The Band Envelopes of Unsymmetrical Rotator Molecules. I. Calculation of the Theoretical Envelopes

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the higher melting form could be obtained by recrystallization from a polar solvent, ether, would seem to be in accord with this. The origin of the single absorption peaks and their relative sharpness is discussed. An explanation for the former, that is, for the observation of what seems to be simply the pure vibration frequency

of the group giving rise to the absorption is suggested, considering the absorbing group as constrained to lie in one or more particular orientations in the molecule by forces which prevent the group departing from such orientations by more than an amplitude small compared with that of rotation around the $C-O$ bond.

The Band Envelopes of Unsymmetrical Rotator Molecules.

I. Calculation of the Theoretical Envelopes *

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Since the majority of molecules of chemical interest are too heavy to permit resolution of the rotational structure of the infra-red bands, it is of interest to find what information can be derived from a study of the band envelopes. Considerations of the type which Gerhard and Dennison have made for symmetrical molecules have been extended to the unsymmetrical rotator. By the use of an approximation method the envelopes of the three elementary types of band have been calculated for nine different sets of molecular parameters.

INTRODUCTION

THE number of molecules with moments of inertia small enough to permit the resolution and analysis of the rotational structure of the infra-red bands appears to be rather limited. In the majority of cases of interest to the chemist it is an idealization to speak of the bands as consisting of lines, since the spacing of the theoretical lines is less than their breadth must be under the conditions of experiment. Gerhard and Dennison[1] have considered the unresolved bands of symmetrical rotators and have shown that useful information can be obtained from the separations and relative intensities of the maxima. They have calculated a number of band envelopes which we have found very useful in qualitative comparisons. However, the majority of molecules are unsymmetrical and their calculations are inapplicable since with even moderate asymmetry the appearance of the bands is materially modified, especially near their centers.

We have recently observed the spectra of a number of moderately heavy unsymmetrical molecules and have found that the bands may vary considerably in appearance and frequently exhibit distinctive features. For example: In some cases there is only one broad maximum, in others there may be as many as five peaks of unequal intensity. The significance of these features has not always been immediately obvious but their variability suggests that useful information may be obtained from the shapes of the band envelopes alone. To make this possible the theoretical envelopes for various types of molecules must, of course, be known.

The discussions of the unsymmetrical rotator bands which have been given in the literature are quite inadequate for our purposes. Both Dennison[2] and Nielsen[3] have presented diagrams giving the positions and intensities of a few lines as functions of asymmetry, but these plots can give no idea of the intensity distribution in a band since only lines of very low J value are included. Aside from this fact they are restricted

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[1] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

[2] D. M. Dennison, Rev. Mod. Phys. **3**, 2 (1931).
[3] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

to planar molecules. The elaboration of such diagrams to the point where they would be of general use is not practical owing to the amount of labor involved in calculating every line of appreciable intensity. Since we are not interested at all in individual lines it seems more sensible to follow a procedure similar to that used by Gerhard and Dennison for the symmetrical molecule. Even this is difficult in the unsymmetrical rotator case, but we have devised a method for calculating the intensity distribution in a band which can be carried out with a reasonable amount of labor. The method involves a number of approximations but the errors should not be excessive and the results are indeed justified by satisfactory agreement between calculated and observed band envelopes.

In the unsymmetrical rotator case one finds a number of complications which are not present in the symmetrical molecule. Two of these concern us at this point. In the first place it is comparatively seldom that the bands are of any simple type. If symmetry elements are entirely lacking the electric moment or change of moment may have components along all three principal axes of inertia. It is convenient, however, to consider any band as being built up of the three elementary types of structure which would be expected if the electric moment were parallel to the minor, intermediate or major axis in turn. We shall follow Nielsen in designating these structures by the letters A, B and C, respectively. There has been no consistent usage followed in the literature but it is convenient to adopt the convention that the three principal moments of inertia shall be designated by the same three symbols and always in the order $A < B < C$. The reciprocals, designated by small letters, will consequently be in the reverse order: $a > b > c$. An "A" band shall be one in which the electric moment or change of moment is parallel to the minor or A axis, etc.

