

INFRARED BANDS OF SLIGHTLY ASYMMETRIC MOLECULES

BY HARALD H. NIELSEN

MENDENHALL LABORATORY, OHIO STATE UNIVERSITY

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ABSTRACT

As an aid in the interpretation of the infrared spectra of nearly linear, slightly asymmetric molecules, calculations have been made upon molecular models of varying degrees of asymmetry in order to determine the general characteristics of their infrared bands. A_x , A_y , and A_z have been chosen as the principal moments of inertia and the atoms comprising the molecule have been taken to be coplanar such that $A_x = A_y + A_z$. For convenience of calculation, a parameter ρ has been chosen where $\rho = A_z / A_y$ and calculations have been made for ten values of ρ , varying in steps of $\Delta\rho = 0.02$ from $\rho = 0.20$ to $\rho = 0.00$. In the computation of the intensities of lines, Boltzmann factors were used corresponding to a largest moment of inertia $A_x = 2.0 \times 10^{-39}$ gm · cm². As in the work of Dennison on completely asymmetric molecules, of which this is essentially an extension, charts have been prepared depicting the general characteristics of the three types of bands which may occur.

Type A bands. Type A bands arise from vibrations of the electric moment along the z -axis or least axis of inertia and may be seen to consist of P , Q , and R branches. The members of the P and R branches are not single lines as in the symmetric rotator, but are groups of closely spaced lines spreading out as ρ increases. The Q branch also is complex and decreases in intensity as ρ decreases finally vanishing in the limiting linear case where $\rho = 0$.

Type B bands. Type B bands arise from vibration of the electric moment along the y -axis or intermediate axis of inertia. They too may be seen to consist, not of single lines, but of groups of closely spaced lines. As ρ decreases the spacing between these groups becomes coarser and coarser until finally where $\rho = 0$, this type of band vanishes completely. Type B consists essentially only of one branch.

Type C bands. Type C bands arise from vibrations of the electric moment along the x -axis or the largest axis of inertia and for the class of molecules here considered are very similar to type B bands. As in the former case the spacing between line groups becomes coarser and coarser, the band finally vanishing completely where $\rho = 0$.

THE infrared rotational-vibrational bands of molecules belonging to the symmetrical rotator class have been fairly well understood for several years, a fact which may be ascribed to their relative simplicity and because solutions to the problem of the symmetric rotator in the quantum mechanics¹ have been available for some time. In bands of this kind, each line may be described as due to certain definite quantum transitions and the spacings between the lines have certain definite meanings in terms of the moments of inertia of the molecules.

Only recently, however, have quantum mechanics solutions to the asymmetric rotator been made available² and in bands arising from such mole-

¹ D. M. Dennison, *Phys. Rev.* **28**, 318-333 (1926); F. Reiche and H. Rademacher, *Zeits. f. Physik* **39**, 444 (1926); R. de L. Kronig and J. J. Rabi, *Phys. Rev.* **29**, 262 (1927).

² H. A. Kramers and G. P. Ittmann, *Zeits. f. Physik* **53**, 553-565, (1929); S. C. Wang, *Phys. Rev.* **58**, 730-734 (1929); O. Klein, *Zeits. f. Physik* **58**, 730-734 (1929).

cules, the relations of the spacings between lines to the molecular constants are far less apparent. In infrared bands such as those of water vapor³ and hydrogen sulphide⁴ the fine structure lines cannot be arranged in a linearly spaced series and the chief difficulty in their interpretation lies in the inability to ascribe to the observed lines definite quantum transitions. Another complication is, that what frequently is observed as a relatively intense line may indeed be a group of lines lying very close together, incompletely resolved, arising from many different quantum transitions.

In view of these difficulties, it has seemed important to make calculations on molecular models of various degrees of asymmetry, more clearly to understand what would be the general appearances of their bands. In a recent number of *Reviews of Modern Physics*, Dennison⁵ has given two charts illustrating the characteristics of two of the kinds of bands that may occur in completely asymmetric molecules. The purpose of this paper is to extend the work of Dennison and give similar charts demonstrating what will be the behavior of the bands of slightly asymmetric molecules, namely those which approach the linear rotator as their limit. In a later paper it is hoped to discuss characteristic examples of the spectra of such molecules.

