expected; it has not been found possible to analyse the frequencies attributable to this band due to their limited extent and the strong overlapping lines of the A_o band. Of those frequencies which are singly assigned and free from disturbances due to neighbouring lines, 450 were considered suitable for the determination of constants.

The frequencies have been processed both by the combination difference method (section 6.4) and by the full-scale solution procedure for all constants (section 6.3). For the former, 140 combinations were obtained using lines once only; this restriction (substantiated on p. 181) imposed

Table 7.1.

A_0 Band : Rotational constants, in cm^{-1}.

1) Rotational

	This work		D.&K. (14)	
	Ground State	Excited State	G.State	E.State
D	(6) 1.21487	(6) 1.06840	1.215	1.067
α	(2) 8.19038	(2) 7.68331	8.189	7.682
b	(3) -0.009841	(3) -0.007299	-0.0095	-0.0084
D_E	(2) -6.368 x10^{-4}	(1) -5.047 x10^{-4}		
D_{EJ}	(4) -4.33 x10^{-5}	(5) -6.18 x10^{-5}		
D_J	(6) -2.33 x10^{-6}	(6) -3.23 x10^{-6}		
D_4	(5) 2.81 x10^{-5}	(6) 2.85 x10^{-5}		
D_5	(6) 1.35 x10^{-7}	(5) 8.2 x10^{-8}		
D_6	(9) 3.12 x10^{-7}	(7) 7.2 x10^{-8}		

2) Vibronic

σ_{oo} = 28,312.569 (1) (D.&K. 28,312.66)

3) Perturbation

I = 125.3 ±1 cm^{-1}

d = 0.020 ± .002

c = 0.0004 ± .0003

the rejection of about 40 combinations. The results of this analysis are presented separately in section 8.2.

For the full-scale treatment, the full 450 frequencies could not be used because of the limitations of the storage capacity, of the computer and 100 of them (somewhat arbitrarily selected) were discarded.

The energy formula used to describe the frequencies was made up from the rigid rotor and centrifugal distortion terms for both states (2 x 9 = 18 in all), the vibronic frequency, and the three parameters I, d and e used to describe the one Lide perturbation (see section 5.4) expected in the region of high K'. The initial values for the ground state were derived from previous analyses of other bands (to be described later) and those for the excited state rigid rotor constants were the values given in Dieke and Kistiakowsky's paper, as was also that for the vibronic frequency. The results of least squares solution for the total of 22 constants are presented in table 7.1. The standard deviation of the residuals between the observed frequencies and the frequencies calculated from the final constants was 0.0081 cm^{-1} (0.0079 cm^{-1} after discarding a single impossibly large residual, 0.045 cm^{-1}). This value is considerably lower than the corresponding figure obtained for the other bands investigated and its significance is discussed in section 9.3. The constants obtained from the solution will be considered separately below.

Table 7.2.

A_o Band : Differential constants*

Constants	Differential Δx	$r_{x''x'}$	Stand. Error	Derived ex. state const	Stand. Error
D	-0.14646	0.981	1.1^{-5}	1.06828	5.6^{-5}
α	-0.50707	0.891	8.6^{-5}	7.68350	2.0^{-4}
b	0.002541	0.607	2.5^{-6}	-0.007300	4.4^{-6}
D_E	1.1321^{-4}	0.768	1.2^{-6}	-5.050^{-4}	2.4^{-6}
D_{EJ}	-1.341^{-5}	0.822	2.8^{-7}	-6.16^{-5}	5.8^{-7}
D_J	-0.897^{-6}	0.955	2.0^{-8}	3.19^{-6}	7.5^{-8}

A_o Band : Inertial constants and moments of inertia.

$A' = \overset{(15)}{8.75172}$ cm^{-1} $\qquad I_a' = \overset{(3)}{1.92684}$ amu.Å^2

$B' = \overset{(6)}{1.12449}$ " $\qquad I_b' = \overset{(8)}{14.9964}$ "

$C' = \overset{(5)}{1.01232}$ " $\qquad I_c' = \overset{(7)}{16.6579}$ "

$$\Delta = \overset{(12)}{-0.2653} \text{ amu.Å}^2$$

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* **Note.** In this table, and in several others later, powers of 10 are indicated thus: $2.0^{-8} = 2.0 \times 10^{-8}$.

(i) The accuracy obtained for the rigid rotor constants is better than that obtained for other bands in this work except in their determination by the combination difference method. The differential quantities and the "derived" excited state constants are presented in table 7.2, together with their standard errors. The standard errors of the differential quantities are quite significantly lower than those of either of the two quantities from which they were derived, (see table 7.1). Because of the difficulty of attributing the correct standard errors to the "derived" excited state constants (discussed in section 6.6), we have used here the constants of table 7.1 to derive the inertial constants and moments of inertia, given in table 7.2, and later, in section 9.5 for purposes of comparison with the constants of other bands. The relations used to obtain the inertial constants etc., and their standard errors, have been given in section 6.6 (that is we have employed the known correlation coefficients between D, α and b in the determination of the standard errors). The value obtained for the inertial defect, -0.2653 amu.Å^2, is some distance from that reported by Robinson (-0.280 amu.Å^2) for this band; however, he states that his analysis was a preliminary one, and our value is to be preferred.

(ii) The differential centrifugal distortion constants are also given in table 7.2, as are the "derived" excited state constants obtained from them. Here again, the standard errors of the differential quantities are significantly lower than those of the quantities from which they were obtained.

(iii) A highly accurate value for the vibronic frequency is reported in table 7.1. Similarly accurate values for other bands enables excited state vibrational frequencies to be determined to about 0.005 cm^{-1}, but it is doubtful whether much practical use can be made of vibrational frequencies determined to this degree of accuracy, since present-day theories of vibrations are considered excellent if they can account for the observed frequencies to better than about 1 cm^{-1}, when recalculated from the force constants.

(iv) The values reported in table 7.1 for the perturbation parameters indicate a very weak perturbation indeed. Table 7.3 below gives the magnitude of the perturbation calculated from these output values.

Table 7.3.

	J'	8	12	16	20	24	28
K' =	7	0.001	0.005	0.012	0.018	0.027	0.036
K' =	8	0.000	-0.006	-0.013	-0.024	-0.037	-0.052

In order to ascertain whether or not this perturbation was real, a selected number of frequencies (169) in the region most likely to be affected by the perturbation (i.e. K' = 5 to 10) were used in two parallel runs. In the first, it was attempted to fit the frequencies to an energy formula containing no perturbation terms, while in the second, allowance was made for the parameters I and d (from the original run, e was considered to be negligibly small, see table 7.1)); in the second, as initial input, I and d were set to the values reported in table 7.1 (it is necessary to have initially non-zero values for those parameters as otherwise their coefficients in the equations of condition would be zero - see table 6.2). For both runs, the input values for the molecular parameters were those obtained from the first, full-scale solution but only the constants D', α', D_K', D_{KJ}' and D_J' were solved for, D_4, D_5 and D_6 were set to zero.

The least squares fits obtained for the two runs were almost identical, and in particualar, no discontinuities in the residuals could be traced in the case where the perturbation was ignored. However, the fact that in the second run, the inversion splitting I emerged with a value of 123 ±4 cm^{-1} and that d emerged with a standard error of 40% suggests that although the perturbation may be too small to be apparent on visual inspection of the residuals, there is sufficient information in the frequencies to enable meaningful perturbation parameters to emerge from the normal equations. Indeed, if no perturbation were present, we would expect I to emerge with a standard error of the same magnitude as itself. We conclude therefore that the perturbation is probably real, and in this we are supported by the fact that the value of I that we obtain is in excellent agreement with the inversion splitting obtained from the vibrational analysis. We have still to account for the very small magnitude of the perturbation in the light of the findings from the A_2 band (in the next section); discussion on this point is deferred until section 9.5.

ADDENDUM

Very recently we have shown beyond doubt that no perturbation is present in the A_0 band. In two least squares runs, which we have just completed, the values 100 and 150 cm^{-1} were used as initial approximations for the inversion frequency I. If a Lide perturbation were present, we would expect the refined values of I to approach the value 125 cm^{-1} on successive iterations. The values of I, with their corresponding d, are given in the following table.

	Initial	It. 1	It. 2	It. 3	It. 4
I_1 =	100	100.0	100.0	100.0	100.0
d_1 =	0.015	0.007	0.004	0.002	0.001
I_2 =	150	156.9	164.9	-807.7	51852.5
d_2 =	0.015	0.018	0.002	-0.38	30.4

We attribute the behaviour of I in the first of these to a special feature of the least squares solution procedure which need not be given here; the last few values for d indicate a completely unobservable perturbation. In the second run, on iteration, d becomes so small that the normal equations matrix is almost singular, after this the solutions are meaningless. There is no indication in either case of a drift towards I = 125. We conclude therefore:

1) There is no Lide perturbation in the A_0 band.
2) Lide's theory must be critically re-examined.
3) The K' = 8 perturbation in the A_2 band is now unlikely to be a simple 'Lide' perturbation, and some other explanation must be sought for it.
4) The A_0 band is completely free from perturbations; rotational constants should therefore be determined for it using equations of condition containing no perturbation terms. This is expected to improve the standard errors of the constants that emerge over those (already excellent) reported in section 7.2 above.

7.3. The A_2 band.

The A_2 band was also one of those investigated by Dieke and Kistiakowsky (14) and the remarks made in the previous section with regard to their work, apply equally here. Apart from the work of Stace (5) and Raynes (6), no other high dispersion work has been reported on this band. Stace measured 156 frequencies and he stated that they had an accuracy of from 0.02 to 0.04 cm^{-1}. Raynes measured 789 frequencies for this band (from about 4000 fringe measurements) and his values are listed in table A1 of the Appendix; he showed that the precision of measurement of the frequencies was about the same as that obtained in the present work for the A_0 band, i.e. of the order 0.0035 cm^{-1}.

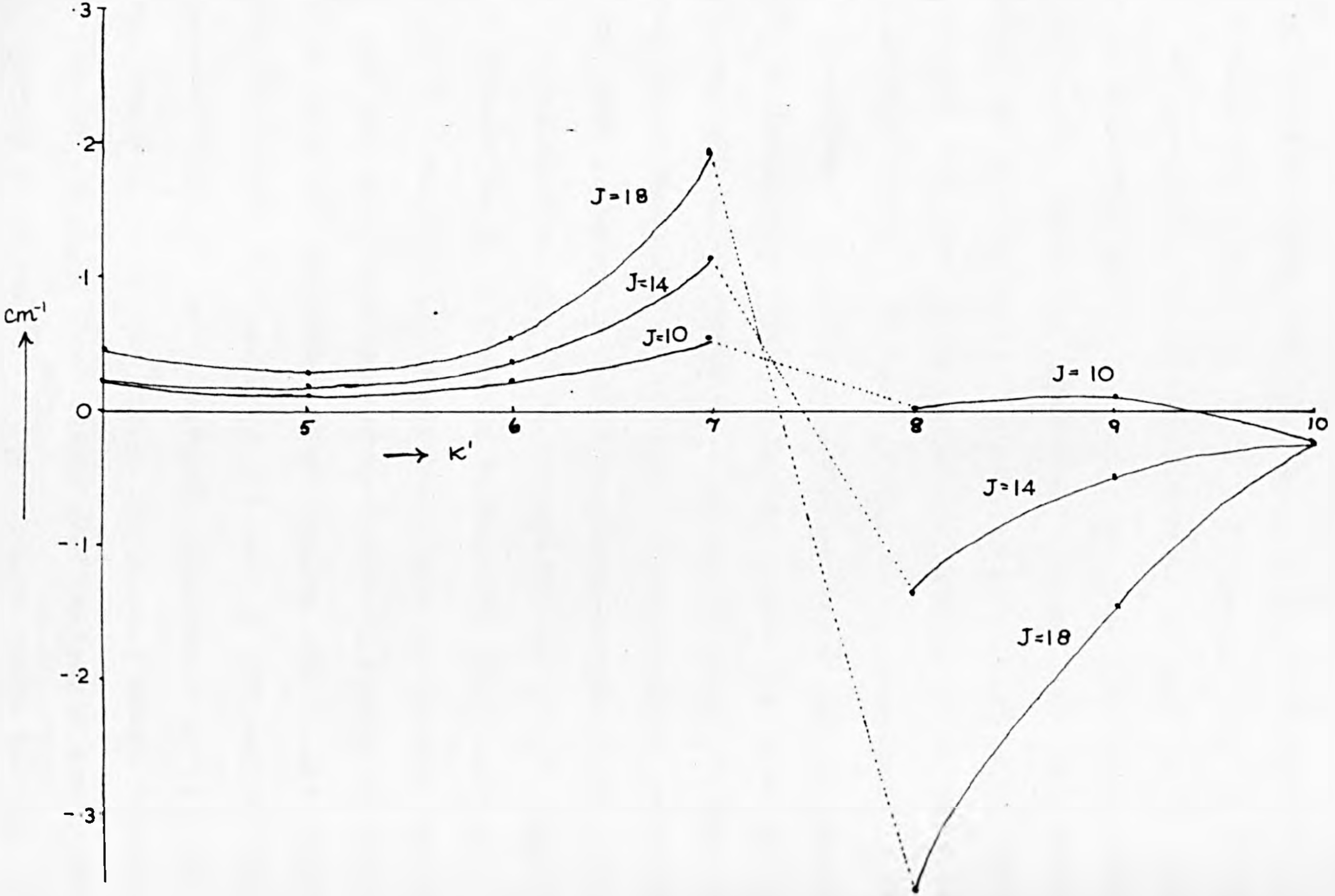
Using Raynes's frequencies, a full analysis of the A_2 band was carried out by Dr. Poole, and his assignments are those listed in table A1. In this analysis, Poole demonstrated conclusively that the A_2 band, and therefore the whole A series, was of type-B in agreement with the findings (on rather weaker evidence) of Dieke and Kistiakowsky. He also discovered and mapped the perturbations (77) in the high K' region and the K' = 0 region, described later in this section. The rigid rotor, distortion, vibronic, and perturbation constants determined by him were used as the starting point for the refinement procedure described later.

The first contribution of the present work was the re-measurement of the high frequency end of the spectrum from the strong absorption plates of set 2. It was hoped that a few extra assignments in this region would enable some of the sub-branches rR J 10 and rR J 11 to be mapped and allow a fuller picture of the high K' perturbation to be obtained. The frequencies are reported in table A2 of the appendix; it can be seen that very few extra assignments have been made. This is because the stronger absorption for these plates has brought up the weak lines of the neighbouring C_1 band and they overlap the high frequency end of the A_2 band to a great extent. A large percentage of the lines reported in table A2 undoubtedly belong to the C_1 band and their profusion makes unambiguous assignment of the weak, high K' lines of the A_2 band impossible. The new frequency values have, however, been employed in the analysis wherever they duplicate Raynes's values since in general, they are determined from a larger number of fringe measurements.

For the final full-scale determination of constants, 304 lines were chosen as singly assigned and free from disturbance. They also provided 90 uncorrelated combinations for the determination of the ground state constants and this work is reported in chapter 8. The chief difficulty connected with this band is in accounting correctly for the perturbations in the excited state levels. As mentioned earlier, there are two of these, one affecting the levels with high K', mainly K' = 7 and 8, and the other which seems to be confined largely to levels with K' = 0.

FIGURE 7.1

A_2 BAND. OBSERVED PERTURBATIONS IN HIGH K' LEVELS



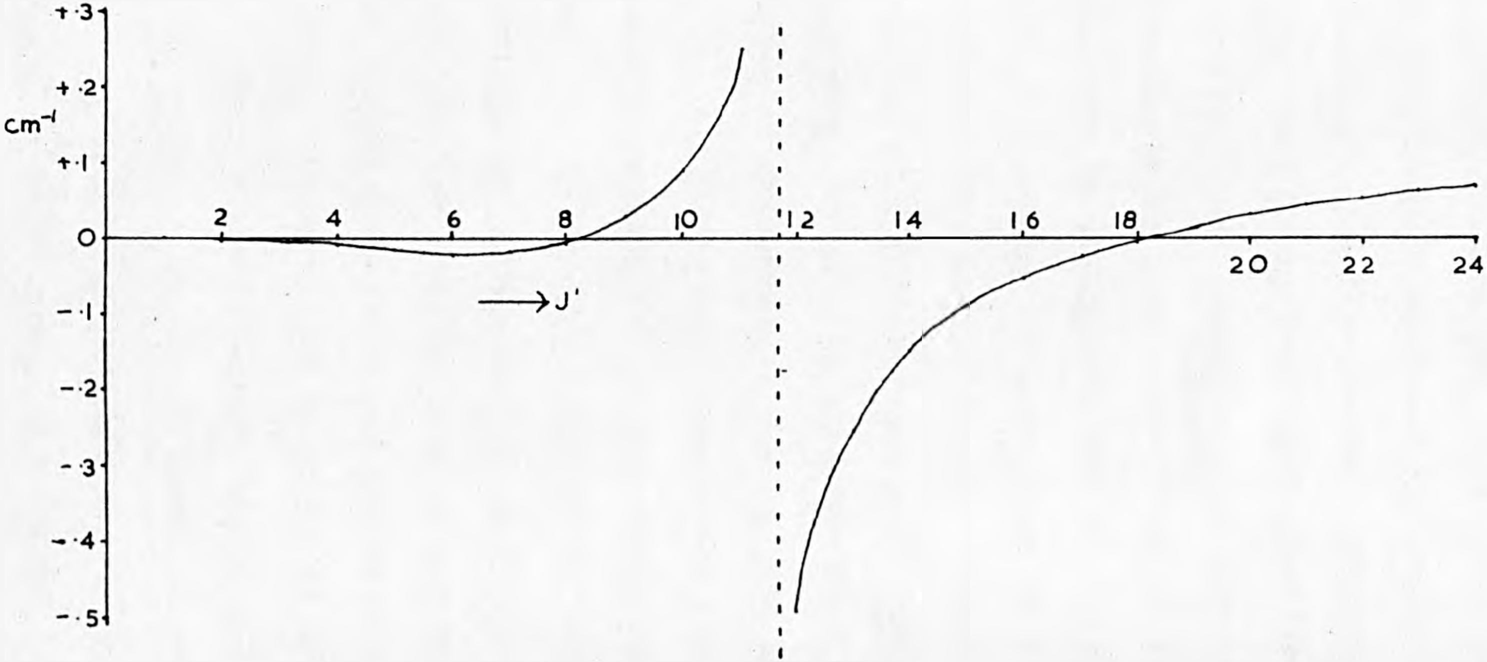
The first of these is believed to be a straightforward Lide type of perturbation (see section 5.4). Its magnitude is plotted against K', for selected values of J', in fig. 7.1; the points represent smoothed experimental values derived in effect by subtracting the calculated, unperturbed frequency from the observed frequency. Derived in this way, the points contain besides the perturbations, the errors of fitting the energy formula to the frequencies ; in particular the curves contain the effects of any inadequacy of the centrifugal distortion formula at these high K' values. The perturbations are therefore to be viewed against a zero line, which is not necessarily the horizontal zero line of fig. 7.1; in fact it appears from the figure that the line of zero perturbation is somewhat bent. The general form of the perturbation is very similar, however, to that used for demonstration purposes in section 5.4, fig. 5.2b.(p139). These observed values for this perturbation can be accounted for very well by the perturbation formula given as equation 5.30(p136) in section 5.4. Assuming that the perturbing level is the lower member of an inversion doublet, the rotational constants used to describe the perturbing levels have been taken to be the same as those of the perturbed levels.

The second perturbation is more difficult to account for. Its form is shown in fig. 7.2 where the points represent smoothed values derived from the three sub-branches pP J 1 L, pQ J 1 U and pR J 1 L, all three of which terminated on levels with $K' = 0$. Its form is the same as that used for the second

FIGURE 7.2

A_2 BAND: OBSERVED PERTURBATIONS IN LEVELS WITH $K'=0$

(SMOOTHED VALUES)



example in section 5.4. We have concluded therefore that there exists a perturbing vibronic level a few wavenumbers below the upper level of the A_2 band. For the perturbation to be analogous to the strict Lide type, this perturbing level should be of the same symmetry as that of the (+) level causing the perturbation to levels with high K', mentioned above. At first sight such a level could be the (+) level of the C_1 band which, according to Brand's assignment (23), should have the required symmetry; this would give a value of 175 cm^{-1} for the inversion frequency of the corresponding vibronic state (this value appears not to be unreasonably high since the CH_2 vibration of the C_1 band would be expected to aid quantum mechanical tunnelling through the potential barrier at the planar configuration). However, it has recently been suggested (36) that Brand's assignment for the C_1 band can no longer be justified since the band appears to be a type-C band (see section 7.5). The assignment would then necessarily be to some antisymmetric combination of frequencies and it seems probable that the Brand's assignment of δ_{CH_2} must be changed to the vibration γ'_{CH_2} (see fig. 4.1). The (+) level does not then have the required symmetry for a perturbation of the type considered by Lide and the perturbation may therefore be a normal Coriolis perturbation. In view of the uncertainty, it has been decided to try to account for the observed perturbation by the formulation already developed for a Lide perturbation (and in this it succeeds very well) so that excited state rotational constants, unaffected as far as possible by this perturbation, may be obtained from the frequencies. In the future, when the origin of the perturbation had been settled it may be possible to obtain meaningful parameters for the observed perturbation.

Since it is still quite possible that the perturbation does arise from the (+) level of the C_1 band, the perturbing state rotational constants used for the equation of condition have been assumed to be those of the C_1 band. The perturbation has also been assumed to arise mainly from the $K = 1^+$ levels (and not the 1^- levels) of the perturbing state since this seems much the more likely on examination of the expected perturbations for the two possible cases. This fixes the perturbing level at 15 cm^{-1} below the A_2 band origin,

The full energy formula used then, to describe the frequencies chosen for the least squares analysis is made up from 18 constants required to describe the rotation of the molecule (3 rigid rotor and 6 distortion constants for each level) together with the vibronic frequency and the 6 constants required to describe ~~each of~~ the two perturbations above. Altogether 25 constants were thus employed, this being also the maximum number of variables for an equation of condition permitted by the present storage capacity of the computer. In addition to this run, a supplementary run has been carried out in which the upper state distortion constant D_5, found to be

Table 7.4.

A_2 Band : Rotational constants, in cm^{-1}.

1) Rotational

	This work		D. K. (14)	
	Ground state	Excited state	G.state	E.state
D	$1.21492^{(1)}$	$1.04601^{(1)}$	1.215	1.046
α	$8.19040^{(3)}$	$7.59572^{(3)}$	8.189	7.606
b	$-0.009860^{(6)}$	$-0.006967^{(7)}$	-0.0095	-0.0083
D_K	$-6.481^{(5)} \times 10^{-4}$	$-3.110^{(3)} \times 10^{-4}$		
D_{KJ}	$-3.95^{(1)} \times 10^{-5}$	$-4.69^{(1)} \times 10^{-5}$		
D_J	$-2.85^{(1)} \times 10^{-6}$	$-3.51^{(1)} \times 10^{-6}$		
D_4	$^{(15)}2.0 \times 10^{-6}$	$^{(2)}9.4 \times 10^{-5}$		
D_5	$^{(2)}5.7 \times 10^{-7}$	$^{(15)}3.7 \times 10^{-8}$		
D_6	$^{(3)}2.5 \times 10^{-7}$	$^{(2)}1.5 \times 10^{-6}$		

$\eta'(K) = 0.0^{(3)}$

2) Vibronic

$\sigma_{00} = 30,658.580^{(3)}$ (D.&K. 30,658.67)

3) Perturbation

	1	2
I	123.8 ± .6	14.8 ± .1
d	$7.39(\pm.3) \times 10^{-2}$	$4.2(\pm.3) \times 10^{-2}$
e	$4.3\ (\pm5) \times 10^{-4}$	$6\ (\pm2) \times 10^{-3}$

negligibly small in the first run, was replaced by a term linear in K'. This run also contained rather more data affected by the K' = 0 perturbation than did the earlier run. The extra material consisted mainly of multiply assigned lines (but which seemed undisturbed on the assignment graphs) so that of the constants derived in this run, only the Lide parameters for the low K' perturbation and the linear term in K' have been accepted for use in table 7.4.

The standard deviation of the residuals was 0.015 cm^{-1} for the first run (rather higher for the second) and this, in view of the considerably smaller figure, 0.008 cm^{-1}, obtained for the A_0 band, indicates that the formulation used to describe the perturbations in the excited state levels was not quite adequate. The results given in table 7.4 (and 7.5) will be considered separately as follows.

(i) The rigid rotor constants are obtained with very small standard errors (although not so small as those from the A_0 band). The ground state constants are discussed in section 8.2. The differential constants Δx_i (see section 6.6) are given in table 7.5 together with the inertial constants and moments of inertia for the excited state derived from the constants of table 7.4 (not those of table 7.5 - see section 7.2, sub-section (i) p204); the inertial defect is of the same order as that of the A_0 band. Further discussion is deferred to section 9.5.

(ii)a. The term in K' (γ) is considered to be

insignificant.

Table 7.5.*

A_2 Band : Differential constants.

Constant	Differential Δx	$r_{x''x'}$	Stand. Error	Derived ex. state const.	Stand. Error
D	-0.16891	0.977	2.3^{-5}	1.04583	5.9^{-5}
α	-0.59469	0.851	1.8^{-4}	7.59587	2.5^{-4}
b	0.002893	0.580	6.3^{-6}	-0.006948	7.3^{-6}
D_E	3.371^{-4}	0.796	2.8^{-6}	-3.000^{-4}	3.4^{-6}
D_{EJ}	-0.740^{-5}	0.866	6.6^{-7}	-3.062^{-5}	8.9^{-7}
D_J	-0.660^{-6}	0.971	3.6^{-8}	-2.948^{-6}	8.1^{-8}

A_2 Band : Inertial constants and moments of inertia.

$A' = \overset{(3)}{8.64173}$ cm^{-1} $\qquad I_a' = \overset{(7)}{1.95137}$ amu.Å^2

$B' = \overset{(8)}{1.09893}$ " $\qquad I_b' = \overset{(18)}{15.3451}$ "

$C' = \overset{(8)}{0.99309}$ " $\qquad I_c' = \overset{(19)}{16.9805}$ "

$\Delta = \overset{(26)}{-0.3159}$ amu.Å^2

---

* See note p.203

(ii) The centrifugal distortion constants were also combined to give the Δ quantities reported in table 7.5; here again the standard errors of the latter are considerably lower than those of the separate constants.

(iii) The vibronic frequency is obtained with a standard error of 0.0025 cm^{-1} and the remarks made in the previous section regarding such precision apply here also.

(iv) The high K' perturbation delivers a value of 123.8 cm^{-1} for I, although this value may be more in error than the standard error of 0.6 cm^{-1} suggests. In the first place it is quite sensitive to the assumed values for the rotational constants of the perturbing state. In the course of the preliminary work leading up to this final set of constants, values for I ranging from 123 to 126 cm^{-1} have been obtained, the range being largely due to the refinement of the excited state constants and therefore of the adopted perturbing state constants. It can be stated from the results, however, that the inversion splitting for the vibration for which the excited state of the A_2 band is the upper member, has not changed appreciably from the value known for the A_0 band.

(v) A fit, adequate for the present purposes, has been obtained to the K' = 0 perturbation. The value obtained for the analogue of I indicates a perturbing level at about 30644 cm^{-1} and, as mentioned above, this level is provisionally attributed to the (+) level corresponding to the C_1 band.

Further discussion on this point is deferred until section 9.5.

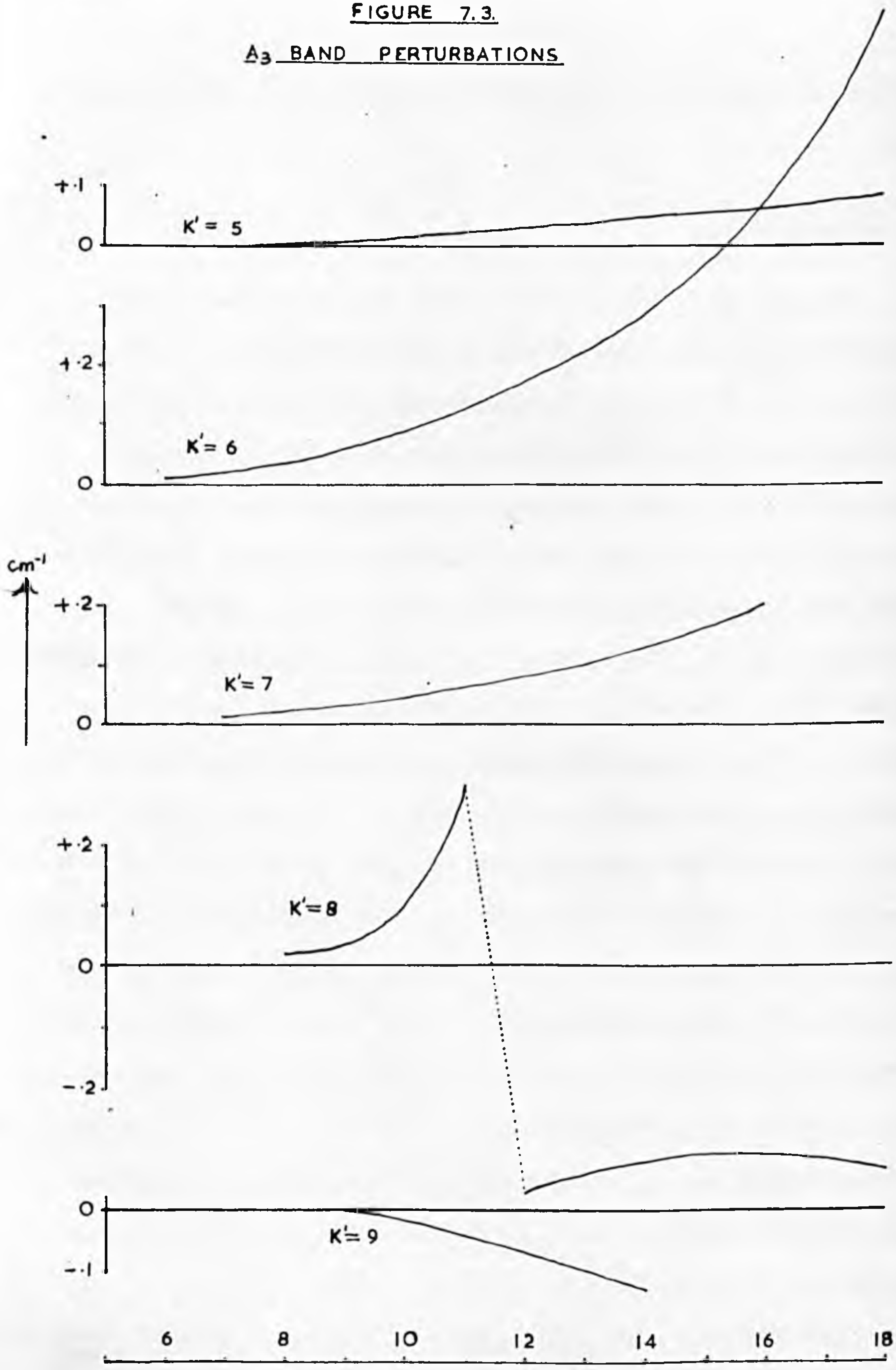
7.4. The A_3 band.

The A_3 band was measured from the spectra of set 1 (photographed and calibrated by Raynes) together with the 60 mm plate of set 2. In all, over 9000 fringe measurements contributed to the 927 frequencies reported in table A4 in the Appendix. Since the band lies so high in frequency, the possibilities for bands overlapping are greatly increased over the other bands studied in this thesis. At the high frequency end of the band, overlapping occurs to a considerable extent with the weaker F_0 band, whose origin is at about 32,000 cm^{-1}; many of the weak unassigned frequencies at the beginning of table A4 are undoubtedly members of this band. Also, many of the sub-branches of the A_3 band are cut short because of overlap by the strong, high frequency end of the B_2 band; the three strong frequencies reported at the end of table A4 certainly belong to this band. It is possible that still more weaker bands underly the A_3 band and account for some of the unassigned lines in the centre of the band, but many, if not most, of these can be accounted for by the necessarily incomplete assignment discussed later in this section.

The analysis has been found quite simple, apart from two

FIGURE 7.3.

A_3 BAND PERTURBATIONS



regions which are greatly affected by perturbations. The sub-branches with low K'' have been found quite regular except for a slight disturbance in the levels with $K'' = 0$. This disturbance take the form of a slight inflection in the curve of (σ_{obs} - σ_{calc}) where this should, in the absence of perturbations, be either straight or smoothly curved. the Quantitatively same effect is shown by all three of the sub-branches in a region where the assignments are quite definite, and it will be discussed at the end of the section.

The region of high K' is, however, greatly affected by perturbations. If we calculate the spectrum in this region from rotational constants derived from the levels with lower K', and compare them with the observed frequencies which are definitely assigned, it is apparent that at least two perturbations are occurring and that their effects overlap greatly. Fig. 7.3 shows the nature of these deviations for the levels $K' = 5, 6, 7, 8$, and 9. It appears that there is a sharp degeneracy of perturbed and perturbing levels at $J' \sim 11.5$, $K' = 8$; its appearence in $K'=8$ would correspond well to a perturbation of the Lide type with a level some 125 cm^{-1} below, ie. the other member of the inversion doublet. However, it is difficult to account for the shape of the perturbation curve if we attribute the approach and departure from degeneracy (necessary to account for the sharp asymptotic behaviour) simply to the differences in the asymmetry terms of the two levels concerned in the perturbation (which we would have to if we assumed that the rotational constants of the two sets were identical), this would lead to a perturbation of opposite sign to that observed. It could, however, be accounted for by allowing the rotational constants D of the two sets to differ by 0.05 cm^{-1}; this is, however, an impossibly large difference for the two members of an inversion doublet. It may ~~also~~ alternatively be accounted for by allowing the rotational constants α to differ and assuming very small values for the parameters d and c (that is, the perturbation would be large only when degeneracy was very close). The true state of affairs may be a combination of these two possibilities although, on the other hand, the source of the perturbation may not even be the inversion doublet. In the absence of any real information to enable a choice to be made, it has been decided to try to account for the observed perturbation by the arbitrary adoption of the first possibility, and then, when more information comes to light about the perturbations in other bands (especially those lower in the spectrum, where identification is likely to be more certain), to re-examine this perturbation. However, when we do account for it on these lines, large deviations in the levels with K' = 6 remain, which cannot be explained on the basis of this single perturbation, since

Table 7.6.

A3 Band : Rotational constants in cm^{-1} ; 1

1) Rotational

	Excited state
D	$1.03552(8)$
α	$7.5563(7)$
b	$-0.00674(2)$
D_{E}	$-1.92(1) \times 10^{-4}$
D_{EJ}	$-6.21(9) \times 10^{-5}$
D_{J}	$-3.43(1) \times 10^{-6}$
D_{4}	$2.7(4) \times 10^{-5}$
D_{5}	$-1.2(2) \times 10^{-7}$
D_{6}	$1.3(5) \times 10^{-6}$

2) Vibronic

$$\sigma_{00} = 31{,}808.633(6)$$

3) Perturbation

	1	2
I	130.90 (±.03)	103.03 (±.2)
d	0.067(±.002)	0.061(±.004)

the levels with K' = 7 seem only to be slightly perturbed. If, however, we assume that there is a second source of perturbation, and that the centre of this perturbation is a little above K' = 6, then the positive perturbation in the levels with K' = 7 due to the first-mentioned source would be partly compensated by the negative perturbations from the second source. We have, therefore, made this assumption, for theppurpose of obtaining a fit of rotational constants to the spectrum; the significance of the perturbation parameters, especially of d and e, will, of course, be subject to further investigation.

For the determination of constants, 369 frequencies, singly assigned and undisturbed, were chosen for the first least squares solution. In view of the uncertain nature of the perturbations affecting the high K' region, it was decided that the solution for the ground state constants as well as those of the excited state would lead to importation of the effects of the perturbation, inadequately accounted for by the perturbation formula, into the values for ground state constants. Accordingly, the best set of ground state constants obtained from other bands was used to obtain the errata; only the excited state constants were solved for in the least squares procedure. The results of such a run are presented in table 7.6. The standard deviation of the residuals after the last iteration was 0.041 cm^{-1}; the high

Table 7.7.

A_3 Band : Rotational constants. 2 ($K' < 5$)

1) Rotational

	Ground state	Excited state
D	$1.21445^{(1)}$	$1.03507^{(1)}$
α	$8.1904^{(8)}$	$7.5579^{(1)}$
b	$-0.009851^{(3)}$	$-0.006735^{(4)}$
D_K	$-6.264^{(2)} \times 10^{-4}$	$-2.484^{(3)} \times 10^{-4}$
D_{KJ}	$-4.73^{(2)} \times 10^{-5}$	$-7.30^{(3)} \times 10^{-5}$
D_J	$-1.67^{(2)} \times 10^{-6}$	$-2.32^{(2)} \times 10^{-6}$

2) Vibronic

$$\sigma_{00} = 31{,}808.624^{(5)}$$

value compared with that for the A_2 and A_0 bands is obviously due to the relatively poor fit in the region where the perturbations are large.

A second run was undertaken with the aim of obtaining rotational constants as far as possible unaffected by the perturbations. For this run, all the frequencies which terminated on levels with $K' \geq 6$ were omitted from the least squares solution. The energy equation was the same as before, that is, the effects of the $K' = 6$ and the $K' = 8$ perturbations were included, the constants used for them being those derived from the run just described; in this way it was hoped to account, sufficiently well, for the overflow of the two perturbations into the levels $K' \leq 5$. The equations of condition for the least squares solution contained the three rigid rotor constants for the two states, the three most significant distortion constants for both states (the first run showed that for present purposes, the remaining three could be neglected as insignificant), and the vibronic energy, a total of 13 constants. 274 frequencies went into this solution and the results are given in table 7.7. The standard deviation of the residuals was 0.024 cm^{-1} indicating that, though better then that for the first run, the energy equation used to describe the frequencies was still not quite adequate; the reason for this will emerge below. The constants taken as definitive are those obtained from the second run, together with the perturbation constants obtained in the first run; they are discussed separately below.

(i) The rigid rotor constants of table 7.7 are all obtained with standard errors comparable to those obtained for the other bands of the A series described in the two previous sections; in particular, the values obtained for the ground state (by the full scale treatment) are in very good agreement with those obtained from the other two bands and also with the values obtained from the combination differences (cf. chapter 8). The slight deviation in the value found for b" is readily accounted for by the slight disturbance in the levels with $K' = 0$, already referred to, and discussed later. The differential constants have been determined as before and they are given in table 7.8 together with the "derived" excited state constants. The inertial constants, moments of inertia and the inertial defect were calculated from the results of the second solution run (table 7.7) and they are also given in table 7.8, together with their standard errors calculated with the aid of the known correlation coefficients. These constants are discussed in relation to those of the other bands, in section 9.5.

(ii) The differential distortion constants are also presented in table 7.8 together with the "derived" excited state constants.

(iii) The vibronic frequency is obtained with very high accuracy, ± 0.005 cm^{-1}.

Table 7.6.

A_3 Band : Differential constants.*

Constant	Differential $\triangle x$	$r_{x''x'}$	Stand. Error	"Derived" ex. state Const.	Stand. Error
B	-0.17938	0.969	3.6^{-5}	1.03536	6.6^{-5}
α	-0.63242	0.625	8.1^{-4}	7.5582	8.3^{-4}
b	0.003116	0.479	3.7^{-6}	-0.006726	4.6^{-6}
D_K	3.780^{-4}	0.379	2.9^{-5}	-2.591^{-4}	2.9^{-5}
D_{KJ}	-2.571^{-5}	0.684	2.2^{-6}	-6.893^{-5}	2.3^{-6}
D_J	-0.648^{-6}	0.962	5.1^{-8}	-2.936^{-6}	8.2^{-8}

A_3 Band : Inertial constants and moments of inertia.

