THE INFRARED SPECTRA OF POLYATOMIC MOLECULES

PART I

DAVID M. DENNISON

UNIVERSITY OF MICHIGAN

INTRODUCTION

WHEN several atoms combine to form a molecule there are many questions which the physicist would like to be able to answer. Perhaps the most important question is whether a given set of atoms can combine or not to form a molecule. The chemists for many years have been able to give an answer through the use of the rules of valence. While this answer has been very satisfactory in its success in justifying known compounds and in predicting new ones, it has not been possible until recently for the physicist to interpret these rules in the light of quantum mechanics. The work of Heitler and London[1] on the formation of homopolar diatomic molecules has shown that valence is to be connected with the symmetry character of the wave functions of the outer electrons in each atom. These ideas have not as yet been applied in detail to molecules with more than two atoms but there is little doubt but that they can be so extended. The question of whether a set of atoms may form a stable molecule depends then, upon the electronic states of the individual atoms.

In the present article we shall not consider the electronic state of the molecule nor spectral bands which involve changes in the electronic energy. Rather it will be assumed that a stable configuration of the atomic nuclei does exist and the problem which we shall attempt to treat is that of the space configuration of the nuclei and of the force functions acting upon the nuclei in the neighborhood of their equilibrium position. Although this neglect of spectra involving a change in the electronic state is a great limitation of the general problem of molecular structure it is partly justified by the fact that so little is known experimentally about such spectra whereas there exists a great body of data on the infrared bands. Undoubtedly more experimental information can be obtained relating to the visible and ultraviolet bands of polyatomic molecules and this may well present one of the most interesting problems to be attacked in the near future.

Recently three very important books have appeared on the subject of infrared spectra by J. Lecomte,[2] by F. I. G. Rawlins and A. M. Taylor[3] and by Cl. Schaefer and F. Matossi.[4] Each of these books summarizes more or less fully the entire field of infrared spectroscopy and together they present descriptions of practically every paper that has appeared on this subject. In view of the existence of these reference books, it would appear to be an

[1] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[2] J. Lecomte, Le Spectre Infrarouge, Paris 1928.

[3] F. I. G. Rawlins and A. M. Taylor, Infrared Analysis of Molecular Structure, Cambridge, 1929.

[4] Cl. Schaefer and F. Matossi, Das Ultrarote Spektrum, Berlin 1930.

unnecessary duplication for us to attempt here any summary of the whole body of infrared data even if it were possible in the space at our disposal. We would like rather to present the methods which are available for the interpretation of infrared spectra and to apply these methods to a set of typical cases. The material will therefore be presented in logical rather than chronological order and should be supplemented by the books which have been quoted above.

Part I comprises an exposition of the methods which may be used for studying the infrared spectra of polyatomic molecules. The order of the sections, the vibrational, the rotational and the symmetry properties of molecules is based upon the appearance of a spectrum as viewed with spectroscopes of progressively higher resolving powers. The gross features of a spectrum are the positions and intensities of the bands and these depend wholly upon the vibrational properties of the molecules. Greater resolution reveals the existence of fine structure in the bands which is to be associated with the rotation of the system and eventually may show certain intensity ratios among these lines which can only be explained when we take into account the symmetry character of the wave functions.

Part II which will appear in a forthcoming issue of The Reviews of Modern Physics will contain a detailed application of these methods to the interpretation of the infrared spectra of a number of the more important polyatomic molecules.

Section 1. The Vibration Spectrum of the Polyatomic Molecule

1. The normal vibrations.

The vibration spectra of diatomic molecules have been investigated in great detail both theoretically and experimentally. A review of the general properties will be interesting since they may be carried over directly to apply to the polyatomic case. Let us suppose that the system consists of two nuclei A and B which have a position of stable equilibrium at the point $r = r_0$.

In Fig. 1 is plotted a typical curve representing the potential energy as a function of the distance between the nuclei. Fig. 2 shows the force $F = dV/dr$ for the same molecule plotted to the same scale.

When the nuclei are very close together the force is very large and in a direction tending to separate them. At $r = r_0$ the force vanishes and the linearity of the curve in this region is a measure of how nearly the oscillator may be considered as simple harmonic for these amplitudes. For larger values of r the force reaches a maximum corresponding to the point of inflection of the potential curve. As r approaches infinity the potential approaches asymptotically a straight line whose height represents the work of dissociation of the molecule. The horizontal lines in Fig. 1 represent the possible energy states, which are discrete below D but continuous above. It is found that the distance between the lower energy levels is nearly constant and is much smaller than the distance D. Thus for HCl we have $h\nu_0/D = 0.026$ and for

CO $h\nu_0/D = 0.023$ where $h\nu_0$ is the distance between the two lowest energy states.

We shall principally be interested in the lowest energy states of vibration where the force function is nearly linear since infrared absorption bands are concerned with transitions from the lowest energy state to those states immediately above. The problem may be treated by the wave mechanics when it is found that the wave functions and energy values of these lowest states are nearly identical with the functions and energy values of the simple harmonic oscillator. The results of this treatment may be summarized for transitions between the lowest states.
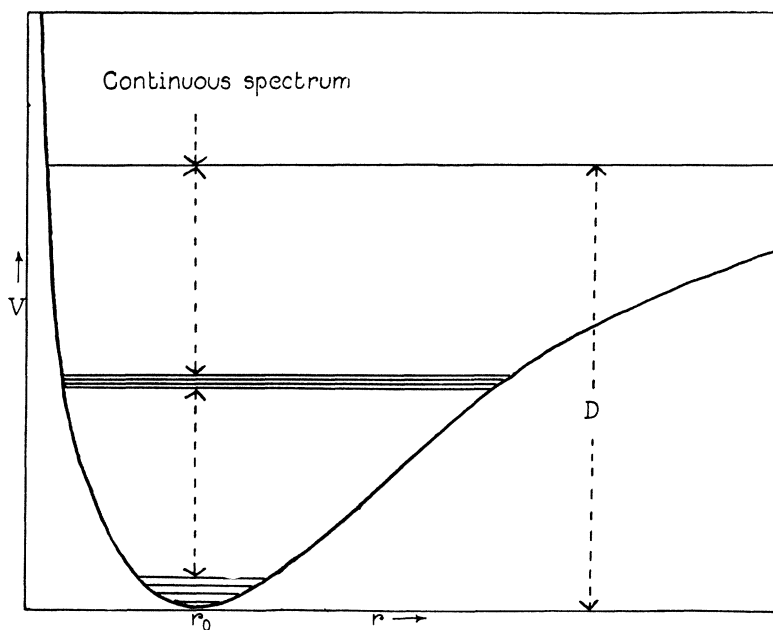

Fig. 1.

1st. The frequency of radiation absorbed or emitted is very nearly the mechanical frequency of motion as computed in the classical manner. The fundamental band corresponds to changes of one unit in the quantum number, the overtones to changes of more than one unit.

2nd. The intensity of radiation is nearly that computed by classical electrodynamics, that is, it depends upon the square of the amplitude of the change of the electric moment.

3rd. The wave function has a value sensibly different from zero only in the immediate neighborhood of the point $r = r_0$ corresponding to the fact that the classical amplitude of the motion is small compared with the equilibrium distance between the atoms.

These general properties may also be shown to hold for the polyatomic

molecule.* Here we have a number s of atomic nuclei which we assume to have a possible equilibrium position. In this section we shall deal with the internal or vibrational degrees of freedom. The whole system has $3s$ degrees of freedom but, of these, three correspond to uniform translation of all particles along the three space directions. In general when the particles do not lie along a straight line there will also be three degrees corresponding to rotations of the whole system about three axes. Thus of internal degrees of free-
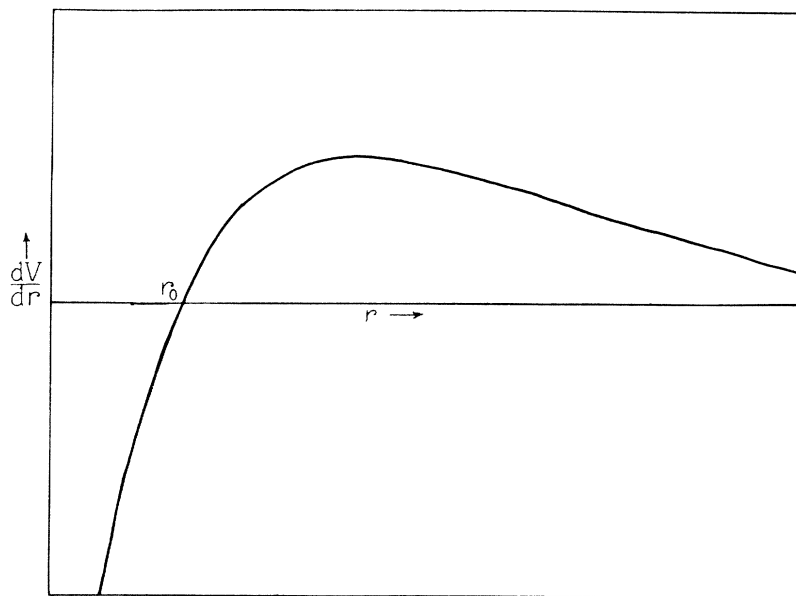

Fig. 2.

dom there will be $n = 3s - 6$. Let there be chosen a set of coordinates $q_1, q_2, \cdots q_n$ giving the displacements from equilibrium, (i.e. in the vibrationless state all q_s are equal to zero). In considering the system either in classical mechanics or in wave mechanics, the first step is to find the Hamiltonian. The kinetic and potential energies assume a simple form in consequence of the property (3) that the amplitude of motion in first approximation may be taken as infinitesimal compared with the normal distances between the nuclei.

$$T = \tfrac{1}{2}(a_{11}\dot{q}_1{}^2 + \cdots + a_{nn}\dot{q}_n{}^2 + 2a_{12}\dot{q}_1\dot{q}_2 + \cdots)$$
$$V = \tfrac{1}{2}(b_{11}q_1{}^2 + \cdots + b_{nn}q_n{}^2 + 2b_{12}q_1q_2 + \cdots)$$

where the a's and b's are constants. A linear transformation may now be affected to the so-called normal coordinates,†

* Perhaps it should be emphasized that these properties depend upon experimental data, namely upon the fact that for real molecules $h\nu_0/D \ll 1$ and that the force field is found to be so nearly linear in the region of the energy states in question.

† See, for example, E. T. Whittaker, "Analytical Dynamics," 2nd edition, p. 178.

$$q_i = \sum_{k=1}^{n} c_{ik} x_k$$

whereby the energies obtain a very simple form.

$$T = \tfrac{1}{2}(\dot{x}_1{}^2 + \dot{x}_2{}^2 + \cdots + \dot{x}_n{}^2)$$

$$V = \tfrac{1}{2}(\lambda_1 x_1{}^2 + \lambda_2 x_2{}^2 + \cdots + \lambda_n x_n{}^2).$$

The λ's are the n roots, distinct or multiple, of the determinant,

$$\left| a_{ik}\lambda - b_{ik} \right| = 0$$

and the coefficients c_{ik} of the linear transformation are given by the first minors of the determinant.

The Hamiltonian may then be written,

$$H = H_1 + H_2 + \cdots + H_n$$

where

$$H_j = \tfrac{1}{2}p_j{}^2 + \tfrac{1}{2}\lambda_j x_j{}^2.$$

It is evident that we have in effect an aggregation of n independent simple harmonic oscillators. The translation into the language of wave mechanics is now particularly simple in that the wave function of the whole system is the product of the wave functions for the individual oscillators and the characteristic value is the sum of the individual characteristic values. This method of treatment is evidently allowed because the system is separable in the n normal coordinates. Thus,

$$\psi^{V_1 V_2 \cdots V_n} = \psi_{(y_1)}^{V_1}\psi_{(y_2)}^{V_2} \cdots \psi_{(y_n)}^{V_n}$$

$$W^{V_1 V_2 \cdots V_n} = W^{V_1} + W^{V_2} + \cdots + W^{V_n}.$$

The quantity $\psi_{(y_i)}^{V_i}$ represents the V_i Hermitian orthogonal function where we have introduced as variable $y_i = (2\pi)^{1/2}h^{-1/2}\lambda_i{}^{1/4}x_i$. The index V_i is an integer 0, 1, 2, and the function $W^{V_i} = (V_i + \tfrac{1}{2})h\lambda_i{}^{1/2}/2\pi$. Reference to the classical theory of small oscillations shows that the system will vibrate with a number n of normal or characteristic frequencies $\nu_1, \nu_2, \cdots \nu_n$. These are given by the relation $\nu_i = \lambda_i{}^{1/2}/2\pi$ and consequently we may write $y_i = 2\pi\nu_i{}^{1/2}h^{-1/2}x_i$ and $W^{V_i} = (V_i + \tfrac{1}{2})h\nu_i$. While the method of derivation of the Hermitian functions and their general expression is given in most of the treatises on the quantum theory, it may be interesting to give the first four of them in normalized form.

$$\psi_{(y)}^{0} = \pi^{-1/4}e^{-y^2/2}$$

$$\psi_{(y)}^{1} = \pi^{-1/4}2^{1/2}ye^{-y^2/2}$$

$$\psi_{(y)}^{2} = \pi^{-1/4}2^{-1/2}(2y^2 - 1)e^{-y^2/2}$$

$$\psi_{(0)}^{3} = \pi^{-1/4}3^{-1/2}(2y^3 - 3y)e^{-y^2/2}$$

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The next problem is that of determining the selection rules and to do this the matrices representing the electric moment of the system must be examined. Let R be the electric moment having three components along three perpendicular axes in the molecule R_ξ, R_η and R_ζ. Any one of these, say R_ξ, will be given, for small displacements of the atoms by a linear function of the original coordinates $q_1, \cdots q_n$, and therefore by a linear function of the normal coordinates.

$$R_\xi = (R_\xi)_0 + \sum A_k x_k$$

$(R_\xi)_0$ is the permanent electric moment in the ξ direction while the coefficients A_k may be determined for any system whose Hamiltonian is known.

The matrix elements in question are

$$R_{\xi V_1{}' \cdots V_n{}'}^{V_1{}'' \cdots V_n{}''} = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} R_\xi \psi_{(y_1)}^{V_1{}''} \cdots \psi_{(y_n)}^{V_n{}''} \psi_{(y_1)}^{V_1{}'} \cdots \psi_{(y_n)}^{V_n{}'} dy_1 \cdots dy_n.$$

A well-known property of the Hermitian orthogonal functions is that the integral

$$\int_{-\infty}^{+\infty} y \psi^{V''} \psi^{V'} dy$$

vanishes unless the integers V'' and V' differ by one unit. In that case

$$\int_{-\infty}^{+\infty} y \psi^V \psi^{V-1} dy = V^{1/2}/2^{1/2}.$$

The matrix elements representing R_ξ will therefore all vanish except; (a) the diagonal elements $R_{\xi V_1 \cdots V_n}^{V_1 \cdots V_n} = (R_\xi)_0$, and (b) those elements for which all the initial and final numbers are the same with the exception of one, say V_k, and this increases or decreases by one unit.*

$$R_{\xi V_1 \cdots V_{k-1}, \cdots V_n}^{V_1 \cdots V_k \cdots V_n} = A_k h^{1/2} V_k^{1/2}/\pi 2^{3/2} \nu_k^{1/2}.$$

This expression for the electric moment gives the desired selection rules and when taken in conjunction with the energy relation shows that the frequencies of radiation which may be absorbed or emitted are just the normal frequencies $\nu_1, \cdots \nu_n$. It has therefore been shown that a wave mechanical treatment of the system yields results identical with those obtained from the classical theory. It must always be remembered that the system we have considered is only an approximation to a real molecule, the simplification lying in the fact that we consider the motion (i.e. values of $\psi\psi^*$ differing from zero) to exist in a region small compared with the inter-atomic distances, and that we take the force fields to be linear near the equilibrium positions. An actual molecule of course only approximates to these conditions and consequently we shall expect that the selection rule deduced above will not be rigorously obeyed and that harmonic and overtone bands corresponding to multiple changes in the quantum numbers will be observed in the spectrum.

* For a single harmonic oscillator with an electric charge e and a mass μ it is easy to show that $A = e/\mu^{1/2}$ and we then obtain the familiar expression for the amplitude of the electric moment $(hVe^2/8\pi^2\mu\nu)^{1/2}$.

Most infrared data on molecules consist of two curves, experimentally determined, giving the spectral energy from a hot source as a function of wave-length. The first curve is taken with a cell containing the gas in question in the path of the radiation, the second is taken with the cell empty, and these curves together yield the percentage transmission of the gas for the range of wave-lengths studied. This final curve giving the transmission as a function of the wave-length or of the frequency will usually show a number of intense regions of absorption corresponding to the fundamental frequencies of the system together with some fainter regions corresponding to the overtones. The appearance of an absorption band depends largely upon the degree of resolution of the spectrometer. With very low resolution it appears without structure, with higher resolution it may be seen to have several adjoining maxima which form the envelope of the band. With sufficiently high resolution the curve will consist of a large number of individual lines, in some cases regularly and in others irregularly spaced. The phenomena of the envelope and of the individual lines are consequences of the rotation of the system and will be dealt with in Section 2. At present we are concerned only with the positions and intensities of each band taken as a whole. Intensity is best defined as the integral of the absorption coefficient over the region of the band in question, $I = \int \alpha d\nu$ where α is related to the percentage transmission T and the cell-length l by Lambert's law.

$$T = e^{-\alpha l}.$$

Unfortunately the intensity I is very difficult to determine experimentally for it is found that with a spectrometer of the usual resolution, Lambert's law is not obeyed. This is due to the fact that the band actually consists of the rotation lines whose width is much narrower than the degree of resolution of the spectrometer. Either of two methods might be employed to remove this difficulty, the fine structure lines may be broadened by examining the gas under a high pressure, or observations may be taken with so little gas in the cell that the transmission T always remains very high. In most of the experimental curves which are available however these conditions do not obtain. Formally for such curves an apparent absorption coefficient and an apparent intensity may be found but these results must be treated with caution. Experience has shown that in absolute amount the true intensity may be as great as ten times the apparent intensity. The errors introduced by comparing the intensities of two bands in the same spectrum are of course not as large as this but they will exist and will tend to make strong bands appear less strong than they actually are.

Leaving aside the difficulties encountered in actually measuring the intensity I, we may consider its relation to the Einstein coefficients and to the matrix elements of the electric moment. The following equation giving the intensity of absorption from the state labeled with the quantum numbers a to the state with numbers b has been very clearly derived by Tolman[5] and his derivation need not be repeated here.

[5] R. C. Tolman, Statistical Mechanics with Applications to Physics and Chemistry, New York 1927 (See page 173 and following).

$$I_b{}^a = (8\pi^3 \nu g_b N_a / 3 c h g_a)(R_a{}^b)^2 (1 - e^{-h\nu/kT}).$$

Here g_a and g_b are the weights of the two states, N_a the number of molecules per cc in the state a and $R_a{}^b$ is $b \rightarrow a$ element of the electric moment. If, as is often the case, R has three components along the three perpendicular axes then

$$(R_a^b)^2 = (R_{\xi a}^b)^2 + (R_{\eta a}^b)^2 + (R_{\xi a}^b)^2$$

When we are interested in comparing the intensities of several fundamental absorption bands, the above formula becomes quite simple. If the experiments have been carried out at room temperature, N_a becomes N the total number of molecules per cc and the factor $(1 - e^{-h\nu/kT})$ may be set equal to unity. This is of course because most of the fundamental bands in question lie at shorter wave-lengths than 20μ and a substitution shows that $h\nu/kT$ is then considerably larger than one. Consider the intensity of the kth fundamental. All the vibrational quantum numbers remain zero excepting V_k which changes from zero to one.

$$(I_1{}^0)_k = (N\pi g_1 / 3 c g_0)(A_k{}^2 + B_k{}^2 + C_k{}^2).$$

This expression is identical with the corresponding classical formula for the intensity. Two special examples will be familiar to the reader. For a linear harmonic oscillator $g_1 = g_0$ and $A^2 = e^2/\mu$ where e is the charge and μ the reduced mass. Let the line of the oscillator be along the ξ axis, when $B = C = 0$. We then see that the energy absorbed per second by each oscillator is $\pi e^2/3\mu c$, just the classical expression. Again we might consider an isotropic oscillator in space. It may then be shown that $g_1 = 3g_0$ and $A^2 + B^2 + C^2 = e^2/\mu$ and thus the energy absorbed per second by each system is $\pi e^2/\mu c$; again a classical result.*

The wave mechanical treatment of the vibration spectrum of molecules may be summarized as follows. To the approximation in which the motions of the atoms are small compared with the inter-atomic distances, the system may absorb or emit radiation with a series of frequencies. These frequencies are the so-called normal frequencies and may be computed with the classical

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* These examples suggest that we may compare the intensity of the kth fundamental band of a polyatomic molecule with the intensity of absorption of an oscillator with the reduced mass μ_k the frequency ν_k and the charge e_k. We then obtain.

$$(I_1{}^0)_k = N\pi g_1 e_k{}^2 / 3 c g_0 \mu_k.$$

This conception becomes useful when we identify the amplitude of the comparison oscillator with the amplitude of some one q_r (or linear combination) of the coordinates of the polyatomic molecule. We may then with Dennison[6] regard e_k as an effective moving charge. A more satisfactory viewpoint is however that of Kemble, Bourgin and Dunham.[7] who write the electric moment E of the molecule as a function of the coordinates $q_1 \cdots q_n$. In this case e_k is the first derivative of E with respect to q_r at the equilibrium position. $e_k = (\partial E / \partial q_r)_0$ showing clearly that we may expect e_k to be the same for only those vibrations ν_k which may be identified with the same coordinate q_r.

[6] D. M. Dennison, Phys. Rev. 31, 503 (1928).

[7] E. C. Kemble and D. G. Bourgin, Nature, 117, 789 (1926); D. G. Bourgin, Phys. Rev. 29, 794 (1927); J. L. Dunham, Phys. Rev. 34, 438 (1929).

theory of small oscillations. The intensity of absorption of the corresponding fundamental bands depends upon the amplitude of the electric moment for the normal vibration in question.

A number of models representing particular molecules have been treated making use of various assumptions to obtain the potential energy function. Historically the first example is that of CO_2 as studied by Bjerrum.[8] He assumed a model having the form of an isosceles triangle with the carbon atom at the apex. He used several forms for the potential function; one in which the potential depended only upon central force fields, that is, only on the distances between the atoms, and others in which the potential was also a function of the apex angle. Hund[9] and Kornfeld[10] examined the spectra of H_2O, H_2S and the CO_3 ion using a model in which the force fields were non-central, the mechanism residing in a polarization of the electron shells surrounding the atoms. Dennison[11,12] found the normal vibrations for models of NH_3 and CH_4 assuming the forces to be central and Nielsen[13] made a like treatment of the CO_3 ion.

In all these investigations, the molecule was assumed to have a certain geometric symmetry in its equilibrium configuration. Thus the atoms of H_2O were to stand at the corners of an isosceles triangle, the NH_3 atoms at the corners of a regular pyramid with the nitrogen atom at the apex, and the atoms of methane formed a regular tetrahedron with the carbon atom in the center. The potential energy function whether dependent upon central forces or not was always assumed to have the same symmetry as the geometric configuration of the molecule.

