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Inversion-Vibration and Inversion-Rotation Interactions in the Ammonia Molecule*

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An attempt has been made to extend the theory of ammonia inversion in order to account for the dependence of the inversion splitting on the full set of vibrational and rotational quantum numbers. The potential energy of ammonia is approximated by a double minimum potential $V(\zeta)$ plus the potential of a system of harmonic oscillators in the remaining five vibrational coordinates. $V(\zeta)$ has been chosen to have the form $V(\zeta) = -2F \cos(\zeta/L) + 2G \cos(2\zeta/L)$ in which ζ is an inversion coordinate and L a constant, $(|\zeta| \leqq \pi L)$. The double minimum wave functions are computed numerically. Inversion-vibration interactions are obtained by developing the parameters F and G, which are regarded as mild functions of the five vibrational coordinates, in a Taylor expansion in the vibrational coordinates. With the exception of the state $2\nu_4{}^0$ this potential accounts for the dependence of the inversion splittings on the vibrational quantum numbers of the two doubly degenerate modes ν_3 and ν_4 (eleven experimental data are fitted with four empirical interaction constants). However, the potential fails to describe completely the interaction between the inversion coordinate and the remaining nondegenerate vibrational coordinate associated with ν_1. Since the task of diagonalizing the complete rotation-inversion Hamiltonian is complicated by the presence of several resonances, the rotation-inversion constants $B^- - B^+$ and $C^- - C^+$ are calculated only from the lowest order vibration-rotation-inversion Hamiltonian. The calculated constants for the pure inversion states $n_2 = 0, 1, 2,$ and 3 and the states $n_2 = 1$ in combination with the remaining vibrational modes agree surprisingly well with the experimentally observed values.

I. INTRODUCTION

Recent investigations of the ammonia spectrum by Benedict *et al.* (*1–4*) and by Garing *et al.* (*5*) have uncovered a wealth of new data revealing the dependence of the inversion splitting on the complete set of vibrational and rotational quantum numbers. In the past, theories of ammonia inversion have aimed at predicting the dependence of the splitting on the quantum number n_2 asso-

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TABLE I

INVERSION SPLITTING IN NH_3 (cm^{-1})

$$\Delta_n = \Delta_n^0 + (B_n^- - B_n^+)[J(J+1) - K^2] + (C_n^- - C_n^+)K^2$$

$n_1 n_2^{\pm} n_3^{l_3} n_4^{l_4}$	Δ_n^0	$B_n^- - B_n^+$	$C_n^- - C_n^+$
$0\ 0\ 0^0\ 0^0$	0.793	−0.005054	0.001998
$0\ 1\ 0^0\ 0^0$	35.81	−0.1817	0.0721
$0\ 2\ 0^0\ 0^0$	284.74	−0.535	0.231
$0\ 3\ 0^0\ 0^0$	512.02	−0.3041	0.1034
$0\ 0\ 1^1\ 0^0$	0.35	−0.0036	0.0007
$0\ 0\ 2^2\ 0^0$	0.43		
$0\ 0\ 0^0\ 1^1$	1.01	0.048	0.011
$0\ 0\ 0^0\ 2^0$	2.24		
$0\ 0\ 0^0\ 2^2$	1.42		
$0\ 0\ 1^1\ 1^1$	0.57		
$1\ 0\ 0^0\ 0^0$	0.99	−0.012	0.003
$1\ 0\ 0^0\ 1^1$	0.86		
$0\ 1\ 1^1\ 0^0$	18.49	−0.0984	0.0429
$0\ 1\ 0^0\ 1^1$	45.4	−0.191	0.097
$0\ 1\ 1^1\ 1^1$	23.68	−0.130	0.054
$1\ 1\ 0^0\ 0^0$	25.55	−0.1265	0.0470

ciated with the mode in which the pyramid height changes most drastically (*6–9*). In this paper an attempt is made to extend the theory to include the dependence of the inversion splitting on the full set of vibrational and rotational quantum numbers n_1, $n_2^{\pm}$, $n_3^{l_3}$, $n_4^{l_4}$, J, and K, where the designation of quantum numbers is that of Benedict *et al.* (*1*).

