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THE STRUCTURE OF THE VIBRATIONAL-ROTATIONAL BANDS OF AN ASYMMETRIC ROTOR

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CONTENTS

The structure of *A*-, *B*- and *C*-type vibrational-rotational bands of an asymmetric rotor is related to the band types of the two limiting symmetric rotors. The effect of the degree of asymmetry and the change in the effective inertial constants between the two vibrational states on the band structure is shown. The type of information which can be obtained from the analysis of asymmetric rotor bands is pointed out.

Introduction

The band structure of the vibrational-rotational bands of symmetric rotors is well understood. In particular, Herzberg (1945) has given a fine presentation of these band structures by considering the total band structure as the sum of various sub-bands. The band structure of the vibrational-rotational bands of an asymmetric rotor is somewhat more complex than those of a symmetric rotor, and it seems desirable to try to bring some order into their structure. Cross, Hainer & King (1944) have made a start in this process. They have broken asymmetric rotor bands down into 'wings', a wing being a group of lines in which K_{-1} or K is held constant while J varies. It seems more desirable to discuss the band structure in terms of sub-bands, each sub-band consisting of three wings, R, P, and Q. Each sub-band is completely specified by a constant value of K_{-1} or K and the parity of the ground-state energy levels. In this way it is possible to preserve an analogy with symmetric rotor-band types. In this paper the structure of asymmetric rotor vibrational-rotational bands will be discussed from the standpoint of sub-bands.

Wherever possible the excellent notation developed by Herzberg (1945) will be used. The only real departure will be to retain the double-suffix notation for designating asymmetric rotor energy levels (King, Hainer & Cross 1943) rather than using the pseudo-quantum number τ. This notation has several advantages which will become apparent,

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the main advantage of interest here being that a close connexion is preserved with the two symmetric rotor limits. In the following discussion a thorough knowledge of symmetric rotor band structure will be assumed, as well as a general knowledge of asymmetric rotor energy levels (Herzberg 1945, p. 45).

Structure of A-type bands

If the change in electric moment lies along the axis of least moment of inertia, during a vibrational transition, the resulting band is called an A-type band. (The convention $I_a < I_b < I_c$ will be used in this discussion.) In the prolate symmetric limit, $I_B = I_C$, a change of electric moment along the axis of least moment of inertia, is a change along the top axis and thus gives rise to a parallel type band. In this limit the asymmetry parameter (King *et al.* 1943)

$$\kappa = \frac{2B - A - C}{A - C} \tag{1}$$

has the value $-1{\cdot}0$; the quantum number of the constant component of the angular momentum will be designated K_{-1}. For an A-type band, in this symmetric limit, the selection rules are well known to be

$$\left.\begin{aligned} &K_{-1} = 0, \quad J - \pm 1, \qquad K_{-1} = 0; \\ &K_{-1} \neq 0, \quad J = 0, \pm 1, \quad K_{-1} = 0. \end{aligned}\right\} \tag{2}$$

If there is to be a correlation between the asymmetric rotor band and the symmetric rotor limit, then one might expect that (2) would furnish the changes in K_{-1}, at least for the strongest transitions.

In the oblate symmetric limit, $I_a = I_b$, $\kappa = +1$, a change in electric moment along the axis of least moment of inertia is a change perpendicular to the top axis and thus gives rise to a perpendicular band. In this limit the quantum number of the constant component of the angular momentum is designated K_{+1} which is shortened to K. The selection rules for an A-type band in the oblate symmetric limit are

$$J = 0, \pm 1, \quad K = \pm 1. \tag{3}$$

Again, if there is to be a correlation between the asymmetric rotor band and this symmetric limit, then (3) should represent the allowed changes in K, at least for the strong transitions. Combining (2) and (3) one obtains

$$\left.\begin{aligned} &K_{-1} = 0, \quad J = \pm 1, \qquad K_{-1} = 0, \quad K = \pm 1; \\ &K_{-1} \neq 0, \quad J = 0, \pm 1, \quad K_{-1} = 0, \quad K = \pm 1, \end{aligned}\right\} \tag{4}$$

as the selection rules for the strong transitions in an asymmetric-rotor A-type band. One would expect these transitions to be strong because they are 'allowed' in both symmetric rotor limits. It is indeed true that the strongest transitions in an A-type band of a rigid asymmetric rotor are those allowed by (4). The general selection rules on K_{-1} and K (Cross *et al.* 1944) are somewhat more relaxed than (4). If we let e stand for the evenness of either K_{-1} or K and o stand for the oddness of K_{-1} or K, the selection rules on K_{-1} and K become

$$ee \longleftrightarrow eo, \quad oe \longleftrightarrow oo. \tag{5}$$

Thus it is seen that in the transition of an A-type band, the parity of K_{-1} does not change while the parity of K must change, hence, changes of $K_{-1} = 0, 2, 4, \ldots$ and of $K = 1, 3, \ldots$

are all allowed. One readily verifies that (4) is a special case of (5). Although (5) allows changes in K_{-1} and K not allowed by (4), the changes forbidden by (4) are generally an order of magnitude weaker than those allowed by (4).

It should also be remembered that in the sub-bands of a perpendicular band of a symmetric rotor the R- or P-branch is strong when $\Delta J = \Delta K$ and weak when $\Delta J \neq \Delta K$. This property is also carried over into asymmetric rotor bands. For those transitions allowed

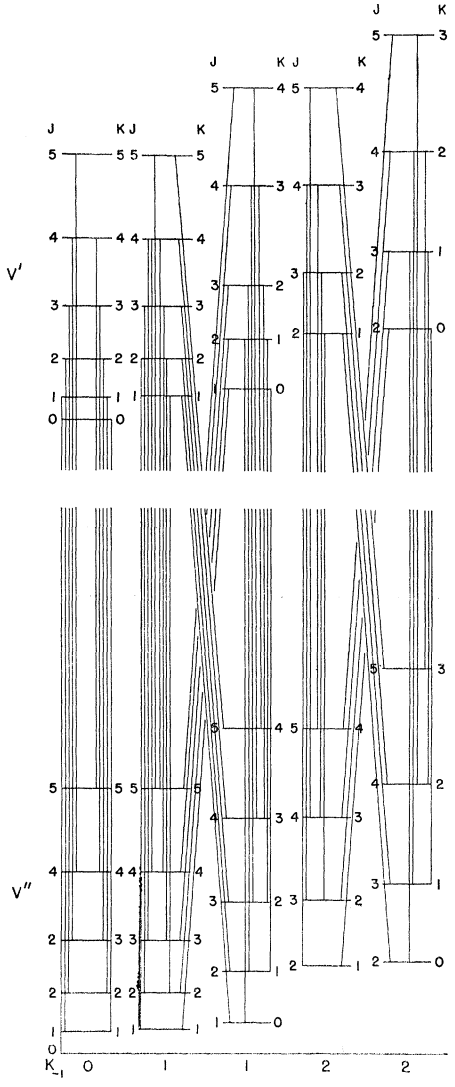

FIGURE 1. Sub-bands of an A-type band.

by (4), the selection rule $\Delta K = 1$ applies to R-branch transitions ($\Delta J = +1$) and the selection rule $\Delta K = -1$ applies to P-branch transitions ($\Delta J = -1$). Thus the selection rules for the strongest transitions of an A-type band can readily be deduced from a knowledge of behaviour in the two symmetric rotor limits.

Cross *et al.* (1944) have grouped the transitions of asymmetric-rotor bands into series of lines which they have called wings. A wing is characterized by a constant value of K_{-1} or K and by the parity of the ground-state energy levels. By combining all the wings with the same ground-state levels one forms a series of sub-bands. Such a sub-band will contain

wings which obey (4) as well as the weaker wings allowed by (5). Only those wings which satisfy (4) will be considered in the following, for they are by far the strongest wings in the sub-bands and give rise to the most easily recognized features in an asymmetric rotor band. One can see that for each K_{-1} or $K \neq 0$, the transitions divided into a sub-band with ground-state levels of even parity (called even sub-bands) and a sub-band with ground-state levels of odd parity (called odd-sub-bands). For K_{-1} or $K = 0$ there is only an even sub-band.

In an A-type band it is natural to specify the sub-bands by a constant value of K_{-1} since this quantum number does not change during a transition. The manner in which the

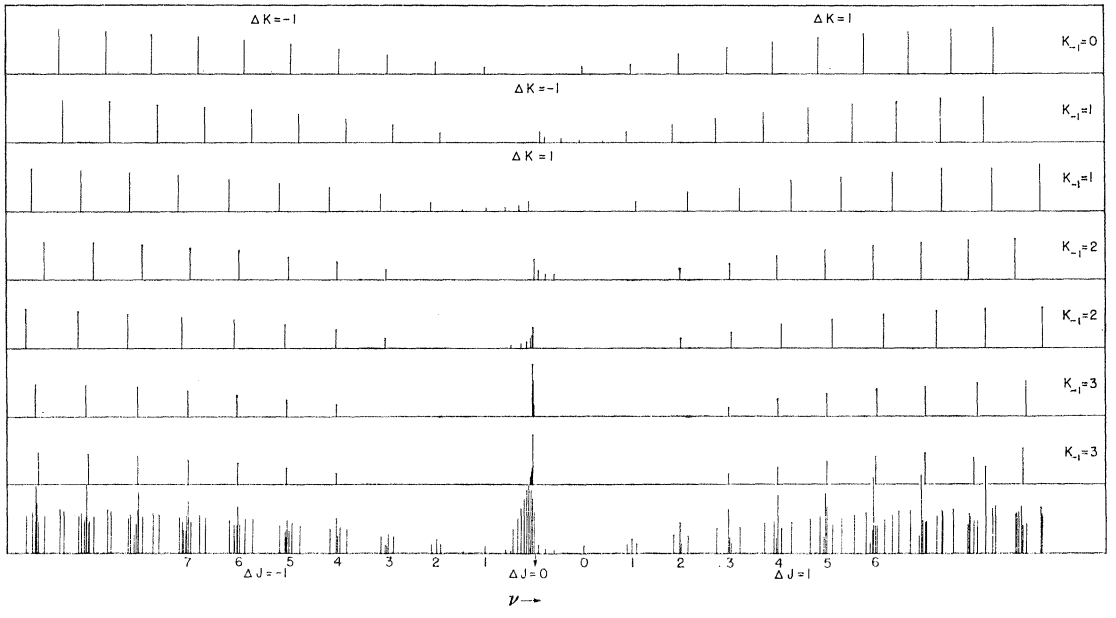

FIGURE 2. The sub-bands of an A-type band of an asymmetric rotor with $\kappa \sim -0{\cdot}9$. The constants used in calculating the energy levels were $A'' = 5{\cdot}241$, $B'' = 3{\cdot}946$, $C'' = 3{\cdot}878$, $A' = 5{\cdot}211$, $B' = 3{\cdot}870$ and $C' = 3{\cdot}855$. The intensities were calculated for $T = 298\,^{\circ}\mathrm{K}$. In the composite spectrum only the first transition of each sub-band Q-branch has been plotted. The parity of the ground-state levels of the $K_{-1} = 0$ sub-band is e. For the sub-bands with $K_{-1} > 0$, the parity of the ground-state levels in the upper sub-band is o while it is e in the lower sub-band.

sub-bands of an A-type band arise is shown schematically in figure 1. Each column of vibrational-rotational levels in the figure is labelled by its value of K_{-1}. The value of K for each level is shown to the right of the line representing that level in the figure. Since for the strongest transitions $\Delta K_{-1} = 0$, the P- and R-branch transitions for a given sub-band take place between the vibrational-rotational levels in the same column. This figure shows clearly why the sub-band with $K_{-1} = 0$ cannot have a Q-branch without violating (4). However, $\Delta J = 0$ transitions can exist for all other sub-bands because the asymmetry removes the K_{-1} degeneracy. The manner in which these $\Delta J = 0$ transitions occur is also indicated in figure 1. All transitions in a given sub-band arise from the same set of ground-state levels, i.e. the same column in the lower vibrational state. From the two sets of levels for each $K \neq 0$, one obtains two P-branches, two Q-branches and two R-branches.