A common feature of all the above mentioned work is that many of the properties of the normal vibrations are independent of the particular constants involved in the potential function and depend only upon the geometric symmetry. These properties which we shall call the character of the vibration, involve the direction of vibration of the electric moment, some information as to its magnitude and a general description of the motions of the individual atoms. The problem of the vibration of groups of atoms possessing geometric symmetry has been considered by C. J. Brester,[14] but his solution while very satisfactory and undoubtedly correct is not in a form suitable for presentation here. It is however possible to obtain the character of the vibration of symmetrical polyatomic molecules through very simple considerations, which may be described as follows. Since the work of Brester has shown that the character of the vibration is independent of the particular values of the forces between the atoms, but depends only upon the geometric configuration, we may examine those limiting cases where some of the forces are extremely weak compared with others. In the next paragraphs some examples

[8] N. Bjerrum, Verh. d. D. Phys. Ges. 16, 737 (1914).

[9] F. Hund, Zeits. f. Physik 31, 81 (1925).

[10] H. Kornfeld, Zeits. f. Physik 26, 205 (1924).

[11] D. M. Dennison, Phil. Mag. 1, 195 (1926).

[12] D. M. Dennison, Astrophys. Journ. 62, 84 (1925).

[13] H. H. Nielsen, Phys. Rev. 32, 773 (1928).

[14] C. J. Brester, Kristallsymmetrie und Reststrahlen, Utrecht 1923.

of the method will be presented where the character of vibration of the simpler cases may be checked by reference to the work of Hund, Dennison, etc., cited above.

2. The triatomic molecule YX₂.

The first problem is that of the triatomic molecules having two equal atoms YX_2 such as H_2O, H_2S, etc. We assume that the atoms lie at the corners of an isosceles triangle, the unequal atom Y being at the vertex, and that the potential function possesses this geometric symmetry. As limiting case, let the force field between the X atoms be very strong compared with the field between the X atoms and the Y atom. Clearly one of the vibrations will be that of a mutual vibration of the X atoms, the Y atom being virtually unaffected, since it is so weakly bound. (See Fig. 3)
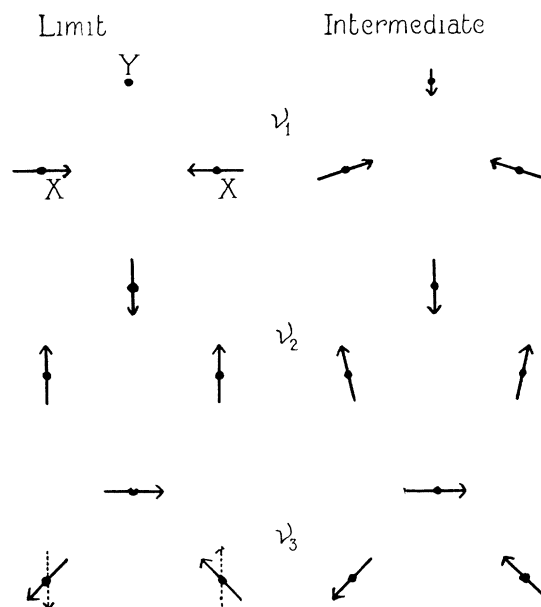

Fig. 3.

This frequency which we call ν_1 does not in the limit have a changing electric moment but it is easy to proceed to an intermediate case. Let the forces between the Y atom and the X atoms grow slowly. The Y atom will be perturbed by the motion of the X atoms but because of the symmetry in the force fields its motion will lie along the bisector of the apex angle. The X atoms will now no longer move along the same line for the whole system must fulfill the mechanical conditions that the linear momenta and also the angular momenta must be constants; in the present instance chosen zero. The direction of the change of the electric moment is clearly along the symmetry line for this vibration ν_1. Its amplitude will depend upon the particular values of the force fields but will not in general vanish.

Returning to the limiting case, consider the vibration of the Y atom rela-

tive to the X atoms. The X atoms are thought of as being so tightly bound that they form a rigid dumbell. The problem becomes similar to the vibration of a mass point elastically bound to a rigid bar. Evidently ν_2 will be one of the normal vibrations, the two X atoms moving in parallel directions and opposed to the motion of the Y atom. In the intermediate case where the force fields are all of the same order of strength, it will be seen that the Y atom will somewhat influence the X atoms so that they no longer move parallel to each other. The motion however is symmetrical about the line bisecting the apex angle and the direction of change of the electric moment is clearly along this line. While the amplitude of the electric moment is dependent upon the constants of the force fields, it will not be difficult to give some estimate of its magnitude. To the extent to which the amplitude of motion of the X atoms may be replaced by the component of their motion along the bisector of the apex angle, the amplitude of the motion of the Y atom relative to the center of gravity of the X atoms is that of an harmonic oscillator having a frequency ν_2 and a mass $\mu = 2mM/(2m+M)$ where m and M are the masses of the X and Y atoms respectively.

The third normal frequency ν_3 results from a tipping of the bar representing the X atoms relative to the Y atom. Because of the mechanical demands on the angular and linear momenta of the system the X atoms do not move along the dotted lines as might be supposed but rather along lines which may be proved to be the sides of the original isosceles triangle. To the approximation that the amplitudes of motion are small compared with the equilibrium distances, the distance between the two X atoms remains a constant and the Y atom moves along a straight line perpendicular to the bisector line. These properties are independent of the relative field-strengths and may be carried over directly to the intermediate case. The direction of the change of the electric moment is for this vibration perpendicular to the line bisecting the apex angle. The magnitude of the displacement of the Y atom relative to the center of gravity of the X atoms is dependent only upon the masses of the particles and the form of the triangle but not upon the force fields. (This obtains since the direction of motion of the particles is independent of the magnitudes of the force fields.) The amplitude of this displacement may be shown to be equal to the amplitude of an oscillator of frequency ν_3 and reduced mass $\mu_3 = 2mM/(2m+M)+2mM^2/(2m+M)^2\tan^2\alpha$ where α is the half-angle at the apex of the isosceles triangle.*

The character of the vibration becomes of particular importance when we come to examine the fine structure of the bands caused by the interaction of the vibration and rotation. We shall consider the H_2O spectrum in detail later but it may be remarked here that of the three fundamental bands, we shall expect two of them ν_1 and ν_2 to possess a similar fine structure since the

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* Continuing the line of thought presented in the footnote to page 287 we may say; let the intensity of this band ν_3 be measured experimentally and found to be I_3. Let us identify the amplitude of the comparison oscillator with the amplitude of motion of the Y atom relative to the center of gravity of the X atoms. The effective change $e_3 = [3\mu_3cI_3/N\pi]^{1/2}$ represents the first derivative of the electric moment E for a displacement of the atoms of the kind involved in the motion ν_3.

direction of vibration of the electric moment is the same. Actually in the observed spectrum we are able to identify with certainty only two of the three fundamental frequencies. Since these are found to have quite different fine structures, we may conclude that one of them is ν_3 while the other may be either ν_1 or ν_2.

It now becomes very interesting and important to examine the deviations from simple harmonic motion when the higher approximations are taken into account. In this case the motion for the vibrations ν_1 and ν_2 deviates somewhat from simple harmonic motion but remains always symmetrical about the bisector line. This means that in general faint overtone bands will appear whose positions are approximately given by $n_1\nu_1 + n_2\nu_2$ where n_1 and n_2 are any set of integers. For all these overtones the direction of the electric moment is along the bisector line and consequently they will all have a fine structure similar to the fundamental bands ν_1 and ν_2. The frequency ν_3 will also have harmonics $n_3\nu_3$ but here the change of the electric moment will be perpendicular to the bisector line for all odd values of n_3 and parallel to it for all even values of n_3. This is true also of the general overtone $n_1\nu_1 + n_2\nu_2 + n_3\nu_3$, that is, the change of the electric moment is along the bisector line for even values of n_3 and perpendicular to it for odd values.

The proof of these statements follows from a wave mechanical treatment. In first approximation the wave function of the vibrations of the system is $\psi^{V_1 V_2 V_3} = \psi_{(y_1)}^{V_1} \psi_{(y_2)}^{V_2} \psi_{(y_3)}^{V_3}$ where $\psi_{(y_i)}^{V_i}$ is the V_i Hermitian orthogonal function with the variable y_i. y_i is simply a constant times the normal coordinate x_i. Set up the rectangular axes ξ and η where ξ is perpendicular to the bisector line and η lies along it; the origin lying at the center of gravity of the system. Now by examining the determinant of the normal vibration problem with regard to the geometric symmetry of the potential and kinetic energies, it may be shown that x_1 and x_2 are even functions of ξ while x_3 is an odd function. That is by reversing the directions right and left $x_1 \rightarrow x_1$, $x_2 \rightarrow x_2$, but $x_3 \rightarrow -x_3$. If the Hermitian functions are examined it is seen that they are odd or even functions of their coordinate, depending upon whether the index number V is an odd or even integer. Consequently $\psi_{(y_1)}^{V_1}$ and $\psi_{(y_2)}^{V_2}$ are even functions of ξ for all values of V_1 and V_2, but $\psi_{(y_3)}^{V_3}$ is an even or odd function depending upon whether V_3 is an even or odd integer.

We now wish to consider higher order approximations and we expand the perturbed wave function in terms of the unperturbed functions. This expansion will have the following property, since the perturbing potential must necessarily be symmetrical in ξ; it will be a series involving only even integers for V_3, when the unperturbed state has an even value of V_3 and will involve only odd integers when the unperturbed state has an odd value of V_3. Thus the perturbed wave functions show exactly the same odd or even character in ξ that the unperturbed functions showed.

The matrix elements of the electric moment in the η direction will be determined by $\int R_\eta \Psi^{V_1'' V_2'' V_3''} \Psi^{V_1' V_2' V_3'} dy_1 dy_2 dy_3$ where these wave functions are the perturbed ones. The component of the electric moment in the η direction R_η must necessarily be a symmetrical function of ξ. (In first approximation

it is proportional to η, $R_\eta = R_0 + A\eta$.) Consequently the integrand will be an even function in ξ only when $V_3{}'' - V_3{}'$ is an even integer. Only under this condition may the integral giving the matrix element be non-vanishing since the limits of the integral correspond to a range of ξ from $+\infty$ to $-\infty$. In a similar way we may show that the matrix elements of the electric moment in the ξ direction can differ from zero, only when $V_3{}'' - V_3{}'$ is an odd integer, thus proving the relationship between the overtones and the direction of the change of the electric moment.

Two special cases of the triatomic molecule may be considered. If all three of the atoms are taken equal and the configuration is that of an equilateral triangle, the two frequencies ν_2 and ν_3 become identical and the system becomes degenerate.*

This degeneration is equivalent to the type of degeneration which exists when a mass particle, free to move in a plane, is elastically bound to a point. The motion, isotropic in a plane, has a frequency independent of the direction
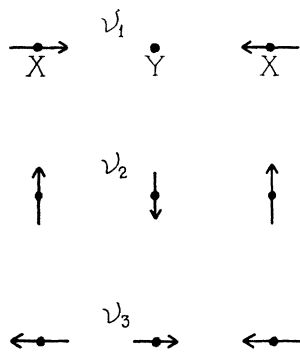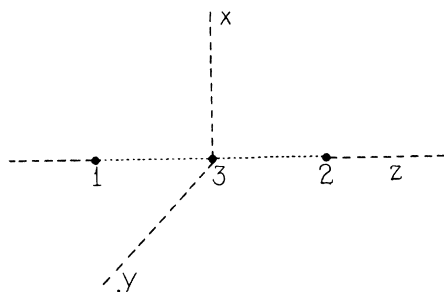

Fig. 4.   Fig. 5.

of vibration in the plane and this is exactly the condition here. It may be shown that the frequency ν_2 is independent of the direction of motion of any one of the three atoms. Of course, as soon as the direction of one atom is chosen, the motion of the other atoms is quite fixed and allows no arbitrariness. In this case of the three equal atoms the motion corresponding to ν_1 becomes particularly simple. All three atoms move on median lines and the triangle formed by them remains equilateral throughout the motion.

The second special case occurs when the three atoms lie along a straight line, a model which probably represents the CO_2 molecule. In the vibration ν_1 the Y atom remains stationary (see Fig. 4) and the change of the electric moment as well as its absolute magnitude is zero during the motion. This frequency is called inactive since it will not be observed in an absorption or emission spectrum for the matrix elements representing the electric moment

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* A simple proof consists in examining the kinetic and potential energy expressions for a system which exhibits a three-fold symmetry. It is then easy to show that the determinant yielding the normal frequencies has two equal roots. Which frequencies become equal may then be determined from one of the problems which has been solved explicitly using a particular potential function, for example using central forces.

are all zero. The frequencies ν_2 and ν_3 are both active and have the property that during the motion the distance between the X atoms remains unchanged. In the non-linear model there existed three frequencies in agreement with the relation previously given $n = 3s - 6$. For the linear model we have only two degrees of rotational freedom and hence we should expect $n = 3s - 5$ or four normal frequencies. The extra frequency arises from the fact that ν_2 is now a double root of the determinant, for the Y atom may move, not only along a line, but in a plane perpendicular to the figure axis. The motion in this plane is obviously isotropic.

Because our interpretation of the CO_2 spectrum rests upon the particular properties of the motion, we shall give a somewhat detailed account of the analysis. Let the X atoms have each the mass m and let their positions be specified by $x_1 y_1 z_1$ and $x_2 y_2 z_2$, where the xyz axes are a perpendicular set of Cartesian coordinates with the z axis lying along the figure axis. (see Fig. 5) Let the Y atom be represented by the mass M and the coordinates $x_3 y_3 z_3$. The kinetic energy of the system is of course,

$$T = (m/2)(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2 + \dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) + (M/2)(\dot{x}_3^2 + \dot{y}_3^2 + \dot{z}_3^2).$$

We now remove the degrees of freedom of rotation and translation by a set of relations of which the typical one is, $mx_1 + mx_2 + Mx_3 = 0$. We need a set of coordinates giving the relative displacements of the particles and these may be chosen as x, y, z giving the displacement of the Y particles relative to the center of gravity of the X particles and q giving the change in the distance between the X particles. Letting this normal distance be a, we have,

$$q = (z_2 - z_1) - a$$
$$x = x_3 - (x_1 + x_2)/2 \quad z = z_3 - (z_1 + z_2)/2$$
$$y = y_3 - (y_1 + y_2)/2.$$

Substituting these values in the expression for T, we find,

$$T = (m/4)\dot{q}^2 + (\mu/2)(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

where

$$\mu = (2mM)/(2m + M).$$

The potential energy is a function of all four variables and to the first approximation is a homogeneous quadratic form. The geometric symmetry is assumed to exist also in the potential energy and hence it must clearly be an even function in the variables x, y, z. It is not necessarily either an even or odd function in q. This demand of symmetry suffices to show that the coefficients of the cross terms vanish and leaves,

$$V^0 = \pi^2 m\nu_1^2 q^2 + 2\pi^2\nu_2^2\mu(x^2 + y^2) + 2\pi^2\nu_3^2\mu z^2.$$

The coefficients of q^2, etc., are of course undetermined constants but in the above expression they are given in terms of the normal frequencies ν_1, ν_2 and ν_3. The system is here so simple that the natural choice of coordinates is also

a choice of the normal coordinates. The mechanical problem is immediately solved and the properties of the motion are seen to be those described in an earlier paragraph.*

For the remainder of the discussion it will be more convenient to make a substitution. Since the force field in the x, y plane is isotropic, it will be more convenient to use polar coordinates, $x = r \cos \phi$ and $y = r \sin \phi$.
Then

$$T = (m/4)\dot{q}^2 + (\mu/2)(\dot{z}^2 + \dot{r}^2 + r^2\dot{\phi}^2)$$

$$V^0 = \pi^2\nu_1{}^2 m q^2 + 2\pi^2\nu_2{}^2\mu r^2 + 2\pi^2\nu_3{}^2\mu z^2.$$

Setting up the appropriate wave equation, it is clear that the general solution is a product of functions each depending upon a single variable (*i.e.* the equation is separable in these coordinates).

$$\psi = \psi_{(\sigma)}^{V_1}\psi_{(\xi)}^{V_2}R_{(\rho)}^{V_2 l}\ e^{\pm il\phi}$$

where

$$\sigma = 2\pi[\nu_1 m/2h]^{1/2}q$$

$$\xi = 2\pi[\nu_3\mu/h]^{1/2}z$$

$$\rho = 2\pi[\nu_2\mu/h]^{1/2}r.$$

The numbers $V_1 V_2 V_3$ and l are all positive integers and the first two functions are the orthogonal Hermitian functions. The energy constant does not contain l and has the form,

$$W^0 = h\nu_1(V_1 + \tfrac{1}{2}) + h\nu_2(V_2 + 1) + h\nu_3(V_3 + \tfrac{1}{2})$$

The part of the wave equation involving the variables ρ and ϕ is simply the wave equation of a plane isotropic oscillator in polar coordinates and the result may be written down immediately. The dependence upon ϕ is $e^{\pm il\phi}$ where l is an integer and the $\pm$ sign indicates two independent solutions. The function R may be expressed

$$R_{(\rho)}^{V_2 l} = \rho^l\ e^{-\rho^2/2}\ \sum_{k=0}^{V_2-l} a_k\rho^k$$

where

$$a_{k+2} = \frac{2k + 2l - 2V_2}{(k+2)(k+2+2l)}a_k.$$

---

* The expressions for the intensities I_1, I_2, and I_3 of the bands ν_1, ν_2 and ν_3 respectively become very simple for the collinear molecule.

$$I_1 = 0 \quad I_2 = 2N\pi e_2{}^2/3\mu c$$

$$I_3 = N\pi e_3{}^2/3\mu c$$

where $\mu = 2mM/(2m+M)$ and e_2 is the first derivative of the electric moment E for a displacement of the Y atom perpendicular to the line joining the X atoms. e_3 is the first derivative for a displacement along the figure axis. In each of these displacements the distance between the X atoms is kept constant and the derivatives are to be computed for the equilibrium configuration.

This function R when multiplied by $e^{\pm il\phi}$ could be called a two dimensional Hermitian orthogonal function expressed in polar coordinates. It may be of interest to give a few of these for the lower values of V_2.

TABLE I.

V_2	l	Wave function
0	0	$\pi^{-1/2}e^{-\rho^2/2}$
1	1	$\pi^{-1/2}\rho e^{-\rho^2/2}e^{i\phi}$
1	1	$\pi^{-1/2}\rho e^{-\rho^2/2}e^{-i\phi}$
2	0	$\pi^{-1/2}(1-\rho^2)e^{-\rho^2/2}$
2	2	$(2\pi)^{-1/2}\rho^2 e^{-\rho^2/2}e^{2i\phi}$
2	2	$(2\pi)^{-1/2}\rho^2 e^{-\rho^2/2}e^{-2i\phi}$

For each value of V_2 there are V_2+1 independent wave functions and since the energy depends only upon V_2 this constitutes the weight of each state. It will in the following be very important to notice the general properties of the wave function. For each value of V_2 there may be a number of values of l the highest one being equal to V_2. The values of l for any given V_2 differ by two units. For each l except $l=0$, there are two wave functions whose dependence upon ρ is the same but which depend upon ϕ as $e^{il\phi}$ and $e^{-il\phi}$.

Up to the present the behavior of this sytem is identical with that already given for any vibrating molecule. The transitions are those for which one and only one of the quantum numbers V_1, V_2 or V_3 changes by one unit and the spectrum consists of three fundamental bands, of which ν_1 has zero intensity because of the symmetry of the motion. The next step in the analysis is to introduce a perturbation, and by so doing give up the assumption that the motion of the atoms is infinitesimal compared with the equilibrium distances between them. The kinetic energy is unchanged but the potential energy becomes V^0+V' where V' is some function of q, z and r. We retain the geometric symmetry of the force fields and consequently V' must be an even function of z and of r but may depend in any way upon q. V' must however be independent of ϕ. To find the changes in the energy due to V', we have recourse to the theory of perturbations of degenerate systems. The first step is to set up the secular determinant. In our case the diagonal elements of the determinant will have the form,

$$\left| \int V'(\psi^{V_1}\psi^{V_3}R^{V_2 l})^2 d\tau - W' \right|.$$

The non-diagonal elements are all zero since they all contain the vanishing integral $\int_0^{2\pi}e^{in\phi}d\phi$ where n is some integer positive or negative but never zero. This vanishing of the non-diagonal elements shows that the coordinate system q, z, r, ϕ is appropriate for studying such a perturbation as V'. The perturbed values of the energy W' are now given by the diagonal elements and we see that they are not all distinct. The set of numbers V_1, V_2, V_3, $+l$, $(l \neq 0)$ gives a value for the perturbed energy W' which is identical with the value for the set

V_1, V_2, V_3, $-l$. The general form of the energy levels is shown diagramatically in Fig. 6 where two pairs of coincident levels are drawn slightly separated. This last degeneracy caused by the falling together of two energy levels whenever $l \neq 0$ cannot be removed by taking into account any number of higher approximations with perturbing functions of the form of V'. It will however be removed by any magnetic field as for example the field caused by the rotation of the molecule as a whole. Such an effect would probably be too small to be observed since the magnetic fields are so weak but it would have the property of splitting up the fine structure lines of a band into doublets whose separation would be a linear function of the ordinal number of the line.
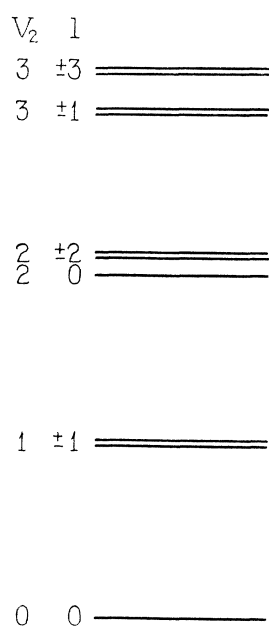
The more important results of this discussion rest upon the form of V' (even function of z and r, independent of ϕ) rather than upon some particular expression, but it may be useful to make a digression and compute W' for a particular V'. We shall suppose that the general function V' is developable in a power series in the coordinates and we retain only the first terms of this expression. If λ is the parameter of smallness and a, $b, \cdots i$ are constants, then

$$V' = \lambda(aq^3 + bqr^2 + cqz^2) + \lambda^2(dq^4 + er^4 + fz^4$$
$$+ gq^2r^2 + hq^2z^2 + ir^2z^2).$$

It is easy to compute W' explicitly as a function of the above constants $\lambda, a, \cdots, i$ and ν_1, ν_2, ν_3 with the aid of the wave functions previously tabulated We shall however merely give the total energy $W = W^0 + W'$ as a function of a number of constants x_{11}, x_{12} etc. since this form will be quite sufficient for most purposes.