In the second place the energy levels of the unsymmetrical rotator are arranged in a most inconvenient fashion and it is not possible accurately to represent the positions and intensities of the rotation lines by simple functions of the moments of inertia.
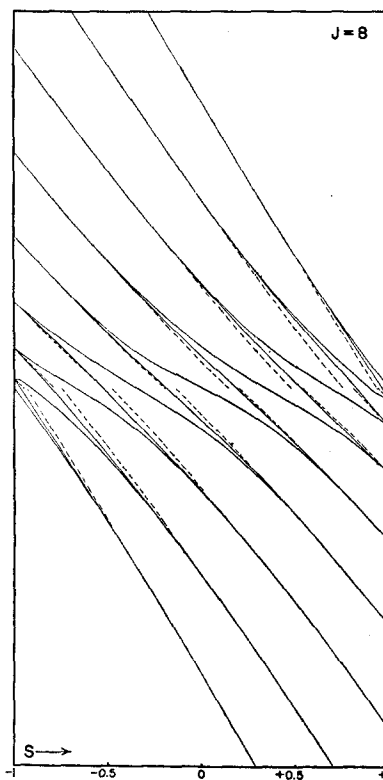

FIG. 1. The energy levels of an asymmetric rotator for $J=8$ plotted as a function of S, with $(a-c)$ and b kept constant. The continuous lines represent the levels given by the exact theory and the dashed lines indicate those given by approximate Eqs. (1) and (2). A horizontal line through the center of the figure would represent the energy $W_b = J(J+1)h^2b/8\pi^2$.

CALCULATION OF THE BAND ENVELOPES

Our first step in the calculation of the band envelopes was to find approximate expressions for the energy levels of the asymmetric rotator which are sufficiently accurate for our purposes and at the same time of a convenient form. These were obtained by an approximate solution of the secular determinant of Wang[4] using second-order perturbation methods.

In any particular case the secular determinant may be written in three different ways. To obtain reasonably accurate values for the energies with only second-order perturbation methods, it is necessary to use different forms depending on the energy ranges with which one is concerned. For levels with energy greater, or less, than $W_b = J(J+1)h^2b/8\pi^2$ the appropriate forms are those in which the diagonal terms are the same

[4] S. C. Wang, Phys. Rev. 34, 243 (1929).

as they would be for symmetrical molecules with the reciprocals of the two like moments of inertia equal to the mean of b and c, or of a and b, respectively.

If one makes an approximation regarding the interaction terms by replacing $(J-\sigma)(J-\sigma+1) \times (J+\sigma)(J+\sigma+1)$ with $[J(J+1)-\sigma^2]^2$, one obtains general solutions for the two cases mentioned above, which may be written as follows:

$$W \approx (h^2b/8\pi^2)\left\{ J(J+1)\left[1-\frac{\rho(5-3S)(1+S)}{8(3-S)}\right]\right.$$
$$\left. +K'^2\frac{\rho(17-14S+S^2)}{8(3-S)}\right\} \quad \text{(Eq. (1)) for } W>W_b,$$

$$W \approx (h^2b/8\pi^2)\left\{ J(J+1)\left[1+\frac{\rho(5+3S)(1-S)}{8(3+S)}\right]\right.$$
$$\left. -K''^2\frac{\rho(17+14S+S^2)}{8(3+S)}\right\} \quad \text{(Eq. (2)) for } W<W_b,$$

where $\rho=(a-c)/b$ and $S=(2b-a-c)/(a-c)$, and K' and K'' are integers with maximum value J.

We prefer to take S as a measure of the symmetry of the molecule rather than Wang's b, since the latter quantity is not uniquely defined but may take three different values depending on how the determinant is written. It will be noted that S takes the values $+1$ for the symmetrical planar molecule, -1 for the symmetrical spindle, and O for those molecules which as regards arrangement of the energy levels we may regard as least symmetrical.

In restricting Eqs. (1) and (2) to their appropriate domains we may make use of an approximation suggested by an equation given in the second paper of Kramers and Ittmann.[5] For the lower limits of K' and K'' we may take $s'J$ and $s''J$, respectively, where

$$s' = (2/\pi) \tan^{-1} [(b-c)/(a-b)]^{\frac{1}{2}}$$

and $s''=1-s'$. The upper limit in each case is of course J.

