

A NEW BAND IN THE ABSORPTION SPECTRUM OF METHANE GAS

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ABSTRACT

The absorption spectrum of methane gas has been examined in the photographic infrared region from 6500A to 9500A in the hope of observing overtones of the known fundamental frequencies. A path length of 10 meters of gas at 70 cm pressure was used. The source of continuous radiation was a tungsten filament and the radiation was analysed with a grating spectrograph having a dispersion of 2.6A per mm at 8000A.

One band which may be attributed to methane was observed at about 8900A and may be identified as the third overtone ($n=0\rightarrow 4$) of the fundamental absorption band at 3.3μ . The fine structure appears to be very complex and irregular, consisting of more than a hundred lines of which about five are very intense.

In an attempt to reconcile the apparent irregularity of this structure with the simple and regular fine structure of the fundamental at 3.3μ , the theory of the overtones of a methane type molecule was examined. It is remarked that the higher energy states corresponding to this mode of vibration are in first approximation degenerate and have a weight $\frac{1}{2}(n+1)(n+2)$. A perturbation representing the anharmonic forces is now introduced and is postulated to have a tetrahedral symmetry. The secular determinant is then constructed and the resulting energy constant is given explicitly for the values $n=0,1,2,3,4$. It is found that for $n=4$ the 15 levels which originally coincided now group themselves into seven neighboring levels having the weights 3,3,3,2,2,1, and 1. These levels may all combine with the vibrationless state $n=0$ and thus it is to be expected that the overtone band under discussion will consist of seven nearly superimposed single bands. These considerations appear to explain the observed degree of complexity although it has not been possible as yet to make a detailed analysis of the positions of the individual lines.

THE infrared absorption spectrum of methane has been observed by Cooley¹ who found a number of bands in the region from 2μ to 8μ but particularly two strong ones at 3.3μ and 7.7μ which are without doubt due to two of the fundamental vibrations of the methane molecule. Higher harmonics of the fundamental at 3.3μ are to be expected in the region of wave-length less than 1μ where they are accessible to photographic investigation. It was therefore determined to search for such bands using a comparatively long light path in the gas (10 meters).

EXPERIMENTAL

The absorption tube was constructed of a piece of lap-welded steel pipe 15 cm in diameter and 5 meters long. Flat steel rings were set in the ends and soldered tightly to the pipe and against these two plate glass windows

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¹ J. P. Cooley, *Astrophys. J.* **62**, 73 (1925).

were sealed with picein wax. Side tubes and drying apparatus for admitting the gases, a water aspirator for rough evacuation of the chamber and a mercury manometer to indicate the pressure were attached.

A tungsten filament provided the source of continuous spectrum. The light passed from the lamp at one end of the tube to a concave mirror of seven meters radius of curvature placed at the other. This mirror reflected the light back through the tube, and focussed it directly on the slit of the spectrograph, a plane mirror being used to deflect the beam from the axis of the tube to the axis of the spectrograph. When observations were made in the region of wave-lengths greater than 8600A a large 45° glass prism was introduced in the convergent beam about one meter in front of the slit. This device produced a short spectrum on the spectrograph slit. Rotation of the prism selected particular regions of wave-length about 1000A in width and thus the scattered light of shorter wave-length which otherwise caused a general fogging on the plates during the long exposures necessary in this part of the spectrum could be easily disposed of. When this prism was not used a red glass filter served to cut out the blue light.

The spectrograph consisted of a concave Rowland grating of 7 meters radius in a Paschen mounting. This instrument gave a dispersion of 2.6A per mm at 8000A. Eastman Extreme Red and Infrared Sensitive plates were used and exposure times varied from 5 minutes to 24 hours, depending on the spectral region under investigation. Second order iron lines served as standards for the determination of wave-lengths.

Pressures in the absorption cell of about 70 cm were used. Even at this pressure the absorption lines seemed quite diffuse and broad so that no advantage was to be gained by pushing the large grating spectrograph to the limit of its resolving power. A similar observation has been made by Badger² in work on the absorption bands of ammonia.

The methane was taken from cylinders of compressed gas supplied by the Matheson Company. It was dried by passing over calcium chloride and through concentrated sulphuric acid but no further attempts were made to purify it. According to the makers this gas was 88% pure containing approximately 7% of ethane, 4% of propane, and 1% of butane. In order to be sure that none of these impurities was responsible for the observed absorption, photographs were taken successively through a 60 cm cell containing each of these gases. In no case could absorption be observed in the region containing the band under discussion. When the 60 cm cell was filled with methane three or four of the strongest absorption lines near 8870A could be detected on the plates, although the absorption was very faint with this relatively short path length.