V₂ 1

3 ±3 ═══════════

3 ±1 ═══════════

2 ±2 ═══════════
2   0 ═══════════

1 ±1 ═══════════

0 0 ──────────

Fig. 6.

$$W/h = \text{constant} + V_1\nu_1 + V_2\nu_2 + V_3\nu_3 + x_{11}V_1{}^2$$
$$+ x_{22}(V_2{}^2 - \tfrac{1}{3}l^2) + x_{33}V_3{}^2 + x_{12}V_1V_2$$
$$+ x_{13}V_1V_3 + x_{23}V_2V_3.$$

This expression differs from the general formula for the vibrational energy of a triatomic non-collinear molecule only in the presence of the factor $(1/3)$ l^2.

We now propose to discuss the intensities of overtone and combination bands for which purpose we must examine the perturbed wave functions. The method of finding them is well-known and we need only sketch the result. A perturbed wave function with the quantum numbers V_1, V_2, V_3 and l becomes, (we select the plus sign in $e^{\pm il\phi}$, the minus sign giving a similar result)

$$U^{V_1V_2V_3l} = \psi^{V_1}\psi^{V_3}R^{V_2l}e^{il\phi} + \sum_\alpha \sum_\beta \sum_\gamma c_{\alpha\beta\gamma}^{V_1V_3V_2l} \psi^{V_1+\alpha} \psi^{V_3+2\beta} R^{(V_2+2\gamma)l} e^{il\phi}.$$

The letters α, β and γ are integers and the range of summation is over all values such that $V_1+\alpha$, $V_3+2\beta$ and $V_2+2\gamma$ are positive integers, omitting the single term where $\alpha=\beta=\gamma=0$. The coefficients of the expansion in the unperturbed wave functions are determined by the integral,

$$C_{\alpha\beta\gamma l}^{V,V,V_2 l} = (\alpha\nu_1 + 2\beta\nu_3 + 2\gamma\nu_2)^{-1} \int V'\psi^{V_1}\psi^{V_3}R^{V_2,l}\psi^{V_1+\alpha}\psi^{V_3+2\beta}R^{(V_2+2\gamma),l}d\tau.$$

It is interesting to notice why further terms do not come into the expansion of the wave functions. The reason that we find the even integer 2β arises from the fact that V' is a symmetrical function in z. If 2β were taken as odd the corresponding coefficient in the expansion would vanish. Again the presence of 2γ rather than γ comes because V' is independent of ϕ. This latter fact also causes the perturbed wave function to have the same dependence upon ϕ as the corresponding unperturbed function.

We are now ready to discuss which transitions giving rise to overtone bands will be allowed. The components of the electric moment perpendicular to the figure axis will be proportional to $r \cos \phi$ and to $r \sin \phi$. The component along the axis is proportional (not necessarily with the same factor) to z. Using the perturbed wave functions and computing the matrix elements representing the electric moment we find,

(a) The elements giving the component of the electric moment perpendicular to the axis, may have values differing from zero, if and only if the change in V_3 is an even integer and the change in V_2 is an odd integer. The change of V_1 may be either odd or even. The change of l must be ± 1.

(b) The elements giving the component of the electric moment along the axis, may have values differing from zero, if and only if the change in V_3 is an odd integer and the change in V_2 is an even integer. The change of V_1 may be either odd or even. The change of l must be zero.

These conclusions rest upon the symmetry properties of the kinetic and potential functions and not upon the order of approximation employed.* We may summarize them by saying that harmonic bands of such a molecule may appear whose positions are roughly given by the expression $n_1\nu_1+n_2\nu_2 +n_3\nu_3$ where the n's are positive or negative integers. Only such bands will appear for which n_2+n_3 is an odd integer. If n_2 is even the change of the electric moment is along the figure axis while if n_2 is odd it lies perpendicular to this axis. One consequence of these results may be of very practical importance in discussing the infrared spectra of triatomic molecules. If the three atoms are collinear and symmetrical, then the sum of the frequencies of any

* One further consideration must be introduced in order to make the proof rigorous. In general the components of the electric moment perpendicular to the figure axis will be $f \cos \phi$ and $f \sin \phi$ where f is some function of r, z and q and in first approximation is equal to r. The component of the electric moment along the figure axis will be F which in first approximation reduces to z. The equality of the two X atoms makes it necessary that quite generally f must be an even function in z and F an odd function in z and that both f and F be independent of ϕ. These properties taken in conjunction with the odd or even character of the wave functions, furnishes a rigorous proof of the above statements regarding the appearance of overtone bands.

two observed bands (overtones, combination bands, or fundamentals) will not be the frequency of an active or observable overtone. For if ν' and ν'' are the two active frequencies then their sum is given by,

$$\nu' = n_1'\nu_1 + n_2'\nu_2 + n_3'\nu_3$$
$$\nu'' = n_1''\nu_1 + n_2''\nu_2 + n_3''\nu_3$$
$$\overline{\nu' + \nu'' = (n_1' + n_1'')\nu_1 + (n_2' + n_2'')\nu_2 + (n_3' + n_3'')\nu_3.}$$

In order that ν' and ν'' may have nonvanishing intensities both $n_2'+n_3'$ and $n_2''+n_3''$ must be odd integers. This means however that $(n_2'+n_2'')+(n_3'+n_3'')$ must be an even integer and hence $\nu'+\nu''$ will be an inactive band.

We shall show in Part II that these results are strikingly confirmed by the observed spectrum of CO_2 making it appear very probable that this molecule is collinear. We hope that the method may be applied to the spectra of many
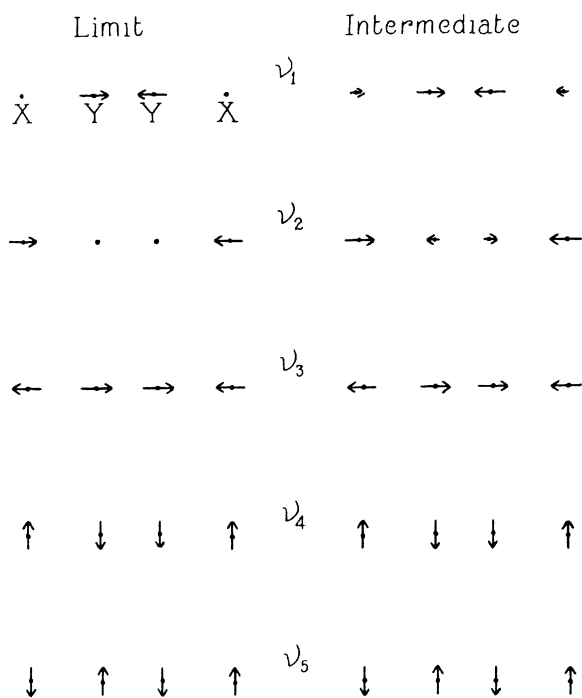

Fig. 7.

other triatomic molecules to show that when systematically the sum of two active frequencies in the spectrum is also a third active frequency, either (a) the molecule is not collinear, or (b) if collinear its potential energy function does not possess the symmetry postulated above. In the light of our present knowledge of the structure of molecules it seems unlikely except in very special cases that a molecule could possess geometric symmetry and fail to have a corresponding symmetry in its potential function.

3. The collinear molecule Y_2X_2

We shall now return to a consideration of the normal vibrations of poly-atomic systems, choosing as an example a model with four atoms, Y_2X_2. Let us consider a special configuration (which it is hoped may later be identified with the acetylene molecule) in which the four atoms are symmetrically placed along a line. (see Fig. 7) The system will have $3 \times 4 - 5 = 7$ degrees of internal freedom, each of which must correspond to a normal vibration.* A simple way to build up the normal vibrations is to start with an assumed force field which while convenient for this purpose would be very unlikely actually to occur. Let the two Y atoms be strongly bound to each other and let the two X atoms be strongly bound to each other but let the forces between the X and Y atoms be very weak. We then obtain in this limiting case a frequency ν_1 corresponding to a mutual vibration of the Y atoms, the X atoms remaining stationary and a frequency ν_2 corresponding to a vibration of the X atoms, the Y atoms remaining stationary. These are each single vibrations and both optically inactive. In the intermediate cases of force fields between all the atoms which are comparable in magnitude, all four atoms will move in both the normal vibrations ν_1 and ν_2 but it is clear that the motion always remains symmetrical and consequently these bands will have zero intensity in an absorption spectrum. The remaining vibrations of the system are concerned with the mutual motion of the Y group against the X group. We have ν_3 in which the Y atoms move as a unit along the axis. This frequency is optically active for all magnitudes of force fields. The Y group may move off the axis in two ways, giving rise to the frequencies ν_4 and ν_5. Of these ν_4 is active and ν_5 inactive for all force fields, the direction of the change of the electric moment in the former case being perpendicular to the axis. Both ν_4 and ν_5 are double frequencies since the motion is isotropic in the plane per-pendicular to the figure axis. We see that this yields seven degrees of internal freedom and completes the number of normal vibrations.

A discussion of which combination bands will be optically active and which will not may be carried out along the same lines employed for the molecule YX_2. The energy in first approximation is a function of five quantum num-bers $V_1, \cdots V_5$.

$$W^0/h = \nu_1(V_1 + \tfrac{1}{2}) + \nu_2(V_2 + \tfrac{1}{2}) + \nu_3(V_3 + \tfrac{1}{2}) + \nu_4(V_4 + 1) + \nu_5(V_5 + 1).$$

The wave functions however require seven indices and we introduce l_4 and l_5 which stand in the same relation to V_4 and V_5 that l did to V_2 in the YX_2 mole-cule. The wave functions are similar to those for the YX_2 molecule. The problem is however somewhat more complicated in form and consequently we shall merely give its solution.

Let the change in a quantum number be denoted by n, $(V_1'' - V_1') = n_1$,

* In a recent paper Mecke[15] has discussed the spectrum of C_2H_2, and the normal vibrations of the molecule as given by him agree completely with those we shall present. Part II will con-tain a treatment of the C_2H_2 spectrum and we shall reserve until that time a critical description of this interesting paper.

[15] R. Mecke, Zeits. f. Physik **64**, 173 (1930).

when the positions of all the infrared bands of the Y_2X_2 molecule will be given by the approximate formula,

$$\nu = n_1\nu_1 + n_2\nu_2 + n_3\nu_3 + n_4\nu_4 + n_5\nu_5.$$

The condition that a band may be optically active, rests with the three numbers n_3, n_4 and n_5 and may be summarized with the following scheme.

	$\parallel$		$\perp$	
	$\mid \Delta l_4 \mid = \mid \Delta l_5 \mid$		$\mid \Delta l_4 \mid + \mid \Delta l_5 \mid \pm 1$	
$n_3 =$ odd	even		even	odd
$n_4 =$ even	odd		odd	even
$n_5 =$ even	odd		even	odd

The first two columns give the condition for the electric moment to vibrate along the figure axis while the last two give the conditions for it to vibrate perpendicular to the figure axis. We notice that only such bands may be optically active for which $n_3 + n_4$ is an odd integer. This carries with it the conclusion that the only two fundamentals which may appear in the spectrum are ν_3 and ν_4 and that any other band which appears must be some combination involving either ν_3, ν_4 or both.

The results which have been obtained for Y_2X_2 depend upon assumptions entirely similar to those employed for YX_2, namely that the molecule is collinear and that the potential energy function possesses the geometric symmetry of the molecule. If the above selection rules are found to be violated then either (a) the molecule is not collinear or (b) its potential function is not symmetrical.
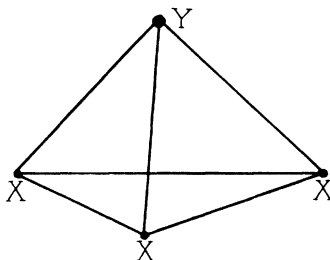

Fig. 8.

4. The symmetrical molecule YX_3.

Another molecule having four atoms but possessing simple properties is the molecule YX_3 where we take a regular pyramid as the normal configuration with the X atoms at the corners of an equilateral triangle forming the base, and the Y atom at the apex of the pyramid. (See Fig. 8.) As limiting case we let the force fields between the X atoms be strong and those connecting the X and Y atoms be very weak. There will be two frequencies ν_1 and ν_2 corresponding to the mutual vibrations of the X_3 group alone which have just

the properties previously described for such a model. In ν_1 the X atoms remain at the corners of an equilateral triangle throughout the motion. For this limiting case the change of the electric moment is zero but in the intermediate cases the Y atom will be influenced by the X atoms and the electric moment will oscillate. This oscillation is clearly along the symmetry axis and accordingly ν_1 will be called a $\parallel$ vibration. ν_2 is a double frequency and in the limit also has no changing electric moment. When however the force fields binding the atoms become of the same order of magnitude, the motion of the X atoms induces a motion to the Y atom. This motion of the Y atom in first approximation is an isotropic vibration in a plane perpendicular to the symmetry axis. In the intermediate case therefore ν_2 remains a double frequency and is a $\perp$ vibration. The remaining normal vibrations of the system may be determined by considering the motion of the X_3 group, taken as a rigid triangle (because of the intense mutual fields), relative to the Y atom. The motion will consist of two sorts, a vibration ν_3 in which the triangle and the mass point Y oscillate with respect to each other, the triangle plane remaining always parallel to itself. This is an active vibration even in the limiting case, with electric moment oscillating parallel to the symmetry axis. When we pass from the limiting to the intermediate cases, we see that in ν_3 the X atoms will also move relative to each other, but because of the symmetry in the potential and kinetic energies, they will always remain at the corners of an equilateral triangle; the length of the side of the triangle of course is not a constant. Thus ν_3 is a single and a $\parallel$ vibration. The last frequency ν_4 is represented by a tipping motion of the triangle relative to the mass point. It is even in the limit, active, $\perp$ and a double frequency. This last statement means that the frequency of vibration is independent of the direction of motion of the Y atom in a plane perpendicular to the axis. Nothing essentially new is introduced by the intermediate cases. We find thus four independent frequencies, two $\parallel$ and two $\perp$. Since the latter are each double, there are six degrees of internal freedom corresponding to the general formula for four atoms.

The above discussion allows us to predict the essential features of the infrared spectrum of the YX_3 molecule. There will be four fundamental absorption bands all of which should appear since their corresponding vibrations are all active. The intensities of the four bands may be widely different and will depend upon the force fields as well as upon the configuration of the molecule. The fine structure of the band ν_1, will be similar to the fine structure of the band ν_3 since they both correspond to a vibration of the electric moment along the figure axis. The pair of bands ν_2 and ν_4 will also have a similar fine structure which however will be unlike that belonging to the pair ν_1 and ν_3. Further questions with regard to fine structure will arise when we come to discuss experimental spectra. What will be the fine structure of a combination band such as $\nu_1+\nu_2$ or $\nu_3+\nu_4$? These problems will involve the introduction of anharmonic force fields and are closely related to the symmetry properties of the wave functions. It appears that we may well postpone their consideration until Section 3.

We may remark on the properties of the normal vibrations when the height of the regular pyramid is zero, that is, when the equilibrium position of the Y atom lies at the center of gravity of the X atoms. The frequency ν_1 now becomes inactive since the motion of the X atoms has no influence on the Y atom. The remaining frequencies remain qualitatively unchanged and accordingly the spectrum of such a molecule as the CO_3 ion where the atoms are known to be coplanar should consist of three active frequencies, of which one ν_3, has an electric moment vibrating perpendicular to the plane while for ν_2 and ν_4 it vibrates in the plane.

These conclusions have been strikingly confirmed and form one of the most successful applications of the theory of vibrations. The important experiments of Cl. Schaefer and his co-workers have demonstrated that any crystal containing the ion CO_3, ($MgCO_3$, $CaCO_3$, etc.) possesses three intense absorption bands lying at about 7μ, 11.5μ and 14μ. These absorption frequencies are a property of the CO_3 ion and correspond to the three active frequencies ν_2, ν_3 and ν_4 of the model YX_3. It is found that the absorption spectrum obtained with light polarized parallel to the crystal axis contains only the band at 11.5μ. If the light is polarized perpendicular to the crystal axis, then only the bands at 7μ and 14μ are observed. Clearly the 11.5μ band is to be identified with the vibration ν_3. Further considerations show that the 7μ band corresponds to ν_2 and the 14μ band to ν_4. The two books by Schaefer and Matossi[4] and by Rawlins and Taylor[3] both contain very adequate and authoritative treatments of the infrared spectrum of the CO_3 group and we shall refer the reader to these works rather than attempt to summarize them further.

5. The symmetrical molecule ZYX_3.

The normal vibrations of one further system will be considered. Let an additional atom Z be added to the model just considered and let Z lie along the symmetry line beyond the Y atom (see Fig. 9). As a limiting case let the force fields holding the Z atom to the YX_3 group be weak compared with the mutual forces within that group. We will then divide the vibrations of the whole system into the mutual vibrations of the YX_3 group and the vibrations of this group relative to the Z atom. The former vibrations are $\nu_1\|$, $\nu_2\perp$, $\nu_3\|$ and $\nu_4\perp$ as previously described. When we let the force fields connecting the Z atom approach those connecting the YX_3 group, the numerical values of the frequencies will be somewhat altered but their general character will not. The motion of the Z atom relative to the YX_3 group gives rise to two frequencies ν_5, corresponding to a motion of the YX_3 pyramid in which each atom moves along a line parallel to the original symmetry axis. The Z atom itself moves along the axis and this vibration is therefore active, single and $\|$. The frequency ν_6 corresponds to a tipping motion of the pyramid relative to the Z atom and is active, double and $\perp$. Nothing new is introduced when we go over to the intermediate cases of force fields. The system as a whole will then possess six independent frequencies, in general all active, of which three are $\|$ and three $\perp$.

An important variation of the model just considered occurs when the Z atom becomes identical with an X atom. This model, YX_4 which we may take to have a high degree of symmetry with the X atoms at the corners of a regular tetrahedron with the Y atom at the center, may well represent such molecules as CH_4 and CCl_4. The normal vibrations of this system are somewhat difficult to obtain from the preceeding case but they are well known from a special treatment of such systems using central force fields.[12] The first frequency ν_1 is perfectly symmetrical, with the X atoms, throughout the motion, remaining at the corners of a regular tetrahedron (the length of
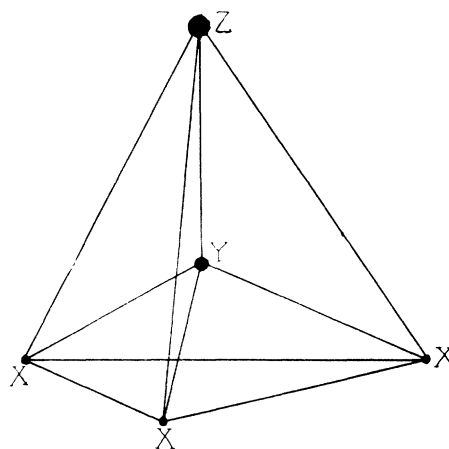
Fig. 9.

whose side of course oscillates). The center of gravity of the X atoms remains fixed at the position occupied by the Y atom and hence ν_1, which is a single frequency, is inactive. The frequency ν_2 is double and corresponds to a motion of the X atoms on the surface of a sphere. The Y atom and hence the center of gravity of the X atoms, remains fixed during the motion and consequently ν_2 is also inactive. The frequencies ν_3 and ν_4 are alike in character but different in magnitude and for central forces ν_3 is always greater than ν_4. These frequencies are triple and are both active. The motion of the Y atom in each case is the motion of a mass particle vibrating isotropically in three dimensions. These four frequencies complete the normal vibrations of the YX_4 molecule and it will be interesting to correlate them with the vibrations of the ZYX_3 molecule. This may be done by considering the limiting case where the force fields connecting the Y atom to the rest of the system vanish. A correspondence may now be obtained between the mathematical solutions for the models YX_3 and YX_4 enabling the following identifications to be made.

This diagram shows how, as the Z atom is made more and more nearly like the X atom, certain of the originally active frequencies ν_1 and ν_4 will become inactive. Moreover certain frequencies such as ν_2, $\perp$ and double combines with ν_3, $\mid\mid$ and single to form ν_3, active and triple.

ZYX_3 YX_4

$\parallel$ (1) ν_1 ⟵————————————⟶ ν_1 (1) inactive

$\perp$ (2) ν_2

$\parallel$ (1) ν_3 ν_2 (2) inactive

$\perp$ (2) ν_4 ν_3 (3) active

$\parallel$ (1) ν_5

$\perp$ (2) ν_6 ⟵————————————⟶ ν_4 (3) active.
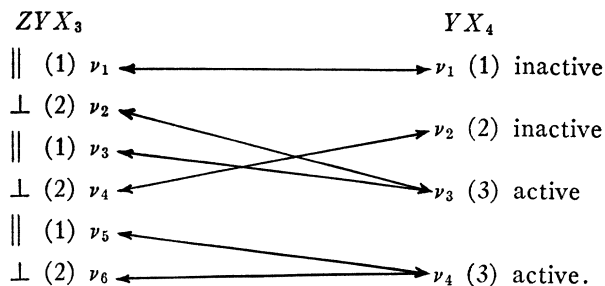
In the foregoing pages a method has been sketched for determining the characteristics of the normal vibrations of molecular systems and it has been applied to a number of simple examples. It was mentioned earlier that a number of these molecules have been examined by various writers, using certain assumed potential functions and obtaining the frequencies by means of the usual mathematical method of small vibrations. A very real difficulty which was always present however was the choice of the potential energy expression. The simplest assumption is that the forces are central but it seems probable that this assumption may well be far from the truth for many molecules. We would think that it would be particularly inappropriate for such molecules as H_2O, (an isosceles triangle) NH_3 (a regular pyramid) and others belonging to these classes, for here the equilibrium configuration of the atoms is determined by forces, such as polarization and the so called "valence" forces which are almost certainly non-central in character. However for molecules having a high degree of symmetry, CO_2 (a linear model), the ion CO_3 (the C lying at the center of an equilateral triangle representing the oxygens) and CH_4 (a regular tetrahedron), the noncentral character of such forces as those of polarization will in first approximation vanish. Consequently for such molecules it may well happen that a model employing a central force potential function will give values for the frequencies and their intensities which are approximately correct. Reference will be made to these explicit solutions when we come to consider the interpretation of the absorption spectra of these molecules.

6. Complex polyatomic molecules.

It is evident that it would be very difficult to apply the theory of normal vibrations to discuss the fundamental frequencies of a very complex molecule possessing say ten or more atoms. In fact unless the potential energy function were of a special and particularly simple form conditioned by a simplicity of the structure, a solution to the normal vibration problem even if found would be virtually useless because of the great number of undetermined constants which must necessarily enter.

The complexity of the mathematical problem of the vibration of a molecule with so many atoms, may be set in correspondence with the fact that the observed infrared spectra of such molecules are indeed far from simple, presenting often from twenty to thirty bands in the regions which have so far

been examined. (1μ to 15μ.) There are however certain surprising regularities which become evident when the spectra of related organic molecules are compared. For example nearly all molecules containing both carbon and hydrogen atoms appear to have an absorption band at about 6.8μ. Much work has been done on these spectra by Coblentz, Lecomte, Bell, Ellis and many others[17] and attempts have been made to arrange the absorption bands with reference to pairs of atoms appearing in the molecule. Such an ordering process seems to have a real significance and yields certain frequencies which are then attributed to pairs of atoms, as for example a C-H frequency, a N-H frequency etc.

