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Further Resolution of Two Parallel Bands of Ammonia and the Interaction between Vibration and Rotation

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The fundamental low frequency parallel band at 10μ and its upper stage band at 16μ have been re-examined under high dispersion. It is found that most of the fine structure lines hitherto reported as single are resolved into multiplets. The positions of the lines may be accounted for accurately by assuming that the energy levels have the form,

$$W^{s,a}/hc=W_V{}^{s,a}/hc+A_V{}^{s,a}(J^2+J-K^2)+C_V{}^{s,a}K^2+F(JK).$$

The superscripts s or a indicate whether the level in question is the lower or the upper of the two levels produced by the double minimum potential. $F(JK)$ is the small centrifugal distortion term calculated by Slawsky and Dennison. The constants $A_0{}^s$, $A_0{}^a$, $A_1{}^s$, $A_1{}^a$, $A_2{}^s$, $C_1{}^s-C_0{}^a$ and $C_1{}^a-C_0{}^s$ are determined from the experimental data. The following vibrational energies are also found, $W_1{}^s=932.24hc$, $W_1{}^a=968.08hc$ and $W_2{}^s=1597.4hc$.

In the discussion of the rotational constants, it is pointed out that two quantities are involved, (a) the average constants, averaged over the two levels of the double minimum, as $\frac{1}{2}(A_v{}^s+A_v{}^a)$, and (b) the difference of the constants, as $A_v{}^a-A_v{}^s$. Recently Shaffer has calculated the theoretical expressions for the averaged constants and has shown how these depend upon the anharmonic terms in the potential energy. A treatment of the difference of the constants is equivalent to a treatment of the change in the splitting of the two levels of the double minimum due to the vibration-rotation interaction. This may be computed from the expression for the splitting of the double minimum levels given by the W-K-B method of approximation. The calculated result for the change in splitting of the first vibration levels is

$$(\delta\Delta/hc)_{\text{theo}}=-0.162(J^2+J)+0.222K^2,$$

which is in excellent agreement with the observed change

$$(\delta\Delta/hc)_{\text{exp}}=-0.17(J^2+J)+0.23K^2.$$

The significance of the agreement is discussed.

Introduction

The general problem of the evaluation of the vibration-rotation energy levels of polyatomic molecules has received considerable attention in recent years and much progress has been made. The present paper contributes to this problem and is concerned with the high resolution of the low frequency parallel bands of ammonia. It will be shown that certain novel features appear here which are produced by the double minimum potential of ammonia and which are not likely to occur in measurable degree in other spectra.

The Hamiltonian function representing a polyatomic molecule is separable only in zeroth approximation and the usual procedure is to develop H as a series involving a number of orders of approximation and to treat these by the methods of perturbation theory. In zeroth approximation the vibration-rotation energy levels of an axially symmetrical molecule, such as ammonia, are given by the expression,

$$W_0/hc=\sum_i \omega_i(V_i+\tfrac{1}{2}d_i)+A_e(J^2+J)+(C_e-A_e)K^2.$$

Here the ω_i are the normal vibration frequencies (expressed in cm^{-1}) and d_i are the degrees of degeneracy of the various normal vibrations.

$$A_e=h/8\pi^2cI_A{}^0,\quad C_e=h/8\pi^2cI_C{}^0,$$

where $I_A{}^0$ and $I_C{}^0$ are the equilibrium values of the moments of inertia for axes perpendicular to and parallel to the symmetry axis, respectively.

When the change of the electric moment due to the vibration lies along the symmetry axis, the selection rules for the rotational numbers are $\Delta J=0$, ±1 and $\Delta K=0$. As is well known this produces a simple band of the so-called parallel type which consists of a positive, negative and zero branch. The lines of the positive and negative branches have the spacing $2A_e$ and are multiple, that is, each line is composed of a number of superimposed components. It is to be expected that in the next order of approximation these component lines may separate slightly from each other.

In the case of the ammonia molecule there is one further circumstance to be recalled.[1] The

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[1] For a review of the ammonia spectrum see D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

nitrogen atom possesses two equivalent positions of equilibrium, one on either side of the plane of the hydrogens. This fact produces a splitting of each energy level into two levels. The doublet separation is small (about 0.66 cm^{-1}) for the ground state but becomes rapidly larger for the excited states of the vibration ν_3. The wave functions characterizing these two states are either symmetrical or antisymmetrical with respect to the plane of the hydrogen atoms, the lower of the two levels of the doublet being symmetrical. Parallel type bands, such as those to be discussed here, correspond to transitions connecting a symmetrical with an antisymmetrical level.