RESULTS

A survey of the spectrum from 6500A to 9500A showed one band extending from 8800A to 9000A. In all over one hundred individual lines could be measured. Some of these were very strong and showed fairly complete

² R. M. Badger, *Phys. Rev.* **35**, 1038 (1930).

absorption but the greater number were very weak and could be measured only with difficulty under the high magnification on the comparator. Table I gives the measured wave-lengths of the lines and eye estimates of the intensities. The last column gives the values of the wave-numbers reduced to

TABLE I. *Wave-lengths and intensities of the lines of a band in the absorption spectrum of methane.*

Int.	I.A.	ν	Int.	I.A.	ν	Int.	I.A.	ν	Int.	I.A.	ν
0*	8798.50	11362.46	0	8837.61	11312.18	1	8872.27	11267.99	0	8910.61	11219.50
0*	8806.15	11352.58	0*	8838.28	11311.32	1	8873.08	11266.96	0	8913.65	11215.68
0	8811.11	11346.19	0	8839.35	11309.95	3	8874.00	11265.79	0*	8916.16	11212.51
1	8812.17	11344.83	2	8842.03	11306.51	0*	8874.74	11264.85	0*	8917.13	11211.29
0	8813.11	11343.62	3	8843.36	11304.81	0	8875.67	11263.67	0*	8919.73	11208.02
1	8814.25	11342.16	0	8844.13	11303.83	0	8876.76	11262.29	1	8921.71	11205.54
1	8814.96	11341.24	0	8845.96	11301.49	1	8877.95	11260.78	0*	8923.53	11203.25
0*	8816.06	11339.82	0	8848.66	11298.04	0*	8879.16	11259.24	0*	8924.71	11201.77
0	8817.04	11338.56	0	8850.44	11295.77	1	8882.83	11254.58	1	8925.96	11200.20
0	8818.32	11336.92	0	8852.25	11293.46	0	8884.94	11251.91	0	8935.84	11187.82
0	8819.78	11335.04	2	8854.44	11290.67	0*	8886.99	11249.31	0*	8937.99	11185.13
0*	8821.02	11333.45	0	8856.35	11288.24	0*	8887.38	11248.82	0*	8940.35	11182.18
1	8822.60	11331.42	4	8859.21	11284.59	0	8888.38	11247.56	0*	8943.01	11178.85
0*	8823.79	11329.89	0*	8860.62	11282.80	0*	8890.36	11245.05	0*	8944.57	11176.90
0	8824.99	11328.35	0*	8861.42	11281.78	0*	8890.87	11244.41	0	8946.26	11174.79
0	8825.68	11327.46	0*	8862.45	11280.47	4	8892.60	11242.22	0	8947.33	11173.46
0	8827.04	11325.72	0	8863.78	11278.78	0*	8893.40	11241.21	0*	8948.78	11171.65
0	8828.15	11324.30	0*	8864.34	11278.06	0*	8896.72	11237.02	0*	8958.47	11159.56
0*	8829.77	11322.23	0*	8864.79	11277.49	0*	8898.20	11235.15	0*	8961.22	11156.13
0*	8830.18	11321.69	0*	8865.54	11276.54	0*	8900.18	11232.65	0	8963.13	11153.76
1	8831.19	11320.40	2	8866.30	11275.57	2	8901.20	11231.36	0*	8966.99	11148.95
1	8831.57	11319.91	2	8867.56	11273.97	0	8902.51	11229.71	0*	8982.97	11129.13
0*	8832.38	11318.87	0*	8868.13	11273.24	0*	8903.46	11228.51	0*	8984.84	11126.81
1	8832.87	11318.25	5	8868.77	11272.43	1	8904.18	11227.60	0*	8986.56	11124.68
2	8836.59	11313.48	0	8870.11	11270.73	0*	8905.69	11225.70	1*	8988.03	11122.86
0*	8837.07	11312.87	1	8871.36	11269.14	0*	8909.41	11221.01	0*	9001.89	11105.73
									0*	9010.14	11095.56

* Measured on one plate only.

vacuum. Independent determinations of the wave-lengths using two different plates indicate that the wave-lengths of the stronger lines are probably accurate to about 0.03A. For the weaker lines, of course, the accuracy is considerably less and errors of 0.1A may be present. Figure 1 gives a graph-

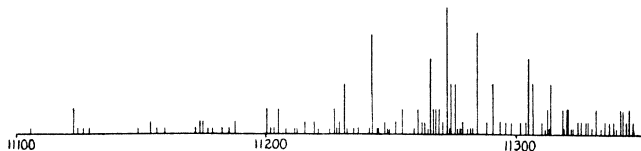


Fig. 1. Graphical picture of the absorption band in methane.

ical picture of the band. The absorption lines are plotted on a frequency scale, the vertical height of the lines representing their intensities.