A further and important empirical law is noticed when spectra of homologous substances are compared. As one atom of a molecule is replaced by another atom or group of atoms, the absorption bands in general undergo slight shifts in position and intensity. In addition to these bands which may be correlated in the several spectra, some new bands may appear and others may disappear.

While it is not our purpose in the present article to discuss in any detail the spectra of very complex organic molecules, we may present the lines along which an analysis might be made. It should be clear from the examples of the simpler polyatomic molecules which have already been considered that in a normal vibration the motion is not confined to any pair of atoms, but rather is shared to a greater or lesser degree by most of the atoms composing the system. Thus when it is found experimentally that an absorption band always appears for molecules containing atoms of carbon and of hydrogen, we may not think that this corresponds to a vibration of one particular pair of atoms C-H to the exclusion of the remaining atoms of the molecule. It cannot however be doubted that the appearance of such a band is dependent upon the presence of carbon and hydrogen atoms in the molecule.

A way out of this difficulty appears to lie in the nature of the construction of many organic molecules. Let us think of a complex system as being made up by joining together a series of groups of atoms (such as the methyl group, the OH group, etc.) which would then be regarded as the building stones of the molecule. In general because of the greater mass of the group, as compared with the individual atoms, the frequencies produced by the inter-vibration of groups taken as units would lie outside the region generally examined, that is, their wave-lengths would lie below 10μ. We might think that the bands which are commonly observed correspond to mutual vibrations within one or another of the groups. The whole system could then be likened to K sets of oscillators, each set containing a number of normal modes of vibration. These sets are more or less weakly coupled to each other and thus the frequencies of any one set will be modified by the presence of the other sets. This type of model would appear to have properties analogous to those observed for many of the complex molecules. Thus there would be frequencies which would be characteristic for each group and since a group will always

[17] See the list of references Cl. Schaefer and F. Matossi, reference 4, pp. 266–285.

contain the same atoms, certain absorption bands may well appear to be characterized by the presence of certain pairs of atoms; in fact in some cases a group consists of just one pair of atoms. Moreover upon substituting one group for another group in the formation of an homologous series, we see that many of the frequencies (those characterized by the unsubstituted groups) would merely undergo small shifts in position and intensity. Some new bands would appear while others would disappear in agreement with the observed data.

A series of papers[18] on molecular dynamics has recently appeared in which attempts are made to analyze with considerable detail the normal vibrations of several complex organic molecules and to these papers the reader who is interested in a further development of the subject is referred.

Section 2. The Rotation of Polyatomic Molecules

1. Introduction.

It has been pointed out earlier that the appearance of the near infrared absorption spectrum of a gas depends largely upon the degree of resolution of the spectrometer used in mapping it. When the spectrum is observed with an instrument of low resolving power, it is found to consist of a series of absorption regions in given positions and with given intensities. These gross features are those which we have discussed in Section 1 and may be correlated with changes in the vibrational energy of the molecule. When such a spectrum is remapped with a spectrometer of sufficiently high resolving power, the absorption regions reveal a distinct structure, the envelopes of the bands, and ultimately are found to consist of a series of fine-structure lines. The presence of these lines is a consequence of the rotation of the molecule and their positions are to be correlated with simultaneous changes in the vibrational and rotational energies of the system. The extent of the fine structure which corresponds to a change of the rotational energy is observed to be of the order of magnitude of 50 to 100 waves/cm. The position of the band, corresponding to the change of the vibrational energy is of the order of 500 to 5000 waves/cm, $(20\mu$ to $2\mu)$.

The possibility for a molecule to possess rotational energy is manifested not only in a fine structure to the near infrared bands but also in the existence of a far infrared absorption spectrum $(\sim100\mu)$. The lines of such a spectrum correspond to changes in the rotational energy alone and they are observed in molecules which possess a permanent electric moment, such as H_2O, NH_3, etc. The far infrared spectra should be the easiest to interpret theoretically but data in this region are extremely difficult to obtain. Moreover as we shall see the far infrared lines are usually not sufficient in themselves to determine all three moments of inertia of a molecule. For these reasons we must be

[18] C. F. Kettering, L. W. Shutts and D. H. Andrews, Phys. Rev. **36**, 531 (1930); D. H. Andrews, Phys. Rev. **36**, 544 (1930); R. C. Yates, Phys. Rev. **36**, 555, 563 (1930); A. B. Lewis, Phys. Rev. **36**, 568 (1930).

prepared to discuss the simultaneous changes in the vibrational and rotational energies of a system which give rise to the fine structure lines in the near infrared.

Fortunately, it is possible to treat the vibration and rotation of a molecule quite separately and then combine the results of these discussions to represent the behavior of an actual system. The validity of this procedure rests finally upon two assumptions, the first of which we have already used, namely, that the amplitudes of vibration of the atoms of a molecule are, for the lower energy states, small compared with the equilibrium distances between the atoms. The second assumption is that the forces between atoms, induced by the rotation are small compared with those interatomic forces giving rise to the vibrations. This latter assumption is equivalent to saying that, at the temperatures at which observations are carried out, the mean rotational frequencies are much smaller than the vibrational frequencies, a condition which is certainly true for all the bands studied up to the present time.

To these approximations the Hamiltonian function may be written as,

$$H = H_V + H_R$$

where H_V depends only upon the mutual coordinates of the atoms and is the function we have already considered in Section 1. H_R, the rotational energy is a function of three coordinates giving the orientation of the system in space. For our problem H_R will have no potential energy term.

The wave equation appropriate to the system will be separable in the mutual and the rotational coordinates and will have the general properties characteristic of separable coordinate problems. The energy constant will be the sum of the energy constants of the two parts of the wave equation,

$$W = W_V + W_R$$

and the wave function will be the product of ψ_V, depending only on the mutual coordinates and ψ_R depending upon the rotational coordinates.

$$\psi = \psi_V \psi_R.$$

The functions ψ_R corresponding to the various rotation quantum numbers, form an orthogonal set, as well as the set ψ_V. We consider that each function ψ_R and ψ_V has been normalized separately. To find the selection rules we must again consider the matrix elements representing the electric moment.

Let us take three perpendicular axes ξ, η, ζ fixed in the molecule and three axes x, y, z fixed in space where the origin of both sets of axes lies at the center of gravity of the system. The electric moment relative to one of the moving axes say ξ will then be (see page 285),

$$R_\xi = (R_\xi)_0 + \sum A_k x_k$$

where $(R_\xi)_0$ is the permanent electric moment in the ξ direction, x_k is the

k^{th} normal coordinate and A_k is a constant. The component of electric moment along a space direction say the x direction is then,

$$R_x = R_\xi \cos \xi x + R_\eta \cos \eta x + R_\zeta \cos \zeta x$$

where the direction cosines between the two coordinate systems will be functions of the rotational coordinates alone, (not of the mutual or normal coordinates). Letting all the vibrational numbers be represented by V and all the rotational numbers by R, we may write the matrix element,

$$(R_x)_{V''R''}^{V'R'} = \int R_x \psi_{V'} \psi_{R'} \bar{\psi}_{V''} \bar{\psi}_{R''} d\tau.$$

It is now convenient to introduce $\rho_{\xi x}, \rho_{\xi y}, \rho_{\eta x},$ etc.
and V_ξ as

$$(\rho_{\xi x})_{R''}^{R'} = \int \cos \xi x \psi_{R'} \bar{\psi}_{R''} d\tau$$

and

$$(V_\xi)_{V''}^{V'} = \int \sum A_k x_k \psi_{V'} \bar{\psi}_{V''} d\tau.$$

Here $(\rho_{\xi x})_{R''}^{R'}$ is the matrix element along the x direction corresponding to a unit electric moment along the ξ direction in the molecule, associated with the change in the rotational quantum numbers from R' to R''. It is independent of the normal vibrations of the system. $(V_\xi)_{V''}^{V'}$ is the matrix element of the electric moment in the molecule along ξ, associated with a change of the vibration numbers. We have already shown that $(V_\xi)_{V''}^{V'}$ is different from zero* only when the individual vibrational numbers change in the following manner,

$$V_1, V_2, \cdots V_k, \cdots V_n \rightarrow V_1, V_2, \cdots V_k \pm 1, \cdots V_n$$

when its value may be explicitly computed in terms of A_k.

Substituting these quantities we obtain

$$(R_x)_{V'R''}^{V'R'} = (R_\xi)_0(\rho_{\xi x})_{R''}^{R'} + (R_\eta)_0(\rho_{\eta x})_{R''}^{R'} + (R_\zeta)_0(\rho_{\zeta x})_{R''}^{R'}$$

$$(R_x)_{V''R''}^{V'R'} = (V_\xi)_{V''}^{V'}(\rho_{\xi x})_{R''}^{R'} + (V_\eta)_{V''}^{V'}(\rho_{\eta x})_{R''}^{R'} + (V_\zeta)_{V''}^{V'}(\rho_{\zeta x})_{R''}^{R'}$$

together with similar expressions for R_y and R_z. The intensity of the transition is of course proportional to the sum of the squares of those matrix elements of R_x, R_y and R_z corresponding to the same change of quantum numbers.

The meaning of the above expressions is clear. The far infrared bands correspond to a change of the rotational numbers alone and such bands will

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* To the approximation in which the intensities of the overtone bands may be neglected in comparison to the intensities of the fundamental bands.

have a finite intensity only when the molecule possesses a permanent dipole moment, that is when $(R_\xi)_0$, $(R_\eta)_0$ and $(R_\zeta)_0$ are not all zero. In this case certain allowed changes of the rotational numbers R may take place; just which changes can be ascertained only when we have the wave function ψ_R given explicitly.

The near infrared bands arise from simultaneous changes in the numbers V and R and the matrix element will be formed from products of the vibrational and the rotational matrix elements. An illustration may show the nature of the bands. In the model representing the H_2O molecule, let the ξ axis be along the bisector of the apex angle of the isosceles triangle, the η axis parallel to the base and the ζ axis be perpendicular to the plane of the triangle. From the symmetry, the permanent electric moment must lie along the ξ axis and therefore the far infrared spectrum will be governed by selection rules given by those elements $\rho_{\xi x}, \rho_{\xi y}$ and $\rho_{\xi z}$ which are different from zero. In the near infrared, the change of the electric moment also lies along the ξ axis for the two frequencies ν_1 and ν_2. The selection rules for the rotational numbers are here identical with those applying to the far infrared band since they depend upon the matrix elements of the same direction cosines. On the other hand the frequency ν_3 has its change of moment along the η axis and consequently the matrix elements involving the rotational numbers are here $\rho_{\eta x}$, $\rho_{\eta y}$, $\rho_{\eta z}$. These will in general be non-vanishing for quite different changes in R and hence the fine structure of the ν_3 band may be expected to be of a quite different character than that of the ν_1 and ν_2 bands.

2. The symmetrical top rotator.

In order to find explicit expressions for the energy constant W_R and the matrix elements of the direction cosines, it is necessary to make use of the Hamiltonian function H_R. This function may be expressed by a variety of coordinates but it will always depend upon the moments of inertia of the molecule about its center of gravity. By choosing ξ, η, ζ to lie along the principal axes of inertia of the body, the Hamiltonian will depend only upon the principal moments of inertia A, B, C, respectively.

In general A, B, and C will be all different but for many of the molecules the geometric symmetry makes at least two of them equal. (CO_2, NH_3, CH_3Cl, etc.). In this event the motion according to classical mechanics becomes very simple as does the analysis by means of the quantum theory. It may be useful to review very shortly the mechanical motion of such a system which we might represent by means of a cylinder. Let the ζ or C axis lie in the axis of the cylinder when it is evident that the two moments of inertia A and B are equal. (Fig. 10.)

As is well known the motion consists of a rotation of the body about its C axis with frequency ω_K coupled with a precession of the C axis about the line of total angular momentum, here chosen as the z space axis. The precession will have a frequency ω_J and the angle θ between the C and z axis will be constant in time. A simple analysis now reveals the following facts. If the total angular momentum has a value P, then,

$$\omega_J = P/2\pi A, \text{ and } \omega_k = \left(\frac{1}{C} - \frac{1}{A}\right)P \cos\theta/2\pi$$

and the total energy is

$$W = P^2/2A + \frac{1}{2}P^2 \cos^2\theta\left(\frac{1}{C} - \frac{1}{A}\right)$$

According to the correspondence principle of Bohr, the selection rules are intimately connected with those frequencies which would be absorbed or emitted on the basis of classical electrodynamics and these may easily be
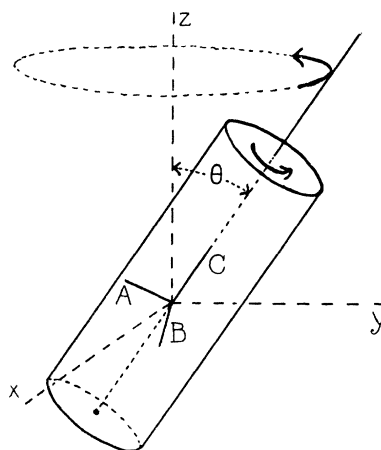

Fig. 10.

seen from the above model. If the electric moment (or change of electric moment) lies along the C axis, it is evident that it will have a constant component along the z axis while its components along x and y will vibrate with
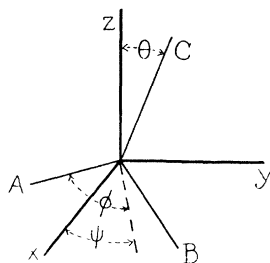
Fig. 11.

frequency ω_J. The frequency ω_K will not appear. If the electric moment lies along A or B, then its component along z will oscillate with the frequency ω_K whereas its components along x and y will have the two frequencies $\omega_J + \omega_K$ and $\omega_J - \omega_K$.

The quantum mechanical treatment of the symmetrical top molecule i.e., the free rotation of a body two of whose principal moments of inertia are equal is well known and the more cumbersome details of the analysis need not be given here.[19] The orientation of the body may best be described by means of the Eulerian angles, θ, ϕ, ψ (see Fig. 11) where θ is the angle between the C and z axes, ϕ is the angle between the A axis and the line formed by the intersection of the AB and xy planes; it accordingly measures the turning of the body about its C axis. The angle ψ is that angle between the x axis and the line formed by the intersection of the AB and xy planes and gives the turning of the whole body about the z axis.* The kinetic energy in these coordinates, giving the rotational energy of a rigid body having two of its principal moments of inertia A and B equal, is well known.

$$T = A/2(\dot{\theta}^2 + \dot{\psi}^2 \sin^2 \theta) + C/2(\dot{\phi} + \dot{\psi} \cos \theta)^2$$

The wave equation may be obtained in the usual manner and when we let the wave function be represented by U, has the form

$$\frac{\partial^2 U}{\partial \theta^2} + \cot \theta \frac{\partial U}{\partial \theta} + \left(\frac{A}{C} + \cot^2 \theta\right)\frac{\partial^2 U}{\partial \phi^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2 U}{\partial \psi^2}$$

$$- 2\frac{\cos \theta}{\sin^2 \theta} \frac{\partial^2 U}{\partial \phi \partial \psi} + \frac{8\pi^2 A W}{h^2} U = 0.$$

It is seen that in the Hamiltonian function both the angles ϕ and ψ are ignorable coordinates and we will expect that the wave function U will have a simple dependence upon these angles. It may be shown that U is separable in the Eulerian angles and has the form,

$$U = \Theta_{(\theta)}e^{iK\phi}e^{iM\psi}.$$

The condition of single-valuedness of U determines that K and M shall have integral values either positive or negative and including zero.

The function Θ is determined by the differential equation

$$\Theta'' + \Theta' \cot \theta - \frac{(M - K \cos \theta)^2}{\sin^2 \theta}\Theta + \sigma\Theta = 0$$

where σ is the constant $\sigma = 8\pi^2 A W/h^2 - A K^2/C$.

It has been found convenient in studying this equation to use the following substitutions,

$$s = |K + M|, \qquad d = |K - M|$$
$$t = \tfrac{1}{2}(1 - \cos \theta), \qquad \Theta = t^{d/2}(1 - t)^{s/2}F.$$

---

* Clearly in the preceding example where the z axis was arbitrarily chosen as the line of total angular momentum we have the following behavior of the Eulerian angles in time, $\theta = \theta_0$ $\phi = 2\pi\omega_K t + \phi_0$, and $\psi = 2\pi\omega_J t + \psi_0$.

The equation which F must satisfy is,

$$t(1 - t)F'' + [\gamma - (\alpha + \beta + 1)t]F' - \alpha\beta F = 0$$

where the constants, α, β, and γ are given by the relations,

$$\gamma = 1 + d, \alpha + \beta = 1 + d + s$$

$$\alpha\beta = \frac{d + s}{2}\left(\frac{d + s}{2} + 1\right) - \sigma - K^2.$$

The equation defining F is the well-known hypergeometric equation and F, the hypergeometric function has the form

$$F = 1 + (\alpha\beta/1\cdot\gamma)t + (\alpha(\alpha + 1)\beta(\beta + 1)/1\cdot 2\gamma(\gamma + 1))t^2 + \cdots .$$

The only solutions of the wave equation which have a meaning for us are those in which the wave function remains finite for all possible values of the coordinates. This condition, when applied here, determines that α shall be a negative integer or zero $\alpha = -p$, $(p = 0, 1, 2, \cdots ,)$ and this in turn determines the possible values of the energy constant W. By a simple calculation we find

$$W = J(J + 1)h^2/8\pi^2 A + \left(\frac{1}{C} - \frac{1}{A}\right)K^2 h^2/8\pi^2$$

where J is some positive integer $J = p + (d + s)/2$.

The relation between J and the quantum numbers K and M suggests the physical significance of these numbers. Evidently J is greater than or equal to $(d + s)/2$. Now several cases occur,

$$(d + s)/2 = \tfrac{1}{2}| K + M | + \tfrac{1}{2}| K - M | = | K | \quad \text{for} \quad | K | \geq | M |$$
$$= | M | \quad \text{for} \quad | M | \geq | K | .$$

Consequently J must be at least as large as $| K |$ or $| M |$ whichever of these two is the greater. Conversely we may say that K and M may have a range of values positive or negative but that $| K | \leq J$ and $| M | \leq J$. These facts suggest that J, K and M may be interpreted as representing angular momenta and it may in fact be shown that the total angular momentum P, the component along the C axis P_c and the component along the z space axis P_z are given by

$$P^2 = J(J + 1)h^2/4\pi^2$$
$$P_c = Kh/2\pi$$
$$P_z \quad Mh/2\pi .$$

The weights of the states may be found very simply. The system is degenerate since W does not depend upon the number M nor upon the sign of the number K. When $K = 0$ we have for each J, $(2J + 1)$ independent wave functions which for a given energy constant, satisfy the wave equation. When $K \neq 0$ there will be for each value of J, K and M two independent

functions satisfying the wave equation (one corresponding to $+|K|$ and the other to $-|K|$). The weights are then,

$$g_{JK} = 2J + 1 \qquad K = 0$$
$$g_{JK} = 2(2J + 1) \qquad K \neq 0.$$

We have now found the energy states of the symmetrical top rotator and the weights of these states as a function of the quantum numbers. The next problem is to determine the selection rules and the intensities. This may be done by examining the matrix elements representing the electric moment. In particular we must find the matrix elements $\rho_{\xi x}$, etc., representing the direction cosines. The analysis (see Dennison and Reiche and Rademaker)[19] is rather involved and we need only give the results here. Taking the ξ, η, ζ axes as lying along the A, B, C axes respectively, the following selection rules are found which correspond exactly to the rules as determined by the correspondence principal. $\rho_{\zeta x}$, $\rho_{\zeta y}$ and $\rho_{\zeta z}$ have elements differing from zero for these changes of the quantum numbers, $\Delta J = \pm 1, 0$, $\Delta K = 0$, $\Delta M = \pm 1, 0$. $\rho_{\eta x}$, $\rho_{\eta y}$ and $\rho_{\eta z}$ (or $\rho_{\xi x}$, $\rho_{\xi y}$ and $\rho_{\xi z}$) are non-vanishing for the changes $\Delta J = \pm 1, 0$, $\Delta K = \pm 1$, $\Delta M = \pm 1, 0$. The explicit expressions for these elements are tabulated in the papers already cited. We are however primarily interested in the intensities of lines and these, because of the degeneracy, depend rather upon certain combinations of the direction cosine elements. Thus a rotator finds itself in a state defined by a given J, K and M and we are interested in the transition to a state defined by J, K where the sign of the K and the value of the new M are immaterial since they do not enter the expression for the frequency of the transition. We therefore define elements A as follows,

$$(A_{J''K''}^{J'K'})^2 = \sum (\rho_{J''K''M''}^{J'K'M'})^2$$

where we sum over (1) all values of M'', (2) the two values $+K''$ and $-K''$ and (3) all the indices of the ρ.* When this is done the following formulae are obtained, where both the K' and K'' are taken as positive.

$$(A_{J\ K}^{J\ K})^2 = \frac{K^2}{4J(J + 1)}$$

$$(A_{J-1\ K}^{J\ K})^2 = \frac{2J - 1}{2J + 1}(A_{J\ K}^{J-1\ K})^2 = \frac{J^2 - K^2}{4J(2J + 1)}$$

$$(A_{J\ K\mp1}^{J\ K})^2 = \frac{(J \pm K)(J \mp K + 1)}{16J(J + 1)}, \quad K \neq 0$$

$$(A_{J\ 1}^{J\ 0})^2 = \frac{1}{8}$$

* The usefulness of this expression depends upon the fact that the sums so obtained are independent of the quantum number M'. It is for this reason that A needs no index M'.

[19] D. M. Dennison, Phys. Rev. **28**, 318 (1926); F. Reiche and H. Rademaker, Zeits. f. Physik **39**, 444 (1926); F. Reiche and H. Rademaker, Zeits. f. Physik **41**, 453 (1927); R. de L. Kronig and J. J. Rabi, Phys. Rev. **29**, 262 (1927); C. Manneback, Phys. Zeits. **28**, 72 (1927).

$$(A_{J-1\ K\mp1}^{\quad J\quad K})^2 = \frac{(J \pm K)(J \pm K - 1)}{16J(2J + 1)}, \quad K \neq 0$$

$$(A_{J-11}^{\quad J\quad 0})^2 = \frac{J - 1}{8(2J + 1)}$$

$$(A_{\ J\ K\pm1}^{\ J-1\ K})^2 = \frac{(J \pm K)(J \pm K + 1)}{16J(2J - 1)}, \quad K \neq 0$$

$$(A_{\ J\ 1}^{\ J-1\ 0})^2 = \frac{J + 1}{8(2J - 1)}.$$

These amplitudes follow the well-known summation rules of Burger and Dorgelo, that is, the total radiation from a state is proportional to the weight of that state. It may easily be verified that the following relations are true,

$$g_{JK}\big[(A_{J\ K}^{\ J\ K})^2 + (A_{J-1\ K}^{\quad J\quad K})^2 + (A_{J+1\ K}^{\quad J\quad K})^2\big] = g_{JK}/4$$

$$g_{JK}\big[(A_{J\ K-1}^{\ J\ K})^2 + (A_{J\ K+1}^{\ J\ K})^2 + (A_{J-1\ K-1}^{\quad J\quad K})^2$$
$$+ (A_{J-1\ K+1}^{\quad J\quad K})^2 + (A_{J+1\ K-1}^{\quad J\quad K})^2 + (A_{J+1\ K+1}^{\quad J\quad K})^2\big] = g_{JK}/4$$

where the factor $\frac{1}{4}$ comes from the fact that we are expressing amplitudes of a Fourier series in the time using the complex $e^{2\pi i \nu t}$ rather than the real $\cos 2\pi \nu t$ form.