As may be seen in Fig. 1, our approximation of the energy levels is entirely adequate except for a small "intermediate" region where the energy

[5] H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58**, 217 (1929).

is not greatly different from W_b. On the scale to which the figure is drawn the levels calculated from Eqs. (1) and (2) cannot be seen to deviate from the actual ones up to the point at which the splitting becomes appreciable. From this point on they diverge along the dashed lines. Fortunately the failure of both equations in the transition region is not very serious. In the first place, only a small fraction of the energy levels are concerned. In the second place, the transitions involving levels in this region are the weakest in the cases where the predicted frequencies are most seriously in error, namely in the $\Delta J = \pm 1$ branches of the B type bands and the $\Delta J = 0$ branches of the A and C type bands. In the remaining cases where the transitions are strong the approximation is not so poor.

In a rough first approximation of the band envelopes we have assumed that the transition probabilities are the same as those of the symmetrical rotator, using of course the rules which will be appropriate for the levels given by the two equations, respectively. This will lead to considerable error only in the "intermediate" region, as has been discussed by Dennison.[6] Since our energy expressions are of the same form as those for the symmetrical rotator the procedure which Gerhard and Dennison[7] have worked out is directly applicable and it does not seem to be necessary to give further details of our calculation except to mention two modifications which must be introduced. In the first place, two sets of calculations have to be made in each case taking account of the two regions of energy levels separately. In the second place, some changes have to be made in the limits of integration to take account of the fact that the lower limits of K' and K'' are $s'J$ and $s''J$, respectively.

Although this first approximation just described gives a reasonably satisfactory representation of the intensity distribution in either the $\Delta J = 0$ or the $\Delta J = \pm 1$ branches of a band, the envelope obtained by combining the two may be considerably in error. It is easy to show that the sum of the transition probabilities between

[6] Randall, Dennison, Ginsberg and Weber, Phys. Rev. **52**, 160 (1937).

[7] The expressions given by Gerhard and Dennison contain several typographical errors and should not be used without careful examination.
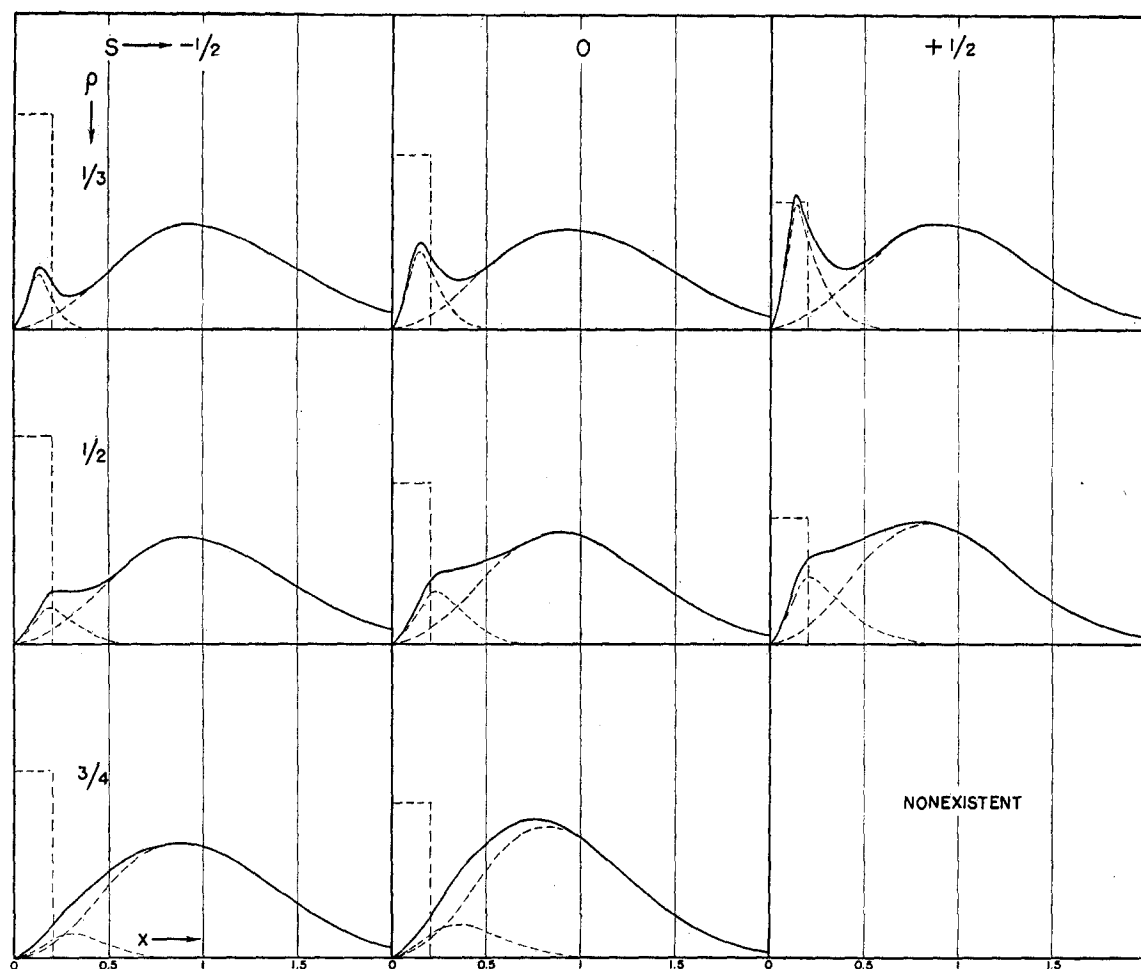
FIG. 2. The A bands (electric moment parallel to the minor axis of inertia) for eight different sets of parameters. The absorption coefficient is plotted as a function of x. One-half the band is shown, with the origin at the left. For further description see text.