It seems very probable that this absorption band is the third overtone ($n=0 \rightarrow 4$) of the fundamental ($n=0 \rightarrow 1$) band at 3.3μ . The first and second

overtone has been previously reported by Ellis³ as lying at 1.69μ and 1.15μ respectively. From the positions of these bands Ellis gives the following formula which is typical for series of this sort.

$$\nu = 3070n - 55n^2.$$

Substituting for $n=4$ we obtain $\nu = 11480 \text{ cm}^{-1}$ which we may compare with the most intense experimental lines at 11280 cm^{-1} . The agreement is satisfactory but could be improved by the formula

$$\nu = 3085n - 66n^2$$

which also represents Ellis' results within his experimental error.

The fine structure of the overtone reported in this paper appears to be very irregular and complex; a feature which seems surprising since the fundamental possesses a simple fine structure consisting of a regular positive, negative and zero branch as might be expected from a molecule whose three moments of inertia are equal. We shall however attempt to show that this overtone should consist of seven nearly superimposed simple bands of varying intensity. These considerations appear to account for the complexity of the observed fine structure even though we have not succeeded in analysing it in detail.

OVERTONES IN THE METHANE SPECTRUM

The normal vibrations of methane have been discussed by Dennison⁴ under the assumption that the molecule may be represented by a regular tetrahedron with the carbon atom at the center. The nine degrees of vibrational freedom give rise to only four independent frequencies ν_1 , ν_2 , ν_3 and ν_4 . Of these ν_1 single, and ν_2 double, are optically inactive. ν_3 and ν_4 are each triple frequencies and are optically active. They may be identified with the two strong bands of methane at 3.3μ and 7.7μ respectively. The band which is being reported in this paper is almost certainly the third overtone of ν_3 ($n=0 \rightarrow 4$) and we shall therefore confine ourselves to a discussion of this vibration. The considerations may be applied without change to overtones of ν_4 and might be extended to cover any general combination of the four fundamental frequencies. In the following work we have derived many important suggestions from two papers by F. Hund⁵ and by W. Elert⁶ on the symmetry properties of the methane type molecule, to which the reader interested in a further development of the subject is referred.

The normal mode of vibration ν_3 (or ν_4) involves the motion of all four of the hydrogen atoms together with the motion of the carbon atom. This system of the normal oscillator ν_3 (or ν_4) may be replaced by a simpler model which will possess all the properties of the ν_3 vibration and which will be found more convenient for discussion. Let a mass particle μ be elastically

³ J. W. Ellis, Proc. Nat. Acad. Sci. **13**, 202 (1927).

⁴ D. M. Dennison, Astrophys. J. **62**, 84 (1925).

⁵ F. Hund, Zeits. f. Physik **43**, 805 (1927).

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

bound to the origin of a rectangular set of axes x, y, z with a potential energy function whose leading term is, $V^0 = 2\pi^2\mu\nu^2(x^2 + y^2 + z^2)$. The remaining terms of the potential function V' may be considered as a perturbing potential and will have only one condition imposed upon them, namely that they must show a tetrahedral symmetry. This model may be visualized by thinking of the hydrogen atoms of methane as being rigidly fixed in space at the corners of a regular tetrahedron. The carbon atom is elastically bound to these four points and has as its equilibrium position the center of the tetrahedron. In first approximation the potential energy is V^0 and the frequency of vibration of the carbon atom is independent of the path of its motion.

When we discuss the model by means of the wave mechanics, we see that the wave equation is separable in the x, y, z coordinates and that in effect we have three independent linear harmonic oscillators each with the same frequency ν . The proper value for the system wave equation is the sum of the proper values for the individual linear oscillators and the wave function is the product of the individual wave functions. Since the theory of the harmonic oscillator and of separable wave equations is so well known, it will only be necessary to give the following results.