We shall now sketch the appearance of the near infrared vibration rotation bands of a symmetrical top molecule. Two types of bands may be produced, || bands in which the electric moment oscillates along the C axis and $\perp$ bands in which the electric moment oscillates perpendicular to the C axis. In certain cases the electric moment might have components both along and perpendicular to C, when the fine structure would consist of an overlaying of the two original types with an intensity ratio equal to the ratio of the squares of the components.

In the || type band we are concerned with the direction cosines $\rho_{\zeta x}\,\rho_{\zeta y}$ and $\rho_{\zeta z}$ and the selection rules are consequently $\Delta J = \pm 1, 0$ and $\Delta K = 0$. Reference to the energy constant W for the symmetrical top shows that the lines of an absorption band will be given by the following expressions where ν_0 is the normal frequency of vibration.

$-$ branch $\quad \nu_{J-1\ K}^{\ J\ K} = \nu_0 - hJ/4\pi^2 A \qquad (J = 1, 2, \cdots)$

0 branch $\quad \nu_{J\ K}^{\ J\ K} = \nu_0$

$+$ branch $\quad \nu_{\ J\ K}^{\ J-1\ K} = \nu_0 + hJ/4\pi^2 A \qquad (J = 1, 2, \cdots).$

Substituting from the formulae on page 287 and page 308 we obtain the following expression for the intensity of a transition,

$$I_{J''K''}^{J'K'} = A g_{J''K''} e^{-W_{J'K'}/kT}(A_{J'K'}^{J''K''})^2$$

where the constant A is,

$$A = [8\pi^3\nu_0 N/3ch \sum g_{JK}e^{-W_{JK}/kT}](V''_{\zeta'\gamma'})^2(1 - e^{-h\nu_0/kT}).$$

In this discussion we have assumed that the vibration frequency ν_0 is very large compared with the fine structure of the band and hence the true frequency of absorption $\nu_{J'K}^{\prime J''K''}$ may be replaced by ν_0. In almost all the applications the number of molecules at room temperature in the normal state (with regard to vibration) may be taken as equal to the total number of molecules, i.e., the factor $(1 - e^{-h\nu_0/kT})$ reduces to unity.

Introducing the notation $\beta = (A/C) - 1$ and $\sigma = h^2/8\pi^2 AkT$ we find for the intensities of the various lines of the $||$ band.*

$$- \text{ branch } I_{J-1}^{J} = A \sum_{K=0}^{J-1}([2](J^2 - K^2)/4J)e^{-\sigma(J^2+J)-\sigma\beta K^2}$$

$$0 \text{ branch } \quad I_J^{J} = A \sum_{J=0}^{\infty} \sum_{K=0}^{J}(K^2(2J + 1)/2J(J + 1))e^{-\sigma(J^2+J)-\sigma\beta K^2}$$

$$+ \text{ branch } I_J^{J-1} = (I_{J-1}^{J})e^{2\sigma J}.$$

The summations are necessary since several transitions give rise to the same spectral frequency. The symbol $[2]$ is to be taken equal to 1 for $K=0$ and 2 for $K \neq 0$. While the intensities are directly functions of σ and β, the general appearance of the band is somewhat independent of their values and we may illustrate it in Fig. 12.

ν_0
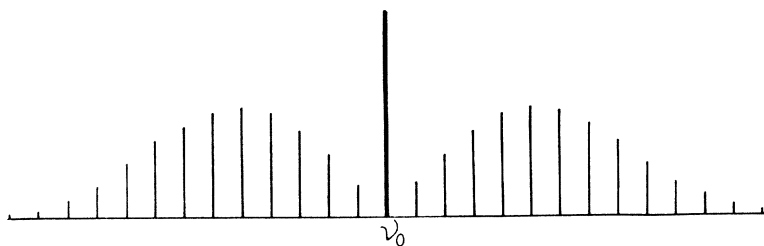
Fig. 12.

The $||$ band becomes the familiar diatomic molecule band when the moment of inertia $C=0$. Clearly the zero branch disappears since $\beta \to \infty$ and all terms of the summation vanish. For the $+$ and $-$ branches we obtain the well-known formulae for the diatomic molecule,

$$I_{J-1}^{J} = (AJ/4)e^{-\sigma(J^2+J)} \text{ and } I_J^{J-1} = (AJ/4)e^{-\sigma(J^2-J)}$$

The perpendicular type band has a considerably more complex fine structure whose general appearance depends largely upon the ratio of the moments of inertia A/C. We may describe it as a series of superimposed single bands where each single band possesses a $+$, 0 and $-$ branch. This picture is very

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* The intensity of a line $I_{J''}^{J'}$, no longer requires the subscript K since the frequencies of the corresponding lines depend upon J but not upon K. It is for this reason that on the right hand side we sum over all possible K values.

helpful when $(A/C)\gg 1$ but might appear misleading when $(A/C)\sim 1$. The Kth single band on the negative side of ν_0.

— branch $\nu_{J-1\ K-1}^{J\ \ K} = \nu_0 - (h/4\pi^2 A)(J + \beta(K - \frac{1}{2})),\quad (J = K,\ K + 1,\ \cdots)$

0 branch $\ \ \nu_{J\ K-1}^{J\ \ K} = \nu_0 - (h/4\pi^2 A)(\beta(K - \frac{1}{2})),$

+ branch $\nu_{J\ \ K-1}^{J-1\ K} = \nu_0 - (h/4\pi^2 A)(-J + \beta(K - \frac{1}{2})),\quad (J = K + 1,\ K + 2,\ \cdots)$

Similar expressions give K^{th} single band on the positive side of ν_0. It must be noticed that the allowed values of J in the $-$ and $+$ branches do not start with 0 but with K and $K+1$, following the structure rule $J \geq K$.
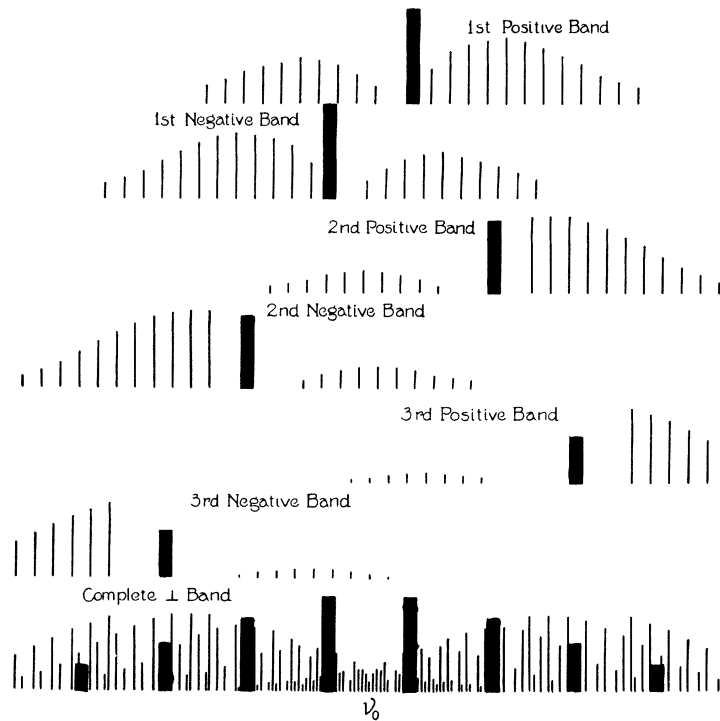
Fig. 13.

The intensity of the absorption lines of the Kth negative single band will be given by the expressions,*

— branch $I_{J-1\ K-1}^{J\ \ K} = (A(J + K - 1)(J + K)/8J)e^{-\sigma(J^2+J)-\sigma\beta K^2}$

0 branch $\ \ I_{J\ K-1}^{J\ \ K} = A \sum_{J=K}^{\infty}((2J+1)(J - K + 1)(J + K)/8J(J+1))e^{-\sigma(J^2+J)-\sigma\beta K^2}$

+ branch $I_{J\ \ K-1}^{J-1\ K} = (I_{J-1\ K-1}^{J\ \ K})((J - K + 1)(J - K)/(J + K - 1)(J + K))e^{2\sigma J}$

* The constant A in these formulae is constructed in a similar manner to the A in the formulae for the $\|$ bands but is of course not equal to it.

In Fig. 13 there is drawn the general appearance of such a $\perp$ band when A/C is taken to be of the order of five, and $\sigma = 0.018$. In the upper part of the figure we have drawn the 1st, 2nd and 3rd single bands on both sides of ν_0. At the bottom all the lines are assembled giving the completed band. More lines would enter due to the 4th, 5th etc. single bands. These would however be weak in the region shown. The following points covering the diagram should be noted. Unless $\beta = (A/C) - 1$ is an exact integer or the inverse of an integer and the convergence factor (interaction between rotation and vibration) is very small, the $+$ and $-$ branch lines of one single band will not fall on the positions of the $+$ and $-$ branch lines of other single bands. This means that the $+$ and $-$ branch lines of all the single bands taken together will form an almost continuous absorption which however may have irregularly spaced stronger and weaker regions because of the accidental falling together of the many fine lines. The zero branches of the single bands are inherently stronger than the individual $+$ and $-$ branch lines (due to the summations) and hence we may expect them to stand out of the more or less continuous background. The ratio of the sum of the intensities of the zero branches to the total background intensity is a function of σ and β but it can be shown to have the order of magnitude unity for $\beta > 1$. The above expressions for the line intensities of the symmetrical top are not always convenient to handle owing to the presence of the summation signs. In most of the applications where σ is not too large these sums may be replaced by integrals and evaluated.

3. The asymmetrical top rotator.

Some of the simpler as well as most of the more complex polyatomic molecules can not be represented by a symmetrical top rotator. For example the model of the water vapor molecule will in general have three principal moments of inertia which are all different. It is true that for any plane model (as H_2O) the sum of the two principal moments lying in the plane is equal to the moment of inertia perpendicular to the plane. Unfortunately this introduces no essential simplification into the equations of motion.

It is well known that the motion of an asymmetrical rotator may be described in classical mechanics as a rotation about either the greatest or least axis of inertia coupled with a precession and nutation (of commensurable period) of this axis about the line of total angular momentum. Thus the motion, although of three degrees of freedom, has only two degrees of periodicity and we shall expect that the energy constant, however complex its form, will be a function of only two quantum numbers. Our first problem is to obtain the energy constant by means of the wave mechanics. This question has been answered successfully by a number of authors[20] using a variety of methods. The simplest method of finding W appears to be that proposed by O. Klein and we shall here follow his work although frequent reference will be made to the papers by Kramers and Ittmann.

[20] E. Witmer, Proc. Nat. Acad. **13**, 60 (1927); S. C. Wang, Phys. Rev. **34**, 243 (1929); H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **53**, 553 (1929); H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58**, 217 (1929); H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **60**, 663 (1930); O. Klein, Zeits. f. Physik **58**, 730 (1929).

The rotator is defined by its three principal moments of inertia A, B, and C whose axes are mutually perpendicular. The total angular momentum of the body P will have components P_1, P_2 and P_3 along the moving axes A, B and C respectively. In classical mechanics, the Hamiltonian function is,

$$H = \tfrac{1}{2}(P_1^2/A + P_2^2/B + P_3^2/C)$$

while the following relations exist between the P_s.

$$P^2 = P_1^2 + P_2^2 + P_3^2 = \text{a constant.}$$

$$\{P_3P_2\} = P_1, \quad \{P_1P_3\} = P_2, \quad \{P_2P_1\} = P_3$$

where $\{\ \}$ is the Poisson bracket symbol. These relations may be translated into the matrix mechanics and furnish equations which the matrices representing the angular momenta must satisfy.

$$H = \tfrac{1}{2}(P_1^2/A + P_2^2/B + P_3^2/C)$$
$$P^2 = P_1^2 + P_2^2 + P_3^2$$
$$P_1P_3 - P_3P_1 = (ih/2\pi)P_2$$
$$P_2P_1 - P_1P_2 = (ih/2\pi)P_3$$
$$P_3P_2 - P_2P_3 = (ih/2\pi)P_1.$$

The last four matrix equations are well known (for example in the theory of the spinning electron) and several matrix representations for the P_s may be given which will satisfy these equations. One which is applicable to our case is that having the following nonvanishing elements.*

$$P_{1\,J\ K+1}^{\ \ J\ K} = iP_{2\,J\ K+1}^{\ \ J\ K} = (h/4\pi)[(J - K)(J + K + 1)]^{1/2}$$

$$P_{3\,J\ K}^{\ \ J\ K} = (h/2\pi)K, \quad J \geqq K.$$

This representation was chosen primarily for the reasons that in it both the angular momentum along C, P_3, and the square of the total angular momentum, P^2, become diagonal matrices. The nonvanishing elements of the matrices representing P_1^2, P_2^2 and P_3^2 may be easily computed.

$$(P_1^2)_{J\ K}^{\ \ J\ K} = (P_2^2)_{J\ K}^{\ \ J\ K} = (h^2/8\pi^2)(J^2 + J - K^2)$$

$$(P_1^2)_{J\ K+2}^{\ \ J\ K} = - (P_2^2)_{J\ K+2}^{\ \ J\ K}$$
$$\qquad = (h^2/16\pi^2)[(J - K)(J - K - 1)(J + K + 1)(J + K + 2)]^{1/2}$$
$$(P_3^2)_{J\ K}^{\ \ J\ K} = h^2K^2/4\pi^2.$$

From these it becomes clear that P^2 is a diagonal matrix whose elements are $(P^2)_{JK}^{JK} = h^2(J^2 + J)/4\pi^2$. These properties of P^2 and P_3 show that in the limiting case where $A = B$ the numbers J and K are identical with those symbols as used in the earlier discussion.

The next step is to examine the matrix representing the Hamiltonian function H when the angular momenta are represented in the above manner. A simple calculation yields,

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* The inverse elements, as $P_{1J\ K}^{\ \ J\ K+1}$, may be easily obtained when we remember that the matrices representing the P_s or any real function of them must be Hermitian.

$$H_{J\ K}^{J\ K} = (h^2/16\pi^2)\{(1/A + 1/B)(J^2 + J - K^2) + 2K^2/C\}$$

$$H_{J\ K+2}^{J\ K} = (h^2/32\pi^2)(1/A - 1/B)\{(J - K)(J - K - 1)(J + K + 1)(J + K + 2)\}^{1/2}.$$

It is evident that for the one case where $A = B$, the Hamiltonian matrix is diagonal and its elements must then represent the energy constant. This agrees with the formula previously obtained for the symmetrical top.

$$(W_{JK})_{A=B} = h^2(J^2 + J)/8\pi^2 A + (1/C - 1/A)h^2K^2/8\pi^2.$$

In general however when $A \neq B$ the matrix representing H is not diagonal and we have the problem of transforming to some other representation in which it will be. It is well known how to perform such a transformation and to obtain the resulting diagonal matrix for H whose terms are now W, the values of the energy constant. The so-called secular determinant is set equal to zero and the resulting equation yields the required values of W. The element of the determinant may be written $|H_m{}^n - W\delta_m{}^n|$ where $\delta_m{}^n$ is the Kroneker symbol and $H_m{}^n$ the matrix elements of the Hamiltonian in the old representation.

For the asymmetrical top the secular determinant becomes rather simple since the only non-vanishing elements are those which are diagonal in J. The number K may take on $2J+1$ values for any given J (see Fig. 14) since $+J \geqq K \geqq -J$ and thus for each J there will be $2J+1$ energy constants W. These will in general all be distinct except in the limiting cases where $A = B$ or $B = C$. Here since the energy is independent of the sign of K there are only $J+1$ distinct W_s as we have already seen. When $A \neq B \neq C$ the $2J+1$ energies must be ordered and we choose, following Kramers and Ittmann to arrange them simply according to their magnitude. We need a new index which may be taken as τ and which will range from $+J$ to $-J$. By definition then $W_{t+1} \geqq W_t$. Perhaps it should be emphasized that this index has no direct relationship with the old letter K. In fact as far as we are aware τ has no simple physical interpretation but serves only as an index by which to arrange the energy constants.

The energy constant as a function of the moments of inertia may be found by solving the secular determinant or may be obtained (Kramers and Ittmann[20]) from the parameter of the Lamé differential equation. Kramers and Ittmann have given W for $J = 0$ to 4 as well as asymptotic formulae for higher values of J. In Table II we have tabulated the W_s for $J = 0$ to 8 using the following notation. We define,

$$\begin{cases} \alpha_1 = 1/A + 1/B - 2/C \\ \beta_1 = (1/A - 1/C)(1/B - 1/C) \end{cases} \qquad 8\pi^2 W_\tau/h^2 = x_\tau + (J^2 + J)/C$$

$$\begin{cases} \alpha_2 = 1/B + 1/C - 2/A \\ \beta_2 = (1/B - 1/A)(1/C - 1/A) \end{cases} \qquad 8\pi^2 W_\tau/h^2 = x_\tau + (J^2 + J)/A$$

$$\begin{cases} \alpha_3 = 1/C + 1/A - 2/B \\ \beta_3 = (1/C - 1/B)(1/A - 1/B). \end{cases} \qquad 8\pi^2 W_\tau/h^2 = x_\tau + (J^2 + J)/B$$

$K =$	J	$J-1$	$J-2$	$\cdots$	$-J$
J	$\frac{h^2}{16\pi^2}\left[\left(\frac{1}{A}+\frac{1}{B}\right)J+\frac{2J^2}{C}\right]-W$	0	$\frac{h^2}{16\pi^2}\left(\frac{1}{A}-\frac{1}{B}\right)[J(2J-1)]^{1/2}$	$---$	0
$J-1$	0	$\frac{h^2}{16\pi^2}\left[\left(\frac{1}{A}+\frac{1}{B}\right)(3J-1)+\frac{2(J-1)^2}{C}\right]-W$	0	$---$	0
$J-2$	$\frac{h^2}{16\pi^2}\left(\frac{1}{A}-\frac{1}{B}\right)[J(2J-1)]^{1/2}$	0	$\frac{h^2}{16\pi^2}\left[\left(\frac{1}{A}+\frac{1}{B}\right)(5J-4)+\frac{2(J-2)^2}{C}\right]-W$	$---$	0
$\vdots$	$---$	$---$	$---$	$---$	$---$
$-J$	0	0	0	$---$	$\frac{h^2}{16\pi^2}\left[\left(\frac{1}{A}+\frac{1}{B}\right)J+\frac{2J^2}{C}\right]-W$

$= 0$

Fig. 14.

The quantity x_r is the rth root of a polynomial appearing in the table. When the polynomial is given with α_s and β_s without subscripts we mean that any pair may be used and that the resulting values of W will be the same. When the α_s and β_s have the subscript i, we mean that each pair $\alpha_1 \beta_1$, $\alpha_2 \beta_2$, $\alpha_3 \beta_3$ will yield distinct values of W. No attempt has been made to give the W_s in their correct order, that is, to give the subscript r but this may easily be found for any problem under actual computation.

TABLE II

$$J = 0$$
$$\overline{W = 0}$$

$$J = 1$$
$$8\pi^2 W/h^2 = \begin{cases} 1/A + 1/B \\ 1/A + 1/C \\ 1/B + 1/C \end{cases}$$

$$J = 2$$
$$8\pi^2 W/h^2 = \begin{cases} 4/A + 1/B + 1/C \\ 1/A + 4/B + 1/C \\ 1/A + 1/B + 4/C \end{cases}$$
$$x^2 - 4\alpha x + 12\beta = 0$$

$$J = 3$$
$$8\pi^2 W/h^2 = 4(1/A + 1/B + 1/C)$$
$$x^2 - 10\alpha_i x + 60\beta_i + 9\alpha_i^2 = 0$$

$$J = 4$$
$$x^3 - 20\alpha x^2 + (64\alpha^2 + 208\beta)x - 640\alpha\beta = 0$$
$$x^2 - 10\alpha_i x + 9\alpha_i^2 + 28\beta_i = 0$$

$$J = 5$$
$$x^3 - 35\alpha_i x^2 + (259\alpha_i^2 + 528\beta_i)x - 225\alpha_i^3 - 4560\alpha_i\beta_i = 0$$
$$x^2 - 20\alpha x + 64\alpha^2 + 108\beta = 0$$

$$J = 6$$
$$x^4 - 56\alpha x^3 + (784\alpha^2 + 1176\beta)x^2 - (22560\alpha\beta + 2304\alpha^3)x + 48384\alpha^2\beta + 55440\beta^2 = 0$$
$$x^3 - 35\alpha_i x^2 + (259\alpha_i^2 + 336\beta_i)x - 225\alpha_i^3 - 2064\alpha_i\beta_i = 0$$

$$J = 7$$
$$x^4 - 84\alpha_i x^3 + (1974\alpha_i^2 + 2296\beta_i)x^2 - (12916\alpha_i^3 + 78896\alpha_i\beta_i)x$$
$$+ 353808\beta_i^2 + 11025\alpha_i^4 + 449848\alpha_i^2\beta_i = 0$$
$$x^3 - 56\alpha x^2 + (784\alpha^2 + 776\beta)x - 2304\alpha^3 - 10584\alpha\beta = 0$$

$$J = 8$$
$$x^5 - 120\alpha x^4 + (4368\alpha^2 + 4176\beta)x^3 - (52480\alpha^3$$
$$+ 235584\alpha\beta)x^2 + (147456\alpha^4 + 2893824\alpha^2\beta$$
$$+ 1797120\beta^2)x - 5308416\alpha^3\beta - 18247680\alpha\beta^2 = 0$$
$$x^4 - 84\alpha_i x^3 + (1974\alpha_i^2 + 1656\beta_i)x^2$$
$$- (12916\alpha_i^3 + 49968\alpha_i\beta_i)x + 11025\alpha_i^4$$
$$+ 200376\alpha_i^2\beta_i + 118800\beta_i^2 = 0$$

In accordance with the general theory it is seen that for each value of J there are $2J+1$ values of the energy, that is, of the index r. It is interesting to follow the energy curves as we change one of the moments of inertia. In

the following discussion let us choose $A \leqq B \leqq C$. In Fig. 15 we plot the energies for $J = 3$, $A = 1$, $C = 2$ against a variable B which of course ranges from 1 to 2. Fig. 15 is typical for all the energy curves and will well repay considerable study. It shows beautifully how the difficulties which beset the older $(J = nh)$ quantum theory are completely avoided by wave mechanics.
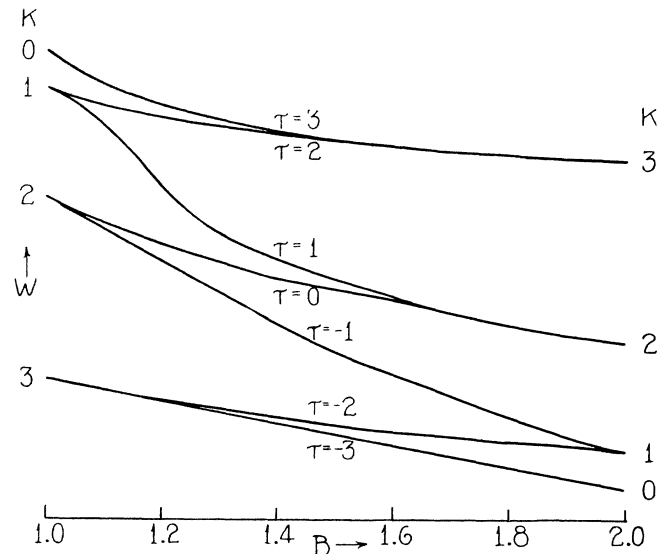

Fig. 15.