$A' = \overset{(10)}{8.5930}$ cm^{-1} $\quad I_a = \overset{(2)}{1.96412}$ amu.Å^2

$B' = \overset{(15)}{1.08597}$ " $\quad I_b = \overset{(21)}{15.5282}$ "

$C' = 0.98417$ " $\quad I_c = \overset{(25)}{17.1344}$ "

$\triangle = \overset{(3)}{-0.3579}$

---

* See Note p.203.

(iv) To account adequately for the perturbations occurring in the excited state levels is the most difficult part of the analysis of this band. The somewhat arbitrary procedure used, was described earlier in this section. It is apparent in the first place that the perturbation parameter d for both perturbations (e was omitted in view of the results from other bands) can be given no physical significance. The values obtained for I for the two perturbations do, however, fix the position of two perturbing levels with something like an accuracy of ± 5 cm^{-1}. The fact that one of the levels probably lies at about 130 cm^{-1} below the excited state level of the A_3 band points to the possibility that we have a Lide type of perturbation and that the level is indeed the (+) level of an inversion doublet. However, a perturbation of a different type would have different selection rules as to the levels allowed to interact, and this might fix the perturbing level some distance from the position assumed above. Further discussion on this point is deferred until section 9.5.

The fixing of the second perturbing level is subject to the same difficulties as those above. That we have not, in fact, accounted adequately for the two perturbations is shown by the large residuals obtained in some of the high K' levels; amounting in some cases to 0.15 cm^{-1}. It is for this reason that the rotational constants are taken from the second (restricted) set of data.

The disturbance in the levels of K' = 0 takes the form shown in table 7.9. The values are all derived from singly assigned frequencies in a region where there is no doubt as to the validity of their assignments.

Table 7.9.

A_3 Band : residuals in K' = 0

J	pPJ 1L	pQJ 1U	pRJ 1L
0			
1	0.019		
2			
3	-0.001		
4	-0.000		
5			-0.028
6		-0.020	-0.031
7		-0.023	
8	-0.046		
9		-0.047	
10	-0.066	-0.049	-0.056
11			
12	-0.078		-0.062
13		-0.034	-0.074
14	-0.078		
15	-0.078	-0.032	-0.071
16	-0.065	-0.014	
17			
18		-0.006	
19		0.021	-0.037
20		0.023	
21			
22	-0.030	0.034	
23	0.004		
24	0.013		

The agreement between the residuals in the first and last columns is very good, making allowance for the random errors of measurement. The values in the central column do show a significant (though small) deviation and this must be attributed to the fact that there, the frequencies originate on a different type of ground state level from the other two, ($K'' = 1^+$ as opposed to $K'' = 1^-$). The least squares procedure, in attempting to correct for these deviations, has attributed part of them to the ground state and has treated the levels $K'' = 1^+$ differently from the levels $K'' = 1^-$ (inevitably, in view of the large $E(b)$'s with opposite signs). This is reflected in and accounts for the slightly high value for the ground state rotational constant b'' mentioned earlier. The source of the disturbance is unknown but it may be due to a very weak perturbation by a vibronic level in the neighbourhood. The high value obtained for the standard deviations of the residuals in the full-scale solution for this band, mentioned earlier, can be almost completely accounted for by these disturbances.

7.5. The C_1 band.

The C_1 band is especially interesting since it is thought that the (+) inversion level corresponding to the (-) level which forms the upper level of this transition, might be responsible for the perturbation occurring in the low K' region of the A_2 band, described in detail in section 7.3. It has not been investigated before, although the C_0 band was analysed by Dicke and Kistiakowsky, and, since the two bands differ only by a single quantum of the excited state carbonyl vibration, they should bear some resemblance to one another. As will emerge below, the present analysis of the C_1 band is very incomplete and in view of the importance of this band, which will become apparent from the discussion in section 9.5, it merits a more complete analysis in the future.

The lines were measured from the two plates containing the strongest absorption of set 2 (the band is much too weak for measurement from the plates of set 1). In all, about 3000 fringes were measured, and these produced the 770 frequencies reported in table A3 of the Appendix. It can be seen from fig. 5.5 p152 which is a print of the kind measured for this band, that although the high frequency end of the band looks quite normal in comparison with fig. 2.3 p38 which is typical of the A series of bands, there is a very noticeable decrease in intensity near the centre of the band. In addition, the fringes appear to be blurred out in this region and this renders their measurement extremely difficult. The weaker frequencies of table A3 are accordingly rather inaccurate and many are probably spurious. Further, the low frequency end of the band overlaps the neighbouring (much stronger) A_2 band.

The analysis of the frequencies has been found very difficult, due largely to the limitations just mentioned. The rR and rQ branches for $K'' \geq 3$ are quite regular and have been analysed in a quite straightforward manner. It

Table 7.10

C_1 Band : Rotational constants (cm^{-1})

1) Rotational

	Excited state
D	$1.0564^{(3)}$
α	$7.694^{(9)}$
b	$-0.0094^{(7)}$
D_E	$-2.6^{(3)}$ $x10^{-4}$
D_{EJ}	$-4.9^{(6)}$ $x10^{-5}$
D_J	$-4.2^{(6)}$ $x10^{-6}$
η	$0.12^{(7)}$

2) Vibronic

σ_{oo} = 31818.9 (± .1)

3) Inertial constant

A' = 8.750 (±.009)

has been found impossible to identify the remaining sub-branches with any certainty, and the determination of constants has been limited to the few definite assignments reported in table A3. Of these, 92 were chosen as singly assigned and reasonably free from disturbance from neighbouring fringes. In view of the relatively small number and limited range, it was decided not to attempt a full scale least squares determination for the ground and excited state constants and the vibronic frequency. Accordingly, the best set of ground state constants available from other bands was employed for determining the errata but were not solved for . The energy formula employed was made up from the three excited state rigid rotor constants together with the three most significant distortion constants and a term linear in K' (the latter to take up any Coriolis perturbation) and finally the vibronic frequency; there were thus eight variables in all to be solved for. The constants obtained are given in table 7.10 together with their standard errors. The standard deviation of the residuals after the final iteration of the solution procedure was 0.052 cm^{-1}; this high value is indicative both of the poor precision of the frequencies and of the inadequacy of the energy formula employed to describe the excited state levels. The constants are considered separately below.

(i) Of the rigid rotor constants, only D' and α' have reliable values, since the information available in the frequencies employed does not permit b' to be obtained with any accuracy. The very high value for b', given in table 7.10, probably has no great accuracy. D' and α' are obtained with much poorer accuracy than in the bands described in the earlier sections of this chapter, but their sum gives the inertial constant A' to be 8.750 ±0.009 cm^{-1}.

(ii) The vibronic frequency is obtained with sufficient accuracy for use in a vibrational analysis. Brand (23) could determine only the frequency of the rR J 3 head for this band, which is the frequency he lists.

(iii) The distortion constants are all obtained with a precision of about 10%.

(iv) The value obtained for the constant whose coefficient was linear in K', here symbolised as η, is high enough to be significant (it produces an energy term of 1.2 cm^{-1} for K'=10) but its standard error of 60% means that little reliance can be placed on its numerical value; it does indicate, however, the probable occurence of some perturbation. A discussion on this point is deferred until section 9.5.

A proper analysis of the band has been left until more reliable frequencies are available for the central portion. To obtain them, stronger absorption is necessary ; but this should not be obtained by raising the pressure of absorbing gas, since still further broadening of the fringes would result. Rather, the pressure should be kept below 20 mm and a longer path of gas employed. The experimental arrangement has only recently been modified so that this could be achieved, but as yet no such spectra have been obtained with it.

Subsequent to this preliminary investigation, it was communicated to the present author by Innes, that the C_0 band, and therefore this C_1 band, was probably type-C, not type-B as reported (on very limited evidence) by Dieke and Kistiakowsky (14) and accepted by Brand (23); the consequences of this important piece of evidence are discussed in section 9.5.

CHAPTER 8.

Results : part 2, the ground state of formaldehyde.

8.1. The microwave spectrum.

The microwave frequencies measured to date for formaldehyde have been reported by Oka, Hirakawa and Shimoda (44). As mentioned earlier, in section 4.2, Oka's procedure for determination of rotational constants was somewhat arbitrary; it was therefore decided to re-examine these data, using the programmes developed for the present work, so that a set of constants consistent with these microwave frequencies could be compared with those obtained from the ultra-violet work.

As mentioned in section 5.3, the fact that the ground state of formaldehyde is planar means that only four independent, non-zero centrifugal distortion constants are needed to describe the centrifugal distortion up to first order. Oka realised this but after an examination of the list of available microwave frequencies, (reproduced in table 8.1 cols. 1,2,3) he concluded that there was not sufficient variety in them to allow unique solution for all seven of the molecular constants (three rigid rotor and four distortion); he therefore computed the four distortion constants from vibrational data obtained from the infra-red spectrum by Blau and Nielson (47). He calculated force constants using a Urey-Bradley potential field, and the τ's obtained are listed in table 8.2 p243 (after conversion to cm^{-1} using c = 299793 km/sec). His rotational constant D, given in table 8 .1,

Table 8.1.

J''	K''_{-1}	K''_{+1}		J'	K'_{-1}	K'_{+1}	Freq.	C.D.C.	Errors	
									This wk.	OKA
1	1	1	-	1	1	0	4829.73	-3.43	0.14	0.00
2	1	2	-	2	1	1	14488.65	-10.76	0.32	-0.03
3	1	3	-	3	1	2	28974.85	-22.89	0.24	-0.29
4	1	4	-	4	1	3	48284.60	-41.21	0.15	-0.01
5	1	5	-	5	1	4	72409.35	-67.52	-0.11	-0.43
6	2	5	-	6	2	4	4954.76	-18.34	-0.13	0.20
7	2	6	-	7	2	5	8884.87	-34.31	-0.29	0.33
8	2	7	-	8	2	6	14726.74	-59.53	-0.47	0.71
9	2	8	-	9	2	7	22965.71	-97.44	-0.73	1.27
10	2	9	-	10	2	8	34100.32	-152.17	-0.72	2.32
12	3	10	-	12	3	9	3225.58	-34.24	0.29	-0.56
13	3	11	-	13	3	10	5136.58	-56.50	0.16	-0.80
14	3	12	-	14	3	11	7892.03	-90.04	0.07	-1.01
15	3	13	-	15	3	12	11753.13	-139.19	0.15	-1.28
16	3	14	-	16	3	13	17027.60	-209.39	0.24	-1.25
17	3	15	-	17	3	14	24068.31	-307.37	0.22	-1.17
18	3	16	-	18	3	15	33270.80	-441.19	0.66	-0.10
19	3	17	-	19	3	16	45063.10	-620.25	0.95	1.43
20	4	17	-	20	4	16	3518.85	-86.09	0.03	-1.94
21	4	18	-	21	4	17	5138.57	-129.60	0.16	-2.42
22	4	19	-	22	4	18	7362.60	-191.49	-0.20	-2.99
23	4	20	-	23	4	19	10366.51	-277.98	-0.21	-3.21
24	4	21	-	24	4	20	14361.54	-397.04	0.10	-2.51
25	4	22	-	25	4	21	19595.23	-558.34	-0.35	-2.31
26	4	23	-	26	4	22	26358.82	-773.64	-0.43	-0.78
27	4	24	-	27	4	23	34982.80	-1057.00	-0.19	2.83
28	4	25	-	28	4	24	45835.58	-1424.66	-0.46	8.03
31	5	27	-	31	5	26	7833.20	-402.82	-0.30	-0.60
32	5	28	-	32	5	27	10608.74	-559.60	-0.27	1.35
33	5	29	-	33	5	28	14211.68	-768.86	-0.27	4.33
34	5	30	-	34	5	29	18841.20	-1044.94	0.32	10.58
35	5	31	-	35	5	30	24730.40	-1405.16	0.53	17.05
								$\sigma =$	0.38	4.16

was derived from the single line $1_{0,1} \leftarrow 0_{0,0}$ whose frequency, since both levels have E(b) = 0, depends only on the distortion constants and D (for all of the other lines $\Delta J = 0$, so that they can contribute no information about D). By applying the calculated distortion correction of -0.030 Mc, he arrived at a value for D of 36419.22 Mc which he considered to have a precision of 0.10 Mc. He then applied the appropriate centrifugal distortion corrections to the rest of the frequencies and solved for the rotational constants α and b, and subsequently with an adjusted value of the distortion constant τ_{xxxx} as well. Although we might not expect the microwave frequencies to deliver τ's which reproduce those calculated from force constants (in view of the lack of variety mentioned above) it seems important that the best set of constants consistent with these frequencies be obtained, together with their standard errors and correlation coefficients.

Accepting Oka's value for D as correct, the frequencies have now been analysed using programme HR 8.45 (see the Appendix p. 315) in which all the remaining six constants were determined simultaneously by least squares; these results (converted to cm^{-1}) are also presented in table 8.2, (p.243), and the differences between the observed and the calculated frequencies are shown in table 8.1, col.5, in comparison with those from Oka's paper, col.6; our calculated centrifugal distortion corrections are given in col.4. The standard deviations of the two sets appear at the foot of the columns. Possibly one factor in the wide variation in Oka's values is that he gave the low J, K transitions a larger weight than the high J, K transitions. He does not state just how this was done, but even so, it is difficult to imagine that this procedure could account for the much poorer fit that he obtained, and it must be concluded that his solution procedure was inferior to the present one*. It is quite informative that the standard errors which emerge for the τ's in our treatment are high, and that the numerical values of the τ's themselves differ so markedly from those calculated by Oka. This supports Oka's conclusion that the distortion constants cannot be determined with any certainty from the microwave frequencies but gives point to the necessity for their determination from the ultra-violet frequencies.

In addition to the above calculations, the frequencies have been analysed using the 6 D formula (see equation 5.24) and the results are compared in table 8.3 with those obtained from the U.V. results. Here, the values of D and D_J are absent from the frequency expressions, hence only seven constants can be solved for. As might be expected, the distortion constants emerge with rather high standard errors.

8.2. Constants from the ultra-violet spectrum.

The ground state constants obtained by solution for all

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* It might be mentioned here that the matrix given by Oka in his paper (44) as table 1, is dimensionally incorrect when used in his equation 6. It is unlikely that this fault is anything but a printing error.

the variables entering into the energy expression for the ultra-violet frequencies of the A_0, A_2 and A_3 bands have already been reported in the previous chapter; for the first two of these bands they are repeated in table 8.3 for purposes of comparison with the values derived by other methods.

As already intimated, the best way for obtaining ground state constants from the ultra-violet frequencies is to remove the effects of the excited state by choosing pairs of lines that contain a common excited state level. The difference between their frequencies gives the frequency of a hypothetical transition between the ground state levels concerned. We can obtain the selection rules for these pseudotransitions from the normal ultra-violet selection rules given earlier in section 5.4; they are given in full below.

$$\begin{array}{ll}
\Delta J = 0 & E^+ \leftrightarrow E^+ \\
 & E^- \leftrightarrow E^- \\
\Delta K = \pm 2 & 0^+ \leftrightarrow 0^+ \\
 & 0^- \leftrightarrow 0^-
\end{array}$$

$$\begin{array}{ll}
\Delta J = \pm 1 & E^+ \leftrightarrow E^- \\
\Delta K = 0, \pm 2 & 0^+ \leftrightarrow 0^-
\end{array}$$

$$\begin{array}{ll}
\Delta J = \pm 2 & E^+ \leftrightarrow E^+ \\
 & E^- \leftrightarrow E^- \\
\Delta K = 0, \pm 2 & 0^+ \leftrightarrow 0^+ \\
 & 0^- \leftrightarrow 0^-
\end{array}$$

(The notation is explained in section 5.2). It can be seen that a wide variety of frequency terms is obtained.

Because of the smaller number of constants required to

Table 8.2.

Ground state constants for formaldehyde (4 τ's)

	Microwave (Oka)	Microwave (this work)	U.V. (C.D.) A_0 band	U.V. (C.D.) A_2 band	U.V. (C.D.) A_3 band	U.V. (C.D.) $A_0+A_2+A_3$ bands
D	(2) 1.214812	(1.214812)	(7) 1.21473	(1) 1.21491	(8) 1.21472	(5) 1.21474
α	(8) 8.1926	(4) 8.1865	(2) 8.19072	(4) 8.19102	(3) 8.19042	(2) 8.19055
b	(1) -0.009827	(1) -0.009846	(3) -0.009839	(7) -0.009834	(4) -0.009832	(3) -0.009837
τ_{xxxx}	-1.345×10^{-5}	(2) -4.592×10^{-6}	(5) -1.168×10^{-5}	(9) -1.299×10^{-5}	(6) -1.126×10^{-5}	(4) -1.173×10^{-5}
τ_{zzzz}	-3.397×10^{-3}	(4) -9.742×10^{-3}	(8) -2.733×10^{-3}	(2) -2.762×10^{-3}	(2) -2.735×10^{-3}	(6) -2.732×10^{-3}
τ_{xxzz}	4.704×10^{-5}	(4) 2.38×10^{-4}	(1) 2.60×10^{-5}	(28) -1.20×10^{-6}	(2) -1.18×10^{-5}	(8) 1.64×10^{-5}
τ_{xzxz}	-1.098×10^{-4}	(1) -2.12×10^{-4}	(9) -9.81×10^{-5}	(2) -7.74×10^{-5}	(1) -6.64×10^{-5}	(7) -8.94×10^{-5}
n	33	32	146	90	100	336
σ_r	0.00014	0.000013	0.012	0.013	0.012	0.013

*After adjustment : 1.308×10^{-5}

describe the frequencies, i.e. only ground state constants, it has been found possible to employ the distortion formulation in terms of the τ's; the programmed route is described in section 6.4. Since also, definitive constants in terms of the 6 D formulation are required in the calculation of excited state constants by the route described in section 6.5, the available combinations have been analysed using the D formulation as well.

The frequencies measured for each of the A_0, A_2 and A_3 bands have been used to provide uncorrelated combinations (between, of course, singly assigned and undisturbed lines) and they have provided 146, 90 and 100 of them respectively, making a total of 336 in all. Each group separately has been analysed, and so has the aggregate of 336; the results obtained for both the τ and D formulations are given in tables 8.2 and 8.3 respectively, together with the standard errors determined by the programme for each constant (printed over the corresponding digits of the constants for brevity). The last two rows give the numbers of frequencies or combinations used and the standard deviations of the residuals for the relevant determinations. (These two quantities do not quite tally in the two tables because a few frequencies were added or removed between the τ and the D sets of determinations.)

We first consider table 8.3 where the D formulation has been employed; it can be seen that neglecting for the moment the constants from the microwave frequencies in the first

Table 8.2.

Ground state constants for formaldehyde (6 D's)

	Microwave (this work)	A_o Band (22 consts.)	A_2 Band (25 consts)	A_o Band (C.D.)	A_2 Band (c.D.)	A_3 Band (C.D.)	$A_o+A_2+A_3$ bands (C.D.)
D	(1.21491)	(6) 1.21487	(1) 1.21504	(7) 1.21468	(1) 1.21491	(1) 1.21478	(5) 1.21474
α	(5) 8.1868	(2) 8.19038	(4) 8.19026	(2) 8.19069	(3) 8.19111	(5) 8.19044	(2) 8.19057
b	(1) -0.009845	(3) -0.009841	(7) -0.009840	(4) -0.009839	(9) -0.009821	(8) -0.009848	(4) -0.009842
D_E	(3) -2.206×10^{-4}	(2) -6.367×10^{-4}	(5) -6.493×10^{-4}	(2) -6.369×10^{-4}	(5) -6.483×10^{-4}	(5) -6.354×10^{-4}	(2) -6.371×10^{-4}
D_{EJ}	(4) -3.79×10^{-5}	(5) -4.34×10^{-5}	(1) -3.83×10^{-5}	(7) -4.32×10^{-5}	(2) -4.25×10^{-5}	(2) -4.48×10^{-5}	(6) -4.32×10^{-5}
D_J	-	(7) -2.33×10^{-6}	(2) -3.00×10^{-6}	(9) -2.18×10^{-6}	(2) -2.53×10^{-6}	(2) -2.32×10^{-6}	(7) -2.29×10^{-6}
D_4	(1) 9.73×10^{-6}	(5) 2.81×10^{-5}	(18) 4.88×10^{-6}	(1) 2.32×10^{-5}	(2) 5.56×10^{-5}	(18) -2.51×10^{-6}	(8) 1.86×10^{-5}
D_5	(3) 2.73×10^{-7}	(7) 1.35×10^{-7}	(2) 1.73×10^{-7}	(2) 2.07×10^{-7}	(3) -4.07×10^{-7}	(3) 4.16×10^{-7}	(1) 2.50×10^{-7}
D_6	(3) 4.74×10^{-8}	(1) 3.12×10^{-7}	(4) 4.14×10^{-7}	(2) 1.51×10^{-7}	(4) 8.78×10^{-7}	(4) -1.99×10^{-7}	(2) 1.19×10^{-7}
n	32	337	304	145	90	107	342
σ_r		0.008	0.015	0.013	0.013)	0.018	0.015

column, the agreement between the various determinations is excellent, and the variation is within the limits to be expected from the quoted standard errors. The values in the last column have been taken as the definitive set and have been used for the determination of the "derived" excited state constants, as mentioned in chapter 7. Comparison of the two sets of constants derived solely from the A_0 band indicates that the full scale determination procedure has given almost as good a set of ground state constants as the combination difference method; this indicates that the excited state of this band is therefore not interfering numerically with the determination of the ground state constants. The energy formulation used for the excited state of this band is therefore entirely adequate. A similar comparison for the A_2 band constants shows almost the same level of agreement for this band also; but the slightly less good agreement between the values for b" indicates that the difficulties connected with the formulation of the $K' = 0$ perturbation present in this band, discussed at length in section 7.3, are causing some numerical disturbance to the ground state constants. Inspection of the values obtained fo~~r~~the three distortion constants D_4, D_5 and D_6 shows that little reliance can be placed on the figures obtained except to give their orders of magnitude; this is of no consequence since the contributions made by those three jointly to the frequencies rises only to about 0.05 cm^{-1} in extreme cases.

Comparison with the microwave constants in column 1 shows that b, D_{EJ} (and D_5) are in good agreement with the ultra-violet results but that the others, α , D_E, D_4 and D_6 are quite significantly different. For the reasons just indicated, the deviations in D_4 and D_6 call for no consideration. The probable reason for the deviations in D_E and α is that they are determined from the microwave frequencies as the difference between the members of asymmetry doublets ($\Delta J = 0$, $\Delta K = 0$); this limits the amount of variation available for their determination from such data, whereas in determination from the ultra-violet frequencies, the pairs of levels used include also many differing in K by two units, and in J by one or two units (this feature is particularly important in its bearing on the determination of b).

We now consider the results in table 8.2, for which the τ formulation was employed. For reasons already enlarged on, these constants are considered to be the ones most appropriate to describe the geometry and centrifugal distortion behaviour of the ground state of formaldehyde. The three rigid rotor constants in the last column have been used to determine the inertial constants and the moments of inertia etc., given below in table 8.4; the relations used for calculating these quantities and their standard errors have been given in section 6.6. (It might be repeated here that the standard errors quoted in table 8.4 are obtained with the aid of the known correlation coefficients between the three variables D, α and b.)

Table 8.4.

$A = \overset{(15)}{9.40529}$ cm^{-1} $\qquad I_a = \overset{(3)}{1.79295}$ amu.Å^2

$B = \overset{(6)}{1.29531}$ " $\qquad I_b = \overset{(7)}{13.0187}$ "

$C = \overset{(4)}{1.13417}$ " $\qquad I_c = \overset{(7)}{14.8683}$ "

$\Delta = +\overset{(9)}{0.0567}$ amu.Å^2

The quantity Δ is the inertial defect defined in equation 6.19. The value obtained is in good agreement with the value 0.0561 amu.Å^2 calculated theoretically by Oka and Morino (46) and (83).

The distortion constants calculated from the ultra-violet work are in good agreement among themselves and the values in the last column are taken to be the best values. The agreement between these and the constants calculated by Oka from vibrational data is also good, especially if we note the experiences of other workers who have tried to correlate τ 's derived from vibrational frequencies and from rotational spectra. An interesting point which emerges from table 8.2 is that the first two distortion constants τ_{xxxx} and τ_{zzzz} emerge with better standard errors from the ultra-violet frequencies than from the microwave frequencies (our treatment, since Oka did not obtain standard errors for his τ's), while the reverse is true for the remaining constants τ_{xxzz} and

Table 8.4.

Centrifugal distortion constants (6 A_i)

$$A_1 = \overset{(2)}{-3.0578} \times 10^{-5}$$

$$A_2 = \overset{(5)}{6.5482} \times 10^{-5}$$

$$A_3 = \overset{(3)}{-3.6657} \times 10^{-5}$$

$$A_4 = \overset{(5)}{11.1443} \times 10^{-4}$$

$$A_5 = \overset{(22)}{4.4656} \times 10^{-4}$$

$$A_6 = \overset{(4)}{1.1813} \times 10^{-4}$$

Correlation coefficients.

	A_1	A_2	A_3	A_4	A_5	A_6
A_1	1.000	-1.000	1.000	0.988	0.972	-0.989
A_2		1.000	-1.000	-0.988	-0.972	0.989
A_3			1.000	0.988	0.971	-0.988
A_4				1.000	0.996	-1.000
A_5					1.000	-0.996
A_6						1.000

τ_{xzxz}. Since, however, each set must be regarded as self-consistent, it is not possible to combine values obtained from the two sources and so the ultra-violet set has been chosen as definitive.

The rotational and disto~~o~~rtion constants obtained from the A_0 band combination differences are given in table 8.5 for the formulation of centrifugal distortion in terms of Kivelson and Wilson's formula (the 6 A formula, equation 5.21). As explained in section 5.3, this formulation gives very poor values for the distortion constants as can be seen in the calculated standard errors. The correlation coefficients between the various A_i are also given in table 8.5. Their extremely high values suggest that a derived set of constants belonging to a better formulation might have had significantly lower standard errors; this is, of course, what has been demonstrated above.

Finally, it might be mentioned that Pillai and Cleveland (81) have calculated theoretical distortion constants for HCHO from the vibrational data of Blau and Nielsen (47); in this work they employed the centrifugal distortion formulation in terms of the constants introduced by Nielsen (69). Their values are given below, but since this formulation has not been used in the present work, no strict comparisons can be made; nevertheless, the first three constants are somewhat closely related to our D_E, D_{EJ} and D_J, and it is therefore interesting that there is a close similarity between these three below and the corresponding three in table 8.3.

$D_K = 6.077 \times 10^{-4}$

$D_{JK} = 4.029 \times 10^{-5}$

$D_J = 2.707 \times 10^{-6}$

$R_5 = 1.123 \times 10^{-5}$

$R_6 = 2.135 \times 10^{-8}$

$\delta = 3.933 \times 10^{-7}$

(The differences in signs arise simply from their respective definitions.)

CHAPTER 9.

Discussion.

9.1. The calibration.

The calibration procedure described at length in chapter 3 deserves some special discussion. As demonstrated by Raynes and by the present work, iron fringes can be measured with a precision of about 0.006 cm^{-1} and, since for most lines from 8 to 12 fringes are measured, the calculated frequencies have a precision approaching 0.002 cm^{-1}. The frequencies used for calibration were (mainly) the international values (37) which had been set up by using combination differences on a large number of assigned iron frequencies. The drawback to using such frequencies is that there is no guarantee that these frequencies, in effect predicted, will correspond exactly to the fringes measured: the presence of a weak unidentified line overlapping one of the standard lines can shift its centre by a significant amount and the measured frequency will be in error. Inspection of table 3.3 indicates that if such interference is present its effects are probably not serious, since the frequencies recalculated from the calibration constants agree with the standard frequencies almost as well as could be expected from the known standard errors. However, iron arc lines are much broader than is desirable for the lines of a calibration spectrum. It would be better if the calibration fringes could be measured individually to something of the order of 0.002 cm^{-1} or better, so that we would not need to rely on a large number of measurements to reduce the standard error of the lines. As yet, the frequencies of the much narrower lines obtained from thorium halide lamps (see Meggers and Stanley (82)) have not been measured sufficiently accurately by enough independent workers for their acceptance as replacing the iron arc standards.

9.2. The absorption frequencies.

As has already been intimated, the absorption frequencies have been measured with a precision considerably higher than has been claimed in the best of previous work. In all, in the present work, some 30,000 individual fringes have been measured (producing almost 3,000 rotational frequencies) and as can readily be imagined, this measurement is by far the most time-consuming and tedious part of the investigation. It is therefore necessary to ensure that the most efficient use of the time is made. Some observations in this regard have already been made in section 3.5.

In Raynes's work and in the early part of the present work, each absorption fringe was measured at least twice. A thorough investigation subsequently showed that the difference between these two measurements was, in general, considerably less (by a factor of five or more) than the standard errors of the frequencies that ultimately emerge. Consequently, a reduction to a single measurement for each fringe was made; no significant loss of accuracy is thereby incurred, and the time of measurement is reduced by almost 50%. It is considered that this advantage easily outweighs the loss of the check for accidental errors of recording etc. which might be discovered as a result of double measurement; any such errors other than minor ones, are practically certain to be detected in the subsequent sorting and assignment of frequencies.

In the next section it is shown that the median of the standard errors of the final frequencies is probably a little more than 0.0035 cm^{-1}. Since for any one frequency the average number of estimations employed is around 9, the standard deviation of a single fringe measurement is of the order 0.010 cm^{-1} (Raynes found 0.009 cm^{-1}). This figure is rather larger than the standard deviation of a single measurement of an iron fringe (0.006 cm^{-1}), which is surprising in view of the much smaller half width of the absorption lines. It seems therefore that the interference with the measurement of a fringe-centre by fluctuations in the grain of the photographic plate, and also by the relatively crowded surroundings in an absorption band, is considerably more important with these absorption fringes than with the broader iron fringes. It would seem likely then that increasing the width of the channels in which the absorption fringes are measured will have a beneficial effect on the precision of measurement. This point is discussed further in section 9.6.

9.3. Statistical methods; the treatment of errors.

It does not appear that previous workers in spectroscopy have made use of statistical methods, beyond the determination of standard or probable errors. From the earlier sections of this thesis, it will be seen that there are a number of ways in which the work has been materially assisted by the use of statistical methods directly as a tool of investigation: for example, in the study of perturbations, even in establishing the possible or probable presence and location of very weak ones; in the use of correlation coefficients; and in the simultaneous solution of normal equations for the totality of constants which may be significantly involved in the frequencies. That this last does not seem to have been previously attempted, at least in ultra-violet work, means that the standard or probable errors often quoted cannot represent (and may grossly misrepresent) the probable accuracy of the quoted values of the constants, when they have been obtained either by ignoring the effects of some terms or by assuming values (necessarily exact) for some of the constants. It seems that this tool is capable of much further development. Some further discussion of the present results, along the more conventional statistical lines, follows.

In view of the large number of rotational frequencies measured in a band, for each of which an estimate of the standard error is available, a statistical examination should

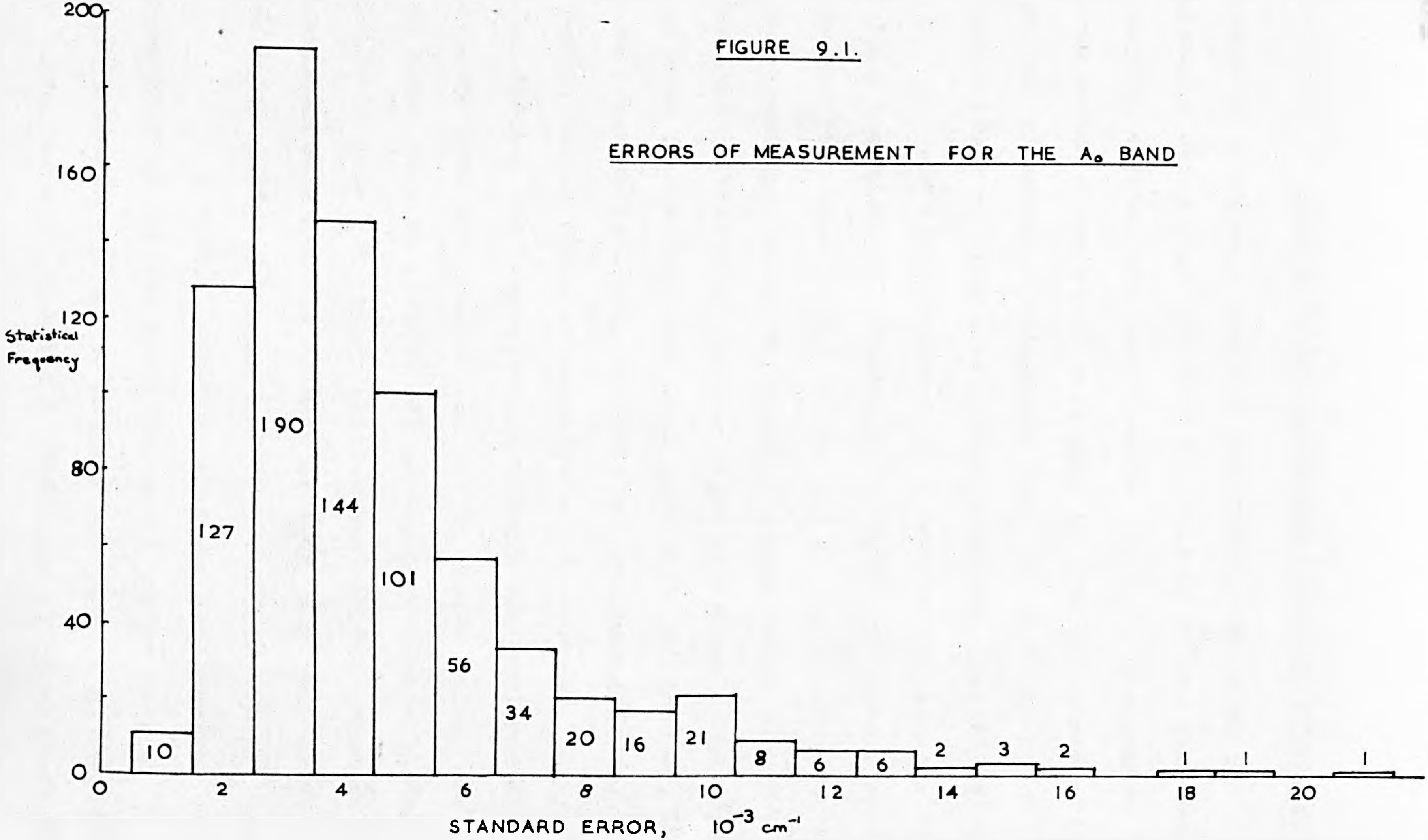

FIGURE 9.1.

ERRORS OF MEASUREMENT FOR THE A_0 BAND deliver some valuable information on the precision of the method, experimental and computational, as a whole. Such a study has therefore been undertaken; for this, the frequencies of the A_0 band shown in table A5 of the Appendix have been chosen, since, firstly, this band is probably less interfered with by superimposed bands and secondly, there is at most only one perturbation to consider (moreover a small one, as shown in section 7.2) the optimum conditions for obtaining a good fit of the molecular constants to the frequency data are present.

Figure 9.1 is a histogram of the (statistical) frequency of standard errors of the frequencies listed in table A5. The total population is 750. As found also by Raynes (6) p.232, in a similar survey of his A_2 band frequencies, most of the errors (here 60%) lie between 0.002 and 0.004 cm^{-1}. The median of the whole population lies at 0.0038 cm^{-1}; this value is slightly larger (probably significantly) than that of Raynes's data (0.0035 cm^{-1}) but this does not indicate that the present set is inferior to the previous set. Probably the reverse is true since the present set includes standard errors derived from three or more observations whereas Raynes confined his investigation to those with five or more; since the standard errors derived from only three or four observations are likely to be significantly larger than those from five or more, the effect of their inclusion is to shift the whole histogram to higher values.

A more interesting quantity than the median is the standard deviation of the whole population of errors which here turns out to be 0.0053 cm^{-1}. If we assume that, (a) the frequencies chosen for the determination of constants for this band are a representative sample of the total population, (b) for the singly assigned lines chosen for this determination, the frequencies used are true estimates for each line, subject only to the errors of measurement (for which we have a measure in the observed standard errors), and (c) the energy formula used to describe the frequencies is adequate (i.e. it contains the correct terms), then the standard deviation of the errors of fitting the energy formula to the frequencies should be identical to the standard deviation of the errors of measurement. The two quantities in fact turn out to be respectively 0.0083 cm^{-1} (see section 7.2) and 0.0053 cm^{-1} (see above). The discrepancy between the two (it is surprisingly small) may readily be accounted for by the following arguments:

(a) The lines chosen for the analysis are assumed single on the basis of a necessarily incomplete analysis; underlying unidentified lines, which may even have an intensity below the level of observability, can shift the peak of an absorption line quite significantly. This argument is strengthened by the fact that certain of the lines do show differences between the observed and recalculated frequencies which are much larger than would be expected from their standard errors. As an example, if we exclude those frequencies, 9 in all, which not being part of a sub-branch which shows a continuous deviation, nevertheless have residuals exceeding 0.020 cm $^{-1}$, then the standard deviation of the set of errors becomes 0.0070 cm^{-1}. If instead we apply the strict criterion of rejection of all observations which show deviations greater than 5 times the probable error (3 times the standard error) of the set (see Margenau and Murphy (84) p. 499), then only one of these large residuals can be rejected; this single rejection reduces the standard error to 0.0078 cm^{-1}.

(b) The energy formula used to describe the lines (detailed in chapter 5) is in several places a first order approximation to a more complex formulation; this is particularly so in the treatment of the Lide perturbation (section 5.4) and also in the treatment of centrifugal distortion (section 5.3). Since, however, the perturbation in this band (A_o) is very small, as demonstrated in section 7.2, the formulation used to describe it is probably entirely adequate; for the distortion formulation this may not be the case, however. Such effects would cause the residuals to deviate by some significant constant or steadily varying amount (superimposed on the errors of measurement); inspection of the residuals shows no significant trends, and it may be concluded therefore that the energy formula is quite adequate for data of the A_o band.

We can apply the above treatment also to the residuals obtained from the least squares solution of constants from the combination differences on the A_0 band; the standard deviation of these residuals is 0.011 cm^{-1}. The standard error of the combination of two frequencies is given by the square root of the sum of their respective variances (σ^2). It is easy to show that the standard deviation of the errors of the whole set of possible combinations is given as $\sqrt{2}$ times the standard deviation of the uncombined frequencies; therefore if we allow all possible combinations of the frequencies represented by the errors in fig. 9.1, then the standard deviations of the errors of the combinations is 0.0075 cm^{-1}. If we assume that the combinations chosen for the least squares determination are a representative selection of these, then this quantity, 0.0075 cm^{-1} should be compared with the 0.011 cm^{-1} mentioned above. The two values bear roughly the same relation to one another as do the earlier pair; this suggests that the chief cause for the discrepency lies in the uncertainties in the true frequencies of the lines, and that the energy formulations used for the two cases are both entirely adequate. In effect this means that both the excited state and ground state energy levels have been adequately formulated.