This sub-band structure is shown schematically in another way in figure 2, for a choice of inertial constants such that the ground state has $\kappa = -0{\cdot}9$, very near to the prolate

symmetric limit. The energy levels used in determining the band in figure 2 were calculated from the expression

$$E(A,B,C) = \tfrac{1}{2}(A+C)\,J(J+1)+\tfrac{1}{2}(A-C)\,E(\kappa), \tag{6}$$

where κ is defined by (1) and $E(\kappa)$ is the root of the reduced energy equation. The roots of $E(\kappa)$, at various intervals of κ have been tabulated (King *et al.* 1943; Townes & Schawlow 1955) hence the calculation of the energy levels is a purely arithmetical procedure. Relative intensities of the transitions were calculated by combining the appropriate Boltzmann factor and nuclear spin factor with tabulated values of the lines strengths (Cross *et al.* 1944; Townes & Schawlow 1955) for the appropriate value of κ. No simple closed expression for the transition positions can be written for an asymmetric rotor band as can be written for simpler rotors. One must calculate the energy levels for each vibrational state according to (6) and take differences to obtain transition frequencies.

In figure 2 only the sub-bands allowed by (4) and with $K_{-1} \leqslant 3$ have been plotted separately. It will be seen that this sub-band structure bears an amazing similarity to that of a parallel band of a symmetric rotor (Herzberg 1945, p. 418). In the lowest line of the figure the sub-bands have been superimposed to give a composite band. This composite band contains not only those sub-bands shown separately above it but also the transitions allowed by (4) belonging to sub-bands with $K_{-1} > 3$. A comparison with a composite parallel type band shows that the composite A-type band is considerably more complex; however, it is conforting to know that even this complex spectrum can be broken down into a series of simple sub-bands.

This spectrum represents a typical A-type band of a slightly asymmetric rotor. However, it should not be regarded as a pattern since different choices of the constants A', B', C' and A'', B'', C'' could give the band a quite different appearance. Equally important, a different value of κ can be expected to give the spectrum a quite different aspect. The value $\kappa = -0{\cdot}9$ is very near to the prolate symmetric limit where an A-type band corresponds to a parallel type band, hence, it is not surprising that a marked resemblance to a parallel type band is found.

Figure 3 is a schematic diagram similar to figure 2 except that the asymmetry parameter κ has a value of $-0{\cdot}5$ for this spectrum. There is still a marked resemblance to a parallel type band although the Q-branches of the sub-bands are now spread out somewhat. The P- and R-branches of the composite band still show a greater complexity than is present in the band of the limiting prolate rotor.

Figure 4 is a schematic spectrum for an asymmetric rotor band with $\kappa = 0{\cdot}5$. Now the sub-band Q-branches are spread out considerably and only the first, and strongest. Q-branch transition for each sub-band remains near the centre. At this asymmetry one can see that the $K_{-1} = 0$ sub-band and the odd, $K_{-1} = 1$, sub-bands are essentially degenerate for all J. At higher values of J, the even K_{-1} sub-band is degenerate with the odd $K_{-1} = 2$ sub-band. This is a result of being very far away from the prolate symmetric limit so that K is a better quantum number than K_{-1}.

In figure 5 a schematic spectrum for $\kappa = 0{\cdot}9$ is shown. At this asymmetry most of the resemblance to a parallel type band has disappeared, even when the sub-bands are still classified by K_{-1}. The composite spectrum has many features of a perpendicular band of a symmetric rotor. The sub-band Q-branches are now completely spread out. The first

transition of each sub-band Q-branch is all that is left near ν_0. The Q-branch transitions with the same value of K are now nearly superimposed giving the composite spectrum a series of Q-branches characteristic of a perpendicular type band. The Q-branches are

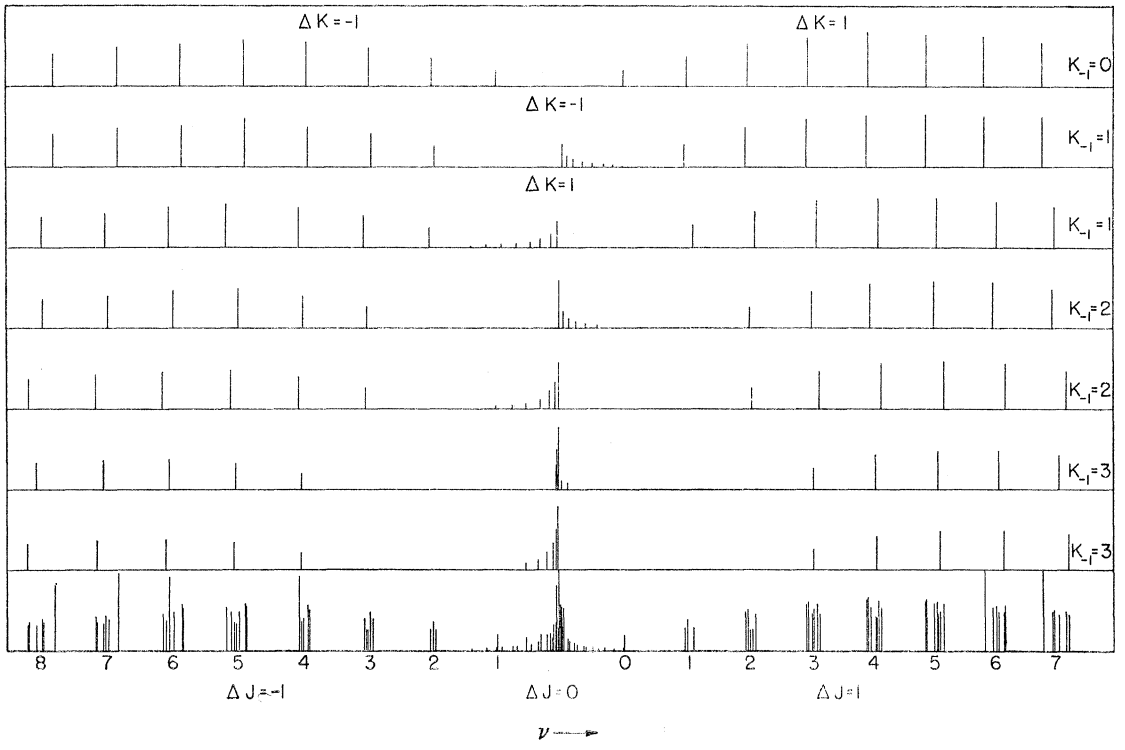

FIGURE 3. The sub-bands of an A-type band of an asymmetric rotor with $\kappa = -0{\cdot}5$. The constants used in calculating the energy levels are $A'' = 5{\cdot}241$, $B'' = 4{\cdot}219$, $C'' = 3{\cdot}878$, $A' = 5{\cdot}211$, $B' = 4{\cdot}194$, $C' = 3{\cdot}855$ cm^{-1}. The intensities were calculated for a temperature of 298 °K.

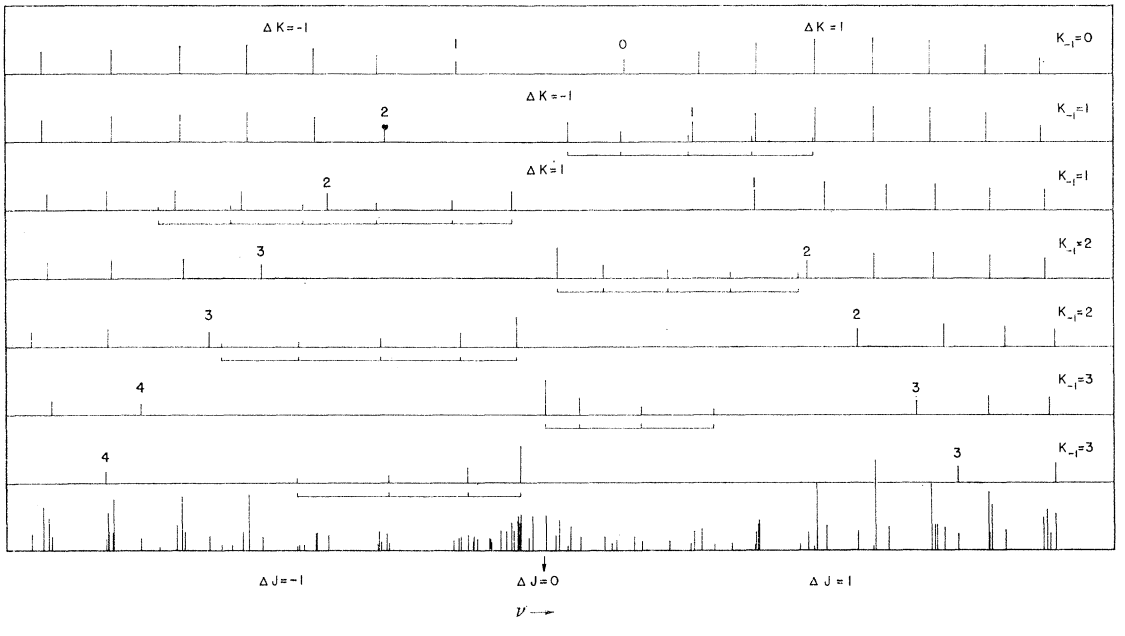

FIGURE 4. The sub-bands and composite band of an A-type band of an asymmetric rotor with $\kappa \sim 0{\cdot}5$. The values of A'', C'', A' and C' are the same as those used in figure 3. The intensities were calculated for $T = 298$ °K.

labelled according to the Herzberg (1945) notation under the composite spectrum. The subscripts are the values of K of the ground-state levels for the various Q branches. The $\Delta K = 1$ Q-branches are at lower frequencies because this is near the oblate limit where $(C-B)$ is negative.

From figures 2 to 5 it is evident that the appearance of an A-type band can vary from great similarity to a parallel type symmetric-rotor band near the prolate limit to great similarity to a perpendicular symmetric rotor band near the oblate limit. In each of these figures the composite bands may be considered as typical but the relative values of A', B', C' and A'', B'', C'' can cause nearly as drastic effects on the band appearance as the degree of asymmetry.