There is no troublesome unstable rotation about the middle moment of inertia with its consequent division of the energies into two distinct classes. The unity that is here achieved between the rotation of the symmetrical top and the asymmetrical top is something that finds no place in a mechanical description of the motion.

The final question which we shall consider is the selection rules of the asymmetrical rotator. Kramers and Ittmann[20] in their third paper have discussed this problem successfully through a consideration of the properties of the Lamé functions. We believe that the following method while less complete will be found simpler. Selection rules imply the finding of all those matrix elements representing the electric moment, which are zero. We shall find a certain number of these vanishing elements without proving that we have found them all. Reference to the work of Kramers and Ittmann shows that this is however the case.

We return to the matrix calculation of the asymmetrical top given by Klein and let $A \leqq B \leqq C$. In the limiting case of $A = B$ we have the energy constant

$$W_{JK} = h^2(J^2 + J)/8\pi^2 A + (1/C - 1/A)h^2 K^2/8\pi^2$$

where the coefficient of K^2 is negative in sign. The wave function is $U_{JKM} = \Theta(\theta)e^{iK\phi} e^{iM\psi}$ where Θ is that part depending upon θ alone. Now we increase B so that it is no longer equal to A. The energy constant will change

somewhat and will now be given an index $J\tau$. Because the energy curves for a given J never cross, we can at least make the identification that the energy state $W_{J,K=0}$ becomes $W_{J,\tau=J}$. Reference to Fig. 15 shows for $J=3$ the values of K when $A=B$ and when $B=C$ and thus indicates the relation between the K and the index τ. The wave function $U_{J\tau M}$ may be expanded in a series in U_{JKM} whose coefficients are the first minors of the secular determinant. Since the secular determinant contains elements which are non-diagonal in the letter K only it is evident that $U_{J\tau M} = \sum_K C_{J\tau M}{}^K U_{JKM}$ where the summation is over the number K alone. When we now think of forming the matrix elements representing the electric moment it is evident that only those will be non-vanishing for changes of J and M which were non-vanishing for the same changes of J and M for the symmetrical top. (Since the wave function $U_{J\tau M}$ is a sum over symmetrical top wave functions having the same letters J and M.) Therefore the selection rules for the asymmetrical top must be $\Delta J = \pm 1, 0$ and $\Delta M = \pm 1, 0$. The changes in M are not pertinent to our present problem since the frequency is independent of M.

To obtain the selection rules for τ, the following property must be noted. The secular determinant has relatively few non-vanishing elements; these are, the principal diagonal and two sub-diagonals displaced one unit to the right and left from the principal diagonal. (See Fig. 16 where for $J=3$ the non-vanishing terms are given by X.)

	+ 3	+ 2	+ 1	0	− 1	− 2	− 3
+ 3	X	0	X	0	0	0	0
+ 2	0	X	0	X	0	0	0
+ 1	X	0	X	0	X	0	0
0	0	X	0	X	0	X	0
− 1	0	0	X	0	X	0	X
− 2	0·	0	0	X	0	X	0
− 3	0	0	0	0	X	0	X

Fig. 16.

It may be proved from the form of the determinant that the wave function $U_{J\tau M}$ is expandable in a series U_{JKM} using *either* odd values of K only *or* even values only. Thus for certain values of τ,

$$U_{J\tau M} = C_{J\tau M}^{-J}U_{J,-J,M} + C_{J\tau M}^{-J+2}U_{J,-J+2,M} + \cdots$$

while for other values of τ,

$$U_{J\tau M} = C_{J\tau M}^{-J+1}U_{J,-J+1,M} + C_{J\tau M}^{-J+3}U_{J,-J+3,M} + \cdots .$$

The asymmetrical rotator was described by the axes ξ, η, ζ lying along the principal moments of inertia A, B, C with respect to the space fixed axes

x, y, z. The connection between these two sets was made by means of the Eulerian angles θ, ϕ, ψ. Consider now the transformation by which $\xi \to -\xi$, $\eta \to -\eta$, $\zeta \to \zeta$. This will be accomplished by letting $\theta \to \theta$, $\phi \to \phi + \pi$, $\psi \to \psi$. Examination of the wave functions of the symmetrical top shows that under this transformation $U_{JKM} \to U_{JKM}$ when K is an even integer but $U_{JKM} \to -U_{JKM}$ when K is odd. This property which we shall call transformation (a) holds unchanged for the asymmetrical top as well since $U_{J\tau M}$ is expandable in the wave functions U_{JKM} using *either* even *or* odd K numbers. Thus for any given value of J the highest state $\tau = J$ is even or $+$ for transformation (a), the next two states $\tau = J - 1$ and $\tau = J - 2$ are odd or $-$, the next two $+$ etc. This is shown in Fig. 17 for $J = 5$.

τ	$J = 5$	a	b
+5		+	−
+4		−	−
+3		−	+
+2		+	+
+1		+	−
0		−	−
−1		−	+
−2		+	+
−3		+	−
−4		−	−
−5		−	+

Fig. 17.

We shall now define the transformation (b) as $\xi \to \xi$, $\eta \to -\eta$, $\zeta \to -\zeta$. The results of applying this transformation to the wave functions may be easiest seen by remarking that changing the axes $\xi \to \zeta$, $\eta \to \eta$, $\zeta \to \xi$ makes (a) turn into (b). The details of the argument need not be given here but the results are as follows, the lowest state $\tau = -J$ is $+$ to transformation (b), the next two higher states are $-$, the next two $+$ etc.

The selection rules follow quickly; if the electric moment R (or its change) lies along the axis of least moment of inertia A, (that is the ξ axis) it is changed into its negative by the transformation (a) but is unchanged by (b). Thus,

Direction of electric moment	(a)	(b)
A	−	+
B	−	−
C	+	−

The matrix elements representing the electric moment along the space axes will depend upon such integrals as

$$(R_{\xi x})_{J''\tau''M''}^{J'\tau'M'} = \int R_{\xi} |\cos \xi x| \, U_{J'\tau'M'} \widetilde{U}_{J''\tau''M''} dV$$

where the direction cosine $|\cos \xi x|$ is $+$ for both transformations (a) and (b). Since the integration is over all space the integral will be non-vanishing only if the integral as a whole is $+$ with regard to both the transformations (a) and (b).

These consideration appear somewhat complicated but may be summarized by a few simple rules. For each group ($2J+1$ in number) of states having the same J, the energy levels are ordered according to their magnitude and given the index τ so that $\tau = +J$ represents the highest and $\tau = -J$ the lowest of the group. Property (a) is then written down. Starting with $\tau = J$ we write $+$, for $\tau = J-1$ and $J-2$, write—, etc. Property (b) makes the level $\tau = -J$, $+$ the levels $\tau = -J+1$ and $-J+2$,—etc. (see Fig. 17 describing the levels where $J = 5$.)

1st. In all cases the allowed transitions are those for which $\Delta J = \pm 1$, 0.

2nd. If the change of electric moment is along the least moment of inertia axis, transitions may occur between levels having unlike signs under (a) and like signs under (b).

3rd. If the change of the electric moment is along the middle moment of inertia axis, transitions may occur between levels having unlike signs under (a) and unlike signs under (b).

4th. If the change of the electric moment is along the greatest moment of inertia axis, transitions may occur between levels having like signs under (a) and unlike signs under (b).

These rules while somewhat different in form are exactly equivalent to those given by Kramers and Ittmann in their third paper. In Fig. 18 we have drawn the allowed transitions between the rotational states $J = 3$ and $J = 4$ of an asymmetrical top rotator when the vibration of the electric moment is along the middle axis of inertia. This diagram is entirely similar to a diagram appearing on page 680 of the third article by Kramers and Ittmann and illustrates the identity of their selection rules and ours.

In addition to giving the selection rules Kramers and Ittmann have also obtained formulae by means of which the intensities of the various lines may be computed. While these formulae probably present as simple a way as any to find the intensities, the actual labor involved in evaluating them is considerable, particularly when the transitions occur between states whose J value is not small.

Recently the author has been engaged in attempting a detailed analysis of the near infrared absorption bands of water vapor, the results of which he hopes to publish in the near future. The methods which were used to obtain the theoretical intensities of the lines are equivalent to those employed by Kramers and Ittmann, although they have a slightly different form and follow a suggestion given by Wang.[20] The secular determinant shown in Fig. 14 allows us to determine the various values of the energy constant W. The sub-minors of this determinant are the coefficients $C_{J\tau M}{}^K$ which appear when the wave function of the asymmetrical rotator is expanded in terms of the wave functions of the symmetrical rotator. Thus by computing the minors of the secular determinant we are enabled to give the wave function of the

asymmetrical rotator in an explicit form. We know the amplitudes associated with transitions between states of the symmetrical rotator (page 313) and hence with the aid of these coefficients we may compute the transition probabilities between states of the asymmetrical rotator. In the proposed paper on the water vapor spectrum it is intended to give many of the transitions between the lower energy states as explicit functions of the moments of inertia of the molecule.
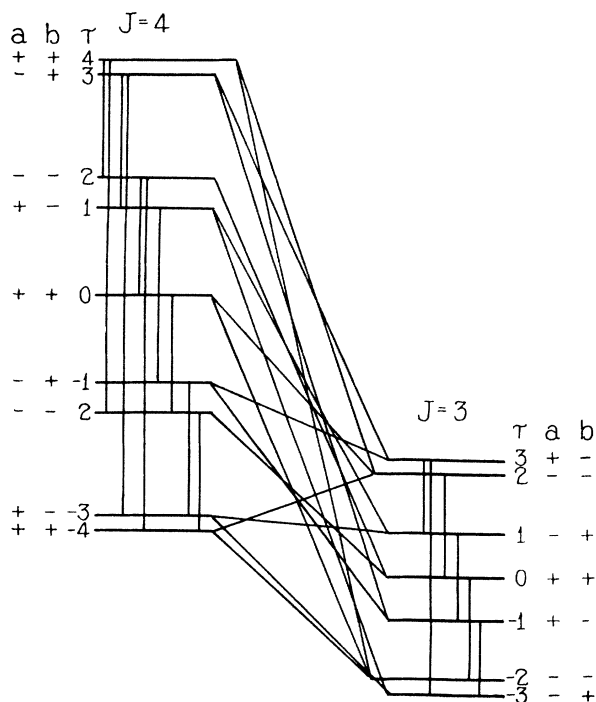

Fig. 18.

The problem of the asymmetrical top rotator may now be considered a solved; for the methods have been described by which we can obtain the ro tational energy levels, the selection rules and eventually the transition prob abilities. In spite of this the reader may have little idea of the general appearance of the infrared bands of an asymmetrical top molecule and we should therefore like to close this section by presenting certain typical diagrams of the absorption lines. A comprehensive picture giving all the possible lines for all ratios of the moments of inertia seems to be out of the question because of the practical difficulties involved. There are an infinite number of lines of which in any particular band perhaps a hundred or more will have intensities sufficiently above their neighbors to be observed by modern infrared spectrometers. Just which transitions correspond to these more intense lines will depend largely upon the moments of inertia of the molecule. Thus for water vapor we believe that most of the intense lines will be included if we consider

ν_0
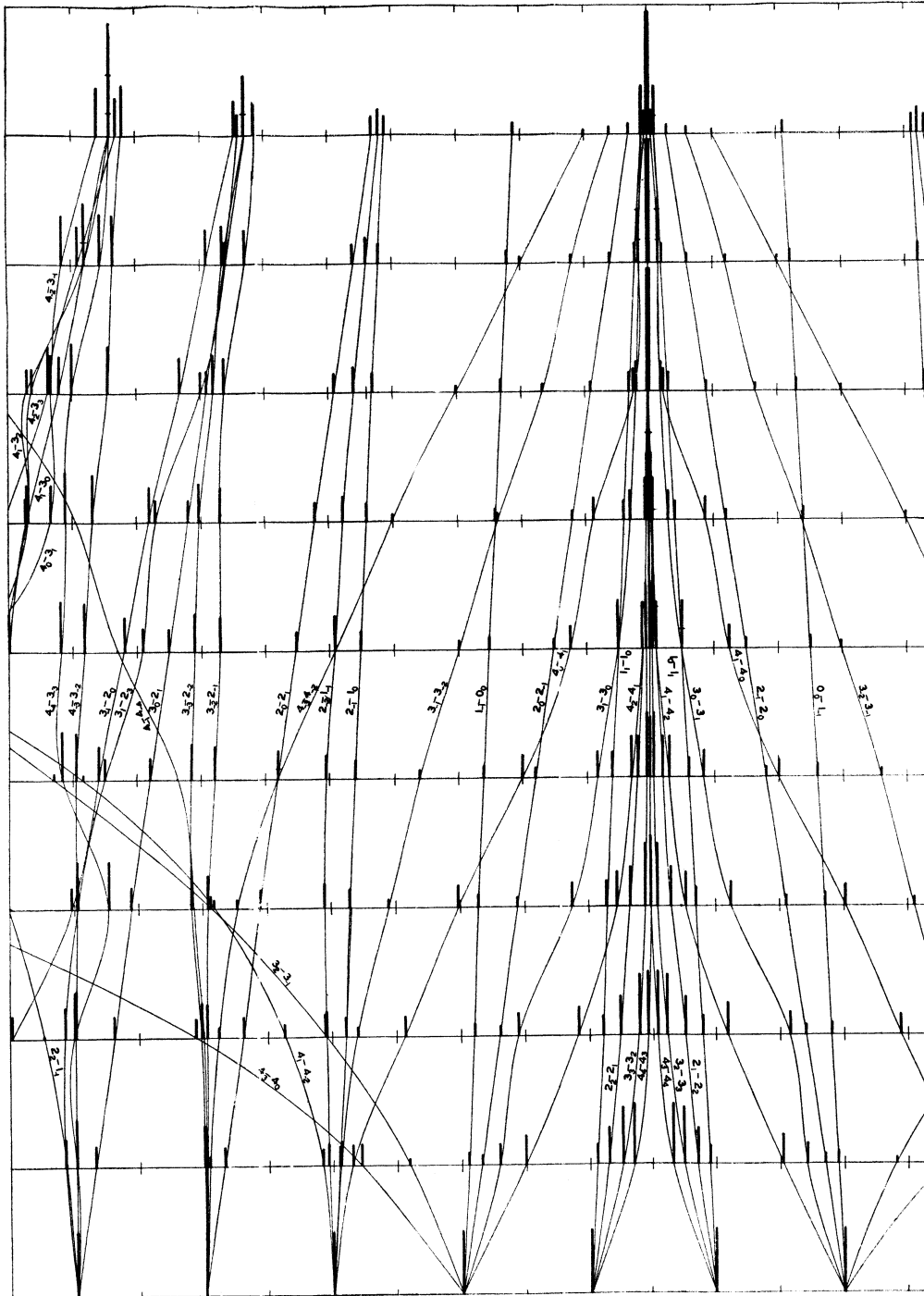
FIG. 19
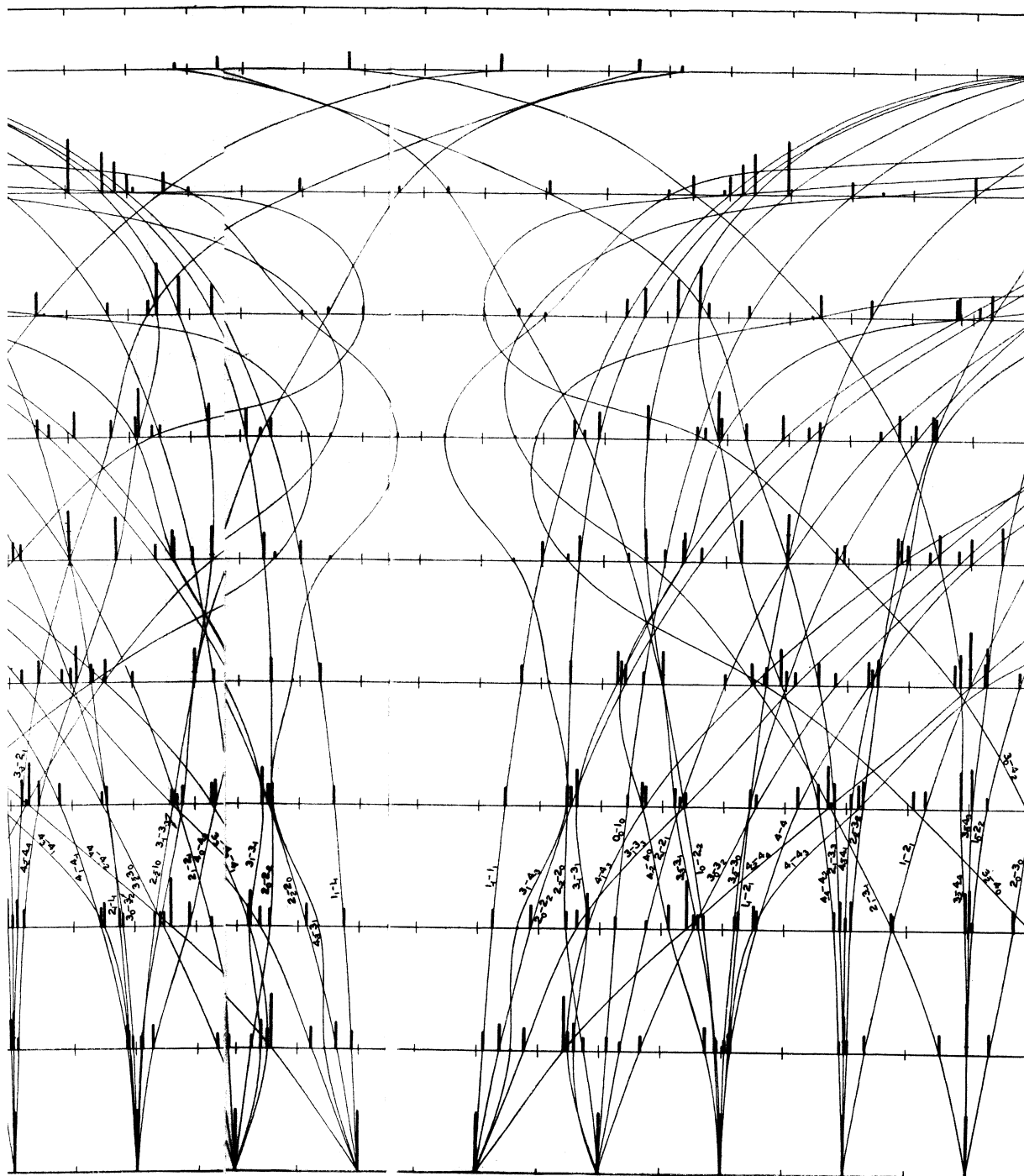
ν_0

Fig. 20

all transitions up to and including the levels for which $J=4$. In a heavier molecule such as sulphur dioxide we should probably need to include levels as high as $J=8$. In any case however the lines near the center of the band will depend upon transitions between the lower states. We have, therefore, in Figs. 19 and 20 plotted the lines using the twenty five levels $J=0, 1, 2, 3, 4$. The Boltzmann factor $e^{-W/kT}$ is taken as unity for all lines.

A second difficulty which is encountered when we attempt to present a general picture of the rotation lines of an asymmetrical top molecule, is that the positions of the lines depend upon the three parameters A, B and C and consequently we should need a three-dimensional graph. We have chosen therefore to draw the rotation lines for one special class of asymmetrical molecules, namely those molecules for which all of the nuclei lie in a plane. A relation then exists among the moments of inertia, $A+B=C$. The simplest representatives of this class of molecules will be the triatomic molecules, for example H_2O, H_2S, etc. and for these as we have seen in Section 1 the electric moment may vibrate either along A, the least axis of inertia, or B, the middle axis of inertia. It is these two types of vibration rotation bands which we show in Figs. 19 and 20 respectively. Both figures are plotted to the same scale, the unit of which is taken as $h/8\pi^2C$ (i.e. two lines separated by x units on the graph have a frequency difference of $xh/8\pi^2C$).

Each of the figures consists of ten sets of lines placed one above the other corresponding to values of $\rho=A/B$ ranging from 1.0 to 0.1. In any one of the sets of lines, the height of a line indicates its intensity. These rotation lines are all symmetrically arranged about the vibration frequency ν_0. In many of the applications where two of the nuclei are equal (H_2O) the intensities of the lines on either side of ν_0 will not be symmetrical but will depend upon the spins of the equal nuclei. This will be described further in Part II.

The lines corresponding to any particular transition are connected by fine lines so that it should be possible to interpolate to find the positions of the lines for any value of ρ. Each line is given a label $(J_{\tau''}{}''-J_{\tau'}{}')$ indicating the rotational levels associated with it. For every line on the plus side of ν_0, $(J_{\tau''}{}''-J_{\tau'}{}')$, there appears a line at an equal distance on the negative side of ν_0 with the label $(J_{\tau'}{}'-J_{\tau''}{}'')$. In both figures the set of lines for $\rho=1.0$ are plotted with the arbitrary equal height of five units.

We wish to emphasize that any conclusions based upon these diagrams must be viewed with some caution since, because of the limitations involved, they do not exactly correspond to any real molecule. The transitions between only a limited number of levels $J=0$ to $J=4$ have been given. We might expect these to be the principal lines for a molecule all of whose moments of inertia were small. If, however, the moments of inertia were small, the Boltzmann factor would be less than unity and consequently the intensity of many of the lines we have plotted would be considerably reduced. On the other hand the fine-structure lines of a molecule with large moments of inertia would contain many more lines, corresponding to transitions between states with J values greater than four. Some of these new lines would fall in the region we have pictured but most of them would fall to either side, extending

the branches of the band. In spite of these limitations we feel that the figures present many of the qualitative features of the fine structure of asymmetrical top infrared bands, particularly the appearance of the centers of the bands.

Fig. 19 shows the structure when the electric moment oscillates along the least moment of inertia axis A. For $\rho = 1.0$ we have a symmetrical top molecule $A = B = C/2$. Here the lines are equally spaced and have been drawn with equal heights. If we examine the fine structure for smaller values of ρ we see that each single line splits into a number of lines. The tendency is to form a zero branch which at first is broad and ill defined but becomes rapidly sharper as ρ decreases. In the limit of $\rho = 0$ we have again a symmetrical top but this time it corresponds to a linear molecule $A = 0$, $B = C$. The zero branch here reduces to a single line but because of the Boltzmann factor (not included in these diagrams) its intensity vanishes. The lines of the positive and negative branches become for $\rho = 0$, equally spaced and we have the typical spectrum of a linear molecule whose electric moment vibrates along the axis. The figure enables us to follow the individual lines between these two extremes $\rho = 1.0$ to $\rho = 0$. The principal characteristic of this diagram is the gathering of the zero branch as ρ decreases.