A_x , A_y and A_z have been chosen as the three principal moments of inertia where $A_x > A_y > A_z$, and in addition the atoms comprising the molecule have been restricted to lie in one plane, hence $A_x = A_y + A_z$. As in Dennison's work, for convenience of calculation a parameter $\rho = A_z/A_y$ has been chosen and the types of bands occurring have been determined for values of $\rho = 0.20$ to $\rho = 0$ where ρ was made to vary in steps of $\Delta\rho = 0.02$.

The energy value of a given rotational state is according to Wang:

$$E = (h^2/8\pi^2)[J(J+1)/2(1/A_x + 1/A_y) + W\{1/A_z - (1/A_x + 1/A_y)/2\}] \quad (1)$$

where W is one of the $2J+1$ roots of the secular determinant which occurs in the Wang-Klein solution of the asymmetric top.

In order to solve this determinant for the values of W , it is first factored into four algebraic equations. These may then in turn be solved for the W 's which in general are functions of a parameter b defined by Wang:

$$b = \frac{(1/A_x - 1/A_y)}{2[1/A_z - (1/A_x + 1/A_y)/2]} \quad (2)$$

The algebraic equations from which the W 's may be calculated have been obtained for the values of J from $J=0$ to $J=10$ by factoring the corresponding secular determinants and are given below. These may be shown to be identical to those obtained by Dennison⁵ who determined them for J values, $J=0$ to $J=8$ from the Lamé functions used by Kramers and Ittmann in their solution to the asymmetric rotator.

³ W. W. Sleator, *Astrophys. J.* **48**, 125 (1918); W. W. Sleator and E. R. Phelps, *Astrophys. J.* **62**, 28 (1925).

⁴ H. H. Nielsen and E. F. Barker, *Phys. Rev.* **37**, 727-732 (1931).

⁵ D. M. Dennison, *Reviews of Modern Physics* **3**, 280 (1931).

$$J = 0 \quad W = 0$$

$$J = 1 \quad W = 0$$

$$W^2 - 2W + (1 - b^2) = 0$$

$$J = 2 \quad W - 1 + 3b = 0$$

$$W - 1 - 3b = 0$$

$$W - 4 = 0$$

$$W^2 - 4W - 12b^2 = 0$$

$$J = 3 \quad W - 4 = 0$$

$$W^2 - 4W - 60b^2 = 0$$

$$W^2 - (10 - 6b)W + (9 - 54b - 15b^2) = 0$$

$$W^2 - (10 + 6b)W + (9 + 54b - 15b^2) = 0$$

$$J = 4 \quad W^2 - 10(1 - b)W + (9 - 90b - 63b^2) = 0$$

$$W^2 - 10(1 + b)W + (9 + 90b - 63b^2) = 0$$

$$W^2 - 20W + (64 - 28b^2) = 0$$

$$W^3 - 20W^2 + (64 - 208b^2)W + 2880b^2 = 0$$

$$J = 5 \quad W^2 - 20W + 64 - 108b^2 = 0$$

$$W^3 - 20W^2 + (64 - 528b^2)W + 6720b^2 = 0$$

$$W^3 - W^2(35 - 15b) + W(259 - 510b - 213b^2) - (225 - 3375b - 4245b^2 + 675b^3) = 0$$

$$W^3 - W^2(35 + 15b) + W(259 + 510b - 213b^2) - (225 + 3375b - 4245b^2 - 675b^3) = 0$$

$$J = 6 \quad W^3 - W^2(35 - 21b) + W(259 - 714b - 525b^2) - 225 + 4725b + 9165b^2 - 3465b^3 = 0$$

$$W^3 - W^2(35 + 21b) + W(259 + 714b - 525b^2) - 225 + 4725b + 9165b^2 + 3465b^3 = 0$$