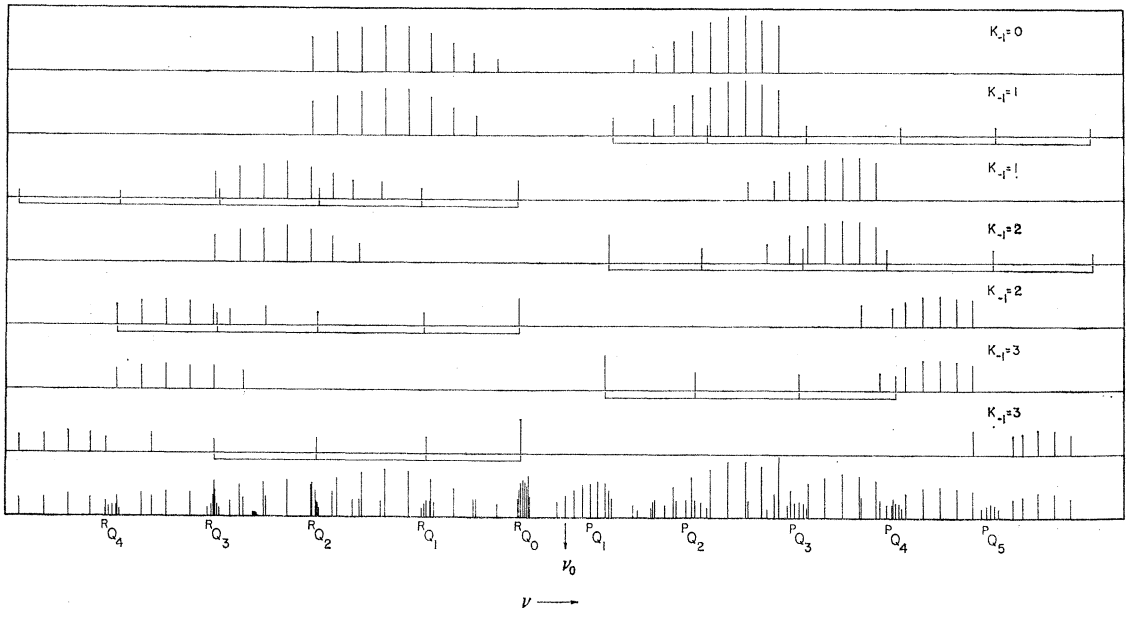

FIGURE 5. The sub-bands and whole band of an A-type asymmetric-rotor band $\kappa = 0{\cdot}9$. The pictured sub-bands are still identified according to the K_{-1} value of the ground-state level. At this asymmetry the band bears an amazing similarity to a perpendicular band of an oblate symmetric rotor. The vestiges of the series of Q-branches are clearly evident and are labelled according to the notation of Herzberg (1945). The inertial constants used for the calculation are $A'' = 4{\cdot}861$ cm^{-1}, $B'' = 4{\cdot}660$, $C'' = 0{\cdot}8340$, $A' = 4{\cdot}841$, $B' = 4{\cdot}640$ and $C' = 0{\cdot}8140$. The intensities are calculated for 298 °K.

In order to illustrate the part inertial constants can play in determining the appearance of bands figure 6 has been prepared. All the bands in this series have the same ground-state energy levels. However, the excited-state energy levels were calculated from the values of A', B', C' given at the left of each spectrum. The excited-state constants used for these bands, although extreme, are not unrealistic. They represent values obtained from the analyses of observed bands of H_2S (Allen & Plyler 1956), the ground state being that given by Cross (1935). The value of κ is about 0·5. This figure should illustrate that such extreme variations in band appearance are to be expected in real spectra. The numbering below the bands gives the ground state J value of the transitions and is intended to help the reader follow the various transitions as the inertial constants are changed. In the Q-branch regions only the first and strongest member of the Q-branch of each sub-band has been plotted.

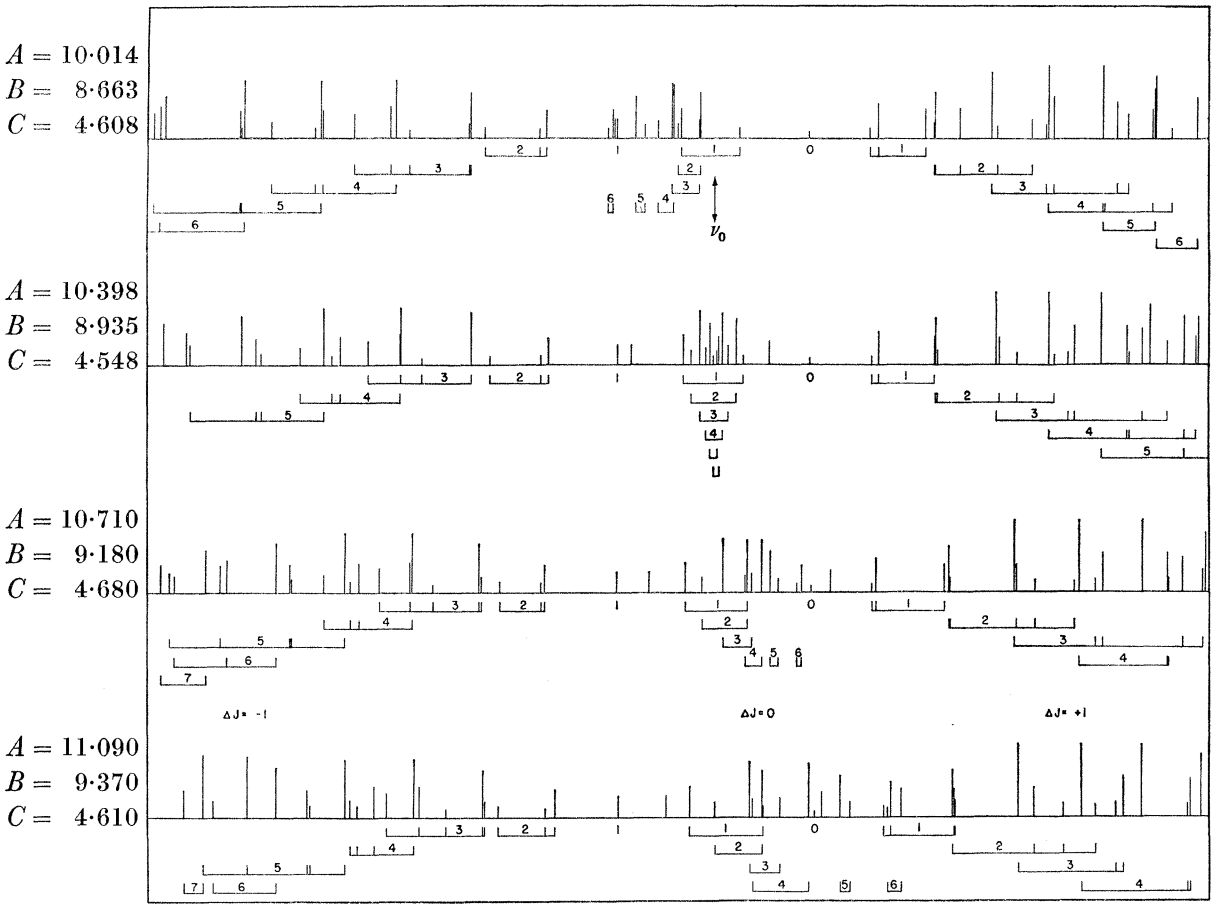

FIGURE 6. Bands of H_2S plotted to show the effect of different excited state constants on the band appearance. The excited state inertial constants are given to the left of the figure. The ground-state constants are $A'' = 10{\cdot}373$, $B'' = 8{\cdot}991$ and $C'' = 4{\cdot}732$. The lines and numbers under the spectra indicate the ground-state J value of the transitions. For the most part only the first transition of a sub-band Q branch has been plotted although a few of the other transitions are plotted when the intensity warrants it. The intensities were calculated for 298 °K and include the nuclear spin factor for H_2S.

The most drastic changes in these bands occur in the Q-branch region. As will be seen below this arises because of the large changes in A'. The convergence of the strongest R-branch lines also changes and it will be seen that this is due largely to changes in C'.

DEPENDENCE OF THE ENERGY LEVELS ON THE INERTIAL CONSTANTS

As an alternative to (6) it is sometimes convenient to express the energy levels of a rigid asymmetric rotor as

$$E(A,B,C) = \alpha A + \beta B + \gamma C, \tag{7}$$

in which α, β, γ are defined by the expressions

$$\left.\begin{aligned} \alpha &= \frac{\partial E(A,B,C)}{\partial A} = \frac{1}{2}\left[J(J+1) + E(\kappa) - (\kappa+1)\frac{\partial E(\kappa)}{\partial \kappa}\right], \\ \beta &= \frac{\partial E(A,B,C)}{\partial B} = \frac{\partial E(\kappa)}{\partial(\kappa)}, \\ \gamma &= \frac{E(A,B,C)}{C} = \frac{1}{2}\left[J(J+1) - E(\kappa) + (\kappa-1)\frac{\partial E(\kappa)}{\partial \kappa}\right]. \end{aligned}\right\} \tag{8}$$

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TABLE 1. THE ENERGY DERIVATIVES OF A RIGID ASYMMETRIC ROTOR

	$\kappa \sim -0{\cdot}9$			$\kappa \sim -0{\cdot}5$			$\kappa \sim 0{\cdot}0$			$\kappa \sim 0{\cdot}5$			$\kappa \sim 0{\cdot}9$		
${}^{J}K_{-1}^{K}$	α	β	γ	α	β	γ	α	β	γ	α	β	γ	α	β	γ
5_{50}	25·000	2·536	2·464	24·917	2·993	2·080	24·695	3·598	1·707	23·538	5·452	1·010	16·325	13·675	0
5_{51}	25·000	2·536	2·464	24·928	2·990	2·082	24·715	3·549	1·736	24·002	4·713	1·284	22·256	6·744	1·000
5_{41}	16·000	7·115	6·885	15·748	8·668	5·583	14·799	11·128	4·073	11·253	16·959	1·788	7·283	21·718	1·000
5_{42}	16·000	7·115	6·885	15·785	8·492	5·723	15·283	9·827	4·890	14·277	11·508	4·215	13·115	12·885	4·000
5_{32}	9·000	10·746	10·254	8·284	15·048	6·667	6·699	19·340	3·961	5·878	20·880	3·241	11·790	14·210	4·000
5_{33}	9·000	10·720	10·280	8·788	12·297	8·915	8·640	12·720	8·640	8·915	12·297	8·788	10·280	10·720	9·000
5_{23}	4·000	14·210	11·790	3·241	20·880	5·878	3·605	20·053	6·342	6·667	15·048	8·284	10·254	10·746	9·000
5_{24}	4·000	12·885	13·115	4·215	11·508	14·277	4·717	10·173	15·110	5·723	8·492	15·785	6·885	7·115	16·000
5_{14}	1·000	21·718	7·283	1·788	16·959	11·253	3·634	12·062	14·360	5·583	8·668	15·748	6·885	7·115	16·000
5_{15}	1·000	6·744	22·256	1·284	4·713	24·002	1·645	3·731	24·624	2·082	2·990	24·928	2·464	2·536	25·000
5_{05}	0	13·675	16·325	1·010	5·452	23·538	1·596	3·819	24·585	2·080	2·993	24·917	2·464	2·536	25·000
6_{60}	36·000	3·042	2·958	35·915	3·577	2·508	35·652	4·264	2·084	34·434	6·219	1·347	23·612	18·388	0
6_{61}	36·000	3·042	2·958	35·915	3·576	2·508	35·657	4·251	2·091	34·686	5·830	1·484	31·539	9·461	1·000
6_{51}	25·000	8·632	8·368	24·730	10·321	6·948	23·810	12·710	5·480	19·200	20·147	2·652	10·617	30·383	1·000
6_{52}	25·000	8·632	8·368	24·737	10·280	6·973	24·002	12·225	5·773	22·063	15·434	4·503	19·288	18·712	4·000
6_{42}	16·000	13·246	12·754	15·410	16·817	9·773	13·145	22·724	6·131	9·284	29·388	3·328	16·677	21·323	4·000
6_{43}	16·000	13·245	12·755	15·582	15·990	10·428	14·861	17·941	9·198	14·341	18·881	8·778	16·093	16·907	9·000
6_{33}	9·000	16·983	16·017	7·622	25·510	8·868	6·176	29·648	6·176	8·868	25·510	7·622	16·017	16·983	9·000
6_{34}	9·000	16·907	16·093	8·778	18·881	14·341	9·021	18·295	14·684	10·428	15·990	15·582	12·755	13·245	16·000
6_{24}	4·000	21·323	16·677	3·328	29·388	9·284	5·240	24·506	12·254	9·773	16·817	15·410	12·754	13·246	16·000
6_{25}	4·000	18·712	19·288	4·503	15·434	22·063	5·482	12·807	23·711	6·973	10·249	24·737	8·368	8·632	25·000
6_{15}	1·000	30·383	10·617	2·652	20·147	19·200	5·014	13·641	23·344	6·948	10·321	24·730	8·368	8·632	25·000
6_{16}	1·000	9·461	31·539	1·484	5·830	34·686	1·977	4·480	35·543	2·508	3·576	35·915	2·958	3·042	36·000
6_{06}	0	18·388	23·612	1·347	6·219	34·434	1·963	4·506	35·531	2·508	3·577	35·915	2·958	3·042	36·000