In Fig. 20 we see the fine-structure lines when the electric moment oscillates along the middle axis of inertia B. The lines for the case $\rho = 1.0$ must be identical with those in Fig. 19 for we have the same symmetrical top molecule in each case with the electric moment vibrating perpendicular to the symmetry axis. As before when ρ decreases, each line splits up into a number of individual lines. However, there is here no tendency for a zero branch to form but rather the lines diverge from the center leaving a distinct gap. As ρ approaches zero the whole structure becomes very coarse relative to the structure of Fig. 19 and in the limit all lines would go to infinity. This is what we should expect when we remember that in the limit the spacing of the lines depends upon $1/A$ and here A approaches zero. The principal feature of this spectrum is the formation of a well defined gap in the center of the band over the major portion of the range of ρ.

These characteristics may be set in immediate correspondence with the appearance of the fundamental bands of water vapor at 2.7μ and 6.6μ. The former possesses a broad zero branch at its center while the latter has a distinct gap or region of no absorption at its center. This correspondence will be described in detail in Part II.

While a triatomic molecule can not have vibration bands in which the electric moment oscillates along the greatest axis of inertia C, other plane molecules (for example OCH_2) may. The properties of such a band might be sketched. For $\rho = 1.0$, the fine structure would not resemble that of Figs. 19 or 20 but would possess a sharp intense zero branch. The lines of the positive and negative branches would be equally spread but with a spacing constant twice that of the foregoing examples. As ρ decreased, all lines would become multiple as before. In particular, the sharp zero branch would become broad and badly defined but would still retain its intensity. Near the limit for ρ

approaching zero the spacing of the lines would become very coarse and eventually each line would approach a corresponding line in the diagram 20 for in the limit of $\rho = 0$ the B and C axes become equivalent.

SECTION 3. THE SYMMETRY PROPERTIES OF POLYATOMIC MOLECULES

1. Introduction.

In order to interpret the infrared spectra of polyatomic molecules it is necessary first of all to understand the mechanism of the vibration and rotation of the molecules which determine the spectral frequencies. In addition to this however, the spectra of many of the molecules which have been examined experimentally present certain features, the explanation of which rests upon the quality of two or more of the atomic nuclei forming the molecule. The properties of systems having several equal particles was originally studied by Heisenberg[21] and first applied by him to a discussion of the spectrum of helium. The principal features of such systems may be described by showing that the energy states together with their associated wave functions may be separated into a number of classes. Each class will have a certain symmetry character which is determined by the behavior of the wave functions when the like particles of the system are interchanged. It has been proved rigorously that no transitions, whether induced by radiation or by collisions, may take place between states possessing different symmetry characters. While this proof is quite simple even for the general case we believe that it may be more helpful for the reader to present it for the case where the system contains only two like particles. The particles may be labeled 1 and 2 and their coordinates (three each) may be denoted by x_1 and x_2 respectively. The wave functions of this system divide themselves into two classes which have been called symmetrical ψ^s and antisymmetrical ψ^a, having the following properties. ψ^s and ψ^a are functions of the coordinates x_1 and x_2, and when the two like particles are interchanged $x_1 \rightarrow x_2$, $x_2 \rightarrow x_1$, the symmetrical wave functions are unchanged while the antisymmetrical wave functions change their sign. Thus

$$\psi_n^s(x_1 x_2) = \psi_n^s(x_2 x_1)$$
$$\psi_n^a(x_1 x_2) = -\psi_n^a(x_2 x_1).$$

The transition probability between any two states, n'' and n', whether spontaneous or induced by external forces, will depend upon matrix elements $F_{n'}{}^{n''}$ representing some function of the coordinates F. In radiative transitions F is the electric moment of the system but in certain collision problems it may be a more complicated function of the coordinates. The point is that F must be a symmetrical function of the coordinates $F(x_1, x_2) = F(x_2, x_1)$ since the interchanging of the two exactly equal particles cannot affect the behavior of the system towards any external forces. It now becomes clear

[21] W. Heisenberg, Zeits. f. Physik **38**, 411 (1926); W. Heisenberg, Zeits. f. Physik **39**, 499 (1926).

that the matrix elements of F between two states of different symmetry character must vanish,

$$F^{n''}_{n'(s \to a)} = \int \int \widetilde{\psi}^s_{n'} F \psi^a_{n'} dx_1 dx_2 = 0$$

since the integration is over the same range of x_1 and x_2 and since the integrand as a whole is antisymmetrical in these coordinates.

Let us now return to the consideration of systems with several like particles. The energy states may be divided into a number of classes characterized by the symmetry properties of their associated wave functions. No transitions may occur from a state of one class to a state of any other class. Thus a system with r different classes would behave exactly like r different systems since no inter-combinations are possible. As is well known this is not what is observed in nature, for all the energy states of a system may intercombine under suitable conditions, although the transition probabilities may be very small indeed. The solution to this difficulty is given by the exclusion rules which say that of all the thinkable or r classes of states of a system only one class actually exists in nature. When the like particles in the system are electrons we have the Pauli Exclusion Principle which allows only the one class to exist which is totally antisymmetrical. That is, the wave functions are such that they change sign whenever any pair of electrons of the system are interchanged. The success of this principle in interpreting the periodic system of the elements is too well known to need mention here.

When the like particles of the system are protons there exist exclusion principles which are entirely similar to the Pauli Principle and which limit the total number of symmetry classes which exist in nature to one single class. For protons the work that has been done on the hydrogen molecule shows that the wave functions are antisymmetrical with respect to the interchange of any two protons. For more complex nuclei it appears that the single symmetry class which exists is either totally symmetrical or totally antisymmetrical depending upon whether the nucleus contains an even or odd number of particles. The question of which exists will not, however, form a part of our immediate problem.

The reader might easily have gained the impression from the foregoing paragraphs that further discussion of the possible symmetry classes of the wave functions of polyatomic molecules will be unnecessary since only one such class actually occurs. This impression would be misleading for the following reason. The energy of a polyatomic molecule may be expressed as the sum of a number of terms of descending order of magnitude, (1) the electronic energy, (2) the vibrational energy, (3) the rotational energy, (4) the spin energy of the nuclei, (assuming, as is usually the case, that the nucleus possesses a spin). In first approximation the Hamiltonian of the system is separable in the sets of coordinates having to do with the energies (1), (2), (3) and (4) and consequently the total wave function of the system may be written as a product of wave functions.

$$\Psi = (\psi_E)(\psi_V)(\psi_R)(\psi_S).$$

The exclusion principle demands that Ψ shall be of a certain symmetry class, either symmetrical or antisymmetrical depending upon the type of nuclei involved. Other than this demand, however, the exclusion principle does not limit the symmetry class to which a part of the wave function, say ψ_V, may belong. Thus if there are only two equal nuclei and if Ψ is to be antisymmetrical with respect to them, there are eight possible ways in which this may be accomplished. These may be written very shortly by adopting the notation (s, a, a, s) to indicate a function symmetrical in the electronic and spin parts of the wave function and antisymmetrical in the vibrational and rotational parts. The product of two functions both of which are antisymmetrical is of course a symmetrical function.

$$1\text{---}(a, s, s, s) \qquad\qquad 5\text{---}(s, a, a, a)$$
$$2\text{---}(s, a, s, s) \qquad\qquad 6\text{---}(a, s, a, a)$$
$$3\text{---}(s, s, a, s) \qquad\qquad 7\text{---}(a, a, s, a)$$
$$4\text{---}(s, s, s, a) \qquad\qquad 8\text{---}(a, a, a, s).$$

Similarly for two equal nuclei there are eight possible ways in which the total wave function may be made symmetrical.

When the system contains more than two equal particles there will be many symmetry classes to which each part of the wave function may belong. There will then be very many ways in which the demands of the exclusion principle may be realized.

We will discuss one additional feature of the general theory before proceeding to a detailed consideration of the symmetry classes of particular molecules, namely the transition probabilities. In the above scheme it will be noted that the states 1, 2, 3 and 8 are antisymmetrical as regards that part of the wave function depending upon the electronic, vibrational and rotational coordinates. The states 4, 5, 6 and 7 are symmetrical in these coordinates. Thus if there were no nuclear spin, no transitions of any kind could take place between these two groups of states. The existence of a nuclear spin will however allow these transitions to occur but it may be shown that their probability is exceedingly small. To understand this we have only to remember that the transition probabilities will depend upon the matrix elements $F_{n'}{}^{n''}$ mentioned above. Now the function F can depend only in very small degree upon the spin coordinates since the magnetic moments of the nuclei are so very small that their influence upon any external fields will be nearly negligible. This has as a result that the matrix elements corresponding to transitions between states of different symmetry in the spin coordinates will be so small that we may quite disregard them for spectroscopic purposes. A well-known example of the noncombining character of these groups of states is furnished by hydrogen gas, H_2 which normally consists of molecules in the two sets of states, (s,s,s,a) and (s,s,a,s). Under suitable experimental conditions the one modification (s,s,s,a) alone may be produced and it is found to be very stable, with a mean time of transition to states of the (s,s,a,s) group, expressable in years.

2. The molecule YX₂.

In applying the above considerations to the energy states of polyatomic molecules, we shall treat* first the simplest case which may occur, namely, a triatomic molecule two of whose nuclei are equal YX_2. The results may also be applied without change to some more complex molecules with two equal nuclei, such as formaldehyde $O = C <^H_H$. The total wave function may be divided into the product of four functions depending upon the electronic, the vibrational, the rotational and the spin states respectively. The first of these need not concern us since the electronic state is unaltered during the transitions giving rise to infrared bands. We shall consider successively the symmetry characters of the vibrational, rotational and spin wave functions. It will prove convenient to treat first the non-collinear molecule YX_2.

On page 291 of Section I it was remarked that the vibrational wave function which depends upon the three numbers V_1, V_2 and V_3, behaves in the following manner for a reversal of the directions right and left in the isosceles triangle. The wave function remains unchanged when V_3 is an even integer. However, when V_3 is an odd integer the wave function upon reversing the directions right and left, retains its form but changes its sign.

This means that the character of the vibrational part of the wave function is symmetrical for even values of V_3 and antisymmetrical for odd values of V_3 and is independent of the quantum numbers V_1 and V_2.

Let us now examine the symmetry character of that part of the wave function depending upon the rotation. Two cases may occur.

(a) The least moment of inertia A may fall along the bisector of the apex angle as in Fig. 21. Reversing the two atoms X will be accomplished by the
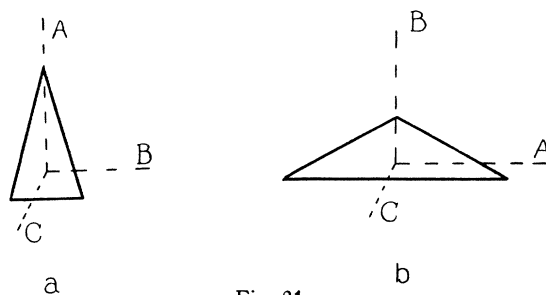
Fig. 21.

following transformation of the Eulerian angles. (Let θ be the angle between the A axis and the space axis z) $\theta \rightarrow \theta$, $\phi \rightarrow \phi + \pi$, $\psi \rightarrow \psi$. The symmetry characters may be easily established by examining the limiting case where $A \leq 0$ and $B \leq C$, and extending this to the general case of $A \neq B \neq C$, remembering that the symmetry character of a level is independent of the parameters. It is then found that the character is a function of the index τ but not of J or M. The lowest level $\tau = -J$ is always symmetrical, the next two $\tau = -J+1$,

* Many of the results discussed in the following pages appeared first in a paper by F. Hund.[22]

[22] F. Hund, Zeits. f. Physik **43**, 805 (1927).

$\tau = -J+2$ are antisymmetrical, the next two symmetrical, etc. (see Fig. 22 illustrated for $J=3$).
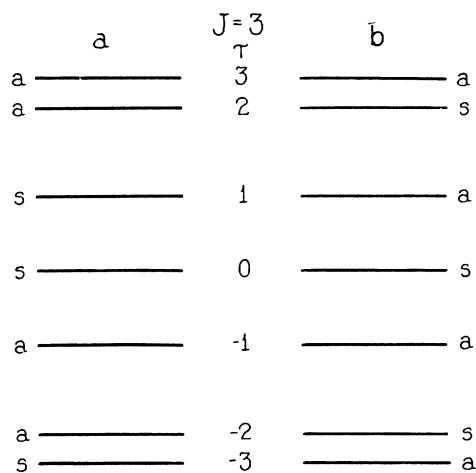
Fig. 22.

(b) The middle moment of inertia B may fall along the bisector of the apex angle and here reversing the nuclei amounts to the transformation, $\theta \rightarrow \pi - \theta$, $\phi \rightarrow -\phi$, $\psi \rightarrow \psi + \pi$. The symmetry character may be established by examining the limiting case where the asymmetrical top approaches the symmetrical top. For a given value of J the levels are alternately symmetrical and antisymmetrical, and are independent of the number M. For even J the highest and lowest levels $\tau = J$ and $\tau = -J$ are symmetrical whereas for odd J they are antisymmetrical. This is shown in Fig. 22 for $J=3$.

The fine structure lines of the near infrared bands correspond to simultaneous changes in vibrational and rotational quantum numbers defining the levels.* As we have already said transitions may occur only between levels having like symmetry characters, that is, the total wave function must be *either* symmetrical in both initial and final states *or* antisymmetrical in both states. Applying this we see that in a near infrared band corresponding to an even change in the vibrational quantum number V_3, the fine structure lines will be the result of transitions between rotational levels having the same symmetry character. If the change of V_3 is odd, the transitions will be between rotational levels of opposite symmetry character. These rules do not contradict any of the general selection rules already found for the asymmetrical rotator but rather form a part of them. This obtains because the oddness or evenness of the wave functions used to determine the general selection rules are intimately connected with the symmetry characters of these functions.

We may next consider the modification when the three atoms lie along a straight line as is perhaps the case in CO_2. It is easily seen that the symmetry character as regards the vibrational part of the wave functions has the same

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* The spin modifications will be considered in a later paragraph.

dependence upon the quantum numbers V_1 and V_3, that it had above. The character of the wave function is independent of V_1; it is symmetrical for the even values of V_3 but antisymmetrical for the odd values. In the collinear model the vibration ν_2 has somewhat changed its significance since it takes on many of the properties of a rotation. It may be simplest to describe the system (now including both the vibration and the rotation) by means of the old coordinates (see page 295) q, z and r together with the Eulerian angles. Of the Eulerian angles, the one which we here designate by ϕ, corresponds exactly with the angle ϕ which was used in describing the vibration alone. (see Fig. 23). The wave equation is separable in these coordinates and the energy constant may be divided into a vibrational and rotational part,

$$W = h\nu_1(V_1 + \tfrac{1}{2}) + h\nu_2(V_2 + 1) + h\nu_3(V_3 + \tfrac{1}{2}) + (h^2/8\pi^2 I)(J^2 + J - l^2),$$

where I is the moment of inertia of the molecule about a line perpendicular to its figure axis. The interaction terms between the vibration and rotation
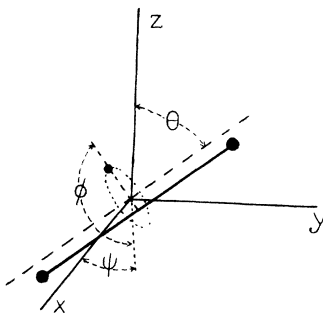
Fig. 23.

have as usual been neglected. The wave function may be written as follows where $\psi_\sigma^{V_1}$, etc. have their old significance.

where

$$U_{V_1 V_2 V_3 lJ M} = \psi_{(\sigma)}^{V_1}\psi_{(\xi)}^{V_3}R_{(\rho)}^{V_2 l}t^{d/2}(1 - t)^{s/2}Fe^{il\phi}e^{iM\psi}$$

$$d = |\, l - M\,|, \quad s = |\, l + M\,|, \quad t = \tfrac{1}{2}(1 - \cos\theta)$$

and F is the hypergeometric function as defined in the section on the symmetrical top. It will be remembered that there are two independent wave functions when $l \neq 0$, one using $+l$ and the other $-l$ but both having the same energy constant W.

An interchange of the two X atoms may be effected by the transformation, $\theta \rightarrow \pi - \theta$, $\phi \rightarrow -\phi$ and $\psi \rightarrow \psi + \pi$. An examination of the behavior of the wave function shows that it possesses the following characteristics. For the series of states where $l = 0$, all states with even J are symmetrical in the part of the wave function depending upon the quantum numbers V_2, l, J and M and antisymmetrical for odd values of J. When $l \neq 0$ there are two energy levels which coincide as has been pointed out. Closer examination shows that one of these is symmetrical for an interchange of the nuclei and the other antisymmetrical. Fig. 24 illustrates the character of the states of $l = 0$ and $l = 1$ where

a symmetrical state is represented by a full line and an antisymmetrical state by a dotted line. The coincident levels for $l = 1$ are drawn slightly separated in the figure.

$l = 0$	J	$l = 1$
- - - - - - - - - -	3	= = = = = = = = =
——————	2	= = = = = = = = =
- - - - - - - - - -	1	= = = = = = = = =
——————	0	
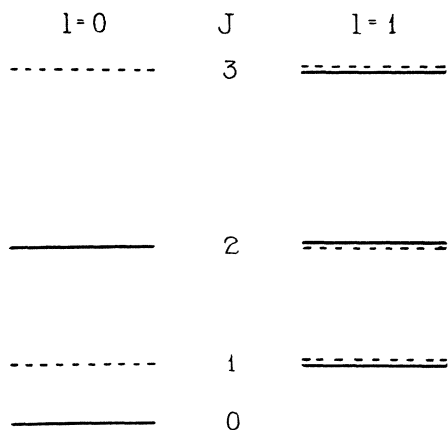
Fig. 24.

These properties will play an important role in interpreting the fine-structure lines of the near infrared bands. In accordance with the exclusion principle we shall assume that in nature only such energy states of the molecule exist which correspond to wave functions of one symmetry class (in the present case to either symmetrical or to antisymmetrical functions). Thus in the spectrum of CO_2, since the oxygen nucleus possesses no spin, we will expect the fundamental bands to have every alternate fine structure line completely absent. However, a band corresponding to the transition V_2, $1 \to 2$ and l, $1 \to 2$ would have every line present.

The last step in the analysis of the symmetry characters of the wave functions of the YX_2 molecule will consist in a description of the properties of the nuclear spin wave functions. While the treatment is entirely equivalent to that for the homopolar diatomic molecule it may be of interest to give some of the details here.

We let each X nucleus have a spin of s units, that is an angular momentum $sh/2\pi$ and we may suppose that these spins are oriented by means of an external magnetic field.* Let m be the component of s along the field. It may take on the values s, $s-1$, $s-2$, $\cdots$, $2-s$, $1-s$, $-s$; in all $(2s+1)$ different values. The part of the wave function depending upon the spin of the first nucleus may be designated by $U_1{}^{m'}$, and that depending upon the spin of the second nucleus by $U_2{}^{m''}$. If we neglect the interaction between the two spins, the part of the wave function depending upon both spins will be $U_1{}^{m'} U_2{}^{m''}$.

Clearly there will be $(2s+1)^2$ such spin wave functions and we shall now proceed to examine their symmetry characters. An interchange of the two

---

* The separation of the levels induced by the external magnetic field is of course of much too small an order of magnitude to be observed experimentally.

X nuclei evidently transforms $U_1{}^{m'} U_2{}^{m''}$ into $U_2{}^{m'} U_1{}^{m''}$. Of the original $(2s+1)^2$ functions there are $(2s+1)$ for which $m'=m''$. The wave functions of this group are unchanged when we interchange the X nuclei and consequently these functions have a symmetrical character. All the remaining functions $(2s(2s+1)$ in number) for which $m'\neq m''$ can be grouped into pairs as follows $U_1{}^{m'} U_2{}^{m''}$ and $U_1{}^{m''} U_2{}^{m'}$. The two energy levels of one of these pairs evidently exactly coincide and therefore the states of a pair are degenerate. This degeneracy may be removed when we take into account the interaction between the two spins themselves. When this is done however it is found that the appropriate wave functions are not $U_1{}^{m'} U_2{}^{m''}$ and $U_1{}^{m''} U_2{}^{m'}$ but rather the following linear combinations $(1/2^{1/2})(U_1{}^{m'}U_2{}^{m''}+U_1{}^{m''} U_2{}^{m'})$ and $(1/2^{1/2})(U_1{}^{m'}U_2{}^{m''}-U_1{}^{m''} U_2{}^{m'})$. Upon now interchanging the X nuclei it is clear that the first of these has a symmetrical character and the second an antisymmetrical character. Thus we have shown that of the original $(2s+1)^2$ spin functions $(s+1)$ $(2s+1)$ are symmetrical and $s(2s+1)$ are antisymmetrical. We shall assume that for polyatomic molecules having two equal particles as for homopolar diatomic molecules, only one modification exists in nature, that is, the wave function as a whole must be either symmetric for all levels or antisymmetric for all levels. A closer discussion of *which* exists, symmetric or antisymmetric levels, will depend essentially upon the character of the electronic wave functions, a subject we do not propose to treat.

We shall expect that the fine structure of the near infrared bands of molecules having two equal particles, may be described by two sets of lines, the one set arising from transitions between two levels both of which are symmetrical in the part of the wave function depending upon vibration and rotation. The levels giving rise to the other set have wave functions whose vibration-rotation part is antisymmetrical for an interchange of the equal particles. Intercombination lines between the two sets of levels will be much too faint to be observed due to the smallness of the spin interactions. The ratio of intensity of these two sets of lines will be $(s+1)/s$ where s is the spin in units of $h/2\pi$ associated with each of the equal nuclei. All the levels giving *both* sets of lines, are *either* symmetrical in the vibration-rotation-spin part of their wave functions or antisymmetrical in these functions.