$$W^3 - 56W^2 + W(784 - 336b^2) - 2304 + 9984b^2 = 0$$

$$W^4 - 56W^3 + W^2(784 - 636b^2) - W(2304 - 34144b^2) - 483840b^2 + 55440b^4 = 0$$

$$J = 7 \quad W^3 - 56W^2 + W(784 - 784b^2) - 2304 + 20736b^2 = 0$$

$$W^4 - 56W^3 + W^2(784 - 2296b^2) - W(2304 - 99360b^2) - 870912b^2 + 353808b^4 = 0$$

$$W^4 - W^3(84 - 28b) + W^2(1974 - 2324b - 1162b^2) - W(12916$$

$$- 52948b - 70660b^2 + 13636b^3) + 11025 - 308700b - 847098b^2 + 566244b^3 + 61425b^4 = 0$$

$$W^4 - W^3(84 + 28b) + W^2(1974 + 2324b - 1162b^2) - W(12916$$

$$\begin{aligned}
& + 52948b - 70660b^2 - 13636b^3 + 11025 + 308700b - 847098b^2 \\
& - 566244b^3 + 61425b^4 = 0 \\
J = 8 \quad & W^4 - W^3(84 - 36b) + W^2(1974 - 2988b - 2250b^2) - W(12916 \\
& - 68076b - 127620b^2 + 39420b^3) + 11025 - 396900b - 1455930b^2 \\
& + 1477980b^3 + 363825b^4 = 0 \\
& W^4 - W^3(84 + 36b) + W^2(1974 + 2988b - 2250b^2) - W(12916 \\
& + 68076b - 127620b^2 - 39420b^3) + 11025 + 396900b - 1455930b^2 \\
& - 1477980b^3 + 363825b^4 = 0 \\
& W^4 - 120W^3 + W^2(4368 - 1656b^2) - W(52480 - 138528b^2) + 147456 \\
& - 2428416b^2 + 118800b^4 = 0 \\
& W^5 - 120W^4 + W^3(4368 - 4176b^2) - W^2(52480 - 430848b^2) \\
& + W(147456 - 12266496b^2 + 1797120b^4) + 92897280b^2 \\
& - 92897280b^4 = 0 \\
J = 9 \quad & W^4 - 120W^3 + W^2(4368 - 3096b^2) - W(52480 - 243360b^2) - 147456 \\
& - 4068864b^2 + 668304b^4 = 0 \\
& W^5 - 120W^4 + W^3(4368 + 7056b^2) - W^2(52480 - 702720b^2) \\
& + W(147456 - 19528704b^2 + 6441984b^4) + 145981440b^2 \\
& - 291962880b^4 = 0 \\
& W^5 - W^4(165 - 45b) + W^3(8778 - 7380b - 4086b^2) - W^2(172810 \\
& - 387630b - 536130b^2 + 100710b^3) + W(1057221 - 7388820b \\
& - 19565154b^2 + 11135340b^3 + 822149b^4) - 893025 + 40186125b \\
& + 189344790b^2 - 268964550b^3 - 45052805b^4 + 9398025b^5 = 0 \\
& W^5 - W^4(165 + 45b) + W^3(8778 + 7380b - 4086b^2) - W^2(172810 \\
& + 387630b - 536130b^2 - 100710b^3) + W(1057221 + 7388820b \\
& - 19565154b^2 - 11135340b^3 + 822149b^4) - 893025 - 40186125b \\
& - 189344780b^2 + 268964550b^3 - 45052805b^4 - 9398025b^5 = 0 \\
J = 10 \quad & W^5 - W^4(165 - 55b) + W^3(8778 - 9020b - 6886b^2) - W^2(172810 \\
& - 473770b - 865810b^2 + 224290b^3) + W(1057221 - 9030780b \\
& - 30555954b^2 + 23531860b^3 + 6390549b^4) - 893025 + 49116375b \\
& + 288482310b^2 - 542218050b^3 - 346473045b^4 + 62214075b^5 = 0 \\
& W^5 - W^4(165 + 55b) + W^3(8778 + 9020b - 6886b^2) - W^2(172810 \\
& + 473770b - 865810b^2 - 224290b^3) + W(1057221 + 9030780b \\
& - 30555954b^2 - 23531860b^3 + 6390549b^4) - 893025 - 49116375b \\
& + 288482310b^2 + 542218050b^3 - 346473045b^4 - 62214075b^5 = 0 \\
& W^5 - 220W^4 + W^3(16368 - 5456b^2) - W^2(489280 - 932800b^2)
\end{aligned}$$