The values of these derivatives are readily calculated using published energy tables of $E(\kappa)$. The quantity $\partial E(\kappa)/\partial\kappa$ can be determined over a suitable range of κ from these same tables. Examples of these derivatives for various ranges of κ are given in table 1. In these tables the increment of κ used was $\Delta\kappa = 0{\cdot}1$ which is rather large. However, it is easily seen from the table that the change in these derivatives with κ is really quite small. These derivatives have the further advantage that they do not depend explicitly on the values of A, B, and C but merely on their ratio as defined by κ in (1).

By substituting the numerical values of α, β and γ for a given level into (7) one can ascertain immediately the relative importance of the three inertial constants in determining the energy of that level. As an example, using the values of α, β, γ for 6_{60} level with $\kappa = 0$, one finds

$$E_{6_{60}}(A, B, C) = 35{\cdot}65A + 4{\cdot}264B + 2{\cdot}084C. \tag{9}$$

Equation (9) shows that the value of A very nearly determines the energy of this level. Furthermore, one can see from table 1 that this is true over the whole range of κ except very near the oblate limit where the level depends very nearly equally on A and B. On the other hand the level 6_{61} depends predominantly on A throughout the complete range of κ, and except very near the oblate limit the dependence of this pair of levels on A is essentially the same. This pair of levels in each J give rise to the first Q-branch transition in each of the sub-bands. Figures 2 to 5 show clearly that these transitions are the strongest transitions in the composite Q-branch. This series of transitions may be described symbolically by the expression

$$J_{J0} \rightleftharpoons J_{J1}, \tag{10}$$

it being understood that one of these rotational levels is in the ground vibrational state and one is in the excited vibrational state. Neglecting for the minute the small dependence of these levels on B and C, and assuming the α values are the same in both vibrational states, the transition frequency becomes

$$\nu = \nu_0 + \alpha(A' - A''), \tag{11}$$

in which ν_0 is the frequency of vibration. Thus one finds that the frequency of the strongest transitions in the Q-branch of an A-type band is determined essentially by the difference in the A constants between the two vibrational states. This effect shows up very clearly in figure 6. From the top spectrum to the bottom spectrum the quantity $(A' - A'')$ becomes increasingly positive and thus the Q-branch transitions shown are shifted to successively higher frequencies.

One may also consider the state 6_{06} at $\kappa = 0$. The expression for the energy of this level is

$$E_{6_{06}}(A, B, C) = 1{\cdot}963A + 4{\cdot}506B + 35{\cdot}531C. \tag{12}$$

Here the dependence on C is an order of magnitude greater than it is on the other inertial parameters except near the prolate limit where the dependence on B and C is nearly equal. The dependence of the level 6_{16} is predominantly on C throughout the whole range of κ. Those two levels in fact have almost identical dependence on C except very near the prolate limit. These properties are generally true for the lowest two levels in a given J. Now the R- and P-branch transitions in the $K_{-1} = 0$ and the odd $K_{-1} = 1$ sub-bands occur between levels of this type, i.e.

$$\left.\begin{aligned} &J_{0J} \rightleftharpoons (J+1)_{0,\,J+1} \quad (a) \\ \text{and} \quad &J_{1J} \rightleftharpoons (J+1)_{1,\,J+1} \quad (b). \end{aligned}\right\} \tag{13}$$

It will be noticed in table 1 that $\gamma \sim J^2$ for these two lowest levels in each J. Making use of this approximation and also the fact that the energy dependence on B and A is small, one can write the transition frequencies as

$$\left.\begin{aligned} \nu &\sim \nu_0 + (J+1)^2 C' - J^2 C'' = \nu_0 + (2J+1)\, C' + (C' - C'')\, J^2, \quad \Delta J = +1, \\ \nu &\sim \nu_0 + J^2 C' - (J+1)^2 C'' = \nu_0 - (2J+1)\, C'' + (C' - C'')\, J^2, \quad \Delta J = -1. \end{aligned}\right\} \tag{14}$$

Thus one sees that the transition frequencies of the P- and R-branch of these two sub-bands are essentially determined by C' or C'' and the convergence of divergence of the P- and R-branches is, in this approximation, determined by the difference between the C values in the two vibrational states.

A perusal of table 1 will show that the other levels do not generally depend predominantly on only one of the inertial parameters and hence no generalizations can be made concerning them. However, these observations about the two highest and two lowest levels in a given J can be extremely useful in band analysis.

ΔF_2 values of an A-type band

The sub-band structure is very useful in determining ΔF_2 values (Herzberg 1945). Each sub-band may be treated just as a band of linear molecule. Ground-state energy differences may be determined just as for simpler types of rotors, i.e.

$$\left.\begin{aligned} \Delta F_2''(J) &= R(J-1) - P(J+1), \\ K_{-1}\,&\text{constant}, \quad |\Delta K| = 2 \end{aligned}\right\} \tag{15}$$

and analogously for the excited state energy differences one finds

$$\left.\begin{aligned} \Delta F_2' &= R(J) - P(J), \\ K_{-1}\,&\text{constant}, \quad |\Delta K| = 2. \end{aligned}\right\} \tag{16}$$

Equations (15) and (16) apply only to those transitions of the sub-bands allowed by (4) but since these are by far the strongest sub-bands they will be the most important ones. The dependence of these ΔF_2 values on the inertial parameters is readily found, with the help of (7), to be

$$\Delta F_2(J, K_{-1}) = [\alpha(J+2) - \alpha(J)]\, A + [\beta(J+2) - \beta(J)]\, B + [\gamma(J+2) - \gamma(J)]\, C. \tag{17}$$

The dependence on the inertial parameters of the first few ΔF_2 values in the sub-bands with low values of K_{-1} are shown in table 2. From table 1, one can see that in most of the κ range $\alpha \sim K_{-1}^2$. Since for the sub-bands under considerations $\Delta K_{-1} = 0$, the dependence of the ΔF_2 values on A would be expected to be small; this indeed turns out to be the case. One can see that except very close to the oblate limit these ΔF_2 values have essentially no dependence on A. Thus from experimental ΔF_2 values for these sub-bands one would not expect to obtain a very good value of A. However, these ΔF_2 values have a dependence on B and C such that good values of these parameters can be obtained. In order to obtain any information about A from an A-type band it is necessary to assign transitions for which $\Delta K_{-1} > 0$. The strongest set of wings (2) would be those for which $|\Delta K_{-1}| = 2$, $\Delta K = 1$ (Cross *et al.* 1944). The line strengths for these transitions are an order of magnitude smaller than for the transitions allowed by (4). Thus in an observed spectrum these transitions will

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TABLE 2. DEPENDENCE OF ΔF_2 VALUES ON α, β AND γ FOR VARIOUS VALUES OF κ (A-TYPE BAND)

	$\kappa \sim -0{\cdot}9$			$\kappa \sim -0{\cdot}5$			$\kappa \sim 0{\cdot}0$			$\kappa \sim 0{\cdot}5$			$\kappa \sim 0{\cdot}9$		
ΔF_2	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
$K_{-1} = 0$															
2_{02}–0_{00}	0	2·962	3·038	0·046	2·605	3·349	0·240	2·058	3·702	0·652	1·395	3·953	0·962	1·038	4·000
3_{03}–1_{01}	0	4·808	5·192	0·202	3·192	6·606	0·721	1·658	7·621	1·240	0·797	7·963	1·476	0·524	8·000
4_{04}–2_{02}	0	6·465	7·535	0·597	2·113	11·290	0·954	1·133	11·913	1·064	0·928	12·008	1·008	0·992	12·000
5_{05}–3_{03}	0	7·867	10·133	0·808	1·260	15·932	0·875	1·161	15·964	0·820	1·196	15·954	0·988	1·012	16·000
6_{06}–4_{04}	0	8·961	13·043	0·704	1·501	19·795	0·779	1·315	19·916	0·792	1·254	19·954	0·988	1·012	20·000
$K_{-1} = 1$															
3_{13}–1_{11}	0	1·000	3·000	0·025	2·281	7·694	0·114	2·026	7·860	0·306	1·719	7·975	0·476	1·524	8·000
4_{14}–2_{12}	0	1·476	4·524	0·091	2·670	11·239	0·345	1·930	11·725	0·720	1·313	11·967	0·970	1·030	12·000
5_{15}–3_{13}	0	4·268	13·732	0·259	2·432	15·308	0·531	1·705	15·764	0·776	1·271	15·953	0·988	1·012	16·000
6_{16}–4_{14}	0	5·059	16·941	0·256	2·160	19·447	0·632	1·550	19·818	0·788	1·263	19·948	0·988	1·012	20·000
$K_{-1} = 1$															
3_{12}–1_{10}	0	4·476	1·524	0·037	7·203	2·760	0·227	6·547	3·176	1·394	4·808	3·798	2·808	3·192	4·000
4_{13}–2_{11}	0	10·396	3·604	0·166	9·172	4·662	1·184	6·339	5·477	3·338	2·828	7·834	4·396	1·604	8·000
5_{14}–3_{12}	0	13·242	4·759	0·751	8·756	8·493	1·357	4·515	11·184	3·189	2·860	11·950	3·077	2·923	12·000
6_{15}–4_{13}	0	15·987	6·013	1·486	6·975	13·538	2·830	3·302	15·867	2·510	3·493	15·896	2·972	3·028	16·000
$K_{-1} = 2$															
4_{23}–2_{31}	0	6·970	7·030	0·036	7·747	7·277	0·214	6·192	7·594	0·760	5·330	7·910	1·402	4·598	8·000
5_{24}–3_{22}	0	8·885	9·115	0·215	7·508	10·277	0·717	6·173	11·110	1·723	4·492	11·785	2·885	3·115	12·000
6_{25}–4_{23}	0	10·742	11·258	0·467	7·747	13·786	2·268	5·615	15·117	2·213	3·960	15·827	2·996	3·034	16·000
$K_{-1} = 2$															
4_{22}–2_{20}	0	7·504	6·495	−0·392	10·905	3·487	0·677	11·890	3·787	0·790	9·695	3·515	4·419	5·581	4·000
5_{23}–3_{21}	0	10·018	7·982	−0·557	15·072	3·484	0·326	12·711	4·963	3·907	6·845	4·723	7·730	2·270	8·000
6_{24}–4_{22}	0	12·780	9·220	−0·233	17·088	5·145	2·156	10·674	9·170	5·634	4·517	11·849	5·297	4·703	12·000
ΔF_2 values with $\Delta K_{-1} = 2$															
3_{31}–1_{11}	8·000	1·524	0·476	7·975	1·719	0·306	7·886	1·974	0·140	7·694	2·281	0·025	7·524	2·476	0
4_{32}–2_{12}	8·000	4·598	1·402	7·910	5·330	0·760	7·655	6·070	0·275	7·277	6·697	0·036	7·030	6·970	0
5_{33}–3_{13}	8·000	7·244	1·756	7·763	10·016	0·321	7·526	10·694	−0·220	7·509	10·578	−0·187	8·804	9·196	0
6_{34}–4_{14}	8·000	12·505	1·495	7·767	15·211	−0·898	7·676	15·365	−1·041	8·708	13·677	−0·385	10·785	11·785	0