The energy of the system in first approximation is

$$W^0 = h\nu(n + 3/2) \quad n = 0, 1, 2, \dots$$

while the wave function ψ will be given in terms of three positive integer indices n_1, n_2, n_3 .

$$\psi = \psi_{(x)}^{n_1} \psi_{(y)}^{n_2} \psi_{(z)}^{n_3}.$$

In this expression $\psi_{(x)}^{n_1}$ is the n_1^{th} Hermitian orthogonal function having as its argument the variable $[4\pi^2\mu\nu/h]^{1/2}x$. The relation between the $n_s, n_1 + n_2 + n_3 = n$ shows that all the states for which n is not equal to zero are degenerate. For each value of n there will exist a number g_n of independent solutions to the wave equation. This number, which represents the weight of the n^{th} state may be easily found to be

$$g_n = \left(\frac{1}{2}\right)(n + 1)(n + 2).$$

For simplicity we shall represent a wave function by the symbol $(n_1 n_2 n_3)$. Thus the lowest vibrational state has the single wave function (000) while the first state possesses three independent wave functions (100), (010) and (001), any linear combination of which will be a solution of the wave equation.

In first approximation as has been seen, for any value of n there will be g_n coincident energy levels. In higher order of approximation however when we take into account the anharmonic terms in the potential function, not all of these levels will exactly coincide and the purpose of the discussion is to determine the grouping of the levels. The method we shall employ is the familiar theory of perturbations of degenerate systems. For any particular value of n , the wave functions may be given the designation ψ_{n_m} where m is an index running from 1 to $\frac{1}{2}(n+1)(n+2)$. Let the perturbing potential

energy be V' and the perturbed addition to the energy constant be W' . The so-called secular determinant is then constructed with the elements $|\int V'\psi_{nm}\psi_{nm}'dxdydz - W'\delta_m^{m'}|$ where $\delta_m^{m'}$ is the Kroneker symbol. Setting the secular determinant to zero provides $\frac{1}{2}(n+1)(n+2)$ values for W' not all of which however need be distinct.

In our problem the secular determinant for small values of n becomes very simple since many of the elements vanish because of the tetrahedral symmetry of V' . Let the four corners of the tetrahedron be joined by six straight lines. Construct three axes each of which bisects one of the three opposite pairs of lines. These three axes which are mutually perpendicular, have an origin at the center of gravity of the system, and may be chosen as our x, y, z axes.

The potential function $V = V^0 + V'$ is a function of x, y and z and must have the symmetry of the tetrahedron. A little inspection discloses the following properties.

$$\begin{aligned} V(x, y, z) &= V(y, x, z) = V(z, y, x) \\ &= V(-x, -y, z) = V(-x, y, -z) = V(x, -y, -z). \end{aligned}$$

Thus the potential V or V' is unchanged by any permutation of the coordinate axes x, y, z . It is further unchanged if any two of the axes are reversed in direction. These properties describe the most general type of function having tetrahedral symmetry.

In constructing the elements of the secular determinant we may use the notation,

$$\alpha_{n_1 n_2 n_3}^{n_1' n_2' n_3'} = \int (n_1' n_2' n_3') V'(n_1 n_2 n_3) dx dy dz.$$

If we now remember that the Hermitian orthogonal function is an even or odd function of x depending upon whether n is an even or odd integer, it becomes evident that only those elements are non-vanishing for which $(n_1' + n_1)$, $(n_2' + n_2)$ and $(n_3' + n_3)$ are either all even integers or all odd integers. It is further clear from the symmetry properties of V' that,

$$\alpha_{n_1 n_2 n_3}^{n_1' n_2' n_3'} = \alpha_{n_2 n_1 n_3}^{n_2' n_1' n_3'} \text{ etc.}$$

The results of these considerations will now be tabulated for $n=0, 1, 2, 3, 4$. In every case values of the energy constant W' are given. The number in parenthesis immediately preceding W' indicates the number of levels having this value of the energy. This last degeneration (falling together of levels) can never be removed by introducing higher order perturbing terms provided they retain the symmetry of the tetrahedron.

