

REVIEWS OF MODERN PHYSICS

VOLUME 12

JULY, 1940

NUMBER 3

The Infra-Red Spectra of Polyatomic Molecules. Part II

DAVID M. DENNISON*

University of Michigan, Ann Arbor, Michigan

INTRODUCTION

IT is now nearly ten years since the first part of the article on the "Infra-red spectra of polyatomic molecules" appeared in the *Reviews of Modern Physics*.¹ Part I contained a description of the theoretical methods by which the infra-red spectrum of a molecule might be interpreted, thus leading to a determination of the molecular constants. It was intended that Part II, containing the application of these methods to particular spectra, would follow shortly, and, in fact, the greater portion of the manuscript was actually prepared. It was unsatisfactory, however, and was never published. The unsatisfactoriness arose from the fact that at that time there existed no single polyatomic spectrum which could be understood with any degree of completeness. In some instances a vital piece of experimental datum was lacking, while in others a further development of the theory was necessary.

At the present time the situation is quite changed, for it may be said that there exist twenty or more spectra which have been adequately explained. The number of these spectra is now so great that it does not seem feasible in

the space available here to describe each of them in detail.† The author has elected, rather, to select five typical molecules, CO₂, H₂O, NH₃, the methyl halides and CH₄, and to treat their spectra quite fully. To some extent these may serve as examples for many other polyatomic molecules, although it must be admitted that certain features which may be essential for the description of a particular spectrum have not been included. We think, for example, of the phenomenon of hindered rotation as it occurs in ethane or methyl alcohol.

It has been interesting in the preparation of this article to observe the theoretical advances and changes in viewpoint which have been made during the past ten years. It is gratifying to find that the methods set forth in Part I are still valid and form the backbone for the analysis of a polyatomic spectrum. They must be supplemented, however, by various additional theories, such as those describing the resonance interaction of frequencies and their overtones, the vibration-rotation interaction and the effects of an internal angular momentum.

Let us consider briefly the usual procedure in analyzing a spectrum. The first step is the corre-

* The major portion of this article was written while the author was on leave at the California Institute of Technology. He wishes to acknowledge his indebtedness to the staff of the Institute, and particularly to Professor Linus Pauling, for placing all their facilities at his disposal. During this period the author was assisted by a Fellowship from the John Simon Guggenheim Memorial Foundation, which he also wishes gratefully to acknowledge.

† Of the recent books dealing with the infra-red spectra of polyatomic molecules we would like to mention, *Infrared and Raman Spectra* by G. B. B. M. Sutherland (Methuen, 1935); *Molekülspektren* by H. Sponer (Springer, 1936) and *Vibrational Spectra and Structure of Polyatomic Molecules* by T. Y. Wu (National University of Peking, 1939). This last book contains a particularly full account of the experimental spectra and their interpretation.

lation of the infra-red and Raman frequencies with the normal modes of oscillation of the system. If the configuration of particles representing the molecule possesses any symmetry properties, the n normal frequencies may be divided into a number of symmetry classes of which the i th class will contain say n_i frequencies. The vibrations of each symmetry class (the irreducible representations of group theory) will have certain properties, i.e., the infra-red or Raman activity, the direction of oscillation of the electric moment, etc., which will be very useful in identifying the observed frequencies of the molecule. The process of classifying the vibrations and of determining their symmetry properties may be accomplished through the aid of group theory, and this method in the hands of Wilson, Teller and others has proved to be very powerful. In Part I similar results were obtained by what was called the method of limiting force fields. This method may be described and rationalized in the following manner. It has been proved with the aid of group theory that the division of the normal vibrations into symmetry classes and that the properties of each class of vibrations depends upon the symmetry of the molecule and not at all upon the magnitude of the forces. This fact suggests that we may set up a model which possesses the symmetry of the molecule being discussed, but where the forces are chosen to be of such a simple nature that the vibrations and resulting motions of the system may be determined by inspection, or at least by an easy calculation. These vibrations will of course be quite different from the actual vibrations of the molecule since they are derived from limiting or extreme types of force fields. On the other hand, one may be certain that these vibrations will possess exactly the same symmetry properties as those of the true motion. It is often possible to find the vibrations for several different types of limiting force fields and thus to obtain checks upon the calculation. The author has found this method to be very convenient and rapid for determining the symmetry properties of the vibrations, as well as other results, such as the product rule, the sum of the ζ_s and the activity of the various overtones.

A second and a powerful guide in the identifica-

tion of the normal frequencies of a molecule arises from the fact that the forces which bind together the atoms in one group in a given molecule are only slightly changed when one considers the same group in a different molecule. Thus the hydroxyl group possesses a frequency in the region of 3700 cm^{-1} whether the group occurs in water vapor or in methyl alcohol. Similarly, the vibrations of the methyl group are relatively independent of the molecule in which the group finds itself.

After the infra-red and Raman frequencies of the molecule have been identified one may wish to obtain explicitly the potential function of the system. This will be a function of the mutual displacements of the particles from their equilibrium configuration. It is usual to assume that the potential may be developed as a power series in the displacement coordinates. The linear terms are of course absent since these are displacements from equilibrium. The quadratic terms are those which determine the normal modes of oscillation and will be discussed first. The cubic and quartic contributions may be treated as perturbations of the normal vibrations.

A nondegenerate system possessing n normal frequencies will have n displacement coordinates, and consequently the quadratic combinations of these coordinates will require $\frac{1}{2}(n)(n+1)$ coefficients. It is easy to show, however, that the potential of a system having symmetry properties and for which the normal vibrations may be divided into symmetry classes, contains but $\frac{1}{2}\sum n_i(n_i+1)$ independent coefficients where the sum is carried over the various symmetry classes. This means that the symmetry of the molecule reduces the number of constants which are necessary to specify the zeroth-order potential. As an extreme example we might cite the case of methane. This molecule has nine degrees of internal freedom and thus, were it not for the symmetry, the potential would contain 45 arbitrary constants. However, there are but four normal frequencies of which ν_1 and ν_2 each belong to different symmetry classes while ν_3 and ν_4 belong to a third class. We therefore conclude that the methane potential will actually require but five independent constants.

Although the symmetry greatly reduces the number of coefficients appearing in the quadratic

portion of the potential function, in general the number of constants will be greater than the number of normal frequencies and hence cannot be determined by them alone. (The only exception to this statement is when each normal frequency belongs to a different symmetry class. This occurs in triatomic linear symmetrical molecules of which CO_2 is an example.) Several ways around this difficulty have been devised. In the first place, if the molecule in question contains hydrogen atoms, then the corresponding molecule with deuterium replacing the hydrogen will furnish additional data for determining the potential constants. It is assumed that the forces are not affected by the substitution. In principle this method could be employed for any isotopic molecules, but the accuracy is generally very low except in the hydrogen-deuterium case. A second source of data which may be useful in fixing the potential constants is the spacing of the fine structure lines of molecules which possess axial or spherical symmetry. The spacing is determined by the internal angular momentum associated with the vibrational motion and depends upon the squares of the potential constants. It is, for this reason, a sensitive method of finding the potential. The normal frequencies themselves depend only upon the square root of the potential constants; however, the experimental values of the frequencies are known with higher precision than the fine structure spacings.

In the case of a complicated molecule, the number of data which may be found by the foregoing methods is still too small to evaluate the general potential. Recourse has been made to a different procedure which has considerable physical interest and promise. This consists in postulating a form for the potential function which is plausible and which one hopes will furnish an adequate approximation to the actual potential. The assumed form will depend upon a fewer number of constants than the general potential and consequently these can be evaluated. In the past, three lines of approach have been used. Studies of molecules such as H_2O , NH_3 and CH_4 containing hydrogen and one heavy atom have shown that the potential closely approximates a valence type potential, that is, it depends upon changes in the bond distances and changes in the bond angles only.

Thus the normal frequencies of these molecules may be well expressed in terms of just two constants. On the other hand, the potential functions of molecules containing only heavy atoms (for example CCl_4), seem better to follow a central force function. It will be shown that in the intermediate case of the methyl halides, a satisfactory compromise between these forms can be made.

A second approach lies in the assumption that a complicated molecule may be thought of as composed of a number of groups of atoms, and that the potential is the sum of the functions for each group, together with terms which determine the binding between groups. This method also reduces the number of constants which are required. Finally, it is found that the force constants which describe a group of atoms—say the methyl group—are relatively independent of the molecule in which the group finds itself. The information available at present indicates that this last assumption holds to within 10 percent or better. We wish to call attention to the fact that these methods of introducing a plausible but simplified form for the potential may only be considered to be satisfactory when there exist a sufficient number of checks on the experimental data with which one may substantiate the assumptions involved.

The zeroth order, or quadratic portion of the potential function, the evaluation of whose constants we have just discussed, determines the normal frequencies. These differ slightly—by from 1 to 5 percent—from the observed positions of the infra-red and Raman bands because of the influence of the anharmonic forces. The task of obtaining the normal frequencies is often a difficult one and implies that a rather complete analysis of the spectrum has been made. Usually this point has been neglected in the past and the observed positions of the fundamental bands have been substituted directly into the equations for the determination of the potential constants. The errors which are introduced in doing this are often surprisingly large. Since the potential constants are proportional to the squares of the frequencies the errors will usually lie between 2 and 10 percent but in certain cases, because of the sensitiveness of the functions, they may be considerably larger. In the case of CO_2 and H_2O ,

the spectrum is known with sufficient completeness so that the normal frequencies are well determined. This is, unfortunately, not so for either NH_3 or CH_4 , but a method based on the product rule and the internal angular momentum has been devised which we believe allows the normal frequencies to be obtained from the observed fundamentals with a fair degree of accuracy.

The potential function of a polyatomic molecule is actually a complicated function of the displacement coordinates. As has been mentioned, we approximate the potential by developing it as a power series in the coordinates. The quadratic terms give rise to an energy constant W_0 which is equal to $\sum h\omega_i[n_i + (d_i/2)]$ where d_i is the degree of degeneration of the i th normal vibration. As soon as the cubic and quartic portions of the potential power series development are considered the problem becomes non-separable and we employ the usual perturbation methods. In the simplest case where no accidental degeneration occurs between the frequencies and their overtones it may readily be shown that the energy constant is augmented by a term of the form

$$\sum_{i,k} X_{ik}[n_i + (d_i/2)][n_k + (d_k/2)].$$

The quantities X_{ik} are linear functions of the coefficients of the quartic terms in the potential and quadratic functions of the cubic coefficients. Clearly, the X_{ik} as well as the normal frequencies ω_i may be determined for a given molecule providing the positions of a sufficient number of the fundamental and overtone bands are known from experiment. The explicit equations connecting the X_{ik} and ω_i with the coefficients of the potential function may readily be obtained but, unfortunately, they will not serve for their immediate evaluation since there are a greater number of coefficients than there are relations. The following procedure may be adopted when the fine structure of a considerable number of the bands have been observed and analyzed.

The Hamiltonian of a polyatomic molecule depends both upon the vibration and upon the rotation of the system, and is in general not separable. It may, however, be written as $H = H_V + H_R + H_{VR}$ where H_V is a function of

the vibrational coordinates alone and H_R determines the rotation of a rigid molecule. If the possibility of internal angular momenta is neglected, $H_R = P_\alpha^2/2A_0 + P_\beta^2/2B_0 + P_\gamma^2/2C_0$ where P_α , P_β and P_γ are the components of the total angular momentum and A_0 , B_0 and C_0 are the equilibrium values of the moments of inertia. The term H_{VR} contains the vibration-rotation interaction and is usually small enough to be treated as a perturbation. The effect of this term in first approximation has been shown by Wilson and Howard² to be of the following sort. The rotational energy levels of the vibrating molecule will be just those of a fictitious rigid rotator whose moments of inertia A , B and C are linear functions of the vibrational quantum numbers. In fact,

$$1/A = 1/A_0 + \sum_i a_i(n_i + d_i/2).$$

The constants a_i are found to be linear functions of the cubic coefficients in the potential development. Thus if the fine structure of a sufficient number of the bands of the molecule in question have been analyzed, the effective moments of inertia and consequently the a_i and the A_0 , B_0 , C_0 may be evaluated. From the a_i the cubic coefficients of the potential can be calculated. The cubic coefficients, together with the X_{ik} and ω_i will fix the values of the quartic coefficients of the power series development of the potential function. The method which has just been outlined is unfortunately not very direct, and the resulting accuracy with which the coefficients are determined is often not great. In spite of these defects, it seems to be the only feasible approach at present available towards a detailed knowledge of the potential function of a polyatomic molecule.

Certain modifications must be introduced when there exists a resonance interaction between the vibrational levels. This phenomenon, which was first discovered by Fermi³ in a discussion of the spectrum of CO_2 , appears to occur quite frequently in many polyatomic spectra and may play an essential role. Thus if one frequency ω_i is approximately equal to twice another frequency $2\omega_k$, these levels may interact strongly through the term $q_i q_k^2$ in the cubic part of the potential. If the resonance is nearly perfect, as it

is in CO_2 , the interaction will greatly affect both the positions and the intensities of the bands. When $\omega_i \cong 3\omega_k$ or when $\omega_i \cong \omega_k$, the interaction is accomplished only through the quartic terms and quadratic combinations of the cubic terms in the potential, and its influence upon the spectrum is therefore usually smaller. This will be illustrated in the analysis of the water vapor spectrum.

In each of the molecular spectra which will be discussed in this article, we have endeavored, first of all, to determine the vibrational and rotational energy levels of the molecule from the most accurate experimental data which are at present known. These are then subjected to a theoretical treatment with the view of obtaining the molecular potential function as well as the molecular dimensions. Wherever possible, cross checks are adduced which serve to verify the theory which has been employed. In the majority of instances a very good agreement is found.

The infra-red wave-lengths which appear in the literature are usually measured in air, and these have been reduced to vacuum wave-lengths in order to obtain more accurate values for the energy levels. The physical constants were taken from a private communication kindly furnished by Professor R. T. Birge and we shall use $h = 6.624 \times 10^{-27}$ and the mass of the hydrogen atom $m = 1.6734 \times 10^{-24}$ g. The atomic weights of hydrogen, deuterium, carbon, nitrogen and oxygen used in evaluating the molecular constants were assumed to be 1.00813, 2.01473, 12.00398, 14.00750 and 16.00000, respectively.

CARBON DIOXIDE

The qualitative, as well as the quantitative, features of the infra-red spectrum of carbon dioxide lead unambiguously to the conclusion that the molecule is both linear and symmetrical. Molecules of this type possess three normal modes of vibration, of which one is doubly degenerate. (See reference 1, p. 292.) The frequency ν_1 corresponds to a motion in which the oxygen atoms oscillate symmetrically with respect to the carbon. This vibration, since it evidently possesses no changing electric dipole moment, will be completely inactive in the infra-red, but will appear strongly in the Raman

spectrum. The frequency ν_3 may be described as an oscillation of the carbon atom with respect to the oxygen atoms along the symmetry axis of the molecule. This vibration possesses a changing electric moment and will be strongly infra-red active. It may easily be shown that the fine structure associated with this band consists of a series of uniformly spaced lines corresponding to a positive and negative branch, but with no zero branch. Finally, the vibration ν_2 consists of a motion of the carbon atom against the oxygens in a line perpendicular to the symmetry axis of the molecule. The motion is doubly degenerate since there are two directions perpendicular to the symmetry axis along which the molecular forces are evidently identical. In the motions corresponding to both ν_2 and ν_3 the distance between the two oxygen atoms does not change. The frequency ν_2 is infra-red active and its fine structure consists again of uniformly spaced lines, but with the addition of a strong zero branch. Since the CO_2 molecule possesses a center of symmetry, those frequencies, which are active in the infra-red, will not appear in the Raman spectrum, and vice versa.

These predictions are completely confirmed by the experimental spectrum of CO_2 . The infra-red spectrum consists principally of two intense bands, one centering near 667 cm^{-1} and the other at about 2349 cm^{-1} . Both bands possess fine structures consisting of uniformly spaced lines, but the band at 667 cm^{-1} has a strong zero branch. Clearly, this must be identified with ν_2 , while the band at 2349 cm^{-1} which has no zero branch must be ν_3 . Neither of these frequencies appears in the Raman spectrum, whose principal feature is a pair of strong lines at 1285 and 1388. The average of these lines, 1337 cm^{-1} , may be taken to be the symmetrical frequency ν_1 .

The explanation of the fact that the Raman spectrum contains two lines rather than one was given by Fermi,³ who remarked that the first overtone of the frequency ν_2 (i.e., $2\nu_2 = 1334 \text{ cm}^{-1}$) lies very close to ν_1 . The existence of a small perturbation would cause these levels to resonate and interact with each other. The resulting levels would be somewhat separated from each other, and the wave functions would be linear combinations of the original wave functions. It is easy to show that the potential function of

TABLE I. *Vibrational energy levels of CO₂.*

(n_1, n_2, n_3)	$(W - W_0)/hc$ OBS.	$(W - W_0)/hc$ CALC.
(0 1 0)	667.3	667.3
(0 2 ₀ 0)	1285.5	1285.8
(1 0 ₀ 0)	1388.4	1388.1
(0 2 ₂ 0)	1335.4	1335.4
(0 3 ₁ 0)	1932.4	1931.9
(1 1 ₁ 0)	2076.6	2077.1
(0 3 ₂ 0)	—	2004.3
(0 0 ₀ 1)	2349.4	2349.4
(0 4 ₀ 0)	2553.6	2547.4
(1 2 ₀ 0)	—	2675.8
(2 0 ₀ 0)	2804.4	2798.8
(0 4 ₂ 0)	—	2583.4
(1 2 ₂ 0)	2761.3	2762.2
(0 2 ₀ 1)	3609	3613.2
(1 0 ₀ 1)	3716	3715.6
(0 4 ₀ 1)	4859	4852.8
(1 2 ₀ 1)	4981	4981.4
(2 0 ₀ 1)	5108	5104.3
(0 6 ₀ 1)	6077	6074.5
(1 4 ₀ 1)	6231	6231.4
(2 2 ₀ 1)	6351	6354.4
(3 0 ₀ 1)	6510	6518.9
(0 0 ₀ 3)	6976	6973.1
(0 0 ₀ 5)	11496.5	11496.5
(0 2 ₀ 5)	12672.4	12672.4
(1 0 ₀ 5)	12774.7	12774.7

CO₂ does contain a term which is capable of producing the interaction, and an estimate of its magnitude is in conformity with the observed separation of the levels. If the resonance is nearly perfect, as it is here, the stabilized wave functions will contain about 50 percent each of the original functions. This accounts for the fact that the two Raman lines are of nearly equal intensity.

Let us now turn to the quantitative side of the problem. The infra-red spectrum of CO₂ contains, in addition to the two strong fundamental bands, a large number of weaker bands which are to be ascribed to harmonics and combination tones of the fundamentals. These have been the subject of many experimental investigations and, in all, some twenty-five bands have been located whose positions extend from 600 cm⁻¹ to 12,775 cm⁻¹. These latter, which lie in the photographic infra-red, were observed by Adams and Dunham⁴ in the light reflected from the planet Venus, and attest to the great quantity of CO₂ which must exist there. The fine structure, which corresponds to a simultaneous change in the rotational energy, has been measured in nine of the bands, and will prove to be of great importance in the solution of the problem. Our immediate task, however, is the location of the

band centers; that is, a determination of the energy levels of the nonrotating molecule.

The vibrational energy levels may be labeled by means of the numbers n_1 , n_2 and n_3 , which are to be associated with the frequencies ν_1 , ν_2 and ν_3 , respectively. The motion corresponding to ν_2 is doubly degenerate, as has been mentioned, and consequently another quantum number is required to describe the levels. This is conveniently chosen to be l , and denotes the angular momentum in units of \hbar which arises from the vibrational motion ν_2 . The selection rules are easily obtained (reference 1, p. 297) and may be stated as follows. An active infra-red band whose fine structure shows a zero branch, that is, one in which the oscillation of the electric moment is perpendicular to the symmetry axis, will result when Δn_2 is odd, Δn_3 is even and $\Delta l = \pm 1$. An active infra-red band having no zero branch (change of electric moment along the symmetry axis) will occur if Δn_2 is even, Δn_3 is odd and $\Delta l = 0$.

One further remark must be made on the designation of the levels. The very close resonance between ν_1 and $2\nu_2$ means that a degeneracy may be said to exist originally between certain levels which is later removed by a perturbing or coupling term in the potential energy. It will be shown that only those levels may interact which have the same value of l . The stabilized wave functions of the levels after interaction are linear functions of the original wave functions, and consequently the original method of describing a level (n_1, n_2, n_3) is no longer suitable. This situation may be taken care of by enclosing the levels in brackets. Thus the two levels which give rise to the principal Raman lines are

$$\left\{ \begin{array}{l} (1, 0_0, 0) \\ (0, 2_0, 0) \end{array} \right\}.$$

The best experimental determinations of the vibrational energy levels of CO₂ are given in Table I, where the first column identifies the level, and the second column gives its value as measured above the ground state. A few comments must be made on the numbers appearing in this table since they differ slightly from those heretofore used. In the first place, the experimental wave-lengths are measured in air and

these have been reduced to vacuum by means of the corrections proposed by Rusch.⁵ Secondly, it will be noticed that a number of levels may be reached in several ways and consequently may be evaluated from a number of independent measurements. As an example we might consider the levels

$$\left\{ \begin{array}{l} (1, 0_0, 0) \\ (0, 2_0, 0) \end{array} \right\}.$$

These were determined by Martin and Barker⁶ as the sum of the transitions from

$$(0 0_0 0) \rightarrow (0 1_1 0) \text{ and } (0 1_1 0) \rightarrow \left\{ \begin{array}{l} (1, 0_0, 0) \\ (0, 2_0, 0) \end{array} \right\}$$

who in this way found the values 1388.2 and 1285.2 cm^{-1} .^{*} A second method of finding these levels is from the difference bands

$$\left\{ \begin{array}{l} (1, 0_0, 0) \\ (0, 2_0, 0) \end{array} \right\} \rightarrow (0 0_0 1)$$

as measured by Barker and Adel,⁷ together with the frequency $(0 0_0 1)$ observed by Martin and Barker and, more recently, by Cameron and Nielsen.⁸ These yield 1388.67 and 1285.86 cm^{-1} . The average of the infra-red determinations is therefore 1388.43 and 1285.53.