The methods for treating the interaction between the vibration and rotation of polyatomic molecules have been discussed by Wilson and Howard[2] and have recently been applied in detail to the pyramidal XY_3 molecule by Shaffer.[3] This treatment leads to an expression of the following type for the energy of a level not involving a perpendicular vibration.[4]

$$W^s/hc = W_V{}^s/hc + A_V{}^s(J^2+J) + (C_V{}^s - A_V{}^s)K^2 + F(JK). \quad (1)$$

The first term $W_V{}^s$ represents the vibrational energy. The quantities $A_V{}^s$ and $C_V{}^s$ are functions of the vibrational numbers, in first approximation linear functions. The superscript s indicates that the level in question is the lower member of the doublet pair caused by the double minimum character of the potential; the upper level will be designated with the superscript a. Shaffer's formula does not contain the superscript s or a, of course, since he did not consider effects arising from the double minimum potential.

The fact that $A_V{}^s$ and $A_V{}^a$ may differ from each other is indicated by the following qualitative argument. Consider the case where $K=0$. This corresponds to the classical motion in which the molecule is rotating about an axis perpendicular to the axis of the pyramid. The centrifugal force tends to force the hydrogen atoms away from the nitrogen and to make the apex angle of the pyramid more acute. In other words the centrifugal distortion *raises* the barrier separating the two equivalent equilibrium positions of the nitrogen atom. Accordingly, the doublet separation, which is a very sensitive function of the barrier height, will be decreased and therefore $A_V{}^a - A_V{}^s$ must be negative. On the other hand when $K=J$ the energy levels correspond to the classical motion of rotation about the axis of the pyramid. The centrifugal forces will clearly tend to make the apex angle of the pyramid more obtuse and hence in effect will *lower* the barrier height. Thus we may expect $C_V{}^a - C_V{}^s$ to be positive. It will appear that the experimental data are in accord with these predictions.

The last term in Eq. (1), namely $F(JK)$, represents what may be called the centrifugal distortion of the molecule. It is small, depends principally upon quartic combinations of the quantum numbers J and K and is in first approximation independent of the vibrational state; hence no superscript s or a is necessary. $F(JK)$ has been calculated by Slawsky and Dennison.[5] Recently Foley and Randall[6] have measured under high dispersion lines of the pure rotation spectrum of ammonia. They were thus able to determine $F(J,K)-F(J-1,K)$ experimentally and their results are in almost perfect agreement with the calculated formula, particularly when the new values of the molecular force constants[1] are used.

$$F(J,K) - F(J-1,K) = -0.00294J^3 + 0.00279JK^2. \quad (2)$$

The frequencies of the lines constituting a parallel type band may be written out easily from the energy expression Eq. (1). For example, the positive branch lines of the band corresponding to the change $0_s \rightarrow 1_a$ in the vibrational number are given by

$$\nu_{1,a,J,K}^{0,s,J-1,K} = (W_1{}^a - W_0{}^s)/hc + (A_1{}^a + A_0{}^s)J + (A_1{}^a - A_0{}^s)J^2 + (C_1{}^a - C_0{}^s - A_1{}^a + A_0{}^s)K^2 + F(J,K) - F(J-1,K). \quad (3)$$

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[2] E. B. Wilson and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

[3] W. H. Shaffer, J. Chem. Phys. **9**, 607 (1941).

[4] In the case of the perpendicular frequencies there occur additional terms due to the Coriolis forces.

[5] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939).

[6] H. M. Foley and H. M. Randall, Phys. Rev. **59**, 171 (1941).

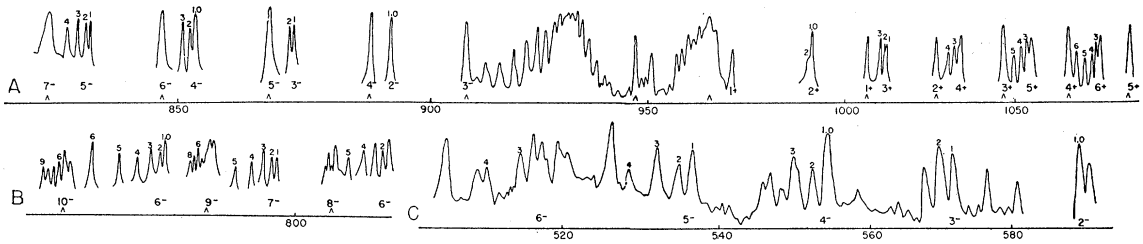

FIG. 1. Curves A and B: The double 10μ band with partially resolved Q branches. The $0_s \rightarrow 1_a$ component with center at 968.08 cm^{-1} is marked Λ. Center of the $0_a \rightarrow 1_s$ band lies at 931.58 cm^{-1}. Curve C: A part of the P branch of the 16μ band $1_a \rightarrow 2_s$.