The currently available data on the inversion splitting in NH_3 are summarized in Table I. Although the inversion splitting depends mainly on the quantum number n_2, it is clear that it also exhibits a significant dependence on the remaining vibrational quantum numbers n_1, $n_3^{l_3}$, and $n_4^{l_4}$. This leads immediately to the conclusion that there must exist interactions between the inversion coordinate and the remaining vibrational coordinates. In the present paper a scheme is proposed for describing and evaluating these interactions. The potential energy function for ammonia is represented, in lowest approximation, by a double minimum potential involving the inversion coordinate plus the potential of a system of uncoupled harmonic oscillators involving the five remaining vibrational coordinates.[1] Interactions are obtained by interpreting the parameters occurring in the double minimum potential as mild functions of the remaining vibrational coordinates through the use of a Taylor series expansion. In a similar fashion the vibration-rotation interactions affecting the inversion splitting have

[1] By treating the remaining degrees of vibrational freedom by means of uncoupled harmonic oscillators, the usual anharmonicities involving *only these* degrees of freedom are ignored. Although these are important for a complete description of the spectrum it is felt that they will not contribute significantly to the inversion splitting.

been introduced and calculated. These lead to numerical values which can be compared with the experimental quantities $B^- - B^+$ and $C^- - C^+$.

II. INTERNAL COORDINATES AND THE VIBRATIONAL KINETIC ENERGY

As a method of specifying a set of internal coordinates for ammonia it is convenient to start with a Cartesian reference frame fixed in space and with origin at the center of mass of the molecule as shown in Fig. 1. Let x_i, y_i, and z_i be the Cartesian coordinates of the ith atom with respect to this reference frame. The subscripts $i = 1, 2$, and 3 refer to hydrogen atoms and $i = 4$ to the nitrogen atom. In either of the two equilibrium configurations of the molecule the nitrogen atom lies on the z-axis and the number three hydrogen atom is chosen to lie in the $y - z$ plane. The twelve Cartesian coordinates of the four atoms can be replaced by six internal coordinates u_i $(i = 1, \cdots 6)$ by means of the following scheme where m is the mass of a hydrogen atom and M the mass of the nitrogen atom.

$$
\begin{aligned}
x_1 &= -\frac{\sqrt{3}}{2}u_1 - \frac{\sqrt{3}}{2}u_3 - \frac{1}{2}u_4 - \frac{M}{M+3m}u_6, \\
y_1 &= -\frac{1}{2}u_1 + \frac{1}{2}u_3 - \frac{\sqrt{3}}{2}u_4 - \frac{M}{M+3m}u_5, \\
z_1 &= -\frac{M}{M+3m}\left[u_2 + \left(\frac{u_2}{u_1}\right)u_5 + \sqrt{3}\left(\frac{u_2}{u_1}\right)u_6\right], \\
x_2 &= \frac{\sqrt{3}}{2}u_1 + \frac{\sqrt{3}}{2}u_3 - \frac{1}{2}u_4 - \frac{M}{M+3m}u_6, \\
y_2 &= -\frac{1}{2}u_1 + \frac{1}{2}u_3 + \frac{\sqrt{3}}{2}u_4 - \frac{M}{M+3m}u_5, \\
z_2 &= -\frac{M}{M+3m}\left[u_2 + \left(\frac{u_2}{u_1}\right)u_5 - \sqrt{3}\left(\frac{u_2}{u_1}\right)u_6\right], \\
x_3 &= u_4 - \frac{M}{M+3m}u_6, \\
y_3 &= u_1 - u_3 - \frac{M}{M+3m}u_5, \\
z_3 &= -\frac{M}{M+3m}\left[u_2 - 2\left(\frac{u_2}{u_1}\right)u_5\right]. \\
x_4 &= \frac{3m}{M+3m}u_6, \\
y_4 &= \frac{3m}{M+3m}u_5, \\
z_4 &= \frac{3m}{M+3m}u_2.
\end{aligned}
\tag{1}
$$