Transitions from the ground state to these levels cannot, of course, occur in the infra-red, but they are the strongest lines appearing in the Raman spectrum. They have been measured in carbon dioxide gas by Dickinson, Dillon and Rasetti⁹ who found the values 1387.7 and 1285.1, as well as by Langseth and Nielsen¹⁰ who obtained 1388.9 and 1285.8. The averages of the Raman determinations, 1388.30 and 1285.45, are in good agreement with the averages of the infra-red measurements. It is difficult to estimate the accuracy, but we should imagine that the error is smaller than 0.5 cm^{-1} .

In a similar manner, the pair of levels

$$\left\{ \begin{array}{l} (1, 1_1, 0) \\ (0, 3_1, 0) \end{array} \right\}$$

may be found from several infra-red bands as well as from the Raman spectrum. The various

^{*} A recalculation of the fine structure lines of the bands at 13.9μ and 16.2μ shows that the residuals may be made substantially smaller by raising the frequency of the band center of the former by 0.2 cm^{-1} and by lowering that of the latter by 0.2 cm^{-1} .

evaluations are again quite consistent, and the best averages appear to be 2076.6 and 1932.4 cm^{-1} . In this case, the infra-red bands are not resolved into their fine structure and it becomes necessary to determine their centers from the positions of the zero branches. A small correction (from 0.1 to 0.8 cm^{-1}) must be applied to the observed maxima of the zero branches to find the true band centers owing to the fact that the fine structure shows some convergence. The amount of this convergence will be discussed later. The correction is equal to the displacement of the most intense line of the zero branch. The values of many of the higher harmonic and overtone bands are taken from the paper by Barker and Wu.¹¹

The data which have thus far been presented serve to fix the positions of the band centers and consequently the vibrational energy levels. A second and a highly important source of information lies in the fine structure of those bands which have been resolved, since through it we may determine the moment of inertia of the molecule as well as several of the potential constants. The fine structure of the fundamental band ν_3 was first resolved by Martin and Barker,⁶ and later, in considerably greater detail, by Cameron and Nielsen.⁸ These latter investigators were able to obtain a very satisfactory fit for the positions of their lines by means of the formula,

$$\nu_3 = 2349.4 \pm 0.780J - 0.0031J^2,$$

where, for the positive branch, J assumes only odd values, and for the negative branch, only even values. This peculiar numbering of the lines corresponds to the fact that only half of the usually possible rotational states actually exist, and depends upon the identity of the oxygen nuclei. It was shown in Part I that the fine structure lines of the linear symmetrical molecule YX_2 should exhibit an alternation in intensity[†] of magnitude $s/(s+1)$ where $s\hbar$ is the spin of the X nucleus. In this case, the alternate lines are completely missing in confirmation of the zero spin of oxygen. The numbering of the lines shows, moreover, that in the normal unexcited state of the molecule, only those states occur for which the total angular momentum number J is even.

[†] Except for those bands where $l \neq 0$ in both the initial and final states.

From this we may conclude that the electronic wave function describing the normal state must be symmetrical for an interchange of the two oxygen nuclei.

Besides the fundamental ν_3 , the fine structures of six other bands have been resolved. The fundamental ν_2 was measured by Martin and Barker and the lines are well represented by

$$\nu_2 = 667.3 \pm 0.780J + 0.00045J^2.$$

The difference bands

$$\left\{ \begin{array}{l} (0, 2_0, 0) \\ (1, 0_0, 0) \end{array} \right\} \rightarrow (0, 0_0, 1)$$

which were observed by Barker and Adel yield*

$$\nu = 960.76 \pm 0.7763J - 0.00311J^2$$

and

$$\nu = 1063.57 \pm 0.7763J - 0.00335J^2.$$

The bands observed in the atmosphere of Venus were resolved by Adams and Dunham who give the following expressions:

$$\nu = 11496.5 \pm 0.769J - 0.0153J^2,$$

$$\nu = 12672.4 \pm 0.769J - 0.0150J^2$$

and

$$\nu = 12774.7 \pm 0.769J - 0.0156J^2.$$

It will be advantageous at this point to organize the data on the fine structure of the bands, and for this purpose we shall write the formula for that part of the energy which depends upon the rotation of the molecule. It will be shown later that this energy is given by the expression

$$W_R = (J^2 + J - l^2)(h^2/8\pi^2A)[1 + \alpha_1(n_1 + \frac{1}{2}) + \alpha_2(n_2 + 1) + \alpha_3(n_3 + \frac{1}{2})],$$

where A is the equilibrium moment of inertia, and the constants α_1 , α_2 , α_3 give the interaction between vibration and rotation and, as will be proved, are themselves functions of the potential constants. The lines of the positive branch of an absorption band corresponding to a transition from the state n_1'', n_2'', n_3'' to the state n_1', n_2', n_3' are then given by†

$$\nu_{J, n_1'n_2'n_3'}^{J-1, n_1''n_2''n_3''} = \nu_0 + (h/8\pi^2Ac) \{ J[2 + \alpha_1(n_1'' + n_1' + 1) + \alpha_2(n_2'' + n_2' + 2) + \alpha_3(n_3'' + n_3' + 1)] + J^2[\alpha_1(n_1' - n_1'') + \alpha_2(n_2' - n_2'') + \alpha_3(n_3' - n_3'')] \}.$$

The experimentally determined convergences will thus fix the constants α_1 , α_2 , α_3 , and these may be set back into the coefficient of J in order that the moment of inertia A may be found. The convergence of ν_3 gives $h\alpha_3/8\pi^2Ac = -0.0031$. This is in good agreement with the harmonic $5\nu_3$ observed in the Venus atmosphere which yields $5h\alpha_3/8\pi^2Ac = -0.0153$. The best average of these values would appear to be

$$h\alpha_3/8\pi^2Ac = -0.00307.$$

The fundamental ν_2 serves to evaluate α_2 and we find

$$h\alpha_2/8\pi^2Ac = +0.00045.$$

The formula given above for the rotational energy levels will hold only for those states which show no resonance interaction, such as ν_2 , ν_3 and $5\nu_3$. It is also valid for the sum of the energies for any group of levels in resonance interaction, but the calculation of the values for an individual level will be reserved until later.

The sum of the convergences observed by Barker and Adel for the difference bands will thus allow us to determine that

$$(h/8\pi^2Ac)(2\alpha_3 - \alpha_1 - 2\alpha_2) = -0.00646.$$

From the previously evaluated constants α_2 and α_3 we find

$$h\alpha_1/8\pi^2Ac = -0.00058.$$

* All values are corrected for vacuum wave-lengths.

† The effect of the term involving l^2 is merely to shift the position of the band center. It will prove more convenient to lump this term with the vibrational energy and we shall consequently omit it here.

The sum of the two resonating Venus bands gives

$$(h/8\pi^2Ac)(10\alpha_3 + \alpha_1 + \alpha_2) = -0.0306$$

from which

$$h\alpha_1/8\pi^2Ac = -0.0008.$$

The accuracy of this latter determination is much less than that of the former since we are here dealing with the difference between two rather large quantities and since the number of observed rotation lines is considerably smaller. We shall consequently adopt the former value. Although the arithmetic indicates that α_3 is determined to three significant figures and α_1 and α_2 to two figures, a careful review of the data shows that the errors involved in each of them might be as large as ± 0.0001 .*

It is now possible to evaluate the constant $h/4\pi^2Ac$. The term linear in J of the fundamental ν_3 yields the value, 0.786 while ν_2 gives 0.782. The sum of the two difference bands gives 0.782 while the Venus bands yield the two values 0.787 and 0.787. These figures are in accord with the measurements by Houston and Lewis¹² of the rotational Raman spectrum of CO_2 gas who found the number 0.786. We shall adopt the average and let $h/4\pi^2Ac = 0.785$ and thus obtain $A = 71.30 \times 10^{-40}$ g cm². The distance between the oxygen nuclei then becomes 2.317×10^{-8} cm.

An analysis of the carbon dioxide spectrum has been made by Adel and Dennison¹³ who succeeded in correlating the observed energy levels and in determining the potential constants of the molecule. Our discussion will follow in the main along the lines of their investigation; however it appears possible to simplify some of the calculations and, moreover, to correct some errors which exist in their papers.† The method proposed by Wilson and Howard² for the evaluation of the Hamiltonian of semirigid molecules may readily be adapted to our problem, and proves to be very suitable.‡ In this method a set of rotating axes is introduced which serve as a framework for the description of the normal modes of vibration. The rotating axes are defined by the condition that the angular momentum associated with the normal modes of vibration shall, in first order, vanish with respect to them. Analytically this means that

$$\sum_i m_i (r_i^0 \times \dot{r}_i) = 0,$$

where r_i is the vector, in the rotating axis system, to the i th particle and r_i^0 is the equilibrium value of that vector.

The coordinates which we shall use in defining the vibratory motion of the molecule are essentially those appearing in the papers by Adel and Dennison. Let q measure the change in distance between the two oxygen nuclei and be positive for an increase in distance. Let x , y and z be the components of

* The difference bands

$$(0 \quad 1_1 \quad 0) \rightarrow \left\{ \begin{matrix} 0 & 2_0 & 0 \\ 1 & 0_0 & 0 \end{matrix} \right\}$$

observed by Martin and Barker afford a certain test of the self-consistency of the work. These bands lie close to the intense fundamental ν_2 and are partially overlaid by it. Nevertheless, the positive branch of the high frequency band and the negative branch of the low frequency band are clearly resolved and accurately measured. Knowing the fine structure of the bands

$$\left\{ \begin{matrix} 0 & 2_0 & 0 \\ 1 & 0_0 & 0 \end{matrix} \right\} \rightarrow (0 \quad 0_0 \quad 1)$$

as well as that of the fundamentals ν_2 and ν_3 , we readily calculate the fine structure of the band in question. We find $\nu = 719.9 \pm 0.780J - 0.00041J^2$ and $\nu = 617.9 \pm 0.780J - 0.00017J^2$ where the only adjustment which has been made has been to find the best values for the band centers. The agreement between the observed and calculated lines is remarkably good. In these formulas the J must be an even integer for the positive branch lines and odd for the negative branch, in distinction to the former cases, since here l goes from $1 \rightarrow 0$ and the symmetry character of the initial and final states is reversed.

† Some of these errors are merely algebraic in nature, but there are a few which arise from the fact that the Hamiltonian which was used was not complete. I wish to take this opportunity to thank Dr. Ta-You Wu, Dr. A. Adel and Professor H. H. Nielsen, all of whom independently discovered certain of the errors and communicated them to me.

‡ In its original form the analysis of Wilson and Howard applies only to nonlinear molecules. However, the extension to linear molecules, as has been pointed out by Sayvetz, reference 14, is easily accomplished by noticing that one of the Eulerian angles, ψ , enters as a constant parameter and may be set equal to zero.

a vector connecting the carbon nucleus with the center of gravity of the oxygens. These components are to be taken along the axes of the moving coordinates defined above and z will be chosen to be parallel to the line joining the equilibrium positions of the oxygen nuclei. The x axis is immediately fixed providing, in the Eulerian angles which connect the moving axes with a set of space fixed axes, we let ψ be a constant, for example, zero. The calculations will be considerably freer from numerical constants if at the outset, q , x , y and z are replaced by dimensionless coordinates which are proportional to them. These will be chosen as σ , ξ , η , ζ where

$$\begin{aligned}\sigma &= 2\pi(\omega_1 mc/2h)^{\frac{1}{2}}q, & \xi &= 2\pi(\omega_2 \mu c/h)^{\frac{1}{2}}x, \\ \eta &= 2\pi(\omega_2 \mu c/h)^{\frac{1}{2}}y & \text{and} & \zeta = 2\pi(\omega_3 \mu c/h)^{\frac{1}{2}}z.\end{aligned}$$

Here ω_1 , ω_2 , ω_3 are the normal frequencies of oscillation expressed in waves per cm, m is the mass of an oxygen atom and μ is the reduced mass $2mM/(2m+M)$. c is the velocity of light.

A straightforward application of the method of Wilson and Howard, leads to the following Hamiltonian:

$$H = [(P_\alpha^2 + P_\beta^2) - 2(P_\alpha p_\alpha + P_\beta p_\beta) + (p_\alpha^2 + p_\beta^2)]/2A(1 + \sigma h^{\frac{1}{2}}/2\pi c^{\frac{1}{2}}A^{\frac{1}{2}}\omega_1^{\frac{1}{2}})^2 + (2\pi^2 c/h)[\omega_1 p_\sigma^2 + \omega_2(p_\xi^2 + p_\eta^2) + \omega_3 p_\zeta^2] + V.$$

In this formula A is the equilibrium moment of inertia of the molecule, P_α , P_β , P_γ are the components of the total angular momentum vector, while p_α , p_β , p_γ may be described as a local angular momentum taken with respect to the moving axes. More exactly,

$$p_\alpha = p_\zeta \eta - p_\eta \zeta, \quad p_\beta = p_\xi \zeta - p_\zeta \xi, \quad p_\gamma = p_\eta \xi - p_\xi \eta.$$

p_γ may be shown to be equal to P_γ . The quantities p_ξ , p_η , p_ζ and p_σ are of course the momenta which are canonically conjugate to their respective variables.

The potential energy V is a function of the vibrational coordinates only and has the following properties. Since the coordinates represent displacements from the equilibrium configuration, V must be a minimum with respect to each of them. The carbon dioxide molecule possesses a center of symmetry at the carbon atom and consequently V must be an even function of ζ . This symmetry also imposes the condition that V must be a function of the distance $\rho = [\xi^2 + \eta^2]^{\frac{1}{2}}$. The exact form of the potential function is of course unknown and recourse will be made to the usual device of assuming that V is an analytic function and that it may be developed as a power series in the coordinates. It will be assumed that the coefficients of the higher powers become successively smaller and may be treated as higher orders in a perturbation calculation. If V is analytic only even powers of ρ will appear and of course the center of symmetry guarantees that the same is true for ζ . These considerations lead to the following expression,

$$V = V_0 + \lambda V_1 + \lambda^2 V_2 + \dots,$$

where

$$\begin{aligned}V_0 &= \frac{1}{2}hc(\omega_1 \sigma^2 + \omega_2 \rho^2 + \omega_3 \zeta^2), \\ \lambda V_1 &= hc(a\sigma^3 + b\sigma\rho^2 + c\sigma\zeta^2), \\ \lambda^2 V_2 &= hc(d\sigma^4 + e\rho^4 + f\zeta^4 + g\sigma^2\rho^2 + h\sigma^2\zeta^2 + i\rho^2\zeta^2).\end{aligned}$$

The problem of obtaining the eigenvalues of the system is made somewhat simpler if we consider first of all only those terms in the Hamiltonian which do not contain the total angular momenta P_α , P_β , P_γ . This means that we shall obtain the energy W_V of the nonrotating molecule, which may be used to correlate the observed band centers as given in Table I. In zeroth order the Hamiltonian has the form $H_0 = (2\pi^2 c/h)[\omega_1 p_\sigma^2 + \omega_2(p_\xi^2 + p_\eta^2) + \omega_3 p_\zeta^2] + V_0$. The solution was derived in some detail in Part I, and yields,

$$W_V^0/hc = \omega_1(n_1 + \frac{1}{2}) + \omega_2(n_2 + 1) + \omega_3(n_3 + \frac{1}{2}).$$

The remaining terms in the Hamiltonian of the nonrotating molecule are now treated by the method of perturbations and lead to the following result:*

$$W_V/hc = \omega_1(n_1 + \frac{1}{2}) + \omega_2(n_2 + 1) + \omega_3(n_3 + \frac{1}{2}) + X_{11}(n_1 + \frac{1}{2})^2 + X_{22}(n_2 + 1)^2 + X_{33}(n_3 + \frac{1}{2})^2 \\ + X_{11}(l^2 - 1) + X_{12}(n_1 + \frac{1}{2})(n_2 + 1) + X_{13}(n_1 + \frac{1}{2})(n_3 + \frac{1}{2}) + X_{23}(n_2 + 1)(n_3 + \frac{1}{2}).$$

The constants $X_{11} \cdots X_{23}$ are related to the constants appearing in the development of the potential function V by means of the formulas,

$$X_{11} = \frac{3}{2}d - 15a^2/4\omega_1, \\ X_{22} = \frac{3}{2}e - b^2/2\omega_1 - b^2/8(2\omega_2 + \omega_1) + b^2/8(2\omega_2 - \omega_1), \\ X_{33} = \frac{3}{2}f - c^2/2\omega_1 - c^2/8(2\omega_3 + \omega_1) + c^2/8(2\omega_3 - \omega_1), \\ X_{11} = -\frac{1}{2}e + b^2/8(2\omega_2 + \omega_1) - b^2/8(2\omega_2 - \omega_1) - h/8\pi^2Ac, \\ X_{12} = g - 3ab/\omega_1 - b^2/2(2\omega_2 + \omega_1) - b^2/2(2\omega_2 - \omega_1), \\ X_{13} = h - 3ac/\omega_1 - c^2/2(2\omega_3 + \omega_1) - c^2/2(2\omega_3 - \omega_1), \\ X_{23} = i - bc/\omega_1 + (\omega_3/\omega_2 + \omega_2/\omega_3)h/8\pi^2Ac.$$

The expression for the vibrational energy just set down takes no account of any possible resonance between the frequencies and is the result of a second-order perturbation. The first-order change in the energy vanished since the terms comprising λV_1 are each odd in one of the coordinates. It is evident that when $\omega_1 \cong 2\omega_2$, as is the case in CO_2 , the coefficients X_{22} , X_{11} and X_{12} may become indefinitely large and the perturbation method employed breaks down completely.

The procedure employed by Adel and Dennison in the solution of the problem consisted in treating the first-order perturbation separately, finding the stabilized wave functions, and using these in a second-order calculation to find the resulting energy of the system. A reconsideration of the problem shows that this may be accomplished in a more straightforward manner as follows. We begin with the zeroth-order solution in which $\lambda V_1 = \lambda^2 V_2 = 0$. With these wave functions, the matrix $|H_b^a|$ representing the complete Hamiltonian of our problem may now be calculated. It will of course contain diagonal elements of order λ^0 and λ^2 but no elements in λ for the reason cited in the last paragraph. There will also exist off diagonal elements in λ , λ^2 , etc. Our problem is to diagonalize this Hamiltonian and thus obtain the eigenvalues of the system. It is well known that these are the roots of the determinant $|H_b^a - \delta_b^a W_b| = 0$. The standard method of approximating the roots is to assume that in the calculation of W_a , the remaining roots W_b are nearly equal to the zeroth-order energies, namely, $W_b^0 = H_{0b}^b$. The result of doing this is to transform from the original determinant to one in which the off diagonal elements contain only quadratic and higher powers of λ . New terms are introduced into the diagonal elements which are of order λ^2 and contain resonance denominators $W_a^0 - W_b^0$. The method obviously fails in any case when $W_a^0 \cong W_b^0$, as has been pointed out.

The difficulty may be rather simply obviated. We may carry out the standard method of approximation for all such levels for which W_a^0 is not equal or nearly equal to W_b^0 . This leaves us with a determinant composed of square boxes, centered about the diagonal, which contain those elements whose unperturbed energies are approximately equal. The diagonal elements are just the energy levels as given earlier, with the one difference that those terms in X_{22} , X_{11} and X_{12} which possess the nearly vanishing resonance denominators are to be omitted. The off diagonal elements outside the boxes begin with terms of order λ^2 while those within the boxes have terms in λ . The final step in obtaining the eigenvalues is merely to diagonalize each of the boxes separately. This is comparatively simple since in our case most of the boxes have only two elements on a side and none have more than four.

* The calculation as originally performed by Adel and Dennison contains a few small errors which are here corrected. The contribution from the term $(p_\alpha^2 + p_\beta^2)/2A(1 + \sigma h^2/2\pi c^2 A^2 \omega_1^2)^2$ agrees with the result computed by Weinberg and Eckart, reference 15, and appears in the constant X_{23} . The term $-h/8\pi^2Ac$ in X_{11} comes from the rotational energy, which will be discussed later.

It will be interesting to carry out this process in detail for a particular pair of levels, for example, the levels

$$\begin{Bmatrix} (1, 0_0, 0) \\ (0, 2_0, 0) \end{Bmatrix}.$$

The small determinant whose roots give the energy values is

$$\begin{vmatrix} (W_{V^{1,0_0,0}} - W)/hc & -b/\sqrt{2} \\ -b/\sqrt{2} & (W_{V^{0,2_0,0}} - W)/hc \end{vmatrix}.$$

The off diagonal term comes from the expression $b\sigma\rho^2$ which occurs in λV_1 and is the $(1, 0_0, 0) \rightarrow (0, 2_0, 0)$ element. The diagonal elements are just what they would have been, had there existed no resonance. The roots of the determinant may be expressed conveniently as $W_{\pm} = \frac{1}{2}(W_{V^{1,0_0,0}} + W_{V^{0,2_0,0}}) \pm \frac{1}{2}\Delta$ showing that the sum of the two levels is unaffected by the resonance. The separation between the levels is given by $\Delta = (\Delta_0^2 + \Delta_1^2)^{\frac{1}{2}}$ where Δ_0 is the separation that would have existed without resonance, namely, $\Delta_0 = W_{V^{1,0_0,0}} - W_{V^{0,2_0,0}}$. Δ_1 in this case is easily seen to be $\sqrt{2}|b|/hc$.