levels of a given J value is independent of the symmetry of the molecule. Consequently this sum for any unsymmetrical molecule is the same as for the symmetrical rotator. A similar rule applies to transitions between levels which have J values differing by unity. In our approximation these rules are violated, though the ordinary sum rules are obeyed. This has the result that in the B type bands the branches with $\Delta J = 0$ are robbed of a considerable fraction of their intensity while the $\Delta J = \pm 1$ branches are augmented by the same amount. In the A and C type bands the errors are in the opposite direction and are less serious.

Since the symmetrical rotator intensity expression must hold fairly well for transitions between the highest and lowest energy levels,

respectively, it is evident that these errors must arise from a serious failure in the intermediate region. Besides the failure with respect to the normal transitions there are of course additional transitions which have no analog in the symmetrical rotator case. We have found it difficult to estimate the total contribution of these, though general considerations seem to show that it cannot be large. We shall assume that it may be ignored, which seems to be justified by the observations on the rotation spectrum of water vapor. Out of a total of well over two hundred lines of sufficient intensity to be observed only eight could be identified as due to anomalous transitions, and none of these was very strong.[6]

Considering this assumption to be justified it is possible to apply a simple correction to the
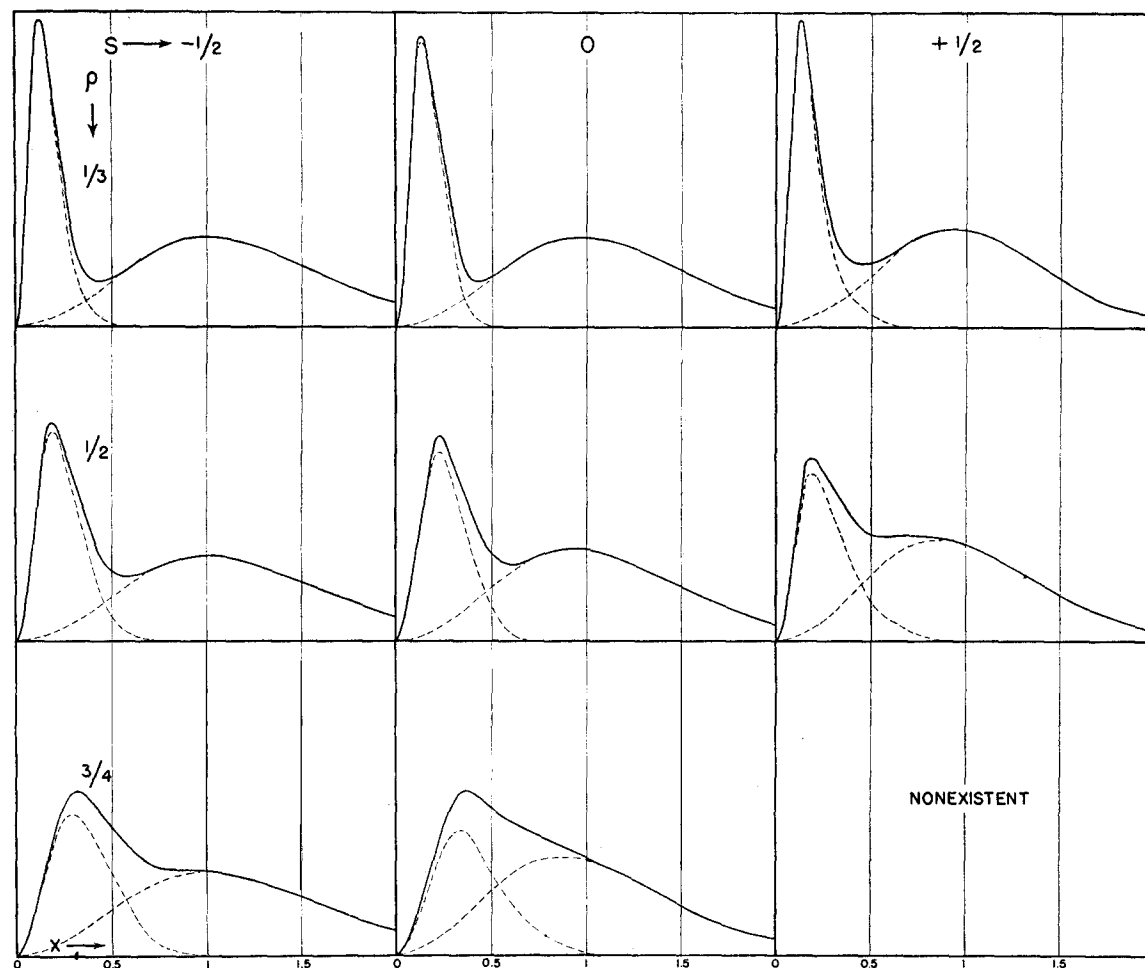
FIG. 3. The B bands (electric moment parallel to the intermediate axis of inertia).

band envelopes which takes into account the errors resulting from our approximation regarding the intensities. Actually of course we must expect that the symmetrical rotator expressions fit fairly well for the highest and lowest levels but fail more and more badly as one approaches the "intermediate" region. To compensate for this precisely would be difficult but it is simple to calculate two limiting envelopes between which the theoretically correct one should lie. In the one case one may assume that the intensity expressions are adequate except in the very center of the "intermediate" region where they abruptly fail, in the other case that they fail uniformly throughout.

In the former case the deficit or excess of the sum of probabilities for any set of transitions $(J \rightarrow J')$ may be accounted for by attributing it

all to one transition in the very center of the "intermediate" region. Correction envelopes may then be calculated in a very simple manner, which have to be added to or subtracted from the envelopes obtained in our first approximation.

In the latter case the correction may be made by multiplying the probabilities of any given set of transitions by a constant factor. Since this factor is independent of J, one needs merely to multiply the ordinates of the $\Delta J = 0$ and the $\Delta J = \pm 1$ branches by the appropriate constants before adding them to obtain the total envelope.