A similarly detailed treatment of the errors obtained for the A_2, A_3 or the C_1 bands has not been attempted, since for these bands the magnitude of the deviations caused by the interference of underlying frequencies from different bands, as well as from unidentified frequencies of the same band, and the difficulties of accounting adequately for the perturbations found in them, is likely to vitiate any comparison of observed and predicted errors. The investigation for the A_0 band does, however, indicate that for a band sufficiently well separated from other bands, the rotational frequencies can be measured to very high accuracy, mostly better than ± 0.004 cm^{-1}, and that the treatment of rotational energies outlined in chapter 5 can make full use of this accuracy in accounting for rigid rotor energies, centrifugal distortion and for small perturbations.

9.4. The ground state constants.

The ground state constants have been discussed at length in section 8.2. Here, a summary of the conclusions will be given.

In the first place it has been shown that the set of constants derived from the combination differences in the ultra-violet frequencies is significantly superior to that derived from the microwave spectrum.

The centrifugal distortion has been described by the τ, the A and the D formulations, discussed in section 5.3. The constants obtained for the 6A's of Kivelson and Wilson's formula have been shown to produce energy terms, for a given level, which are much larger than the total centrifugal distortion itself. It has been shown that this behaviour leads to numerical difficulties which can be obviated by using the derived formulation in terms of the D's of equation 5.24. The numerical values obtained for the D's from the ultra-violet combinations have been used in the determination of the "derived" excited state constants.

The definitive set of constants has been obtained using the τ formulation. From this set the moments of inertia about the three principal molecular axes have been determined as:

$$I_a = 1.79295_2 \pm 0.00003 \text{ amu.}\mathring{A}^2$$
$$I_b = 13.0186_6 \pm 0.0006 \text{ "}$$
$$I_c = 14.8683_2 \pm 0.0006 \text{ "}$$

The inertial defect of 0.0567_1 amu.$\mathring{A}^2$ is in very good agreement with the value 0.0561 amu.$\mathring{A}^2$ predicted by Oka and Morino (46) and (84) on the basis of the effect of the zero point vibrations. Used in conjunction with the same quantities for the dideuterated molecule, these moments of inertia should deliver precise information on the geometry of the ground state, better in fact than that obtainable from any other source at the present time.

The final centrifugal distortion constants are:

$$\tau_{xxxx} = -1.17_3 \; (\pm.04) \times 10^{-5} \text{ cm}^{-1}$$
$$\tau_{zzzz} = -2.732 \; (\pm.006) \times 10^{-3} \text{ "}$$
$$\tau_{xxzz} = 1.6_4 \; (\pm.8) \times 10^{-5} \text{ "}$$
$$\tau_{xzxz} = -8.9_4 \; (\pm.7) \times 10^{-5} \text{ "}$$

These values are in quite good agreement with the τ's calculated from force constants derived from the infra-red frequencies. It would be interesting to discover the degree of consistency of these τ's with the force constants of the molecule.

9.5. The excited state of formaldehyde.

The information obtained in the present work on the excited state of formaldehyde is derived mainly from the analyses of the bands of the A series. The excited states of these bands differ only in the numbers of quanta of the excited state vibration ν_{CO}; we might expect then, a smooth variation in the rotational constants (rigid rotor and centrifugal distortion) along the series. Unfortunately, although the bands A_0, A_2 and A_3 have been analysed in detail, the A_1 band has not, as yet, been investigated, so that there is an important gap in the series. In this section we will compare the rotational constants of the A series of bands and show that there is indeed a very smooth variation along the series. Following this, the perturbations found in the excited state levels will be discussed; since some of these are due to "accidental" degeneracies of other vibrations, we can expect only perturbations of the Lide type to show any smooth variation along the series. The work on the C_1 band will be considered

Table 9.1.

Comparison of excited state rotational constants : A series.*

	A_0	A_1 (interpolated)	A_2	A_3
A'	(15) 8.75172	8.695	(3) 8.64173	(10) 8.59301
B'	(6) 1.12449	1.1110	(8) 1.09893	(15) 1.08599
C'	(5) 1.01232	1.0025	(8) 0.99309	(15) 0.98417
Δ	(12) -0.2653	-0.288	(26) -0.3159	(3) -0.3579
D_K'	(1) -5.047^{-4}	-3.8^{-4}	(3) -3.110^{-4}	(3) -2.484^{-4}
D_{KJ}'	(5) -6.18^{-5}	-5.0^{-5}	(1) -4.69^{-5}	(2) -7.30^{-5}
D_J'	(6) -3.23^{-6}	-3.0^{-6}	(1) -3.51^{-6}	(8) -2.32^{-6}

* See note, p.203.

in the light of the recent suggestion (53) of its type-C character, and finally some comments will be made on the series a_0 to a_2.

Firstly, however, we will consider the vibrational energies derived from the analyses of the A series. If we take Dieke and Kistiakowsky's value (14) for the vibronic origin of the A_1 band, then the successive quanta of the ν_{co} vibration have the following values: $0 \rightarrow 1$, 1182.5 cm^{-1}; $1 \rightarrow 2$, 1163.5 cm^{-1}; $2 \rightarrow 3$, 1150.0 cm^{-1}. These figures show the regular expected decrease due to anharmonicity. If the A_4 and A_5 bands are analysed (and their analysis should present no more difficulty than that of those bands which have already been analysed) we might expect very precise data on the effects of anharmonicity in this relatively simple system.

A series: the rigid rotor constants.

In table 9.1, the inertial constants* (in cm^{-1}) and the inertial defect* (in amu. $Å^2$) are compared for the three bands investigated (the values for the A_1 band are interpolated). As far as can be judged, all four quantities do, in fact show a very smooth increase along the series and this is in accord with the expected lengthening of the C-O

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* Obtained from the full scale solution of section 6.3 and not from the "derived" excited state constants of section 6.6.

bond due to the increasing number of quanta of ν_{CO}. Their standard errors were determined by the methods explained in section 6.5, that is by making use of the correlation coefficients between the quantities D, α and b from which the inertial constants A, B and C are calculated. The degree of precision obtained for the constants is very satisfactory and some of the constants are obtained to an accuracy better than 1 in 30,000. When used in combination with data of similar accuracy for the deuterated molecule, we might expect a very high precision in the calculated geometry of the excited state levels concerned.

A series: distortion constants.

The three most significant distortion constants in the D formulation (see section 5.3), D_E, D_{EJ} and D_J are also presented in table 9.1 for the three bands. It can be seen that whereas D_J shows sensibly no variation along the series, the D_E exhibits a large, but smooth, variation, D_{EJ} varies less regularly. We might attribute this behaviour to the fact that D_{EJ} is in effect a cross term, and it will be interesting to see whether or not D_{EJ} for the A_1 band does turn out to be close to the interpolated value given here. We might hope that eventually, when sufficient bands for both HCHO and DCDO have been analysed, that these centrifugal distortion constants can be correlated with force constants developed for quite a complex potential field (this latter would, of course, have to be adequate to account for the inversion).

The remaining distortion constants D_4, D_5 and D_6 have not been listed in table 9.1. Reference to sections 7.2 to 7.4 will show that they are obtained with very high standard errors (so high, in fact, that statistically, the values obtained for the constants in most cases can not be regarded as significant), and in accord with this, calculation shows that their summed effect in the spectrum is very small, amounting to only about 0.015 cm^{-1} in extreme cases. (This does not mean, of course, that their collective effect can be ignored; they form part of a self-consistent set of constants, and must accordingly be used, with the values given.) This behaviour is due, no doubt, to the fact that formaldehyde is close to the symmetric rotor limit.

A series: perturbations.

We first consider those perturbations believed to be of the Lide type (see section 5.4). The main evidence that such perturbations are present in the spectrum is that there appears to be a perturbing level at 125 cm^{-1} below the origin of the A_2 band (see section 7.3) and this could very well be accounted for by the fact that the inversion splitting for the A_0 band is known to be of this order (see section 7.2 and below). It is reasonable to suppose that the influence of the ν_{CO} vibration which is predominantly a carbonyl strengthening vibration, would have a minimal effect on the ability of the two hydrogens to tunnel through the potential barrier; we might therefore predict an inversion splitting of about 125 cm^{-1}, for the A_2 band and this is in accordance with the observed behaviour. The behaviour of the other bands (A_0 and A_3) does not, however, fit in with the pattern to be expected on the basis of the findings in the A_2 band (the A_2 band was the first to be investigated in the present work). In section 7.4, it was shown that in the A_3 band a perturbation centred on the rotational levels with K' = 8 could be due to a perturbing level at somewhat more than 125 cm^{-1} below the origin of the A_3 band itself. The form of the perturbation as it approached degeneracy could not, however, readily be correlated with Lide's theory unless we assumed impossibly large values for the rotational constants of this perturbing level (these should approximate to those for the perturbed state). It was concluded in section 7.4 that there did appear to be a perturbing level close to the region predicted for the lower member of the inversion doublet but that it could not be positively identified with this lower inversion level. In section 7.2, dealing with the A_0 band, a very small perturbation was reported in the region expected for a Lide perturbation. It is very hard to explain why there should be such a large difference between the magnitude of the Lide perturbations in the A_0 and the A_2 bands. If the

A_1 band shows similar behaviour to the A_0 band we shall have to cast doubt on the occurrence of Lide perturbations in the spectrum and will have to account in a different way for the high K perturbation in the A_2.band.[‡] It might be mentioned here that the evidence for the occurrence of a Lide perturbation in the spectrum of dideuterated cyanamide (71) is very limited though there the observed discrepancies in the lines concerned are difficult to account for in any other way.

The other perturbations found in the bands investigated are probably of a normal Coriolis character. The perturbation in the levels $K' = 0$ in the A_2 band can be correlated with the lower inversion member of the C_1 band (see section 7.3). If it turns out to be the case that the assignment for the C_1 band contains the antisymmetric vibration γ'_{CH_2} (see below), then the product of the symmetry species of its (+) level and of the excited state level of the A_2 band contains the species of the rotations R_x and R_z in the C_s symmetry group, (see table 4.2).[*] We thus have the possibility of a normal Coriolis perturbation but this has not been investigated further in the present work. Some support, or otherwise, for this hypothesis might be forthcoming

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[*] It should be mentioned here that the choice of axes for this representation have been chosen to go over into the C_{2v} frame as the molecule becomes planar; this is not in accord with the usual identification of the principal axes for a C_s molecule but those chosen are obviously more convenient here.

[‡] N.B. also, the addendum p.207.

from the analysis of the A_1 band; the (+) level corresponding to the (-) level of the C_0 band is expected to lie in roughly the same relative position to the excited state of the A_1 band as is the situation in the next higher members of the two progressions.

The origin of the two remaining perturbations in the A_3 band, one a large perturbation affecting mainly the levels with K' = 6 and the other a minute perturbation in the K' = 0, are more difficult to account for. Ostensibly, one of them may be caused by the (+) level of the "F_0" band (see below) whose origin lies about 200 cm^{-1} above the origin of the A_3 band; but there are a large number of combinations of excited state vibrations that could occur in the vicinity (not all of which need necessarily produce observable absorption bands), and so the unambiguous assignment of the perturbing levels will be very difficult.

Clearly much work remains to be done on the nature of these perturbations, and, in particular, analysis of the A_1 band should help to clarify some points.

The C_1 band and the C series of bands.

As mentioned in section 7.5, the present analysis of the C_1 band has been very incomplete, due both to lack of time and to the difficulties inherent in the frequencies obtained from the present sets of plates. It is possible that analysis on the basis of type-C selection rules (see below) might help to clarify the analysis of the region near the centre of the band. Some of the difficulty however, is connected with the unexpectedly low intensity of the central portion of the band, since the fringes obtained in this region are very weak and their measurements are likely to be in error. It is possible that some of this loss of intensity might be due to the effect of C-axis selection rules, as described below, but it is tempting to ascribe it to a rotational-vibrational mixing phenomenon of the type postulated by Pople and Sidman (51) to account for the intensity of the parallel bands of formaldehyde. For this, these workers predicted that the intensities of the various sub-branches should be proportional to the quantum number K (i.e. to the amount of rotation about the z axis) as well as depending on the other factors described in detail in section 5.5 of this thesis. This would mean that the sub-branches terminating on K' = 0 should have zero intensity; it is unfortunate that the present analysis is inadequate to confirm or deny this hypothesis.

It has been mentioned above, and elsewhere in this thesis, that the C_0 band and therefore the C series of bands, has been found to obey type-C selection rules (53); this leads to the assignment of the C_0 band to the combination of excited state vibrations γ_{CH_2} (0^-) + γ'_{CH_2}, which is antisymmetric to the operations of the symmetry group C_s (see fig. 4.1). It is this γ'_{CH_2} vibration that Pople and Sidman (51) suggested would play some part in breaking down the selection rules which forbid this electronic transition (though the effect of the symmetric vibration γ_{CH_2}, was expected to, and indeed does, play the major part). Their suggestion therefore deserves a fuller, in particular a more quantitative investigation.

Finally, in connection with the C series, it is thought strange by the present author that the C series of bands should terminate abruptly at the member C_1 (especially since the C_1 band is noticeably stronger than the C_0 band), and that the band actually observed in the position expected for the C_2 band, is assigned by Brand (23) to the vibrations $\nu_{CH} + \gamma_{CH_2}(1-)$ as "F_0". A superficial examination of the high resolution pictures obtained in this work for this band indicates that it seems to be of the same general character as the bands of the C series; that is, the spacing of the rR heads is similar and there is the same low intensity in the central region. It therefore seems probable that "F_0" should now be re-assigned as "C_2". A still more superficial examination of Brand's F_1 band (this band only just appears in our photographed range and is appreciably outside the properly focussed region) seems to indicate that there are two bands there, possibly C_3 and some other band;

the setting of those points must await further experimental work.

The a series of bands.

Observation of transitions to the (+) members of the inversion doublets corresponding to the (−) levels of the A series of bands have been reported by Brand (23) up to the member a_2. The present high dispersion work on the A_2 band has shown no trace of frequencies attributable to an a_2 band (although we believe that we have located its excited state level by perturbations in the levels of the A_2 band, as shown in section 7.3) and we therefore believe that Brand's observation is spurious. A cursory examination of the A_1 band seems to indicate that the rotational structure in the region where the a_1 band is expected to lie belongs to the A_1 band. It seems that only for the a_0 band is there evidence in the spectrum. Robinson and diGiorgio (25) have published low temperature absorption pictures where the a_0 band is seen to stand out from the rotational structure of A_0 band, better than it does in the room temperature plates of the present work (see fig 2.3, p. 39). In our analysis of the A_0 band we have found a few lines unassignable to the A_0 band and we assume that they are due to a_0. It seems that the main evidence for the location of the (+) inversion levels will come from perturbations of the Lide type, discussed at length elsewhere in this thesis.

9.6 Further work.

(i) Although significant further increase in the absolute accuracy of the absorption frequencies is unlikely until a more exact means of calibrating the spectrum than the iron arc spectrum is found, several experimental modifications might be made to increase the precision of measurement and also to extend the useful range of the instrument. At present, as it is described in the early part of this thesis, the apparatus may be used for the photography and thence the reduction of absorption fringes between the rough limits 2700 Å and 3800 Å. Although many molecules have band systems within this region, it is obviously desirable to be able to extend potential measurement both into the visible and further down in the quartz ultra-violet.

The long wavelength limit is caused by the falling off of the resolution of the quartz Littrow optics and the consequent inability to resolve adjacent fringes lying one order apart - the condition for the formation of channels. Thus a secondary instrument with greater resolving power is called for, a grating spectrograph with a suitable high quality grating being the obvious solution. As a corollary to the use of higher resolution, the consequent increase in dispersion which could be obtained, would increase the width of the channels, so rendering the measurement of fringes, especially of weak ones, more precise. Pilot work on these lines has recently been carried out by Mr. D.C. Lindsey with very encouraging results.

The limiting factor at the low wavelength end of the range is the inordinate time of exposure required to obtain a suitable dense spectrum. For instance, at 2700 Å, the exposure found necessary was 6 hours; in this time, unless strict temperature control is in force, the temperature can vary sufficiently to cause the channels to blur out and eventually disappear, (1°C would be sufficient to completely blur out the channels). Besides the need for a light source of much higher intensity at these wavelengths, several other modifications could be made to make more efficient use of the available light. At each quartz/air surface in the optical train, about 5% of the incident radiation (much more at each prism face) is lost by reflection, so that a reduction in their number would be beneficial. Two surfaces could be saved by combining the two radiation filters into one, while four could be saved by removing the windows of the Lummer plate housing; this latter procedure might not be so dangerous with the present set-up as it would have been in the earlier, more open one. Also the replacement of the quartz Littrow optics (6 surfaces) by a grating would improve matters in this respect, but the efficiency of blazing would have to be very high to achieve a positive improvement. A further possibility which was tried in the present work is to place a concave mirror behind the lamp thus almost doubling the intensity. No detrimental effects due to the fact that the source is no longer strictly incoherent were detectable from a somewhat superficial examination.

It is now possible, with the apparatus in its present design, to move the light source back to allow a longer absorption cell to be employed. This is necessary if a proper investigation into the weaker formaldehyde bands is to be made. It may even be necessary to employ a multiple pass cell but the optics must be carefully designed to fill the horizontal aperture of the Lummer plate, and also to ensure that the final image (the effective source) is as nearly as possible incoherent; the additional reflection losses in such a system may well be serious, however.

(ii) The most time-consuming part of an investigation of a single band is in the actual measurement of the fringes; the subsequent operations of the analysis are almost entirely governed by the delay in the availability of the computer. The obvious way to lessen the time of measurement is to make it as nearly automatic as possible. At first sight, the best method would be to scan photometrically either the spectrograph camera, the photographic plate, or an enlargement of the latter. The first possibility is ruled out by the very small area available for photometry; a sampling area of about 5 x 15 μ (possibly somewhat greater with the wider channels envisaged above) would be the maximum allowable, and the light available in such a small area would require an extremely sensitive photo-multiplier. The second possibility is ruled out on similar grounds. The third possibility seems to offer some chance of success, although here the size of the grain enlarged from the photographic plate would necessitate a sampling area rather larger than the optimum for accurate estimation of a fringe peak. The most feasible method of speeding up the measurement would be to employ the present visual estimation procedure and to make all the subsequent recording automatic. Thus the measuring carriage would be attached to some digitising equipment to record the movement across a channel. Measurement techniques along these lines (notably for use in engineering) have been developed by several workers, employing a Moiré fringe method of digitising the transverse movement, the counting being done electronically. Application of such a method to fringe measurements would merely require that when a fringe-peak has been centred (visually, as at present, the depressing of a switch would transfer the current reading to a buffer store and thence to punched tape, ready for input to the computer. Although a few difficulties can be foreseen, this technique should result in a time saving of considerably more than 50%; a further advantage would be the virtually complete elimination of the errors that at present may occur by the manual transfer of many thousands (about ½ million in the present work) of digits. It is anticipated that the possibilities of this technique will be examined further.

(iii) The analytical procedure described in chapter 6 has been developed fully, and the only significant further improvement would be to replace the intermediate manual analytical stage, between computation of the spectrum and extraction of constants from the assigned frequencies, by a programmed technique; this is likely, however, to require such involved programming that the effort would not be justified (the manual procedure takes only a few days to complete). A few improvements to the programmes as they stand may be called for; chiefly, this will consist of generalising them to make them applicable to larger asymmetries than those found in formaldehyde, or to rewrite the selection rules for some of them to make them useful for type A and C bands.

(iv) The next absorption band of formaldehyde which should be investigated is obviously the A_1 band, so that a complete picture of the A series of bands is obtained. Approximate rotational constants for the preliminary analysis may readily be obtained by interpolation between those constants known for the remaining three bands. This process gives the following values:

$D' = 1.0569 \text{ cm}^{-1}$

$\alpha' = 7.638$ "

$b' = -0.00714$ "

$D_E' = -4.2 \times 10^{-4} \text{ cm}^{-1}$

$D_{EJ}' = -5.0 \times 10^{-5}$ "

$D_J' = -3.5 \times 10^{-6}$ "

The ground state constants are of course known to very high accuracy while the remaining excited state distortion constants may be neglected in the initial stages. The value for σ_{00} obtained by Dieke and Kistiakowsky (14) of 29,495.12 cm^{-1} will be adequate. We might predict a 'Lide' perturbation in the region of high K', but its magnitude cannot be predicted with any certainty and it may initially be neglected. The A_1 band is at present under investigation by Mr. D.C. Lindsey.

After this band, several others merit attention. The B series should be investigated since Dieke and Kistiakowsky noted the possible occurrence of a 'rotational perturbation' in the levels of the excited state. Also, since the (+) inversion level corresponding to the (-) level of the B bands lies some 400 cm^{-1} away, perturbations of the strict Lide type are likely to be negligible. The C series beginning with C_0 deserves more attention, as already outlined in section 9.5.

Repetition of those investigations on the spectrum of dideuterated formaldehyde will provide sufficient information for a thorough survey of the molecular geometry of formaldehyde in several excited vibronic states.

The other information derived from the rotational analysis, in particular the centrifugal distortion constants and the parameters describing the various perturbations, should provide very useful data for a thorough survey of the internuclear forces of formaldehyde in its first excited state. It should enable force constants for quite an elaborate force field to be determined with the aid of the known vibrational frequencies. Then, if possible, the energies of the unknown vibrations of the first excited state might be determined and the source of some of the perturbations in the observed bands identified.

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ROTATIONAL ANALYSIS OF SOME VIBRONIC BANDS IN THE $^1A' \leftarrow {}^1A_1$ SYSTEM OF FORMALDEHYDE

James Ernest Parkin

Volume 2

Appendices

Contents

Appendix 1

The inversion of a symmetrical matrix (modified Choleski procedure)

We require the inverse B, of a symmetrical matrix A, i.e.

$$B = A^{-1}$$

We first find a new matrix Y such that

$$A = Y^T . Y \qquad (A1)$$

and such that all its elements below the leading diagonal are zero. Then the elements y_{ij} of Y, are given in terms of the elements a_{ij} of A by the following relations:

Case $i = j = 1$

$$y_{11} = \sqrt{a_{11}}$$

Case $i = j \neq 1$

$$y_{ii} = \sqrt{a_{ii} - \sum_{s=1}^{i-1} y_{si}^{2}}$$

Case $i = 1 < j$

$$y_{1j} = \frac{a_{1j}}{y_{11}}$$

Case $i < j \ (i \neq 1)$

$$y_{ij} = \frac{1}{y_{ii}} \left[a_{ij} - \sum_{s=1}^{i-1} y_{si} . y_{sj} \right]$$

If we calculate the elements of Y in the order : y_{11}; y_{12}, y_{13}, ... y_{1n}; y_{22}; y_{23}, ... y_{2n}; ... y_{nn}; it can be seen that for a given y_{ij}, only previously calculated elements are required for its evaluation. Y^T is then known, of course by $y^T_{ji} = y_{ij}$.

We now premultiply both sides of equation A1 by B, whence :

$$B.A = B.Y^T.Y$$

$$= I$$

$$B.Y^T = Y^{-1}$$

It can readily be shown that Y^{-1} has only zero elements below its diagonal, and that its diagonal elements are $y_{ii}^{-1} = 1/y_{ii}$; as will appear below, its remaining elements need not be evaluated.

If we now represent Y^{-1} as Z and Y^T as X, then

$$z_{ij} = \sum_{s=1}^{n} b_{is}.x_{sj} \qquad (A2)$$

We have the relations

$$z_{ii} = 1/y_{ii}$$

$$z_{ij} = 0 \qquad (i > j)$$

$$z_{ij} = ? \qquad (i < j; \text{ not needed})$$

and

$$x_{ij} = y_{ji} \qquad (i \geqslant j)$$

$$x_{ij} = 0 \qquad (i < j)$$

therefore equation A2 becomes

$$z_{ij} = \sum_{s=j}^{n} b_{is}.y_{js} \qquad (A3)$$

whence we have the following cases:

Case $i = j$

$$1/y_{jj} = \sum_{s=j}^{n} b_{js}.y_{js}$$

Case $i > j$

$$0 = \sum_{s=j}^{n} b_{is}\, y_{js}$$

From these we have

Case $i = j = n$

$$b_{nn} = 1/y_{nn}^{2}$$

Case $i = j \neq n$

$$b_{jj} = \frac{1}{y_{jj}}\left[\frac{1}{y_{jj}} - \sum_{s=j+1}^{n} b_{js}\cdot y_{js}\right]$$

Case $i > j$

$$b_{ij} = -\frac{1}{y_{jj}}\left[\sum_{s=j+1}^{n} b_{is}\cdot y_{js}\right]$$

Since B is symmetrical, $b_{ji} = b_{ij}$, so the elements b_{ij} with $i < j$ need not be calculated (it is because of this circumstance that the upper elements of Z are not required).

If we calculate the elements of B in the order : b_{nn}; $b_{n,n-1} \ldots b_{n,1}$; $b_{n-1,n-1} \ldots b_{n-1,1}$; ...; b_{11}, setting $b_{ji} = b_{ij}$ at each stage, it can again be seen (as for Y) that for a given b_{ij}, only previously calculated elements are required (bearing in mind that $b_{ji} = b_{ij}$).

Appendix 2

Computer Programmes*

(a) Standard Programmes

(i) Routine 95 The calculation of asymmetric rotor energies.

Since the calculation of asymmetric rotor energies plays an important part in several of the programmes described later, the procedure has been programmed as a Mercury Autocode Routine; that is, it is a self-contained Routine that can be inserted into a chapter of any programme requiring the calculation. The Routine makes provision either for the calculation of the reduced energy $E(b)$ alone, or for the calculation, as well, of the quantities $E'(b)$ and $E''(b)$. These last two differential quantities are determined by calculating $E(b-\delta b)$, $E(b)$ and $E(b+\delta b)$; the differentials are then given by :

$$E'(b) = \frac{E(b+\delta b) - E(b-\delta b)}{2\delta b}$$

$$E''(b) = \frac{E(b+\delta b) + E(b-\delta b) - 2E(b)}{\delta b^2} \qquad \text{(A4)}$$

---

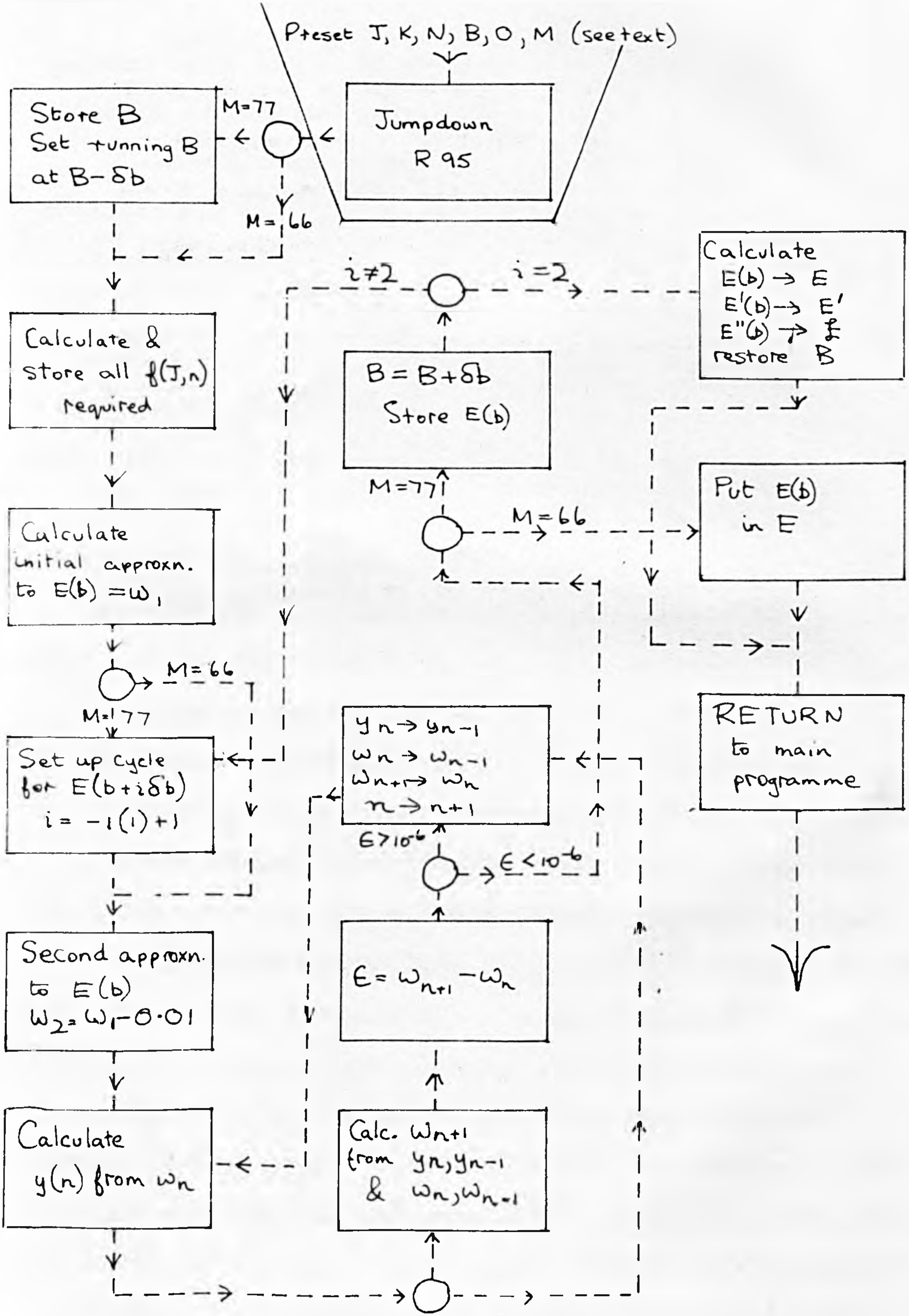
* Since the programmes used have a wide applicability, which in some cases can be further widened by relatively minor modification, the following descriptions contain some reference to organisational details; this is in order to facilitate the use and possible modification of the programmes by subsequent workers. In the block diagrams, the symbols appearing outside the blocks are signals, used for organisation purposes.

For the present work we have set δb at 0.001, after proving that this is sufficiently small for the expressions A4 to hold to the required degree of accuracy. The selection between the two types of calculation is made by presetting a parameter M, (66 for E(b) alone and 77 for the additional differential quantities).

As indicated in chapter 5, section 5.2, the programme requires an initial approximation to E(b) better than K^2 as the first stage in an iteration process, for those levels with $K \leqslant 3$. As stated in section 5.2, these approximations are obtained from an empirical series expansion up to the third power in the argument J, the coefficients of the expansion being calculated for each value of K^+ or K^-. Since the zeroth order coefficient is just K^2, 21 coefficients are required for a given value of b and these are stored in a standardised part of the computer store, ready for use by the Routine (actually 24 coefficients are input, the 4th, 5th and 6th being zeros for the non-existent $K = 0^-$). Since in ultra-violet work for which the Routine is specifically designed, two markedly different values of b are commonly encountered (i.e. for two different vibronic levels), the Routine is designed to allow for two values of b, and if the second value differs sufficiently from the first to make it worth while to use a second set of coefficients, these are also read in. The appropriate set is called into play by specifying another

FIGURE A1: ROUTINE 95

CALCULATION OF ASYMMETRIC ROTOR ENERGIES



parameter, O, (O (zero) for the first set, 1 for the second set). The calculating procedure is exactly that described in section 5.2; the secular determinant is expanded as a recursion formula and its numerical value, y, is obtained as a function f(w) of an approximation, w, to a required root. When two values y_1 and y_2 are obtained from two approximations w_1 and w_2, the second differing from the first by some arbitrary amount (0.01 is employed at present), then a better approximation, w_3, is obtained by the method of 'regula falsi', described in section 5.2.

A block diagram of the routine is shown in fig. A1 opposite. The following parameters must be preset before entering the routine:

J and K for the two quantum numbers J and K.

N for the value of γ ; 0 and 1 for a U and an L level respectively.

O and M are set as signals as explained above.

B is set as the value of b.

The answers are found in the following variable stores:

E(b) in E
E'(b) in E'
E"(b) in £

The main indices are left unchanged by the routine while the primed indices are destroyed. The special variables apart from E, E' and £ are not used.

It has been found that on the average, about 10 E(b)'s can be computed every second.

(ii) Programme - 102. The solution of normal equations.

This programme and its modifications have been programmed by Dr. Poole. Besides solving the normal equations to obtain the solutions, x_i, they also calculate the standard error, σ_i, of each solution x_i, and the correlation coefficients, r_{ij}, between every pair of solutions x_i and x_j.

If we express the normal equations in the form:

$$A \bar{x} = \bar{d}$$

(see section 6.3 p. 172 et seq.) then the solutions $\bar{x}$ are given by

$$\bar{x} = A^{-1} \bar{d}$$

We therefore calculate the inverse matrix $B = A^{-1}$ by the procedure outlined in Appendix 1. This matrix is then post-multiplied by the vector $\bar{d}$ of the right hand sides of the normal equations to deliver the solutions $\bar{x}$. The inversion procedure as formulated in Appendix 1 is particularly amenable to automatic computation, especially when the A matrix is of order 5 or 6 or more. Since, however, it entails much arithmetic involving destructive cancellations, many more decimal digits must be retained throughout than are needed in the final result, to ensure accuracy. As mentioned elsewhere, we employ double length arithmetic in the computation by Mercury; that is, 17 decimal digits are used for all operations. Nevertheless, for matrices of low order, say up to n = 5 or 6, the much faster single length arithmetic (to 8 or 9 digits) suffices; our Programme - 100 is for this case. In the present work, however, such matrices have rarely been met and we have employed exclusively the double-length technique. When computed, the vector $\bar{x}$ is printed out to 9 significant figures.

If at the same time that we compute the normal equations we also determine the sum of the squares of the right hand sides of the m equations of condition, then we can use it with the n solutions (when found) to obtain the sum of the residuals, $\sum\epsilon^2$; then the variance, σ^2, of the input data is given by:

$$\sigma^2 = \left(\sum\epsilon^2 - \bar{x} \, . \, \bar{a}\right)/(m-n)$$

(this is a normal statistical procedure). This quantity gives a measure of the precision of the input data, as fitted by the least-squares solutions found. The variance and covariance matrix is then given by $\sigma^2 \, . \, B$; its elements are

$$\sigma_i^{\,2} = \sigma^2 b_{ii}$$

and $r_{ij}\,\sigma_i\,\sigma_j = \sigma^2 b_{ij} = \sigma^2 b_{ji}$

whence the standard errors, σ_i, of the solutions x_i

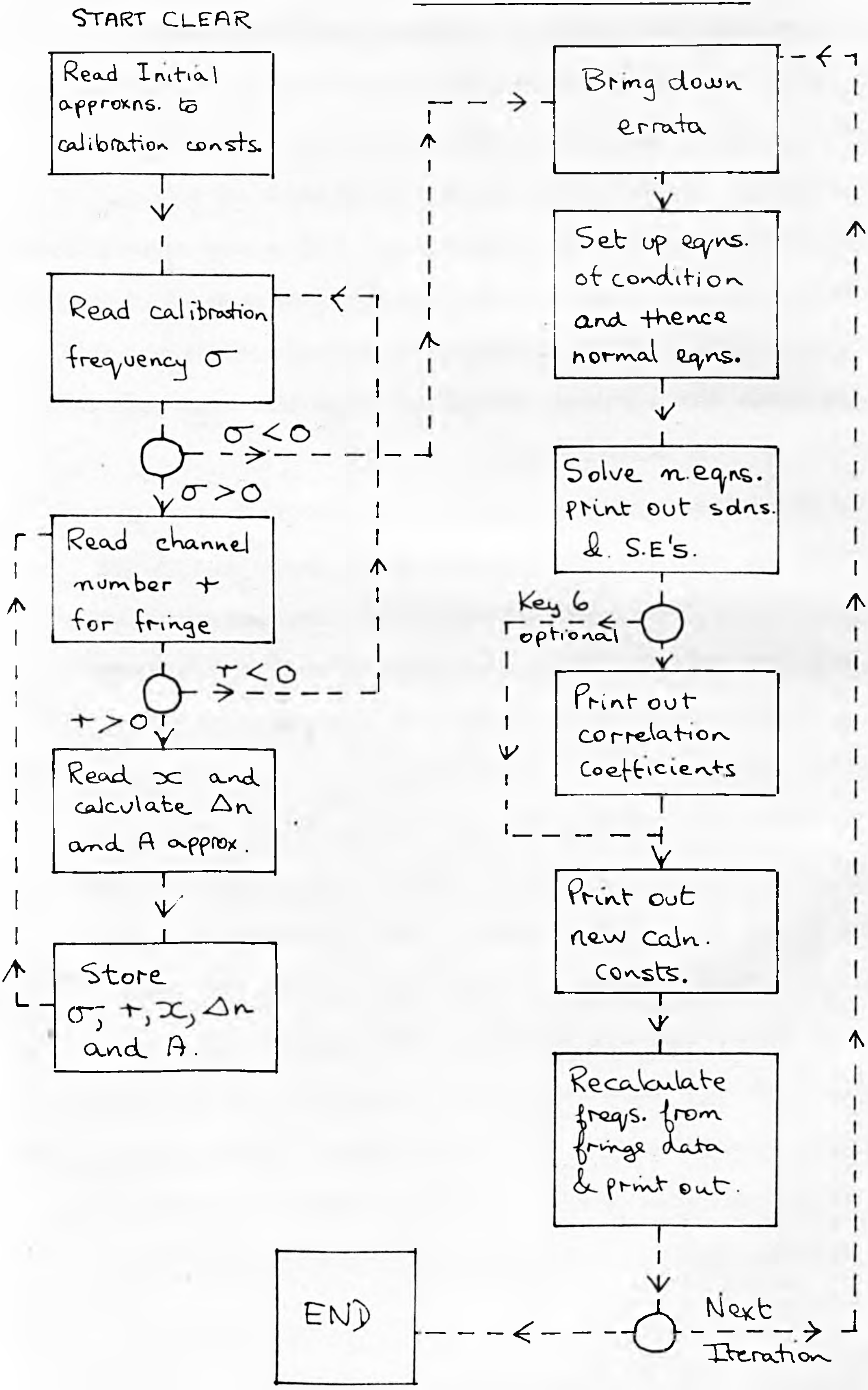
are known, and the correlation coefficients matrix (r_{ij}) is set up. The σ_i are printed out, this time to 3 significant figures, as are the r_{ij} when called for (manually by way of computer keys). As an index to the precision of the inversion procedure, the two matrices A and B are multiplied, and the resulting matrix, (which should of course approximate to the unit matrix of the appropriate order) is scanned and the element with the largest deviation from the unit matrix is printed out for inspection.

Recently, the full programme was condensed into a single chapter, and the final inspection stage (of AB) described was omitted since tests showed that with the matrices being employed in the present work, rounding errors reduced the precision of the solution by only 2 or 3 powers of ten below the full 17 digits of the computation.

As written at present, the programme makes provision for a normal equations matrix of order $\leqslant 31$, which is more than enough for the present work. The programme has been employed with great success in those programmes described later where least squares solutions are called for. We have found that the time required to complete an inversion is roughly proportional to the third power of the order of the matrix; as an example, a 25 x 25 matrix can be inverted in about 6 minutes while a 7 x 7 matrix requires only about 20 - 30 seconds.

FIGURE A2 HR 950

LUMMER PLATE POLYNOMIAL



(b) Programmes connected with frequency determination.

(i) HR9.50 Lummer plate polynomial.