The stabilized wave functions may now be obtained from the minors of the determinant. Thus if the nonstabilized functions are designated by the symbols $(1, 0_0, 0)$ and $(0, 2_0, 0)$, the upper state W_+ has the wave function, $(1, 0_0, 0)(\Delta + \Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}} - (0, 2_0, 0)(\Delta - \Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}$ while the lower state function is $(1, 0_0, 0)(\Delta - \Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}} + (0, 2_0, 0)(\Delta + \Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}$. One further property is easily proved. If $W_{V^{1,0_0,0}}$ is increased by a small amount δ and $W_{V^{0,2_0,0}}$ by ϵ (this situation occurs when we consider the rotation vibration interaction), then the upper state W_+ will be increased by $\delta(\Delta + \Delta_0)/2\Delta + \epsilon(\Delta - \Delta_0)/2\Delta$ and W_- by $\delta(\Delta - \Delta_0)/2\Delta + \epsilon(\Delta + \Delta_0)/2\Delta$.

Up to this point we have evaluated the eigenvalues for the energy of the nonrotating molecule. The final step will be to consider those terms of the Hamiltonian which depend upon the total angular momenta P_α , P_β and P_γ . There are two of these, the first being $(P_\alpha^2 + P_\beta^2)/2A(1 + \sigma h^{\frac{1}{2}}/2\pi c^{\frac{1}{2}}A^{\frac{1}{2}}\omega_1^{\frac{1}{2}})^2$. Now $P_\alpha^2 + P_\beta^2 + P_\gamma^2$ is the square of the total angular momentum and possesses the eigenvalue $(J^2 + J)h^2/4\pi^2$. P_γ is the component of the angular momentum along the axis of the molecule. It also is represented by a diagonal matrix whose eigenvalues are $lh/2\pi$. Consequently $P_\alpha^2 + P_\beta^2$ is already diagonalized and is equal to $(J^2 + J - l^2)h^2/4\pi^2$. The term $[1 + \sigma h^{\frac{1}{2}}/2\pi c^{\frac{1}{2}}(A\omega_1)^{\frac{1}{2}}]^{-2}$ may be expanded in a power series in σ and each term treated by the usual perturbation methods. The linear term by combining with the matrix elements of λV_1 yields contributions containing the anharmonic constants a , b and c , while the quadratic term may be evaluated by taking the diagonal elements of σ^2 .

The second term in the Hamiltonian may, to the approximation to which we are working, be replaced by $-(P_\alpha p_\alpha + P_\beta p_\beta)/A$. P_α and P_β contain no diagonal matrix elements (see reference 1, p. 318) and consequently this term gives no first-order addition to the energy. The second-order perturbation calculation is straightforward, although rather lengthy, and results in an addition to the energy constant of

$$[(J^2 + J - l^2)h^3/16\pi^4 A^2 c][[(n_2 + 1)\omega_2/(\omega_2^2 - \omega_3^2) + (n_3 + \frac{1}{2})\omega_3/(\omega_3^2 - \omega_2^2)].$$

Collecting these results we find that the rotational energy of the molecule together with the rotation-vibration interaction may be expressed by means of a formula of the type given earlier where

$$\begin{aligned} \alpha_1 &= 3h/4\pi^2 c A \omega_1 + 3ah^{\frac{1}{2}}/\pi(cA\omega_1^3)^{\frac{1}{2}}, \\ \alpha_2 &= h(\omega_3^2 + 3\omega_2^2)/8\pi^2 c A \omega_2(\omega_2^2 - \omega_3^2) + bh^{\frac{1}{2}}/\pi(cA\omega_1^3)^{\frac{1}{2}}, \\ \alpha_3 &= h(\omega_2^2 + 3\omega_3^2)/4\pi^2 c A \omega_3(\omega_3^2 - \omega_2^2) + ch^{\frac{1}{2}}/\pi(cA\omega_1^3)^{\frac{1}{2}}. \end{aligned}$$

The first step in the determination of the potential constants of CO_2 is to find the numerical values of the ten quantities ω_1, \dots, X_{23} together with the interaction constant b . The most obvious way of doing this, namely, to employ the eleven

best experimental data on the band centers, does not prove to be satisfactory for it may be shown that small changes in the frequencies (of the order of the experimental errors) will seriously affect the values of the constants. A further

TABLE II. *Potential constants of CO₂.*

$\omega_1 = 1351.2$	$a = -30$	$d = 1.5$	$g = 1.9$
$\omega_2 = 672.2$	$b = 71.3$	$e = \begin{cases} +0.5 \\ -3.7 \end{cases}$	$h = 8.9$
$\omega_3 = 2396.4$	$c = -250$	$f = 6.4$	$i = -25.7$

datum by which this uncertainty might be eliminated would be, for example, $\Delta_0 = W_V^{1,0_0,0} - W_V^{0,2_0,0}$, namely, the difference which would exist between the two levels (1, 0₀, 0) and (0, 2₀, 0) had there been no resonance interaction. The value of Δ_0 may be arrived at from the following experimental data. The convergence observed in the difference bands observed by Barker and Adel together with the convergence of the fundamental band ν_3 serves to determine the convergence of the resonating levels

$$\begin{Bmatrix} (1 & 0_0 & 0) \\ (0 & 2_0 & 0) \end{Bmatrix}.$$

The convergence factors α_1 , α_2 and α_3 have already been obtained and thus we may calculate the convergence which would have existed in the absence of resonance. These data when substituted into the appropriate equation yield* $\Delta_0 = 16.7 \text{ cm}^{-1}$. The value of Δ_0 as just calculated may well be in error by as much as 10 percent and this uncertainty constitutes one of the unsatisfactory phases of our discussion of the CO₂ spectrum.

The band centers, in conjunction with Δ_0 , may be used to compute the molecular constants. We have attempted in each instance to employ the most accurately known bands or combination of bands.

$$\begin{aligned} \omega_1 = 1351.2, & \quad X_{11} = -0.3, \quad X_{12} = 5.7, \\ \omega_2 = 672.2, & \quad X_{22} = -1.3, \quad X_{13} = -21.9, \\ \omega_3 = 2396.4, & \quad X_{33} = -12.5, \quad X_{23} = -11.0. \\ b^2 = 5081, & \quad X_{ii} = 1.7, \end{aligned}$$

Since there are 23 observed levels which have been used to obtain 10 constants, there will exist 13 independent checks upon the adequacy of the theory. The third column of Table I lists the calculated levels and it is seen that the agreement is very satisfactory. Such discrepancies as do

* The fact that Δ_0 is positive and of this order of magnitude is indicated by the observation that the high frequency Raman line is stronger than the low frequency by a factor of about 1:0.57. See I. Hansen, reference 63, for a discussion of this point.

exist may be attributed to either of two causes; on the one hand they are of the order of the experimental errors, and on the other they are likewise of the order of the deviations to be expected from a theory which uses a power series development.

The convergence factors α_1 , α_2 and α_3 have been shown to be functions of the first-order potential constants a , b and c and may be used for their evaluation. Substituting the numerical values for the normal frequencies and for the moment of inertia we find

$$\begin{aligned} h\alpha_1/8\pi^2Ac &= 0.000684 + 4.20a \times 10^{-5}, \\ h\alpha_2/8\pi^2Ac &= -0.000307 + 1.40b \times 10^{-5}, \\ h\alpha_3/8\pi^2Ac &= 0.000429 + 1.40c \times 10^{-5}. \end{aligned}$$

From the observed values for these convergence factors one readily obtains $a = -30$, $b = +54$ and $c = -250 \text{ cm}^{-1}$. The second constant b has already been evaluated far more accurately from the resonance interaction and found to be $b = \pm 71.3 \text{ cm}^{-1}$. The failure to obtain a better check is puzzling; possibly it has its origin in the fact that experimental convergence which is here involved is very small, $+0.00045$, and is difficult to determine precisely.

The second-order potential constants are now to be found from the expressions connecting them with the quantities X_{11} to X_{23} . The results of this calculation are collected in Table II and expressed in waves per cm. It will be noticed that there are two methods of obtaining the constant e , from X_{22} and from X_{ii} , and that the values thus found fail to agree except in as far as they both give e to be small. This point will be discussed in the following paragraph.

The analysis of the carbon dioxide spectrum has been, in the main successful. A theoretical derivation of the vibration-rotation energy levels has been given which is based upon a model for which the potential function is developed as a power series in the displacement coordinates. Thirteen constants, ω_1 , ω_2 , ω_3 , a , \dots , i and A , the moment of inertia, are involved. The energy levels are determined directly as functions of fifteen quantities $\omega_1 \dots X_{11}$, \dots , X_{23} , b^2 , $\alpha_1 \dots \alpha_3$ and A and it is shown that these serve to predict with high accuracy the twenty-three band centers and the seven rotational fine structures which have been experimentally measured. There ap-

WATER VAPOR

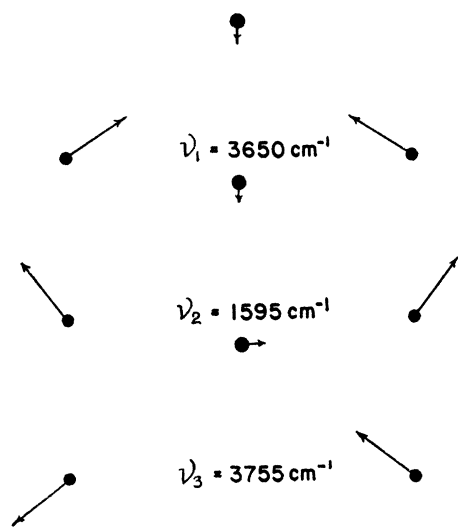


FIG. 1. The normal vibrations of water vapor.

pears to be no doubt but that an adequate method has been devised for calculating the vibration-rotation energy levels of the carbon dioxide molecule. On the other hand, the determination of the potential constants of the power series development is much less certain. The two checks upon the self-consistency of the method, the calculation of b from α_2 and of e from X_{22} and X_{11} , are not well satisfied. We feel that this is an illustration of the difficulty of employing a power series development for the potential function which breaks off at a certain order. Since the potential constants of one order are often quite unequal (thus in Table II $i \gg d$), it seems likely that some terms of the next higher order will have an appreciable effect which should not be neglected.

As an example of the ability of the theory to predict the energy levels of the molecule we shall consider the fundamental band ν_3 of C^{13}O_2 ¹⁶ which has been observed by A. H. Nielsen.¹⁶ The negative branch has been well resolved but the positive branch is badly overlaid by the ν_3 band of normal CO_2 . Nielsen finds the band center to lie at 2283.8 cm^{-1} (corrected to vacuum). This quantity may now be calculated from the theory which predicts that the band center should be at 2283.9 cm^{-1} , in nearly perfect agreement with the observation.

The rotation-vibration spectrum of water vapor is very extensive and has been the subject of many investigations. It begins in the far infra-red, at about 500μ , and extends with very few gaps to about the middle of the visible spectrum. It has been accurately mapped from 135μ to 5700A . The molecule, which may be represented by an isosceles triangle with an apex angle of about $104^\circ 31'$, possesses a permanent electric moment and consequently exhibits a pure rotation spectrum. Since no two of the moments of inertia are equal, the molecule belongs to the class of asymmetric rotators and accordingly its fine structure lines will be very irregularly spaced; a prediction which is fully borne out by experiment. The pure rotation spectrum reaches its maximum intensity around 50μ , from which point it slowly decreases until at about 15μ only a few lines are observable and these only with long columns of the saturated vapor. At about 8.5μ an intense absorption again sets in, this time due to the outer edge of a fundamental vibration band.

The water vapor molecule possesses three normal modes of vibration, which are illustrated in Fig. 1. While all three frequencies should be both infra-red and Raman active, only two of the fundamentals, ν_2 and ν_3 , are directly observed in the infra-red. These correspond to the intense regions of absorption centering around 1595.0 and 3755.4 cm^{-1} , respectively. The Raman spectrum, on the other hand, contains only one strong line at 3650 cm^{-1} which must be identified with ν_1 . Undoubtedly this frequency does appear in the infra-red, but it is probably rather weak and is overlaid by the intense absorption due to ν_3 which falls close to it. A very qualitative explanation for the intensity distribution between the Raman and infra-red spectra is suggested by the fact that the apex angle in water vapor is rather obtuse and that for a linear molecule we have the rigorous selection rules that only ν_1 is Raman active while only ν_2 and ν_3 appear in the infra-red.

The absorption of water vapor in the near and photographic infra-red is strong and is due to the harmonics and overtones of the fundamental frequencies. The intensity of the lines decreases

as we proceed into the visible region until they can only be observed by using very long path lengths. They are most accurately measured as atmospheric lines in the solar spectrum.

We begin our discussion of the experimentally determined energy levels of the water molecule by considering the rotational energy levels of the molecule in its lowest vibrational state. The theory of the asymmetrical rotator was developed in Part I, where it was shown that the eigenvalues of the levels are given as the roots of certain algebraic equations and are functions of the three moments of inertia. The states are designated by the symbol J_τ where J determines the total angular momentum of the system, τ is an index which runs from $+J$ to $-J$ and denotes the ordering of the levels as regards their magnitude within any J group. Each level is furnished with a symbol $(++)$, $(+-)$, $(-+)$ or $(--)$ which fixes the symmetry class to which the state belongs. The permanent electric moment of the water molecule lies along the axis of the middle moment of inertia and it was shown that in this case the selection rules for the pure rotation spectrum are such that $\Delta J = \pm 1$ or 0 and that transitions may occur only between the symmetry classes $(++) \leftrightarrow (--)$ and $(+-) \leftrightarrow (-+)$.

In a recent paper Randall, Dennison, Ginsburg and Weber¹⁷ have measured the far infra-red spectrum of water vapor under high dispersion from 18μ to 75μ . These observations, supplemented by the work of Wright and Randall,¹⁸ serve to determine many of the rotational energy levels. The combined measurements do not extend to frequencies below 74 cm^{-1} and consequently it is difficult from these data alone to calculate the lowest rotational states. Fortunately, however, the analyses of the rotational structure of the water bands occurring in the solar spectrum which have been made by Mecke¹⁹ and his collaborators furnish the requisite information. A careful study of Mecke's work shows that it is most reliable in its identification of the transitions between the low lying states and consequently is particularly valuable for our purpose. In many cases energy differences between levels may be determined both from the solar bands and from the far infra-red measurements and it is found that these agree to within a few hundredths of a cm^{-1} , attesting to the high

accuracy of both sets of observations. The results of this analysis are collected in Table III. The numbers differ slightly from those previously given for two reasons. In the first place all the wave-lengths have been corrected to vacuum, and in the second place a more complete use has been made of the information which may be obtained from the solar bands. The far infra-red spectrum of water vapor affords a beautiful example of the application of the theory of the

TABLE III. The rotational energy levels of the water molecule.

J_τ	W/hc	J_τ	W/hc	J_τ	W/hc
++ 0 ₀	0	++ 7 ₄	1216.38	++ 10 ₆	2254.53
+ - 1 ₁	42.36	+ - 7 ₃	1059.87	+ - 10 ₅	2254.53
- - 1 ₀	37.14	- - 7 ₂	1059.68	- - 10 ₄	2054.55
- + 1 ₋₁	23.76	- + 7 ₁	931.33	+ - 10 ₃	2054.55
++ 2 ₂	136.15	++ 7 ₀	927.76	++ 10 ₂	1875.72
+ - 2 ₁	134.88	+ - 7 ₋₁	842.51	+ - 10 ₁	1875.24
- - 2 ₀	95.19	- - 7 ₋₂	816.65	- - 10 ₀	1725.84
+ - 2 ₋₁	79.47	+ - 7 ₋₃	782.42	+ - 10 ₋₁	1719.36
++ 2 ₋₂	70.08	++ 7 ₋₄	709.44	++ 10 ₋₂	1614.07
+ - 3 ₃	285.46	+ - 7 ₋₅	704.30	+ - 10 ₋₃	1581.53
- - 3 ₂	285.26	- - 7 ₋₆	586.46	- - 10 ₋₄	1538.31
- + 3 ₁	212.12	- + 7 ₋₇	586.25	+ - 10 ₋₅	1446.37
++ 3 ₀	206.35	++ 8 ₈	1789.36	++ 10 ₋₆	1438.19
+ - 3 ₋₁	173.38	+ - 8 ₇	1789.36	+ - 10 ₋₇	1293.80
- - 3 ₋₂	142.30	- - 8 ₆	1591.11	- - 10 ₋₈	1293.22
- + 3 ₋₃	136.74	- + 8 ₅	1591.11	+ - 10 ₋₉	1114.69
++ 4 ₄	488.19	++ 8 ₄	1411.59	++ 10 ₋₁₀	1114.69
+ - 4 ₃	488.19	+ - 8 ₃	1411.59	+ - 11 ₁₁	3217.73
- - 4 ₂	383.93	- - 8 ₂	1255.98	- - 11 ₁₀	3217.73
+ - 4 ₁	382.47	+ - 8 ₁	1255.98	+ - 11 ₉	2974.13
++ 4 ₀	315.70	++ 8 ₀	1131.88	++ 11 ₈	2974.13
+ - 4 ₋₁	300.33	+ - 8 ₋₁	1122.89	+ - 11 ₇	2740.73
- - 4 ₋₂	275.23	- - 8 ₋₂	1052.72	- - 11 ₆	2740.73
+ - 4 ₋₃	224.71	+ - 8 ₋₃	1006.19	+ - 11 ₅	2522.46
++ 4 ₋₄	221.94	++ 8 ₋₄	983.04	++ 11 ₄	2522.46
+ - 5 ₅	742.18	+ - 8 ₋₅	885.69	+ - 11 ₃	2322.25
- - 5 ₄	742.18	- - 8 ₋₆	882.97	- - 11 ₂	2322.20
+ - 5 ₃	610.34	+ - 8 ₋₇	744.20	+ - 11 ₁	2144.66
++ 5 ₂	610.16	++ 8 ₋₈	744.13	++ 11 ₀	2143.55
+ - 5 ₁	508.80	+ - 9 ₉	2225.87	+ - 11 ₋₁	2000.24
- - 5 ₀	503.90	- - 9 ₈	2225.87	- - 11 ₋₂	1983.73
+ - 5 ₋₁	446.39	+ - 9 ₇	2010.19	+ - 11 ₋₃	1898.12
++ 5 ₋₂	416.00	++ 9 ₆	2010.19	++ 11 ₋₄	1839.71
+ - 5 ₋₃	399.44	+ - 9 ₅	1810.76	+ - 11 ₋₅	1810.79
- - 5 ₋₄	326.50	- - 9 ₄	1810.76	- - 11 ₋₆	1694.32
+ - 5 ₋₅	325.27	+ - 9 ₃	1631.58	+ - 11 ₋₇	1690.74
++ 6 ₆	1045.14	++ 9 ₂	1631.44	++ 11 ₋₈	1525.31
+ - 6 ₅	1045.14	+ - 9 ₁	1477.46	+ - 11 ₋₉	1525.02
- - 6 ₄	888.74	- - 9 ₀	1475.14	- - 11 ₋₁₀	1327.30
+ - 6 ₃	888.70	+ - 9 ₋₁	1360.56	+ - 11 ₋₁₁	1327.30
++ 6 ₂	757.72	++ 9 ₋₂	1340.70	- - 12 ₆	3033.01
+ - 6 ₁	756.78	+ - 9 ₋₃	1283.02	+ - 12 ₅	3033.01
- - 6 ₀	661.54	- - 9 ₋₄	1216.37	+ - 12 ₋₉	1774.85
+ - 6 ₋₁	649.03	+ - 9 ₋₅	1202.04	- - 12 ₋₁₀	1774.85
++ 6 ₋₂	602.71	++ 9 ₋₆	1080.51	+ - 12 ₋₁₁	1558.07
+ - 6 ₋₃	552.94	+ - 9 ₋₇	1079.20	++ 12 ₋₁₂	1558.07
- - 6 ₋₄	542.74	- - 9 ₋₈	920.25	++ 13 ₋₁₀	2042.51
+ - 6 ₋₅	447.17	+ - 9 ₋₉	920.25	+ - 13 ₋₁₁	2042.51
++ 6 ₋₆	446.66	++ 10 ₁₀	2702.61	- - 13 ₋₁₂	1806.94
+ - 7 ₇	1394.96	+ - 10 ₉	2702.61	+ - 13 ₋₁₃	1806.94
- - 7 ₆	1394.96	- - 10 ₈	2471.83	+ - 14 ₋₁₃	2073.81
+ - 7 ₅	1216.38	+ - 10 ₇	2471.83	++ 14 ₋₁₄	2073.81

asymmetrical rotator. It is shown by Randall, Dennison, Ginsburg and Weber that the calculated spectrum agrees almost perfectly with the observed spectrum both as regards the positions of the lines and their intensities. An interesting feature is that the rotational energy levels deviate somewhat from the positions which are predicted by the asymmetrical rotator equation. The reason for this lies in the centrifugal force correction to the energy levels which may assume values as large as 280 cm^{-1} for the high energy state 11₁₁. For the lower states where this correction is not too great, it may be calculated by the method proposed by Wilson and Howard.² The computation is somewhat long but it has yielded good agreement for those states to which it has been applied. Empirically the centrifugal force correction may be found by subtracting the observed energy levels from those which are calculated by the asymmetrical rotator theory. This correction will be approximately independent of the vibrational state and consequently the numbers which are found for the normal state may be employed in the evaluation of the rotational energies of the higher vibrational states.