$$\begin{aligned}
& + W(5395456 - 46095104b^2 + 3165184b^4) - 14745600 \\
& + 639452160b^2 - 252702720b^4 = 0 \\
W^6 - 220W^5 + W^4(16368 - 11396b^2) - W^3(489280 - 2215840b^2) \\
& + W^2(5395456 - 138188864b^2 + 20438704b^4) - W(14745600 \\
& + 3177400320b^2 - 2697416640b^4) - 21897216000b^2 \\
& + 77803545600b^4 - 2031480000b^4 = 0
\end{aligned}$$

The selection rules for the asymmetric rotator have been correctly stated by Kramers and Ittmann⁶ in their third paper and again in a more simple manner by Dennison.⁵ In both papers, it is shown that there are three sets of rules depending upon whether the electric moment vibrates along the x -axis, the y -axis or the z -axis. In accord with these, asymmetric molecules may in general have, as we shall see, three different kinds of infrared bands.

The intensity with which a line will occur in the spectrum corresponding to a given quantum transition is expressed by the relation:⁷

$$I_{J'\tau'}^{J\tau} = K(A_{J\tau}^{J'\tau'})^2 N(J) g_J / g_{J'} e^{-E(J,\tau)/kT} \quad (4)$$

where $N(J)$ is the number of molecules in the state J , g_J and $g_{J'}$, the *a priori* probabilities of the initial states and final states respectively. $A(J'\tau'/J\tau)$ are the amplitudes which in the case of the symmetric rotator are well known.¹ For the asymmetric rotator, the amplitudes for a $(J, \tau, M - J', \tau', M')$ transition can be calculated from the already known amplitudes of the symmetric rotator and from the characteristic functions. Once the values of W have been obtained, a set of matrix equations may be obtained from which these characteristic functions may be determined. The actual $J\tau - J'\tau'$ intensity can then be found by summing over all the Zeemann components. Kramers and Ittmann⁶ have, however, devised a method which, while it is entirely equivalent to the above procedure, seems more adaptable for numerical work. This method was here used for the most asymmetrical case (i.e. $\rho = 0.2$) and the results compared with those given by the symmetric amplitudes for corresponding transitions. The divergence between the two was found to be so slight that in the remaining cases, the latter were used. Certain transitions may of course occur here for which there are no corresponding ones in the symmetrical case, but for the range of molecules under consideration, these take place with an intensity only slightly different from zero, and may well be neglected.

A complete picture of each of these types of bands should of course include the most intense lines of the spectrum, i.e., those which will be intense enough to be distinguishable from neighboring lines. Just how many values of J will be needed to do this must depend to a large extent upon the moments of inertia of the molecule, since for larger values of the energy the Boltz-

⁶ H. A. Kramers and G. P. Ittmann, *Zeits. f. Physik* **60**, 663-681 (1930).

⁷ R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, New York, 1927.

mann factor of Equation (4) becomes an important item in determining the intensity of a line. For example; in the case of lighter molecules, only a few values of J might be required, while for heavier molecules, several might be necessary.