The conversion of the fringe co-ordinates r, x to frequency values σ involves a function of 2 polynomials, here conventionally called the Lummer plate polynomial; its nine coefficients are the calibration coefficients. This programme is used for determining the best set of 9 coefficients, by a least squares procedure, from an initial approximate set, using the fringe measurements of a number of standard frequencies (the calibration frequencies) spread over the range to be calibrated (See section 3.4). A block diagram is given in table A 2.

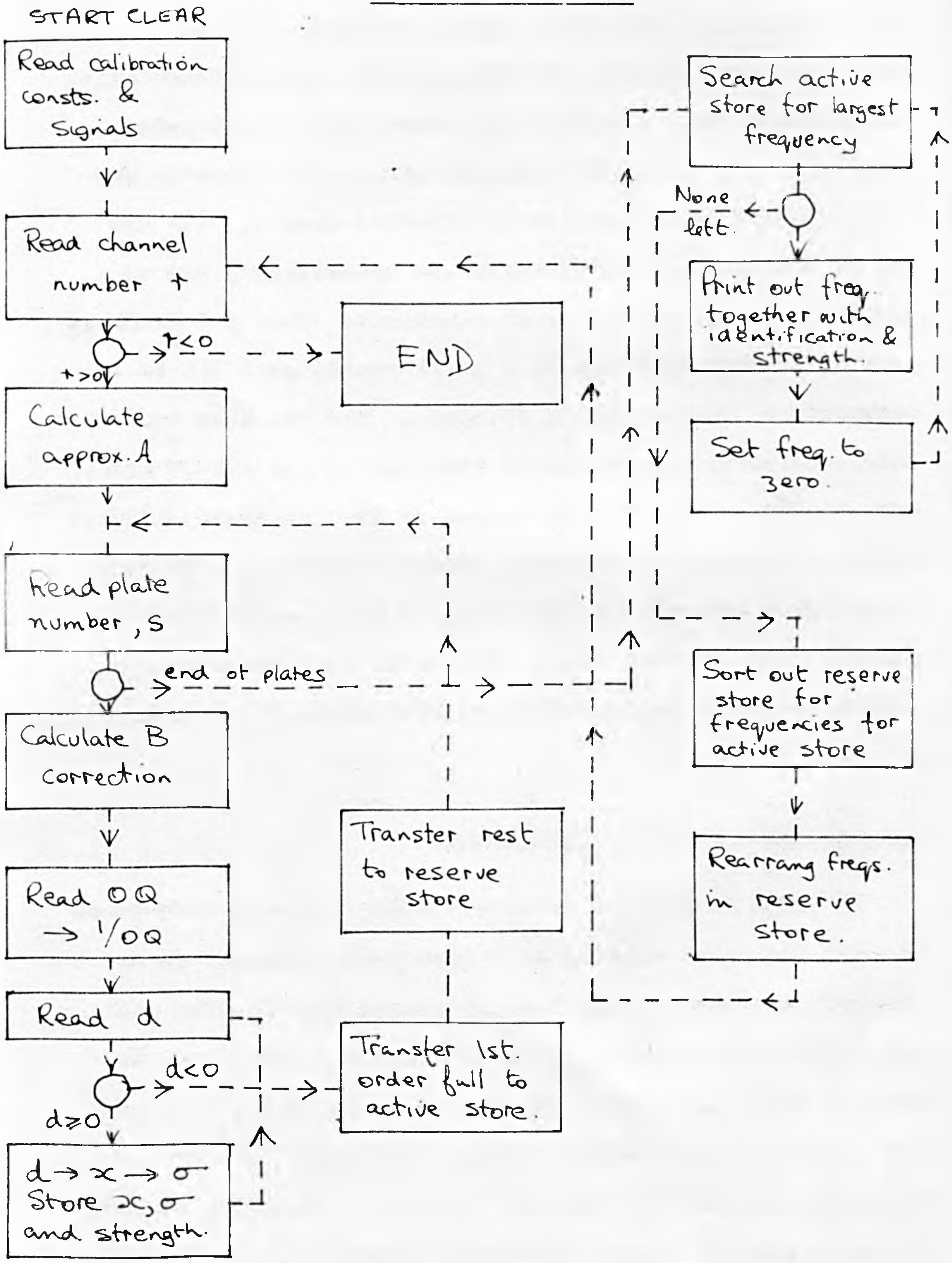
For every measured fringe of every calibration frequency, the channel number t, and the x value are read in and stored, together with the standard value of the frequency, σ, and first approximate values for n and A calculated fringe by fringe from the current set of approximations to the coefficients. After the list is complete, each set of σ, t, x, Δ n and A in turn is brought to the fast store of the computer, the corresponding equation of condition is set up, and its contribution to the normal equations computed; on completion of the list, the normal equations matrix is complete. (Since A and Δ n are not independent of one anther (see section 3.4) they are determined in a short iterative cycle, i.e. an initial value for Δ n allows an approximation to A to be found, and this in turn gives a better value for Δ n.) The normal equations are solved using the least squares procedure of Programme - 102 (app. 2(a) (ii).). Correlation coefficients are calculated and output from the computer along with the solutions (corrections to the input values of the coefficients) and their standard errors. The new set of calibration coefficients are constituted, and used to obtain a new set of normal equations. This procedure is continued iteratively until a sufficiently good fit to the calibration frequencies is obtained. The standard and recalculated values for these frequencies are output after each iteration so that the course of the solution procedure may be followed. In practice, three iterations have been found ample even when a crude set of input calibration coefficients has been used. The total time for a single calibration run, employing three iterations, is a little over 10 minutes.

(ii) LR 1.4 Ordered Frequencies.

A given absorption frequency occurs four or five times between the O- and Q-lines in neighbouring channels on an absorption print. Since several prints are measured each for a different pressure of absorbing gas, some 10 to 20 fringes are usually measured for each frequency. Fringes are measured consecutively along a channel and any one frequency occurs only once in a channel; hence the measurements of fringes of any particular frequency, occurring in consecutive channels, are found in the record book, separated

FIGURE A3, HR 1.4.

ORDERED FREQUENCIES



by those fringes of other frequencies. The function of programme HR 1.4 is both to calculate the frequencies themselves from the fringe measurements, and to sort the calculated frequencies into numerical order so that all the estimates of a given frequency are placed in juxtaposition, ready for inspection and averaging by a subsequent programme. It has been written in the 'Pig-F' machine language of the Mercury computer, since this technique is more amenable to the complex sorting process involved in the procedure than is the simpler Autocode language. A block diagram is given in table A3.

The data tape is prepared in such a way as to facilitate the sorting process; thus data is read in for consecutive channels starting with the channel with the highest number (highest frequency); for a given channel, all the measured fringes from every used plate are input in turn, and their frequencies are computed from the calibration and appropriate 'b-correction' coefficients. Some 70% to 80% of these frequencies are transferred to a reserve store to await the data of successive channels. The fringes lying at less than one order difference from the 0-line are transferred to an active store with the measurements of the same frequencies from previously input channels. The latter are also sorted out into orders and to facilitate this sorting procedure; for this, four input constants are read in at the head of the data tape, these being the x values corresponding to order differences of 1, 2, 3 and 4 from the 0-line. The frequencies are stored in parts of both the reserve and active stores, determined uniquely by the plate number from which they came and by their channel number (or rather by the difference of their channel number from the currently input one); the importance of this provision will emerge later. Besides the frequency, the x value is also stored in a uniquely determined part of the computer store.

As each fringe measurement is read, its estimated strength and character are also read in and stored. The strength on the visually estimated scale is represented by a digit in the range from 0 to 9. Inaddition, provision is also made for a single character describing the character of the fringe; absence of such a character on the tape indicates a 'good' fringe, well separated from near-neighbours. The following teleprinter "characters" are used to indicate deviations from these properties.

) the fringe is merged with, yet resolved from a neighbouring fringe, usually about 0.1 cm^{-1} away; two such fringes will therefore occur as a pair.

(that the fringe is probably double, yet the two members are unresolved; resolution of these fringes is often obtained on prints with weaker absorption.

n the fringe is very weak and might possibly be spurious.

x the fringe measurement is interfered with either by photographic disturbance (dust marks etc.) or by a strong fringe in a neighbouring channel; such a fringe is not used in the later averaging procedure unless it is the only recorded observation of a particular frequency.

Output

When the current channel-ful of data (from all plates) has been read in and the frequencies computed and stored, the active store is scanned and the location of the highest frequency noted. From its location, the plate number and channel number are reconstituted and printed out, together with the x value. These three quantities enable a given frequency estimation to be traced back to the original print and fringe, should any question about its verity arise. The frequency is then printed out to four decimals, followed by the strength and character.

Each frequency in the store, after it has been so used, is set to a negative value so that it cannot be used again by the sorting procedure. The active store is then scanned again for the highest frequency and so on until the store is exhausted. The reserve stores are then sorted and those frequencies which will match with the next input channel are transferred to the active store, the rest being replaced in reserve.

The limitations imposed on the programme by reason of the limited storage of the computer are that fringes from only four plates are allowed, and that a maximum of six fringes are allowed in any one order of a single channel; these limitations do not seriously limit the applicability of the programme.

We have found that about 5,000 fringes can be processed in about 30 minutes.

(iii) HR 1.6 Mean frequencies and standard errors.

This programme is designed to read frequencies from the output tapes of HR 1.4, in prescribed groups (each group containing all of the estimates of one frequency), but with rejection of prescribed individuals, and then to find the mean and standard error for each group. The prescription is by way of a second tape, a steering tape, set up as the result of examination of the output list from HR 1.4, and read concurrently with the frequency tape. For each group, and therefore for each final mean frequency, the steering tape also contains the estimated strength, compounded from all the individual estimates, together with the "character" of the frequency. The conventions used for the character differ somewhat from those of the previous programme, they are as follows:

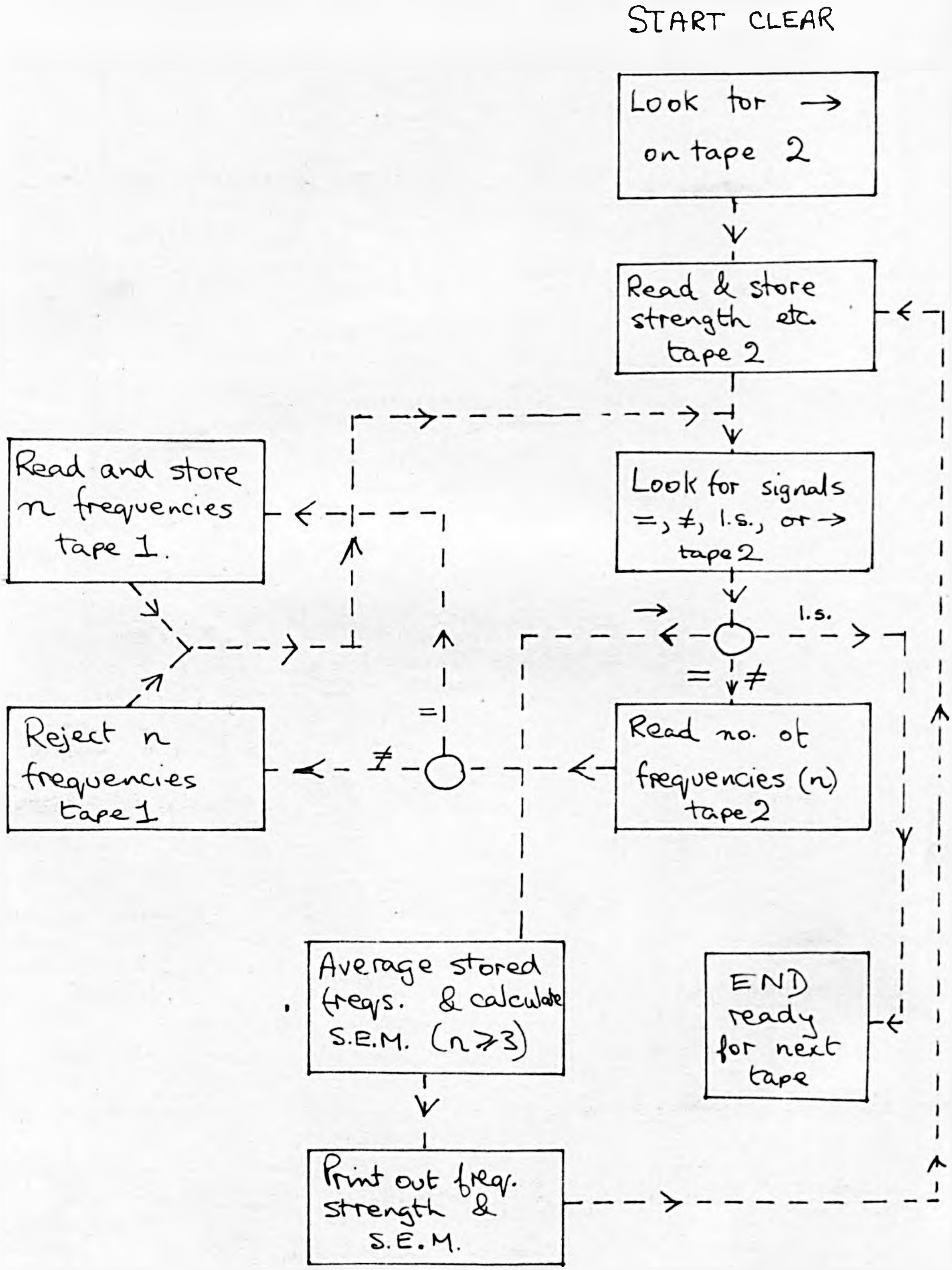
)	the frequency has a just-resolved near neighbour; where resolution is only just attained, the apparent frequencies of the lines will be shifted closer together and therefore such frequencies should be used with caution in the analysis of the band.
))	the frequency is probably the mean of overlying fringes; it should therefore have a multiple assignment in the analysis.
n	the frequency may be spurious
*	the frequency value is uncertain; therefore in the analysis, it must not be used for the determination of constants.

Once all the frequencies of a group have been read into the computer, the set is averaged and the standard error of the mean calculated. The mean frequency and intensity are then output from the computer, followed by the standard error. If the group contains less than three estimates, the standard error cannot be calculated, and so instead the letters F or FF are output, signifying one or two estimates respectively.

Because of the large numbers of frequencies which have to be read in and then averaged in groups, and because the information on the steering tape must be exactly in step with the groups of frequencies, the steering tape sometimes contains an error which causes the groups to get out of step.

FIGURE A4. HR 1.6.

MEAN FREQUENCIES AND STANDARD ERRORS



In order to minimise the effects of such an error, a check has been programmed to make use of a run-out (a length of blank tape) always inserted for this purpose between blocks of 50-100 frequencies on the main tape; whenever one or more frequencies before one of these run-outs is to be rejected from the averaging process, the computer is caused to ignore all characters on the frequency tape until it meets three consecutive blank characters, this can only occur at a length of run-out. In most of these cases (themselves infrequent) the two tapes are thus brought back into step ready for the next group of frequencies; the incorrectly handled groups then stand out on the final tape since when odd frequencies, not belonging to a group, are used in that group, the standard error becomes impossibly large. Since there are usually only a few of these frequencies, the errors are corrected manually.

The programme is very fast; about 10,000 frequencies can be processed in about 15 minutes. A block diagram is given in table A 4.

(iv.) Further programmes.

Programme HR1.3A has been written to calculate δq's from the calibration constants and the measurements of the fringes. These δq's are used in order to obtain the b-correction polynomial appropriate for an individual plate (see section 3.5).

FIGURE A5. HR4.35

U.V. SPECTRUM AND ASSIGNMENTS

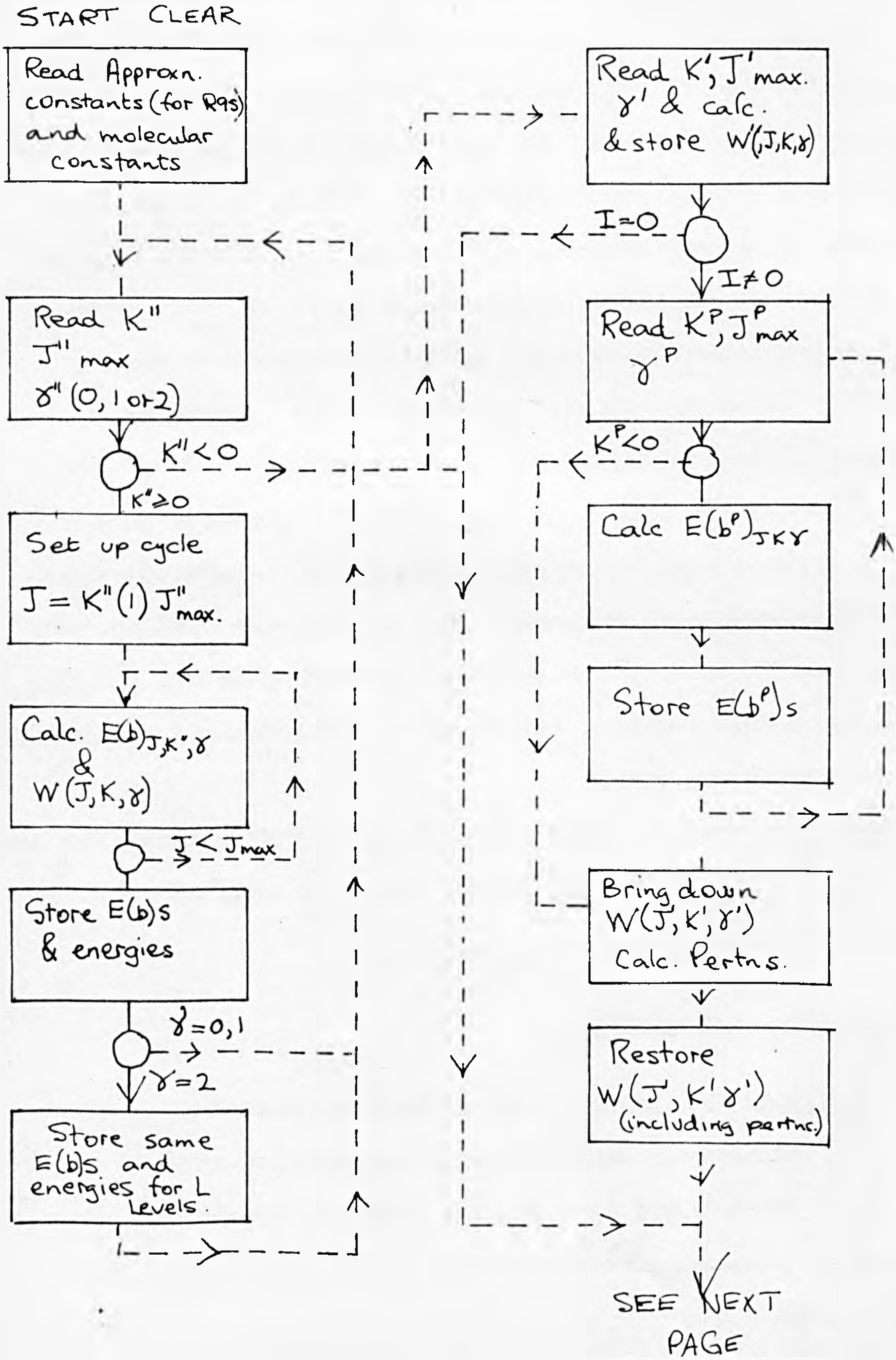


FIGURE A5 CONTINUED

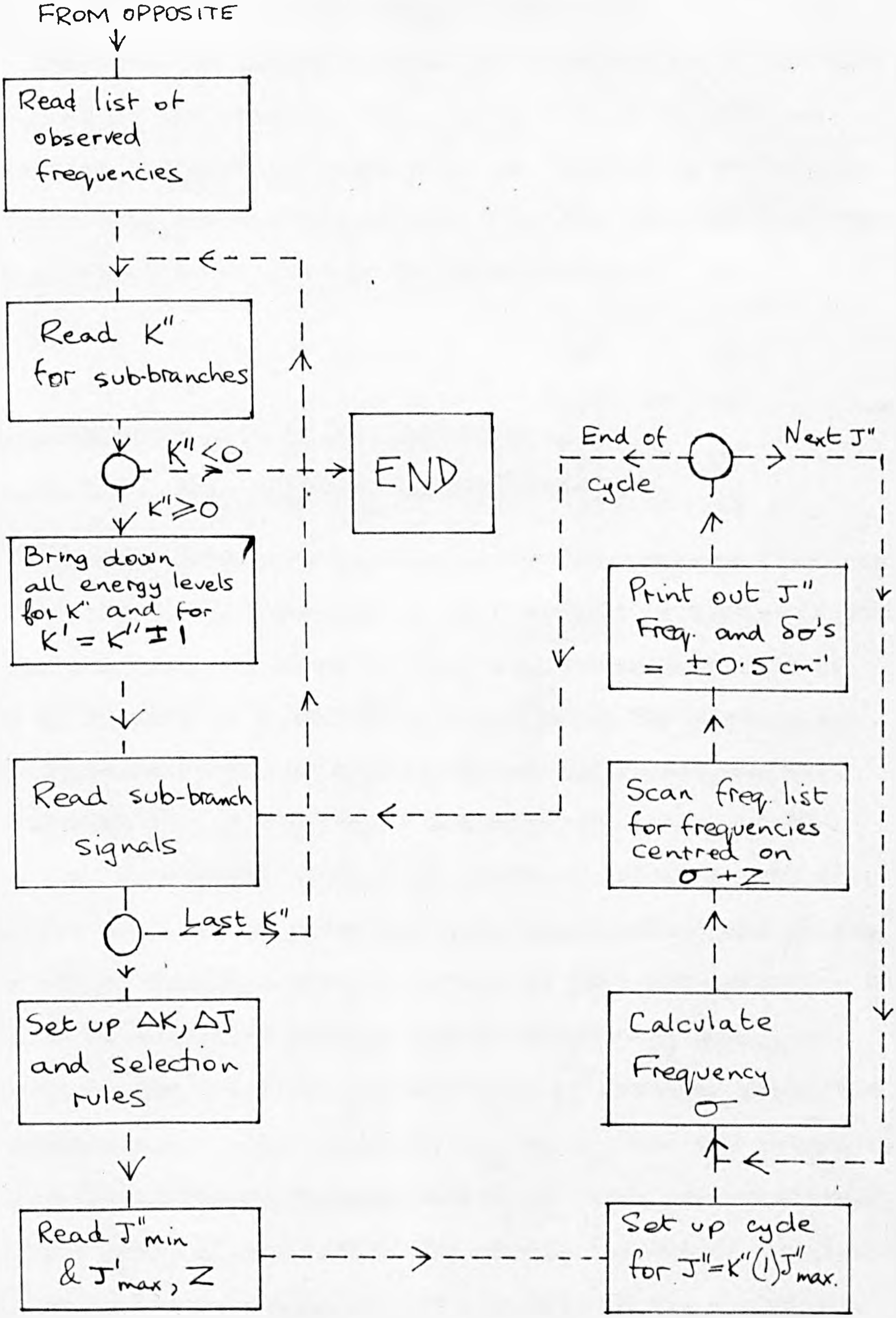


Table of constants for HR 4.25

(and HR 8.55)

$c_0 = D''$

$c_1 = \alpha''$

$c_2 = b''$

$c_9 = D'$

$c_{10} = \alpha'$

$c_{11} = b'$

$c_3 = D_E''$

$c_4 = D_{EJ}''$

$c_5 = D_J''$

$c_6 = D_4''$

$c_7 = D_5''$

$c_8 = D_6''$

$c_{12} = D_E'$

$c_{13} = D_{EJ}'$

$c_{14} = D_J'$

$c_{15} = D_4'$

$c_{16} = D_5'$

$c_{17} = D_6'$

$c_{18} = \overline{\sigma}_{oo}$

$c_{19} = I_1$

$c_{20} = d_1$

$c_{21} = e_1$

$c_{22} = I_2$

$c_{23} = d_2$

$c_{24} = e_2$

$c_{25} = D^p{}_1$

$c_{26} = \alpha^p{}_1$

$c_{27} = b^p{}_1$

$c_{28} = D^p{}_2$

$c_{29} = \alpha^p{}_2$

$c_{30} = b^p{}_2$

c_{31} = identification number

Programme HR 1.7 calculates the frequencies at the base (0-lines) of the channels for a given set of calibration constants; the results facilitate the tracing on the prints of fringes or frequencies missing from the analysis and therefore possibly overlooked in the measurement.

(c) Programmes used in the analysis.

(i) HR 4.35 U.V. Spectrum and Assignments.

The main points in connection with the spectrum programme have already been discussed in section 6.2. A block diagram of the programme is shown in fig. A 5 pp303-304. The data tape is made up firstly of a sub-title identifying the particular run, followed by the 48 approximation constants (for the calculation of the E (b)'s, - see page 286) and by 32 molecular constants. These latter are given in detail in the table opposite since their order has been standardised and is the same (apart from the last constant) as that for programme HR 8.55 to be described later. The constants C_{19} to C_{24} are parameters for two Lide perturbations of the type described in section 5.4. The constants c_{25} to c_{30} are the rotational constants for the perturbing levels of these perturbations. The last constant identifies the particular set of rotational constants; in our convention, it consists of the wavelength of the band under consideration plus a running number corresponding to the successive refinements of the constants.

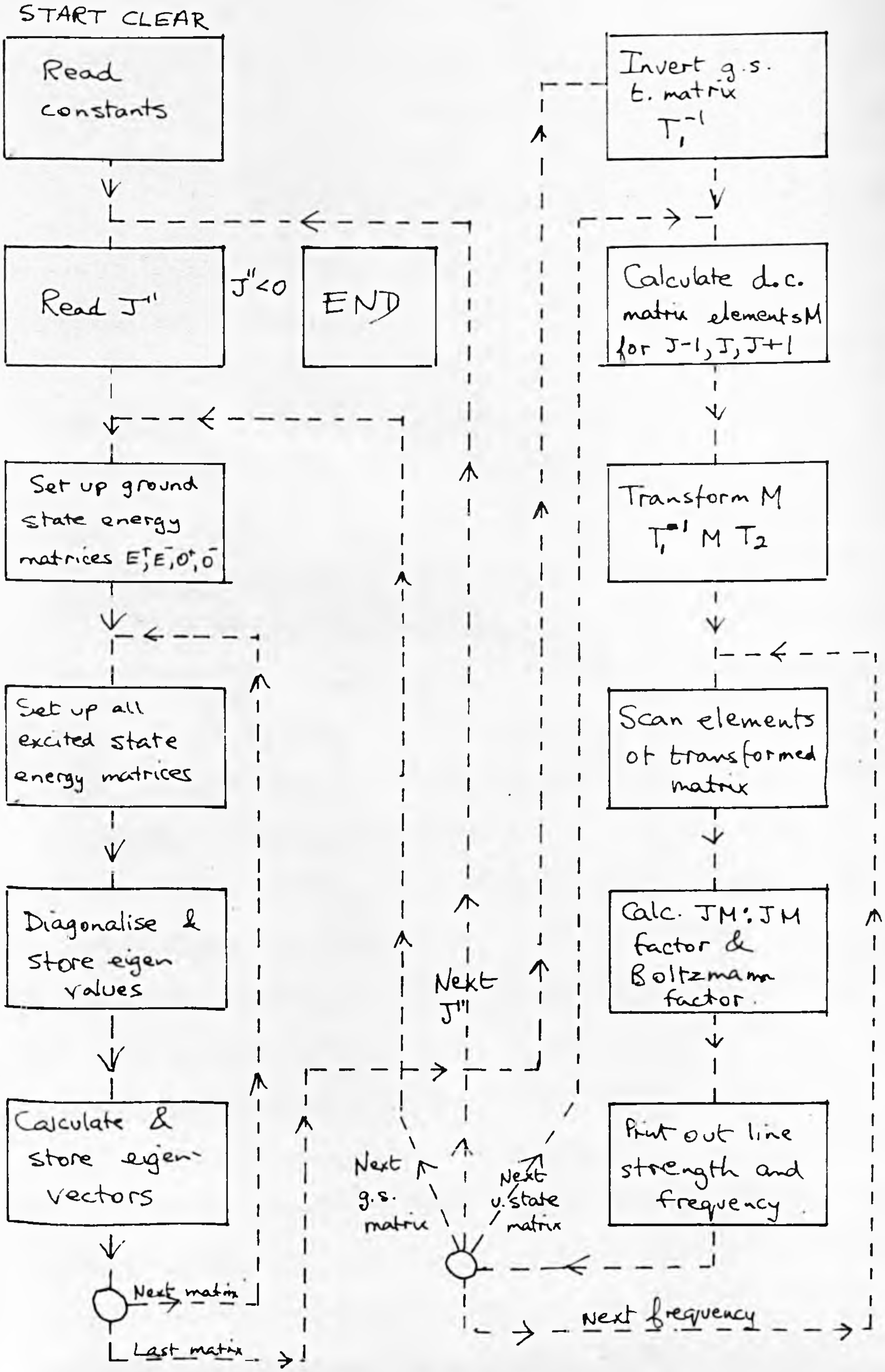
Next on the data tape come the specifications for all the energy levels involved in the spectrum, beginning with the ground state levels, followed by the excited state levels and finally the perturbing state levels (if any). The energies are computed and stored as each specification is read in.

The computer then reads in the list of observed frequencies and strengths, (the output tape of HR. 1.6) ignoring the rest of the material on each line of input. Finally, the sub-branches required are specified. As each frequency is calculated, the computer scans the frequency list for frequencies lying within a small prescribed range (e.g. ± 0.5 cm^{-1}) about the calculated frequency plus some input parameter Z, (this latter provision allows one to make some allowance for any expected drifts between the calculated frequencies and the correctly assigned frequencies, e.g. in the earlier stages of analysis, arising from inaccurate constants); and points out the deviations. The form of the output is that shown in table 6.1 p166. About 30 minutes computing time is required to produce the frequencies and deviations for a single band.

A modification of this programme, HR4.30, calculates only the expected frequencies of the band; in all respects but those connected with the assignment procedure above, it is identical with HR 4.35.

FIGURE A6. HR 5.15

LINE STRENGTHS AND FREQUENCIES



The assignments are completed manually, by inspection and plotting, when necessary, of the deviations throughout each sub-branch, in the manner described in detail in chapter 6.

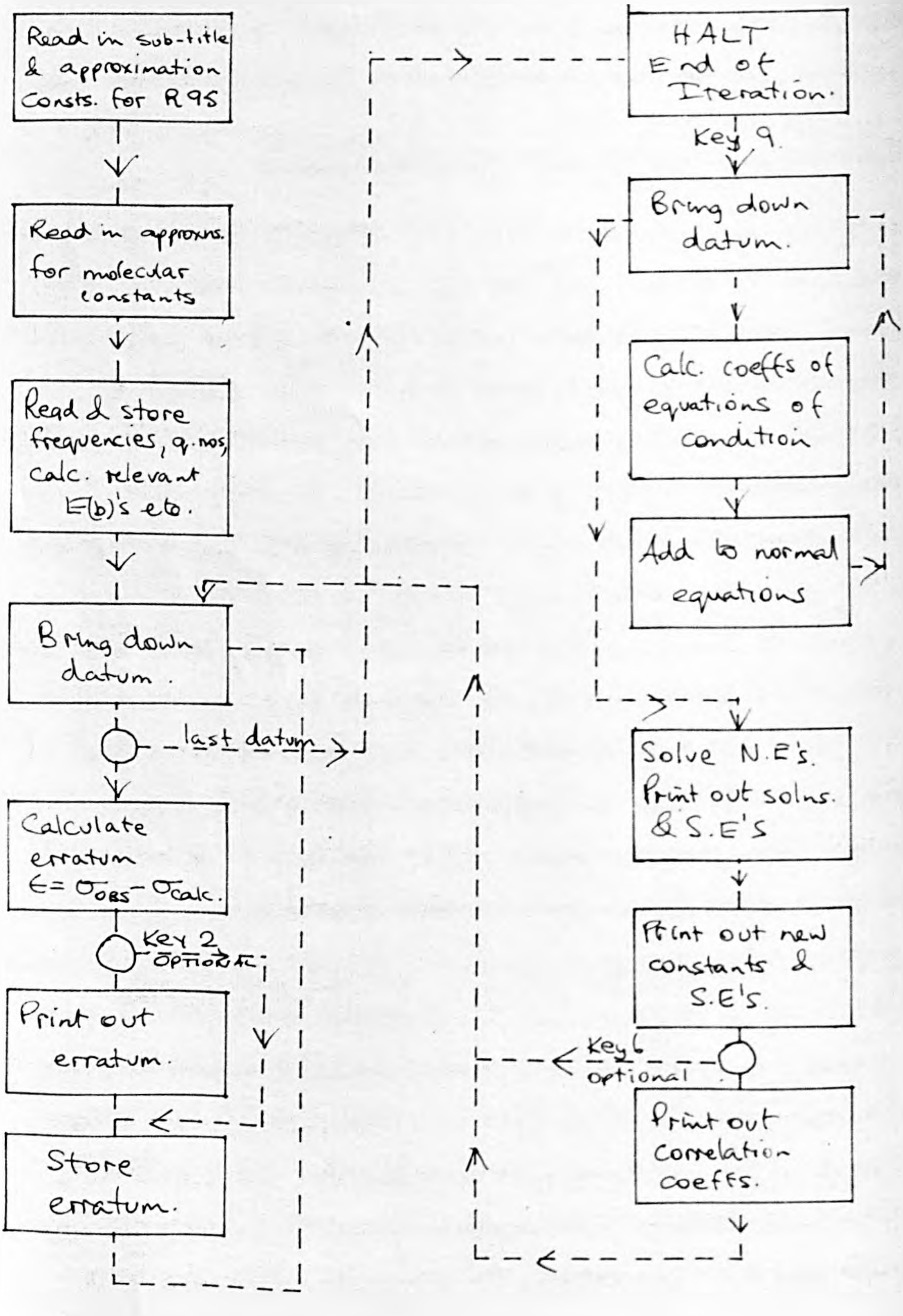
(ii) HR 5.15 Line strengths and frequencies.

This programme allows the line strengths and frequencies of any allowed transitions for the asymmetric rotor to be computed. Provision is made for either a, b or c axis transition moments; transitions involving J,K $\leqslant$ 40,40 may be calculated, this limit being set by the fast storage capacity of the present computer. A block diagram is given in fig. A6.

In calculating the energy levels for the frequencies and also for the Boltzmann factor, the rigid rotor approximation has been used it being sufficient for the purposes of the present prog. (see p. 149); the two sets of molecular constants are therefore first read in. At the same time the maximum values of ΔK and K" respectively that are needed in the output are specified, so that unnecessary output is not obtained. The required values of J" are then read in one at a time. For each J" the computer sets up the appropriate asymmetric rotor energy matrices for all the possible transitions involving the current J", and successively diagonalises them and stores the eigenvalues; the diagonalisation procedure is that described by Bennett, Ross and Wells (74). From these eigenvalues, the eigenvectors which together make up the transformation matrix are computed using the energy matrix elements and the eigenvalues, by the method described by

FIGURE A7. HR8.55

MOLECULAR CONSTANTS FROM U.V. FREQUENCIES



Gora (75), and the vectors are collected together making up the transformation matrices (which diagonalise the original energy matrices). Once all this material has been computed and stored, the J,K elements of the symmetric rotor, direction cosine matrices are set up as described in section 5.5, and transformed to the asymmetric rotor representation by means of the transformation matrices already computed. This transformed matrix is then scanned and the appropriate elements picked out and multiplied by the remaining factors of the direction cosines and by the Boltzmann facto. The resulting line strengths are then printed out together with the associated line specifications and frequencies in blocks, each block having a common value of ΔK, ΔJ and J''.

As an example of the speed of the programme when used with the Mercury computer, for b axis transitions with $\Delta K = \pm 1$ and $J'' = 40$, all the transitions are calculated and output in a little over 20 minutes. This involves 16 matrix diagonalisations 4 inversions and 12 matrix multiplications, each operation being performed on matrices of order 20 or so.

(iii) HR 8.55 Molecular constants from UV frequencies.

This programme has been described in detail in section 6. of this thesis. A block diagram is given opposite, in fig. A7.

At the head of the data tape there are the approximation constants for the E(b) determination (see p.286) and the input approximations to the molecular constants; these are in the order shown on p.305 as for the spectrum programme, except that c_{31} is omitted. The frequency data are presented in blocks, each block containing all the chosen frequencies of a single sub-branch. For this pupose, those sub-branches that are degenerate at low J", but are split at higher J" by the asymmetry are considered as three distinct sub-branches; the degenerate lines are treated as the means of the two individual transitions; the coefficients of their equations of condition are also calculated as means. As each frequency is read, various signals and parameters which uniquely identify it are set up, then, for the levels entering into the frequency, all of the required E(b), E'(b) and E"(b) are computed; the whole of this information relating to the frequency is then stored as a block (a "datum") for future use. The form of a datum is given in the table overleaf.

When all the data have been read in, the next chapter of the programme brings down each datum in turn and calculates the frequency of the line from the current approximations to the molecular constants. This quantity is subtracted from the observed frequency to give the "erratum" for the next least squares solution. Provision is made to print out each erratum as it is calculated, since the completed array of errata provides an indication of the goodness of the fit obtained to the observed frequencies, for the current set of molecular constants; since this item of output is not usually required until the final iteration, it may be bypassed by setting one of

Datum for HR 8,55*

y_0 = U/L/D, $\triangle K$, K'', $\triangle J$

y_1 = J'', γ'', γ', spare

y_2 = observed frequency

y_3 = erratum ($\sigma_{obs} - \sigma_{calc}$)

	1st transition	2nd transition (for a D freq. only)	
$E(b)''$ =	y_4	y_{10}	
$E'(b)''$ =	y_5	y_{11}	
$E''(b)''$ =	y_6	y_{12}	
$E(b)'$ =	y_7	y_{13}	
$E'(b)'$ =	y_8	y_{14}	
$E''(b)'$ =	y_9	y_{15}	
$E(b^p)_{K-1}$ =	y_{16}	y_{18}	Pertn 1
$E(b^p)_{K+1}$ =	y_{17}	y_{19}	
$E(b^p)_{K-1}$ =	y_{20}	y_{22}	Pertn. 2
$E(b^p)_{K+1}$ =	y_{21}	y_{23}	

*It will be recalled that the designations U, L, D specify transitions originating on a +, −, and degenerate level respectively.

....

the keys on the console of the computer. When all the errata have been computed, the comuter halts, since this stage represents the end of an iteration. The operator then decides whether or not to continue with the iterative procedure. If so, the next chapter again brings down the data in turn; the coefficients of the equations of condition (see table 6.2, p.177) are calculated for each datum, and the normal equations are set up in the usual way. When this stage has been completed, Programme-102 (p.289) is called in to solve the normal equations, and the solutions and standard errors are output from the computer; these solutions give the improved values of the molecular constants of the ground state and of the excited state.

The correlation coefficients may be output or ignored as required (usually only one set is needed in a run) by setting another of the console keys.

The improved values of the molecular constants are now substituted for the previously used values, the errata are replaced by newly calculated values, ready for the next iteration of the above procedure (or for final print-out). As many iterations as desired may be carried out; in practice, three are found to suffice.

In operation, the various stages require about the following times:

Input of 350 frequencies and calculation of E(b)s etc.	12 mins.
Calculation and print-out of errata, per iteration	5 mins.
Setting up and solution of normal equations per iteration (order 25)	12 mins.

(iv) HR 8.45 Molecular constants from microwave data.

This programme follows the same general course as the previous one, the differences being:

1) The experimental data are input by specifying each individual combining level together with the frequency; this obviates the need for selection rules.