Recently Fuson, Randall and Dennison²⁰ have obtained the pure rotation spectrum of D₂O throughout the region from 26μ to 139μ . The lines resemble those of H₂O in their chaotic and irregular appearance but they possess an average separation which is only half as great. An analysis of the spectrum was made in the following manner. A discussion of the effective moments of inertia of H₂O leads to a method of estimating with high precision the moments of inertia of the ground state of D₂O. From these, the energy levels are calculated from the formulas of the asymmetric rotator. A correction must now be made for the centrifugal force stretching which is based upon the similar correction for H₂O. Armed with these trial levels, the spectrum is calculated both as regards the positions and the intensities of the lines. It is found that this calculated spectrum agrees so well with the observed spectrum that it is possible unambiguously to identify the lines. Small adjustments are now made which result in further increasing the accuracy and self-consistency with which the rotational levels of D₂O are finally determined.

TABLE IV. *The vibrational levels of water vapor.*

$(n_3 n_1 n_2)$	W/hc OBS.	W/hc CALC.
(001)	1595.0	—
(002)	3151.0	—
(010)	3650	—
(100)	3755.41	—
(101)	5330.8	5330.6
(110)	7251.0	7250.4
(111)	8807.05	8805.52
(120)	10613.12	—
(300)	11032.36	—
(121)	12151.22	[12148.46]
(301)	12565.01	[12567.74]
(130)	13830.92	—
(310)	14318.77	—
(131)	15347.91	[15346.27]
(311)	15832.47	[15834.12]
(132)	16821.61	16822.70
(140)	16899.01	16894.25
(320)	17495.48	17482.60

The vibrational states are to be labeled by means of the three quantum numbers n_1 , n_2 and n_3 , and a given level will be designated by the symbol (n_3, n_1, n_2) . In all, some fifteen overtone and harmonic bands have been measured and these, together with the three fundamentals furnish us with the eighteen vibrational levels which are shown in Table IV.

In a recent paper Darling and Dennison²¹ have considered the problem of the vibration-rotation states of the water molecule. We shall here review the methods which they used and the results which were obtained. For the details of the calculation the reader is referred to the original article. The Hamiltonian function for a semirigid molecule may be written in the form

$$H = \frac{1}{2} \sum_{\alpha\beta} \mu^{\frac{1}{2}} (P_\alpha - p_\alpha) \mu_{\alpha\beta} \mu^{-\frac{1}{2}} (P_\beta - p_\beta) \mu^{\frac{1}{2}} + \frac{1}{2} \sum_k \mu^{\frac{1}{2}} p_k \mu^{-\frac{1}{2}} p_k \mu^{\frac{1}{2}} + V.$$

The P_α are the components of the total angular momentum while the p_α are the components of the angular momentum in the rotating coordinate system defined by Wilson and Howard. $\mu_{\alpha\beta}$ are the cofactors of a determinant μ which contains the moments of inertia which are themselves functions of the normal coordinates. The p_k are the momenta conjugate to the normal coordinates q_k .

In the case of the water molecule, there are three normal coordinates and these are illustrated in Fig. 1. The potential will be a function

of the normal coordinates which, we shall assume, can be developed as a power series. It will prove convenient to introduce the dimensionless variables x_i which are related to the normal coordinates q_i by the expressions

$$x_i = 2\pi[\omega_i c/h]^{\frac{1}{2}} q_i.$$

The ω_i are the normal frequencies expressed in waves per cm; c is the velocity of light. The symmetry of the molecule evidently imposes the condition that V must be an even function of q_3 or x_3 . If λ is the parameter of the development, we have

$$V = V^0 + \lambda V_1 + \lambda^2 V_2 + \dots,$$

where

$$V^0/hc = \frac{1}{2}(\omega_1 x_1^2 + \omega_2 x_2^2 + \omega_3 x_3^2),$$

$$\lambda V_1/hc = \alpha_1 x_1^3 + \alpha_2 x_2^3 + \alpha_3 x_1^2 x_2 + \alpha_4 x_1 x_2^2 + \alpha_5 x_1 x_3^2 + \alpha_6 x_2 x_3^2,$$

$$\lambda^2 V_2/hc = \beta_1 x_1^4 + \beta_2 x_2^4 + \beta_3 x_3^4 + \beta_4 x_1^2 x_2^2 + \beta_5 x_1^2 x_3^2 + \beta_6 x_2^2 x_3^2.$$

We may remark that the symmetry condition would allow $\lambda^2 V_2$ to contain additional terms of the sort $x_1 x_2 x_3^2$, $x_1 x_2^3$ and $x_1^3 x_2$. Since these are odd in at least one coordinate they will not contribute to the energy, at least in orders up to the third.

The first problem of the theory is the evaluation of the band centers, that is, the energy of the vibrating, but not rotating, molecule. This may be accomplished by setting the components of total angular momentum P_α equal to zero and calculating the eigenvalues by the familiar perturbation methods. The result is that the vibrational energy has the form,

$$Wv/hc = \sum_k \omega_k (n_k + \frac{1}{2}) + \sum_{k \geq l} X_{kl} (n_k + \frac{1}{2})(n_l + \frac{1}{2}).$$

The six quantities X_{kl} are found as explicit functions of the twelve anharmonic constants $\alpha_1 \dots \beta_6$.

An expression of this type was obtained by Bonner²² and applied to the water vapor spectrum. The nine quantities ω_k and X_{kl} were evaluated from nine of the measured band centers; the remaining band centers could then be calculated and compared with the observations. The resulting check was moderately good with one important exception. The fundamental

frequency ν_1 , measured as a Raman line, was predicted to lie some forty or fifty wave numbers below its observed position. The solution of this difficulty appears to lie in the near equality of the two frequencies ω_1 and ω_3 , which may accordingly give rise to resonance effects. This resonance is not of first order since the normal vibrations ω_1 and ω_3 belong to different symmetry classes. It may easily be shown that the vibrational levels of the YX_2 molecule belong to either of two symmetry classes which may be characterized by the evenness or oddness of the vibrational number n_3 . It is therefore clear that the overtone levels which may resonate are of the sort (n_3, n_1, n_2) and (n_3+2, n_1-2, n_2) .

The matrix elements in the Hamiltonian connecting these states are all off diagonal and they are all of second order. Thus the calculation of the X_{kl} will be unaffected, since these depend upon second-order elements on the diagonal but only upon the first-order off diagonal elements. This is in contrast to the situation in carbon dioxide where the resonance effects are of first order and consequently much larger. The method of deducing the final energy levels is now to diagonalize separately those portions of the Hamiltonian matrix which contain the elements in question. The off diagonal terms of these portions of the Hamiltonian consist of an interaction b . A short calculation shows that

$$b_{n_3+2, n_1-2, n_2}^{n_3, n_1, n_2} = \frac{1}{2} \gamma hc [n_1(n_1-1)(n_3+1)(n_3+2)]^{\frac{1}{2}},$$

where

$$\gamma = \frac{1}{2} \beta_5 - \alpha_5^2/\omega_1 + \alpha_1 \alpha_5/2\omega_1 + \alpha_3 \alpha_6/4(2\omega_1 - \omega_2) - \alpha_3 \alpha_6/4(2\omega_1 + \omega_2).$$

There exists also a small contribution to γ from the kinetic energy part of the Hamiltonian but in the case of water vapor this term is negligible.

The procedure is now quite straightforward. By using ten data from the table of band centers we calculate the ten constants. The remaining eight band centers may then be computed and compared with the experimental values. This is done in Table IV where a bracket around two numbers means that their sum was used in fixing the constants but not the individual values. The agreement is seen to be very satisfactory.

The constants obtained in this manner are

$$\begin{aligned}\omega_1 &= 3825.32, & X_{11} &= -43.89, & X_{12} &= -20.02, \\ \omega_2 &= 1653.91, & X_{22} &= -19.50, & X_{13} &= -155.06, \\ \omega_3 &= 3935.59, & X_{33} &= -46.37, & X_{23} &= -19.81, \\ & & |\gamma| &= 74.46, & W_0/hc &= 4631.25.\end{aligned}$$

It is clear that although we have at this point a method for calculating any of the centers of the water vapor bands we are not yet in a position to evaluate the twelve potential constants $\alpha_1 \cdots \beta_6$ since we possess only seven quantities X_{kl} and γ which involve them. Moreover the actual displacements corresponding to each normal coordinate are also unknown. These may however be obtained in the following way. Let us consider the Cartesian axes x and y whose origin lies at the center of gravity of the system and whose y axis is parallel to the line joining the equilibrium positions of the two X atoms. We now choose the x component of the change (increase) of distance between X atoms to be the coordinate q . Let y be the y component of the displacement of the Y atom with respect to the center of gravity of the X atoms. The final coordinate x is equal to $x_1 + b\theta$, where x_1 is the x component of the displacement of the Y atom against the center of gravity of the X atoms, θ is the angle between the line joining the X atoms and the x axis, while b is the equilibrium distance between the Y atom and the line joining the X atoms. From the conservation of angular momentum it is easily shown that $x = (1 + \mu b^2/2ma^2)x_1$. Here μ is the reduced mass $2mM/(2m+M)$ and $2a$ is the equilibrium distance between the X atoms.

The kinetic energy of the vibrating system may be calculated in the usual manner and is

$$2T = [\mu/(1 + \mu b^2/2ma^2)]\dot{x}^2 + \mu\dot{y}^2 + \frac{1}{2}m\dot{q}^2.$$

The general potential function will contain only four constants (since it must be even in the coordinate x) and may be written

$$2V = ax^2 + by^2 + cq^2 + 2dyq.$$

The normal frequencies are given in terms of the roots ($\lambda_i = 4\pi^2\omega_i^2 c^2$) of a determinant and may be expressed as follows:

$$\begin{aligned}\lambda_1\lambda_2 &= 2(bc - d^2)/m\mu, \\ \lambda_1 + \lambda_2 &= b/\mu + 2c/m, \\ \lambda_3 &= a(1 + \mu b^2/2ma^2)/\mu.\end{aligned}$$

The first minors of the determinant yield the relationships between the displacement coordinates and the normal coordinates q_1, q_2, q_3 .

$$\begin{aligned}q &= \delta_{11}q_1 + \delta_{12}q_2, \\ y &= \delta_{21}q_1 + \delta_{22}q_2, \\ x &= \delta_{33}q_3.\end{aligned}$$

The four potential constants a, b, c and d cannot be determined from the three normal frequencies of H_2O alone but could easily be evaluated if we possessed the corresponding frequencies for D_2O . While the spectrum of heavy water vapor is not known nearly as precisely nor as completely as that of normal water vapor it seems possible to fix the following values of the D_2O constants with considerable accuracy. (See reference 21 for fuller details.)

$$\begin{aligned}\omega_1 &= 2758.06, & X_{11} &= -22.81, & X_{12} &= -10.56, \\ \omega_2 &= 1210.25, & X_{22} &= -10.44, & X_{13} &= -81.92, \\ \omega_3 &= 2883.79, & X_{33} &= -24.90, & X_{23} &= -10.62, \\ & & W_0/hc &= 3385.74, & |\gamma| &\cong 42.\end{aligned}$$

The difference between the zero-point energies of H_2O and D_2O has recently been measured by Rossini, Knowlton and Johnston²³ using a calorimetric method. Their result of 1243.0 ± 7.6 cm^{-1} is in very good agreement with our spectroscopic value of 1245.5 cm^{-1} .

The potential constants as well as the connection between the displacement and the normal coordinates may now be evaluated.

$$\begin{aligned}a &= 10.672 \times 10^5 \text{ dynes/cm}, & c &= 3.134, \\ b &= 7.181, & d &= 3.159, \\ \delta_{11} &= 1.1468 \text{ m}^{-\frac{1}{2}}, & \delta_{12} &= 0.8276 \text{ m}^{-\frac{1}{2}}, \\ \delta_{21} &= 0.4391 \text{ m}^{-\frac{1}{2}}, & \delta_{22} &= -0.6084 \text{ m}^{-\frac{1}{2}}, \\ \delta_{33} &= 0.9283 \text{ m}^{-\frac{1}{2}},\end{aligned}$$

An examination of the displacements for each normal mode of oscillation reveals that in water vapor the vibration ω_1 is such that the H atoms move very nearly along the O-H bond directions whereas in the vibration ω_2 they move nearly perpendicular to the bond directions. This suggests that the potential function is of the so-called valence type. To show this, the potential may be rewritten as a function of $\delta r_1, \delta r_2$ and $\delta\gamma$, the changes in the two bond distances and the bond angle, respectively. R is the equilibrium O-H distance and the constants are

expressed in dynes/cm. We find

$$2V = 8.428(\delta r_1^2 + \delta r_2^2) + 0.7678R^2\delta\gamma^2 \\ + 2(0.1051)\delta r_1\delta r_2 + 2(0.2521)R\delta\gamma(\delta r_1 + \delta r_2).$$

A strictly valence potential would mean that the coefficients of $\delta r_1\delta r_2$ and of $R\delta\gamma(\delta r_1 + \delta r_2)$ would be zero.

We shall now return to the Hamiltonian function and consider the terms which involve P_α and thereby obtain the rotational eigenvalues and the vibration-rotation interaction. In zeroth order these terms yield the familiar expression for the rigid asymmetrical rotator, $P_\alpha^2/2I_\alpha^0 + P_\beta^2/2I_\beta^0 + P_\gamma^2/2I_\gamma^0$. I_A^0 , I_B^0 and I_C^0 are the equilibrium values of the moments of inertia and since the H_2O molecule is plane we have the relation $I_C^0 = I_A^0 + I_B^0$. A perturbation calculation on the remainder of the terms in the Hamiltonian shows that the rotational energy (when the vibration-rotation interaction is included) may be developed as a series containing quadratic, quartic, etc. combinations of the components of total angular momentum P_α . The quartic combinations, as has been pointed out by Wilson and Howard,² represent the effects of the centrifugal forces upon the rotational levels and are not, in first approximation, functions of the vibrational state. They give rise to the deviations between the calculated and observed energy levels which were discussed earlier in connection with the pure rotation spectrum of H_2O . Their influence becomes almost negligible for the lower rotational states and we may ignore them for the present.

The principal part of the rotational energy contains the quadratic combinations of angular momenta P_α and may be shown to have the form

$$W_R = P_\alpha^2/2I_A + P_\beta^2/2I_B + P_\gamma^2/2I_C.$$

TABLE V. Values of $\Delta = I_C - I_A - I_B$ for the water molecule.

$(n_1 n_2)$	Δ_{OBS}	Δ_{CALC}	$(n_3 n_1 n_2)$	Δ_{OBS}	Δ_{CALC}
(0 0 0)	0.077	0.076	(1 2 1)	0.262	0.226
(0 0 1)	.304	.241	(3 0 1)	.215	.207
(1 0 0)	.063	.064	(1 3 0)	.071	.057
(1 0 1)	.222	.228	(3 1 0)	.050	.047
(1 1 0)	.122	.064	(1 3 1)	.254	.221
(1 1 1)	.327	.228	(1 3 2)	.393	.386
(1 2 0)	.061	.061	(1 4 0)	.120	-.004
(3 0 0)	.045	.042	(3 2 0)	.176	-.006

This means that the rotational energy levels are just those which are predicted by the theory of the rigid asymmetrical rotator but where the equilibrium moments are replaced by so-called effective moments of inertia. The effective moments are functions, in first approximation linear functions, of the vibrational quantum numbers. Thus

$$I_A = I_A^0 [1 + \sum a_k (n_k + \frac{1}{2})], \\ I_B = I_B^0 [1 + \sum b_k (n_k + \frac{1}{2})], \\ I_C = I_C^0 [1 + \sum c_k (n_k + \frac{1}{2})].$$

The nine quantities $a_1 \cdots c_3$ are functions of the normal frequencies, the δ_{ik} which connect the normal and the displacement coordinates and of the six first-order anharmonic constants $\alpha_1 \cdots \alpha_6$. These expressions, which are rather long and will not be reproduced here, have been calculated by Shaffer and Nielsen²⁴ and by Darling and Dennison. A very interesting feature is that, despite the fact that H_2O is a plane molecule, in general $I_C \neq I_A + I_B$. However, it turns out that $\Delta = I_C - I_A - I_B$ is independent of the anharmonic constants $\alpha_1 \cdots \alpha_6$. This is a very important point for it means that we may calculate Δ at once for each band and compare it with the experimental Δ . This has been done in Table V. The calculated numerical value of Δ for the water molecule is

$$\Delta = [0.1644(n_2 + \frac{1}{2}) - 0.0122(n_3 + \frac{1}{2})] \times 10^{-40},$$

where the coefficient of $(n_1 + \frac{1}{2})$ is so small as to be negligible. The agreement is very satisfactory and is best for those levels which are best known experimentally, i.e., the normal state (0 0 0) and the more intense solar bands (1 2 0) to (3 1 0). We regard this as a real and significant test of the theory of the water vapor spectrum.

The theory also predicts that the effective moments of inertia should be linear functions of the vibrational quantum numbers. A study of the data shows that this is essentially the case, although small discrepancies exist which are of the order of the experimental errors. The following procedure was adopted. The effective moments of inertia were obtained from the analyses of the fine structure as given by Mecke. The small correction produced by the quartic terms in P_α was subtracted. The seven most accurately observed bands, (0 0 0) and (1 2 0) to (3 1 0),

were selected and their moments fitted to a linear formula which was subject to two conditions; first, that $I_C^0 = I_A^0 + I_B^0$, and second, that the Δ must be equal to the calculated Δ . In the case of resonating levels, such as (1 2 0) and (3 0 0) etc., it is necessary to combine the moments of inertia by means of an expression which is identical with the equation which was used to calculate the convergence factors for the various resonating levels in carbon dioxide.

The following result is attained,

$$I_A \times 10^{40} = 1.0229 + 0.0213(n_1 + \frac{1}{2}) \\ - 0.1010(n_2 + \frac{1}{2}) + 0.0486(n_3 + \frac{1}{2}),$$

$$I_B \times 10^{40} = 1.9207 + 0.0398(n_1 + \frac{1}{2}) \\ - 0.0249(n_2 + \frac{1}{2}) + 0.0077(n_3 + \frac{1}{2}),$$

$$I_C \times 10^{40} = 2.9436 + 0.0611(n_1 + \frac{1}{2}) \\ + 0.0385(n_2 + \frac{1}{2}) + 0.0441(n_3 + \frac{1}{2}).$$

A comparison between the observed moments and the moments calculated from the above formulas shows a very good agreement. The errors appear to be of the order of the experimental errors and are smallest for those bands which are best known.

The equilibrium values for the moments of inertia lead to an O-H distance of 0.9580A and a valence angle of $104^\circ 31'$.

It is now possible to evaluate the six quantities $a_1 \cdots c_3$ which enter the theoretical expressions for the effective moments of inertia and through them to calculate the six anharmonic constants $\alpha_1 \cdots \alpha_6$. The accuracy of their determination is not very great since the effects which they produce are small. The six quantities X_{ik} (used to calculate the band centers) are functions of the twelve anharmonic constants $\alpha_1 \cdots \beta_6$. Since we now know the α_5 it is a simple matter to obtain the β_5 . The zeroth, first- and second-order potential constants of the water molecule are collected in Table VI. They are all expressed in the units of cm^{-1} .

One further test of the theory may be made. The resonance interaction constant γ which was found to have the value $|\gamma|_{\text{obs.}} = 74.46 \text{ cm}^{-1}$, is a function of the anharmonic potential constants. A substitution yields $\gamma_{\text{calc.}} = -71.5 \text{ cm}^{-1}$. This agreement is remarkably good especially when one considers the many steps which have been involved in the calculation.

In reviewing the present status of the problem of the water molecule we begin by pointing out that methods have been devised by which we may calculate the many energy states associated with the vibration-rotational motion. The procedure consists in first calculating the band centers by means of the ω_k , X_{ik} and γ . Following this the effective moments of inertia for the state in question will yield the rotational energies through the use of the asymmetrical rotator formula. Finally a small correction due to the centrifugal stretching is to be applied. While this correction may be approximately calculated it would appear to be easier to find it by subtracting the observed rotational energy levels of the normal state from their computed values. These numbers are listed in the paper by Randall, Dennison, Ginsburg and Weber.¹⁷ The results of the various tests which have been made on the self-consistency of these methods furnish definite information on the degree of accuracy which may be attained.

In addition to allowing us to calculate the energy levels, the theory evaluates the coefficients in the series of terms which represent the potential function. The results show that the potential is far from being harmonic. The coefficients of the terms which connect the motions ω_1 and ω_3 , namely, $x_1 x_3^2$ and $x_1^2 x_3^2$ are unusually large. This no doubt accounts both for the resonance between the levels $(n_3 n_1 n_2)$ and $(n_3 + 2, n_1 - 2, n_2)$ and for the fact that they appear to be the most intense overtones in the spectrum. On the other hand, the size of the anharmonic coefficients is somewhat disturbing because it tends to invalidate the assumptions which underlie the perturbation theory. However, the results appear to show that the method of using a power series development is still applicable to the case of the water molecule.