$$\begin{array}{l} n = 0 \quad g_0 = 1 \\ (1)W' = \alpha_{000}^{000} \end{array} \quad \begin{array}{l} n = 1 \quad g_1 = 3 \\ (3)W' = \alpha_{100}^{100} \end{array}$$

$$n = 2 \quad g_2 = 6$$

$$\begin{aligned} (3)W' &= \alpha_{110}^{110} \\ (2)W' &= \alpha_{200}^{200} - \alpha_{020}^{200} \\ (1)W' &= \alpha_{200}^{200} + 2\alpha_{020}^{200} \end{aligned}$$

$$n = 3 \quad g_3 = 10$$

$$\begin{aligned} (1)W' &= \alpha_{111}^{111} \\ (3)W' &= \alpha_{210}^{210} - \alpha_{021}^{201} \\ (3)W' &= \frac{1}{2}(\alpha_{300}^{300} + \alpha_{210}^{210} + \alpha_{021}^{201}) \\ &\quad + \left[\frac{1}{4}(\alpha_{300}^{300} + \alpha_{210}^{210} + \alpha_{021}^{201})^2 - \alpha_{300}^{300}(\alpha_{210}^{210} + \alpha_{021}^{201}) + 2(\alpha_{120}^{300})^2 \right]^{1/2} \\ (3)W' &= \frac{1}{2}(\alpha_{300}^{300} + \alpha_{210}^{210} + \alpha_{021}^{201}) \\ &\quad - \left[\frac{1}{4}(\alpha_{300}^{300} + \alpha_{210}^{210} + \alpha_{021}^{201})^2 - \alpha_{300}^{300}(\alpha_{210}^{210} + \alpha_{021}^{201}) + 2(\alpha_{120}^{300})^2 \right]^{1/2} \end{aligned}$$

$$n = 4 \quad g_4 = 15$$

$$\begin{aligned} (3)W' &= \alpha_{310}^{310} - \alpha_{130}^{310} \\ (3)W' &= \frac{1}{2}(\alpha_{310}^{310} + \alpha_{211}^{211} + \alpha_{130}^{310}) \\ &\quad \pm \left[\frac{1}{4}(\alpha_{310}^{310} + \alpha_{211}^{211} + \alpha_{130}^{310})^2 - \alpha_{211}^{211}(\alpha_{310}^{310} + \alpha_{130}^{310}) + 2(\alpha_{112}^{310})^2 \right]^{1/2} \\ (2)W' &= \frac{1}{2}(\alpha_{400}^{400} + \alpha_{220}^{220} - \alpha_{040}^{400} - \alpha_{202}^{220}) \\ &\quad \pm \left[\frac{1}{4}(\alpha_{400}^{400} + \alpha_{220}^{220} - \alpha_{040}^{400} - \alpha_{202}^{220})^2 - (\alpha_{400}^{400} - \alpha_{040}^{400})(\alpha_{220}^{220} - \alpha_{202}^{220}) \right. \\ &\quad \left. + (\alpha_{022}^{400} - \alpha_{220}^{400})^2 \right]^{1/2} \\ (1)W' &= \frac{1}{2}(\alpha_{400}^{400} + \alpha_{220}^{220} + 2\alpha_{040}^{400} + 2\alpha_{202}^{220}) \\ &\quad \pm \left[\frac{1}{4}(\alpha_{400}^{400} + \alpha_{220}^{220} + 2\alpha_{040}^{400} + 2\alpha_{202}^{220})^2 - (\alpha_{400}^{400} + 2\alpha_{040}^{400})(\alpha_{220}^{220} + 2\alpha_{202}^{220}) \right. \\ &\quad \left. + (2\alpha_{220}^{400} + \alpha_{022}^{400})^2 \right]^{1/2}. \end{aligned}$$

A certain independent check on the above calculations may be made in the following manner. Suppose that V' possesses not only tetrahedral symmetry but spherical symmetry as well. This would mean that the α_s would be unchanged by a rotation of the x, y, z axes and this would lead to certain relations between them. Thus in the case $n=2$, it may be shown that if V' has spherical symmetry $\alpha_{200}^{200} - \alpha_{020}^{200} = \alpha_{100}^{110}$ and therefore instead of three groups of energy levels for the tetrahedron we obtain only two energy levels for the sphere (one with the weight 5 and the other with the weight 1). These results for a spherical potential may be obtained independently by introducing the spherical coordinates r, θ, ϕ in which case V' is a function of r alone. The results of applying these two methods were compared for the values of n under discussion and found to agree, thus furnishing at least one check on the numerical calculations. It may be of interest to state how the seven groups of levels for the tetrahedron for $n=4$ degenerate into three groups of levels (with the weights 9, 5, and 1) for the sphere. Let the perturbed energy W' be given an index running from 1 to 7 and corresponding

to the energies in the above table ($n=4$) respectively. When the tetrahedral symmetry degenerates into spherical symmetry we have the three levels, $W_1' = W_3' = W_5' = W_7'$, $W_2' = W_4'$ and W_6' .