Type A

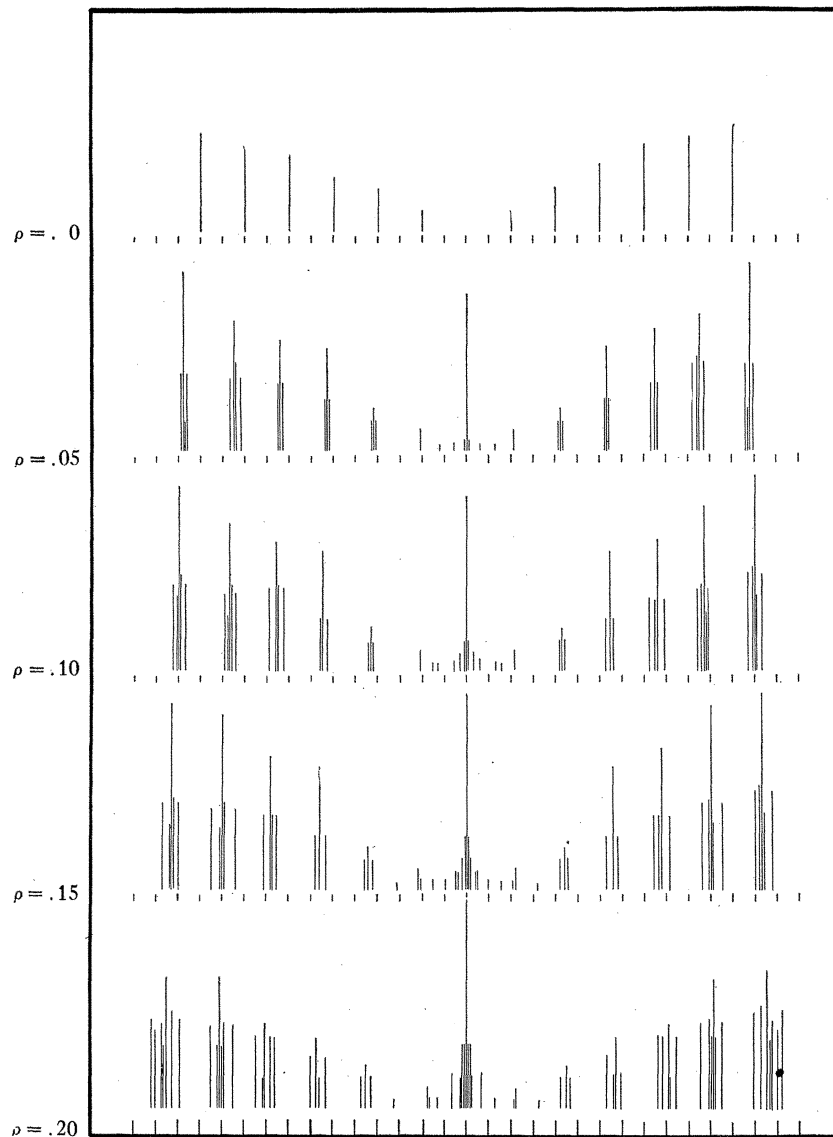


Fig. 1.

Thus for such molecules as formaldehyde ($\begin{matrix} \text{H} \\ \diagup \\ \text{H} \end{matrix} - \text{C} = \text{O}$) where two of the moments of inertia are quite large (of the order of 2.0×10^{-39} gm·cm²) and the third small, a fairly good idea as to the appearance of the bands, especially

near the center, may be had with values of J up to say $J=6$. Since it is thought that these calculations will prove most useful to molecules of just this kind, Boltzmann factors have been used throughout corresponding to a largest moment of inertia. $A_x = 2.0 \times 10^{-39}$ gm·cm². The forty-nine levels of $J=0, 1, 2, 3, 4, 5, 6$ were used to determine the positions of the lines in these bands. The results of these computations are plotted in Figures 1, 2 and 3.