AMMONIA

The ammonia molecule has the geometric form of a regular pyramid. The hydrogen nuclei lie at the corners of an equilateral triangle while

TABLE VI. *Potential constants of the water molecule.*

$\omega_1 = 3825.32$	$\alpha_1 = -322$	$\alpha_4 = 216$	$\beta_1 = 39$	$\beta_4 = -116$
$\omega_2 = 1653.91$	$\alpha_2 = -47$	$\alpha_5 = -909$	$\beta_2 = 2$	$\beta_5 = 212$
$\omega_3 = 3935.59$	$\alpha_3 = 1$	$\alpha_6 = 160$	$\beta_3 = 35$	$\beta_6 = -108$

the nitrogen occupies the apex of the pyramid. Since the molecule, which belongs to the class of symmetrical rotators, has a permanent electric moment, it exhibits an absorption in the far infra-red which should consist primarily of a uniformly spaced set of lines. These have been observed, first by Badger and Cartwright²⁵ and later, under higher dispersion, by Wright and Randall.¹⁸ The molecule possesses four normal modes of vibration. (See reference 1, p. 300.) Of these, ν_1 and ν_3 belong to one symmetry class which may be characterized by the fact that the nuclei move symmetrically with respect to the axis of the pyramid. The change of the electric moment is consequently parallel to the molecular axis and these bands are called \parallel bands. ν_1 lies at 3336 cm^{-1} while the center of the absorption band ν_3 is at 949.9 cm^{-1} . The remaining frequencies, ν_2 and ν_4 , are such that the change of the electric moment is perpendicular to the symmetry axis of the molecule. Since the molecule possesses axial symmetry as regards the normal modes of oscillation both ν_2 and ν_4 are doubly degenerate. ν_2 appears only very weakly as a group of irregularly spaced lines in the region of 3μ and is badly overlaid by the ν_1 band. From measurements of the difference band, $\nu_2 - \nu_3$, Barker³³ concludes that the center of the ν_2 absorption should be at 3414 cm^{-1} . The frequency ν_4 manifests itself as an intense absorption band whose center appears to be at 1627.5 cm^{-1} .

In addition to the energy of rotation and of vibration just discussed there is a contribution to the energy of the system which arises from the so-called tunnel effect. There are two entirely equivalent equilibrium positions for the nitrogen nucleus with respect to the three hydrogen nuclei. It is impossible to transform from one configuration to the other by a rotation, but only by a finite displacement of the particles such as that by which the nitrogen passes through the plane of the hydrogens. It was shown in Part I that this circumstance will produce a doubling of all of the energy levels of the molecule. The magnitude of the doubling depends markedly upon the vibrational state. Thus in the ground state the separation of the levels is 0.66 cm^{-1} , in the fundamental vibrational state ν_1 it is about 0.9 cm^{-1} and in ν_3 it is 35.7 cm^{-1} .

The three sources of energy, the rotation, the vibration and the tunnel effect are of course interrelated and in a certain sense must be discussed simultaneously. However, it may be somewhat clearer to focus our attention on each one successively. The far infra-red spectrum as observed by Wright and Randall consists of a series of doublets whose average spacing is about 19.89 cm^{-1} . The fact that the lines are double arises from the tunnel effect since for these lines only those transitions are allowed which connect one of the double minimum states with another of these states. The average doublet separation of 1.32 cm^{-1} represents twice the separation of the two lowest tunnel states. In many ways the pure rotation spectrum of ammonia is similar to a \parallel type vibration band. The zero branch of this band corresponds to a transition in which the rotational quantum numbers do not change but where the system goes from one of the tunnel states to the other. This absorption should lie at 0.66 cm^{-1} or at a wave-length of about 1.5 cm and has been measured experimentally by Cleeton and Williams²⁶ using short electromagnetic waves produced by an oscillator tube. The pure rotation lines, as observed by Wright and Randall show some convergence and the center of gravity of the doublets may be represented by the formula $\nu = 19.89J - 0.00178J^3$. This convergence, which is caused by the centrifugal force stretching of the molecule has been treated recently by Slawsky and Dennison²⁷ using the method outlined by Wilson and Howard.² They show that, in addition to the conventional expression for the energy of a symmetrical rotator, i.e.,

$$W_R = (J^2 + J)\hbar^2/2A + K^2\hbar^2(\frac{1}{2}C - \frac{1}{2}A)$$

there are additional terms which are proportional to powers of $(J^2 + J)$ and of K^2 . The coefficients of these terms are functions of the vibrational constants of the molecule. Explicitly for NH_3 the correction to the rotational energy is*

$$\begin{aligned} \delta W/hc = & -0.000625(J^2 + J)^2 + 0.000799(J^2 + J) \\ & - 0.000630K^4 - 0.00189K^2 \\ & + 0.000950(J^2 + J)K^2. \end{aligned}$$

* *Note added in proof.*—A substitution of the potential constants derived in this article into the Slawsky and Dennison formula would probably give a more reliable estimate of the centrifugal force correction to the rotational energy.

The effect of this contribution is to separate the rotation lines into groups of multiplets whose average positions will exhibit a convergence which is approximately proportional to J^3 . In the case of the lines observed by Wright and Randall the multiplet separation is too small to be distinguishable but it should be easily measurable for the higher members of the series. The quantitative agreement obtained by Slawsky and Dennison in fitting the observed lines is almost perfect.

The moment of inertia A as determined from the far infra-red lines is 2.814×10^{-40} . The moment of inertia about the axis of the pyramid, C , cannot be found from these lines and is in fact very difficult to obtain even from the \perp vibration bands due to a vibration-rotation interaction which will be discussed later. It may be inferred in a number of ways, (1) from the solution of the double minimum problem, (2) from the measurements by Barnes of the far infra-red spectrum of ND_3 and (3) from the observations by Migeotte and Barker on the vibration band ν_3 of ND_3 . (We have corrected these latter observations to give the line spacing of the molecule in its normal state, namely, $2B_0 = 10.276$.) The values obtained by these three procedures are very consistent and lead to the following molecular dimensions and moments of inertia:

		NH_3	ND_3
H-H distance	$= 1.631 \times 10^{-8}$ cm	$A = 2.814$	5.447
N-H distance	$= 1.014$	$C = 4.452$	8.898
Height of pyramid	$= 0.377$		
H-N-H angle	$= 107^\circ 3'$		

The problem of obtaining the normal modes of vibration of the pyramidal molecule YX_3 is a simple one, although it will turn out that an exact evaluation of the potential constants is more difficult. We begin by recognizing that vibrations belonging to different symmetry classes may be treated separately. Geometric coordinates appropriate for each symmetry class will be introduced. (For detailed descriptions and figures see reference 27.) For the two \parallel frequencies we use a coordinate ζ which denotes a motion of the X atoms in their plane in which each atom approaches the axis of the pyramid by the amount $\zeta/3^{1/2}$. The second coordinate will be z , which measures the displacement of the Y

atom along the axis and away from and relative to the X_3 plane. Since these two coordinates correspond to displacements of the particles which are respectively perpendicular to each other the kinetic energy is just the sum of the two kinetic energies. Clearly,

$$2T_{\parallel} = m\dot{\zeta}^2 + \mu\dot{z}^2,$$

where μ is the reduced mass $3mM/(3m+M)$. The potential energy will be a general quadratic form in ζ and z and consequently will have three coefficients.

$$2V_{\parallel} = az^2 + b\zeta^2 + 2cz\zeta.$$

The normal frequencies of the parallel motions may now be found in the usual manner ($\lambda_i = 4\pi^2\omega_i^2 c^2$)

$$\begin{aligned}\lambda_1 + \lambda_3 &= a/\mu + b/m \\ \lambda_1\lambda_3 &= (ab - c^2)/\mu m.\end{aligned}$$

The perpendicular frequencies are only slightly more difficult. Let x represent the displacement of the Y atom from a line drawn perpendicular to the X_3 plane and through the center of gravity of the X atoms. Since there are two directions possible for any displacement which is perpendicular to the symmetry axis we must have a complementary coordinate y . The second pair of coordinates ξ and η denote the two motions of the X_3 atoms in their plane which correspond to the double frequency of the X_3 system. A short calculation yields the following expression for the kinetic energy where k is defined in terms of the moments of inertia and the masses $k = \mu C/2Am$

$$2T_{\perp} = mk(\dot{x}^2 + \dot{y}^2) + m(\dot{\xi}^2 + \dot{\eta}^2).$$

The potential energy is a quadratic form which is subject to the condition that the coordinates x, y or ξ, η must enter equivalently. Thus,

$$2V_{\perp} = \alpha(x^2 + y^2) + \beta(\xi^2 + \eta^2) + 2\gamma(x\xi + y\eta).$$

The normal frequencies are then given by

$$\begin{aligned}\lambda_2 + \lambda_4 &= \alpha/mk + \beta/m \\ \lambda_2\lambda_4 &= (\alpha\beta - \gamma^2)/m^2k.\end{aligned}$$

It is evident that the four fundamental frequencies of NH_3 will not serve to determine the six potential constants. However, it would appear to be easily possible with the additional aid of the fundamental bands of ND_3 . These

have been observed by Migeotte and Barker²⁸ who found, $\nu_1=2419$, $\nu_2=2555$, $\nu_3=747.3$ and $\nu_4=1191$ cm^{-1} . We shall consider the \perp vibrations first. Since there are four data and only three potential constants, there must exist an interrelation. This relation, often called the product rule, is that

$$(\omega_2\omega_4)^2_{\text{NH}_3}/(\omega_2\omega_4)^2_{\text{ND}_3}=(m^2k)_{\text{ND}_3}/(m^2k)_{\text{NH}_3}.$$

From a knowledge of the moments of inertia we calculate that this ratio should be 3.503. On the other hand, a substitution of the numerical values for the frequencies yields the result 3.340. The reason for this discrepancy lies in the fact that we have not used the normal frequencies; but, rather, the frequencies of the fundamental bands which differ from them by the anharmonic terms. A similar situation arose in the case of water vapor, and this example may be worth citing since there both the normal and the fundamental frequencies are known. In H_2O the frequencies ω_1 and ω_2 belong to the same symmetry class and the product rule is

$$(\omega_1\omega_2)^2_{\text{H}_2\text{O}}/(\omega_1\omega_2)^2_{\text{D}_2\text{O}}=(m\mu)_{\text{D}_2\text{O}}/(m\mu)_{\text{H}_2\text{O}}.$$

The calculated value of the ratio, 3.592 is just equal to the ratio of the squares of the products of ω_1 and ω_2 . However, the ratio of the squares of the products of the positions of the fundamental bands is only 3.431.

In general there is no way out of this difficulty short of a complete analysis of the overtone bands which will thus yield the normal frequencies. If one disregards the distinction between the normal frequencies and the positions of the fundamental bands, predictions of frequencies will be made which will differ from the true frequencies by the order of the anharmonic corrections, that is by from 1 to 5 percent. The force constants, which depend upon the squares of frequencies, may be incorrect by as much as 10 percent or more.

In certain cases, of which the present instance is one, it seems possible to estimate the values of the normal frequencies with some degree of precision. We begin by writing the relation between the normal frequency ω_i and the position of the fundamental band ν_i in the following manner $\omega_i=\nu_i(1+\alpha_i)$. Clearly $\nu_i\alpha_i$ is the correction due to the anharmonicity. We shall

assume that the corresponding quantities ω_i^* and ν_i^* for the isotopic molecule obey the equation,

$$\omega_i^*=\nu_i^*(1+\alpha_i\omega_i^*/\omega_i)\cong\nu_i^*(1+\alpha_i\nu_i^*/\nu_i).$$

This assumption states that the anharmonic correction varies nearly as the square of the normal frequency. A study, both of the theoretical expressions for the anharmonic corrections and of the existing cases where the ω_i and ν_i are known, shows that the approximation is a very good one, particularly for such molecules as NH_3 and ND_3 where all the frequencies transform with about the same factor.* We possess one relation between the normal frequencies, namely the product rule,

$$(\omega_2\omega_4)^2_{\text{NH}_3}/(\omega_2\omega_4)^2_{\text{ND}_3}=(m^2k)_{\text{ND}_3}/(m^2k)_{\text{NH}_3}.$$

Substitution of our expressions for ω_2 and ω_4 , yields an equation between α_2 and α_4 .

A second equation may be obtained from the observed spacing of the fine structure lines of the perpendicular bands. It will be shown in detail later that the fine structure spacing $\Delta\nu_i$ determines the value of a quantity δ_i which is proportional to the squares of the potential constants. By elimination we may thus obtain a relation between the δ_i , the normal frequencies and the masses. In the present instance this is

$$\begin{aligned} & [mk(\omega_2^2+\omega_4^2)]_{\text{NH}_3} \\ & - [mk(\omega_2^2+\omega_4^2)]_{\text{ND}_3} = (k_{\text{NH}_3}-k_{\text{ND}_3}) \\ & \quad \times [(m\delta_2^{\frac{1}{2}}\omega_2^2+m\delta_4^{\frac{1}{2}}\omega_4^2)/(\delta_2^{\frac{1}{2}}+\delta_4^{\frac{1}{2}})]_{\text{ND}_3}. \end{aligned}$$

The observed spacings $\Delta\nu_i$ of ND_3 give $\delta_2=0.533=1/\delta_4$. We thus obtain a second relation connecting α_2 and α_4 which when combined with the first equation results in the numerical values $\alpha_2=0.0610$ and $\alpha_4=0.0356$. The normal frequencies ω_2 and ω_4 of NH_3 are then 3622 and 1685.4, while those of ND_3 are 2670 and 1221.6 cm^{-1} . The potential constants α , β and γ are now obtained from a simple substitution and are found to be 10.494, 4.098 and 4.168×10^5 dynes/cm, respectively.†

* It might have been slightly more logical to let $\nu_i=\omega_i(1-\alpha_i)$ and $\nu_i^*=\omega_i^*(1-\omega_i^*\alpha_i/\omega_i)$. The difference between the results obtained with these two sets of expressions lies well within the uncertainty of the method, however.

† The sign of γ is not determined directly but it can be fixed from the fact that, as Howard²⁹ has shown, the potential function for ammonia must be nearly of the valence type.

The values of α_2 and α_4 appear to be very reasonable. The type of forces which are present in the ammonia molecule is not very different from that in the water vapor molecule. In the latter case, since we know both the ω_i and ν_i , we may calculate the α_i directly. The two high frequencies ω_1 and ω_3 which lie at 3825.32 and 3935.59 cm^{-1} , respectively, have the same value of α , namely 0.0480, while ω_2 at 1653.91 has $\alpha_2=0.0369$. It will be seen that these do not differ greatly from the corresponding figures for the α_i of NH_3 which have just been calculated. We may remark in passing that if one sets $\alpha_2=\alpha_4=\alpha$, the product rule alone will serve to fix the normal frequencies. This procedure while less accurate than that which we have used, gives, in the case of water vapor, results for the normal frequencies with a maximum error of only 0.8 percent.

The situation with respect to the parallel frequencies is much more uncertain since the existence of the double minimum potential greatly affects the vibration ω_3 and makes it far more anharmonic than would normally be the case. This is immediately shown by the fact that in the product rule,

$$(\omega_1\omega_3)^2_{\text{NH}_3}/(\omega_1\omega_3)^2_{\text{ND}_3} = (m\mu)_{\text{ND}_3}/(m\mu)_{\text{NH}_3}.$$

The right-hand side of the expression is 3.392 while the left-hand side, if we use the positions of the fundamentals, is only 3.078. We offer the following suggestions for estimating approximately the normal frequencies. The frequencies ω_1 and ω_2 are of about the same magnitude and the motions corresponding to both involve essentially displacements along the N-H bonds but no change in the bond angles. We therefore assume that the difference between ω_1 and ν_1 will be proportionately equal to the difference between ω_2 and ν_2 . In this way we set $\omega_1=3539 \text{ cm}^{-1}$ for NH_3 and 2524 for ND_3 . The frequency ν_3 is very anharmonic because of the double minimum potential. The Manning double minimum potential, which will be described later furnishes a means of calculating the frequency for infinitesimal amplitude. A substitution yields $\omega_3=1051$ and 806.6 cm^{-1} for NH_3 and ND_3 , respectively. The four frequencies which we have estimated when substituted into the left-hand side of the product rule give the number 3.338.

Finally we adjust the frequencies ω_3 to 1055 and 803.4, respectively, in order to satisfy the product rule exactly.

With these normal frequencies the potential constants become $a=3.171$, $b=6.811$ and $c=3.078 \times 10^5$ dynes/cm. Again the sign of c is not determined directly but it must be such that the forces are approximately of the valence type. It is apparent, in view of the anharmonic character of the motion and of the uncertainties inherent in our estimates of the normal frequencies, that these latter potential constants are not determined with as great precision as the constants governing the perpendicular vibrations. However, we believe that we have furnished the means of calculating the normal modes of vibration of the ammonia molecule with considerable accuracy. The normal frequencies of the molecules NH_2D and ND_2H may be computed using the formulas derived by Salant and Rosenthal.³⁰ The positions of the fundamental bands might then be obtained by estimating appropriate values for the α_i . (See the discussion of the deuterio-methanes.)

A number of harmonic and overtone bands have been observed but unfortunately not a sufficient number to allow a complete analysis of the spectrum. The few anharmonic constants which can be deduced are of the expected order of magnitude. One interesting group of overtones are those which appear to form the series $n\nu_1$. These extend into the visible spectrum and may be approximately fit by the formula $\nu=3397n-61n^2$. The identification of this series as $n\nu_1$ is somewhat misleading, however, since there are in reality many superimposed bands due to the fact that $\nu_1 \cong \nu_2 \cong 2\nu_4$. Thus even the first member of the series $n=1$ contains four bands, of which two are $\nu_1=3336 \parallel$, $\nu_2=3414 \perp$. The first overtone of ν_4 also falls in this region and consists of two components, a parallel and a perpendicular band. The \parallel band has been observed both in the Raman spectrum and in the infra-red and falls at 3219 cm^{-1} . It may interact with ν_1 by means of a cubic term in the anharmonic potential. The resonance is of the same type as that in CO_2 but far less complete. The \perp component of $2\nu_4$ cannot resonate with ν_2 except through very high order anharmonic terms.

The fine structure of the \parallel bands is of the type to be expected for a symmetrical rotator (we neglect for the moment the doubling of the lines which arises from the double minimum potential) and consists of a strong zero branch together with a nearly uniformly spaced set of lines which constitute the positive and negative branches. The average spacing of the lines, $h/4\pi^2A$, is equal to the spacing of the far infra-red lines and fixes the moment of inertia perpendicular to the figure axis. The fine structure of the \perp bands is similar to that described in Part I but exhibits a phenomenon which was not known at the time Part I was written. Qualitatively it consists of a series of uniformly spaced zero branches, each of which is the center of a group of fine structure lines. In many cases these latter will combine to give the appearance of an irregular and chaotic band; in others they may blend together to form a more or less continuous background out of which the zero branches rise. The spacing of the zero branches, in contrast with that predicted by the older theory, is not determined by the moments of inertia alone but is equal to

$$[(1-\zeta_i)/C-1/A]h/4\pi^2.$$

The analysis which leads to this formula was first proposed by Teller³¹ and later somewhat amplified by Johnston and Dennison.³² The central idea underlying the theory is as follows. The normal modes of vibration corresponding to the \perp bands, are doubly degenerate and may be described as two identical harmonic oscillations at right angles to each other. Such a pair of oscillators may be combined to give a circular motion and hence may produce an angular momentum along the symmetry axis. An exact analysis shows that the eigenvalues of the angular momentum associated with a \perp fundamental ν_i are $\pm\zeta_i\hbar$. The quantity ζ_i is not necessarily an integer and proves to be a function of the normal mode of vibration. The component of the total angular momentum of the system along the symmetry axis must, however, be $\pm K\hbar$ where K is an integer, equal to or less than J . Roughly one may say that the rotation of the molecule supplies the additional, and non-integral, angular momentum which when added to $\pm\zeta_i\hbar$ produces $\pm K\hbar$. The resulting formula

for the rotational energy is

$$W_R = (J^2 + J)\hbar^2/2A + K^2\hbar^2(\frac{1}{2}C - \frac{1}{2}A) \mp \zeta_i K\hbar^2/C + \zeta_i^2\hbar^2/2C$$

and may be shown to predict a fine structure for a \perp band consisting of zero branches with the spacing given earlier.

An important point which was made by Teller is that the sum of the ζ_i for the fundamentals belonging to any symmetry class is independent of the force constants and a function only of such quantities as the moments of inertia. Thus it was shown³² that for the YX_3 molecule, $\zeta_2 + \zeta_4 = C/2A - 1$. The individual ζ_i may be calculated as a function of the force constants of the molecule and for the present case,

$$\zeta_i = (C/2A - \delta_i)/(1 + \delta_i),$$

where $\delta_i = 2mA\gamma^2/\mu C(m\lambda_i - \beta)^2$.

The fine structure of the perpendicular bands of ND_3 have been measured by Migeotte and Barker²⁸ who found the values $\Delta\nu_2 = 5.2$ and $\Delta\nu_4 = 1.7$ cm^{-1} . The sum $\Delta\nu_2 + \Delta\nu_4$ may be shown to be independent of the potential constants and equal to $(3/C - 5/2A)h/4\pi^2$. Substituting the figures for the C and A of ND_3 we obtain 6.8 which is in good agreement with the observed number 6.9 cm^{-1} . (Actually $\Delta\nu_2$ and $\Delta\nu_4$ as well as $\Delta\nu_2 + \Delta\nu_4$ are negative rather than positive numbers. This merely means that the molecule nearly resembles a disk in its inertial properties.) We shall adjust $\Delta\nu_2$ to 5.15 and $\Delta\nu_4$ to 1.65, a change which is well within experimental error, in order to preserve the self-consistency of the solution. The following constants for ND_3 may now be found, $\zeta_2 = 0.185$, $\zeta_4 = -0.368$ and $\delta_2 = 1/\delta_4 = 0.533$. This last value was employed in the determination of the molecular potential constants.