be much harder to find and assign correctly. However, if they can be assigned then the ΔF_2 values can be found for which $\Delta K_{-1} = 2$. Some examples of these ΔF_2 values together with their dependence on the inertial parameters are given at the bottom of table 2. These ΔF_2 values have a sizable dependence on A, so only provided enough transitions with $\Delta K_{-1} = 2$ can be assigned can one obtain an accurate value of A. However, these transitions are forbidden in the prolate limit and only have appreciable intensity near the oblate limit where it is still small compared with the transitions in the $\Delta K_{-1} = 0$ sub-bands. Thus in a practical sense there is a real limitation on the information which can be obtained from the analysis of an A-type band. Only in the case of light molecules for which the band structure is well-spread out and under conditions of highest resolution can one hope to get a complete set of inertial parameters from an analysis of an A-type band. One should bear in mind that ΔF_2 values may also be obtained from the use of Q-branch transitions. This is only true if the Q-branch is sufficiently resolved to enable one to make unique assignments. This again requires very high resolution even for relatively light molecules. Since in general these ΔF_2 values will have $\Delta K_{-1} = 0$, these new ΔF_2 values will not help in determining A.

Values of the inertial constants may be obtained from the ΔF_2 values by using the sum rules first proposed by Mecke (Herzberg 1945, p. 50) bearing in mind that these rules hold for effective moments of inertia only as long as centrifugal distortion effects can be ignored. Constants may also be derived using the appropriate forms of equation (17) and solving the set of equations, so found, by the method of least squares. This procedure also neglects centrifugal distortion effects.

C-TYPE BANDS

There is a symmetry to be found between A-type bands and C-type bands. Much of the previous discussion of A-type bands is true for C-type bands provided the roles of A and C, K_{-1} and K, and oblate and prolate are reversed. A C-type band results when the electric moment change during the transition is along the principal axis of largest moment of inertia. Such a change corresponds to a parallel band in the oblate symmetric limit and a perpendicular band in the prolate limit. Thus one is led to the following selection rules for the strong transitions of the sub-bands

$$\left.\begin{aligned} &\Delta J = \pm 1, \quad \Delta K_{-1} = \pm 1, \quad \Delta K = 0, \quad K = 0; \\ &\Delta J = 0, \pm 1, \quad \Delta K_{-1} = \pm 1, \quad \Delta K = 0, \quad K \neq 0; \end{aligned}\right\} \tag{18}$$

the general selection rules being

$$ee \longleftrightarrow oe, \quad eo \longleftrightarrow oo, \tag{19}$$

i.e. the parity of K does not change while the parity of K_{-1} must change.

By sorting the transitions of a C-type band according to their value of K rather than K_{-1}, one finds a sub-band structure for the transitions allowed by (18) which is very analogous to the sub-band structure of A-type bands. The same figures 2 to 5 show just how these bands are made up provided the roles of K_{-1} and K are interchanged and κ is set equal to $-\kappa$.

The strongest transitions in the Q-branch of a C-type band are those for which

$$J_{0J} \rightleftharpoons J_{1J}. \tag{20}$$

As shown earlier these levels, which give rise to the Q-branch transitions in (20), are those which depend mainly on C throughout most of the κ range. The equation for a C-type band which is analogous to (11) is

$$\nu \sim \nu_0 + \gamma(C' - C''); \tag{21}$$

thus the frequency of the strongest Q-branch transitions depends mainly on the difference between the effective values of C in the two vibrational states. The P- and R-branch transitions in the two sub-bands of lowest K value are

$$\left.\begin{aligned} J_{J,0} &\rightleftharpoons (J+1)_{J+1,0} \quad (a), \\ J_{J,1} &\rightleftharpoons (J+1)_{J+1,1} \quad (b) \end{aligned}\right\} \tag{22}$$

and the equation analogous to (14) for their frequency becomes

$$\left.\begin{aligned} \nu &\sim \nu_0 + (2J+1)\,A' + (A' - A'')\,J^2, \quad \Delta J = +1, \\ \nu &\sim \nu_0 - (2J+1)\,A'' + (A' - A'')\,J^2, \quad \Delta J = -1. \end{aligned}\right\} \tag{23}$$

By comparing (21) and (23) with (11) and (14) one finds that the roles of A and C are interchanged in the two types of band.

One can also obtain ΔF_2 values from the sub-bands of a C-type band. These have the same form as (15) and (16) provided the conditions on K and K_{-1} are interchanged. The dependence of the ΔF_2 values on the inertial parameters for a C-type band is illustrated in table 3. One finds that it is now the C constant for which one finds little information in a C-type band. One must seek transitions with $\Delta K > 0$ in order to obtain ΔF_2 values with a sizable dependence on C. These are the weaker transitions in a C-type band and hence subject to the same difficulties as the $\Delta K_{-1} > 0$ transitions in an A-type band. However, one can see from this discussion the complete symmetry which exists between the A- and C-type bands of an asymmetric rotor.

Because of this symmetry between these two types of bands, one can combine the $\Delta F_2''$ values obtained from the ground states of both an A- and C-type band to obtain very good values for the ground-state parameters. Since the effective inertial constants of the two excited states will be different one cannot combine the excited state values. However, if the ground-state values are known then one can obtain the excited state constants by solving by least squares a series of equations derived from (7)

$$\nu - E'' = \alpha' A' + \beta' B' + \gamma' C' + \nu_0. \tag{24}$$

An equation of the type (24) may be set up for each observed and assigned transition in the band. In this way one may completely determine the excited state constants.

B-TYPE BANDS; SELECTION RULES AND RELATIVE INTENSITIES

A B-type vibrational-rotational band arises when the change in electric moment during a vibration is along the principal axis of intermediate (B) moment of inertia (Herzberg 1945). In the prolate symmetric limit ($\kappa = -1$) the B-axis is perpendicular to the top axis, thus a B-type band corresponds to a perpendicular band in this symmetric limit. The selection rules for this type of symmetric-rotor band are

$$\Delta J = 0, \pm 1, \quad \Delta K_{-1} = \pm 1. \tag{25}$$

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TABLE 3. DEPENDENCE OF ΔF_2 VALUES ON α, β AND γ FOR VARIOUS VALUES OF κ (C-TYPE BAND)

	$\kappa \sim -0{\cdot}9$			$\kappa \sim -0{\cdot}5$			$\kappa \sim 0{\cdot}0$			$\kappa \sim 0{\cdot}5$			$\kappa \sim 0{\cdot}9$		
ΔF_2	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
$K=0$															
2_{20}–0_{00}	4·000	1·038	0·962	3·953	1·395	0·652	3·761	1·942	0·297	3·349	2·605	0·046	3·038	2·962	0
3_{30}–1_{10}	8·000	0·524	1·476	7·963	0·797	1·240	7·723	1·453	0·824	6·606	3·192	0·202	5·192	4·808	0
4_{40}–2_{20}	12·000	0·992	1·008	12·008	0·928	1·064	11·967	1·024	1·009	11·290	2·113	0·597	7·535	6·465	0
5_{50}–3_{30}	16·000	1·012	0·988	15·954	1·196	0·840	15·992	1·145	0·883	15·932	1·260	0·808	10·133	7·867	0
6_{60}–4_{40}	20·000	1·012	0·988	19·954	1·254	0·792	19·924	1·298	0·778	19·795	1·501	0·704	13·039	8·961	0
$K=1$															
3_{31}–1_{11}	8·000	1·524	0·476	7·975	1·719	0·306	7·886	1·974	0·140	7·694	2·281	0·025	3·000	1·000	0
4_{41}–2_{21}	12·000	1·030	0·970	11·967	1·313	0·720	11·786	1·808	0·406	11·239	2·670	0·091	4·524	1·476	0
5_{51}–3_{31}	16·000	1·012	0·988	15·953	1·271	0·776	15·829	1·575	0·596	15·308	2·432	0·259	13·732	4·268	0
6_{61}–4_{41}	20·000	1·012	0·988	19·948	1·263	0·788	19·871	1·443	0·685	19·447	2·160	0·256	16·941	5·059	0
$K=1$															
3_{21}–1_{01}	4·000	3·192	2·808	3·798	4·808	1·394	3·729	6·342	0·379	2·760	7·203	0·037	1·524	4·476	0
4_{21}–2_{11}	8·000	1·604	4·396	7·834	2·828	3·338	6·816	5·661	1·523	4·662	9·172	0·166	3·604	10·396	0
5_{41}–3_{21}	12·000	2·923	3·077	11·950	2·860	3·189	11·520	3·786	2·694	8·493	8·756	0·751	4·759	13·242	0
6_{51}–4_{31}	16·000	3·028	2·972	15·896	3·493	2·510	15·994	3·049	2·957	13·538	6·975	1·486	6·013	15·987	0
$K=2$															
4_{32}–2_{12}	8·000	4·598	1·402	7·910	5·330	0·760	7·655	6·070	0·275	7·277	7·747	0·036	7·030	6·970	0
5_{42}–3_{22}	12·000	3·115	2·885	11·785	4·492	1·723	11·283	5·827	0·890	10·277	7·508	0·215	9·115	8·885	0
6_{52}–4_{32}	16·000	3·034	2·996	15·827	3·960	2·213	15·347	5·155	1·498	13·786	7·747	0·467	11·258	10·742	0
$K=2$															
4_{22}–2_{02}	4·000	5·584	4·419	3·515	9·695	0·790	2·844	11·774	−0·618	3·487	10·905	−0·392	6·495	7·504	0
5_{32}–3_{12}	8·000	2·270	7·730	4·723	6·845	3·907	5·422	11·793	0·785	3·484	15·072	−0·557	7·982	10·018	0
6_{42}–4_{22}	12·000	4·703	5·297	11·849	4·517	5·634	10·061	8·892	3·047	5·145	17·088	−0·233	9·220	12·780	0
ΔF_2 values with $\Delta K=2$															
3_{13}–1_{11}	0	2·476	7·524	0·025	2·281	7·694	0·114	2·026	7·860	0·306	1·719	7·975	0·476	1·524	8·000
4_{23}–2_{21}	0	6·970	7·030	0·036	6·687	7·277	0·214	6·192	7·594	0·760	5·330	7·910	1·402	4·598	8·000
5_{33}–3_{31}	0	9·196	8·804	−0·187	10·578	7·509	−0·246	10·746	7·500	0·321	10·016	7·763	1·756	7·244	8·000
6_{43}–4_{41}	0	11·215	10·785	−0·385	13·677	8·708	−0·915	15·133	7·792	−0·898	15·211	7·767	1·495	12·505	8·000