Thus the fact that the quantities A and C are functions of the vibrational state introduces a convergence in the series through the term proportional to J^2. Moreover since K may take on the values, 0, 1, $\cdots$, $J-1$, each line which was formerly single will be split into a multiplet of J components. The spacing of the lines in a multiplet will be quadratic. Since, as has been pointed out, the A and C depend upon whether the superscript is s or a, the convergence and the multiplet spacing of the complementary vibrational band $0_a \rightarrow 1_s$ may be very different from that of the band $0_s \rightarrow 1_a$. The intensities of lines in a multiplet are interesting. Because of the proton spin, when K is a multiple of three the line in question is enhanced by the factor two. The state where $K=0$, J is even and the vibration superscript is s does not exist and consequently lines involving a transition to it are absent. Likewise, states where $K=0$, J is odd and the superscript is a do not occur.

The bands which have been chosen for the present investigation are the long wave parallel bands corresponding to the following changes in the vibrational quantum number V_3, $0_s \rightarrow 1_a$, $0_a \rightarrow 1_s$ and $1_a \rightarrow 2_s$. The first two bands lie at about 10μ while the third has its center at about 16μ. The next section describes the experimental procedure and results, and shows that the observed lines may be adequately represented by means of a formula of the type of Eq. (3). In the last section an attempt is made to calculate $(A_V{}^a - A_V{}^s)$ and $(C_V{}^a - C_V{}^s)$ theoretically.

EXPERIMENTAL[7]

The spectrometer employed for these observations has already been described.[8] For the 10μ band an absorption cell 12 cm long with KBr windows was found convenient. The gas pressures ranged from 2 to 5 cm. The resolving power was about 1000 with the slit widths used (about 0.45 mm, corresponding to 0.35 cm^{-1}). For the weaker 16μ band, a cell having an absorption path of two meters was available. Because of its small aperture much wider slits (about 0.9 mm) were necessary, and the resolving power was somewhat less.

The results are shown in Fig. 1. The upper curve is the double 10μ band, its high frequency component, namely $0_s \rightarrow 1_a$, being indicated with Λ. The lower curve is the negative or P branch of the 16μ band ($1_a \rightarrow 2_s$ transition). It is considerably obstructed by many water lines. The positive or R branch of this band is not accessible on account of the strong absorption of atmospheric CO_2. The numbers below the lines in the figure are the initial J values, and those above the lines are the K values. The line frequencies, measured in wave numbers reduced to vacuum, are given in Table I.

A study of Fig. 1 reveals that the 10μ band possesses all the qualitative features predicted by Eq. (3). The lines of this parallel type band are clearly multiple and the multiplet spacing is very different for the band $0_a \rightarrow 1_s$, where it is large, and for the band $0_s \rightarrow 1_a$ where it is so small as to be observable only in the lines of higher ordinal number. The enhancement of the lines where K is a multiple of three is also clear, but the absence of half of the lines where $K=0$ is less apparent since the resolution of the spec-

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[7] During the spring of 1936, Dr. M. V. Migeotte working in this laboratory mapped a part of the positive branch of the 10μ band, and was able to resolve the fine structure of a number of the lines. His results were in substantial agreement with those we have obtained. We wish to acknowledge his priority in resolving this portion of the band, and to thank him for allowing us to examine his measurements.

[8] J. D. Hardy, Phys. Rev. **38**, 2162 (1931).

trometer is not sufficient to distinguish between the lines $K=0$ and $K=1$. However, a study of the positions of the lines shows without question that the theoretically predicted missing lines are indeed absent. Specifically, the separation between the line $K=2$ and the first line of the multiplet, which is either the single line $K=1$ or the merged line of $K=0$ and $K=1$, is systematically larger in the latter case.

The quantitative treatment of the data is not difficult. It is desired to show (a) whether the energy levels may be expressed in the form given by Eq. (1), and (b) to evaluate the constants $A_V{}^s$, $A_V{}^a$, $C_V{}^s$ and $C_V{}^a$. The first step is to eliminate the centrifugal distortion term $F(JK)$. This may be done by subtracting the numerical values given by formula (2) from the observed line positions of the positive branch and adding them to the line positions of the negative branch. One thus obtains lines corresponding to a fictitious molecule which possesses a vibration rotation energy expression in which the centrifugal distortion term $F(JK)$ has been omitted. The second step is to use the combination relation to obtain the difference in energy between two states of the molecule having the same vibrational excitation, 1_s or 1_a, the same K but with values of J differing by two units. From these $2A_1{}^s$ or $2A_1{}^a$ are found by dividing by $(2J+1)$. The results of this procedure are shown in Table II. Note that in the case of the band $0_s \rightarrow 1_a$, which determines $2A_1{}^a$, the multiplet spacing is so small that up to $J=6$ the lines are observed as single. It is seen that the various determinations of $2A_1{}^a$ and $2A_1{}^s$ are quite consistent although the last figure in the average values is no doubt meaningless.