The low frequency perpendicular band ν_4 of NH_3 has recently been observed and analyzed by Barker³³ who concludes that $\Delta\nu_4$ for this molecule is about equal to 3.9 cm^{-1} . From the potential constants α , β and γ together with the masses, $\Delta\nu_4$ may be calculated. We find the value 3.7 cm^{-1} and regard this check as evidence for the correctness of our choice of constants. The sum $\Delta\nu_2 + \Delta\nu_4$ can be computed in the same manner as was done for ND_3 and we obtain 12.0 cm^{-1} . From this it follows that $\Delta\nu_2$ should be

about 8.1 cm^{-1} . This band was also studied by Barker³³ and he reports a spacing of around 16 cm^{-1} . However, the region is so badly overlaid by the band ν_1 that in our opinion a $\Delta\nu_2$ of 8 would fit the observed data quite as well as 16.

The potential function of the pyramidal YX_3 molecule possesses two equilibrium configurations and this leads to a doubling of the vibrational energy levels. In most molecules of this type, as for example PH_3 , AsH_3 , PCl_3 etc., the activation energy, that is, the energy necessary to pass over the barrier separating the minima is so high that the doubling of the levels is unobservably small. In the case of ammonia, however, the height of the barrier is only about 2070 cm^{-1} and the effect assumes importance. An exact treatment of the problem, even neglecting rotation interactions, will involve all of the normal coordinates and appears to be too complex for our present methods. An approximation which uses only the one coordinate q_3 may be justified on the following grounds. The potential is actually a function of the four normal coordinates and possesses two equilibrium positions between which there exists a low pass. In general this pass can be reached by following a path which corresponds to a certain combination of the coordinates. Now in the present case, the coordinates of the perpendicular vibrations, q_2 and q_4 , clearly do not lead towards the pass since they are essentially off axis motions. The coordinate q_1 , which defines a motion in which the hydrogen nuclei move almost exactly towards or away from the nitrogen nucleus, does not materially help the system to go from one minimum to the other. This conclusion is verified by the observation that the doublet separation for the excited state ν_1 is only slightly greater than that of the normal state. The coordinate q_3 , on the other hand, where the hydrogens move perpendicular to the N-H bonds, would seem to lead nearly directly towards the pass, and through this motion, the molecule may transform from the one equilibrium configuration to the other. Experimentally the doublet separation of the excited state ν_3 is about 50 times larger than that of the ground state. We shall accordingly assume that the motion q_3 may be dissociated from the other normal coordinates. In effect this means that we divide the potential function into two parts, one

of which depends upon q_1 , q_2 and q_4 and the other upon q_3 . This latter function will be represented by a symmetrical curve having two minima.

On this basis a solution of the problem has been given by Dennison and Uhlenbeck³⁴ using the W-K-B method of approximation. They found that for levels lying well under the barrier the doublet separation Δ for a pair of levels with the average energy E is given by $\Delta/h\nu = 1/\pi A^2$ where $h\nu$ is the energy difference between pairs of doublets and

$$A = \exp \left[(1/h) \int_0^{x_1} [2\mu(V-E)]^{1/2} dx \right].$$

They found that the function depends strongly upon the distance between the minima and upon the barrier height but was quite insensitive to other details of the potential curve. Their estimate of the height of the NH_3 pyramid was $0.38 \times 10^{-8} \text{ cm}$. The wave functions of the levels are successively even and odd with respect to the two minima and it is to be noted that in any stationary state of the system the probability of finding the molecule in any one of the two minima is just 50 percent.

A very interesting exact solution of a one-dimensional system having a double minimum has been found by Manning³⁵ and applied to the NH_3 and ND_3 molecules. Manning used the potential $V = -A \text{ sech}^2(r/2\rho) + B \text{ sech}^4(r/2\rho)$. This function is symmetrical and has minima at $\pm r_0$ where, $\text{sech}^2(r_0/2\rho) = A/2B$. The height of the barrier, at $r=0$, is $(2B-A)^2/4B$ above the minimum. While this potential function has the correct general form, there is no reason to suppose that it represents the actual potential of ammonia. Since, however, the splitting of the

TABLE VII. Levels for ν_3 and its overtones.

	NH_3		ND_3	
	Calc.	Obs.	Calc.	Obs.
0_s	0	0	0	0
0_a	0.83	0.66	<0.2	—
1_s	935	932.4	746.0	745.6
1_a	961	968.1	748.5	749.0
2_s	1610	1597.5	1379	1359
2_a	1870	1910	1434	1429
3_s	2360	2380	1852	1830
3_a	2840		2140	2113
4_s				2495
4_a				2868

levels has been shown to be quite insensitive to the details of the potential we might suppose that it will give a good description of the energy levels. That this is indeed the case may be seen in Table VII where we compare the calculated and observed levels for ν_3 and its overtones. The evaluation of the eigenvalues of Manning's potential is very laborious and we give here the energy levels as he published them. These employ the following values for the constants, $A = 109,619 \text{ cm}^{-1}$, $B = 66,551 \text{ cm}^{-1}$, $8\pi^2 c \mu \rho^2 / h = 2.885 \times 10^{-2} \text{ cm}$. It is probable that a somewhat better agreement might be achieved through a further adjustment of the constants. The quantity μ represents the reduced mass for the vibration in question. Manning considered that the motion was principally of the valence type, the hydrogen atoms moving perpendicularly to the N-H bonds, and he took $\mu = 4.60 \times 10^{-24} \text{ g}$. From this assumption the equilibrium height of the ammonia pyramid may be deduced to $0.37 \times 10^{-8} \text{ cm}$. Manning points out that the reduced mass will vary with the amplitude of the motion and at the center of the barrier where $r=0$, $\mu = 4.07 \times 10^{-24} \text{ g}$. If this were the mass the calculated height of the pyramid would turn out to be $0.40 \times 10^{-8} \text{ cm}$. It seems probable that these two values represent upper and lower limits. It will be remembered that the height as found from the line spacing of NH_3 and ND_3 bands was 0.377×10^{-8} . Unfortunately even this value is not too accurately determined since it is a sensitive function of the spacings.

The energy levels of ND_3 may be calculated as soon as a reduced mass for the motion is chosen. The constants A and B are unchanged and Manning takes $8\pi^2 c \mu \rho^2 / h = 4.899 \times 10^{-2}$. The agreement with the experimental levels is remarkably good and might be still further improved by slightly altering the values of the constants. In our opinion, however, such refinements would not be particularly valuable since the real difficulty is that the system cannot be so simply treated by means of a one-dimensional model. The potential is actually a function of four coordinates and the wave equation is not rigorously separable.

The experimental observations which are listed in Table VII have been taken from several sources; the lower levels of NH_3 are from the

work of Sheng, Barker and Dennison³⁶ while the values of 2_a and 3_s for NH_3 come from the studies by Benedict³⁷ of the ultraviolet absorption bands. Benedict also determined many of the other levels of NH_3 and ND_3 and his results are in substantial agreement with those quoted here.

A recent investigation³⁶ of the fine structure of the fundamental ν_3 of NH_3 has shown that the rotation lines are not single, as predicted by the simple theory, but consist of closely spaced multiplets. The data may be accurately reproduced by assuming that the usual rotational energy $W_R = (J^2 + J)\hbar^2/2A + K^2\hbar^2(\frac{1}{2}C - \frac{1}{2}A)$ is augmented by a δW which is a linear function of $(J^2 + J)$ and K^2 . This means that the rotation-vibration interaction may be accounted for by replacing the true moments by effective moments of inertia. Since the coefficient of K^2 is not the same in the initial and final states, a line, say the $J \rightarrow J-1$ line, will consist of $J-1$ components corresponding to the possible values for K . The observations yield the following results for the energy correction δW for the states 1_s , 1_a and 2_s :

$$\begin{aligned}(\delta W)_{1_s}/hc &= 0.113(J^2 + J) - 0.267K^2, \\(\delta W)_{1_a}/hc &= -0.062(J^2 + J) - 0.030K^2, \\(\delta W)_{2_s}/hc &= 0.24(J^2 + J) - 0.54K^2.\end{aligned}$$

Qualitatively, these values may be readily understood. Thus when $J=K$ the molecule is rotating about its symmetry axis and the centrifugal force will tend to lower the barrier which separates the two equal minima. This means that the doublet spacing of the two states 1_a and 1_s should increase, i.e., $[(\delta W)_{1_a} - (\delta W)_{1_s}]_{J=K}$ must be positive. On the other hand, when $K=0$, the molecule rotates about a line perpendicular to the symmetry axis, and the potential barrier will be raised by the centrifugal force. Thus $[(\delta W)_{1_a} - (\delta W)_{1_s}]_{K=0}$ must be negative. It will be seen that these predictions are indeed verified. Sheng, Barker and Dennison have attempted a semiquantitative analysis of the problem which is based upon the centrifugal force distortion of the Manning potential. Their calculated values for δW are in fair agreement with the experimental values. A complete, quantitative discussion of the phenomenon appears to be quite difficult since it apparently will involve certain details of the interaction between the various modes of oscillation which are at present not known.

THE METHYL HALIDES

The methyl halide molecule may be represented by a model in which the methyl group has the form of a regular pyramid while the halogen nucleus is situated along the axis of the pyramid beyond the carbon nucleus. These molecules belong to the class of symmetrical rotators and, since they possess permanent electric moments, they should have pure rotation spectra consisting of lines with the spacing $h/4\pi^2A$. These lines will lie in the far infra-red (say from 200 or 300μ towards longer wave-lengths) and have not as yet been observed. There exist six normal modes of vibration (see reference 1, p. 302); three belonging to one symmetry class and three to another. These symmetry classes are very similar to those of the molecule YX_3 and will be called \parallel and \perp . In the first of them the nuclei move symmetrically with respect to the molecular axis and the change of the electric moment is along the axis. We designate the \parallel frequencies with odd subscripts, ν_1 , ν_3 and ν_5 . The remaining frequencies ν_2 , ν_4 and ν_6 are such that the displacements of the halogen nucleus, the carbon nucleus and the center of gravity of the hydrogen nuclei are perpendicular to the molecular axis.

The vibration spectra of the methyl halides as observed by Bennett and Meyer³⁸ and by Barker and Plyler³⁹ exhibit three \perp bands which may be readily identified with ν_2 , ν_4 and ν_6 . There are, however, four \parallel type bands. Of these one may conclude that the two lowest ones are surely ν_3 and ν_5 since they are in about the positions one would expect and show a reasonable behavior in passing along the series of the methyl halides. The two remaining \parallel bands lie close to 2900 cm^{-1} , are of about equal intensity and are separated from each other by about 100 cm^{-1} . Adel and Barker⁴⁰ put forward the reasonable hypothesis that the frequency ν_1 resonates strongly with the parallel component of $2\nu_4$ which falls at about this place. There appears to be no very certain way of obtaining the true value of ν_1 short of an analysis of the complete spectrum including many overtone bands. From a consideration of the positions of the two resonating levels with respect to twice the frequency ν_4 , Linnett⁴¹ estimates the probable value of ν_1 . We shall adopt his figures and have included them in Table VIII which lists the

TABLE VIII. *Fundamental frequencies of methyl halides.*

	CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I
ν_1	2862	2920	2930	2940
ν_3	1460	1356	1305	1252
ν_5	1048	732	610	532
ν_2	2987	3045	3061	3074
ν_4	1476	1460	1450	1445
ν_6	1200	1020	957	885

fundamental frequencies of the methyl halides.

The fine structure of the parallel bands is normal in all respects and the spacing of the lines yields A , the moment of inertia about a line perpendicular to the molecular axis. Unfortunately this spacing is so small that, except for methyl fluoride, it has not been accurately measured. The observations of Bennett and Meyer on the band ν_3 of methyl fluoride when corrected to give the B_0 of the normal state lead to the value $A = 32.94 \times 10^{-40}$ for that molecule.

A knowledge of A is of course not sufficient to determine the molecular dimensions without additional assumptions regarding the methyl group. It will appear when we calculate the moment of inertia C that the CH₃ group in the methyl halides probably differs only slightly from its form in the methane molecule. We shall assume that the C-H distance is unchanged throughout the methyl halide series and is equal to its value in methane, namely, $1.093 \times 10^{-8}\text{ cm}$. The halide-carbon-hydrogen angle would be equal to about 109.5° if the structure of the CH₃ group were the same as in methane while if the CH₃ were coplanar, as might be expected for the ion, the angle would be 90° . Linnett estimates that this angle is probably in the neighborhood of 107.5° and we shall also choose this value for all the methyl halides. The F-C distance may now be calculated to be $1.396A$. The electron diffraction measurements⁴² are in good agreement, yielding the value $1.42 \pm 0.02A$.

The spectroscopic measurements of the moment of inertia A of the remaining methyl halides are not very accurate. Barker and Plyler obtain A for CH₃Cl to be about 50×10^{-40} while the doublet separation of the positive and negative branches of the parallel bands of CH₃Br and CH₃I leads to the estimates 89 and 99×10^{-40} , respectively. It would appear that a more reliable procedure is to make use of the electron diffrac-

tion data on the carbon-halogen distance as has been done by Sutherland⁴³ and by Linnett.⁴¹ In Table IX we present the most probable values of the moments of inertia as they are now known.

The fine structure of the perpendicular bands has been mapped by Bennett and Meyer and found to consist of a uniformly spaced series of lines which may be identified with the zero branch lines described in Part I. Every third line is enhanced by the factor 2 due to the spin of the hydrogen nuclei. The positive and negative branches associated with the zero branches combine to form a general background of absorption. The spacing of the zero branch lines varies from one perpendicular band to the next; a phenomenon which is caused by the interaction between the rotation and the internal angular momentum associated with the vibration. Thus in methyl fluoride, $\Delta\nu_2 = 7.5$, $\Delta\nu_4 = 11.5$ and $\Delta\nu_6 = 5.65$ cm^{-1} . Just as in the case of the ammonia molecule, the spacing of the zero branch lines is $[(1 - \zeta_i)/C - 1/A]h/4\pi^2$ where $\zeta_i h$ is the internal angular momentum. Johnston and Dennison³² have shown that the sum of the ζ_i for all three perpendicular bands is equal to $C/2A$ and thus the sum of the spacings $\Sigma\Delta\nu_i$ is $(3/C - 7/2A)h/4\pi^2$. From the observed $\Sigma\Delta\nu_i$, which for the series of molecules CH_3F to CH_3I is 24.65, 27.15, 28.32 and 28.5 cm^{-1} , respectively, together with the values of A , we may calculate the moments of inertia C . These are given in the last column of Table IX. It is seen that they are nearly equal to the moment of inertia of methane which will be derived in the next section of this article. The fact that they are a little larger would tend to verify the assumption that the $X-C-H$ angle is indeed somewhat less than the tetrahedral angle. In fact, the calculated value of C based upon a $C-H$ distance of 1.093 Å and an $X-C-H$ angle of 107.5° is 5.46×10^{-40} . Actually, however, we do not believe that the experimental data are

known with sufficient accuracy to be able adequately to substantiate this conclusion.

The analytical problem of finding the normal vibrations of the ZYX_3 molecule has been solved by Rosenthal and Voge.⁴⁴ The general potential function contains twelve constants and the six frequencies are given in terms of these together with the masses and relative dimensions of the molecule. It is clearly impossible in the case of the methyl halides to evaluate the twelve constants of the general potential function from the six fundamental frequencies and attempts have been made by Sutherland and Dennison,⁴⁵ by Slawsky and Dennison⁴⁶ and by Linnett⁴¹ to introduce a physically plausible potential function which will contain a fewer number of constants. Before describing these we remark that here, as in the preceding molecules which have been studied, we have the ever present difficulty that the data which are known are the positions of the fundamentals rather than the true normal frequencies. This means that any predictions of frequencies which will be made, may well contain errors of the magnitude of the anharmonic contributions and that the values of the potential constants will be correspondingly falsified. We shall make no attempt to estimate the normal frequencies themselves. Whenever the spectra of the isotopic molecules containing deuterium shall have been measured, it will be possible to make a solution which follows that made in the case of the ammonia molecule.

The potential function used by Slawsky and Dennison and by Linnett is based upon the following reasoning. (The Sutherland and Dennison discussion, although quite satisfactory, treats only the \parallel frequencies.) Various investigations^{29, 47} have shown that molecules containing hydrogen atoms and one other atom such as H_2O , NH_3 and CH_4 possess potential functions which are nearly of the valence type, that is, the potential depends principally upon the squares of the displacements along the bonds and upon the squares of the changes in the bond angles. On the other hand, molecules containing several heavy atoms, as for example CCl_4 , definitely cannot be represented by means of a valence potential. It is therefore reasonable to assume that the potential of the methyl halide molecules consists of a valence potential which applies to the methyl

TABLE IX. Moments of inertia of methyl halides.

	$(C-X)_{\text{DIST}}$	A	C
CH_4	1.093	5.33	5.33
CH_3F	1.40	32.94	5.49
CH_3Cl	1.71	58.3	5.50
CH_3Br	1.90	84.3	5.48
CH_3I	2.2	118	5.57

group and of a nonvalence potential which describes the forces binding the halogen to the methyl group. Analytically this may be expressed in the following manner through the use of five arbitrary constants. Let δr_i , ($i = 1, 2, 3$), be the change in distance between a hydrogen nucleus and the carbon nucleus and let δx_0 be the change in distance between the carbon and the halogen nucleus. $\delta\alpha_i$ is the change in one of the three H—C—H bond angles and $\delta\beta_i$ is the change in an H—C—halogen angle. It is convenient dimensionally to introduce the normal C—H distance, namely R , although this has no influence upon the resulting frequencies.

$$2V = k_1 \Sigma (\delta r_i)^2 + k_2 R^2 \Sigma (\delta\alpha_i)^2 + k_3 R^2 \Sigma (\delta\beta_i)^2 + c (\delta x_0)^2 + 2k_4 R (\delta x_0) \Sigma (\delta\beta_i).$$

The coordinates δr_i , δx_0 , $\delta\alpha_i$ and $\delta\beta_i$ are redundant and are not appropriate for an analytical treatment of the normal vibrations. However, the transformations which connect them with the nine coordinates employed by Voge and Rosenthal may be made and the explicit formulas for calculating the frequencies in terms of the five potential constants k_1 , k_2 , k_3 , k_4 and c are given by Slawsky and Dennison.⁴⁶ Although both Slawsky and Dennison as well as Linnett use the same form for the potential they proceed along different lines in the evaluation of the constants. Since both methods contain certain virtues and also certain disadvantages we shall describe the results of each separately.

Slawsky and Dennison start with the assumption that the potential constants which relate to the CH₃ group, namely k_1 and k_2 , will remain approximately the same throughout the series and that they will have the same value that they have in CH₄. The four frequencies of methane may be represented fairly satisfactorily by a valence type of potential with $k_1 = 4.878 \times 10^5$ and $k_2 = 0.443 \times 10^5$ dynes per cm. The average deviation between the calculated and the observed frequencies is only 1.5 percent. Consider first the perpendicular frequencies of the methyl halides. These are functions of k_1 , k_2 and k_3 only. If k_1 and k_2 are assumed to have the values which they possess in methane, there remains but one constant and this was adjusted by substituting the observed value of ν_6 into the equation. In this way k_3 was found to be 0.810, 0.596, 0.536 and

0.463×10^5 for the series CH₃F to CH₃I. The remaining frequencies ν_2 and ν_4 were then calculated and a surprisingly good agreement with the experimental figures resulted. The maximum deviation was 1.7 percent while the average was only 0.5 percent. The motion corresponding to the perpendicular frequencies is completely specified by k_1 , k_2 and k_3 and consequently the internal angular momenta, the ζ_i and the spacing of the zero branch lines $\Delta\nu_i$ for each of the perpendicular bands may be calculated. The resulting agreement with the experimental values is again very good, particularly when one remembers that the ζ_i are proportional to squares of the potential constants. As a typical example of the figures, the $\Delta\nu_2$, $\Delta\nu_4$ and $\Delta\nu_6$ calculated for CH₃F were 6.9, 12.0 and 5.5 cm⁻¹ whereas the corresponding observed values are 7.5, 11.5 and 5.6 cm⁻¹.

The treatment of the parallel frequencies is less satisfactory. These are functions of all five constants and the process employed was first to substitute the k_1 , k_2 and k_3 already found. The remaining constants k_4 and c were then determined with the aid of the observed frequencies ν_3 and ν_5 . The final frequency ν_1 could then be computed. One difficulty which appeared upon applying the method was that in the case of CH₃Cl and CH₃F the solutions for k_4 and c were complex. The nearest real numbers were taken and the final agreement between the observed and calculated frequencies was quite good with a maximum deviation of 2.8 percent and a much smaller average deviation.

The advantage of the procedure just outlined consists in its simplicity. The potential function, with the two constants evaluated from methane, contains but three arbitrary parameters for each methyl halide and with these the six frequencies and the $\Delta\nu_i$ may be calculated. The agreements are good. The disadvantages lie in the fact that the assumptions are not completely fulfilled. The fact that the methane frequencies cannot be expressed exactly with a valence type potential makes it almost certain that our potential, which is of the valence form as far as the CH₃ group is concerned, cannot be rigorously correct. This criticism of course applies equally to Linnett's treatment since he uses the same potential form. The second difficulty lies with the assumption of the invariance of the constants k_1 and k_2 through-

TABLE X. Constants for methyl halide molecules.

	k_1	k_2	k_3	k_4	c
CH ₃ F	4.71	0.433	0.792	-0.594	5.64
CH ₃ Cl	4.90	0.438	0.587	-0.325	3.35
CH ₃ Br	4.95	0.432	0.529	-0.325	2.83
CH ₃ I	5.00	0.432	0.460	-0.293	2.32

out the methyl halides. A study of the calculated frequency ν_2 shows that in going from CH₃F to CH₃I this decreases by 3 cm⁻¹. This is a mass effect due to the changing halogen atom and depends essentially only upon the assumption of the invariance of k_1 . Actually the observed ν_2 increases by 87 cm⁻¹. This can be understood only if k_1 increases by about 6 percent in going from CH₃F to CH₃I. Lastly, a comparison of the value of the constant c with the values obtained by Sutherland and Dennison and by Linnett indicates strongly that the above method of finding both c and k_4 is probably not an accurate one. The unsatisfactoriness of this determination of c and k_4 is emphasized by the fact that the original solution led to complex values.