2) There is only set of molecular constants to be solved for since the combining levels are in the same vibronic state. Programme HR 8.45 is written with the centrifugal distortion in terms of the four τ's for a planar molecule. A modification HR 8.45A, is written in terms of the six D's while a further modification HR 8.46, uses Kivelson and Wilson's six A's.

3) The use of the τ formula means that for the calculation of the energy of and the coefficients for the centrifugal distortion, the two matrices, the H-matrix and the U-matrix (see section 5.3) must be calculated and stored.

(v) HR 8.60 Molecular constants from UV combination differences.

This programme is essentially the same as the programme HR 8.45 for microwave frequencies; the only difference is that now, provision is made for degenerate frequencies as described earlier in connection with programme HR 8.55. Modifications HR 8.65 and HR 8.70 differ from HR 8.60 only in that for them, the centrifugal distortion is treated in terms of the six D's and the six A's respectively; they are therefore similarly essentially the same as the microwave programmes HR 8.45A and HR 8.46.

(vi) Further programmes

A programme, HR 10.0, calculates perturbations of the Lide type; this has been found useful in the investigation of the forms of these perturbations.

Programme HR 11.0 computes energy levels from input rotational constants and may be used for obtaining predicted combination differences; those observed in the course of analysis of a band may then be checked for arithmetical errors.

A further programme, HR 2.3, calculates and tabulates the reduced energies $E(b)$ and the derivatives $E'(b)$ for the asymmetric rotor; the tables obtained are found to be very useful in the early stages of an analysis.

Appendix 3.

Lists of Frequencies and Assignments

Table A1

A_2 Band, part 1* (ref. section 7.3)

Key.

Along each line, the following quantities appear, in the order given.

Mean frequency, in cm^{-1}

Estimated strength, scale 1 to 9

Standard error of the mean frequency

A = 0.000 - 0.002 cm^{-1}

B = 0.002 - 0.004 cm^{-1}

C = 0.004 - 0.006 cm^{-1}

D = 0.006 - 0.008 cm^{-1}

E = 0.008 - 0.010 cm^{-1}

F = more than 0.010 or less than 4 estimates

Assignments - see p. 156 for explanation of the notation

* Note: these frequencies are due to Kaynes (6) and the assignments to Dr. Poole (see section 7.3).

30,000 +

```
456.955.1F  PQ30,3U
456.373.1F  PQ26,5U
455.605.1F
455.057.1F
454.615.1F
454.401.1F  PP24,3U
453.992.1F
453.604.2F  PQ21,7?
453.460.1F  PP21,5

   EITHER
453.282.1F)
453.194.1F)
    OR
453.238.1F) PQ13,9?

452.518.2C
        )→  PP16,7
452.442.1F  PQ24,6
450.766.1F  PQ18,8?

450.697.1F  PP13,8  PP9,9?
450.292.2C  PP19,6
448.485.1F  PQ14,9?
448.395.1F
447.232.1F
446.263.1F

  EITHER
446.164.1F)
446.100.1F)
   OR
446.139.1F)  PQ22,7?  RP30,1U

  EITHER
444.892.1F)
444.805.1F)
   OR
444.819.1F) PP10,9?

444.619.1B  PP17,7
443.877.1B  PQ25,6  PP14,8  PP22,5
443.308.1F  PQ15,9?

442.825.1F
442.628.1F
442.497.1F
441.726.1F
441.445.1F  PP20,6
440.618.1F
438.969.1F  PP11,9?
436.592.1F
436.454.1F  PP18,7
433.950.1F  PP23,5
```

479.940.1C	PP28,1L	
479.673.1F	PP8,8	
479.563.1F	PP23,3L	
478.513.1F	PQ28,3U	
477.427.1F	PP22,3U	
475.985.1F	PQ21,6	
474.868.1F	PP16,6	
474.544.1F	PP9,8	
473.992.3C	PP13,7	PQ18,7
473.797.1F	PQ24,5	
473.100.1F	PQ14,8?	
471.595.3B	PP19,5	PQ29,1U
470.944.1F	PQ28,3L	
470.650.1F		
470.208.2F	PP24,3L	
469.729.1F	RP28,1U	
469.653.1F		
469.550.1F	PP29,1L	
469.088.2A	PP10,8	
468.804.1F		
468.494.1F	PQ22,6	
467.987.1F	PQ29,3U	PQ15,8?
467.601.1F	PQ19,7	
467.398.1F		
467.221.1F		
467.165.3B	PP14,7	
466.993.1F	PP17,6	
466.196.1F	PP23,3U	
465.447.1F		
465.217.1F	PQ25,5	
464.934.1F		
464.397.1F		
463.816.1F		
463.308.2F	PP11,8	
463.187.1F		
462.687.2B	PP20,5	
462.232.1F		
461.844.1F	PQ11,9?	
460.902.2F		
460.737.1F	PQ20,7?	
460.638.1F	PQ23,6	
460.003.3D	PP15,7	
459.922.1F		
458.850.2F	PP18,6	PP30,1L
458.045.1F	RP29,1U	
457.736.1F	PQ12,9?	
457.153.1F	PP12,8	

505.510.2F	PQ12,7		
504.501.2C	PQ20,5		
503.729.1C	PP15,5		
503.505.1F	RP25,1U		
503.446.1F			
502.992.4B	PP8,7		
502.845.2F	PP12,6		
502.498.1F	PQ17,6		
501.804.1F	PQ23,4L		
501.114.2B	PQ13,7		
500.914.1F	RP26,0U		
500.300.2E	PP18,4U	PQ25,3L	
499.815.2C	PP26,1L		
498.297.1F	PQ26,3U?	PP20,3U	
~~498.187.1F~~			
497.878.3B	PP9,7		
497.376.3B	PQ21,5	PP21,3L	
496.666.1F			
496.375.4B	PQ18,6	PP13,6	PQ14,7
496.193.3C	PP16,5		
496.063.1F			
495.965.1F			
494.047.1F			
493.477.1B	PQ27,1U		
493.318.1F	PQ9,8?		
492.824.1F			
492.418.4B	PP10,7	RP26,1U	
492.113.1F	PP19,4L		
491.331.2B	PQ15,7		
490.895.2C	PQ26,3L		
490.028.2C	PP27,1L		
489.965.2F?	PQ19,6	PQ10,8?	
489.855.2D	PQ22,5		
489.652.1E			
488.594.2C	PQ27,3U	PP22,3L	
488.350.3B	PP17,5		
488.115.1F	PP21,3U		
487.810.1F			
486.738.1F			
486.608.3B	PP11,7		
485.854.2B	PQ16,7		
484.401.1F			
483.150.1F	PQ20,6		
482.677.1F	PP20,4U?	PQ28,1U	
482.350.2D	PP15,6		
482.011.1D	PQ23,5		
480.661.1C			
480.467.3C	PP12,7		
480.309.1E			
480.139.3C	PP18,5	PQ17,7	

528.041.1F			
527.911.1F	PQ12,6		
527.367.3B	PP23,1L		
526.322.2B	PQ22,3L		
526.000.2C	PP17,3U		
525.393.3C	PP8,6		
524.975.2B	RP23,1U		
524.638.1F	PQ20,4L		
524.260.5B	PP12,5	PQ23,3U	PQ24,1U
524.083.1F	PP15,4L		
523.979.2F	PP15,4U		
523.896.3C	PQ17,5		
523.754.2F			
523.631.1F			
522.413.2F	PQ7,7		
522.157.1F	PP18,3L		
521.130.1F			
520.823.1F			
520.258.2C	PP9,6		
519.987.1F	RP24,0U		
519.709.1F	PQ8,7		
518.784.1F	PQ14,6		
518.489.2C	PP24,1L		
518.045.2D	PQ21,4U	PQ23,3L	
517.774.5A	PQ18,5	PP13,5	
517.392.1F	PQ21,4L		
517.222.1F	PP18,3U		
516.648.2D	PP16,4L	PQ9,7	
516.053.2B	PQ24,3U		
514.954.1F			
514.805.2C	PP10,6		
514.347.2F	RP24,1U	PQ25,1U	
514.118.1B	PP19,3L		
513.691.2D	PQ15,6		
513.289.2B	PQ10,7		
511.634.1F			
511.470.1F			
511.309.3D	PQ19,5		
510.898.4B	PP14,5		
510.742.1F	PQ22,4U		
510.562.1F	RP25,0U		
510.454.4F			
509.580.2D	PQ11,7		
509.315.3B	PQ24,3L	PP25,1L	
508.986.2B	PP11,6		
508.751.1F	PP17,4L		
507.784.4B	PP7,7		
507.352.1F	PQ25,3U		
505.924.2F	PP20,3L		

549.942.1F	PQ16,4L		
549.642.3C	PP14,3U		
549.474.1F			
549.360.4B	PQ12,5		
548.966.3B	PQ19,3L		
547.872.1F			
547.166.1F	PQ6,6		
546.793.5B	PP8,5		
546.695.3F	RP21,0U		
546.495.3D	PQ20,3U		
545.502.2D	RP21,1U		
544.907.5B	PQ13,5		
544.472.4F	PP12,4	PP15,3L	
544.338.3F	PQ17,4U	PQ22,2U	
544.208.4B	PP21,1L		
)>	PQ17,4L		
544.095.4F			
543.331.2B	PR21,5?	PQ22,1U	
542.294.1F			
542.161.3C	PQ8,6	PP15,3U	PP16,2U
541.794.3C	PQ20,3L		
541.669.5A	PP9,5		
540.177.4B	PQ14,5		
539.490.3B	PQ21,3U		
539.078.2C	PQ9,6		
538.338.1F	PQ18,4U		
538.045.3B	PP13,4	PQ18,4L	RP22,0U
537.299.2B	PP16,3L		
537.058.2F			
536.465.1F			
536.192.5B	PP10,5		
535.936.3B	PP22,1L		
535.709.1F	PQ10,6		
535.359.2C	PQ23,2U	RP22,1U	
535.062.4B	PQ15,5		
534.629.3B	PP6,6		
534.268.4B	PQ21,3L	PP16,3U	
533.942.1F	PQ23,1U		
533.198.2F			
532.225.1F	PP17,2U		
532.096.3B	PQ22,3U		
531.955.2F	PQ11,6	PQ19,4U	
531.479.1F	PQ19,4L		
531.132.1F			
530.384.5B	PP11,5		
530.202.3D	PP7,6		
529.862.2C	PP17,3L		
529.657.4B	PQ16,5		
529.119.1F	RP23,0U		
528.241.1F			

```
567.924.1F   RQ27,3U??  RQ28,3L??
567.342.2B   PP15,2L  PQ18,2L
567.137.6A   PP8,4  PP18,1L
566.228.4B   PQ7,5
565.163.4B   PQ17,3U  PR16,5
564.986.3B   RP19,1U
564.308.4B   PP12,3L
563.818.3F
563.673.2F
563.512.5B   PQ8,5
563.405.4D   PP12,3U

563.199.2B   RP19,0U
562.765.1F
562.141.4D   PQ17,3L
562.008.3F   PP9,4
561.521.1F   PR17,5
561.143.3B   PQ20,1U
560.862.2C   PQ20,2U
560.674.2F   PP16,2L
560.485.5B   PQ14,4  PQ9,5

560.159.5B   PP5,5
559.841.2F
         )>  PP19,1L
559.765.3F
559.380.3F
         )>  PQ18,3U
559.262.3E
557.884.2C   PP13,3L
557.098.5B   PQ10,5
556.840.1F   RQ28,3U??
556.525.4B   PP10,4

556.041.6A   PP6,5
555.739.3B   PQ18,3L
555.507.2B   PQ15,4U
555.387.3D   PQ15,4L  RP20,1U
555.046.1F   RP20,0U

 EITHER
553.805.1F)  PP17,2L
   OR
553.846.1F)
553.759.1F)


553.388.4B   PQ11,5
553.084.3B   PR19,5?  PQ19,3U
552.794.2E   PQ21,2U
552.611.1F
552.402.2D   PQ21,1U
552.152.4B   PP20,1L
551.587.6B   PP7,5  PP15,2U
551.347.3B   PP14,3L
550.730.3B   PP11,4
550.509.1F
550.108.1F   PQ16,4U
```

```
584.285.4B  PP4,4
583.974.5B  PQ13,3L
583.872.3F  PQ8,4
583.351.4B  RP17,1U
583.081.2B  RQ23,1U??
582.296.3B  PQ17,2U  PR8,5
581.659.1F
581.383.5B  PP9,3L  PR9,5
581.152.4B  PP9,3U
580.857.6B  PQ9,4  PP16,1L
580.723.5B  PQ16,2L  PQ14,3U  RP21,3U
580.503.3C  PP5,4

580.105.2F  PR10,5
579.781.3E  PP13,2L  PR23,3L??
579.084.4B  PQ14,3L
578.718.3B  RP17,0U
578.537.2D  PR11,5  RQ26,3U??
577.610.3D
577.500.5C  PQ10,4  PQ18,1U
576.734.1F
576.500.3F  PR12,5  PP12,2U
576.396.4F  PP6,4
576.000.5C  PP10,3L

575.859.5C  PQ15,3U
575.605.5B  PP10,3U  PQ18,2U
574.581.1F  PR24,3L??
574.310.4B  RP18,1U
        )>  PQ17,2L
574.161.5B  PR13,5  PP17,1L
573.795.5D  PQ15,3L
        )>  PQ11,4
573.699.5B  PP14,2L
573.243.1F
573.064.1F

571.932.3B  PP7,4
571.693.1F
571.506.1E  PR14,5
571.087.2C  RP18,0U
570.644.5A  PQ16,3U  PQ5,5
570.301.4B  PP11,3L
569.684.5B  PP11,3U  PQ12,4
569.530.4C  PQ19,1U
568.735.1F  PP13,2U
568.581.4B  PQ6,5
        )>  PR15,5
568.468.3B  PQ19,2U
568.160.4B  PQ16,3L
```

598.745.2F	PR17,3U
598.503.2F	RQ24,3U??
598.071.3C	PQ13,2L
597.423.1F	
597.003.4B	PQ10,3U
596.853.4E	RQ21,1U?? PP9,2U
596.500.5B	PQ10,3L
596.192.1F	
595.656.6A	PP6,3
595.381.1F	

595.217.2F	RQ25,3L??
594.580.3B	
594.318.4C	PQ15,2U
594.116.1F	PR18,3U
593.441.6B	PQ11,3U
593.311.6B	RP15,0U PP14,1L
592.709.5C	PQ14,2L PQ11,3L PQ4,4
592.382.5A	PQ16,1U
592.082.3C	RP16,1U

591.888.1F	
591.695.1F	RQ25,2L
591.384.1F	
591.175.6D	PP11,2L PP7,3
590.981.2E	PQ5,4
590.538.3D	PP10,2U (RP20,3U)
590.039.3B	RQ22,1U??
589.872.2B	
589.711.1F?	
589.641.2F	

589.409.5B	PQ12,3U
589.037.1F	
588.941.4D	PQ6,4 PR21,3L??
588.890.3F	
588.830.4F	
588.621.3B	
588.549.3F	PQ12,3L PQ16,2U
588.325.4B	
588.154.1F	
587.251.5C	PP15,1L

586.900.2C	PQ15,2L
586.570.4D	PQ7,4
586.478.5B	PP8,3L
)>	RQ26,3L??
586.342.5C	PP8,3U
586.135.4B	RP16,0U
585.783.1F	
585.593.2E	PP12,2L
585.500.1F	
585.245.5F	PQ13,3U
585.146.4F	PQ17,1U
584.484.1F	PR22,3L??

```
610.425.3F  PP7,2L
610.286.4F  PP11,1L
       )→   PQ5,3
610.190.6F  PR15,3L
610.081.7B  RQ19,1U?  PR14,3U

608.965.5C  PQ12,2U  RP18,3U
608.804.3F
608.501.4B  RP14,1U
608.214.6C  PQ6,3
608.140.5F
607.959.3D  PP7,2U
607.775.3B  PQ11,2L
607.482.1F  RR26,0U
607.351.2A  PR16,3L

607.249.1F
606.996.7B  PP3,3
       )→   RP13,0U
606.866.5D
606.705.4D  PR15,3U
605.914.6D  PQ7,3U
605.792.5C  PQ7,3L
605.589.6B  PQ14,1U
605.184.5B  PP12,1L
604.523.4B  PQ13,2U
603.656.3F  RQ24,3L??
603.552.6B  PP4,3  RQ20,1U??

603.269.5B  PQ8,3U
603.052.6B  PQ12,2L  PQ8,3L
602.595.2D  PP8,2U
602.313.2F
601.801.2C
601.534.2F
601.371.3B  PP9,2L
601.055.2F
600.787.3C  PR18,3L
600.437.4B  RP15,1U

600.294.6B  PQ9,3U  RP14,0U
599.998.6B  PQ9,3L  (RP19,3U)
599.768.6C  PP5,3

  EITHER
599.654.4C)
   OR
599.643.4F) PQ14,2U

599.203.5B  RQ24,2L  PQ15,1U
598.888.5B  PP13,1L
```

622.778.4F	PR5,3 PR6,3 PR7,3L
)>	PQ11,1U
622.661.8C	PQ8,2U
622.501.8B	PQ7,2L RQ17,1U?? PR4,3 PR7,3U PQ11,1U
622.224.4D	PR8,3L RQ19,2U RR23,1U
622.000.3D	PP4,2L
621.860.3C	PR8,3U
621.653.1F	PR3,3
621.339.4C	PR9,3L PP4,2U
621.135.3B	
620.818.3C	PR9,3U RQ19,0U??
620.262.3F	PR10,3L
619.94 .6F	RQ21,2L
)>	PP9,1L
619.84 .6F	PQ9,2U
619.682.3F	RQ22,3L??
619.506.5F	RP11,0U
619.402.5F	PQ8,2L PR10,3U
619.215.2F	
618.696.4C	RR24,0U
618.434.4D	PP5,2L
618.157.2F	RQ22,1L
617.961.4B	
617.640.2F	PR11,3U RP17,3U
617.488.4C	
617.296.3C	PP5,2U
617.061.3B	PR12,3L
616.787.5C	PQ12,1U
616.651.5D	PQ10,2U RQ20,0U??
616.509.4F	
616.367.6A	RQ18,1U? RQ22,3U??
615.926.2F	PQ9,2L
615.492.4F	PR12,3U
615.219.6A	PP10,1L
615.051.3E	PR13,3L
614.596.2E	PP6,2L
614.299.1F	RQ20,2U
614.087.1F	
613.522.1F	
613.357.5C	RP12,0U
613.251.5D	PQ3,3 RQ22,2L RR25,0U
612.994.5B	PQ11,2U PR13,3U
612.816.3C	PR14,3L PP6,2U
612.571.2D	RQ23,1L
612.220.2D	
612.024.4F	PQ10,2L
611.912.6C	PQ4,3 RQ23,3L??
611.490.6B	PQ13,1U

```
638.60  .6F  PQ7,1U
        )>   RQ18,2L
638.50  .7F
638.096.3C   RQ18,1L
637.920.2F   RR20,0U
637.358.3F   PR13,2L
637.098.4B   RP10,1U
636.836.4A   RQ17,2U
636.599.1F
636.266.4D   RP8,0U

636.054.6A   PP5,1L   RQ15,0U
635.493.5B   PR14,2L   PR20,1L
635.192.8B   PQ8,1U
634.910.1F   RR26,3U
634.610.3B   RR21,1U
634.404.1F   RQ20,3L
634.137.6B   RQ15,1U
633.854.1F   RP13,2U
633.489.4F   RQ19,1L   RR21,0U   RP15,3U
633.282.3E   PR15,2L

632.544.4F   PQ2,2U   RQ19,2L   RQ16,0U
632.406.6B   PP6,1L   RQ20,3U
631.669.3D   PQ3,2U   RP13,1L
631.414.7B   PQ9,1U
631.086.2F   PQ3,2L
630.992.3E   RP9,0U
630.851.2F   PR16,2L
630.514.6C   PQ4,2U   RP11,1U
629.766.1D   RQ18,2U
629.514.3B   PQ4,2L

629.076.2D   PQ5,2U
628.802.3B   RQ17,0U   RR22,0U
628.485.7B   PP7,1L   RQ16,1U??   RR22,1U
627.553.2C   PQ5,2L
627.296.4F
        )>   PQ6,2U
627.198.7B   PQ10,1U   RQ21,3L??
626.550.1F   RP14,1L
626.421.2F   RQ20,2L   RP16,3L
625.772.1F   RP16,3U

625.364.4D   RP10,0U
625.243.4D   PQ6,2L   PP3,2L
625.150.3E   PQ7,2U
624.913.3F   PP3,2U   RQ18,0U   PR18,2L
624.627.2E   RQ21,3U
624.316.7B   PP8,1L
623.886.1E   RR23,0U
623.546.5C   RP12,1U   RQ21,1L
623.087.1F
```

654.021.6B	RQ9,0U	RQ17,3L			
653.712.1F	RP10,2U				
653.166.6F	RQ17,3U				
653.043.7C	PR14,1L	RR16,0U			
651.492.4B	RQ10,0U				
651.182.4B	RR18,1U				
650.923.6B	PR15,1L				
650.722.4D	RP9,1L				
)>	RR24,3U				
650.599.5B	RQ15,1L				
650.195.3D	RP5,0U				
649.972.5D	PQ1,1U				
649.576.7A	RQ12,1U	RQ16,2L	RR17,0U		
649.118.6C	PQ2,1U	RP8,1U			
648.726.3C	RQ11,0U				
648.473.6B	PR16,1L				
648.160.4F	RP13,3L				
648.043.5C	PP1,1L				
647.840.7B	PQ3,1U	RQ18,3L			
647.575.1F	RP11,2U	RP16,5			
646.688.5C	RQ16,1L	RQ18,3U			
646.245.4F	RP10,1L				
646.165.6B	PQ4,1U				
645.942.6C	RR19,1U	RP6,0U	RR18,0U		
645.810.6C	RQ12,0U				
645.685.5B	PR17,1L				
645.434.4C	PP2,1L				
645.180.1F					
644.743.7A	RQ13,1U				
644.060.7B	PQ5,1U				
643.590.2E	RQ16,2U				
643.280.3B	RP9,1U				
643.126.2F					
642.725.4C	RQ13,0U				
642.575.7B	PP3,1L	PR7,2L	PR18,1L		
642.491.4F	PR6,2L	RQ17,1L	PR8.2L		
642.037.3B	PR5,2L	PR9,2L	RR19,0U		
641.532.8C	PQ6,1U	RP11,1L			
641.263.5B	RP7,0U	RP14,3L	RQ19,3L	PR4,2L	PR10,2L
640.923.3B	RP12,2U	RP14,3U			
640.454.4F	RR20,1U				
640.261.2F	PR11,2L				
640.044.1F					
639.709.3F	RQ19,3U	RP17,5			
639.571.7B	RQ14,1U				
)>	RQ14,0U				
639.439.7B	PP4,1L				
639.226.4C	PR19,1L				
638.981.1F	PR12,2L				
638.888.1F					

```
670.885.5B  RR8,0U   RQ16,4
670.504.6C  RQ11,2U   RQ14,3L
670.221.4A  RQ14,3U
669.834.3A  RR1,0U   RP4,1L   RP7,2U
669.718.2F
669.642.4B  RR9,0U
669.277.8C  RQ7,1U vRQ9,1L
668.904.5A  RR14,1U
668.229.5A  RR0,0U   RP4,1U   RQ12,2L
668.110.5B  RR10,0U
667.838.1F  RR22,3L?

666.764.6B  RQ10,1L   RP10,3
666.470.2C  RP5,1L
666.175.3B  RR11,0U
666.032.7B  RQ8,1U   RQ12,2U
665.317.5B  RQ2,0U   RQ15,3L
664.964.6B  RR15,1U   RQ15,3U   RQ17,4
664.473.5B  RQ3,0U
664.050.7A  RP5,1U   RQ13,2L   RR12,0U
         )→ RQ11,1L
663.929.3F
663.365.5B  RQ4,0U

662.877.2D  RP6,1L
662.457.6A  RQ9,1U
662.312.3F  RQ19,5   RP14,5
661.978.5C  RQ5,0U
661.725.4C  RR13,0U
661.350.2F
661.126.3D  RQ13,2U
660.806.7E  RP11,3   RR16,1U
660.341.5B  RQ6,0U
659.815.4C  RQ16,3L

659.702.8B  PR7,1L   PR8,1L
659.480.9F  PR6,1L   RP6,1U   RQ14,2L   RP9,2U
659.401.7F  PR9,1L
659.264.4F  RQ16,3U
659.051.4F  RP7,1L   RR14,0U
658.960.8F  PR5,1L   PR10,1L
658.471.8C  RQ10,1U   RQ7,0U
658.214.5B  PR4,1L
657.764.6B  RP3,0U   RQ13,1L   PR11,1L
657.230.7B  PR3,1L   PR11,1L

656.311.7B  RQ8,0U   PR12,1L
656.148.7B  RR17,1U   RR15,0U
655.880.4B  PR2,1L
655.690.2C  RQ14,2U
655.375.2B
655.000.5E  RP8,1L
654.845.6B  PR13,1L
654.687.4D  RQ15,2L   RP12,3L
654.539.4F  RP7,1U   RP12,3U
654.289.7A  RQ11,1U   PR1,1L   RQ14,1L
```

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686.415.6C   RQ15,5   RQ13,4   RR18,3U
686.278.4B   RR2,1L
685.808.8B   RR2,1U   RR16,1L   RR7,1U
685.423.2F   RR16,2L?
684.683.6B   RR1,1L   RQ7,2L
684.574.8E   RR17,1L   RR8,1U
          )> RR1,1U
684.46 .4F   RQ7,2U
683.851.6B   RQ11,3
683.180.3F   RR18,1L   RR19,3L?
682.957.5B   RR9,1U

682.218.3C   RP7,3
682.072.3B   RQ8,2L
681.591.5B   RR19,1L   RQ8,2U   RQ14,4   RR19,3U
680.902.6C   RR10,1U   RQ16,5
679.987.4B   RR20,1L   RQ2,1L
679.803.5E
        )>   RQ12,3L
679.694.4E   RQ12,3U
679.507.3C   RQ2,1U
679.219.4F   RQ3,1L

679.095.3F   RQ9,2L
678.896.2F   RR16,2U
678.807.3F
678.603.2F   RP5,2
678.30 .6F   RQ9,2U   RR20,3L?   RQ3,1U
678.20 .6F   RQ4,1L   RR21,1L
677.771.1F   RP10,4
677.407.2C   RP8,3
676.912.6B   RQ5,1L
676.600.6B   RQ4,1U

676.355.3F   RQ15,4   RR20,3U   RR22,1L
675.778.2F   RQ10,2L
675.668.6C   RR12,1U   RP12,5
675.388.6F   RQ6,1L
675.292.5F   RQ13,3L
675.112.5C   RQ17,5   RQ13,3U
674.690.4C   RQ10,2U
674.543.6B   RQ5,1U
674.234.1F   RR17,2U   RR23,1L?
673.610.6B   RQ7,1L

673.250.1F   RR21,3L?
672.604.5C   RR5,0U
672.491.6B   RR13,1U   RR4,0U
672.363.5D   RR6,0U
672.182.5C   RQ11,2L   RP9,3
672.080.6C   RQ6,1U
671.983.5F   RR3,0U   RP3,1U
671.803.4C   RR7,0U
671.584.7B   RQ8,1L
671.115.4C   RR2,0U
```

```
701.790.5F   RR14,3L
701.719.4F   RR6,2L
        )>   RR5,2L
701.567.6C   RR14,3U  RR7,2L  RR5,2U  RR6,2U
701.249.6B   RR4,2  RR7,2U  RQ5,3
700.913.2C   RR8,2L
700.723.5B   RQ12,5
700.480.6B   RR3,2  RR8,2U
700.048.2F   RR9,2L
699.408.5B   RR2,2

699.238.6B   RR9,2U  RQ6,3  RR20,5
698.755.5C   RR15,3L  RQ10,4  RR10,2L
698.395.4D   RR15,3U  RR18,4  RP8,5
697.650.2C   RR10,2U  RQ18,9?
697.342.3B   RR11,2L
696.852.6B   RQ7,3  RQ16,7
696.302.4B   RQ13,5
695.677.1F   RR11,2U
695.398.3B   RR16,3L
694.931.2B   RQ11,4

694.809.2C   RR16,3U
694.118.6B   RQ8,3
693.678.1F
693.380.1E   RR13,2L
693.16 .1F   RR12,2U  RP9,5
692.119.2C   RQ3,2
691.553.5A   RQ14,5
691.039.7B   RR14,2L  RQ9,3  RQ17,7  RQ19,9?
690.833.6F   RQ12,4  RR17,3U  RP5,3
690.750.8B   RR8,1L  RR9,1L  RQ4,2

690.552.6B   RR7,1L  RR10,1L
690.157.5B   RR6,1L  RR11,1L
690.021.3F
689.547.6A   RR5,1L  RR12,1L
689.061.4D   RQ5,2
688.839.4D   RR13,1L
688.693.6B   RR4,1L
688.470.1F   RR22,5
688.343.1F   RR15,2L
687.988.4C   RR14,1L

687.608.8A   RR3,1L  RR18,3L?  RQ10,3  RP10,5
687.03  .7F  RR4,1U  RR5,1U  RQ6,2L
        )>   RR15,1L  RR14,2U
686.93  .5F  RQ6,2U

  EITHER
686.638.7B)
   OR
686.68  .2F) RP6,3
686.61  .7F) RR3,1U  RR6,1U
```

724.599.5B	RR7,4		
724.463.5C	RR4,4		
724.118.1F	RR18,7		
723.966.4D	RR8,4		
722.995.4B	RR9,4		
722.840.5C	RR14,5		
721.684.4D	RR10,4		
721.116.1F	RQ11,7	RR17,6	
720.739.1F	RQ9,6		
720.154.3F	RQ6,5		
720.013.3B	RR11,4		
719.719.4C	RR15,5		
718.071.2C			
717.776.3C	RQ7,5		
717.382.1F	RQ10,6	RR18,6	
716.989.1F	RQ12,7		
716.704.1F			
716.336.3C	RR16,5		
715.613.3B	RR13,4		
715.047.4B	RQ8,5		
713.841.8B	RR5,3	RR6,3	
713.579.7C	RR7,3		
713.428.7B	RR4,3		
712.933.7B	RR8,3	RR14,4	
712.694.7B	RR3,3		
712.342.2F	RR17,5	RQ5,4	RQ13,7
711.963.7B	RR9,3	RQ9,5	
710.623.6B	RR10,3		
710.265.2F	RQ6,4		
709.800.2C	RR15,4		
708.970.6B	RR11,3		
708.562.5B	RQ10,5		
707.895.2C	RQ7,4		
707.563.1F	RQ14,7		
706.91 .4F	RR12,3L		
706.81 .4F	RR12,3U		
706.385.1F	RR16,4		
705.147.3C	RQ8,4		
704.842.4C	RQ11,5		
704.565.4B	RR13,3L		
704.390.4B	RR13,3U		
704.005.2E	RR19,5		
703.720.1F	RQ17,9??		
703.458.1F			
702.964.4B	RQ4,3		
702.605.1B	RR17,4		
702.393.1F	RQ15,7		
702.089.4C	RQ9,4		

761.312.1F	RR9,9		
760.880.1F			
760.759.1F			
759.976.1F	RR10,9		
758.276.1F	RR11,9		
757.030.1F			
756.785.1F	RR8,8		
756.413.1F			
756.238.1F	RR12,9		
755.775.1F	RR9,8		
754.428.1F	RR10,8		
753.899.1F	RR13,9		
752.738.1F	RR11,8		
751.195.1F	RR14,9		
750.874.4B	RR7,7		
750.677.1F	RR12,8		
750.195.4C	RR8,7		
749.159.4C	RR9,7		
748.282.1F	RR13,8		
747.793.3C	RR10,7		
746.096.3B	RR11,7		
745.696.1F			
745.505.1F	RR14,8		
744.306.1F			
743.932.1C	RR12,7		
743.523.3B	RR6,6		
743.238.2C	RR7,6		
742.602.2C	RR8,6		
741.573.2B	RR9,6	RR13,7	
740.301.1F	RR10,6		
738.775.1F	RR14,7		
738.638.1F	RR11,6		
736.849.1F			
736.641.1F	RR12,6		
735.788.1F			
735.620.1F	RR15,7		
734.743.7A	RR5,5	RR6,5	
734.489.5B	RR7,5		
733.848.5B	RR8,5		
732.870.5B	RR9,5		
732.152.1E	RR16,7		
731.562.5B	RR14,6	RR10,5	
729.982.4F			
729.883.4C	RR11,5		
728.602.1F	RR15,6		
728.347.2B	RQ9,7	RR17,7	
727.873.4B	RR12,5		
725.524.5B	RR13,5		
725.229.1F	RR16,6		
724.877.6B	RR5,4	RR6,4	RQ10,7

Table A2

A_2 Band, part 2 (ref. section 7.3)

Key

As for table A1. p317

except * = probably spurious

30,000+

763.249.1F
763.318.1F ●
763.433.1F
763.577.2E
763.653.1F ●
763.874
+-.05.2F
764.405.1E
764.541.1F
764.642.1F ●
764.952.2D

765.163.1F ●
765.287.1F ●
765.369.1F ●
765.462.1F ●
765.870.1F
765.962.1F ●
766.114.1F ●
766.26 .2F
766.34 .2F
766.44 .2F

766.843.2F ●
766.924.3D
767.035.1F
767.279.1F ●
767.515.1F
767.65 .1F
767.985.1F
768.14 .1F
768.232.1C
768.325.1F ●
768.729.2E

755.956.1F	•
756.136.3D	
756.252.5C	RR12,9
756.405.2F	
756.545.2F	
756.796.5B	RR8,8
756.923.1F	•
757.06 .2F	
757.19 .1F	
757.311.1F	•
757.437.1F	
757.55 .1F	
757.613.1D	
757.736.1F	
757.86 .1F	
758.081.1F	
758.282 +-.05.4C	RR11,9
758.472.2E	
758.636.1F	•
758.740.1F	
758.903.1F	•
759.039.1F	•
759.144.1F	
759.234.1F	•
759.321.1D	
759.494.1F	
759.650.1E	
759.80 .1F	
759.969.4C	RR10,9
760.150.1F	•
760.274.1F	•
760.377.3F	
760.580.2F	
760.74 .1F	•
760.877.2D	
761.001.2F	
761.14 .2F	
761.306.4B	RR9,9
761.580.2F	
761.682.1F	•
761.774 +-.05.2B	
761.861.1C	
761.998.1F	
762.305.1F	•
762.654.1F	
762.78 .1F	•
762.860.2F	
762.969.1F	•
763.062.1F	
763.14 .1F	•

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747.96 .2F
748.116.3E  RR15,9
748.317.3F  RR13,8
748.50 .1F
748.676.1F
748.83 .1F
749.154.8B  RR9,7
749.288.3F
749.389.2B
749.587.1F  •

749.701.1F  •
749.788.1F
749.861.1F
749.94 .2F
750.040.3F  •
750.182.8B  RR8,7
750.382.2F
750.57 .3F
750.689.4F  RR12,8
750.879.8B  RR7,7

751.025.2F
751.165.3C  RR14,9
751.414.1F  •
751.552.1F
751.670.1F  •
751.755.1E
751.843.1F  •
751.936.1F  •
752.102.1F  •
752.208.1E

753.299.1F  •
752.447.1F
752.753
  +-.05.5D  RR11,8
752.881.1F  •
753.066.1F  •
753.132.2F  •
753.320.2D
753.657.1F  •
753.882.4C  RR13,9
754.030.2F  •

754.25 .1F  •
754.420.3D  RR10,8
754.562.1F
754.701.1F  •
754.777.2D
755.014.1D
755.17 .1F  •
755.37 .1F
755.47 .1F
755.774.4C  RR9,8
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739.266.1F  •
739.430.1F
739.544.1F
739.693.1F
739.859.1F
740.009.1F  •
740.154.1B
740.316.6B  RR10,6
740.567.2D
740.662.1D

740.945.2F  RR17,9
741.129.1F  •
741.298.2F
741.571.8B  RR9,6  RR13,7
741.800.2F
741.979.1F
742.079.2F  •
742.235.1F  •
742.353.1F
742.596.7C  RR8,6

742.820.1F
742.937.2F
743.231.7B  RR7,6
743.312.5F  •
743.513.7A  RR6,6
743.688.3F  •
743.773.2D
743.931.7B  RR12,7
744.160.2F
744.353.2B

744.508.1F  •
744.708.2F  RR16,9
744.897.2F  •
745.001.2F
745.113.2F
745.221.2F
745.333.1F  •
745.48 .2F  RR14,8
745.61 .2F
745.74 .2F

746.090.7B  RR11,7
746.29 .2F
746.506.1F
746.619.1F  •
746.867.1F
747.049.1F
747.319.1F  •
747.428.1F
747.655.1D
747.786.8B  RR10,7
```

	732.260.3F		
	732.396.2F	RR19,9	
	732.507.1F	•	
	732.659.1F	•	
	732.870.9C	RR9,5	
	733.003.4F		
	733.149.2F		
	733.285.2F	RQ11,9	
	733.389.3F		
	733.471.2F		
	733.839.9D	RR8,5	
	734.178.4F		
	734.298.5F	RR13,6	
†	(734.481.9B)	RR7,5	
†	(734.735.9A)	RR5,5	RR6,5
	735.284 +-.05.3F	RR17,8	
	735.631.4C	RR15.7	
	735.807.3F		
	736.021.1F		
	736.208.1F	•	
	736.404.1F	•	
	736.493.1F	•	
	736.651.5B	RR12,6	
	736.79 .3F	RR18,9	
	736.969.2F		
	737.079.1C	RQ10,9	
	737.251.1F	•	
	737.610.1F		
	737.710.1F	•	
	737.876.1F		
	738.001.1F	•	
	738.171.1F		
	738.292.1E		
	738.426.2F		
	738.519.2F		
	738.632.6A	RR11,6	
	738.749.6B	RR14,7	
	738.911.2D		
	739.010.1F		
	739.197.2E		

† ( ) = too strong to be reliable; use Raynes values (table A1) instead.

723.283.1F	•		
723.408.2F			
723.513.1F	•		
723.614.2F			
723.787.2F	RQ8,6		
723.973.8C	RR8,4		
724.125.5B	RR18,7		
724.251.3F			
724.467.9F	RR4,4		
724.607.9C	RR7,4		
724.866.9B	RR5,4	RR6,4	RQ10,7
725.076.2F			
725.238.4C	RR16,6		
725.365.3F			
725.513.8B	RR13,5		
725.632.4F			
725.783.1F			
726.096.1D			
726.194.1F			
726.546.3C	RQ7,6		
726.836.1F			
726.951.1F			
727.145.1F	•		
727.262.1F			
727.438.1F			
727.600.2F	RR20,9		
727.691.4F	•		
727.865.8B	RR12,5		
728.027.4E			
728.134.2F			
728.355.6B	RQ9,7	RR17,7	
728.594 +-.05.4E	RR15,6		
728.842.2F			
729.002.1F	•		
729.184.1F	RQ12,9		
729.610.1F	•		
729.879.9B	RR11,5		
730.024.4F			
730.242.2F			
730.352.1F	•		
730.498.1F	•		
730.811.1F	•		
730.917.1F	•		
731.090.2D			
731.186.2F	RR18,8		
731.303.2F			
731.396.3F	•		
731.548.9B	RR14,6	RR10,5	
731.806.3F			
732.162.5C	RR16,7		

```
714.699.2F   RR20,7
715.052.8C   RQ8,5
715.605.6B   RR13,4
715.847.1F
716.039.1F   •
716.344.8C   RR16.5
716.464.3F
716.576.2F
716.664.1F   •
716.990.5B   RQ12,7

717.071.2F
717.375.4D   RQ10,6
717.565.3F
717.770.8B   RQ7,5
717.915.4F   RR12,4
718.062.6B
718.932.1D   RQ13,8
719.097.2E
719.167.2E
719.320.1F

719.489.3F
719.574.4D   RR19,7
719.708.9E   RR15,5
720.004.8D   RR11,4
720.141.8D   RQ6,5
720.223.4F
720.341.2D
720.743.4C   RQ9,6
721.097.4C   RQ11,7
721.186.2F

721.454.3E
721.675.8C   RR10,4
721.989.2F   •
722.145.1F   •
722.308.2E
722.428.1F
722.529.3D   RR21,9
722.682.3F
722.844.9B   RR14,5
722.995.9D   RR9,4

EITHER
723.156.3F
OR
723.099.3F
723.209.3F
```

Table A3

C_1 Band (ref. section 7.5)

Key

The following quantities appear in the order given.