TABLE I. *Observed positions of lines in the bands at 10μ and 16μ.*

	R BRANCH			*P* BRANCH		
TRANSITION	*J*	*K*	ν_{vac}	*J*	*K*	ν_{vac}
$0_a \rightarrow 1_s$	5→6	3	1053.11	2→1	0,1	892.05
		4	1051.42	3→2	1	872.52
	4→5	3	1032.05		2	871.70
	3→4	1	1013.06	4→3	0,1	853.66
		2	1012.47		2	852.70
	2→3	0,1	992.55		3	851.30
				5→4	1	834.73
					2	833.96
					3	832.61
					4	830.60
				6→5	0,1	816.48
					2	815.55
					3	814.13
					4	812.53
					5	809.68
$0_s \rightarrow 1_a$	5→6		1084.59	1→0		948.21
	4→5		1065.49	3→2		908.15
	3→4		1046.34	4→3		887.93
	1→2		1007.51	5→4		867.80
				9→8	6	783.39
					7	782.75
					8	782.14
				10→9	6	763.55
					7	762.87
					9	761.35
$1_a \rightarrow 2_s$	2→1	0,1	590.32	5→4	1	536.14
	3→2	1	571.41		2	534.74
	4→3	0,1	553.96		3	531.99
		2	551.93		4	528.49
				6→5	3	515.38

TABLE II. *Values of constants* A_1.

J	*K*	$2A_1{}^s$	*J*	$2A_1{}^a$
5→6, 5→4	3	20.111	5→6, 5→4	19.780
	4	20.121	4→5, 4→3	19.772
4→5, 4→3	3	20.120	3→4, 3→2	19.773
3→4, 3→2	1	20.113	1→2, 1→0	19.773
	2	20.137		
2→3, 2→1	0,1	20.116	Average	19.774
	Average	20.120		

In a similar way the combination relations may be used to determine the $2A_0{}^s$ and $2A_0{}^a$; these are given in Table III.

The spacings of the lines composing a given multiplet furnish the means of determining such quantities as $(C_1{}^s - C_0{}^a - A_1{}^s + A_0{}^a)$. The procedure of course is to divide by $2K+1$ the interval between two lines having the same J but with K values differing by unity. The results appear in Table IV.

For the 16μ band which corresponds to the vibrational transition $1_a \rightarrow 2_s$, it is not possible to use combination relations since only one branch could be measured experimentally. However, since the energies of the 1_a levels are known, those of the 2_s levels may be found. From them the following numerical values are obtained:

$$2A_2{}^s = 20.36,$$
$$C_2{}^s - C_1{}^a - A_2{}^s + A_1{}^a = -0.50.$$

Finally the centers of each of the three bands may be located with considerable precision. The interval between the ground levels 0_s and 0_a is taken from observations of Wright and Randall.[9]

$$W_0{}^s/hc = 0,$$
$$W_0{}^a/hc = 0.66,$$
$$W_1{}^s/hc = 932.24,$$
$$W_1{}^a/hc = 968.08,$$
$$W_2{}^s/hc = 1597.4.$$

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[9] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

TABLE III. *Values of constants A_0.*

J	K	$2A_0^a$	J	$2A_0^s$
6→5, 4→5	3	19.876	5→4, 3→4	19.887
5→4, 3→4	1	19.873	3→2, 1→2	19.890
	2	19.884		
4→3, 2→3	0,1	19.877	Average	19.888
	Average	19.877		

It will appear in the next section that certain combinations of A and C are susceptible of theoretical estimation. For convenience we list these below. The data do not seem to warrant the retention of more than two significant figures.

$$A_0{}^a-A_0{}^s=-0.00_5,$$
$$A_1{}^a-A_1{}^s=-0.17,$$
$$(C_1{}^a-C_0{}^s-A_1{}^a+A_0{}^s)-(C_1{}^s-C_0{}^a-A_1{}^s+A_0{}^a)$$
$$=0.23\cong(C_1{}^a-C_1{}^s)-(A_1{}^a-A_1{}^s).$$

In the next section it will be shown that there are theoretical arguments for supposing that both $A_0{}^a-A_0{}^s$ and $C_0{}^a-C_0{}^s$ are small. Experimentally $A_0{}^a-A_0{}^s$ is indeed small and it is safe to conclude that $C_0{}^a-C_0{}^s$ is also negligible. Hence the approximation in the last equation is probably quite good and $C_1{}^a-C_1{}^s=+0.06$.