In Figure 1 is shown the type of band arising when the electric moment changes along the least axis (Z -axis) of inertia. This type of band we designate as type A. It consists of P , Q and R branches of which the Q branch diminishes as ρ approaches zero. This becomes apparent by inspection of Equation (1), for keeping A_x constant, then as ρ decreases, the energy values where $W \neq 0^*$ become greater and greater while at the same time the corresponding Boltzmann factors become smaller and smaller until in the limiting case, the linear rotator where $\rho=0$, they become zero. In the latter case the Q branch vanishes completely, as is well known from the HCl-like spectra. From Figure 1 it is clear that to give a complete picture of this type of band showing all the line groups that would be observable in the case of the molecule which we have chosen, many more values of J would be required than have here been used. From the six values used, however, a fairly good idea may be had how the band appears near the center and how each line in the linear case becomes a group of closely spaced lines as ρ becomes different from zero. The scale to which these values have been plotted is indicated on the diagram where the unit is taken as $h/8\pi^2 A_x$. Hence two lines on the diagram which are separated by say n units differ in frequency by an amount $nh/8\pi^2 A_x$. It should also be pointed out that in such cases where two lines were found to lie extremely close together they have been plotted as one line of their combined intensities.

In Figure 2 is shown the kind of band arising when the electric moment vibrates along the intermediate (y -axis) of inertia and it is denoted as type B. It should be emphasized that the scale to which these values have been plotted is much smaller than before. The unit used and indicated in Figure 2 is taken as $5h/8\pi^2 A_x$. As is indicated in the diagram, as ρ decreases, the spacing between lines or groups of lines becomes coarser and coarser until in the limiting case where $\rho=0$, this type of band completely vanishes. In other words the ratio between the spacings of groups of lines in type B and in type A becomes larger and larger as ρ decreases. The reason for this becomes clear upon inspection of the selection rules and of the energy equation (1). It was pointed out in the preceding section that as ρ is decreased, the energy values where $W \neq 0$ become larger and larger. The increase of spacing in type B as ρ is decreased is inherent with this same effect since the permitted transitions are just between such levels which as they increase in energy, also spread farther and farther apart. One observes, moreover, that as the spacing between lines increases, corresponding lines on opposite sides of the center of

* For the molecules which we are here dealing with, one of the W values for each value of J is found to be practically zero. In fact its value decreases with ρ and where $\rho=0$ this value of W becomes identically zero.

the band begin to vary widely in their intensities. It is evident that this should be so for the line on one side of the center corresponding to one on the other side of the center arising from a $J'\tau' - J''\tau''$ transition is a line arising from a $J''\tau'' - J'\tau'$ transition; the ratio of their intensities being given by:

$$\lambda = e^{-\frac{(E''-E')}{kT}} \quad (5)$$

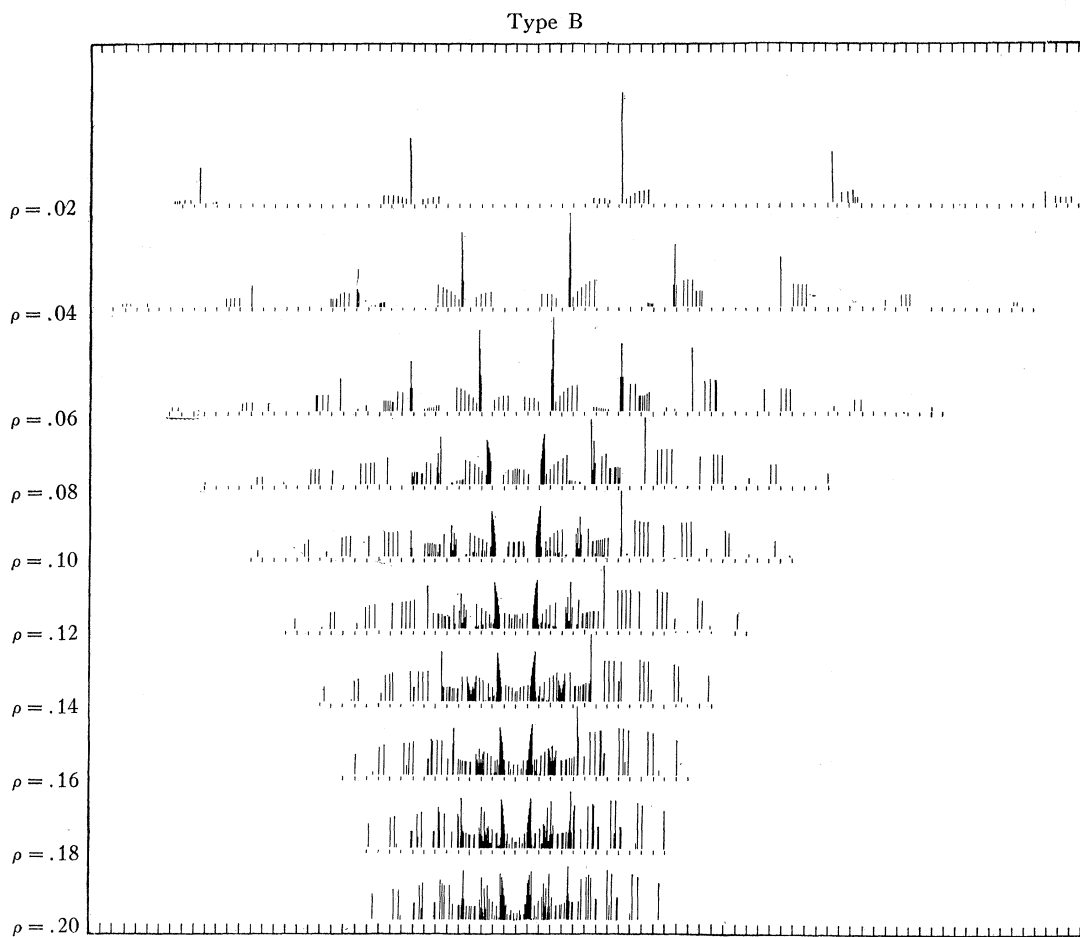


Fig. 2.

If now E'' represents increasingly more and more energy as ρ decreases than does E' , then by (5) the ratio of intensities of these corresponding lines must become smaller and smaller. It is evident that the degree to which these differences in intensity of corresponding lines about the center take place depends entirely upon the values of the moments of inertia. As was earlier pointed out, these calculations have been made for a molecule for which $A_x = 2.0 \times 10^{-39}$ gm · cm², but for any other molecule where the moments of inertia are much different these intensities may be somewhat invalid.

As in type A, it is clear that more values of J would be required to give a complete description of these bands. Near the center, however, a fairly complete representation of the structure of the bands exists. The main difference in this region of adding more values of J would be to intensify line groups and to further fill in the background between such groups. It is believed that a fair representation of the lines is given out to about three lines from the center. As before when two lines lie too close together to be plotted separately they have been plotted as one line with their combined intensities.