Mean frequency

Strength on visual scale from 0 to 9

Character - see p.300

) = close near neighbour (occurs in pairs).

)) = probably double

n = probably spurious

* = frequency uncertain

Standard error of mean frequency

(F = 1 estimate, FF = 2 estimates)

Assignments (see p.156 for an explanation of the notation)

30,000 +

778.087	1•	FF
777.769	1•	F
777.449	1	0.014
777.318	1•	FF
777.197	1•	F
777.088	1	FF
776.817	1•	FF
776.305	2))	FF
776.188	2	0.009
776.014	2	0.011
775.811	1	0.016
775.596	1•	FF
775.470	1•	F
775.063	2	0.008
774.818	1•	F
774.553	1)	F
774.386	1	FF
774.227	2)•	F
773.788	1	0.015
773.512	2)	0.008
773.334	1)	0.006
773.170	1•	F
773.067	1	FF
772.960	1•	F
772.405	1•	F
772.254	2	0.008
771.921	1	FF
771.766	2)	0.011
771.612	2)	FF
771.287	1	0.010
771.147	1	FF
771.078	1•	F
770.921	1	0.013
770.684	2	0.008
770.509	1	FF
770.136	1	F
770.019	1	F
769.899	1•	F
769.794	1)	FF
769.667	1)	FF
769.340	1	F
769.038	1•	F
768.904	1•	F

788.773	1•	F
788.586	1•	F
788.435	1)•	FF
788.300	1	FF
788.129	2)	FF
787.994	3)	0.003
787.914	2)	FF
787.741	2	0.007
787.563	1	FF
787.478	1•	F
787.241	1•	FF
787.070	2)	FF
786.975	2)	0.008
786.869	2)•	F
786.708	1)	FF
786.452	1•	F
786.300	1	0.020
786.116	1	FF
785.964	1)•	F
785.628	1	0.012
785.450	1	0.015
785.212	1	0.018
785.083	1)	0.013
784.934	2))	0.008
784.576	4	0.006
784.420	2)	FF
784.286	2)	0.011
784.163	1•	FF
783.980	1	FF
783.807	1	0.007
783.060	1	0.010
782.434	1)	FF
782.307	1)	FF
782.013	1•	F
781.803	2))	0.009
781.486	1•	F
781.396	1•	F
780.633	1))	0.011
780.398	4	0.004
780.202	2	0.015
779.993	1•	F
779.636	1	0.012
779.318	1	FF
778.916	1	0.011
778.602	1•	F

798.995	2)	0.012	
798.686	1	F	
798.259	1•	F	
797.986	1•	F	
797.626	1)	F	
797.510	2)	0.016	
797.297	3)	0.013	
797.139	4)	0.009	
797.021	2)	FF	
796.912	2•	FF	
796.552	2)	FF	
796.446	2)	0.008	
795.991	1	F	
795.839	2)	F	
795.593	1•	F	
795.062	1•	0.025	
794.966	1	FF	
794.785	2	0.009	RQ21 3L
794.674	1•	F	
794.393	2	0.013	
794.320	2)•	F	
794.094	1	0.007	
793.853	1•	F	
793.572	1•	F	
793.464	1•	FF	
793.070	1	0.002	
792.913	2•	F	
792.787	1	0.008	
792.585	1•	F	
792.404	1•	F	
792.192	2	0.007	RQ21 3U
791.601	2))	0.009	
791.341	3))	0.011	
791.100	2)	0.005	
790.980	1•	F	
790.858	1	F	
790.548	1	F	
790.379	2)	0.009	
790.254	2)	FF	
790.077	1	FF	
789.933	1)•	F	
789.754	1•	FF	
789.528	1	FF	
789.308	1•	F	
788.983	1	0.010	
788.881	1	0.005	

807.033	3))	0.011	
806.779	2	0.005	
806.579	1•	F	
806.332	4	0.012	RQ19 3U
806.180	4)•	F	
806.029	2•	F	
805.921	2•	0.016	
805.665	2)	F	
805.534	4))	0.007	
805.393	2)	FF	
805.297	1)	FF	
805.176	1)	FF	
805.034	1	F	
804.906	1•	F	
804.814	1	0.018	
804.669	1•	F	
804.497	1•	F	
804.408	3	0.011	
804.132	1)	0.004	
804.023	1)	FF	
803.828	2	0.007	
803.578	1•	F	
803.322	2)	FF	
803.160	2)	F	
802.792	1	F	
802.460	1•	F	
802.141	1	FF	
802.032	3)	FF	
801.941	4)	0.008	
801.827	3)	F	
801.684	2)	0.015	
801.523	3)	0.012	RQ20 3L
801.422	2)	F	RQ20 3L
801.258	1•	F	
801.156	1•	FF	
800.972	2•	F	
800.872	1•	F	
800.717	2•	F	
800.594	2	0.004	
800.404	1•	F	
800.241	2•	F	
799.768	3)	0.011	
799.648	4)	0.007	
799.482	1	FF	RQ20 3U
799.142	2))	0.009	

816.833	3)	0.007	
816.672	3)	0.004	
816.559	3)	0.004	
816.314	2)	FF	
816.178	2)	0.008	
815.729	1•	F	
815.538	1	FF	
815.102	2)	0.008	
814.991	2)	F	
814.755	2	0.004	RP16 5
814.511	2	0.006	
814.355	1	F	
813.963	3)	0.005	RQ18 3L
813.856	3)	FF	
813.747	2)•	F	
813.581	2)•	F	
813.406	3))	0.007	
812.857	2	0.010	RQ18 3U
812.609	1•	F	
812.310	1	FF	
812.200	1)•	FF	
812.110	2))	0.009	
811.807	1•	F	
811.628	2	FF	
811.395	2)	FF	
811.293	2)	F	
811.189	2)	FF	
811.033	2)	0.015	
810.872	3)	0.006	
810.669	3)	0.011	
810.478	2)	F	
810.374	2)	0.008	
810.215	2)•	F	
809.992	2•	F	
809.841	3	0.009	
809.626	1•	F	
809.232	2))	F	
808.983	1	0.007	
808.720	1•	FF	
808.204	3	0.006	
808.069	2	0.006	
807.892	2	0.011	RQ19 3L
807.570	2•	F	
807.435	1•	F	
807.191	1	F	

	825.890	2)	0.015				
	825.798	1	0.011	RQ18	4		
	825.688	1	0.005				
	825.413	2•	F				
	825.275	2)	0.010	RQ16	3L		
	825.120	1)	FF				
	824.973	2)	0.001				
	824.578	4)	0.011	RQ16	3U	RQ20	5
	824.457	4)	0.007	RP11	3	RQ20	5
	824.327	2)	0.017	RP11	3		
	823.992	1•	FF				
v	823.815	1•	F				
	823.605	1•	FF				
	823.269	1•	F				
	823.147	1•	F				
	822.946	2)	F				
	822.791	2)	0.005				
	822.627	3)	0.007				
	822.415	2	0.004				
	822.137	2	0.009				
	821.918	1)	F	RP15	5		
	821.772	1	FF				
	821.504	1•	F				
	820.912	1))	0.010				
	820.466	1	F				
	820.355	2•	F				
	819.892	1	0.009				
	819.761	2)	F				
	819.700	4)	0.003	RQ17	3L		
	819.567	3)	0.007				
	819.380	1•	F				
	819.240	1•	F				
	819.097	3))	0.007				
	818.927	3)	0.006	RQ17	3U		
	818.827	2•	FF				
	818.700	2•	F				
	818.573	1	0.003				
	818.425	2	0.009				
	818.045	1•	F				
	817.703	1•	0.017	RQ21	5	RP14	4
	817.431	1	FF				
	817.311	1•	FF				
	817.184	2)	FF				
	817.086	1)•	F				
	816.997	1	FF				

835.777	1	FF		
835.519	3)	0.003	RP13	5?
835.391	3)	FF	RP 9	3
835.190	5	0.005	RQ14	3L
834.898	3	0.007	RQ14	3U
834.642	1	FF		
834.135	2•	0.012		
833.839	3)	0.006		
833.735	1)	F		
833.585	1	FF		
833.044	1	FF		
832.954	1•	FF	RR22	3U
832.798	2	F		
832.602	1	F		
832.296	2)	0.015		
832.163	2)	0.011		
832.057	1	FF		
831.787	3))	0.007	RQ17	4
831.592	1	FF		
831.455	1	F		
831.255	1	F	RR23	3L
830.987	3	0.006	RQ19	5
830.730	2)	F		
830.619	2)	0.017	RP12	4
830.395	3	0.006	RQ15	3L
830.277	1)	F		
830.104	2)	0.019	RP10	3
829.942	3)	0.008	RQ15	3U
829.741	2)	0.006		
829.547	2	0.003		
829.327	1	FF		
829.053	3	0.008		
828.880	2	0.009	RP14	5
828.517	1	FF		
828.219	1	0.012		
828.118	1	F		
827.857	1)	F		
827.741	1•	FF		
827.613	2•	F		
827.473	3	0.005		
827.161	1•	F		
826.797	2)•	FF		
826.478	2))	0.011		
826.081	2)	0.007		

845.738	3)	F			
845.656	1)	FF			
845.503	2)	0.012			
845.177	2)	F			
845.039	3)	0.006			
844.877	2	F			
844.697	2•	F			
844.533	2)•	FF			
844.361	4))	0.006			
843.972	4)	0.009			
843.843	4)	0.007	RQ12 3U	RR20 3U	RQ12 3L
843.628	2	F	RQ12 3U		
843.237	2	0.008			
842.874	3	0.006	RQ17 5		
842.510	2)	FF			
842.364	2)	FF	RQ15 4		
842.156	2	0.016	RP10 4		
841.758	2)	0.007			
841.632	3)	FF	RP12 5		
841.467	2)	FF			
841.349	2•	F			
841.220	2)	0.013			
840.997	3))	0.009			
840.767	2	F			
840.487	3•	F			
840.334	4)	0.006	RP 8 3		
840.095	2	F			
839.650	3)	0.006	RQ13 3L		
839.463	4	0.004	RQ13 3U		
839.284	2	0.014			
839.022	2	0.000			
838.630	2	0.007	RR21 3U		
838.507	2•	F			
838.376	2	0.006			
837.989	2)	0.006			
837.818	2)	FF			
837.466	2	FF			
837.296	2•	F			
837.083	5)	0.005	RQ18 5		
836.938	3	F			
836.792	1	0.016			
836.579	3)•	F	RP11 4		
836.420	2•	FF	RR22 3L		
836.302	2•	F			
836.202	3	0.008			

854.410	5	0.006	RQ 9 3	RR13 2U
854.098	2)	0.006	RR18 3L	
853.756	3)	0.006	RQ 3 2	
853.623	3)	0.006	RR23 5	RQ15 5
853.470	1•	F		
853.310	3	0.004	RP10 5?	
852.995	3)	0.007	RR18 3U	
852.716	2)	FF		
852.595	3)	0.005	RQ 4 2	
852.503	2)	F	RQ 4 2	
851.956	1•	FF		
851.763	1)	0.007	RQ13 4	
851.666	1)	0.007	RQ13 4	
851.574	2)•	F		
851.448	2)	F		
851.207	6	0.005	RQ10 3	
851.003	4	0.006	RQ 5 2	
850.803	3)	F	RQ 5 2	
850.628	2)	F		
850.525	2)	0.007		
850.405	3)	0.012	RQ19 7	
850.285	2)•	F		
850.130	2	FF	RR19 3L	
849.917	1	0.012		
849.731	1•	FF		
849.603	1	F		
849.185	1	F		
849.020	4)	0.008		
848.899	2)	FF		
848.701	4)	0.006		
848.606	5)	0.002	RR19 3U	
848.491	3)	0.012	RQ16 5	
848.347	4)	0.006		
848.146	2•	F		
848.002	4)	0.008	RR15 2U	
847.863	4)	0.010	RR24 5	
847.666	6)	0.004	RQ11 3	RP11 5?
847.427	3)	0.012		
847.211	5	0.008	RQ14 4	
846.871	3	0.010		
846.700	2	F		
846.539	3	0.007		
846.141	2•	F		
846.032	1)	FF		
845.903	5)	0.006	RR20 3L	

```
862.988  3)  F      RR 8  2U
862.877  5)  0.008  RQ13 5   RR 9  2L
862.540  2   F
862.408  3)  FF     RQ17 7
862.238  4)  0.010  RQ17 7   RR 3  2

862.088  5)  0.007  RR10 2L  RQ 6  3   RR 9  2U
861.839  2   0.014  RR10 2L
861.665  2   FF
861.463  1   F
861.266  1   FF

861.114  4   0.006  RR16 3L  RR 2  2
860.791  2)  F      RR10 2U
860.696  2)• FF     RR11 2L
860.600  2)• 0.008  RR16 3U
860.515  3)• 0.007  RR16 3U

860.415  2)• F
860.325  1•  F
860.185  2   FF
859.853  5   0.006  RQ11 4   RQ 7  3
859.544  1   0.003  RQ 11 4

859.395  1•  FF
859.221  2   0.011  RR12 2L
859.124  1   FF
859.000  1   F      RR22 5
858.868  1•  F

858.628  3•  F
858.391  3)  0.005  RQ14 5?  RQ16 6
858.042  1•  F
857.838  1   0.008
857.708  2)  0.011  RR17 3L

857.589  2)  F
857.471  2   F      RR13 2L
857.298  6   0.004  RQ 8  3
857.011  2)  FF     RR17 3U
856.932  2)  0.006  RR17 3U  RR12 2U

856.673  1•  F
856.548  1   0.009  RQ18 7
856.087  1•  F
855.892  2)  0.006  RQ12 4
855.710  1)  F

855.512  1   FF     RR14 2L
855.184  2   FF
855.035  1   FF
854.893  1   0.008
854.760  1•  F
```

871.164	3)	F	RR12 3U			
871.072	2•	F				
870.870	4	0.004	RQ11 5			
870.556	1	F				
870.467	2	F				
869.896	1	FF				
869.761	1)	FF				
869.623	1	F	RR17 4			
869.477	2	FF				
869.309	3)	0.006	RQ 8 4			
869.214	2)	FF	RR13 3L			
869.104	3)	0.007	RR13 3U			
868.888	2	F				
868.773	1	0.002	RR20 5			
868.697	1•	F				
868.549	1	0.009				
868.473	3	FF	RQ14 6			
868.325	1•	FF				
868.205	1•	F				
867.832	1	0.004	RQ16 7			
867.700	1	F				
867.397	1	F				
867.261	2	F				
867.075	3)	FF				
866.989	4)	0.006	RQ12 5			
866.900	3)	0.005	RR14 3L			
866.804	2)	F				
866.671	3)	F				
866.580	3)	FF	RR14 3U			
866.487	3)	0.006	RQ 9 4			
866.365	1	F				
865.670	1	FF				
865.576	2	0.005	RQ 4 3			
865.235	1	F				
865.064	1	F				
864.553	2	0.011				
864.413	1	FF				
864.156	4)	0.006	RR15 3L	RR21 5		
863.996	7	0.004	RQ 5 3	RR21 5	RR 6 2L	RR 7 2L
863.751	7	0.006	RR15 3U	RR 6 2U	RR 6 2L	RR 7 2L
863.633	5)	FF	RQ15 6	RR 7 2U		
863.499	4)	0.010	RR 5 2	RR 7 2U	RR 8 2L	
863.359	3)	F				
863.249	4)	F	RQ10 4			
863.086	4)	0.002	RR 4 2			

881.556	1	F				
881.302	2)	FF	RR13 4			
881.204	3)	0.008	RR13 4			
881.013	2	F	RQ11 6?			
880.836	3)	0.005	RR17 5			
880.645	2	F				
880.451	3	0.004	RQ 8 5			
880.155	1	F				
879.388	1	FF				
878.859	2)	0.007	RR14 4			
878.388	1)	FF	RR22 7			
878.274	1)	F				
878.080	1•	FF				
877.772	1)	0.002	RQ14 7			
877.592	3	0.005	RQ 9 5			
877.496	2)	F				
877.380	1	F				
877.296	2•	F				
877.146	3)	0.005	RR18 5	RQ12 6?		
877.004	3	F				
876.854	8)	0.004	RR 6 3			
876.701	8)	0.003	RR 5 3	RR 7 3		
876.320	6)	0.007	RR 8 3			
876.150	7)	0.004	RR15 4	RR 4 3		
875.511	4	0.002	RR 9 3			
875.312	7	0.003	RR 3 3			
874.864	1	0.003				
874.735	2	F				
874.601	2	FF				
874.429	7	0.005	RQ10 5	RR10 3		
874.155	1	FF	RQ 6 4			
873.923	1	FF				
873.585	1	F				
873.410	2	F				
873.272	1	F				
873.044	7	0.004	RR16 4	RR11 3	RR23 7	RR19 5
872.838	2	FF				
872.684	1	F				
872.500	2	F				
871.961	1)	F	RQ 7 4			
871.827	1	F				
871.574	1	FF				
871.489	1	FF				
871.413	1	FF				
871.269	4)	0.004	RR12 3L			

894.140	1)	FF		
894.000	1)	FF		
893.871	1)	0.007	RQ10 7	
892.875	1	F		
892.715	1	F		
892.408	4	0.005	RR13 5	RR19 7
892.008	1*	F		
891.873	1*	F		
891.768	1	F		
891.602	1	F		
890.911	1	FF		
890.718	1	F		
890.579	1	0.008		
890.466	2	F		
890.309	1	0.015	RQ11 7	
890.062	3)	0.007	RR14 5	
889.772	2)	FF		
889.044	2	F		
888.892	4)	0.005	RR 6 4	
888.757	5)	0.003	RR 5 4	RR 7 4
888.367	3)	0.004	RR 8 4	
888.200	4)	0.004	RR 4 4	RR 20 7
887.903	2	F		
887.628	3)	0.007	RR 9 4	
887.216	3	0.006	RR15 5	
886.495	4	0.003	RR10 4	RQ12 7
886.144	1*	F		
885.794	1	FF		
885.419	2	F		
885.269	2)	0.008	RQ 6 5	
885.069	3)	0.009	RR11 4	
884.924	2	F		
884.722	2	F		
884.563	1	0.010	RQ10 6?	
884.177	3	0.007	RR16 5	
883.978	1	FF		
883.736	1	F		
883.568	1)	F		
883.436	2)	0.011	RR21 7	
883.325	2)	0.007	RR12 4	
883.101	2)	FF		
882.998	3)	0.005	RQ 7 5	
882.404	1	FF		
882.304	2)	0.007	RQ13 7	
881.777	1	F		

909.319	)	FF	RR14 7	
908.799	2)	0.007	RR 9 6	
908.475	1	F		
908.290	1	F		
908.211	1	F		
908.003	1	F		
907.710	3	0.008	RR10 6	
907.382	1	F		
907.186	1	F		
906.636	3)	0.008	RR15 7	
906.320	1	0.008	RR11 6	
906.216	1	FF		
905.852	1	F		
905.663	1	FF		
905.024	1	F		
904.939	2	F		
904.648	1	FF		
904.531	2)	0.004	RR12 6	
904.083	1	F		
903.925	1	F		
903.824	1	F		
903.592	2•	0.011	RR16 7	
903.009	1	FF		
902.888	1	F		
902.766	1	F		
902.541	1	0.004		
902.422	2	F	RR13 6?	
902.153	1	FF		
901.942	1	F		
901.358	1	F		
900.211	2•	0.011	RR17 7	
899.996	8)	0.005	RR 6 5	RR14 7
899.829	8)	0.004	RR 5 5	RR 7 5
899.444	5	0.004	RR 8 5	
898.683	5	0.004	RR 9 5	
898.062	1	F		
897.583	5	0.002	RR10 5	
897.087	1	F	RQ 9 7?	
896.734	1	FF		
896.640	2	F		
896.520	3	0.006	RR18 7	
896.174	5)	0.004	RR11 5	
895.698	2	F		
894.610	1	F		
894.430	4	0.005	RR12 5	

934.336	1	0.005	RR 9 9	
933.222	1	0.003	RR10 9	
931.774	1	0.007	RR11 9	
931.647	1	F		
930.000	1	0.017	RR12 9	
928.029	1)	F		
927.898	1)	0.016	RR13 9	
927.481	1	F	RR 8 8	
927.269	1	F	RR 8 8	
926.749	1	F		
926.571	1)	FF	RR 9 8	
925.433	1)	F	RR17 9	RR10 8?
923.929	1	F	RR11 8?	
922.774	1*	F		
922.690	1*	FF	RR15 9	
919.539	1	FF	RR16 9	
919.342	4	0.002	RR 7 7	
918.880	3	0.002	RR 8 7	
918.117	3	0.003	RR 9 7	
917.533	1	F		
917.014	3	0.005	RR10 7	
916.367	1	F		
915.580	3	0.005	RR11 7	
914.760	2	0.007		
914.539	1	FF		
913.983	1	FF		
913.833	3	0.005	RR12 7	
913.606	1	F		
913.455	1	F		
913.068	1	F		
912.813	1	F		
912.717	2	F		
912.403	2	FF		
912.295	1	0.014		
911.897	1	F		
911.744	3	0.006	RR13 7	
911.246	1	F		
910.784	1	F		
910.675	1	F		
910.169	4)	0.007	RR 6 6	
910.035	3)	FF	RR 7 6	
909.935	2	FF		
909.761	1	F		
909.574	3	0.003	RR 8 6	
909.455	2)	FF		

Table A4

A_3 Band (ref. section 7.4)

Key

As for table A3 p343

30,000+

1606.102	2	0.005		
1605.605	0	F		
1605.064	2))	0.008		
1604.817	2)	0.005		
1604.698	2)	FF	PP18 6	
1604.566	2	0.008		
1603.989	1)•	FF	PP25 3L	PP12 8
1603.764	1)	0.008	PP25 3L	PQ12 9
1602.538	1	0.002		
1601.860	1	0.007		
1601.469	0	FF	PQ29 3L	
1600.919	2)	0.004		
1600.749	2)	0.006		
1600.079	1	0.007		
1599.857	0)	F		
1599.714	0)	FF	PP29 1U	
1599.239	0	F	PQ13 9	
1599.080	1	F		
1598.964	2	0.004	PP16 7	
1598.716	1	FF	PP24 3U	
1598.559	1	FF	PP24 3U	
1598.369	1	0.005	PP21 5	
1597.467	2	0.004	PP 9 9	
1596.812	1	0.011		
1596.339	1	0.008	PQ30 3U	
1595.729	1	0.005	PP19 6	
1595.499	0•	FF		
1593.448	3	0.004		
1593.102	2	0.005		
1592.875	4	0.003		

1626.071	1	0.006	PQ17 7
1625.600	2))	0.007	PQ23 5?
1625.305	2	0.007	PQ23 5?
1624.592	2	0.003	
1623.867	2))	0.005	RP27 1U PP23 3L RP28 0U
1623.033	1	0.009	PP28 1L
1622.859	0n	F	
1622.516	1	0.010	PP22 3U
1622.115	2	0.004	PP 9 8
1621.873	2	0.008	
1621.431	1	0.006	PP16 6
1621.204	3	0.003	PP13 7
1620.296	1	0.012	PQ21 6
1620.098	4)	0.003	
1619.974	3)	0.003	
1619.800	1	0.011	PQ18 7
1619.231	1	0.009	PQ28 3U
1618.237	0	F	
1617.853	1	0.008	
1617.492	3•	0.006	PP19 5
1617.076	2n	F	
1616.798	3	0.005	PQ24 5
1616.459	1	0.006	PP10 8
1615.622	2	0.006	
1615.311	1n	F	
1615.087	2	0.005	
1614.874	1	0.004	
1614.134	2	0.006	PP14 7
1613.967	0n	F	PP24 3L
1613.210	3	0.005	PP17 6
1613.011	1n	FF	
1612.509	1))	0.008	PQ10 9?
1612.197	2	0.006	PP29 1L PQ22 6
1611.913	2))	0.005	RP28 1U
1610.386	1))	0.010	PP11 8
1609.953	1	0.007	
1609.417	2)	0.005	
1609.293	2)	0.006	
1608.913	1	0.012	PQ11 9
1608.511	1	0.014	
1608.328	2	0.004	PP20 5?
1607.966	0	F	PQ29 3U
1607.802	2	0.007	
1606.899	1	FF	
1606.722	3	0.003	PP15 7

1645.686	2	0.012	
1644.935	1	FF	RP26 0U
1644.272	2))•	0.011	PP20 3U
1643.827	3	0.002	PP26 1L PP13 6
1643.642	3	0.004	PQ25 3L
1643.262	2)	0.008	
1643.125	4)	0.002	PQ14 7 PP16 5
1642.627	1	0.004	PP21 3L
1642.066	2	0.007	
1641.858	3))	0.004	PQ18 6 PQ21 5
1641.512	1	0.003	
1640.713	1	0.009	PQ 9 8
1640.356	4)	0.008	
1640.253	5)	0.004	PP10 7 PQ26 3U
1638.486	1	0.005	
1638.324	2	0.003	
1637.756	2	0.003	PQ15 7
1637.590	1	0.013	
1637.270	1	FF	
1637.141	1	FF	PQ10 8
1636.825	3)	0.005	
1636.698	2)	0.007	PP14 6 PQ27 1U
1636.101	1	0.005	
1635.701	1	0.005	RP26 1U
1634.951	3))	0.004	PQ19 6 PP17 5
1634.261	3	0.004	PP11 7
1633.854	2	0.004	PQ22 5?
1633.755	1)	FF	
1633.616	3)	0.006	PP21 3U PP27 1L PQ26 3L
1633.352	2	0.005	PP22 3L
1633.041	2	0.005	
1632.855	1	0.010	
1632.516	0	FF	
1632.102	2	0.003	PQ16 7
1631.785	0	F	
1631.073	0	FF	
1630.723	1n	0.008	
1629.971	1•	0.009	PQ27 3U
1628.954	3	0.004	
1628.541	1•	FF	
1628.295	1	0.010	
1627.882	4	0.004	PP12 7 PQ20 6
1627.428	1	0.008	PP 8 8
1627.033	1	FF	
1626.384	3	0.003	PP18 5

1662.249	3	0.006	PQ23 3L	PQ21 4L
1661.795	3	0.003		
1661.574	1n	F		
1661.401	1•	F		
1660.943	2	0.007	PQ10 7	
1660.715	3	0.004		
1660.280	4	0.002	PP19 3L	PQ15 6
1659.902	0	FF		
1659.398	3	0.003		
1659.204	3	0.003	PQ24 3U	
1658.562	3)	0.007	RP24 1U	
1658.440	4)	0.004	PP14 5	
1658.305	2n	FF	PQ25 1U	
1658.074	3)	FF		
1657.886	4)	0.005		
1656.957	4	0.004	PQ11 7	PP11 6
1656.641	2•	F	PQ19 5?	
1656.421	2	0.004		
1656.108	5	0.003	PP 7 7	
1655.562	0•	FF	PP17 4L	
1655.255	3))	0.006	PP17 4U	
1655.009	2	F	RP25 0U	
1654.486	2	0.013	PQ16 6	
1654.349	3)	0.004	PP19 3U	
1654.192	3)	FF		
1654.123	4)	0.003	PQ22 4L	
1653.776	3	0.004	PP25 1L	
1653.108	1	0.005	PQ24 3L	
1652.719	2	0.004	PQ12 7	
1651.886	4	0.005		
1651.615	3)	0.006	PP20 3L	
1651.376	1	F		
1651.182	4	0.003	PP 8 7	
1650.966	4	0.003	PP15 5	
1650.520	3	0.005	PP12 6	
1649.902	3	0.004	PQ25 3U	
1649.409	4	0.003	PQ20 5	
1648.386	1	0.006	PQ17 6	
1648.095	2	0.004	PQ13 7	
1647.579	1))	0.008	PQ26 1U	
1647.234	1	0.011	RP25 1U	
1647.046	1	0.014	PP18 4L	
1646.651	4))	0.006	PP18 4U	
1646.431	1•	F		
1645.909	4	0.004	PP 9 7	

1679.398	3	0.004	PQ 21 3L
1679.002	2)	FF	PP14 4
1678.867	4)	0.003	PQ23 1U PP 7 6
1678.664	5	0.002	PP11 5
1677.513	2	0.009	PQ19 4U?
1677.182	1)	0.003	PQ19 4L PP20 2L
1677.022	2)	0.006	PR13 7
1676.790	3	0.004	PP17 3L
1676.435	3)*	0.014	
1676.287	5*	0.003	PQ22 3U PQ16 5
1675.371	2	0.006	PQ12 6
1674.470	3	0.003	RP23 0U
1673.922	3	0.005	PP 8 6
1673.696	2n	F	
1673.354	2	0.004	
1673.073	3	0.005	PP17 3U
1672.877	1	F	
1672.650	4	0.003	PP23 1L
1672.291	5	0.003	PP12 5
1671.980	1	F	
1671.575	3*	FF	PP15 4L
1671.499	2*	0.005	PP15 4U
1671.014	3)	0.005	PQ22 3L
1670.879	2)	0.006	PR15 7?
1670.641	1	0.010	PQ13 6 PQ 7 7
1670.369	2	0.006	PQ20 4U?
1670.115	4	0.002	PQ17 5
1669.611	2n	FF	RP23 1U
1669.353	1n	F	PQ24 2U?
1668.676	4))	0.004	PP18 3L PQ24 1U PP 9 6
1668.025	3	0.004	PQ23 3U
1667.749	1	F	PQ 8 7
1666.608	1	FF	
1666.303	1	0.010	
1665.545	5	0.002	PP13 5
1665.074	2n	F	
1664.934	2	0.005	RP24 0U
1664.517	4	0.004	PQ 9 7
1663.942	2*	0.007	PP18 3U
1663.735	3)	0.003	PP16 4L
1663.608	3)	0.005	PP16 4U PQ18 5
1663.385	4)	0.002	PP24 1L
1663.276	2)	FF	
1662.964	2*	0.007	PP10 6
1662.647	3	0.004	

1696.757	1	FF	PQ16 4L		
1696.063	2	0.005			
1695.645	5	0.003	PP 8 5		
1695.010	2	0.004	PQ19 3L		
1694.867	2	0.003	PQ19 3L		
1694.393	2	FF			
1694.253	2))	0.008			
1693.315	2)	0.012	PQ 7 6		
1693.210	2)	0.002	PP18 2L		
1692.853	4	0.003	PP12 4	RP21 0U	
1692.450	5	0.002	PQ13 5		
1692.106	4	0.002	PP15 3L		
1691.700	4	0.004	PQ20 3U		
1691.419	1•	F			
1691.038	3	0.003	RP21 1U		
1690.620	3)	0.005	PQ17 4L		
1690.444	4)	FF	PQ 8 6		
1690.339	6))	0.003	PP21 1L	PQ21 2L	PP 9 5
1689.920	4	0.003	PP15 3U		
1689.354	1n	F			
1688.842	1	0.007			
1688.610	2	0.003	PQ22 1U		
1687.938	1	0.014			
1687.383	6)	0.003	PQ20 3L	PQ14 5	
1687.242	3)	0.002	PQ 9 6		
1686.939	1	FF			
1686.345	2	0.009	PR 8 7		
1686.105	3	0.005	PP13 4		
1685.910	1	0.006			
1685.371	2	0.005	PP19 2L		
1684.685	6)	0.002	PP10 5		
1684.569	4)	0.003	PP16 3L		
1684.249	3))	0.004	PQ21 3U	PQ18 4?	
1683.762	2•	FF	RP22 0U		
1683.626	2	0.004	PQ10 6		
1683.449	3	0.002	PP 6 6		
1683.292	2	0.006			
1682.737	1	0.002			
1682.004	4	0.003	PQ15 5		
1681.663	5))	0.003	PP16 3U	PP22 1L	PQ22 2L
1680.748	1	0.004			
1680.476	3	0.002	RP22 1U		
1680.333	1	0.007			
1679.960	1n	F			
1679.678	2	0.004	PQ11 6		

1710.949	3	0.004	PP 9 4
1710.365	2	FF	
1710.018	3	0.005	RP19 0U
1709.385	6	0.002	PP 5 5
1708.977	5)	0.004	PQ 9 5
1708.859	4)	0.004	PQ17 3L
1708.661	2	F	PP14 2U
1708.430	1n	F	
1708.034	4	0.003	PQ14 4 PP16 2L
1707.344	2•	FF	PR17 5
1707.211	4	0.002	PQ20 1U
1706.926	2	0.004	PR32 1L
1706.585	5))′	0.003	PP19 1L PQ19 2L
1706.193	5))	0.005	PP13 3L PQ20 2U
1705.581	3	0.009	
1705.369	7)	0.005	PP10 4 PQ18 3U PQ10 5
1705.176	6)	0.003	PP 6 5
1705.006	4	0.005	PP13 3U
1704.475	1	0.007	PR11 6
1704.225	3	0.005	
1703.399	2	0.009	RQ26 1U
1703.144	2•	FF	
1702.669	3)	0.003	PQ15 4U
1702.564	3)	0.010	PQ15 4L
1702.098	4	0.003	PQ18 3L
1701.729	2•	F	RQ26 2U
1701.630	2•	FF	RP20 0U
1701.442	5))	0.002	RP20 0U PQ11 5
1701.266	3	0.003	RP20 1U
1701.006	3	0.005	
1700.814	2	FF	PP17 2L
1700.601	5	0.002	PP 7 5
1700.325	1	F	
1699.951	2	0.011	
1699.509	2	FF	PP15 2U
1699.275	4	0.003	PP14 3L PP11 4
1698.910	2	FF	
1698.730	5)	0.005	PQ19 3U
1698.605	4)	0.002	PP20 1L PQ20 2L
1698.092	3))	0.007	PQ21 1U PR19 5
1697.952	3	0.006	
1697.788	4)	0.006	PQ21 2U?
1697.652	4)	0.002	PP14 3U
1697.119	5	0.002	PQ12 5
1696.914	1	F	PQ16 4U

1725.995	6	0.004	PQ10 4
1725.778	5	0.003	PP 6 4 RP21 3U
1725.597	3	0.006	
1725.304	3	0.003	PP12 2U
1724.932	5	0.003	PP10 3L
1724.734	3	0.006	
1724.557	5	0.003	PP10 3U
1724.328	6	0.002	PQ18 1U
1724.012	1	0.004	PR12 5
1723.564	2	0.005	
1723.137	5	0.002	PQ15 3U
1722.316	2))	FF	PR30 1L RQ24 2U
1722.052	5))	0.003	PQ11 4
1721.877	3	0.003	PQ18 2U
1721.781	2	FF	PP14 2L
1721.631	5	0.002	PP17 1L
1721.429	3	0.003	PQ17 2L PR13 5
1721.210	6	0.001	PQ15 3L PP 7 4
1721.046	3	0.004	RP18 1U
1720.344	1n	F	
1719.739	3	0.003	PQ 5 5
1719.505	1	0.008	
1719.353	1	0.004	
1719.024	4))	0.004	PP11 3L RQ24 1U
1718.657	1	FF	
1718.439	5	0.003	PP11 3U PR14 5
1718.277	4	0.003	RP18 0U
1717.725	4)	0.004	PQ12 4
1717.596	5)	0.003	PQ16 3U PQ 6 5
1716.667	1	FF	
1716.264	4	0.003	PP 8 4
1715.974	4	0.003	PQ19 1U
1715.222	5)	0.004	PQ16 3L
1715.079	5)	0.003	PR15 5 PQ 7 5 PP15 2L
1714.808	2	0.012	PR31 1L
1714.273	6	0.002	PP18 1L PQ19 2U PQ18 2L
1713.939	1	FF	
1713.153	3	0.007	PQ13 4
1713.009	3	FF	PQ13 4
1712.767	5	0.003	PP12 3L
1712.484	2	0.008	
1712.200	4	0.002	PQ 8 5 RQ25 2U
1711.924	4	0.004	PP12 3U
1711.689	5	0.002	PQ17 3U
1711.370	4	0.003	RP19 1U PR16 5 RQ25 1U

1739.488	4	0.003	RP16 1U			
1739.291	1	0.008	RP19 2L			
1738.792	1	F				
1738.406	2	0.006	RP20 1L			
1738.211	3	0.004	PQ 6 4			
1737.922	2	0.009	PR20 3L			
1737.701	6	0.002	PQ12 3U			
1737.346	1n	F	RR28 0U			
1736.803	6	0.002	PQ12 3L			
1736.665	1n	F	PR28 1L			
1736.391	1n	F				
1736.235	1	FF	RR27 1U			
1736.062	2	0.001	RP20 3U			
1735.776	6)	0.002	PQ 7 4	PP 8 3L	PR15 4U	
1735.627	6)	0.008	PQ 7 4	PP 8 3U	PQ16 2U	
1735.375	7	0.002	PP15 1L			
1735.031	1	0.008				
1734.705	1	0.005	PQ15 2L			
1734.489	1	0.005	PR19 3U			
1734.268	4	0.003	PP12 2L	RQ22 1U		
1733.904	6	0.003	PP 4 4	RP16 0U		
1733.383	1	0.004				
1733.183	6	0.002	PQ13 3U	PR21 3L		
1732.812	4	0.003	PQ 8 4	PP11 2U		
1732.549	1n	F				
1732.299	5	0.003	PQ17 1U	PR16 4L		
1732.002	5))	0.002	PQ13 3L	PR 6 5	PR16 4U	RQ23 2U
1731.617	1	0.005	PR 7 5			
1731.340	1	0.004				
1730.800	1	0.008	RP20 2L	PR 8 5		
1730.499	6	0.004	PP 9 3L	RP17 1U		
1730.293	5	0.002	PP 9 3U	RQ27 1L	RR29 0U	
1730.021	4	0.002	PP 5 4			
1729.619	4	0.006	PQ 9 4	PR 9 5		
1729.403	2n	F				
1728.948	4	0.002	PQ17 2U			
1728.657	6	0.002	PP16 1L			
1728.330	6	0.003	PQ14 3U			
1728.135	5))	0.003	PR22 3L	PP13 2L	PR10 5	PQ16 2L
1727.448	1	FF				
1726.799	6	0.002	PQ14 3L	RQ23 1U		
1726.361	4)	0.004				
1726.211	5)	0.005	PR11 5	RP17 0U		