The experimental data and their analysis appear to be very satisfactory. The consistency shown in Tables II, III, and IV demonstrates that these vibration rotation energy levels of the ammonia molecule may be expressed by a formula of the type of Eq. (1). Moreover the qualitative predictions regarding the effect of centrifugal forces upon the rotational constants A and C are verified since $A_1{}^a-A_1{}^s$ is observed to be negative, whereas $C_1{}^a-C_1{}^s$ is positive.

DISCUSSION

In considering the interaction between vibration and rotation it is best to divide the effects into two classes: (a) the effects which are independent of the double minimum nature of the potential energy, and (b) effects which may be attributed solely to the double minimum potential. Of these, the former will determine the average values of A and C (averaged over the two levels caused by the double minimum), that is, $\frac{1}{2}(A_V{}^s+A_V{}^a)$ and $\frac{1}{2}(C_V{}^s+C_V{}^a)$. The latter will fix the interval between the two levels of any pair resulting from the double minimum. From Eq. (1), this separation, $\Delta\nu$, is given by

$$\Delta\nu/hc=(W_V{}^a-W_V{}^s)/hc$$
$$+(A_V{}^a-A_V{}^s)(J^2+J-K^2)+(C_V{}^a-C_V{}^s)K^2.$$

(a) The methods of treating the vibration-rotation interactions which are independent of the double minimum potential are well known and, as already stated, have been applied in detail to the pyramidal molecule XY_3 by Shaffer.[3] They consist in developing the Wilson and Howard form of the Hamiltonian in a series of approximations and of treating each term by perturbation theory. This procedure does not distinguish between the levels s and a and consequently will describe the average values of the A and C for these levels. Shaffer finds, essentially,

$$\tfrac{1}{2}(A_V{}^s+A_V{}^a)=A_e-\sum\alpha_i(V_i+\tfrac{1}{2}d_i),$$
$$\tfrac{1}{2}(C_V{}^s+C_V{}^a)=C_e-\sum\gamma_i(V_i+\tfrac{1}{2}d_i).$$

The subscript i ranges over all the normal frequencies and the V_i are the corresponding quantum numbers. The quantities α_i and γ_i are functions of the masses, the normal frequencies and of those anharmonic terms in the potential which are cubic in the normal coordinates. There are eight of these unknown cubic constants and it is thus evident that the fine structures of at least eight of the ammonia bands must be measured before this part of the problem can be solved in detail. Before turning our attention to (b) we may remark that the average values of A_V and C_V depend essentially upon the potential function in the neighborhood of the equilibrium configuration, that is upon the region where the wave function is large. On the other hand, the doublet separation is determined by the behavior of the potential near the barrier. A study of the doublet separation is thus capable of furnishing information about the molecule at points which are distant from the equilibrium configuration.

(b) Since the Hamiltonian function proposed by Wilson and Howard is exact, it might furnish a starting point for the calculation of $A_V{}^a-A_V{}^s$ and $C_V{}^a-C_V{}^s$. It is very complicated however and the particular series development used in (a) would probably not be applicable here. Certain approximations may be made which greatly simplify the work and which appear to be well justified physically. The principal assumption is that the normal coordinate x_3 associated with the band ν_3 at 10μ, leads directly over the lowest part of the pass connecting the two equivalent equilibrium configurations of the molecule. This assumption must be very nearly true since it is known experimentally that the doublet separations for the excited states of the vibrations ν_1, ν_2 and ν_4 differ only slightly, if at all, from the doublet separation 0.66 cm^{-1} of the ground state. On the other hand, the doublet separation of the first excited state of ν_3, is 35.9 cm^{-1}, about 50 times that of the ground state. We may conclude that the motions associated with x_1, x_2 and x_4 do not lead from one equilibrium configuration to the other except by way of a very high potential barrier. This is also a plausible conclusion when the actual motions associated with these coordinates are considered.

Since the subject of our study is the doublet separation and since this depends almost wholly upon x_3 we shall ignore the remaining coordinates. The actual Hamiltonian will be approximated by one which is a function of x_3 alone, the other coordinates being given their equilibrium values, namely zero. The normal coordinate x_3 describes a deformation in which the hydrogen atoms move symmetrically with respect to the axis of the pyramid, and in first approximation the N−H bond distances are unchanged. Thus, whatever the value of x_3, the molecule retains its axial symmetry. The moments of inertia are of course functions of x_3 but the products of inertia are always zero. Under these assumptions, the Hamiltonian takes on a very simple form. We express it in terms of y rather than of x_3 where y is the actual displacement of each hydrogen relative to the nitrogen atom, taken, however, along the path of the normal coordinate x_3.

$$H=(P_\alpha{}^2+P_\beta{}^2)/2I_A+P_\gamma{}^2/2I_C+p^2/2\mu+V.$$

P_α, P_β and P_γ are the components of the total angular momentum of the system. The combinations occurring here may be diagonalized at once leading to a Hamiltonian which contains only the vibrational coordinate y and its conjugate momentum p.