Similarly, in the oblate-symmetric limit ($\kappa = +1$) a B-type band also corresponds to a perpendicular band, the selection rules being those given in (25) with K replacing K_{-1}. If there is to be a correlation between the selection rules for an asymmetric rotor and those in the two symmetric-rotor limits, one might expect that (25) would furnish the selection rules, at least for the strong transitions. Such reasoning leads to the selection rules

$$\Delta J = 0, \pm 1, \quad \Delta K_{-1} = \pm 1, \quad \Delta K = \pm 1. \tag{26}$$

Equation (26) does indeed give the selection rules for the strongest transitions of a B-type band. The general selection rules (Cross *et al.* 1944) may be stated as

$$ee \longleftrightarrow oo, \quad eo \longleftrightarrow oe. \tag{27}$$

These selection rules require that the parity of both K_{-1} and K must change during a transtion. This allows both K_{-1} and K to change by 1, 3, 5, ... Thus it is readily seen that (26) is a special case of (27). Just as in the case of A- and C-type bands, transitions involving multiple changes in K_{-1} or K are very much weaker than the transitions allowed by (26). Another important property of perpendicular bands concerns the relative intensities of the branches in a sub-band. A sub-band will have a strong branch when $\Delta J = \Delta K$, i.e. for a sub-band with ΔK (or ΔK_{-1}) $= 1$, the R-branch will be much stronger than the P-branch, whereas the converse is true when ΔK (or ΔK_{-1}) $= -1$. This property will play an important part in the subsequent discussion of the relative intensity of the wings which make up a sub-band.

Sub-band structure

As in the case of A- and C-type bands, a sub-band of a B-type band will be characterized by a constant value of K_{-1} or K and the parity of the ground-state energy levels. The proper grouping of the strong wings to produce the sub-bands of a B-type band is given in table 4. There will be a wing with each of the given designations for each value of K_{-1} or K. Once again there is an even and an odd sub-band for each K_{-1} or $K \neq 0$ while only the even sub-band exists for K_{-1} or $K = 0$.

One finds that for the even sub-bands there is only one R-branch wing and that in this wing the change in both K_{-1} and K is $+1$. This wing satisfies the condition $\Delta J = \Delta K$ in both symmetric limits, thus one would expect the R-branches of the even sub-bands to be relatively strong regardless of the value of κ. On the other hand there are two P-branch wings for the even sub-bands with K_{-1} or $K > 2$. In one of these wings $\Delta K_{-1} = 1$ while $\Delta K = -1$. Since this wing satisfies the condition $\Delta J = \Delta K$ only in the oblate limit, one would expect this wing to be very weak near the prolate limit and increase in intensity as one approaches the oblate limit. For the other P-branch wing, $\Delta K_{-1} = -1$ and $\Delta K = 1$, so that one concludes that this wing will be strong near the prolate limit and decrease to extreme weakness near the oblate limit. In the discussion below it will be seen that these predictions are amply borne out by the facts. There is only one P-wing in the even sub-band K_{-1} or $K = 1$ because K_{-1} and K must both be less than J.

In the odd sub-bands there is only one P-branch wing for which both K's change by -1. Since this wing satisfies the condition $\Delta J = \Delta K$ at both symmetric limits, it is relatively intense throughout the whole range of κ. There are, however, two R-branch wings for the odd sub-bands, one with $\Delta K_{-1} = 1$, $\Delta K = -1$ and the other with $\Delta K_{-1} = -1$, $\Delta K = 1$.

By applying the intensity condition as before one finds that the former will be strong in the prolate limit and weak near the oblate limit while the converse is true in the latter case.

TABLE 4. SUB-BAND STRUCTURE OF B-TYPE BANDS

R-wing	Q-wing	P-wing	
${}^{be}R_{11}$	${}^{be}Q_{1\bar{1}}$ ${}^{be}Q_{\bar{1}1}$	${}^{be}P_{1\bar{1}}$ ${}^{be}P_{\bar{1}1}$	even sub-bands
${}^{bo}R_{1\bar{1}}$ ${}^{bo}R_{\bar{1}1}$	${}^{bo}Q_{1\bar{1}}$ ${}^{bo}Q_{\bar{1}1}$	${}^{bo}P_{\bar{1}\bar{1}}$	odd sub-bands

The wing designation is that given by Cross *et al.* (1944). R, Q, P mean $\Delta J = 1, 0, -1$, respectively, the superscript b indicates a change of electric moment along the B axis, the superscripts e and o designate the evenness or oddness of the ground-state levels, while the subscripts show the changes in K_{-1} and K.

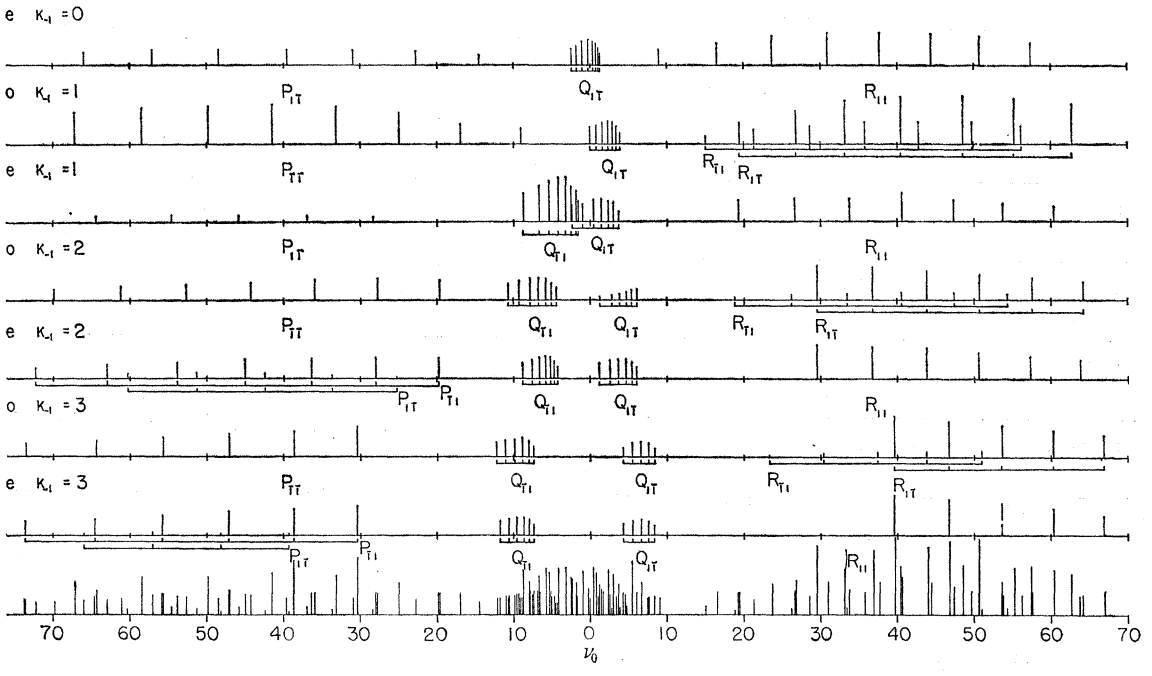

FIGURE 7. A calculated spectrum for an asymmetric rotor with $\kappa = -0{\cdot}9$. The top seven lines show the individual sub-band with $K_{-1} \leqslant 3$, while the lowest line shows the composite spectrum obtained by superimposing the sub-bands. The inertial constants used to calculate the spectrum are $A'' = 5{\cdot}241$, $B'' = 3{\cdot}946$, $C'' = 3{\cdot}878$, $A' = 5{\cdot}200$, $B' = 3{\cdot}870$ and $C' = 3{\cdot}800$. The relative intensities were calculated for a temperature of 300 °K.

In order to discuss the properties of the sub-bands further, it is now necessary to decide whether one will classify the sub-bands on the basis of K_{-1} or K. This choice will have no effect on the general conclusions so, for convenience, the sub-bands discussed here have been chosen so that the value of K_{-1} is constant. On this basis the sub-bands with $K_{-1} \leqslant 3$ have been plotted in figure 7 for an asymmetry of $\kappa = -0{\cdot}9$. It can be seen that all the wings in the even sub-band $K = 0$ are reasonably intense. The fact that the wing ${}^{e}P_{1\bar{1}}$ seems strong in this sub-band apparently violates the intensity condition. It must be remembered that this condition applies only to the relative intensity and it will be seen that this wing does indeed increase in intensity as the oblate-symmetric limit is approached. The ${}^{e}P_{1\bar{1}}$ wing is, however, very weak in the even sub-bands with $K_{-1} \neq 0$. They are, in fact, so weak that

one would have difficulty identifying them in an observed spectrum. The lowest line in the figure is a composite spectrum including all the sub-bands plotted above it. In the composite spectrum one will find it difficult to identify the ${}^{e}P_{1\bar{1}}$ transitions because of their weakness. The transitions in the even sub-bands which belong to the wings ${}^{e}P_{\bar{1}1}$ are relatively quite intense so that one has little difficulty identifying them in the composite spectrum. In the R-branches of the even sub-bands there is only one wing, ${}^{e}R_{11}$, and as was predicted earlier is quite intense. In the P-branch of the odd sub-bands the one wing ${}^{o}P_{\bar{1}\bar{1}}$ is strong as predicted. Of the two R-branch wings the ${}^{o}R_{1\bar{1}}$ is much stronger than the ${}^{o}R_{\bar{1}1}$ as one would expect. Again, it is very difficult to identify the transitions of the weak wings ${}^{o}R_{\bar{1}1}$ in the composite spectrum. The Q-branches are quite intense in each sub-band and for the most part pretty well spread out. However, in the composite spectrum the Q-branches are so badly overlapped that it is extremely difficult to identify the individual transitions with any degree of confidence. This situation makes the Q-branch transitions of little use for the purposes of analysis.