1751.411	1	FF	PR 8 4		
1751.050	2	0.007	RP18 1L		
1750.794	2))	0.006	RQ21 2U		
1750.582	4))	0.004	RR26 0U	PP 9 2L	
1750.316	4	0.004	PR17 3L	PR 9 4	
1750.157	1	FF	RQ23 2L		
1749.702	4	0.004	PR16 3U	PR26 1L	
1749.470	7	0.002	PP 5 3		
1749.244	6	0.002	PQ 9 3U		
1748.917	6)	0.003	PQ 9 3L		
1748.782	4)	0.003	RQ20 1U	PR10 4	
1748.549	4	0.003	RP14 0U		
1748.170	4	0.004	RP15 1U		
1747.867	6	0.002	PP13 1L		
1747.420	4))	0.006	PQ14 2U		
1747.244	1	FF			
1746.996	6	0.003	PQ15 1U		
1746.853	2)	FF	PR11 4		
1746.401	3))	0.004	PQ13 2L	RP18 3L	
1746.162	2	0.006	PP 9 2U		
1745.933	2)	0.008	RP19 3U		
1745.733	5	0.002	PQ10 3U		
1745.440	3)	0.004	PP10 2L		
1745.251	7	0.002	PP 6 3	PQ10 3L	
1745.105	2	FF	PR17 3U		
1744.748	2	0.004	RP19 1L	PR12 4	
1744.392	3	0.004			
1744.146	2)	0.007	RR27 0U		
1744.031	3)	0.004	RR26 1U		
1743.649	1	0.015			
1743.401	2	0.006	PR27 1L		
1742.794	1	0.004			
1742.345	2)	0.008	PR19 3L		
1742.156	2))	0.006	PQ 4 4	PR13 4	
1741.876	7)	0.007	PQ11 3U		
1741.787	7)	0.002	PP14 1L	PQ15 2U	
1741.666	6)	0.008	PQ15 2U	RQ21 1U	RQ22 2U
1741.364	5)	0.005	RP15 0U		
1741.237	6)	0.002	PQ11 3L		
1740.662	7	0.003	PP 7 3	PQ14 2L	
1740.347	2	0.005	PQ 5 4		
1740.159	2	0.006			
1740.000	2	FF	PR18 3U	PP11 2L	
1739.871	5	0.003	PQ16 1U		
1739.709	2	0.007	PP10 2U		

1763.701	2)	0.004			
1763.531	3	0.005	PR12 3U		
1763.398	2	0.011	RP16 2L		
1763.060	6	0.002	PQ 3 3	RP16 1L	
1762.806	3	0.006	RR24 0U	RQ22 1L	
1762.698	4	0.005	PR13 3L		
1762.543	6))	0.004	PP 6 2U	RQ18 1U	
1762.110	4	0.003	RP12 0U		
1761.593	7))	0.003	PQ 4 3	RR24 1L	PQ11 2U
1760.997	4	0.004	PQ10 2L		
1760.695	2	0.007	PR13 3U		
1760.422	1	0.005			
1760.289	1n	F			
1760.100	2)	0.012	PR14 3L	PP 7 2L	
1759.964	7)	0.003	PQ13 1U		
1759.826	6)	0.004	PQ 5 3		
1759.465	1	F	RQ20 2U		
1759.336	1	F	RP20 5?		
1759.137	7	0.003	PP11 1L		
1758.884	1	0.008	RR24 1U		
1758.595	1n	F			
1758.172	1n	F			
1758.047	1	FF			
1757.760	3)	FF			
1757.644	7)	0.004	PP 7 2U	PQ 6 3	RQ22 2L
1757.474	3)	FF	PP 7 2U	PR14 3U	
1757.319	4	0.003	PQ12 2U		
1757.119	4)	0.005	PR15 3L	RP17 1L	RP16 2U
1756.988	3)	F			
1756.836	7	0.002	PP 3 3	RR25 0U	RQ23 1L
1756.526	6	0.003	RP14 1U	PQ11 2L	RP18 3L
1755.905	1)n	F	PR25 1L		
1755.755	5	0.003	PR25 1L	RQ19 1U	RP17 2L
1755.455	6	0.002	RP13 0U	PP 8 2L	
1755.237	6)	0.003	PQ 7 3U		
1755.110	6)	0.003	PQ 7 3L		
1754.364	1n	F			
1753.825	4)	0.008	PR16 3L	PR15 3U	
1753.673	8)	0.002	PP12 1L	PQ14 1U	
1753.334	7	0.001	PP 4 3		
1752.750	2)	0.008	PR 5 4	PR 6 4	
1752.576	5	0.005	PQ13 2U		
1752.402	6	0.002	PQ 8 3U		
1752.205	6	0.003	PQ 8 3L	PP 8 2U	PR 7 4
1751.652	4	0.003	PQ12 2L		
1751.518	2	FF	PR 8 4	RR25 1U	

1776.031	7	0.002	PQ10 1U
1775.788	2	0.004	RP17 4 RQ18 2U
1775.651	1	FF	RQ17 0U
1775.534	2n	F	PR12 2U
1775.379	6))	0.003	RQ16 1U
1775.233	3)	FF	PP 3 2L
1774.895	5	0.004	PP 3 2U PQ 6 2L
1774.665	3	0.005	
1774.546	5	0.003	RP10 0U RP14 1L PQ 7 2U
1774.323	2	0.005	PR17 2L RQ20 1L
1774.126	2	0.005	RP14 2U RQ20 1L
1773.815	7	0.002	PP 8 1L RR22 0U
1773.300	1	0.007	RP16 3L
1772.745	4	0.002	RP16 3U RR22 1U
1772.243	4	0.003	PR 5 3 PR 6 3L
1772.077	7)	0.006	PR22 1L PR 6 3U RP12 1U PQ 7 2L PR 4 3
1771.906	6)	0.006	PR22 1L RR 7 3L PP 4 2L PQ 8 2U PR 4 3
1771.662	4	0.002	PR 7 3U RQ20 2L
1771.414	1	F	RQ18 0U PR 3 3
1771.144	8	0.001	PR 8 3L PQ11 1U PP 4 2U
1770.825	2	0.007	PR 8 3U RP15 2L PR18 2L
1770.381	1	F	
1770.084	3	0.005	PR 9 3L
1769.560	3	0.005	PR 9 3U
1769.217	7	0.001	PP 9 1L
1769.058	7	0.002	RQ17 1U
1768.884	5	0.004	RP15 1L PQ 9 2U
1768.721	5)	0.003	PR10 3L PQ 8 2L
1768.612	4)	0.006	RQ21 1L
1768.465	4	0.003	RP11 0U RR23 0U RP19 5
1768.209	2	0.006	PP 5 2L
1767.946	3	0.004	PR10 3U
1767.813	1	F	RQ19 2U
1767.111	4)	0.010	PP 5 2U
1766.964	6)	0.004	PR11 3L PR23 1L
1766.648	1n	FF	
1766.171	1	FF	
1765.936	5)	0.005	PR11 3U RR23 1U
1765.774	7)	0.003	PQ12 1U RP15 2U
1765.451	4	0.002	PQ10 2U
1765.223	1	FF	RQ23 4U
1765.047	4	0.004	PQ 9 2L PR12 3L RP17 3L
1764.755	1	FF	RQ21 2L
1764.493	5)	0.006	RP13 1U
1764.327	8)	0.002	PP10 1L PP 6 2L

1788.058	7	0.003	PQ 7 1U
1787.674	1	F	PR 7 2U?
1787.453	1	FF	
1787.194	7	0.002	RQ14 0U RQ14 1U
1786.961	2	0.008	PR12 2L
1786.386	3	0.004	PR 8 2U
1786.054	5)	0.004	RP10 1U
1785.918	6)	0.002	PP 5 1L
1785.781	5)	0.003	RP 8 0U RP17 5
1785.549	3	0.003	RR20 1U
1785.293	5	0.003	PR19 1L RP12 1L RQ19 3U
1785.085	2)	F	PR13 2L
1784.961	2)•	0.004	RP13 2L
1784.883	2)	FF	
1784.490	7	0.002	RQ18 1L PQ 8 1U
1784.032	1	FF	RP16 4
1783.650	3	0.004	RR20 0U
1783.460	3	0.008	RQ15 0U
1783.300	3•	0.008	RQ17 2U
1782.985	2	F	
1782.806	2	FF	PR14 2L
1782.528	2	0.003	PQ 2 2U
1782.166	6	0.002	PP 6 1L PQ 2 2L
1781.897	2	0.007	RP13 2U
1781.673	2)	0.009	
1781.567	3)	0.010	PQ 3 2U
1781.413	6	0.002	RQ15 1U
1781.191	5	0.002	PR20 1L RP15 3L
1781.014	3	0.006	PQ 3 2L
1780.808	2	0.006	RP15 3U
1780.486	7)	0.004	PQ 9 1U
1780.332	6)	0.002	RP 9 0U PQ 4 2U PR15 2L
1779.950	3	0.005	RP13 1L
1779.538	3	0.005	RQ19 1L?
1779.295	7	0.003	RP11 1U RR21 1U PQ 4 2L
1778.828	4	0.003	RR21 0U
1778.705	3	FF	PQ 5 2U
1778.315	3	0.009	PP 2 2L RQ19 2L
1778.147	7	0.003	PP 7 1L PP 2 2U RP14 2L
1777.496	2	0.003	PR16 2L RQ20 3U
1777.313	4	0.005	PQ 5 2L RP18 5
1776.907	3)	0.007	
1776.787	5)	0.005	PR21 1L PQ 6 2U
1776.491	1	F	
1776.286	1	FF	

1800.519	1	0.008	
1800.227	7	0.003	RR16 0U RQ10 0U RQ17 3L
1800.022	6	0.003	PQ 1 1U RP 5 0U
1799.864	4	0.004	RP 9 1L
1799.546	2	0.004	RP14 4

1799.431	4	0.005	RQ17 3U
1799.132	7	0.003	PQ 2 1U
1798.516	2)•	FF	
1798.385	7	0.002	PR15 1L RP 8 1U
1798.050	7))	0.004	PP 1 1L RQ15 1L

1797.822	7	0.003	PQ 3 1U RQ12 1U RP11 2L
1797.304	5	0.003	RQ11 0U RQ19 4 RR18 1U
1797.046	4	0.003	RQ15 2U
1796.432	4	0.004	RR17 0U RQ16 2L
1796.030	7	0.002	PQ 4 1U RP11 2U RP13 3L

1795.620	7)	0.003	PR16 1L RP 6 0U RP13 3U
1795.479	5)	0.003	PP 2 1L
1795.210	3	0.005	RP10 1L
1794.313	2	0.009	
1794.157	4))	0.003	RQ12 0U

1793.962	2)n	F	RP16 5
1793.793	8))	0.004	PQ 5 1U RQ16 1L
1793.687	5)	0.002	RQ18 3L

1793.113	1	FF	
1792.912	2n	F	
1792.635	8)	0.007	PP 3 1L RQ18 3U RQ13 1U
1792.482	8)	0.005	PP 3 1L RQ18 3U PR17 1L RR18 0U RP 9 1U
1791.963	2	0.003	RP15 4

1791.816	2	0.003	PR 6 2L PR 7 2L
1791.486	5	0.004	RR19 1U RP12 2 L PR 5 2L PR 8 2L
1791.159	7	0.002	PQ 6 1U
1790.847	5	0.002	RP 7 0U RQ13 0U PR 9 2L
1790.701	3	FF	RQ17 2L

1790.356	4	0.005	RP11 1L RQ16 2U
1790.128	1	FF	PR 3 2L
1789.840	2	0.005	PR10 2L RQ20 4?
1789.376	6	0.003	PP 4 1L
1789.215	6	0.003	RQ17 1L RP12 2U

1789.073	6	0.003	PR18 1L
1788.756	2	0.004	RP14 3L PR 6 2U
1788.575	2	FF	PR11 2L
1788.476	2	0.006	RP14 3U
1788.194	3)	FF	RR19 0U

1813.483	1	FF	RP12 4			
1813.230	3)*	FF				
1813.131	4)*	0.002	RQ 4 0U			
1812.493	7))	0.002	RR12 0U	RP 6 1L	RQ11 1L	
1812.234	4	0.003	RQ15 3L			
1812.067	5	0.004	RR15 1U			
1811.819	5)	0.003	RQ15 3U	RQ13 2L		
1811.666	4)	0.005	RQ 5 0U			
1811.375	7	0.002	RQ 9 1U			
1810.887	2	0.011	RQ17 4	RP 2 0U		
1809.992	3)*	0.006				
1809.841	5)*	0.004	RR13 0U	RQ 6 0U		
1809.286	6	0.003	RP11 3	RQ12 1L	RP 9 2L	RP14 5
1809.012	8))	0.003	RP11 3	PR 6 1L	PR 7 1L	RP 6 1U
1808.799	7	0.002	PR 8 1L	RQ13 2U	RR19 2U	
1808.603	6))	0.004	PR 5 1L			
1808.487	6	0.012	RP 7 1L	RP 9 2U		
1808.243	8	0.002	PR 9 1L			
1807.950	8)	0.002	PR 4 1L			
1807.853	3)	FF	RQ 7 0U			
1807.714	2	0.003	RP 3 0U			
1807.411	7	0.003	PR10 1L	RR16 1U		
1807.217	7	0.003	RQ10 1U			
1807.031	6	0.003	PR 3 1L	RQ14 2L		
1806.860	5	0.004	RR14 0U			
1806.664	2	FF	RP13 4			
1806.393	3	0.006	RQ16 3L			
1806.236	6	0.002	PR11 1L			
1805.807	7	0.002	PR 2 1L	RQ13 1L	RQ16 3U	
1805.583	4	0.003	RQ 8 0U			
1805.086	1	0.013				
1804.748	7	0.001	PR12 1L			
1804.298	5	0.003	RQ18 4	PR 1 1L	RP 8 1L	
1804.055	4)	0.006	RP 4 0U			
1803.924	4)	0.004	RP 7 1U			
1803.646	5	0.002	RR15 0U	RP10 2L		
1803.168	3)	0.004	RQ 9 0U	RQ14 2U		
1802.972	7)	0.002	RR 9 0U	PR13 1L		
1802.708	7	0.002	RP12 3U	RQ11 1U	RP12 3L	
1802.483	5	0.004	RP12 3U	RR17 1U	RP10 2U	
1802.341	1n	F	RR20 2U			
1802.021	5	0.003	RQ14 1L			
1801.848	4))	0.006	RQ15 2L			
1801.184	1	0.011				
1800.831	6	0.003	PR14 1L			

1824.446	1n	F	RR18 2L?
1824.323	4	0.007	RQ10 2L
1824.132	5	0.003	RQ 5 1U
1823.694	5	0.003	RR12 1U
1823.351	2•	FF	
1823.203	4))•	0.008	RQ10 2U RP12 5
1822.915	7)	0.006	RQ 7 1L RQ15 4
1822.801	5)	0.004	RQ13 3L RP 3 1L
1822.641	5	0.001	RQ13 3U
1822.237	6	0.002	RR 4 oU RR 5 oU
1821.852	7	0.002	RR 3 oU RR 6 oU RP 3 1U
1821.548	7	0.002	RQ 6 1U
1821.138	6)	0.002	RR 7 oU
1820.977	5))	0.005	RR 2 oU RR20 3U RQ17 5 RP 9 3
1820.731	7	0.002	RQ 8 1L
1820.465	3	0.004	RQ11 2L
1820.204	5	0.003	RR13 1U
1820.049	5	0.003	RR 8 oU
1819.844	4	0.005	RR 1 oU RP11 4
1819.616	2	0.005	RP 4 1L
1819.362	1	0.009	RP 7 2L
1819.084	1	FF	RP 7 2U
1818.868	4))	0.004	RQ11 2U
1818.565	7	0.002	RQ 7 1U RR 9 oU
1818.255	6	0.002	RR 0 oU RQ 9 1L
1817.998	2	0.008	RP 4 1U
1817.707	4	0.003	RQ14 3L
1817.443	5	0.003	RQ14 3U
1817.239	2	FF	
1817.096	2	0.004	RQ16 4
1816.866	4	0.003	RQ10 oU
1816.639	1n	F	
1816.317	6	0.004	RR14 1U RQ12 2L RP13 5
1816.175	3	0.008	RP 5 1L
1815.928	2))	0.011	RQ 1 oU RR20 2L RQ19 6
1815.656	1n	F	
1815.531	6	0.002	RQ10 1L
1815.343	3	FF	RQ 2 oU
1815.183	8))	0.003	RQ 2 oU RQ 8 1U RP10 3
1814.804	6	0.002	RR11 oU RR21 3U RR18 2U
1814.593	4	0.003	RQ18 5
1814.449	3)	0.005	RP 8 2L
1814.326	3)	0.009	RQ 3 oU
1814.080	2))	0.009	RQ12 2U RP 8 2U
1813.729	3	0.004	RP 5 1U

1837.472	5)	0.003	RR17	3L	RR12	1L		
1837.298	5)	0.002	RR 3	1L				
1836.636	6	0.004	RR17	3U	RR 4	1U		
1836.491	6	0.004	RR 5	1U	RR13	1L		
1836.327	7	0.003	RR 3	1U	RQ 6	2L		
1836.202	4	0.009	RQ 6	2U				
1836.040	7)	0.003	RR 2	1L				
1835.911	7)	0.005	RQ10	3	RR 6	1U	RP 6	3
1835.571	5	0.003	RR 2	1U	RP10	5		
1835.225	3	0.005	RR14	1L	RR15	2L	RQ16	6
1834.959	6	0.002	RR 7	1U				
1834.529	5)	0.004	RR 1	1L				
1834.380	4)	0.002	RR 1	1U				
1834.158	1	0.008	RR14	2U				
1833.872	4	0.003	RR15	1L	RQ 7	2L		
1833.541	6	0.002	RQ13	4	RR 8	1U	RQ 7	2U
1833.096	1	0.008	RR18	3L				
1832.804	4	0.003	RQ15	5				
1832.375	1	0.005	RR16	1L				
1831.886	6)	0.004	RQ11	3	RR18	3U	RR16	2L
1831.707	6)	0.004	RR 9	1U				
1831.494	1	0.006	RP12	6?				
1831.222	1	0.012	RP 7	3				
1831.022	2	0.006	RQ 8	2L				
1830.542	2))	0.010	RQ 8	2U	RR17	1L		
1829.998	1	0.010	RR15	2U				
1829.836	3	0.004	RQ 2	1L				
1829.427	6))	0.004	RR10	1U	RP11	5		
1829.328	2)•	F	RQ 2	1U				
1828.996	5	0.002	RQ 3	1L	RQ17	6		
1828.815	1n	F	RR18	1L				
1828.458	1	0.008	RQ14	4				
1828.225	1	FF	RR17	2L?				
1828.033	5)	0.003	RQ 3	1U				
1827.887	6)	0.002	RQ 4	1L	RQ 9	2L		
1827.552	5)	0.003	RQ12	3L				
1827.432	5)	0.002	RQ12	3U				
1827.069	5	0.003	RQ16	5	RQ 9	2U		
1826.772	5	0.003	RR19	3U	RR11	1U		
1826.498	6	0.002	RR19	3U	RQ 5	1L		
1826.297	5	0.003	RQ 4	1U	RP 8	3		
1825.945	1	0.003	RP10	4				
1825.411	1	0.009	RR16	2U				
1825.211	1	0.009						
1824.842	5	0.002	RQ 6	1L				

1851.478	1	0.008	RQ13 6				
1850.849	5	0.004	RR 5 2	RR 6 2L			
1850.636	6	0.003	RR 4 2	RR 6 2U			
1850.406	5	0.002	RQ 5 3	RR 7 2L			
1850.255	3	0.004	RQ 9 4				
1850.121	4)	0.005	RR 7 2U				
1849.997	4)	0.009	RR 3 2				
1849.661	3	0.005	RR 8 2L				
1849.168	3	0.003	RR 8 2U				
1849.004	5	0.003	RR 2 2				
1848.754	4	0.004	RR14 3L				
1848.516	4))	0.003	RR14 3U	RR 9 2L			
1848.229	6	0.002	RQ 6 3				
1848.056	2n	F	RR17 4				
1847.934	4	0.003	RQ12 5				
1847.732	3	0.006	RR 9 2U	RQ15 7			
1847.122	3	0.004	RR10 2L				
1846.628	3	0.004	RQ10 4				
1846.386	1n	F	RQ14 6	RR22 7?			
1845.989	3	0.004	RR10 2U				
1845.695	5	0.003	RQ 7 3				
1845.346	4	0.002	RR15 3L	RR11 2L			
1844.950	3	0.003	RR15 3U				
1844.311	1n	F					
1844.094	1n	F					
1843.870	1	FF	RP10 6				
1843.699	2)	0.006	RR11 2U				
1843.514	2)	0.009	RR18 4				
1843.257	5	0.002	RR12 2L	RQ13 5			
1842.800	6)	0.001	RQ 8 3				
1842.645	4)	0.003	RQ11 4				
1842.081	1n	F					
1841.850	1	0.004	RQ16 7				
1841.708	3)	0.004	RQ 3 2				
1841.583	2)	0.004	RR16 3L				
1840.996	4)	0.005	RR16 3U	RR12 2U	RQ15 6		
1840.865	2	F	RR13 2L				
1840.260	3	0.002	RQ 4 2				
1840.037	1	0.009	RP 5 3				
1839.653	7)	0.005	RR 7 1L	RR 8 1L			
1839.479	8)	0.003	RQ 9 3	RR 6 1L	RR 9 1L		
1838.989	6	0.002	RR 5 1L	RR10 1L			
1838.478	3)*	FF	RQ 5 2				
1838.297	7))	0.004	RQ14 5	RQ12 4	RR 4 1L	RR11 1L	RR14 2L
1837.817	1	FF	RR13 2U	RP11 6			

1869.254	4)	0.002	RR14 5		
1868.471	2	0.006	RQ 6 5		
1868.142	2	0.004	RR13 7	RQ 9 6	
1867.436	3	0.003	RR11 4		
1867.036	1	0.005			
1866.570	1n	F			
1866.151	1n	F			
1865.939	4	0.003	RQ 7 5	RR15 5	
1865.116	2	0.004	RR12 4		
1864.582	1n	F			
1864.493	1	0.006	RQ10 6		
1864.161	1	FF			
1864.049	1n	F			
1863.310	1	0.008	RR19 7		
1863.050	4	0.003	RQ 8 5		
1862.823	7)•	0.005	RR 5 3		
1862.701	7)•	0.005	RR 6 3		
1862.551	8)	0.003	RR 4 3	RR13 4	
1862.270	7	0.001	RR 7 3	RR16 5	
1861.930	6	0.003	RR 3 3		
1861.635	1n	F			
1861.426	6	0.002	RR 8 3		
1861.067	1	FF	RQ 5 4		
1860.535	1	0.009	RQ11 6		
1860.228	6	0.001	RR 9 3		
1860.041	1n	F			
1859.809	4	0.004	RQ 9 5		
1859.448	2	0.003	RR14 4		
1858.928	1	0.012	RQ 6 4		
1858.660	6	0.002	RR10 3		
1858.330	3	0.006	RR17 5	RQ13 7	
1856.712	5	0.002	RR11 3		
1856.403	3	0.008	RQ 7 4		
1856.221	4	0.002	RQ10 5	RQ12 6	
1856.035	2	0.004	RR15 4		
1854.617	1n	F			
1854.431	4)•	0.004	RR12 3L		
1854.327	4)•	0.007	RR12 3U		
1854.155	2	0.004	RR18 5		
1853.519	3	0.003	RQ 8 4		
1853.149	1	FF	RQ14 7		
1852.440	2	0.004	RR21 7?		
1852.241	6	0.003	RQ 4 3	RQ11 5	RR16 4
1851.762	4)	0.003	RR13 3L		
1851.608	4)	0.004	RR13 3U		

1891.257	3	0.003	RR 6 6		
1890.794	3	0.004	RR 7 6		
1890.622	1*	FF	RR14 8		
1889.960	2	0.003	RR 8 6		
1889.768	3	0.006	RR12 7		
1889.132	2	FF			
1888.771	3	0.004	RR 9 6		
1888.460	1	0.010	RR16 9		
1887.998	1n	F			
1887.169	4))	0.003	RR13 7	RR10 6	RR15 8
1885.635	0n	F			
1885.318	2	0.006	RR11 6		
1884.318	1	0.007	RR17 9		
1884.066	2	0.003	RR14 7		
1883.344	1	0.016	RR16 8?		
1882.983	7))	0.002	RR 5 5	RR 6 5	RR12 6
1882.492	5	0.003	RR 7 5		
1881.678	5	0.002	RR 8 5		
1880.879	1*	0.015			
1880.638	2)	FF	RR15 7		
1880.515	5)	0.003	RR 9 5		
1879.838	0n	F	RR18 9		
1878.975	5	0.002	RR10 5		
1878.629	1	0.012	RQ 8 7		
1878.182	1n	F			
1877.945	1n	F			
1877.730	1n	F			
1877.343	1	0.005	RR14 6		
1877.090	4	0.002	RR11 5		
1876.849	2	0.005	RR16 7		
1875.766	1n	F			
1875.366	1	0.008	RQ 9 7		
1874.836	4	0.002	RR12 5		
1874.032	1	0.008	RR15 6		
1873.468	5))	0.003	RR 5 4	RR 6 4	
1873.259	5	0.003	RR 4 4		
1872.950	4	0.004	RR 7 4		
1872.696	1	0.007	RR17 7		
1872.468	1n	F			
1872.179	5))	0.003	RR13 5	RR 8 4	
1871.361	1n*	FF	RQ 8 6		
1870.927	4	0.003	RR 9 4		
1870.299	1n*	FF	RR16 6		
1869.840	1	0.002	RQ13 9		
1869.384	3)	0.004	RR10 4		

1910.351	0	F		
1910.722	0	F		
1909.697	1	FF		
1907.189	2	0.003	RR 9 9	
1906.893	0	FF		
1906.131	1n	FF		
1906.014	1n	F		
1905.734	1n	F		
1905.602	1	0.006	RR10 9	
1905.441	1•	FF		
1904.738	1•	FF		
1904.364	1n	F		
1904.240	1n	F		
1903.643	1	0.006	RR11 9	
1903.316	1	0.006	RR 8 8	
1903.238	1n	0.003		
1902.669	1•	FF		
1902.102	1	0.005	RR 9 8	
1901.811	1	FF		
1901.684	1n	F		
1901.355	1	0.008	RR12 9	
1900.937	1n	F		
1900.550	1	0.008	RR10 8	
1900.055	1n	F		
1900.520	0	0.008		
1899.824	0	FF		
1898.746	1)	F	RR13 9	
1898.623	1)	0.007	RR13 9	RR11 8
1898.477	1	0.010		
1898.023	4	0.003	RR 7 7	
1897.789	1n	FF		
1897.483	1•	0.015		
1897.189	4	0.002	RR 8 7	
1896.744	1n	F		
1896.351	1	0.003	RR12 8	
1896.042	3	0.005	RR 9 7	
1895.646	1	0.011	RR14 9	
1894.639	3	0.004	RR10 7	
1893.671	1))	0.011	RR13 8	
1893.570	1n	FF		
1893.296	1n	F		
1893.217	1	FF		
1892.023	3	0.006	RR11 7	
1891.866	1)n	F		
1891.694	1	FF		

Table A5

A_0 Band (ref. section 7.2)

Key

As for table A3 p343

(See also section 9.3 for an investigation of the standard errors of this band.)

27,000 +

1092.133	o	F	PP16 8	
1091.631	o	F		
1091.402	o	F	PP24 5?	
1091.271	o	0.014		
1088.530	1	0.004	PP13 9	
1086.973	o	F	PQ19 9	
1085.038	o	0.005	PP17 8	PQ26 7?
1084.283	o	0.007	PP20 7	
1082.281	o	0.010	PP14 9	
1081.846	o	FF	PP25 5?	
1081.670	o	FF		
1079.928	o	F	PP23 6	
1077.975	o	F		
1077.702	o	FF	PP18 8	
1075.933	o	0.007	PP21 7	
1075.744	o	0.011	PP15 9	
1071.749	o	FF		
1070.657	o	FF	PP24 6?	
1070.468	o	FF	PP 12 10	
1068.924	o	FF	PP16 9	
1068.883	o	FF		
1068.735	o	F		
1067.843	o)	F		
1067.741	o)	F		
1067.332	o•	F	PP22 7	
1066.216	o	FF		
1065.091	o	F		
1063.445	o	F		
1061.925	o	F		
1061.765	o•	FF	PP17 9	
1059.041	o	F		
1058.364	o	0.015	PP23 7	
1056.750	o	FF		
1054.315	o	FF	PP18 9	

1120.159	0	FF	PP31	1L		
1120.022	0	0.016	PQ12	9		
1119.524	1	0.002	PQ25	5U		
1119.062	0*	FF	RP30	1U		
1118.170	1	0.003	PP21	5		
1117.776	0	0.008	PP12	8		
1117.464	0	0.008				
1117.074	0	F				
1116.171	0	F	PQ13	9		
1114.636	1	0.004	PP16	7		
1114.373	0	FF	PQ25	6?		
1114.158	1	0.008	PQ22	7		
1113.896	0	0.006	PP19	6		
1112.332	0	0.005				
1112.002	1	F	PQ14	9		
1111.816	0	0.018	PP13	8		
1111.464	0*	FF				
1111.221	0	F				
1110.881	0	F				
1110.626	1	0.026	PP 9	9		
1110.290	1	0.016				
1110.045	1	0.010	PP32	1L		
1109.527	1	0.004	PP22	5		
1107.636	0	0.002	PQ15	9		
1107.495	1	0.004	PP17	7		
1107.328	0	FF	PQ23	7		
1105.863	0	0.012	PP20	6		
1105.528	1	0.004	PP10	9	PP14	8
1104.752	0	F				
1104.380	1	F				
1103.885	0	F				
1102.941	0	0.004	PQ16	9		
1102.397	0	F				
1102.211	0	F				
1101.845	0	F				
1100.573	0))	0.004	PP23	5		
1100.165	2)	0.004	PP11	9		
1100.059	1)	0.006	PP18	7		
1099.026	0	0.006	PP15	8		
1098.043	0	0.005				
1097.880	0	F	PQ17	9		
1094.490	1	0.005	PP12	9		
1092.762	0	F	PQ25	7		
1092.554	0	F	PQ18	9		
1092.316	0	0.004	PP19	7		

1138.416	1	0.005	PP21	4L	PQ18	7
1137.531	0	0.005	PP24	3L		
1137.303	0	0.012	PP21	4U		
1136.913	0	F				
1136.226	1	0.008	PP16	6		
1135.860	0	F	PQ22	6?		
1135.392	0	F	PQ14	8		
1135.243	0	FF	PQ25	5U		
1135.086	0	FF	PQ25	5L		
1134.697	0	F				
1134.567	2	0.003	PP19	5		
1134.276	2))	0.004	PP13	7		
1133.883	0	0.004	PP 9	8		
1133.293	0	0.011	PQ30	3U	PQ29	3L
1132.789	1	0.005	PQ19	7		
1131.693	0	FF				
1131.525	0	0.004	PP23	3U		
1130.901	0	F	PQ15	8?		
1130.716	0	F				
1130.509	0	F	RP30	0U		
1130.003	1	0.005	PP30	1L	PP22	4L?
1129.804	0	0.003	PQ 9	9	RP29	1U
1129.367	0	F				
1129.077	1	0.004	PP17	6		
1128.931	1	FF	PQ23	6	PP10	8
1128.798	1	0.008				
1128.026	2	0.003	PP14	7		
1127.513	0	F	PQ26	5U		
1127.329	0	FF	PQ26	5L		
1126.860	1	0.005	PQ20	7	PQ10	9
1126.524	1	0.005	PP20	5		
1125.426	0	F				
1124.658	0	FF				
1124.413	0	F				
1124.199	0	FF				
1123.865	0	FF				
1123.578	0	0.010	PQ11	9		
1123.451	1	0.00[illegible]	PP11	8		
1121.815	0	F	PQ24	6		
1121.631	0	0.005	PP18	6		
1121.484	2	0.003	PP15	7		
1121.252	0	FF	PQ17	8	PP23	4L?
1120.803	0	F	PP24	3U		
1120.667	1	0.007	PQ21	7		
1120.481	0	F	PP26	3L		

1157.309	0	F				
1156.900	4	0.003	PP16	5		
1156.716	2))	0.007				
1156.503	2	0.006	PQ22	5		
1156.319	4	0.002	PP 9	7		
1155.871	1	0.003	PP13	6		
1154.620	0	FF	PP19	4L		
1154.386	1	0.005	PQ19	6		
1154.094	0	0.003	PQ25	4L	PP19	4U
1153.828	1))	0.005	PP22	3L		
1153.433	2	0.004	PQ15	7		
1152.730	1	0.004	PQ28	1U		
1152.005	1	0.008	PQ28	3U		
1151.634	1	0.005	PP21	3U	PQ27	3L
1151.256	3	0.003	PP10	7		
1150.674	0	0.007	RP27	1U		
1150.062	0	F	PQ10	8?		
1149.930	0	F				
1149.745	3	0.003	PP17	5	PQ23	5
1149.611	3	0.004	PP14	6	RP28	0U
1149.134	0	0.010				
1148.948	1	0.004	PP28	1L		
1148.723	2	0.005	PQ16	7		
1148.514	1	0.004	PQ20	6		
1147.850	0	FF				
1146.857	1	0.006	PQ11	8		
1146.663	0•	FF	PP20	4L		
1145.898	3	0.003	PP11	7		
1145.775	1	0.006	PP20	4U	PP23	3L
1144.822	0	0.007				
1144.175	0	F				
1143.722	2	0.005	PQ17	7		
1143.454	2	FF				
1143.069	1	0.008	PP15	6		
1142.870	0	0.011	PQ29	3U		
1142.641	1))	0.006	PQ24	5	PQ28	3L
1142.310	3	0.003	PP18	5	PQ21	6
1142.067	0	FF				
1141.511	0	0.009				
1140.940	0	0.003	PQ27	4U		
1140.246	3	0.003	PP12	7		
1139.990	0	F				
1139.614	0	0.009	PP29	1L		
1139.511	0	FF	PQ13	8		
1138.639	1	0.005	PP 8	8		

1169.663	1	0.007	PP17 4L	
1169.350	4)	0.004	PP17 4U	PQ11 7
1169.193	4)	0.005	PQ20 5	PP20 3L
1168.957	0	F	PQ23 4L	
1168.697	0	0.010	PQ25 3L	
1168.231	1	F		
1168.015	0	F		
1167.737	0	0.011	RP26 0U	
1167.487	2	0.005	PP11 6	
1166.824	1	0.003	PP26 1L	
1166.626	0	0.013		
1166.394	0	0.005	PQ27 2U	
1165.814	2	0.004	PQ12 7	
1165.581	4	0.002	PP 7 7	
1165.355	1))	0.006	PQ17 6	
1164.896	0	F		
1163.750	4	0.002	PP15 5	
1163.597	1	F		
1163.388	0	F		
1163.016	2	0.004	PQ21 5	
1162.823	0	0.002		
1162.438	0	0.004	PQ27 1U	
1162.262	0	FF	PP18 4L	
1161.972	3)	0.004	PQ13 7	
1161.815	2)	0.006	PP12 6	PP18 4U
1161.686	2	FF	PQ24 4L	
1161.563	1	0.004	PP21 3L	
1161.339	0	0.010		
1161.102	4	0.004	PP 8 7	
1160.947	1	0.002	PP20 3U	
1160.812	2•	0.007	PQ27 3U	RP26 1U
1160.361	0	0.007	PQ26 3L	
1160.019	1	0.007	PQ18 6	
1158.902	0	FF		
1158.782	0	FF	RP27 0U	
1158.386	0	F		
1158.013	2	0.002	PP27 1L	
1157.855	2	0.004	PQ14 7	

1186.320	2	0.005	PP17 3U			
1186.058	4	0.003	PQ17 5			
1185.227	1))	0.004	PQ25 2U			
1184.979	1	0.004	PR16 7	RP24 0U		
1184.714	0	F	PQ24 2L			
1184.540	2	0.004	PQ24 3U			
1184.362	1	0.005	PQ23 3L			
1184.077	0	F				
1183.617	4	0.004	PP15 4L	PP18 3L	PP24 1L	PQ13 6
1183.440	2	0.010	PP15 4U			
1182.934	0	F				
1182.689	3	0.004	PP 8 6			
1182.512	5	0.002	PP12 5	PQ21 4L		
1182.055	0	0.011	PR17 7	PP18 2U		
1181.262	0	0.007	PQ25 1U			
1180.951	0	FF				
1180.723	4	0.003	PQ18 5	RP24 1U		
1180.500	1	0.006	PQ 7 7			
1180.095	0	0.006				
1179.949	0	0.007				
1179.462	1	0.003	PQ14 6			
1178.862	0	0.010	PR18 7			
1178.276	2	0.003	PP18 3U			
1178.156	2	0.003	PQ 8 7			
1177.908	2	0.005	PP 9 6			
1177.459	0	FF				
1177.025	2	0.005	PQ25 3U			
1176.727	3))	0.006	PP16 4L	PQ24 3L		
1176.536	5	0.001	PP13 5	PP16 4U	PP19 3L	RP25 0U
1176.116	1	0.004	PQ26 2U			
1175.918	1))	0.007	PQ22 4L			
1175.502	2)	0.004	PQ 9 7			
1175.375	3)	0.008	PP25 1L			
1175.123	3	0.003	PQ19 5	PQ15 6		
1174.256	0	F				
1173.973	0	0.012				
1172.842	2))	0.003	PP10 6			
1172.574	2	0.004	PQ10 7			
1172.357	1	0.003				
1172.185	0	0.012				
1171.986	0	0.006	PQ26 1U			
1171.811	0n	F	PP19 2U			
1170.847	1	0.003	RP25 1U			
1170.309	4	0.003	PP14 5	PQ16 6		
1169.830	2	0.005	PP19 3U			

1202.114	1	0.006	PQ 7 6		
1201.321	2	0.004	PP19 2L	RP22 0U	
1201.164	3	0.003	PP15 3U		
1200.801	1	0.010	PQ18 4U		
1200.425	1	0.012	PQ22 2L	PQ18 4L	
1200.195	4	0.002	PQ14 5		
1199.761	2	0.003	RP22 1U	PQ 8 6	
1199.390	4	0.003	PP22 1L		
1199.095	1	0.004	PQ23 1U		
1198.907	0	F			
1198.622	5	0.002	PP 9 5	PQ21 3L	
1198.328	3	0.005	PQ22 3U		
1197.450	0	0.012			
1197.179	3))•	0.004	PP16 3L	PQ 9 6	
1196.368	3))	0.004	PP13 4		
1196.038	2	0.006	PR10 7		
1195.772	4	0.004	PQ15 5		
1195.566	0	FF			
1195.275	2	0.004	PQ19 4U		
1194.908	1	F	PR11 7		
1194.740	2	0.006	PQ19 4L		
1194.468	1	0.005	PP20 2L		
1194.161	3)	0.005	PQ10 6		
1194.051	3)	0.009			
1193.938	3)	0.004	PP16 3U	PQ24 2U	
1193.752	2	0.008			
1193.542	5	0.002	PP10 5	PR12 7	
1193.267	2	0.005	RP23 0U		
1192.233	1	0.007			
1191.826	2	0.006	PR13 7	PP17 2U	
1191.653	5	0.002	PQ23 3U	PQ22 3L	PP23 1L
1191.364	3	0.004	PP 6 6		
1191.051	4	0.003	PQ16 5		
1190.518	2	0.004	PP17 3L		
1190.306	2	0.004	RP23 1U	PQ24 1U	
1190.064	2))	0.004	PP14 4		
1189.599	1	0.010			
1189.442	2	0.008	PQ20 4U		
1189.191	0	F			
1188.913	0	FF			
1188.786	0	F	PQ20 4L		
1188.168	5	0.003	PP11 5		
1187.414	3))	0.005	PQ12 6		
1187.168	3	0.003	PP 7 6		