$$H=p^2/2\mu+V+\hbar^2(J^2+J-K^2)/2I_A+\hbar^2K^2/2I_C.$$

It will prove convenient to rearrange the terms in the Hamiltonian; let,

$$H=p^2/2\mu+V+\delta V+W_R{}^0,$$

where $W_R{}^0$ is a constant equal to $A_e(J^2+J-K^2)+C_eK^2$ and

$$\delta V=\hbar^2(J^2+J-K^2)(1/2I_A-1/2I_A{}^0)+\hbar^2K^2(1/2I_C-1/2I_C{}^0).$$

The problem has now been brought to such a form that it differs from the usual double minimum problem in only two respects, (1) the potential is increased by δV and (2) the energy constant of the whole system is increased by $W_R{}^0$. This last point will, of course, have no effect upon the quantity to be calculated, namely the splitting of the levels caused by the double minimum potential.

This splitting has been calculated by Dennison and Uhlenbeck[10] using the W-K-B approximation.

They find

$$\Delta=2\hbar\nu/A^2,$$

where

$$A^2=\exp\left[(2/\hbar)\int_0^{y_1}[2\mu(V-E)]^{\frac{1}{2}}dy\right].$$

The origin for the coordinate y is chosen to be the equatorial plane through the nitrogen atom, that is, at the center of the barrier separating the two equilibrium positions for the hydrogens. y_1 is the first root of $V-E=0$.

In the present calculation V must be increased by δV and E by δE, the latter to take account of

TABLE IV. *Values of constants.*

J	K	$C_1{}^s-C_0{}^a-A_1{}^s+A_0{}^a$	J	K	$C_1{}^a-C_0{}^s-A_1{}^a+A_0{}^s$
6→5	4	−0.300	10→9	7	−0.020
	3	−0.213		8	−0.024
	2	−0.266	9→8	7	−0.016
	1	−0.240		6	−0.024
5→4	3	−0.273			
	2	−0.256		Average	−0.021
	1	−0.243			
4→3	2	−0.270			
	1	−0.251			
3→2	1	−0.266			
5→6	3	−0.258			
3→4	1	−0.210			
	Average	−0.254			

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[10] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932).

the fact that the average of the levels s and a may be slightly shifted by δV. A^2 can be developed since δV is small. Thus $\Delta+\delta\Delta=2\hbar\nu/A^2$ and

$$A^2=\exp\left[(2/\hbar)\int_0^{y_1+\delta y_1}[2\mu(V+\delta V-E-\delta E]^{\frac{1}{2}}dy\right]$$

$$=\exp(2/\hbar)\left[\int_0^{y_1}[2\mu(V-E)]^{\frac{1}{2}}dy\right.$$

$$+\int_0^{y_1}\mu(\delta V-\delta E)[2\mu(V-E)]^{-\frac{1}{2}}dy$$

$$\left.+\tfrac{1}{2}[2\mu(\delta V-\delta E)]^{\frac{1}{2}}_{y=y_1}\delta y_1\right].$$

The first term in this exponent gives Δ while the next two determine $\delta\Delta$. The third term may be expected to be negligible in comparison with the second since the integrand is so small in the region y_1 to $y_1+\delta y_1$. A numerical calculation indicates that it contributes less than one percent to $\delta\Delta$ and consequently we shall ignore it. If we assume that $\delta\Delta$ is small, the exponential may be developed[11] and we obtain,

$$\delta\Delta=-(2\Delta/\hbar)\int_0^{y_1}\mu(\delta V-\delta E)[2\mu(V-E)]^{-\frac{1}{2}}dy.$$

It does not appear to be possible to evaluate this integral by any means other than numerical quadrature. We have chosen to use for V the double minimum potential proposed by Manning.[12]

$$V/hc=a\ \mathrm{sech}^4(y/2\rho)-b\ \mathrm{sech}^2(y/2\rho).$$

This function has the correct general form but there is no reason to suppose that it is the best function for describing the ammonia molecule. However, it is well known that the splitting of the levels is rather independent of the particular form of the potential. The constants obtained by Manning from the data for ammonia are $a=66{,}551$, $b=109{,}619$ and $\rho=0.04793(\hbar/c\mu)^{\frac{1}{2}}$. The mean energies E are not given directly by Manning but only the energy differences. A calculation yields as the value for the first excited state $(E_1{}^s+E_1{}^a)/2hc=-43{,}692.0$.