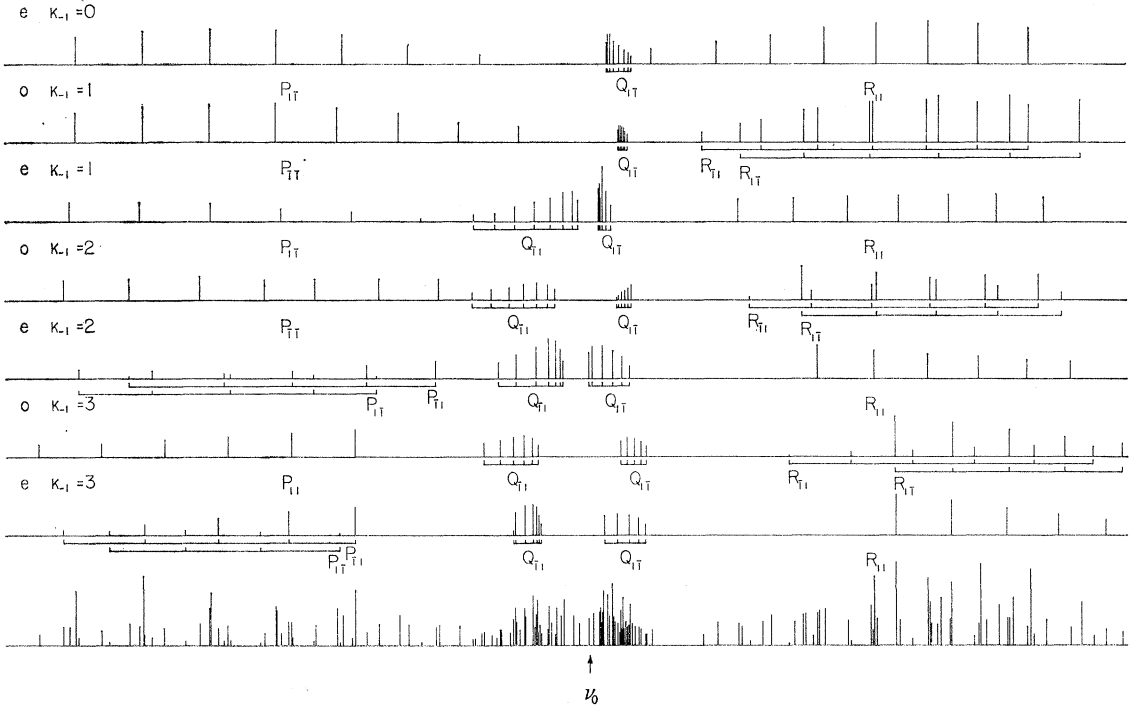

FIGURE 8. A calculated spectrum for an asymmetric rotor with $\kappa = -0{\cdot}5$. The arrangement is the same as figure 7. The inertial constants used to calculate the spectrum are $A'' = 4{\cdot}241$, $B'' = 4{\cdot}218$, $C'' = 3{\cdot}878$, $A' = 5{\cdot}200$, $B' = 4{\cdot}150$ and $C' = 3{\cdot}800$.

Figure 8 is a plot similar to figure 7 except that the value of κ is $-0{\cdot}5$. At this degree of asymmetry one finds that the wings ${}^{e}P_{1\bar{1}}$ and ${}^{o}R_{\bar{1}1}$ are increasing in intensity especially for $K_{-1} = 0, 1, 2$. For the higher values of K_{-1} the increase in intensity is not nearly as marked. Again, the Q-branch transitions are badly overlapped in the regions on each side of the band centre. The particular patterns assumed by the Q-branches in this figure are very sensitive to the relative values of the inertial constants in the two vibrational states. In general the Q-branches will spread from the centre as shown even for excited state constants considerably different from those used in the figures.

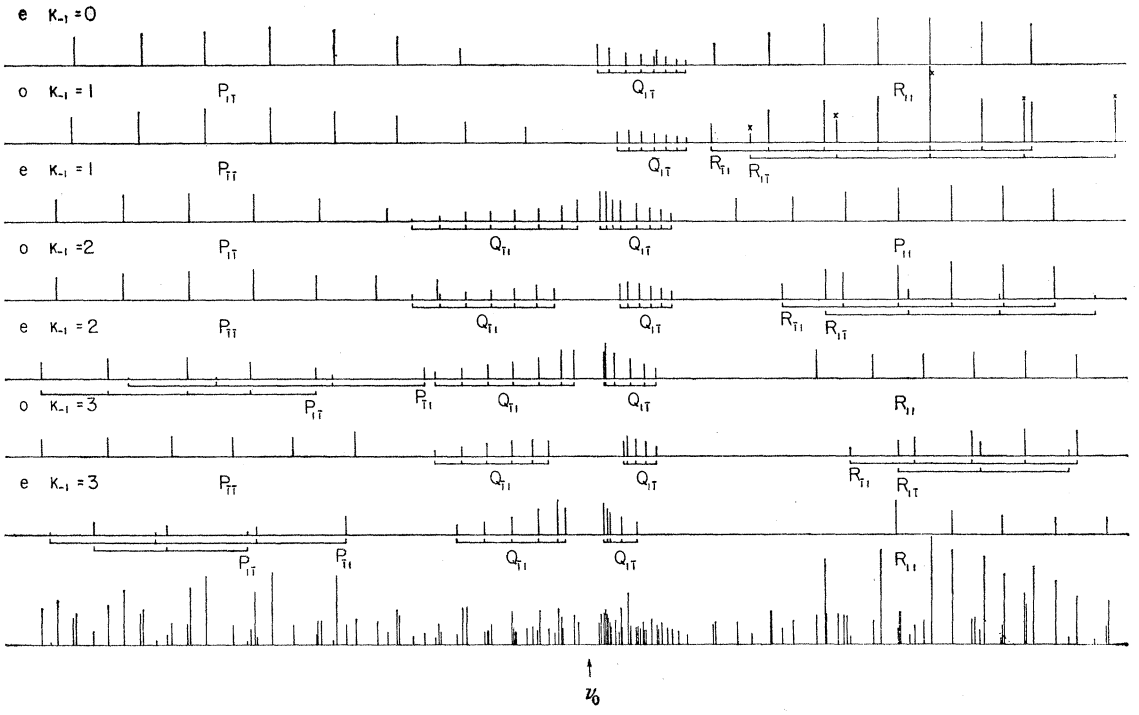

FIGURE 9. A calculated spectrum for an asymmetric rotor with $\kappa = 0{\cdot}5$. The arrangement is the same as in figure 7. The inertial constants used to calculate the spectrum are $A'' = 5{\cdot}241$, $B'' = 4{\cdot}900$, $C'' = 3{\cdot}878$, $A' = 5{\cdot}200$, $B' = 4{\cdot}850$ and $C' = 3{\cdot}800$.

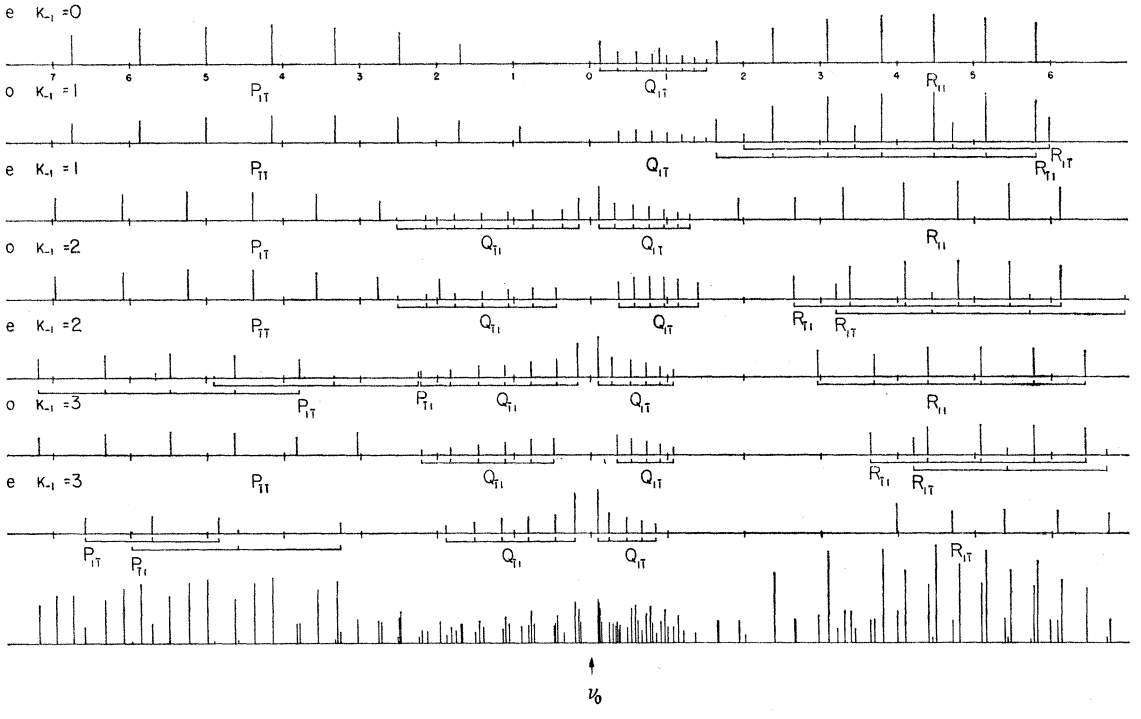

FIGURE 10. A calculated spectrum for an asymmetric rotor with $\kappa = 0{\cdot}9$. The arrangement is the same as in figure 7. The inertial constants used to calculate the spectrum are $A'' = 5{\cdot}241$, $B'' = 5{\cdot}173$, $C'' = 3{\cdot}878$, $A' = 5{\cdot}200$, $B' = 5{\cdot}130$ and $C' = 3{\cdot}800$.

Figure 9 shows the situation when $\kappa = 0{\cdot}5$. At this degree of asymmetry the wings ${}^{o}R_{\bar{1}1}$ and ${}^{e}P_{\bar{1}1}$ are seen to be slightly stronger than the wings ${}^{o}R_{1\bar{1}}$ and ${}^{e}P_{1\bar{1}}$. This condition is just what one would expect from an application of the intensity criterion. The Q-branches are now spread out considerably which would seem to make for ease of identification of these transitions in an observed spectrum. Figure 10 presents the situation for a value of $\kappa = 0{\cdot}9$. This asymmetry is as close to the oblate limit as $\kappa = 0{\cdot}9$ is to the prolate limit and the relative intensities of the two R-wings in the odd sub-bands and the two P-wings in the even sub-bands are quite the reverse in figures 7 and 10. It is thus seen that the relative intensities of the wings in the sub-bands behave in just the manner one predicts from a consideration of their behaviour in the two symmetric-rotor limits.

Dependence of B-type transitions on the inertial constants

The P- and R-branch transitions of the $K_{-1} = 0$ and the odd $K_{-1} = 1$ sub-bands involve the lowest two levels in a given J as follows

$$\left.\begin{aligned} J_{0,J} &\rightleftharpoons (J+1)_{1,J+1}, \\ J_{1,J} &\rightleftharpoons (J+1)_{0,J+1}, \end{aligned}\right\} \tag{28}$$

where one of these rotational levels is in the ground vibrational state and the other is in the excited vibrational state. These energy levels are the ones which were shown to depend mainly on C and the transitions between them are approximately represented by equation (14). Thus these transition frequencies are essentially determined by the values of C' and C'' while the convergence of the R- or P-branch is determined by the difference $(C'-C'')$ just as was true for A-type bands. If the sub-bands had been classified according to the value of K, then one would need to use the arguments appropriate to the transitions of the $K = 0$ and odd $K = 1$ sub-bands of a C-type band. The selection rules would give

$$\left.\begin{aligned} J_{J,0} &\rightleftharpoons J_{J+1,1}, \\ J_{J,1} &\rightleftharpoons J_{J+1,0}, \end{aligned}\right\} \tag{29}$$

and the transition frequencies would be given approximately by equation (23). In this case one finds the dependence is on A', A'' and $A'-A''$ rather than on the C's.

ΔF_2 values of a B-type band

The sub-band structure is useful in determining ΔF_2 values from the transitions of a B-type band, but not quite as straightforward as it was in the case of A- and C-type bands. In principle the frequency difference between any two transitions with the same excited state represents a difference in energy between two ground-state levels. If the difference is taken between two transitions with the same ground state then the result is the energy difference between two excited state levels. Since the sub-bands have been classified according to their ground-state values of K_{-1}, the $\Delta F_2'$ values for the excited state are readily obtained from each sub-band. However, only part of the ground state $\Delta F_2''$ values may be obtained from each sub-band. This is a direct result of the selection rules which require the parity of both K_{-1} and K to change during the transition. The remaining $\Delta F_2''$ values are readily obtained by combining the transitions of the K_{-1} sub-band with those of the $K_{-1}+2$ sub-band. These two sub-bands must have the same parity. The method by which the $\Delta F_2'$ and $\Delta F_2''$ values are obtained is presented in table 5.