It turns out that the corrected envelopes obtained by these two different procedures do not differ materially. This is, of course, to be expected since in any given set of transitions the probability changes rather rapidly from one line to the next and a small part of the total set is
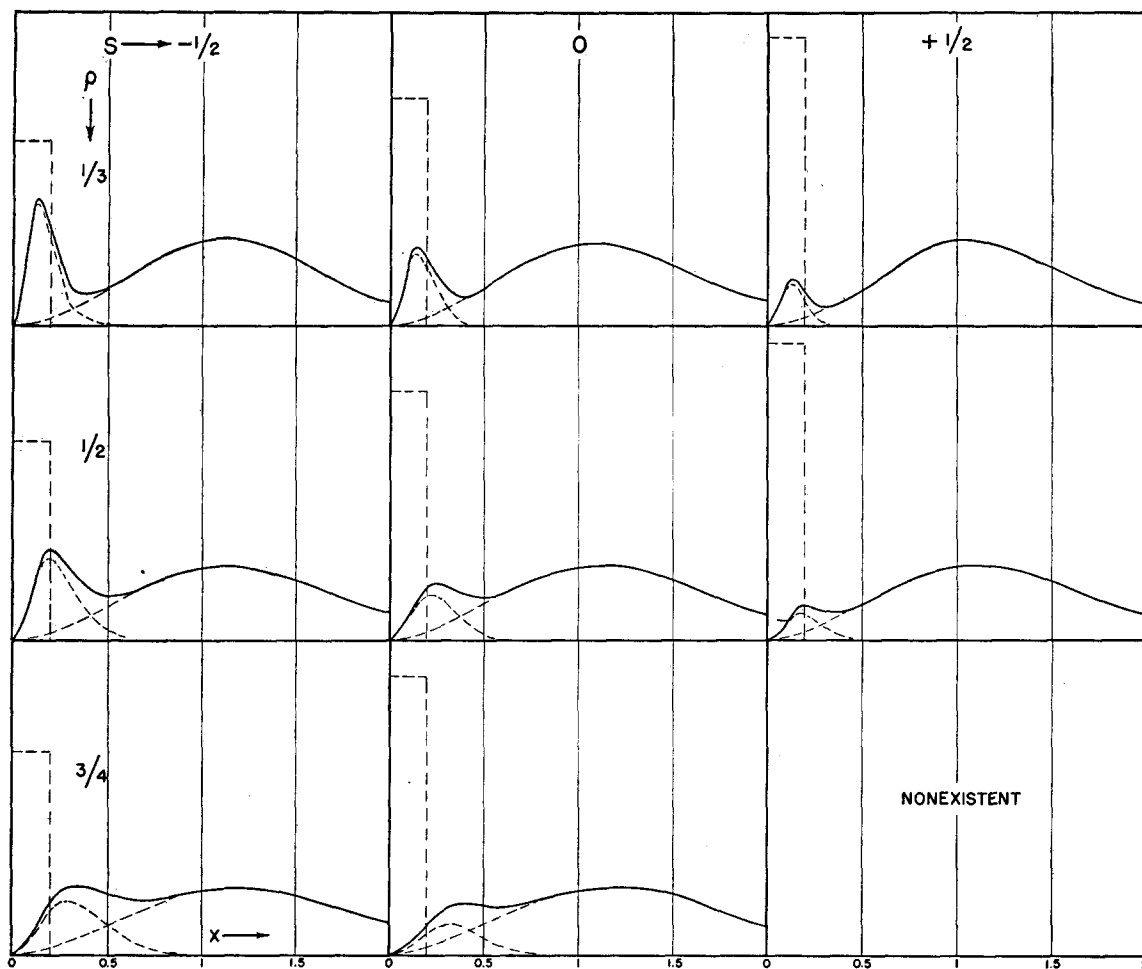
FIG. 4. The C bands (electric moment parallel to the major axis of inertia).

responsible for a large part of the intensity. Consequently we have been satisfied to calculate the envelopes by the second method and believe that they deviate less from the ideal theoretical ones than observed bands will normally do, owing to

the nonrigidity of real molecules and other factors which we have not taken into account.