The quantity δV may be found by writing out the moments of inertia I_A and I_C. These will be expressed first as functions of two variables, r, the distance between a hydrogen and the nitrogen atom, and α, the angle between a N−H bond and the equatorial plane through the nitrogen.

$$I_A=[3mM/(3m+M)]r^2\sin^2\alpha+\tfrac{3}{2}mr^2\cos^2\alpha,$$
$$I_C=3mr^2\cos^2\alpha.$$

The motion corresponding to the frequency ν_3 is, to a high degree of approximation, one in which r remains constant and α alone varies. The relationship between α and y is then, $\alpha=\alpha_0 y/y_0$ where y_0 is the distance along the arc from the equatorial plane to the equilibrium position and α_0 is the equilibrium value of the angle. From previous work[1] these are known to be, 0.386×10^{-8} cm and 21° 49.7′, respectively. Actually the assumption that r is a constant is not quite justified and will be modified later. It is very instructive, however, to carry out the computation under this assumption and that will be done first. δV is then determined as a function of y and the only quantity not yet discussed is δE. δE is the change in the average position of the levels s and a caused by the rotation. Since this change, for example the term $\frac{1}{2}(A_{V^s}+A_{V^a})-A_e$, is proportional to $V+\frac{1}{2}$, it is evident that for the first excited state,

$$\delta E/hc=\tfrac{3}{2}[\tfrac{1}{2}(A_1{}^s+A_1{}^a)-\tfrac{1}{2}(A_0{}^s+A_0{}^a)]$$
$$\times(J^2+J-K^2)+\tfrac{3}{2}[\tfrac{1}{2}(C_1{}^s+C_1{}^a)$$
$$-\tfrac{1}{2}(C_0{}^s+C_0{}^a)]K^2.$$

Introducing the observed values we obtain,

$$\delta E/hc=0.05(J^2+J-K^2)-0.16K^2.$$

The contribution due to δE turns out to be $\delta\Delta/hc=0.007(J^2+J)-0.029K^2$, which is considerably smaller than that due to δV.

The numerical evaluation of the integral determining $\delta\Delta$ for the first excited state is not difficult. Near the point $y=y_1$ the integrand becomes infinite but this portion could be ob-

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[11] The approximation of developing the exponential is only justified as long as the integral occurring in the exponent is small compared with unity. A substitution of the numerical values to be obtained later shows that this is true for the lines actually used in the analysis. For lines of large ordinal numbers where the multiplet spacings are correspondingly large, this will no longer be the case and it is probable that the energy levels cannot be expressed in the form of Eq. (1).

[12] M. F. Manning, J. Chem. Phys. 3, 136 (1935).

tained through an exact integration where, however, the potential was approximated by a straight line. Multiplying the integral by the observed splitting in the absence of rotational interaction, namely $\Delta/hc=35.8$ we find,

$$\delta\Delta/hc=-0.105(J^2+J)+0.194K^2.$$

It will be recalled that the observed change of splitting is

$$(\delta\Delta/hc)_{\text{obs}}=-0.17(J^2+J)+0.23K^2.$$

Clearly this first theoretical estimate of $\delta\Delta$ is only moderately satisfactory. It was based upon the assumption that the distance r between each hydrogen and the nitrogen atom remains constant throughout the motion. This point may now be reexamined. The normal coordinate treatment of the problem yields not only the frequencies but also the motion associated with each frequency. Thus it is easy to show from the normal frequency determinant that, in the motion ν_3, the hydrogen atoms oscillate along lines which make an angle β_0 with the symmetry axis of the pyramid where

$$\cot\beta_0=\sqrt{3}(m\lambda_3-b)/c.$$

The quantities b and c are potential constants the latest values of which are given in reference 1. A substitution yields $\beta_0=16°\,7.2'$. The lines along which the hydrogens would travel under the assumption that r remains constant are easily found from the known equilibrium configuration of the ammonia molecule. These lines make an angle $\alpha_0=21°\,49.7'$ with the axis of the pyramid.

Thus as the hydrogen atoms move toward the equatorial plane through the nitrogen, the distance r *decreases* and at such a rate that the angle between the line along which they move and the line perpendicular to the N–H bond is $\alpha_0-\beta_0=5°\,42.5'=0.10$ radian. If this motion were to continue from the equilibrium position all the way to the equatorial plane r should be set equal to

$$r_0[1-0.10(\alpha_0-\alpha)]\cong r_0[1-0.10\alpha_0(1-y/y_0)].$$

This last approximation depends upon the fact that the distance along the actual path is very nearly equal to the distance along the arc for such a small angle $\alpha_0-\beta_0$.