TABLE 5. THE COMBINATION OF WINGS TO BE USED TO DETERMINE ΔF_2 VALUES FROM THE R- AND P-BRANCHES OF THE SUB-BANDS OF A B-TYPE BAND

excited state	ground state
${}^{be}R_{11}(K_{-1})-{}^{be}P_{1\bar{1}}(K_{-1})$	${}^{bo}R_{\bar{1}1}(K_{-1})-{}^{bo}P_{\bar{1}\bar{1}}(K_{-1})$
${}^{be}R_{11}(K_{-1})-{}^{be}P_{\bar{1}1}(K_{-1})$	${}^{bo}R_{1\bar{1}}(K_{-1})-{}^{bo}P_{\bar{1}\bar{1}}-(K_{-1}+2)$
${}^{be}P_{1\bar{1}}(K_{-1})-{}^{be}P_{\bar{1}1}(K_{-1})$	${}^{bo}R_{\bar{1}1}(K_{-1}+2)-{}^{bo}R_{1\bar{1}}(K_{-1})$
${}^{bo}R_{\bar{1}1}(K_{-1})-{}^{bo}P_{\bar{1}\bar{1}}(K_{-1})$	${}^{be}R_{11}(K_{-1})-{}^{be}P_{\bar{1}1}(K_{-1}+2)$
${}^{bo}R_{1\bar{1}}(K_{-1})-{}^{bo}P_{\bar{1}1}(K_{-1})$	${}^{be}R_{11}(K_{-1})-{}^{be}P_{1\bar{1}}(K_{-1})$
${}^{bo}R_{1\bar{1}}(K_{-1})-{}^{bo}R_{\bar{1}1}(K_{-1})$	${}^{be}P_{\bar{1}1}(K_{-1}+2)-{}^{be}P_{1\bar{1}}(K_{-1})$

The number in parentheses denotes the K_{-1} value of the sub-band to which the wing belongs.

Since it is very difficult to assign complete Q-branch wings only the ΔF_2 values which can be obtained from P- and R-branch transitions will be discussed. According to table 5 there are six possible types of ΔF_2 values, three which can be obtained from the even sub-bands and three from the odd sub-bands. Four of these possible combinations involve both P- and R-branch transitions. These ΔF_2 values are summarized in table 6. The wings which would be used to obtain these differences for the excited state are also indicated in the table. To find the wings which should be used to obtain the corresponding ground-state differences, one has only to refer to table 5, where the correlation is given.

An examination of these ΔF_2 values reveals that they fall into two groups. One group is identical with that which is obtained from an A-type band, while the other group is identical with that which would be obtained from a C-type band. The dependence of these two groups of ΔF_2 values on the inertial constants is contained in tables 2 and 3. The A-type ΔF_2 values have practically no dependence on A while the C-type ΔF_2 values have practically no dependence on C. The fact that both A- and C-type ΔF_2 values may be obtained from the same B-type band is an indication that more information can be obtained from an analysis of a B-type band than one can obtain from the analysis of either an A- of C-type band.

A third group of ΔF_2 values can be obtained from the two R-wings of the odd sub-bands and the two P-wings of the even sub-bands. These ΔF_2 values involve precisely the same transitions as the other two groups of ΔF_2 values which have been discussed. Thus this new set of ΔF_2 values is not independent of the first two groups and can in fact be deduced by properly combining the A- and C-type ΔF_2 values. In any least squares treatment for the determination of the inertial constants, the inclusion of all three sets of ΔF_2 values will give the P- and R-branch transitions a double weight.

Although in principle one can determine accurately six inertial parameters of a molecule (A, B, C in both vibrational states) from the analysis of a B-type band, there are in practice certain limitations. From figure 7 it is apparent that the ${}^{o}R_{\bar{1}1}$ and ${}^{e}P_{1\bar{1}}$ wings are extremely weak near the prolate-symmetric limit so that the chance of identifying them in an observed spectrum is very small. Unless these transitions can be assigned it is not possible to determine the ΔF_2 values characteristic of a C-type band. This means the available information is reduced to that which is available from the analysis of an A-type band. Thus the A-constant is very poorly determined. On the other hand, it can be seen from figure 10 that the wings ${}^{o}R_{1\bar{1}}$ and ${}^{e}P_{\bar{1}1}$ are extremely weak near the oblate limit. For this reason the A-type ΔF_2 values will be very difficult to obtain and one is reduced to having only those ΔF_2 values which can be obtained from the analysis of a C-type band. In this case the C constant is not determined.

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In figures 8 and 9 one finds that all wings in the P- and R-branches are strong enough to be identified, especially for the lower values of K_{-1}. Thus in the region $-0{\cdot}5 \leqslant \kappa \leqslant 0{\cdot}5$ one should be able to obtain accurate values for the three inertial constants in both the vibrational states.

If the Q-branch region is sufficiently resolved so that the transitions can be uniquely assigned, then one can obtain additional ΔF_2 values. Since these ΔF_2 values involve new

TABLE 6. SUMMARY OF ΔF_2 VALUES WHICH CAN BE OBTAINED FROM THE P- AND R-BRANCHES OF A B-TYPE BAND

	A-type ΔF_2 values		C-type ΔF_2 values*	
$K_{-1}=0, e$		${}^eR_{11}$–${}^eP_{1\bar{1}}$		
	3_{13}–1_{11}			
	4_{14}–2_{12}			
	5_{15}–3_{13}			
	6_{16}–4_{14}			
	7_{11}–5_{15}			
	8_{18}–6_{16}			
$K_{-1}=1, o$		${}^oR_{\bar{1}1}$–${}^oP_{\bar{1}\bar{1}}$	$K_{-1}=1, o$	${}^oR_{\bar{1}1}$–${}^oP_{\bar{1}\bar{1}}$
	2_{02}–0_{00}		2_{20}–0_{00}	
	3_{03}–1_{01}		3_{21}–1_{01}	
	4_{04}–2_{02}		4_{22}–2_{02}	
	5_{05}–3_{03}		5_{23}–3_{03}	
	6_{06}–4_{04}		6_{24}–4_{04}	
	7_{07}–5_{05}		7_{25}–5_{05}	
	8_{08}–6_{06}		8_{26}–6_{06}	
$K_{-1}=1, e$		${}^eR_{11}$–${}^eP_{1\bar{1}}$		
	4_{23}–2_{21}			
	5_{24}–3_{22}			
	6_{25}–4_{23}			
	7_{26}–5_{24}			
	8_{27}–6_{25}			
$K_{-1}=2, o$		${}^eR_{\bar{1}1}$–$P_{\bar{1}\bar{1}}$	$K_{-1}=2, o$	${}^oR_{1\bar{1}}$–$P_{\bar{1}\bar{1}}$
	3_{12}–1_{10}		3_{30}–1_{10}	
	4_{13}–2_{11}		4_{31}–2_{11}	
	5_{14}–3_{12}		5_{32}–3_{12}	
	6_{15}–4_{13}		6_{33}–4_{13}	
	7_{16}–5_{14}		7_{34}–5_{14}	
	8_{11}–6_{15}		8_{35}–6_{15}	
$K_{-1}=2, e$		${}^eR_{11}$–${}^eP_{1\bar{1}}$	$K_{-1}=2, e$	${}^eR_{11}-{}^eP_{\bar{1}1}$
			3_{31}–1_{11}	
			4_{32}–2_{12}	
	5_{33}–3_{31}		5_{33}–3_{13}	
	6_{34}–4_{32}		6_{34}–4_{14}	
	7_{35}–5_{33}		7_{35}–5_{15}	
	8_{36}–6_{34}		8_{36}–6_{16}	
$K_{-1}=3, o$		${}^oR_{\bar{1}1}$–${}^oP_{\bar{1}\bar{1}}$	$K_{-1}=3, o$	${}^oR_{1\bar{1}}$–${}^oP_{\bar{1}\bar{1}}$
			4_{40}–2_{20}	
	5_{23}–3_{21}		5_{41}–3_{21}	
	6_{24}–4_{22}		6_{42}–4_{22}	
	7_{25}–5_{23}		7_{43}–5_{23}	
	8_{26}–6_{24}		8_{44}–6_{24}	
$K_{-1}=3, e$		${}^eR_{11}$–${}^eP_{1\bar{1}}$	$K_{-1}=3, e$	${}^eR_{11}$–${}^eP_{\bar{1}1}$
			4_{41}–2_{21}	
			5_{42}–3_{22}	
	6_{43}–4_{41}		6_{43}–4_{23}	
	7_{44}–5_{42}		7_{44}–5_{24}	
	8_{45}–6_{43}		8_{45}–6_{25}	

* The origin of the ΔF_2 values given in the table make these excited state ΔF_2 values. These same ΔF_2 values may be found for the ground state as shown in table 5.

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transition assignments they will be independent of the ΔF_2 values obtained from the P- and R-branches alone. For this reason these new ΔF_2 values can furnish important checks on the ΔF_2 values obtained from the P- and R-branches. Such checks can be very helpful in verifying quantum number assignments.

The inertial parameters can be determined from the ΔF_2 values using the methods described earlier. It should be remembered that this discussion has been based on the semi-rigid rotor approximation, i.e. a rigid rotor with effective moments of inertia in each vibrational state.

The theory of centrifugal distortion has been worked out by Kivelson & Wilson (1952). To include the correction for centrifugal distortion there are six additional constants (other than A, B, C) to be evaluated for each vibrational state. If sufficient information is known concerning the potential function and geometry of the molecule, one can calculate the correction and apply it level by level. If, as is usually the case, such information is not available then these constants must be determined by the least squares fitting of the data. The energy equation including centrifugal distortion is

$$E = E_0 + A_1 E_0^2 + A_2 E_0 J(J+1) + A_3 J^2(J+1)^2 + A_4 J(J+1)\langle P_z^2\rangle + A_5\langle P_z^4\rangle + A_6 E_0\langle P_z^2\rangle. \quad (29)$$

Methods of evaluation of $\langle P_z^4\rangle$ and $\langle P_z^2\rangle$ are given by Kivelson & Wilson. E_0 is given by either (6) or (7).

The complex structure of asymmetric rotor bands is considerably simplified when it is considered as a composite spectrum made up of sub-bands. This method preserves a close correlation with the bands of the two limiting symmetric-rotor cases thus enabling one to make judicious use of the large body of information about symmetric rotors which is available. This presentation should give an insight into the patterns of related transitions which are most useful in band analysis. An understanding of the sub-band structure is the key to assigning quantum numbers in an observed spectrum.

Once the process of assigning quantum numbers to the observed spectrum is complete, the sub-band treatment enables one to see simply how much information can be deduced from the spectrum. The amount of information which can be obtained from the analysis of an A- or C-type band alone is limited. However, by combining the ground state ΔF_2 values of an A- and a C-type band, the ground-state inertial constants can be completely determined. Similarly in a B-type band, the amount of information which can be obtained is limited near the two symmetric-rotor limits. However, in regions of moderate and large asymmetry one can obtain as much information about the ground state from the analysis of one B-type band as can be obtained by combining the data of an A- and a C-type band.

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