In Figs. 2, 3, 4 and 5 will be seen the three types of band envelopes for nine different sets of parameters. To save space only one-half the
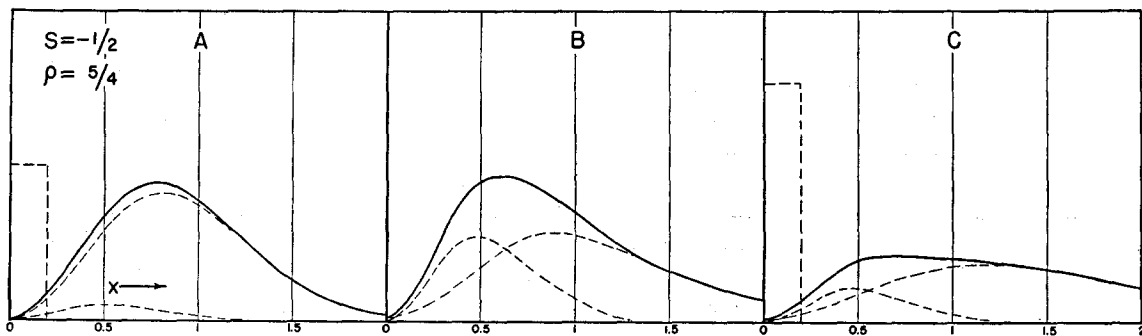
FIG. 5. The A, B and C bands for a molecule with $S = -\frac{1}{2}$ and $\rho = \frac{3}{4}$.
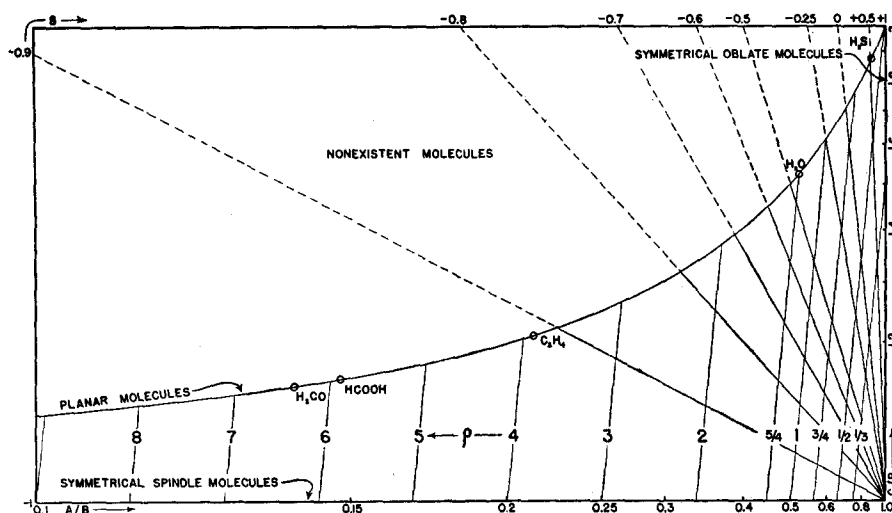
FIG. 6. Lines with constant S and with constant ρ plotted in a field with the dimensions a/b and c/b. The scales provided are in units of A/B and C/B rather than of the reciprocals.

band is shown in each case, with the origin at the left. The absorption coefficient has been plotted against x, where $x = (\nu - \nu_0)\pi(2B/kT)^{\frac{1}{2}}$, so that the figures are adaptable to molecules with any absolute moments of inertia and to any temperature. The frequencies are to be expressed in reciprocal seconds and B (the intermediate moment of inertia) and k in the usual units. The continuous lines represent the total envelopes while the dashed lines indicate the $\Delta J = 0$ and the $\Delta J = \pm 1$ branches from which they are composed. In the A and C type bands the area of the dashed rectangle at the left represents one-half the amount of intensity in the collected "Q" branch. In the approximation to which we worked this branch should appear as a line of zero width. Actually this will not be the case, but in our experience the observed central branches have a width which is mainly due to the stretching of the molecule and to the difference in rotational constants in the normal and excited states and is much greater than would be expected for a rigid molecule with no interaction between rotation and vibration. In most cases this central branch can be well represented by a Gaussian function with width about $0.166x$ at half-height.

Our calculations have been confined to highly unsymmetrical and consequently little elongated molecules. These have been least investigated and seemed to us most interesting. The envelopes of spindle-shaped and slightly unsymmetrical molecules have become familiar through the investigation of several good examples.

Since one may wish to compare our curves with the envelopes of the "perpendicular" bands of the symmetrical rotator calculated by Gerhard and Dennison it may be worth while to call attention to the following facts. As S approaches $+1$ the A and B bands degenerate into perpendicular bands, which is likewise true of the B and C types when S approaches -1. In both limiting cases when $S = \pm 1$, $\rho S = -\beta$, where β is the parameter which Gerhard and Dennison have used to describe the symmetrical molecule.

Figure 6 may be of some assistance in the rapid estimation of the parameters S and ρ in any actual case. The lines of constant S and constant ρ are represented in a field with the dimensions a/b and c/b. For convenience the scales attached have been given in units of A/B and C/B, rather than of their reciprocals. Some molecules whose moments of inertia have been determined with some precision are located on the plot. It is of interest to note that in the extreme right portion of the figure the parameter S varies rapidly with the moments of inertia.

In a paper to follow we shall show how our calculated band envelopes have been of assistance in the interpretation of some observed bands.