The spiral path postulated for the hydrogen particles has one unsatisfactory feature, namely that it makes an inward cusp at the equatorial plane. This may be eliminated by adding a further term to the expression for r; let,

$$r=r_0[1-0.10(\alpha_0-\alpha)+(0.05/\alpha_0)(\alpha_0-\alpha)^2]$$
$$\cong r_0[1-0.05\alpha_0+0.05\alpha_0(y/y_0)^2].$$

This function satisfies the condition imposed by the normal coordinate treatment, namely $(dr/d\alpha)_{\alpha=\alpha_0}=0.10$, and has no cusp at the equatorial plane since $(dr/d\alpha)_{\alpha=0}=0$. We are well aware that very little reliance can be placed upon this estimate for r. It must be emphasized that the normal coordinate treatment can only give information concerning the displacements near the equilibrium configuration. Our function contains this information and is otherwise merely plausible.

The integral determining $\delta\Delta$ may now be recomputed. It yields the result,

$$(\delta\Delta/hc)_{\text{theo}}=-0.162(J^2+J)+0.222K^2.$$

The agreement between $(\delta\Delta)_{\text{theo}}$ and $(\delta\Delta)_{\text{obs}}$ is almost perfect and some remarks should be made concerning its significance. The change in the splitting of the levels is an effect which depends upon the potential energy function of the molecule at some distance from the equilibrium configuration, namely in the region near the potential barrier. From the motion near the equilibrium configuration we have estimated the manner in which the molecule most easily passes from one equilibrium position to the other, that is, we have estimated the distance r as a function of α. This estimate was admittedly very rough but the fact that it leads to a correct value of $\delta\Delta$, indicates that it must be of the correct order of magnitude.

The agreement may be interpreted as furnishing information on the trustworthiness of the potential constants which have been used. It will be recalled that these were obtained[1] from estimates of the normal frequencies of the ammonia molecule and not, as in the usual procedure, from the positions of the fundamental bands. This latter method was employed by Slawsky and Dennison and led to rather different values for the constants. A substitution of the older constants yields the angle $\beta_0 = 28° 40'$ and thus would predict that as the hydrogens approach the equatorial plane, the distance r *increases.* This result would have destroyed the agreement between the calculated and observed separation of the double minimum levels. One further point may be noted. If the potential of the ammonia molecule was of the valence type and contained no cross product term between the change in the valence angles and the change in valence distance, the angle β_0 may be computed readily and is $22° 1'$. This also predicts an increase of r, although only a slight one, as the hydrogens approach the plane and consequently would not lead to the very satisfactory agreement which we have obtained.

The change in the splitting of the ground level may be calculated in a similar fashion. It will be considerably smaller, partly because the integral is smaller but principally because the splitting itself $\Delta_0/hc = 0.66$ is so small. We find

$$A_0{}^a - A_0{}^s = -0.0011,$$
$$C_0{}^a - C_0{}^s = 0.0005.$$

The first of these values was determined experimentally and found to be $A_0{}^a - A_0{}^s = -0.00_5$. The agreement is satisfactory although not very significant.

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The Vibration-Rotation Energies of Polyatomic Molecules

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The quantum-mechanical Hamiltonian function, H, for the general vibrating-rotating polyatomic molecule of N atoms has been expanded by the method of Wilson and Howard to second order of approximation. It has been practicable to obtain solutions of the Schrödinger equation $(H-E)\psi = 0$ for asymmetric molecules, axially symmetric molecules and linear molecules. Expressions for the anharmonic terms occurring in the vibration energy, the effective moments of inertia, the amplitudes of the internal angular momentum of oscillation and the centrifugal distortion coefficients are derived so that when the normal coordinates are known the vibration-rotation energies of a polyatomic molecule may be calculated from the results given. Tetrahedrally symmetric molecules and models in which internal rotation occurs are regarded as anomalous cases and are not treated.

I. INTRODUCTION

RECENTLY a number of papers have appeared in which the form of the vibration-rotation energies of certain polyatomic molecular models[1] have been derived to a second order of approximation. The method followed has in each instance been equivalent to that delineated by Wilson and Howard,[2] although the details have varied slightly from case to case. The method consists essentially in approximating by the method of the perturbation theory to three items, namely: the energy of the atomic nuclei oscillating anharmonically about their positions of equilibrium in a set of body-fixed coordinates; the effective moments of inertia of the molecule regarded as a semi-rigid rotator and the distortion of the molecular energies due to the centrifugal forces.

An inspection of the final results in these papers reveals that they are nearly always of the same form. Thus, for example, the oscillational energy always consists of a set of terms linear in the

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[1] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933); W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939); W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 895 (1939); W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 1051 (1939); B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940); Ta-You Wu, J. Chem. Phys. **8**, 489 (1940); S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941); W. H. Shaffer, J. Chem. Phys. **9**, 607 (1941); W. H. Shaffer and A. H. Nielsen, J. Chem. Phys. **9**, 847 (1941).

[2] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 262 (1936).