The method which Linnett employs consists in evaluating the five constants k_1 , k_2 , k_3 , k_4 and c for each of the methyl halides separately by using the five best known frequencies, namely ν_2 , ν_4 , ν_6 , ν_3 and ν_5 . It is then possible to calculate the remaining frequency ν_1 and he obtains in every case a very good check with the experimental value. The advantage of this procedure is that the potential constants so obtained are undoubtedly more accurate than those found by Slawsky and Dennison and should constitute a better description of the molecule. We list these constants in units of 10⁶ dynes per cm in Table X.

A study of the figures shows that the H-C-H constant k_2 is practically invariant throughout the series but that k_1 increases by about 6 percent as expected. From this increase Linnett estimates, by using Badger's rule, that the C-H distance may decrease by about 0.01A. The values of k_1 , k_2 and k_3 do not differ greatly from those employed by Slawsky and Dennison and it is thus reasonable to suppose that a recalculation of the $\Delta\nu_i$ would not essentially alter the numbers previously obtained.

The only unsatisfactory point in this treatment is that there exist so few independent checks

which might prove or disprove the solution. The very good agreement between the calculated and observed ν_1 is to a certain extent illusory since under a potential of the valence type where, moreover, $k_1 \gg k_2$, the frequency ν_1 is determined almost directly by the value of ν_2 . In spite of this remark we feel that the simplified potential function with the values of the five constants given above, must closely approximate to the actual potential function of the methyl halide molecules. A test of this belief may be made whenever the experimental spectra of the deuteromethyl halides are obtained.

METHANE

The methane molecule, the last of the series of molecules to be discussed in this article, possesses a very high degree of symmetry. The four hydrogen nuclei occupy the corners of a regular tetrahedron at whose center lies the carbon nucleus. The symmetry of this arrangement leads to many simplifications in the spectrum as well as to a number of interesting features which are characteristic of the degeneracies of the levels. The system has nine degrees of internal freedom but there are only four normal frequencies. These may be described in the following manner. The motion corresponding to ν_1 is such that the hydrogen nuclei oscillate in phase along the radii of the tetrahedron, that is, directly towards or away from the carbon nucleus which itself remains stationary. ν_1 is a single frequency and the excited levels are nondegenerate. Clearly the electric moment remains zero throughout the motion and consequently the frequency will be inactive in the infra-red. It does appear very strongly in the Raman spectrum, however, and has been observed⁴⁸ to fall at 2914.2 cm⁻¹.

The frequency ν_2 belongs to a different symmetry class. The hydrogen nuclei move upon the surface of the sphere which passes through the four corners of the regular tetrahedron. The normal vibration may be visualized as follows. Two of the hydrogen nuclei, which we might designate as 1 and 2, approach each other while at the same time the nuclei 3 and 4 also approach each other by an equal amount. All the displacements are on the surface of the sphere. Clearly in depicting the motion one might have chosen other

pairs of nuclei, that is, 1 and 3, as well as 2 and 4, to approach and recede from each other. Thus each hydrogen nucleus moves harmonically along a two-dimensional surface. This means that ν_2 will be a double root of the normal frequency determinant. The excited levels will be degenerate and it may easily be shown that, if n_2 is the quantum number, the degree of degeneracy is equal to (n_2+1) . The carbon nucleus, as in the vibration ν_1 , does not take part in the motion and the change of the electric moment is zero. Thus ν_2 will not give rise to absorption in the infra-red spectrum. It is Raman active but since the intensity depends only upon the off diagonal elements of the polarization tensor we might expect it to be faint. It has, in fact, never been observed experimentally, but its first overtone, which resonates weakly with the intense Raman line ν_1 , has been measured⁴⁸ at 3071.5 cm^{-1} . From the arguments which will be given concerning the amount of anharmonicity involved in this vibration it will be estimated that ν_2 probably lies near 1500 cm^{-1} .

The remaining frequencies, ν_3 and ν_4 , both belong to the same symmetry class and are active in the infra-red and in the Raman spectra. They constitute the two strongest regions of infra-red absorption and lie at 3018.4 and 1306.2 cm^{-1} , respectively. Since there is more than one frequency belonging to the same symmetry class, the displacements of the particles will depend upon the potential constants. The motions corresponding to ν_3 and ν_4 may, however, be described as a linear combination of two limiting types of motion. These are the motions which are characteristic (1) of a tetrahedron X_4 with no central particle, and (2) of a central particle Y oscillating against a rigid X_4 tetrahedron. Analytically they may be effected by setting the potential constant e , which will be introduced shortly, equal to zero. The first motion is such that two particles, say 1 and 2, are displaced directly towards each other while the other pair, 3 and 4, are displaced directly away from each other. By choosing other pairs, for example 1 and 3 together with 2 and 4, it is seen that the general motion will allow each particle to oscillate harmonically in three dimensions. The second motion is one in which the central Y particle vibrates harmonically within a rigid tetrahedron. This is also a three-dimen-

sional harmonic oscillator. The weights of the excited states of either ν_3 or ν_4 are equal to $\frac{1}{2}(n_i+1)(n_i+2)$. It must be emphasized that neither ν_3 nor ν_4 possesses these limiting types of motions but rather they are expressible as a linear combination of them. The coefficients of the linear combination are simple functions of the potential constants.

The analytical problem of determining the normal modes of vibration of the methane molecule was first solved by Dennison⁴⁹ using a special potential function which later investigations have shown to be not very suitable. A solution which employs the general potential function and hence contains five constants, has been made by Rosenthal.⁵⁰ We shall here sketch the discussion which is presented in reference 32. The nine internal coordinates will be chosen as follows. Let q_1, q_2, \dots, q_6 be the mutual displacements of the X particles along the edges of the tetrahedron. Let q_1 and q_2 , q_3 and q_4 , q_5 and q_6 relate to the opposite edges of the tetrahedron. The remaining coordinates x, y, z are defined as the components of the vector displacement of the Y particle with respect to the center of gravity of the X_4 particles. It is convenient to let the x, y and z axes be the lines which are perpendicular to the opposite edges of the equilibrium tetrahedron X_4 , 1 and 2, 3 and 4, and 5 and 6, respectively.

The vibrational kinetic energy is given by the expression

$$2T = \mu(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + (5m/8) \sum_i \dot{q}_i^2 - 2(m/8) \sum_{i < k} \dot{q}_i \dot{q}_k + 2(m/4)(\dot{q}_1 \dot{q}_2 + \dot{q}_3 \dot{q}_4 + \dot{q}_5 \dot{q}_6),$$

where m and M are the masses of an X and Y particle, respectively, and where $\mu = 4mM/(4m+M)$. The potential energy contains five constants which may be chosen so that

$$2V = a(x^2 + y^2 + z^2) + b \sum_i q_i^2 + 2c \sum_{i < k} q_i q_k + 2(d-c)(q_1 q_2 + q_3 q_4 + q_5 q_6) + 2e[x(q_1 - q_2) + y(q_3 - q_4) + z(q_5 - q_6)].$$

The determinant whose roots fix the normal frequencies is of course of ninth order but the symmetry properties of the system allow it to be factored into two first-order determinates, the second of which is squared, and a second-order

determinant which is cubed. Explicitly,

$$\begin{aligned}\lambda_1 &= (4b + 4d + 16c)/m, \\ \lambda_2 &= (b + d - 2c)/m, \\ \lambda_3 + \lambda_4 &= a/\mu + 2(b - d)/m, \\ \lambda_3\lambda_4 &= 2[a(b - d) - 2e^2]/\mu m.\end{aligned}$$

We shall discuss the problem of the evaluation of the potential constants along the same lines as those used in the case of the ammonia spectrum. MacWood and Urey⁴⁸ have observed the frequency ν_1 in the Raman spectrum of both CH₄ and CD₄ and report the values 2914.2 and 2084.7 cm⁻¹, respectively. Since there is but a single frequency belonging to this symmetry class, the product rule becomes very simple and is $(\omega_1^2)_{\text{CH}_4}/(\omega_1^2)_{\text{CD}_4} = (m)_D/(m)_H$. We shall set $\omega_1 = (1 + \alpha_1)\nu_1$ and assume that for the isotopic molecule $\omega_1^* = (1 + \alpha_1^*\alpha_1/\omega_1)\nu_1^*$. A substitution of the numbers yields the reasonable values $\alpha_1 = 0.0397$ and $\omega_1 = 3029.8$ and 2143.2 cm⁻¹ for CH₄ and CD₄.

The treatment of the frequency ν_2 differs but slightly from that just given. Unfortunately this frequency has not been observed directly, but its first overtone, $2\nu_2$, appears in the Raman spectrum and has been measured by MacWood and Urey. It will be convenient to let $2\omega_2 = (1 + 2\alpha_2)2\nu_2$ to indicate the fact that the anharmonic correction $4\alpha_2\nu_2$ is of the order of four times its value for the fundamental. Substituting the experimental values $2\nu_2 = 3071.5$ and 2108.1 cm⁻¹ for CH₄ and CD₄, we obtain $\alpha_2 = -0.0474$ and $\omega_2 = 1390.2$ and 983.4 cm⁻¹ for the respective molecules. The negative value for α_2 is somewhat surprising but perhaps understandable. The motion ν_2 is such that as the hydrogen nuclei are displaced from their positions of equilibrium they approach the other hydrogen nuclei. This means that the potential probably rises more steeply than a parabola and hence the anharmonic correction to the energy would be positive rather than negative as it usually is. An objection might be made to our procedure for finding ω_2 based upon the following grounds. $2\nu_2$ appears in the Raman spectrum presumably because it is in resonance interaction with ν_1 and if this interaction is large enough appreciably to affect the positions of the levels, our method would lose its validity. We doubt if this is the case for, while the difference $2\nu_2 - \nu_1$ is 157.3 cm⁻¹ for CH₄, it is only

23.4 cm⁻¹ for CD₄. Such a small difference suggests that the resonance interaction is weak, otherwise it would more widely separate the levels. The effect of resonance would be to raise the $2\nu_2$ of CD₄ by a greater amount than the $2\nu_2$ for CH₄ since the levels lie closer together. This would tend to reduce the value of α_2 . Thus if we could subtract the influence of the resonance, we should make α_2 even more negative than the value which we have calculated. There is no certain way to obtain ν_2 from these data. By assuming that the vibrational energy depends upon n_2 as $(n_2 + 1)\omega_2 + X_{22}(n_2 + 1)^2$ we may calculate ν_2 if $2\nu_2$ and ω_2 are known. We find 1499.4 cm⁻¹. This is at best only an estimate, however, since the energy function is undoubtedly more complicated. Our method of finding ω_2 from $2\nu_2$ of CH₄ and CD₄ does not depend upon this assumption and should be reliable. Nevertheless, it would be very desirable to determine ν_2 more directly in order to check the somewhat unusual negative value of α_2 .

The two active fundamental bands ν_3 and ν_4 were first observed by Cooley⁵¹ who succeeded in resolving and measuring their fine structure. A redetermination of ν_4 under somewhat higher dispersion by A. H. Nielsen and H. H. Nielsen⁵² is in substantial agreement as regards the band center but reveals more detail of the fine structure. Cooley's data has been subjected to a careful analysis by Childs⁵³ who concludes that the band centers of ν_3 and ν_4 lie at (vacuum wavelengths) 3018.4 and 1306.2 cm⁻¹, respectively. The fundamental bands ν_3 and ν_4 of CD₄ have been observed by A. H. Nielsen and H. H. Nielsen⁵⁴ who place their centers at 2259.4 and 996.5 cm⁻¹. We let $\omega_i = (1 + \alpha_i)\nu_i$ as before. The four data on the fundamental bands ν_3 and ν_4 when set in the product rule $(\omega_3\omega_4)_{\text{CH}_4^2}/(\omega_3\omega_4)_{\text{CD}_4^2} = (\mu m)_{\text{CD}_4}/(\mu m)_{\text{CH}_4}$, yield one relation between α_3 and α_4 . A second equation connecting α_3 and α_4 may be found from the internal angular momentum just as was done in the case of the ammonia molecule. (The magnitude of the internal angular momentum and its dependence upon the potential constants will be fully discussed later.) The solution of these two equations is $\alpha_3 = 0.0459$ and $\alpha_4 = 0.0393$. The corresponding values of the normal frequencies are then

TABLE XI. *The fundamental frequencies of deuterio-methanes.*

	ν_1	ν_2	ν_3	ν_4
CH ₄	3029.8 2914.2 2914.2	1390.2 1499.4 $2\nu_2=3071.5$	3156.9 3018.4 3018.4	1357.6 1306.2 1306.2
CH ₃ D	3067.0 2948.5 2982.1	1404.7 ⊥ — 1476.7	3156.6 ⊥ 2283.6 3018.0 2210.1 3030.1 2204.6	1352.0 1174.5 ⊥ 1300.8 1144.7 1306.4 1156.0
CH ₂ D ₂	2234.2M 2170.7 2179.6(?)	1241.2 1393.1M — 1332.9(?)	2336.1G 3099.7M 3156.3L 2260.1 2966.0 3017.8 2255 2974.2 3020	1277.2G 1023.9M 1126.3L 1231.6 994.4 1090.7 1235.1 1035.7 1090.2
CHD ₃	2189.2 2128.2 2141.1	1259.7 ⊥ — 1299.2	2336.9 ⊥ 3128.1 2260.3 2992.0 2268.6 3000	1034.2 1019.5 ⊥ 1004.2 987.4 — 988
CD ₄	2143.2 2084.7 2084.7	983.4 1036.4 $2\nu_2=2108.1$	2336.9 2259.3 2259.3	1026.4 996.5 996.5

$\omega_3 = 3156.9$, $\omega_4 = 1357.6$ for CH₄ and $\omega_3 = 2336.9$, $\omega_4 = 1026.4$ for CD₄.

The calculation of the potential constants may now be performed and leads to the following figures:

$$\begin{aligned} a &= 8.5681 \times 10^5 \text{ dynes/cm}, & d &= -0.4278, \\ b &= 1.6468, & e &= -2.0104. \\ c &= 0.3584, \end{aligned}$$

The sign of e is not directly determined but it may be fixed by the fact that the forces are nearly of the valence type. In the vibration ν_3 , the hydrogens move approximately along the bond directions while in ν_4 they move approximately perpendicular to them.

It may be of interest to calculate the normal frequencies of the remaining isotopic molecules. The necessary formulas have been derived by Rosenthal.⁵⁰ The potential constants which are employed in the Rosenthal formulas are linear combinations of our constants. We list their values below.

$$\begin{aligned} A &= 8.5681 \times 10^5 \text{ dynes/cm}, & D &= 1.4216, \\ B &= 0.5186, & E &= 0.3406. \\ C &= 0.3048, \end{aligned}$$

The molecules CH₃D and CD₃H possess the same symmetry as the methyl halides and there are accordingly six independent frequencies. It was shown in reference 1, p. 304, that in going from the YX₄ molecule to the YX₃Z molecule the single frequency ω_1 goes over to ω_1 while the

double frequency ω_2 goes into the double frequency ω_4 . The triple frequency ω_3 , however, splits into two parts, the frequencies ω_2 and ω_3 of the YX₃Z molecule. The remaining triple frequency ω_4 splits into the single frequency ω_5 and the double frequency ω_6 .

The degeneracies of the levels are completely lost in the molecule CH₂D₂ and there are nine independent frequencies. In spite of this the molecule still retains a number of symmetry properties and the original ninth-order determinant may be factored into one linear, two quadratic and one quartic determinant. The corresponding frequencies may be described as follows. The linear term represents a torsional type of motion for which there is no change of the electric moment. It is accordingly inactive in the infra-red and probably is very weak in the Raman spectrum. The remaining frequencies are all infra-red active. One of the quadratic determinants gives rise to frequencies for which the change of the electric moment lies along the axis of least moment of inertia while the electric moment for the other lies along the axis of greatest moment of inertia. The four frequencies of the quartic determinant represent motions whose electric moment changes along the axis of middle moment of inertia.

We have listed the frequencies of the isotopic methane molecules in Table XI in the following way. The first number is the calculated normal frequency ω_1 , while the number immediately

below it is the calculated position of the band, ν_i . The third number, which is italicized, is the observed position of the band ν_i . The sources of the ν_i of CH_4 and CD_4 have already been cited. The ν_i of CH_3D and the three frequencies of CH_2D_2 at 1035.7, 1090.2 and 1235.1 cm^{-1} are taken from the work of Ginsburg and Barker.⁵⁵ The remaining experimental values were obtained by MacWood and Urey⁴⁸ who examined the Raman spectra of all the deuterio-methanes and by Benedict, Morikawa, Barnes and Taylor^{48a} who measured the infra-red spectra of the same molecules under low dispersion. The assignments are quite certain except perhaps in the case of CH_2D_2 .

The method of obtaining the calculated ν_i from the normal frequencies ω_i was the following. The anharmonic factor α_i of CH_4 was multiplied by the ratio of the normal frequency of the molecule in question to the normal frequency of CH_4 to find the appropriate α_i to be used. Then $\nu_i = \omega_i / (1 + \alpha_i)$. This method is surely of very doubtful validity, particularly in the case of CD_2H_2 where the normal vibrations are quite different from those of CH_4 . The method for estimating the values of ν_i in the column ν_2 would appear to be so unreliable for CH_3D , CH_2D_2 and CD_3H that we have omitted them. The agreement between the calculated and observed ν_i is, on the whole, very satisfactory and quite as good as could be expected under the circumstances.*

The fine structure of the fundamental bands ν_3 and ν_4 was resolved and measured by Cooley.⁵¹ The high frequency band exhibits a very regular structure consisting of a positive, negative and a zero branch. Cooley's data have recently been subjected to a careful re-examination by Childs⁵³ who concludes that the average spacing of the lines in this band is equal to 9.93 cm^{-1} . The low frequency fundamental ν_4 resembles ν_3 in that it also possesses a positive, negative and zero

branch. The mean line spacing is however smaller 5.74 cm^{-1} , and the lines themselves are less regular. In particular, the lines of the negative branch are clearly not single but multiple. The spread of the multiplets and the number of members of each multiplet, increases with the distance of the line from the band center. These effects, which are very clearly shown in the measurements of ν_4 by A. H. Nielsen and H. H. Nielsen, will be discussed later in this article. For the present we shall ignore them and consider the lines to be both single and regularly spaced.

The explanation of the fact that the line spacing in the two fundamentals is not the same was first given by Teller⁵¹ and parallels the discussion of the line spacing in the perpendicular bands of molecules having axial symmetry. The normal modes of vibration corresponding to either ν_3 or ν_4 are degenerate and may be described as a three-dimensional harmonic oscillation. This motion will in general possess an internal angular momentum of magnitude $\zeta\hbar$ which has the quantum-vectorial properties of a spin of magnitude $1\hbar$, that is, it may orient itself parallel, perpendicular or antiparallel to the total angular momentum $J\hbar$ of the system. The effect of the coupling between the internal and the total angular momentum is to split the rotational levels which would otherwise be single and equal to $B_i J(J+1)$ into three levels corresponding to the three respective orientations of $\zeta\hbar$. These are,

$$\begin{aligned} W/hc &= B_i J(J+1) - 2J\zeta_i B_i, \\ W/hc &= B_i J(J+1), \\ W/hc &= B_i J(J+1) + 2(J+1)\zeta_i B_i. \end{aligned}$$

$B_i = \hbar / 8\pi^2 A_i c$, where A_i is the effective moment of inertia for the state ν_i . We have omitted a constant which is additive to all three terms and which is equal to $(\zeta_i^2 - 2\zeta_i) B_i$.

The selection rules are such that in going from $J \rightarrow J+1$ (giving the positive branch in absorption) a transition is made from the ground state, where $\zeta = 0$ and $W/hc = B_0 J(J+1)$, to the first of the excited states listed above. When $J \rightarrow J$, a transition is made to the second state and when $J \rightarrow J-1$ a transition is made to the third state. Applying these rules one finds that the band should present a normal appearance with a positive, negative and zero branch but that

* A calculation of the potential constants of methane was made by Dennison and Johnston, reference 56, which differs from the one we have given in that the positions of the fundamental bands, rather than the normal frequencies, were employed. The potential constants, $A = 7.670$, $B = 0.476$, $C = 0.341$, $D = 1.278$ and $E = 0.313 \times 10^5$ diverge considerably from those we obtained. On the other hand, the calculated frequencies of the isotopic molecules are quite close to our calculated ν_i . This example seems to show that the effect of the anharmonicity may be approximately absorbed by using what may be called "effective" values of the potential constants.

TABLE XII. *Symmetry characters of ν_3 and ν_4 for methane.*

$n_i, (i=3,4)$	CHARACTER
0	A_1
1	F_2
2	A_1+E+F_2
3	$A_1+F_1+2F_2$
4	$2A_1+2E+F_1+2F_2$
5	$A_1+E+2F_1+4F_2$
6	$3A_1+A_2+3E+2F_1+4F_2$

the mean spacing of the lines should be equal to $(B_i+B_0-2\zeta_i B_i) \cong 2B_0(1-\zeta_i)$. The coefficient of J^2 (the convergence factor), is (B_i-B_0) .