1216.291	3	0.003	PQ19 3U		
1215.910	7	0.003	PP 5 5	PP13 3L	PQ21 1U
1215.656	2	0.004	PQ15 4U		
1215.526	1	0.003	PQ15 4L		
1215.025	1	FF	PQ20 2L		
1214.881	5	0.003	PQ10 5		
1214.521	4	0.003	PP13 3U		
1214.392	1	0.007	PP17 2L		
1214.052	4	0.002	PR20 5	PP20 1L	
1213.385	2)	FF	PR13 6	PP10 4	
1213.279	3)	FF			
1212.052	5	0.002	PP 6 5		
1211.646	5	0.003	PQ11 5	PQ19 3L	
1211.436	0	F	PR14 6		
1210.985	2	0.005	PQ16 4U		
1210.792	1	0.004	PQ16 4L		
1210.655	3	0.004	PQ20 3U		
1210.286	1	0.004	PQ22 2U		
1209.884	4	0.003	PP14 3L	PP15 2U	
1209.507	0•	FF			
1209.141	2	0.003	PR15 6	RP21 0U	
1209.004	1	0.004	RP21 1U		
1208.655	0	F			
1208.395	1•	FF			
1208.127	5	0.004	PQ12 5		
1208.001	5)	0.006	PP11 4	PP14 3U	PP18 2L
1207.878	6)	0.004	PP 7 5	PQ21 2L	
1207.632	2	0.004	PQ22 1U		
1207.068	0	FF			
1206.973	0	F			
1206.854	4	0.002	PP21 1L		
1206.516	1n	F	PR16 6		
1206.037	1	0.010	PQ17 4U		
1205.738	2	0.005	PQ17 4L		
1205.312	2	0.003	PQ20 3L		
1204.669	3	0.004	PQ21 3U		
1204.307	4	0.002	PQ13 5		
1204.092	1	FF	PQ 6 6?		
1203.658	3))	0.006	PR15 3L		
1203.382	5	0.002	PP 8 5		
1202.563	0	F			
1202.290	3	0.002	PP12 4	PQ23 2U	

1234.196	2	0.003	PR13 5		
1233.987	5	0.002	PP17 1L		
1233.458	4	0.003	PQ15 3L		
1233.275	1	0.007	PP12 2U		
1232.364	5	0.004	PP10 3L		
1232.183	3))	0.007	PR14 5	RQ26 1U	PP14 2L
1231.931	5)	0.004	PP10 3U		
1231.822	4)	0.004	PP 6 4		
1231.572	3	0.007	PQ19 2U		
1231.434	5)	0.011	PQ11 4	PQ19 1U	
1231.329	5)	0.009	PQ16 3U	RP18 0U	
1230.773	0•	FF			
1229.937	1	0.004	PR15 5		
1228.493	4	0.003	PQ16 3L		
1228.341	1	0.004	PQ18 2L		
1227.936	3	0.003	PQ12 4		
1227.618	5	0.002	PP 7 4	PP18 1L	
1227.351	2	0.006	PR 16 5		
1227.122	4	0.003	PP11 3L		
1226.831	4	0.003	RP19 1U		
1226.614	5	0.002	PQ 5 5	PQ17 3U	
1226.475	5	0.004	PP11 3U	PP15 2L	
1226.008	1	0.006	RQ27 1U	PP13 2U	
1225.760	1	F			
1224.873	4	0.003	PQ 6 5	PQ20 2U	
1224.483	1	0.005	PR17 5		
1224.127	4	0.003	RP19 0U	PQ13 4	
1223.786	3	0.002	PQ20 1U		
1223.363	1	0.003			
1223.188	5	0.002	PP 8 4	PQ17 3L	
1222.808	4	0.002	PQ 7 5		
1221.828	1	0.009	PQ19 2L		
1221.614	5	0.002	PP12 3L	PQ18 3U	
1221.307	1	0.003	PR18 5		
1220.965	5	0.002	PP19 1L		
1220.658	4)	0.004	PP12 3U		
1220.482	5)	0.003	PQ 5 5		
1220.039	2)	FF	PQ14 4U		
1219.956	2)	FF	PQ14 4L		
1218.382	3	0.003	PP 9 4		
1218.045	3	0.003	RP20 1U		
1217.822	5	0.002	PQ 9 5	PR19 5	
1217.597	3	0.003	PQ18 3L		
1216.738	2	0.004	RP20 0U		

1249.134	2	0.003	PQ16 2U		
1248.081	1	0.002	RP21 3L	PR23 3L	
1247.857	3	0.004	PQ 4 4	PP11 2L	
1247.398	4	0.003	PQ12 3U		
1246.974	0	F	RR30 1U		

1246.466	7)	0.005	PQ 5 4	PP10 2U	PP 7 3U
1246.341	7)	0.006	PQ 5 4	PP 7 3L	PQ12 3L
1245.905	6	0.002	PP15 1L	PQ15 2L	
1245.640	4	0.002	PQ17 1U		
1245.392	1	0.006	RP21 3U		

1245.079	3	0.003	RP16 0U		
1244.646	2	0.003	PQ 6 4		
1244.449	2	0.004	RQ24 1U		
1244.238	1	0.006	PR24 3L		

1243.882	1	FF			
1243.738	6))	0.002	PQ13 3U	RP17 1U	PQ17 2U
1243.358	1	0.011			
1242.851	2	0.004	PP12 2L		
1242.718	0	F	PR32 1L		

1242.603	4))	0.005	PQ 7 4		
1242.359	5	0.002	PQ13 3L		
1242.066	5	0.003	PP 8 3L		
1241.916	5	0.002	PP 8 3U		
1241.589	1	0.010			

1240.979	1n	F	RP21 2L?		
1240.451	1	FF	RQ27 3U		
1240.289	4))	0.004	PQ 8 4	PQ16 2L	
1240.088	6	0.002	PP16 1L	PP11 2U	
1239.892	5	0.004	PR 7 5	PR 6 5	PQ14 3U

1239.686	1	0.004	PR 8 5		
1239.331	4	0.002	PP 4 4		
1239.175	1	0.006	PR 9 5	RQ25 2U	
1238.705	4	0.004	PQ18 1U		
1238.333	4))	0.003	PR10 5	RQ25 1U	RP17 0U

1238.070	5	0.002	PQ14 3L		
1237.853	3	0.003	PQ18 2U		
1237.610	5	0.002	PQ 9 4	PP13 2L	
1237.345	5))	0.003	PR11 5	PP 9 3L	
1237.080	4	0.002	PP 9 3U		

1235.878	2	0.005	PR12 5		
1235.740	5	0.002	PP 5 4	PQ15 3U	
1235.397	3	0.003	RP18 1U		
1234.682	4))	0.003	PQ10 4		
1234.515	1	0.006	PQ17 2L		

1262.055	3	0.003	RQ21 1U		
1261.840	6	0.002	PP12 1L		
1261.483	8)	0.003	PP 3 3	PQ 7 3U	PP 8 2L
1261.368	6)	0.005	PQ 7 3L		
1260.962	1	0.005	RP19 1L	RR29 0U	RQ25 0U
1260.586	1	0.005	PR17 3U		
1260.370	2	0.004	PR29 1L	PQ12 2L	
1260.060	0	FF	RR28 1U		
1259.646	1	0.009	PR 6 4	PR 7 4	
1259.452	4	0.003	RP15 1U		
1259.232	5	0.003	PQ 8 3U		
1258.986	5	0.002	PQ 8 3L	PR 9 4	
1258.770	4	0.002	RQ25 3U	PQ14 2U	
1258.555	1	F			
1258.411	6	0.002	PQ15 1U		
1258.155	7)	0.002	PP 4 3		
1258.021	3)	0.010	RP14 0U		
1257.850	2	0.009	PP 8 2U		
1257.454	1	0.006	RQ26 3L		
1257.136	3	0.006	PP 9 2L	PR11 4	
1256.777	7)	0.006	PP13 1L		
1256.670	6)	0.005	PQ 9 3U		
1256.427	2))	FF	RP20 3L	RQ26 0U	
1256.291	6	0.002	PQ 9 3L	RQ22 1U	
1255.873	3)	0.006	RP20 1L	PQ13 2L	
1255.751	2)	0.005	RQ23 2U	PR12 4	
1255.200	0*	FF	PR21 3L	RR30 0U	
1254.749	1	0.009	PR30 1L		
1254.555	7	0.003	PP 5 3		
1254.150	4	0.003	PQ15 2U		
1253.982	1	F	PR13 4U		
1253.847	5	0.003	PQ10 3U		
1253.614	0	FF	RR29 1U		
1253.288	5	0.002	PQ10 3L		
1253.102	1	F			
1252.616	2	0.004	PP10 2L		
1252.365	2	0.006	PP 9 2U		
1252.213	5	0.003	PQ16 1U		
1252.001	1	0.009	PR14 4U		
1251.688	5	0.003	RP16 1U	RP15 0U	
1251.483	6	0.003	PP14 1L		
1251.016	2	0.005	PQ14 2L		
1250.703	8))	0.006	PP 6 3	PQ11 3U	RP21 1L
1250.403	2	0.004	RQ23 1U		
1249.978	5	0.004	PQ11 3L		

1274.689	6	0.002	PQ12 1U		
1274.235	3	0.003	PR13 3L		
1274.024	4)•	0.005	RQ24 1L	RP13 1U	
1273.914	2)•	0.003	PR12 3U		
1273.320	6	0.002	RQ19 1U	PQ10 2U	RQ22 0U
1272.990	2	0.004	PP 5 2L	PR23 2L	
1272.651	2	0.004	PR14 3L		
1272.401	2	0.004	RQ24 3L	RP18 3L	RR26 1U
1271.968	2	0.004	PR13 3U		
1271.811	4	0.003	PP 5 2U	PQ 9 2L	
1271.497	1	FF	RR27 0U		
1271.201	7))	0.002	RP18 3U	PP10 1L	RQ21 2U
1271.034	1	F			
1270.849	3	0.002	PR15 3L	RP17 1L	PR27 1L
1270.431	1	0.009	RP21 5		
1270.269	4	0.002	PQ11 2U		
1270.100	4	0.002	RP12 0U		
1269.669	6	0.003	PR14 3U	PQ13 1U	
1269.390	3	0.007	PP 6 2L	RQ23 0U	
1269.265	1	F	PR16 2U		
1269.108	0	0.004	RQ25 1L		
1268.798	1	0.004	PR16 3L		
1268.334	3	0.003	PQ10 2L		
1267.874	3)	0.004	PQ 3 3		
1267.734	3)	0.004	RQ20 1U		
1267.537	2	0.005	PP 6 2U		
1267.271	2	0.005	RQ24 3U		
1267.050	2	0.004	PR15 3U		
1266.997	1n	F			
1266.856	6)	0.003	RP14 1U	PQ12 2U	
1266.671	8)	0.002	PQ 4 3	PP11 1L	
1266.330	0•	F	RR28 0U	RR27 1U	
1265.962	1	0.004	RP18 1L		
1265.753	1	0.004	PR28 1L		
1265.528	2	0.005	PP 7 2L		
1265.242	5	0.003	PQ 5 3		
1264.751	1	F			
1264.524	3	0.003	RP19 3L	PQ11 2L	
1264.205	7	0.002	PQ14 1U	RP13 0U	
1264.041	3	0.006	PR16 3U	PR18 3L	
1263.630	1)	FF	RQ22 2U		
1263.486	6)	0.003	PQ 6 3		
1262.969	4	0.004	PP 7 2U	PQ13 2U	

1286.789	1	0.004	PQ 2 2U				
1286.694	2	FF	RQ25 5				
1286.520	5	0.004	RP16 3U	RP 9 0U			
1286.332	3	0.007	RQ22 3L				
1286.081	2	0.007	PQ 3 2U				
1285.854	0	FF					
1285.705	1•	0.004	PR19 2L				
1285.588	3•	0.007	RQ19 2U	RR24 0U			
1285.410	2	0.003	PQ 3 2L				
1285.100	4	0.002	RP14 1L	PQ 4 2U	RQ21 2L		
1284.511	2	0.003	PR24 1L				
1283.989	6)	0.003	RQ17 1U	PQ 4 2L	RR24 1U		
1283.877	3)	0.005	PQ 5 2U	RQ19 0U			
1283.498	8))	0.001	RQ22 1L	PQ10 1U	PP 7 1L		
1283.029	2	0.004	RQ22 3U	RR20 2L			
1282.855	0	0.009	RP15 2L				
1282.343	4))	0.005	PP 2 2U	PP 2 2L	PQ 6 2U	PQ 5 2L	
1281.292	4	0.002	RP10 0U				
1281.119	1	0.007	RR25 0U				
1280.817	3	0.002	RP12 1U				
1280.576	4	0.003	PR 7 2U	RQ20 0U			
1280.439	2	0.005	RP15 1L				
1280.194	4	0.004	PR25 1L	PQ 6 2L			
1280.016	1	0.009	PR21 2L				
1279.848	1	0.004	RP17 3L				
1279.581	7))	0.005	RQ23 3L	PP 8 1L	PP 3 2L		
1279.310	7	0.002	PQ11 1U				
1279.112	2•	FF	RP17 3U	PP 3 2U			
1278.902	3	0.004	RQ23 1L				
1278.704	6	0.003	PR 7 3L	RQ18 1U			
1278.496	6))	0.003	PR 6 3U	PR 6 3L	PR 7 3U	PQ 8 2U	PR 8 3L RQ20 2U
1278.187	5	0.003	PR 8 3U	PR 9 3L			
1278.057	2	F	PR 5 3				
1277.754	3	0.005	PQ 7 2L				
1277.591	4	0.003	PR 9 3U	PR10 3L			
1277.404	1	0.006	PR 4 3	PR11 3L			
1277.087	0	0.005	RQ21 0U				
1276.699	4	0.004	PR10 3U				
1276.386	4	0.004	PP 4 2L	RR26 0U			
1276.088	4	0.002	PQ 9 2U				
1275.821	4	0.004	RP11 0U				
1275.647	5)	0.005	PR12 3L	RP16 1L	PR26 1L	PP 4 2U	
1275.515	7)	0.004	PR11 3U	PR12 3L	PP 9 1L		
1275.370	3	0.007	RQ23 3U				
1274.956	3	0.005	PQ 8 2L				

1298.466	5))	0.007	RP11 1L	PR 7 2L	RQ17 2U	
1298.257	2n	F				
1298.088	2	0.005	PR11 2L			
1297.850	1	0.005	PR 6 2L			
1297.630	2	0.003	RR21 0U			
1297.393	2	0.005	PR12 2L			
1297.145	2	0.002	RQ20 3U	PR 5 2L		
1296.697	5	0.003	PP 3 1L			
1296.489	8	0.002	PQ 6 1U	PR13 2L		
1296.164	5))	0.003	RQ19 1L	PR 4 2L	RP 7 0U	
1295.934	4	0.004	RQ15 0U			
1295.762	4	0.002	PR21 1L			
1295.308	1	0.004	PR14 2L			
1295.118	0	0.004	RP13 2L			
1294.867	2	0.002	RP18 5	RR22 1U	PR 3 2L	
1294.650	1}	0.008	PR 5 2U	PR 6 2U		
1294.533	1)	FF				
1294.394	1	0.010	PR 4 2U			
1294.237	2	0.005	RQ24 5			
1294.027	6	0.001	RP15 3L	RQ15 1U	RP12 1L	PR 7 2U
1293.837	8	0.003	PQ 7 1U	PR15 2L	RR22 0U	
1293.719	7	0.003	PP 4 1L			
1293.431	4	0.003	RP10 1U			
1293.133	3	0.002	PR 8 2U	RQ16 0U		
1292.873	1	0.006	RQ 21 3L			
1292.260	5	0.003	PR22 1L	RQ18 2U		
1292.108	3	0.006	RQ 20 1L	RP13 2U		
1291.811	0	0.015	PR 9 2U			
1291.506	3	0.002	RP 8 0U			
1291.111	0n	F				
1290.974	1n	F				
1290.798	7	0.001	PQ 8 1U			
1290.520	6	0.002	PP 5 1L			
1290.305	3	0.005	RQ21 3U	PR17 2L		
1290.005	0	FF	PR10 2U			
1289.836	1	0.004	RR23 0U			
1289.675	2)•	FF	RP13 1L			
1289.549	1)•	0.013	RR23 1U			
1289.101	6	0.002	RQ16 1U			
1288.540	3	0.003	PR23 1L			
1288.144	1	0.008	PR18 2L			
1287.902	2	0.004	RQ21 1L			
1287.755	1	0.007	PR11 2U			
1287.352	7))	0.003	RP11 1U	PQ 9 1U		
1287.090	7	0.002	RP16 3L	PP 6 1L	RQ18 0U	

1310.744	6	0.003	RQ18 3L	PR15 1L		
1310.568	6	0.004	RP 8 1L	RR17 0U		
1310.434	4	0.006	RQ16 2L			
1310.234	6)	0.003	RQ15 1L	RQ 9 0U		
1310.120	3)	0.005	PR 2 1L			
1310.003	3)	0.007	RQ15 2U			
1309.694	4	0.004	RP16 5	RQ18 3U	RP 7 1U	
1309.477	3	0.004	RR19 1U			
1308.947	5	0.003	PR16 1L			
1308.470	4	0.003	RQ22 5	PR 1 1L	RP 4 0U	
1308.193	4	0.002	RQ10 0U			
1307.572	6))	0.003	RQ12 1U	RR18 0U		
1306.998	5)•	0.013	RP15 3L	RQ16 1L		
1306.864	6)•	0.005	RP13 3L	PR17 1L		
1306.729	4	0.003	RP13 3U	RP 9 1L		
1306.405	1	0.005	RP11 2L			
1305.993	4	0.002	RQ11 0U			
1305.808	2	0.003	RP15 4	RQ17 2L		
1305.082	3	0.003	RQ19 3L			
1304.834	3	0.005	RR20 1U			
1304.676	5	0.003	RP 8 1U	RP 5 0U		
1304.510	6	0.002	PR18 1L	RQ16 2U	RR19 0U	
1304.110	1)•	F	RQ21 4U			
1304.005	5)	0.003	PQ 1 1U			
1303.754	2	FF				
1303.608	6)	0.003	RQ19 3U	RQ17 1L	RQ12 0U	
1303.272	7	0.003	RQ13 1U	PQ 2 1U		
1302.643	3	0.003	RP10 1L			
1302.427	1	0.006	RP17 5			
1302.129	7	0.004	PQ 3 1U	PP 1 1L		
1301.869	5	0.004	PR19 1L	PP 1 1L		
1301.553	1	0.005	RQ23 5			
1301.199	4	0.003	RR20 0U	RQ13 0U		
1300.939	2	0.007	RQ18 2L	RP12 2L		
1300.623	7	0.002	RP14 3L	PQ 4 1U	RP 6 1U	
1300.355	1	0.005	RP14 3U			
1299.946	4	0.004	RR21 1U	RQ18 1L		
1299.465	4	0.002	PP 2 1L			
1299.213	4	0.004	RP 9 1U			
1299.111	3	FF	RQ20 3L			
1298.957	5	0.005	PR20 1L			
1298.748	8	0.003	RQ14 1U	PQ 5 1U	PR 9 2L	
1298.619	5))	FF	PR 8 2L	PR10 2L	RQ14 0U	RQ17 2U

1325.366	5))	0.006	RR15 1U	RR 2 0U		
1324.847	7	0.002	RQ 7 1U	RR10 0U		
1324.430	1	0.007	RP 4 1L			
1324.305	3	0.005	RQ12 2U	RR 1 0U		
1324.059	4	0.003	RP10 3			
1323.538	6	0.003	RQ10 1L	RR11 0U		
1323.165	1	0.004	RP14 5			
1322.853	3	0.003	RP 4 1U	RQ13 2L		
1322.633	0n	F	RR20 2U			
1322.389	2	0.009	RR 0 0U	RQ18 4		
1321.967	7)	0.002	RQ 8 1U	RR12 0U		
1321.815	5)	0.002	RR16 1U			
1321.497	3	0.005	RQ20 5			
1321.276	7	0.002	RQ16 3L	RQ11 1L	RP 5 1L	
1320.851	1	0.006	RR25 3L	RP 8 2U		
1320.670	4	0.002	RQ16 3U			
1320.505	0n	F	RR24 3U			
1320.052	4	0.004	RR13 0U	RQ 1 0U		
1319.937	3	0.015	RQ23 7	RQ13 2U	RQ 1 0U	
1319.539	4	0.003	RQ 2 0U			
1318.945	3)	0.003	RQ14 2L			
1318.816	8)	0.002	RQ 9 1U	RQ12 1L	RP 5 1U	RQ 3 0U
1318.641	3	0.004	RP11 3			
1317.951	6))	0.003	RR17 1U	RP 6 1L	RR14 0U	RQ 4 0U
1317.180	0	FF	RR21 2U			
1316.770	4	0.003	RQ 5 0U			
1316.598	2))	0.010	RP15 5	RQ19 4	RP 9 2L	
1316.139	5	0.001	RQ17 3L	RQ13 1L		
1315.716	8)	0.008	PR 8 1L	PR 9 1L	RR15 0U	
1315.589	8)	0.010	PR 8 1L	PR10 1L		
1315.353	9	0.003	RQ17 3U	RQ10 1U	PR 7 1L	RQ 6 0U
1315.158	7	0.002	RQ21 5	PR11 1L	RQ14 2U	
1314.765	6	0.002	PR 6 1L	RQ15 2L		
1314.457	6	0.004	RP 6 1U	PR12 1L		
1314.338	5*	FF	RP 7 1L			
1313.906	7	0.002	RR18 1U	PR 5 1L	RQ 7 0U	
1313.495	6	0.002	PR13 1L			
1313.272	6	0.003	RQ14 1L	RR16 0U		
1312.898	5	0.002	RP12 3	PR 4 1L		
1312.398	1	0.014	RP14 4			
1312.255	6)	0.003	PR14 1L			
1312.141	5)	0.005	RQ 8 0U			
1311.923	2	0.005	RP 3 0U			
1311.602	7	0.002	RQ11 1U	PR 3 1L		
1311.343	1	FF	RR22 2U			

1338.470	7)	0.003	RQ12 3U	RQ 8 2L	RP 7 3	
1338.188	6	0.002	RR10 1U			
1337.968	3	0.003	RQ 8 2U			
1337.784	2	0.003	RQ15 4			
1337.208	2	0.005	RR21 3U			
1336.674	1	0.006	RR17 2U			
1336.468	1	FF	RR20 2L			
1336.286	5	0.002	RR11 1U			
1336.106	1n	F	RR26 5?			
1335.865	3	0.003	RP10 4	RQ 9 2L		
1335.487	2))	0.006	RP12 5	RR22 3L		
1335.106	2	0.003	RQ 9 2U			
1334.701	5	0.005	RQ13 3L			
1334.502	5	0.003	RQ13 3U	RQ 2 1L		
1334.303	1	FF				
1334.012	6	0.003	RP 8 3	RR12 1U	RQ 2 1U	
1333.824	5	0.002	RQ 3 1L	RP 5 2		
1333.420	1	0.006	RQ21 7	RR21 2L		
1333.234	3	0.005	RQ18 5			
1332.980	7)	0.003	RQ16 4	RQ 4 1L	RQ10 2L	
1332.872	6)	0.003	RQ 3 1U			
1332.399	1	0.007	RR18 2U			
1332.059	2	0.005	RR22 3U			
1331.912	6	0.001	RQ 5 1L	RQ10 2U		
1331.423	6	0.003	RR13 1U	RQ 4 1U		
1330.889	1	0.006	RR23 3L			
1330.656	5	0.001	RQ 6 1L			
1330.497	4	0.004	RP11 4	RQ14 3L		
1330.244	5	0.004	RQ 14 3U			
1329.892	3	0.004	RQ11 2L			
1329.544	6	0.002	RQ 5 1U			
1329.183	6	0.002	RP 9 3	RQ 7 1L		
1328.555	3	0.002	RR14 1U			
1328.292	3	0.004	RQ11 2U			
1327.841	2	0.007	RQ17 4			
1327.549	8	0.004	RQ19 5	RQ 8 1L	RR 5 0U	RR 6 0U
1327.371	8	0.003	RQ 6 1U	RR 7 0U		
1327.190	4	0.002	RR 4 0U			
1326.802	4	0.003	RQ22 7	RP 3 1U	RR 8 0U	
1326.486	4	0.003	RR23 3U	RQ12 2L	RR 3 0U	
1325.984	5	0.003	RR24 3L	RQ15 3L	RR 9 0U	
1325.795	1	F	RP 7 2L			
1325.643	6	0.003	RQ15 3U			

1351.448	2)	0.006	RQ18 7			
1351.338	3)	0.005				
1351.086	6))	0.004	RR18 3L	RQ 8 3	RR14 2L	
1350.325	3)	0.004	RQ12 4			
1350.226	3)	0.005	RR18 3U			
1349.796	2	0.004	RR13 2U			
1349.228	1	0.003	RR15 2L			
1348.653	0•	FF				
1348.498	5)	0.002	RQ15 5			
1348.387	7)	0.003	RQ 9 3			
1348.044	7	0.003	RR11 1L	RR12 1L	RR13 1L	
1347.851	6	0.002	RR19 3L	RR10 1L	RR14 1L	
1347.565	6)	0.003	RR 9 1L	RR15 1L		
1347.480	2)•	F	RR24 5			
1347.286	3	0.008	RR16 1L			
1347.114	6	0.002	RR 8 1L	RR14 2U	RQ 3 2	
1346.881	2	0.010	RR17 1L			
1346.490	6))	0.005	RP10 5	RQ13 4	RR 7 1 L	RR18 1L
1346.280	3	0.005	RR19 3U			
1345.975	4	0.002	RQ 4 2			
1345.758	5	0.003	RQ19 7	RP 8 4	RR 6 1L	RR19 1L
1345.404	7	0.001	RQ10 3			
1345.156	1	0.004	RR20 1L			
1344.821	5	0.003	RR 5 1L			
1344.482	4))	0.004	RR21 1L	RQ 5 2		
1344.013	3	0.004	RR20 3L	RR15 2U		
1343.710	6	0.002	RQ16 5	RR 4 1L		
1342.767	3)	0.005	RQ 6 2L	RP 6 3		
1342.650	3)	0.006	RQ 6 2U	RP 6 3		
1342.306	8)	0.008	RQ14 4	RR 5 1U	RR 3 1L	
1342.190	7)	FF	RQ11 3	RR 6 1U		
1342.073	8	0.009	RQ11 3	RR 4 1U		
1341.753	6	0.001	RR 7 1U			
1341.407	5	0.003	RR 3 1U			
1341.161	1	0.004	RP11 5			
1340.907	7	0.003	RP 9 4	RR 8 1U	RR2 1L	
1340.764	3	0.005	RQ 7 2L			
1340.546	3	0.007	RR16 2U	RQ 7 2U		
1340.413	5	0.003	RR 2 1U			
1339.880	2	0.003	RR21 3L			
1339.738	5	0.004	RQ20 7	RR 9 1U		
1339.406	1•	FF	RR19 2L			
1339.161	5	0.004	RR 1 1L			
1339.010	4	0.004	RR 1 1U			
1338.600	7)	0.002	RQ17 5	RQ12 3L		

1368.895	6))	0.003	RR10 3			
1368.488	7	0.003	RR 3 3			
1367.863	5)	0.005	RQ10 5			
1367.745	7)	0.002	RR11 3			
1367.245	2	0.006	RQ 6 4			
1366.744	3	0.003	RQ15 7	RQ13 6		
1366.265	6))	0.001	RR20 5	RR12 3	RR17 4	
1365.731	0	F	RR24 7			
1365.362	0	F	RQ18 9			
1365.174	3	0.004	RQ 7 4			
1364.867	1	F				
1364.591	7	0.002	RR13 3L	RQ11 5		
1364.412	4	0.002	RR13 3U			
1362.923	2)	0.006	RR18 4			
1362.801	3)	0.005	RQ 8 4			
1362.545	5))	0.003	RR14 3L	RQ14 6		
1362.267	4	0.003	RR14 3U			
1361.973	3))	0.006	RR21 5	RQ16 7		
1361.029	4	0.003	RQ12 5			
1360.171	5	0.003	RQ 9 4	RR15 3L		
1359.782	4	0.004	RR15 3U			
1359.310	1	0.005	RR19 4			
1358.764	3	0.002	RQ 4 3			
1358.136	1))	0.008	RQ15 6			
1357.833	4)•	0.004	RR 7 2L			
1357.693	5)•	0.009	RR 6 2L	RR 8 2L		
1357.542	6)•	0.004	RR16 3L	RR 6 2U	RR 7 2U	RR22 5
1357.291	7)	0.005	RQ 5 3	RR 5 2	RR 9 2L	
1357.179	7)	0.005	RQ13 5	RQ10 4	RR 8 2U	
1356.965	4	0.005	RR16 3U			
1356.645	5	0.003	RR 4 2	RR10 2L		
1356.495	5	0.003	RR 9 2U	RR10 2L		
1355.703	4	0.002	RR 3 2			
1355.526	7	0.002	RQ 6 3	RR11 2L		
1355.378	4	0.004	RR10 2U			
1354.580	4	0.003	RR17 3L			
1354.433	5	0.005	RR 2 2	RR12 2L		
1353.901	4	0.003	RQ11 4	RR11 2U		
1353.767	4	0.004	RR17 3U			
1353.436	6	0.002	RQ 7 3			
1352.975	4)	0.003	RQ14 5			
1352.878	3)	0.004	RR13 2L			
1352.628	1	0.005	RR23 5			
1352.048	2	0.002	RR12 2U			
1351.670	1))	0.013	RP 9 5			

1386.568	1	0.005	RR17 6	
1386.088	1	0.003	RQ10 7	
1385.495	0	0.005	RQ 7 6	
1385.186	1	FF	RQ14 9	
1384.950	5	0.002	RR14 5	
1384.371	1	0.006	RR20 7	
1383.273	0	0.008	RR18 6	
1383.133	0	0.010	RQ 8 6	
1382.823	2	0.006	RQ11 7	
1382.596	4	0.003	RR15 5	
1382.219	6	0.003	RR 6 4	RR 7 4
1382.021	5	0.003	RR 8 4	
1381.831	5	0.003	RR 5 4	
1381.483	4	0.002	RR 9 4	
1381.175	5	0.003	RR 4 4	
1380.654	4))	0.005	RR10 4	RQ15 9
1380.482	1	0.010	RQ 9 6	
1380.176	1	0.004	RR21 7	
1379.942	4	0.004	RR16 5	
1379.703	2))	0.019	RR19 6	
1379.509	4	0.003	RR11 4	
1379.250	2	0.003	RQ12 7	
1378.066	4)	0.003	RR12 4	
1377.950	3)	0.005	RQ 6 5	
1377.492	1	0.004	RQ10 6	
1376.973	3	0.003	RR17 5	
1376.315	3	0.003	RR13 4	
1376.015	1	F		
1375.875	4	0.003	RQ 7 5	RQ16 9
1375.673	1	0.009	RR22 7	
1375.365	2	0.004	RQ13 7	
1374.252	4	0.003	RR14 4	RQ11 6
1373.700	3	0.003	RR18 5	
1373.507	4	0.002	RQ 8 5	
1371.885	1	0.005	RR15 4	
1371.182	1	0.004	RQ14 7	
1370.825	5	0.002	RQ 9 5	RQ17 9
1370.490	9	0.002	RR 6 3	RR 7 3
1370.286	8	0.002	RR 8 3	
1370.102	8	0.003	RR19 5	RR 5 3
1369.739	7	0.002	RR 9 3	
1369.440	7	0.002	RR 4 3	
1369.219	3	0.003	RR16 4	

1410.582	1	0.008	RR14 8		
1410.345	4	0.003	RR 9 7		
1409.497	4	0.002	RR10 7		
1408.981	0	0.013	RR17 9		
1408.350	4	0.003	RR11 7		
1406.898	3	0.003	RR12 7		
1405.715	0n	F			
1405.666	0	FF	RR18 9	RR16 8	
1405.549	0	FF		RR16 8	
1405.145	3	0.003	RR13 7		
1403.761	1	F			
1403.196	1	FF			
1403.085	3	0.005	RR14 7		
1402.531	5	0.002	RR 6 6	RR 7 6	RR17 8
1402.314	3	0.002	RR 8 6		
1402.085	1	0.006	RR19 9		
1401.777	3))	0.004	RR 9 6		
1400.918	3	0.003	RR10 6		
1400.731	3	0.002	RR15 7		
1400.177	0	F	RQ10 9?		
1399.785	2	0.007	RR11 6		
1399.270	0	F	RR18 8		
1398.345	2	0.006	RR12 6		
1398.088	3	0.004	RR16 7		
1396.593	1	0.004	RR13 6		
1395.694	0	F	RR19 8		
1395.103	2	0.005	RR17 7		
1394.762	0n	F			
1394.550	2	0.004	RR14 6		
1392.900	8	0.002	RR 6 5	RR 7 5	
1392.691	7	0.003	RR 8 5		
1392.520	7	0.002	RR 5 5		
1392.161	6	0.002	RR 9 5	RR15 6	
1391.805	2	0.003	RR18 7	RQ 8 7	
1391.318	5	0.002	RR10 5		
1390.677	0	F			
1390.180	6	0.002	RR11 5		
1389.536	1	0.005	RR16 6		
1389.364	0	0.010	RQ13 9		
1389.069	1	0.003	RQ 9 7		
1388.737	5	0.002	RR12 5		
1388.265	1	0.005	RR19 7		
1387.653	1n	F	PQ21 8		
1387.149	1)	0.021			
1386.993	5)	0.002	RR13 5		

1432.491	0	FF		
1432.353	0	0.010	RR11 11	
1432.175	0n	F		
1431.824	0n	F		
1431.714	0n	F		
1430.973	0n	F		
1430.847	0	FF	RR12 11	
1430.561	0n	F		
1429.038	0	0.011	RR10 10	RR13 11
1428.807	0n	F		
1427.862	0	0.013	RR11 10	
1427.615	0	FF		
1426.496	0n	F		
1426.036	0n	F		
1424.410	2	0.005	RR 9 9	
1423.541	2	0.004	RR10 9	
1422.374	2	0.006	RR11 9	
1421.732	0n	F	RR16 11?	
1421.052	0n	F		
1420.900	1	0.003	RR12 9	
1420.713	0n	F		
1419.819	0	FF		
1419.412	0n	F		
1419.116	1	0.005	RR13 9	
1418.937	0n	F		
1418.695	0n	F		
1418.459	1	0.006	RR 8 8	
1417.897	1	0.008	RR 9 8	
1417.728	1	F		
1417.346	0	FF		
1417.039	2	0.003	RR14 9	•RR10 8
1415.869	1	0.005	RR11 8	
1414.841	1•	F		
1414.670	1	0.006	RR15 9	
1414.401	1	0.005	RR12 8	
1414.076	1	FF		
1413.938	1	F		
1413.757	1	F		
1412.657	1	0.003	RR13 8	
1412.173	1	F		
1411.980	0	0.007	RR16 9	
1411.761	0	FF		
1411.648	1n	F		
1411.149	5	0.002	RR 7 7	
1410.900	4	0.003	RR 8 7	

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INVERSION DOUBLET INTERACTIONS IN FORMALDEHYDE

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Inversion Doublet Interactions in Formaldehyde

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LIDE[1] recently showed that vibration–rotation interactions of a hitherto unsuspected kind can occur between the member levels of an inversion doublet; he points out that, his formulation is specifically for a molecule with the (non-planar) geometry of cyanamide, but that the qualitative conclusions should have a wider applicability. Millen, Topping, and Lide[2] found evidence of such interaction in the microwave spectrum of cyanamide.

In the ultraviolet absorption spectrum of formaldehyde, we have found, in several places, perturbations of some magnitude, for which it is difficult to find an explanation other than such interactions. The first excited singlet state of formaldehyde is non-planar[3,4] and is geometrically even more closely approximated by Lide's model than is cyanamide itself; perturbations in quantitative agreement with the predictions of Lide's theory may therefore be expected and are in fact found. A rotational level J,K of the 0^- state active in a perpendicular band of this spectrum should be perturbed by interaction with the $J,K-1$ level and the $J,K+1$ level of the 0^+ state. The perturbation is expressible in terms of three parameters, one of which is the inversion frequency, the other two, d_{01} and e_{01}, being also associated with the potential function. Its magnitude is sensibly linear with respect to $J(J+1)$, with the value very nearly zero for $J = K$, and becomes large when $(2K+1)\{A - \frac{1}{2}(B + C)\}$ approaches the inversion frequency.

Our absorption frequencies have been obtained by an interferometric method[5] to high precision, generally of the order of 0·003K. Our analysis of the A_2 band (Brand's notation[3]) reveals a perturbation, strong in sub-branches with $K' = 7$ and $K' = 8$, but not at all negligible over a considerable part of the band, and a second perturbation which is strong in the sub-branches with $K' = 0$ and is of markedly different appearance, especially in that it is very much more localised in the J,K field. A complete numerical analysis has been made, by using about 300 of the 900—1000 recorded frequencies of this band; these were selected as being only singly assigned and free from near or overlapping neighbours. Simultaneous solution was made for the six rotational constants and ten centrifugal distortion constants of the ground and the excited state, the band origin, and the two sets each of three Lide parameters required for the two perturbations described. The first of these perturbations gives 126K for the inversion frequency of the $2\nu'(CO)$ vibronic state involved in this band, and $d_{01} = 7{\cdot}4 \times 10^{-2}$; e_{01} is found to be so close to the level of significance that it can be ignored (the effect of a small e_{01} would be to split the K-degeneracy of the high-K levels but, for the value found, at most a slight broadening ($<$ 0·05K) of the most perturbed lines would occur; the lines concerned are weak ($J' \sim 20$, $K' = 8$) and do not enable us to decide whether there is such broadening). Agreement between the perturbations observed and calculated with these values of the parameters is excellent—to about 0·01K for all singly assigned and apparently single-component lines, and within the resolving limit of our equipment (0·09K) for practically all composite lines, several hundreds of assigned frequencies in all.

The second perturbation referred to above requires a somewhat more refined treatment. For a prolate near-symmetric rotor, Lide's formulation[1] is adequate for levels of high K, but is inadequate for describing a perturbation which is strong in levels of low K, where there is large splitting between members of the asymmetry doublets. To deal with this case we have used a more extended treatment outlined by Lide.[6] Tentatively we regard this second perturbation as arising from analogous interaction between the active 0^- level and the 0^+ level of a vibronically different state. On this assumption, there is again good agreement with observation. The analogue of the inversion frequency here is about 14K, indicating the existence of a 0^+ level at 30,645K above the ground state (since the origin of the A_2 band is 30,658·58K); this may belong to the $\nu'(CO) + \delta'(CH_2)$ state. If so, the corresponding 0^- level, according to our preliminary analysis of the perpendicular C_1 band, is at 30,819K (in agreement with Brand's recording[3] of its R-head of $K'' = 3$ at 30,875K). It would then appear that the inversion frequency of the vibronic state active in the C_1 band is about 174K; the considerable difference between this and the 126K for the $2\nu'(CO)$ state may well be the

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effect of the replacement of a quantum of $\nu'(CO)$ by a quantum of $\delta'(CH_2)$.

Similar perturbations elsewhere in this spectrum have been mapped, but for the bands concerned a similarly complete numerical analysis has not yet been carried out.

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