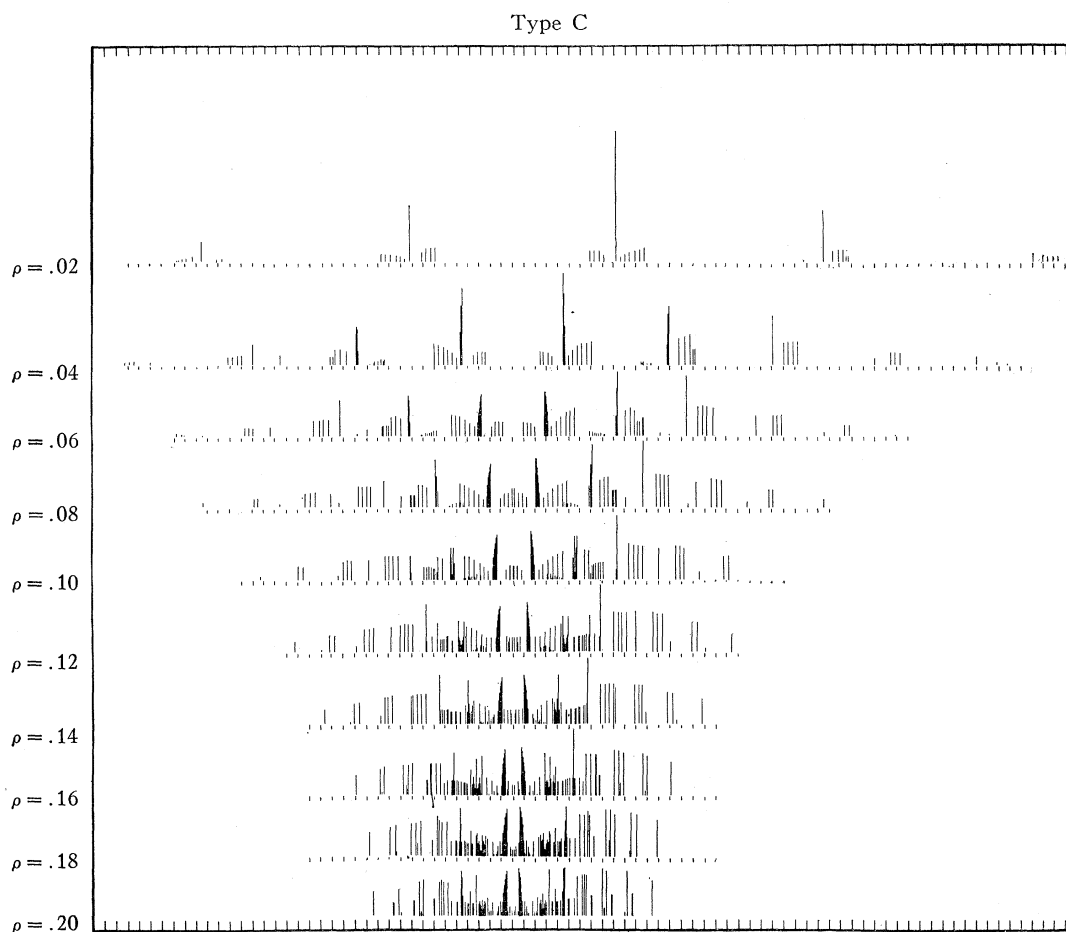


Fig. 3.

In Figure 3 is shown the third type of band which may occur and which has been designated as type C. This type of band originates with vibrations of the electric moment along the largest axis (x -axis) of inertia. Within the range of molecules with which we have been dealing this type of band much resembles type B, and for $\rho = 0$ they would become identical. The main differ-

⁸ F. Hund, *Zeits. f. Physik* **43**, 805 (1927).

ence between the two may be seen from the diagram to be a tendency of the two lines nearest the center to form a *Q* branch while no such tendency exists in the type B band. In our case, however, what has been said about type B bands with respect to spacing and intensities is equally applicable to type C. Figure 3 is plotted to the same scale as Figure 2.

In such molecules where there are two or more identical atoms, each energy level must be classified as symmetric or antisymmetric. The symmetry properties of several kinds of molecules have been discussed by Hund⁸ and more fully by Dennison,⁵ but since the nature of this classification must depend upon the characteristic functions of the respective vibrations as well as upon those for the rotations and must consequently be considered especially for each individual molecule, this has not been taken into account. No generalization whatever can be made about the effect upon the appearance of the band except that it tends to make certain lines appear stronger than others.

By way of summary, it may be stated that as an aid in the interpretation of the infrared bands of the nearly linear slightly asymmetric rotators, calculations have been made on models of varying degree of asymmetry, each characterized by a parameter ρ defined as the ratio between the least to the intermediate moment of inertia. The further restriction that the atoms comprising the molecule shall lie in one plane has also been introduced. Three different types of bands were found to occur depending upon whether the electric moment vibrates along the least, the intermediate or the largest axis of inertia. Of these three types of bands, two were found to resemble one another to a great extent within the range of molecules that have been considered. Three charts summarizing the results of the calculations have been prepared which it is believed represent fairly accurately the general characteristics of the infrared bands of slightly asymmetric molecules, and it is hoped that these may prove themselves of value to the infrared spectroscopist as an aid in classifying and interpreting the spectra of such molecules.