The internal angular momentum $\zeta_i \hbar$ is of course determined by the vibratory motion ν_i and will be a function of the potential constants. The formula connecting these quantities has been derived by Johnston and Dennison³² and is

$$\zeta_i = (\delta_i - \frac{1}{2}) / (\delta_i + 1),$$

where

$$\delta_i = 4\mu e^2 / m(\mu\lambda_i - a)^2;$$

$i=3, 4$. The sum, $\zeta_3 + \zeta_4$, is independent of the potential constants, as has been remarked by Teller, and in the present case is equal to $\frac{1}{2}$. Childs, from his analysis of the Cooley data, comes to the conclusion that the most probable value of B_0 is 5.252 cm^{-1} and that $\zeta_3=0.05$ and $\zeta_4=0.45$. These results may be checked from independent sources. The Raman rotational fine structure of ν_3 together with the infra-red fine structure of the same band yields the very concordant result of $\zeta_3=0.048$.

If $B_0=5.252 \text{ cm}^{-1}$, the effective moment of inertia A_0 of the normal state of CH_4 becomes 5.328×10^{-40} . If we neglect the effect of the zero-point vibration upon the rotational energy, that is, if A_0 is assumed to be the equilibrium moment of inertia, the C-H distance may immediately be calculated to be $1.0927 \times 10^{-8} \text{ cm}$. Ginsburg and Barker⁵⁵ have measured the fine structure of a parallel band of CH_3D . Their data serve to determine $B_0 = h/8\pi^2 A c = 3.879 \text{ cm}^{-1}$, where A is the moment of inertia about an axis which is perpendicular to the symmetry axis. Childs and Jahn⁵⁷ have recently observed an overtone band of CH_3D whose center lies at 9020.84 cm^{-1} . They find that $B_0=3.878$, in excellent agreement with the earlier measurements. This datum fixes the moment of inertia A to be 7.215×10^{-40} and,

assuming a regular tetrahedral structure for the molecule, we find $r=1.0934\text{A}$. The agreement between these two independent determinations of the C-H distance is, in our opinion, remarkably good and seems to argue strongly for the essential correctness of the measurements and their analysis.* We shall adopt 1.093A as the most probable value of the C-H distance.

The fine structure of the fundamental bands ν_3 and ν_4 of CD_4 have been mapped experimentally by A. H. Nielsen and H. H. Nielsen⁵⁴ who report for the average line spacings $\Delta\nu_3=4.52 \text{ cm}^{-1}$ and $\Delta\nu_4=3.42$. The sum of these spacings is equal to $3B$ and thus the moment of inertia from these data is 10.57×10^{-40} and $r_0=1.089\text{A}$. The agreement is again satisfactory. The lines of the band ν_4 fulfill our assumption of single, regularly spaced lines even less well than the lines in the corresponding band of CH_4 and consequently these data are perhaps somewhat less suitable for making a precise evaluation of r_0 . Knowing the potential constants of methane, it is possible to calculate the internal angular momentum associated with the vibrations ν_3 and ν_4 . We obtain $\zeta_3=0.168$ and $\zeta_4=0.332$ and thus the line spacings should be $\Delta\nu_3=4.40$ and $\Delta\nu_4=3.54 \text{ cm}^{-1}$. The differences between the calculated and observed values are not much greater than the experimental errors and we regard the agreement to be real and significant.

The original measurements of Cooley showed that the lines of the fundamental band ν_4 were complex. The more recent work of A. H. Nielsen and H. H. Nielsen succeeded in resolving the fine structure even further and it appears that each line is in reality a multiplet. The number of components and their spread increases as one proceeds away from the band center and the

TABLE XIII. *Multiplication table for symmetry characters.*

	A_1	A_2	E	F_1	F_2
A_1	A_1	A_2	E	F_1	F_2
A_2	A_1	A_2	E	F_2	F_1
E	A_1+A_2+E		F_1+F_2	F_1+F_2	F_1+F_2
F_1			$A_1+E+F_1+F_2$	$A_2+E+F_1+F_2$	$A_2+E+F_1+F_2$
F_2				$A_1+E+F_1+F_2$	$A_1+E+F_1+F_2$

* Childs and Jahn believe that the difference between these determinations is real. They quite rightly remark that such a difference might well exist since the quantity which is measured is the effective and not the equilibrium moment of inertia.

lines of the negative branch are more affected than those of the positive branch. A beautiful and satisfactory explanation of this phenomenon has been given in a series of papers by Jahn⁵⁸ and by Childs and Jahn⁵⁹ and an extension of the theory has recently been published by Shaffer, Nielsen and Thomas.⁶⁰ The methods which are used in calculating the perturbations of the rotational levels are rather complicated and we shall only sketch briefly the underlying ideas; referring the reader to the original papers for more complete details.

Perhaps the best approach to the subject is through a discussion of the symmetry characters of the wave functions describing the levels. These have been derived in explicit form for the YX_4 molecule by Tisza,⁶¹ Jahn⁵⁸ and others. It will prove convenient to write the wave function for the complete system as the product of functions which describe the electronic, the vibrational, the rotational, the tunnel and the nuclear spin contributions. Thus $\Psi = \psi_{el}\psi_V\psi_R\psi_T\psi_S$. This method of treating the symmetry characters of the system is rigorous even though the wave equation is only approximately separable. The tetrahedral symmetry of the molecule imposes the consequence that any part of the wave function (for example ψ_V) possesses one of five symmetry characters, A_1 , A_2 , E , F_1 or F_2 . A function having the character A_1 is totally symmetrical, that is, the wave function is unchanged when any two of the four equivalent particles are interchanged. A function with the character A_2 is antisymmetrical and changes sign upon an interchange of any two particles. Both the states A_1 and A_2 are single. The character E , on the other hand, represents two coincident states. This degeneracy cannot be removed by any perturbation, whatever its magnitude, providing it possesses tetrahedral symmetry. The characters F_1 and F_2 are nearly alike and each describes a state consisting of three coincident levels which again cannot be separated by any tetrahedral perturbation. We shall first discuss the symmetry character of each portion of the wave function separately and then obtain the final symmetry through the use of multiplication rules. In the case of CH_4 , since the protons must obey Fermi-Dirac statistics, the total wave function Ψ must have the character A_2 while in CD_4 ,

the character must be A_1 since the deuterons obey Bose-Einstein statistics.

The electronic wave function describing the normal electronic state has the character A_1 . This may be inferred from the intensities of the fine structure lines of the band ν_3 or ν_4 when taken in conjunction with the symmetry characters of the rest of the wave function.

The vibrational function ψ_V will be set equal to the product $\psi_{n_1}\psi_{n_2}\psi_{n_3}\psi_{n_4}$ where the number n_i

TABLE XIV. Symmetry characters for ψ_R .

J	CHARACTER	J	CHARACTER
0	A_1	8	$A_1+2E+2F_1+2F_2$
1	F_2	9	$A_1+A_2+E+2F_1+3F_2$
2	$E+F_2$	10	$A_1+A_2+2E+2F_1+3F_2$
3	$A_1+F_1+F_2$	11	$A_1+2E+3F_1+3F_2$
4	$A_1+E+F_1+F_2$	12	$2A_1+A_2+2E+3F_1+3F_2$
5	$E+F_1+2F_2$	13	$A_1+A_2+2E+3F_1+4F_2$
6	$A_1+A_2+E+F_1+2F_2$	14	$A_1+A_2+3E+3F_1+4F_2$
7	$A_1+E_12F_1+2F_2$	15	$2A_1+A_2+2E+4F_1+4F_2$

is the quantum number of the i th normal mode of vibration. The function ψ_{n_1} , as one might suspect because of the high symmetry of the motion, possesses the character A_1 for all values of the quantum number n_1 . The function ψ_{n_2} has the character A_1 for $n_2=0$ but the character E for $n_2=1$. Thus the first excited state of the vibration ν_2 , although doubly degenerate, can never be split into two separate levels by any tetrahedral perturbation. The state $n_2=2$ is a triple state and has the character $E+A_1$. This means that a tetrahedral perturbation has the power to split this level into two levels, one having the character E and the other the symmetrical character A_1 . The Raman line $2\nu_2$ at 3071.5 cm^{-1} results from a transition to the sublevel A_1 of $2\nu_2$ since this, and not the sublevel E , may resonate with the excited state ν_1 . The state $n_2=3$ has the character $E+A_1+A_2$. It may be shown that the characters describing $\psi_{n_1}\psi_{n_2}$ will contain only E , A_1 and A_2 and consequently the frequency $n_1\nu_1+n_2\nu_2$ is always inactive in the infra-red.

The symmetry characters of ν_3 and ν_4 are exactly the same and are given in Table XII. Active infra-red transitions may take place from the ground state to any level with either the character F_1 or F_2 . Thus the overtone $4\nu_3$ will consist of three nearly superimposed bands. The

separation will depend upon the anharmonic terms in the potential and in general will be of the usual order of magnitude of anharmonic corrections.

In order to determine the characters of any overtone level $n_1\nu_1+n_2\nu_2+n_3\nu_3+n_4\nu_4$ it is only necessary to know the multiplication table for the characters. This is given in Table XIII. As an example, the character of the level $\nu_2+\nu_3$ is F_1+F_2 while that of $\nu_3+\nu_4$ is $A_1+E+F_1+F_2$.

The symmetry characters of the wave functions ψ_R describing the rotational levels have likewise been given by Jahn and we reproduce them in Table XIV. The rotational levels are highly degenerate and, in the absence of any perturbation have the weight $(2J+1)^2$. Of this quantity, one factor $(2J+1)$, represents the possible orientations of the angular momentum vector $J\hbar$ in space while the other factor, also $(2J+1)$, gives the number of levels falling together by reason of the symmetry of the molecule. Thus the level of $J=3$ is composed of the states $A_1+F_1+F_2$ and, while A_1 is single, F_1 and F_2 are both triple, giving a weight of 7.

The symmetry character of a rotational-vibrational level is at once obtained by multiplication. As an example the state $J=4$ of the first excited vibrational state, $\nu_4=1$, is obtained by multiplying the character $A_1+E+F_1+F_2$ by the character F_2 giving $A_1+A_2+2E+3F_1+4F_2$. The vibration ν_4 possesses an internal angular momentum $\zeta_4\hbar$ and this, as we have seen, splits the rotational level into three levels according as to whether $\zeta_4\hbar$ is parallel, perpendicular or antiparallel to $J\hbar$. Jahn gives tables which show the way in which the symmetry characters follow this division. For $J=4$, the level where the momenta are parallel has the character $A_1+F_1+F_2$. According to the selection rules given earlier, this may connect with the ground state $J=3$ which likewise has (and must have) the character $A_1+F_1+F_2$. The level ($J=4$) corresponding to the perpendicular momenta is $A_2+E+F_1+F_2$ and this connects with the ground state level $J=4$. The level with antiparallel momenta is $E+F_1+2F_2$ and connects with the ground level of $J=5$.

The perturbation caused by the interaction between the internal ($\zeta_i\hbar$) and total ($J\hbar$) angular momenta split the rotational level into three

parts. The result of this was that the lines of the band do not have the spacing $\hbar/4\pi^2A$ but rather $(1-\zeta_i)\hbar/4\pi^2A$. However, the lines remain single as before. An additional perturbation having tetrahedral symmetry may break the level ($J=4$, \parallel angular momenta) $A_1+F_1+F_2$ into three levels with the respective characters A_1 , F_1 and F_2 . Thus the line in question, the fourth line of the positive branch, will divide into three components. The other lines will split in exactly the same fashion and it is clear why the degree of multiplicity increases with the number of the band line.

Jahn⁵⁸ has pointed out that a resonance interaction between the rotational levels of the vibrational state ν_2 and the rotational levels of ν_4 will furnish exactly such a perturbation having tetrahedral symmetry. He has calculated explicitly the effect of these perturbations on the levels up to and including $J=10$. The magnitude of the energy changes depends upon the moment of inertia, the internal angular momentum and inversely upon the difference $\nu_2-\nu_4$ between the band centers. Childs and Jahn⁵⁹ have determined the intensity of the lines and plot the theoretically expected appearance of the fundamental band ν_4 . This resembles in almost every detail the experimentally observed band obtained by A. H. Nielsen and H. H. Nielsen.⁵² The agreement is very striking and furnishes a convincing proof of the validity of the theory. We may remark that our estimate of the position of the fundamental ν_2 is slightly lower than that employed by Jahn. This would increase the amount of the perturbation and also increase the dissymmetry between the positive and negative branches. A study of the theoretical and experimental curves indicates that such a change would somewhat improve the quantitative agreement.

The perturbation employed by Jahn, namely resonance interaction between the rotational levels of ν_2 and ν_4 , is not the only perturbation having tetrahedral symmetry which would cause the lines to split into multiplets, although it is probably the predominant cause in the case of ν_4 . Shaffer, Nielsen and Thomas⁶⁰ have recently completed an extensive and thorough study of the perturbations which may affect the vibration-rotation levels. They calculate the energy changes for a series of vibrational levels (those which

give rise to the fundamental and the principal overtone bands) caused by all the possible resonance interactions as well as by the cubic and quartic anharmonic terms in the potential. The resulting expressions are very complicated but, when taken in conjunction with further experimental investigations of the fine structure of the overtone bands, they should yield interesting information concerning the methane molecule.

The weights of the rotational states, which must be used in obtaining the intensities of the fine structure lines, may be found through a discussion of the symmetry characters of the tunnel and nuclear spin wave functions. A tetrahedron described in a right-hand coordinate system cannot be transformed into a tetrahedron described in a left-hand coordinate system by rotations alone. A finite displacement of the particles is necessary which is similar to the tunneling process in ammonia. The fact that such a tunneling process exists will make each level double. The doublet separation is unobservably small since the potential barrier is very high. It may be shown that the wave function ψ_T describing one of the double levels has the character A_1 while the other has the character A_2 .

The nuclear spin wave function ψ_S has been discussed by Wilson⁶² and we shall quote his results. When the four equivalent particles have the spin $(\frac{1}{2})\hbar$, as is the case for protons, the symmetry character of ψ_S is $5A_1 + E + 3F$. The total wave function $\Psi = \psi_e \psi_v \psi_R \psi_T \psi_S$ must be antisymmetrical, that is, it must have the character A_2 . The number of ways in which this can be realized may be counted readily by using the multiplication table for the symmetry characters. Thus in the normal state the weight of the J th rotational state is $f(2J+1)$ where f takes on the values 5, 3, 5, 11, 13 and 11 for $J=0$ to 5, respectively.

The nuclear spin wave function ψ_S for CD_4 must represent $(2S+1)^4 = 81$ states since the deuteron has the spin \hbar . The separations between the 81 levels are of course far too small to be observed spectroscopically since they depend upon the weak interaction of the nuclear magnetic moments. The symmetry character of ψ_S is $15A_1 + 6E + 18F$ and the complete wave function must have the character A_1 . This gives rise to a different set of weights and f in the above ex-

pression is equal to 15, 18, 30, 51, 63 and 66 for the states $J=0$ to 5. Thus the intensities of the band lines of CD_4 will differ somewhat from those of CH_4 , particularly for those lines near the band centers. Wilson has given tables from which the weights of all the rotational levels for both CH_4 and CD_4 may be obtained.

BIBLIOGRAPHY

1. D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).
2. E. B. Wilson and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).
3. E. Fermi, *Zeits. f. Physik* **71**, 250 (1931).
4. W. S. Adams and T. Dunham, *Pub. A. S. P.* **44**, 243 (1932).
5. M. Rusch, *Ann. d. Physik* **70**, 373 (1923).
6. P. E. Martin and E. F. Barker, *Phys. Rev.* **41**, 291 (1932).
7. E. F. Barker and A. Adel, *Phys. Rev.* **44**, 185 (1933).
8. D. M. Cameron and H. H. Nielsen, *Phys. Rev.* **53**, 246 (1938).
9. R. G. Dickinson, R. T. Dillon and F. Rasetti, *Phys. Rev.* **34**, 582 (1929).
10. A. Langseth and J. R. Nielsen, *Zeits. f. physik. Chemie* **B19**, 427 (1932).
11. E. F. Barker and Ta-You Wu, *Phys. Rev.* **45**, 1 (1934).
12. W. V. Houston and C. M. Lewis, *Proc. Nat. Acad. Sci.* **17**, 229 (1931).
13. A. Adel and D. M. Dennison, *Phys. Rev.* **43**, 716 (1933); **44**, 99 (1933).
14. A. Sayvetz, *J. Chem. Phys.* **7**, 383 (1939).
15. A. Weinberg and C. Eckart, *J. Chem. Phys.* **5**, 517 (1937).
16. A. H. Nielsen, *Phys. Rev.* **53**, 983 (1938).
17. H. M. Randall, D. M. Dennison, N. Ginsburg and L. R. Weber, *Phys. Rev.* **52**, 161 (1937).
18. N. Wright and H. M. Randall, *Phys. Rev.* **44**, 39 (1933).
19. R. Mecke, W. Baumann and K. Freudenberg, *Zeits. f. Physik* **81**, 313, 445 and 465 (1933).
20. N. Fuson, H. M. Randall and D. M. Dennison, *Phys. Rev.* **56**, 982 (1939).
21. B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).
22. L. G. Bonner, *Phys. Rev.* **46**, 458 (1934).
23. F. D. Rossini, J. W. Knowlton and H. L. Johnston, *J. Research Nat. Bur. Stand.* **24**, 369 (1940).
24. W. H. Shaffer and H. H. Nielsen, *Phys. Rev.* **56**, 188 (1939).
25. R. M. Badger and C. H. Cartwright, *Phys. Rev.* **33**, 692 (1929).
26. C. E. Cleeton and N. Williams, *Phys. Rev.* **44**, 421 (1933).
27. Z. I. Slawsky and D. M. Dennison, *J. Chem. Phys.* **7**, 509 (1939).
28. M. V. Migeotte and E. F. Barker, *Phys. Rev.* **50**, 418 (1936).
29. J. B. Howard, *J. Chem. Phys.* **3**, 207 (1935).

30. E. O. Salant and J. E. Rosenthal, *Phys. Rev.* **42**, 812 (1932).
31. E. Teller, *Hand- und Jahrbuch der chemischen Physik* (1934), Vol. 9, p. 125.
32. M. Johnston and D. M. Dennison, *Phys. Rev.* **48**, 868 (1935).
33. E. F. Barker, *Phys. Rev.* **55**, 657 (1939).
34. D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).
35. M. F. Manning, *J. Chem. Phys.* **3**, 136 (1935).
36. Hsi-Yin Sheng, E. F. Barker and D. M. Dennison, *J. Chem. Phys.* (to be published).
37. W. S. Benedict, *Phys. Rev.* **47**, 641 (1935).
38. W. H. Bennett and C. F. Meyer, *Phys. Rev.* **32**, 888 (1928).
39. E. F. Barker and E. K. Plyler, *J. Chem. Phys.* **3**, 367 (1935).
40. A. Adel and E. F. Barker, *J. Chem. Phys.* **2**, 627 (1934).
41. J. W. Linnett, *J. Chem. Phys.* **8**, 91 (1940).
42. L. O. Brockway, *J. Phys. Chem.* **41**, 747 (1937).
43. G. B. B. M. Sutherland, *Trans. Faraday Soc.* **34**, 325 (1938).
44. H. H. Voge and J. E. Rosenthal, *J. Chem. Phys.* **4**, 137 (1936).
45. G. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc.* **148**, 250 (1935).
46. Z. I. Slawsky and D. M. Dennison, *J. Chem. Phys.* **7**, 522 (1939).
47. J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.* **1**, 357 (1933); J. E. Rosenthal, *Phys. Rev.* **46**, 730 (1934).
48. G. E. MacWood and H. C. Urey, *J. Chem. Phys.* **4**, 402 (1936).
- 48a. W. S. Benedict, K. Morikawa, R. B. Barnes and H. S. Taylor, *J. Chem. Phys.* **5**, 1 (1937).
49. D. M. Dennison, *Astrophys. J.* **62**, 84 (1925).
50. J. E. Rosenthal, *Phys. Rev.* **45**, 538 (1934).
51. J. P. Cooley, *Astrophys. J.* **62**, 73 (1925).
52. A. H. Nielsen and H. H. Nielsen, *Phys. Rev.* **48**, 864 (1935).
53. W. H. J. Childs, *Proc. Roy. Soc.* **153**, 555 (1936).
54. A. H. Nielsen and H. H. Nielsen, *Phys. Rev.* **54**, 118 (1938).
55. N. Ginsburg and E. F. Barker, *J. Chem. Phys.* **3**, 668 (1935).
56. D. M. Dennison and M. Johnston, *Phys. Rev.* **47**, 93 (1935).
57. W. H. J. Childs and H. A. Jahn, *Proc. Roy. Soc.* **169**, 428 (1939).
58. H. A. Jahn, *Proc. Roy. Soc.* **168**, 469 and 495 (1938).
59. W. H. J. Childs and H. A. Jahn, *Proc. Roy. Soc.* **169**, 451 (1939).
60. W. H. Shaffer, H. H. Nielsen and L. H. Thomas, *Phys. Rev.* **56**, 895 and 1051 (1939).
61. L. Tisza, *Zeits. f. Physik* **82**, 48 (1933).
62. E. B. Wilson, *J. Chem. Phys.* **3**, 276 (1935).
63. I. Hansen, *Phys. Rev.* **46**, 122 (1934).