We may now summarize the results which have been obtained. The first vibrational state $n=1$ is degenerate and is composed of three coincident levels which will not be separated by any perturbing potential having tetrahedral symmetry.⁷ The fundamental band ($n=0 \rightarrow 1$) is consequently a single band, a result which agrees with the simplicity of its observed fine structure.

The level $n=4$ is composed of seven neighboring levels having the weights 3, 3, 3, 2, 2, 1 and 1 respectively.⁸ All of these levels may combine with the lowest level $n=0$ and therefore the third overtone should consist of seven nearly superimposed bands. The intensity of any one of these bands will depend not only upon the weight of the upper state but also upon the exact nature of the perturbing function V' .

Each of these bands we suppose will have a fine structure consisting of a regular positive, negative and zero branch. By referring to the work of Elert⁶ on the symmetry properties of the wave functions, it may be seen that all the lines of the fine structure will be present with the possible exception of the first line of the zero branch. The intensity distribution will be somewhat irregular due to the spin of the hydrogen nucleus. It is not possible to predict whether the spacing of the lines in the positive and negative branches will be the same for each of the seven nearly superimposed bands since the mechanism of the coupling between rotation and vibration in the methane molecule is not yet understood. It will be remembered that the fine structure lines in the two fundamental bands ν_3 and ν_4 do not have the same spacing in frequency although this was to be expected on the basis of the simple theory involving no interaction between vibration and rotation.

Let us now return to a consideration of the observed structure of the overtone band $n=0 \rightarrow 4$. Although the lines are very irregularly spaced there seems to be a definite convergence on the short wave side of the band. This may be compared with the fact that Cooley¹ found a slight convergence of the fine structure lines of the fundamental band on the short wave side.

Among the hundred or so lines recorded on the plate some five or more lines stand out as being definitely much stronger than the rest and we should

⁷ For the sake of completeness we should remark that Hund⁵ and Elert⁶ have pointed out a further degeneracy arising from the fact that more than one equivalent space equilibrium configuration exists for the methane molecule. In fact each of the levels which we have treated as single is split into two separate levels having reciprocal symmetry character in the wave functions. The magnitude of the separation of these two levels is however very much smaller than the separations which we are considering here and will certainly be far too small to be observed experimentally. We have therefore omitted this type of degeneracy from the discussion.

⁸ It is obviously impossible to determine the W_s' when we do not know the exact form of V' . An estimate based on a potential function having spherical rather than tetrahedral symmetry indicates that the difference between two successive W_s' is smaller than any one of the W_s' but is yet not of an essentially smaller order of magnitude.

like to identify these as the zero branches of the seven single bands which have been predicted by the theory. A difficulty arises however which may make this interpretation untenable. The formula for the positions of the lines of the fundamental band as given by Cooley¹ is,

$$\nu = 3019.3 + 9.771m - 0.0351m^2, \quad m = \pm 1, \pm 2, \dots$$

If the mechanism of the coupling between vibration and rotation were similar to that for a diatomic molecule, the zero branch lines of any of the seven single bands comprising the third overtone would be given by,

$$\nu = A - 4(0.0351)m^2$$

where A is a constant of the order of 12000 cm^{-1} . These zero branch lines would then not fall exactly together but starting from a head on the high frequency side would extend over several waves per cm. Actually the strongest lines on the plates appear to be much sharper than this and seem to have a half width no greater than one wave per cm. We should emphasize however that these considerations lie in the realm of speculation since each single band will probab'y have a different convergence factor whose magnitude can not be predicted without a more complete analysis of the interaction between vibration and rotation for this type of molecule.

Many difficulties lie in the way of a detailed ordering of the observed fainter lines into seven independent series of regularly spaced positive and negative branches. From the theoretical side we do not understand the nature of the coupling between the vibration and rotation and hence we can not be certain of the formulae giving the positions of the fine structure lines. From the experimental side we are not convinced that all the lines necessary for an analysis have been recorded and we believe that many of the lines may be enhanced due to the chance superposition of several faint lines. Our purpose has been rather to show that this overtone band may be expected to possess a complex structure composed of seven bands, each containing some thirty or more lines. The observed spectrum seems to possess about this same degree of complexity.