3. The molecule Y_2X_2.

It may be of interest to sketch the symmetry properties of a collinear model Y_2X_2, such as was discussed on page 299 of the first section. There are two pairs of like atoms and the wave functions may be classified as to their symmetry properties with regard to each pair. Each state which was formerly taken to be single actually will consist of two nearly coincident states with reciprocal symmetry properties. This obtains because there are two positions of equilibrium which may be turned into each other, either by an interchange of the two Y atoms or by an interchange of the two X atoms. (See Fig. 25) The magnitude of the separation between these two levels will in general be far too small to be observed. It is conditioned by the ratio of the energy which would be necessary actually to affect an interchange of one

pair of atoms with respect to the others, to the energy $h\nu_5$ where the frequency is that illustrated in Fig. 7. We shall use the notation proposed earlier in which the quantum numbers V_1, V_2, V_3, V_4 and V_5 have to do with the frequencies of vibration ν_1, ν_2,ν_3, ν_4 and ν_5 respectively. The vibrations ν_4 and ν_5 are each double and consequently we introduce the quantum numbers l_4 and l_5. The wave functions will have the same dependence upon l_4 and l_5 that the wave functions for the collinear model YX_2 have upon l. To make a complete description of the system, it is also necessary to employ the numbers J and M having to do with the rotation of the model. The symmetry properties however are not a function of the magnetic quantum number M.

$$
\begin{array}{cccc}
X & Y & Y & X \\
\bullet\!-\!-\!-\!\bullet\!-\!-\!-\!\bullet\!-\!-\!-\!\bullet \\
1 & 2 & 3 & 4
\end{array}
$$

$$
\begin{array}{cccc}
X & Y & Y & X \\
\bullet\!-\!-\!-\!\bullet\!-\!-\!-\!\bullet\!-\!-\!-\!\bullet \\
1 & 3 & 2 & 4
\end{array}
$$
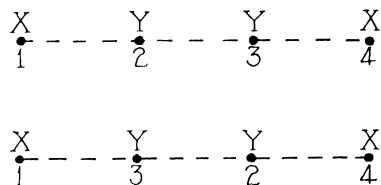
Fig. 25.

The symmetry properties of the states of the model X_2Y_2 may be found through considering what effect the interchange of a pair of equal atoms will have on the wave functions. Thus the part of the wave function depending upon the vibrations ν_1 and ν_2 will be clearly symmetrical for any interchanges; ν_3 is antisymmetrical for an interchange of both pairs, etc. Collecting the results of these considerations we may make the following summary.

(1) For all values of V_1 and V_2, for even values of V_3 and for all values of V_4 and V_5 for which $l_4 = l_5 = 0$, we may classify the states according to the rotational number J. When J is even, there are two nearly coincident states, one of which is symmetrical in both the Y pair and the X pair of atoms while the other is antisymmetrical for an interchange of either the Y pair or the X pair. When J is odd, there are two nearly coincident states one of which is symmetrical in the Y pair and antisymmetrical in the X pair while the other is antisymmetrical in Y and symmetrical in X.

(2) For all odd values of V_3 (coupled with any values of V_1, V_2, V_4, and V_5 for which $l_4 = l_5 = 0$) we again classify the states according to J and find for J odd, two states, one symmetrical in Y and X and the other antisymmetrical in Y and X. For J even, there are two states of which one is symmetrical in Y and antisymmetrical in X while the other is antisymmetrical in Y and symmetrical in X.

(3) When the quantum numbers V_1, V_2, V_3, V_4 and V_5 take on any values but when l_4 and l_5 do not both vanish, we find that for every J value there are four nearly coincident states having the four possible combinations of symmetry properties. These results are shown diagramatically in Fig. 26 where the nearly coincident levels are drawn slightly separated.

The allowed transitions follow from considerations similar to those employed for a system containing only one pair of equal atoms. Transitions

may take place only between levels that have the same symmetry character in the Y pair and the X pair separately. Thus $X_aY_s \rightarrow X_aY_s$, $X_sY_s \rightarrow X_sY_s$, etc. To complete the study of the symmetry properties of this model we should remark the changes which will be introduced when each Y nucleus possesses an angular momentum of $s_1h/2\pi$ and each X nucleus an angular momentum $s_2h/2\pi$. Each state which was taken as single up until now will consist of $(2s_1+1)^2(2s_2+1)^2$ nearly coincident levels. The magnitude of
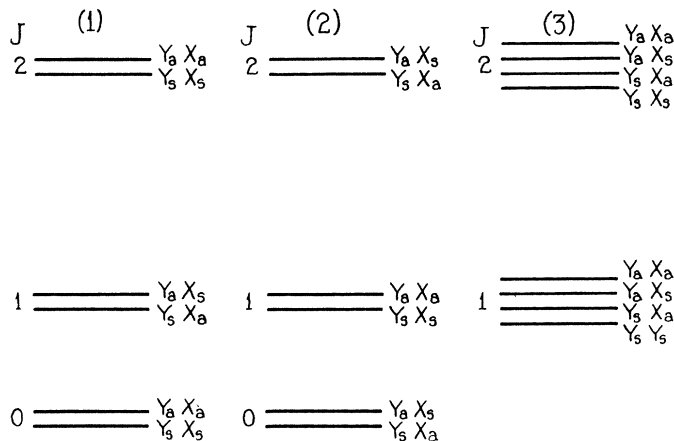
Fig. 26.

the separation of these levels will be too small to be observable since it depends upon the interaction of the magnetic moments of the nuclei with such magnetic fields as those produced by the rotation of the molecule. Of the many nearly coincident states $(2s_1+1)(s_1+1)(2s_2+1)(s_2+1)$ will have spin wave functions (that part of the total wave function depending upon the spins alone) which are symmetrical in both the Y pair of nuclei and the X pair. A number $(2s_1+1)(s_1)(2s_2+1)(s_2+1)$ will be antisymmetrical in the Y pair and symmetrical in the X pair, etc. We hope to apply these considerations in interpreting the spectrum of acetylene C_2H_2.

4. The molecule YX_3.

A very important class of molecules to the infrared spectroscopist are those having three equal atoms and one or more others. The molecules falling in this group whose spectra have been determined are NH_3, PH_3, AsH_3 and the methyl halides. The symmetry properties of these molecules are rather more complex than those of molecules having only two equal atoms and have been investigated in a very important paper by F. Hund.[22] In the following pages we shall attempt to describe the results obtained by him but the proofs will be omitted and the reader referred to the original article.

We begin by considering the vibration of a triatomic molecule having three equal atoms whose equilibrium configuration is represented by an equilateral triangle. Let the three atoms be distinguished by the indices 1, 2

and 3. It may now be shown that the wave functions describing the vibration (or the rotation, or both) will be divided into four symmetry classes which we can label α, β, γ, δ. The wave functions of class α are unchanged when any two of the atoms are interchanged, that is, α is symmetrical in all the indices. The wave functions of class β become negative when any two atoms are interchanged and are thus antisymmetrical. The class γ may be described as being symmetrical for an interchange of two atoms, say 1 and 2, but having neither a symmetrical nor antisymmetrical character for an interchange of either 1 or 2 with 3. The class δ is antisymmetrical for an interchange of a pair say 1 and 2 but neither symmetrical nor antisymmetrical for an interchange of 1 or 2 with 3. It may be shown that the classes γ and δ always occur together and that they are degenerate, their energy levels falling exactly together. No perturbing potential, providing it has the threefold symmetry demanded by the equality of the three atoms, can ever undegenerate these two.

Referring back to page 292 of the first section we remember that when the three atoms of the molecule YX_2 become equal the frequencies ν_2 and ν_3 coincide forming a double frequency which we shall now call simply ν_2 with a quantum number V_2. The weight of each state is now (V_2+1). Hund has shown that the symmetry properties of the wave functions are independent of the number V_1 and have the following dependence upon V_2.

TABLE III.

V_2	V_2+1	Symmetry character
0	1	α
1	2	(γ and δ). These levels coincide and will not be separated by higher order perturbation terms.
2	3	α, (γ, δ)
3	4	α, β, (γ, δ)
$2m$	$2m+1$	α, m pairs of levels having the character (γ, δ)
$2m+1$	$2m+2$	α, β, m pairs of levels having the character (γ, δ)

In first approximation, for every value of V_2 there will be (V_2+1) coincident levels but higher order perturbations will distinguish between some of these. The symmetry character of the wave functions tells us that for $V_2=2m$ there may exist $m+1$ separate levels, m of which have the weight 2. If $V_2= 2m+1$ there may exist $m+2$ separate levels, m of which again have the weight 2.

Following Hund we shall now introduce a further atom Y to produce the molecule YX_3. When the fourth atom Y has its equilibrium position at the center of gravity of the X particles, the molecule will have the following symmetry properties.

The lowest vibration state $V_1=V_2=V_3=V_4=0$ has the symmetrical character α and it may be shown that the symmetry character of the wave functions is independent of the numbers V_1. (We shall employ the notation of Section 1 in which ν_1 is the inactive vibration, ν_2 and ν_4 are active double vibrations lying in the plane of the triangle and ν_3 is the active single fre-

quency whose electric moment vibrates perpendicular to the plane). When $V_2 = V_4 = 0$, we find the character α for all even values of V_3 and the character β for all odd values. The part of the wave function depending upon V_2 or upon V_4 will have just that symmetry character already described for the vibration ν_2 of the molecule X_3. The symmetry character of the wave function for any values of V_1, V_2, V_3 and V_4 may be found by multiplying the wave functions depending upon each of these numbers separately. The behavior of the symmetry character under such a multiplication may be schematically given as follows.

$$(\alpha)(\alpha) = \alpha \qquad (\alpha)(\gamma, \delta) = (\gamma, \delta)$$

$$(\alpha)(\beta) = \beta \qquad (\beta)(\gamma, \delta) = (\delta, \gamma) = (\gamma, \delta)$$

$$(\beta)(\beta) = \alpha \qquad (\gamma, \delta)(\gamma, \delta) = \alpha, \beta, (\gamma, \delta).$$

The most interesting applications of this theory are to molecules where the Y atom does not lie in the plane of the X atoms but rather where the molecule may be represented by a regular pyramid with the Y atom at the apex. A curious feature now obtains in that each state, including the normal state, is no longer single but consists of two nearly coincident states. This is due to the fact that there is not one position of equilibrium but rather two exactly equivalent ones as shown in Fig. 27.
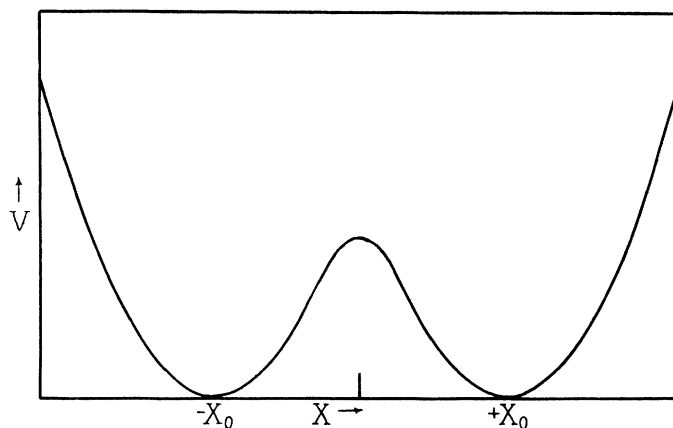
Fig. 27.

The qualitative theory of this phenomenon has been treated by Hund and it may be shown that the two nearly coincident levels have wave functions which are reciprocal in character. By this we mean that the symmetry character of one of the levels is β times that of the other. The separation between these levels is in general very small but is a function of the ratio of the amplitude of the motion of the Y atom relative to the center of gravity of the X atoms, to the normal height of the regular pyramid representing the molecule. We shall expect that this energy difference will be unobservable spectroscopically for all molecules except those where the normal height of the pyramid is small compared with the length of a side of the base.

We are now ready to assemble the parts of the wave function and to determine the symmetry character of the whole as a function of the quantum numbers. The weight of a state (as far as the vibrational numbers is concerned) is $2(V_2+1)$ (V_4+1). In Table IV we have separated the wave functions into the groups having reciprocal character and enclosed them with a bracket. $\{\ \}$ In this table we have given the symmetry character for certain of the vibrational states for which V_2 and V_4 have values different from zero. The rule for constructing the character is to multiply together the symmetry characters for the individual numbers as given in Table III. The symmetry character of a general state for which all the quantum numbers V_1 V_2 V_3 and V_4 have values may be easily obtained, for the symmetry character associated with any value of V_1 or V_3 must be either $\{\alpha/\beta\}$ or $\{\beta/\alpha\}$.

TABLE IV

V_2	V_4	Symmetry Character
0	0	$\left\{\begin{matrix}\alpha\\\beta\end{matrix}\right\}$
1	0	$\left\{\begin{matrix}(\gamma,\ \delta)\\(\delta,\ \gamma)\end{matrix}\right\}$
0	1	
2	0	$\left\{\begin{matrix}\alpha\\\beta\end{matrix}\right\},\ \left\{\begin{matrix}(\gamma,\ \delta)\\(\delta,\ \gamma)\end{matrix}\right\}$
0	2	
3	0	$\left\{\begin{matrix}\alpha\\\beta\end{matrix}\right\},\ \left\{\begin{matrix}\beta\\\alpha\end{matrix}\right\},\ \left\{\begin{matrix}(\gamma,\ \delta))\\(\delta,\ \gamma)\end{matrix}\right\}$
0	3	
1	1	$\left\{\begin{matrix}\alpha\\\beta\end{matrix}\right\},\ \left\{\begin{matrix}\beta\\\alpha\end{matrix}\right\},\ \left\{\begin{matrix}(\gamma,\ \delta)\\(\delta,\ \gamma)\end{matrix}\right\}$
2	1	$\left\{\begin{matrix}\alpha\\\beta\end{matrix}\right\},\ \left\{\begin{matrix}\beta\\\alpha\end{matrix}\right\},\ \left\{\begin{matrix}(\gamma,\ \delta)\\(\delta,\ \gamma)\end{matrix}\right\},\ \left\{\begin{matrix}(\delta,\ \gamma)\\(\gamma,\ \delta)\end{matrix}\right\}$
1	2	

The symmetry character of the wave functions should be of great value in interpreting the structure of the infrared bands of molecules of the YX_3 type. Thus all bands may first be thought of as being composed of two nearly superimposed bands (or groups of bands) corresponding to the energy difference between the levels of reciprocal character $\{\ \}$. Besides this duplicity the higher harmonics will show a splitting when we take into account the anharmonic terms in the potential energy. These anharmonic terms must however possess the three-fold geometric symmetry arising from the equality of the X atoms. Thus, leaving aside the bracket difference in energy, the fundamental bands ν_2 and ν_4 are single bands. Their harmonics $2\nu_2$ and $2\nu_4$ consist of two nearly superimposed bands* and the combination band $\nu_2+\nu_4$ consists of three nearly coincident bands. The reader may easily extend these observations to any desired harmonic or combination band.†

* Of the two upper states giving rise to these two bands, the one $\{(\gamma,\ \delta)/(\delta,\ \gamma)\}$ has twice the weight of the other $\{\alpha/\beta\}$. The intensities of the bands will however not necessarily appear in this ratio since they depend upon the anharmonic terms of the potential energy expression.

† It is interesting to check these results in the following manner. We may start from the unperturbed degenerate problem where the wave functions are given by the quantum numbers

In his paper Hund next discusses the symmetry character of that part of the wave function depending upon the rotation of the molecule. Using the wave functions describing the symmetrical top we shall give their symmetry character as a function of the quantum numbers J,K and M. The symmetry is independent of M. For $K = 0$, the functions have the character α for even values of J and β for odd values. When $K \neq 0$, as we have seen there exist two nearly coincident states the one corresponding to $+K$ and the other to $-K$. If $K \neq 0$ and is divisible by 3, one of these nearly coincident states has the character α, the other β. If $K \neq 0$ and is not exactly divisible by 3, the two nearly coincident states have the characters γ and δ respectively.

Fig. 28.

These results may be combined with the symmetry character of the vibrational part of the wave function and are illustrated in Fig. 28.

Two cases need to be differentiated. In the first (a) the vibrational part of the wave function has the symmetry $\{^\alpha_\beta\}$, (the case of symmetry $\{^\beta_\alpha\}$ may be obtained from it by reversing the upper and lower symbols) and in the second (b) the vibrational part has the symmetry $\{^{(\gamma,\delta)}_{(\delta,\gamma)}\}$. Since there are so many nearly concident levels we have in Fig. 28 drawn all levels as single, relying on the symbols to illustrate their multiplicity.

The possible transitions will be those in which two levels having the same symmetry character may combine. Thus the fundamental ν_1 or ν_3 in which both vibrational states have the character $\{^\alpha_\beta\}$ or $\{^\beta_\alpha\}$ will have a fine structure corresponding to changes of K by some multiple (including zero) of 3. The fundamental ν_2 or ν_4 will have a fine structure in which the letter K may not be a multiple of 3 in both the initial and final states. These rules found from the symmetry are quite consistent with the general selection rules of the rotational energy, for ν_1 and ν_3 are $\|$ vibrations and hence $\Delta J = \pm 1$, 0 and $\Delta K = 0$, while ν_2 and ν_4 are $\perp$ and have a fine structure given by $\Delta J = \pm 1$, 0 and $\Delta K = \pm 1$.

We might continue one step further with the possible applications of this theory. The first harmonics $2\nu_2$ and $2\nu_4$ are, as has been said, composed of two nearly superimposed bands, with an intensity ratio depending upon the anharmonic constants.* The one has as its upper state the symmetry $\{^{(\gamma,\delta)}_{(\delta,\gamma)}\}$ and hence it will have a fine structure entirely similar to that of the fundamental ν_2 or ν_4, that is, it will be a $\perp$ band. The other band has as its upper state the symmetry character $\{^\alpha_\beta\}$ and hence its fine structure will be entirely similar to the fundamental ν_1 or ν_3 and it will be a $\|$ band. Similar considerations may be applied to any overtone of the system YX_3.

Hund has not explicitly discussed the symmetry properties when each of the X atoms possesses a spin $sh/2\pi$ but the extension is very easily accomplished. Each single state will now consist of $(2s+1)^3$ states whose energy levels we may suppose to coincide. Let there exist a magnetic field relative to which the spin vectors of the X nuclei may be oriented. $(2s+1)$ states have the same components of spin for each of the three particles 1, 2 and 3. The spin wave functions for these states are symmetrical for an interchange of any two nuclei and hence have the character α. There will be $(2s+1)6s$ states in which two of the nuclei have the same components of spin along the field axis with the field component of the third nucleus different. A simple computation shows that one third of these states or $2s(2s+1)$ have the symmetry character α, the remainder having the degenerate characters γ or δ. Lastly there are $2s(2s+1)(2s-1)$ states in which all three nuclear components of spin along the field axis are different. Of these one sixth have the character α, one sixth β and two thirds the characters γ or δ. Of all the $(2s+1)^3$ states then, $\frac{1}{3}(2s+1)(2s+3)(s+1)$ have the character α, $\frac{1}{3}(2s+1)(2s-1)s$ the character β and $\frac{1}{3}(2s+1)(s+1)(8s)$ have the degenerate character γ or δ.

As we have said, the introduction of a spin s to the X nuclei makes of each

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* The separation of these bands will in general be large enough to be clearly observable since it depends upon the anharmonic forces and not upon magnetic forces as is the case in the nearly coincident levels caused by the spin.

hitherto single level, $(2s+1)^3$ nearly coincident levels. Their separtion is certainly of much too small an order of magnitude to be observable and consequently the effect of the spin is to change the weights of the states. This is illustrated in Table V for the cases $s = \infty$, $\frac{1}{2}$ and 0 for those states having the vibrational symmetry character $\{^\alpha_\beta\}$ or $\{^\beta_\alpha\}$. (The extension for the vibrational

TABLE V.

J	K	s = ∞			s = ½			s = 0		
		α	β	γ or δ	α	β	γ or δ	α	β	γ or δ
3	3	7·2	7·2	7·8	7·4	7·4	7·8	7·2	7·2	7·0
3	2	7·2	7·2	7·8	7·2	7·2	7·12	7·0	7·0	7·4
3	1	7·2	7·2	7·8	7·2	7·2	7·12	7·0	7·0	7·4
3	0	7·1	7·1	7·4	7·2	7·2	7·4	7·1	7·1	7·0
2	2	5·2	5·2	5·8	5·2	5·2	5·12	5·0	5·0	5·4
2	1	5·2	5·2	5·8	5·2	5·2	5·12	5·0	5·0	5·4
2	0	5·1	5·1	5·4	5·2	5·2	5·4	5·1	5·1	5·0
1	1	3·2	3·2	3·8	3·2	3·2	3·12	3·0	3·0	3·4
1	0	3·1	3·1	3·4	3·2	3·2	3·4	3·1	3·1	3·0
0	0	1·1	1·1	1·4	1·2	1·2	1·4	1·1	1·1	1·0

symmetry character $\{^{(\gamma,\,\delta)}_{(\delta,\,\gamma)}\}$ may be easily performed). The first two columns of the table give the J and K designation of the levels. The remaining numbers in the body of the table give the number of coinciding levels having the symmetry characters α, β, γ or δ. This number of levels is written for convenience as the product of two numbers, the first of which is $(2J+1)$. Again it appears to be more convenient to give numbers proportional to the number of levels rather than the exact numbers themselves. The proportionality factor for any given value of s is of course a constant.

Let us now consider only those states which have the character α or the character β, that is, those states which are either totally symmetrical or totally antisymmetrical in the three equal nuclei. (Exclusion principle). The number of coinciding levels, or the weight of a state for $s = \infty$ is just equal to that which it would be if the three X nuclei were slightly different so that no symmetry considerations would enter. That is the weights of the α or β columns are $(2J+1)$ for $K=0$ and $2(2J+1)$ for $K\neq0$. In the α and β columns for $s=\frac{1}{2}$ we notice that the weights may be described by saying that they are equal to the weights for $s = \infty$ except that they are multiplied by two for those levels for which K is an exact multiple of 3 (including zero). This table will be used to explain why every third line in certain of the bands of the methyl halide molecules is enhanced over its neighbors by a factor of 2.

In the α and β columns for $s=0$ we notice that the weights are different from zero only when K is a multiple of three. These considerations would become of value if the fine structure of any molecule possessing the group O_3 were known.

5. The molecule ZYX₃.

The remarks that have been made in the last paragraphs may be extended almost without change to include the molecule ZYX_3 where the Z nucleus lies along the axis of the YX_3 pyramid. The frequencies ν_1, ν_3 and ν_5 have just the symmetry characters of the frequencies ν_1 and ν_3 of the YX_3 molecule, namely $\{{}^{\alpha}_{\beta}\}$ or $\{{}^{\beta}_{\alpha}\}$. The frequencies ν_2, ν_4 and ν_6 have the vibrational symmetry character $\{{}^{(\gamma,\delta)}_{(\delta,\gamma)}\}$. The structure of any overtone band may be easily found by employing the rules given for the YX_3 molecule. The weights of the rotational states have just the same dependence upon the spin s of the X nucleus.

The problem does however become much more complicated when the Z atom becomes an X atom, forming the methane type molecule YX_4. The symmetry characters of the levels of such a system have been treated by W. Elert[23] but the complexity is so great that we shall not here give any adequate summary of his work. We shall only remark that his treatment shows that the fine structure lines of the fundamental bands ν_3 and ν_4 do not show any marked regularity in the enhancement of the lines caused by the spin of the X nucleus. An enhancement effect does exist but it is neither very pronounced nor obviously regular. (Every fourth line enhanced for example.) This result is in agreement with the experimental data regarding the methane spectrum.

The question of the structure of the vibrational levels V_3 or $V_4 = 0$, 1, 2, 3, 4 has been considered by Dennison and Ingram[16] using a perturbation method. They found that while the levels V_3 or $V_4 = 0$, 1 are single, the other states have three-fold, four-fold and seven-fold levels respectively. It is quite certain that these results of the perturbation calculation could also be obtained from symmetry character considerations following the work of Elert and Hund.

[23] W. Elert, Zeits. f. Physik **51**, 6 (1928).