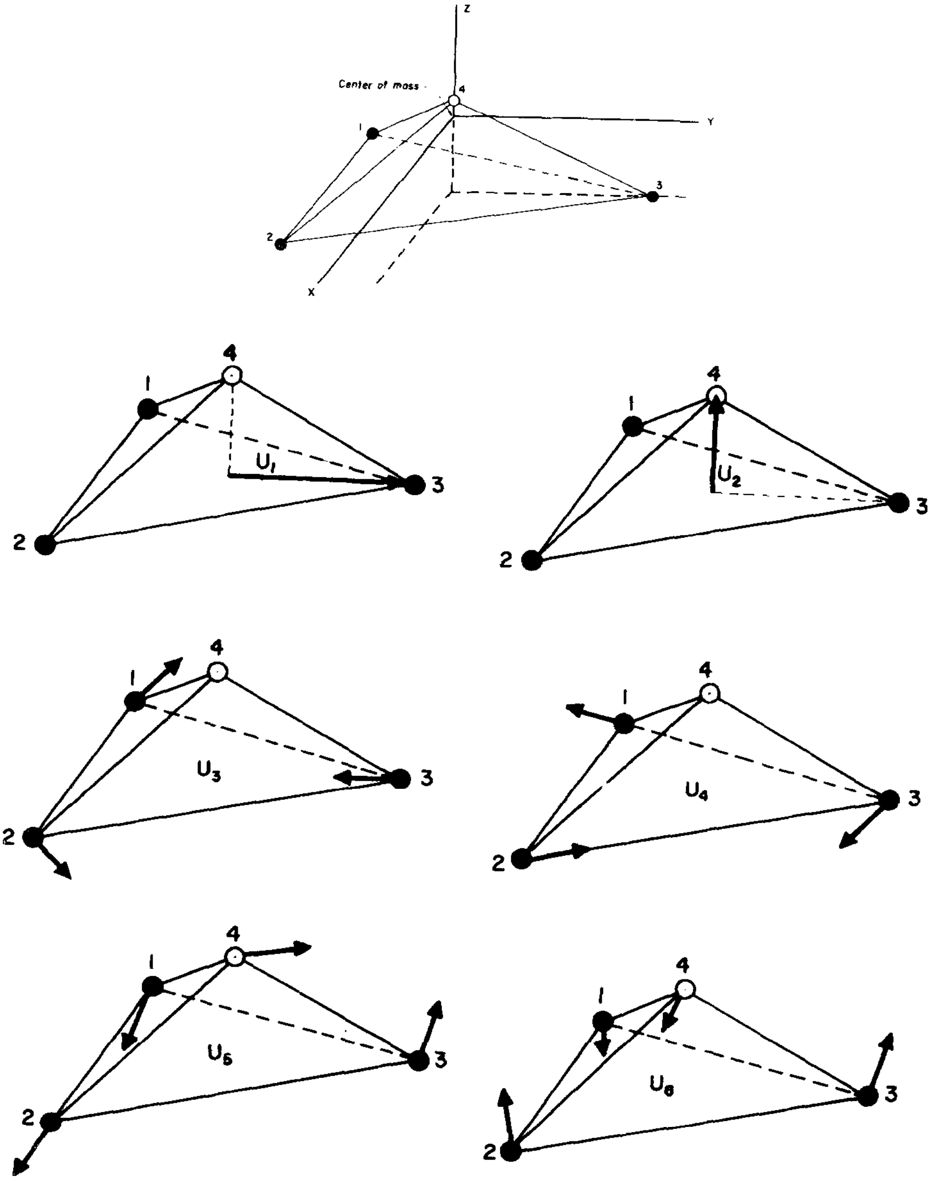

FIG. 1. The internal coordinates

To discover the physical significance of these coordinates consider first the case where $u_3 = u_4 = u_5 = u_6 = 0$. It is apparent from the equations that u_2 is equal to the height of the ammonia pyramid and u_1 equals the distance from a hydrogen atom to the center of the hydrogen triangle. All configurations that arise when $u_3 = u_4 = u_5 = u_6 = 0$ have pyramidal symmetry. That is, the hydrogen atoms form an equilateral triangle and the three N—H bond lengths are equal. On the other hand, the coordinates u_3, u_4, u_5, and u_6 relate to deviations from pyramidal symmetry. The coordinates u_3 and u_4 describe a configuration in which the nitrogen atom remains stationary and the hydrogen atoms undergo displacements parallel to the $x - y$ plane. u_5, however, involves a displacement of the nitrogen atom parallel to the y-axis with a corresponding tipping of the hydrogen triangle while u_6 represents a displacement of the nitrogen atom parallel to the x-axis again with a tipping of the hydrogen triangle. For both u_5 and u_6 all the H—H distances remain invariant.

The two equilibrium configurations are given by

$$u_1 = u_1^0, \qquad u_2 = \pm u_2^0, \qquad u_3 = u_4 = u_5 = u_6 = 0,$$

wherewhere u_1^0 and u_2^0 are approximately 0.94×10^{-8} and 0.38×10^{-8} cm, respectively. Inversion of the molecule through a plane passing through the center of mass and perpendicular to the symmetry axis is accomplished by means of the transformation

$$u_2 \to -u_2, \qquad u_i \to u_i \qquad (i \neq 2).$$

The internal coordinates have been chosen in such a way that for all values of the coordinates and their time derivatives the linear momentum of the molecule remains zero. The angular momentum also remains exactly zero for all motions in which the molecule retains pyramidal symmetry, that is, where $u_3 = u_4 = u_5 = u_6 = 0$, but for all values of u_1 and u_2. For those motions however in which the pyramidal symmetry is destroyed, there will exist small terms in the angular momentum.

A simple calculation yields the vibrational kinetic energy

$$\begin{aligned} T_{\text{vib}} = \frac{1}{2}\Big\{ & 3m\dot{u}_1^2 + \mu\dot{u}_2^2 + 3m(\dot{u}_3^2 + \dot{u}_4^2) \\ & + \mu\rho(u_1, u_2)(\dot{u}_5^2 + \dot{u}_6^2) + \frac{4\mu^2}{3m}(u_5\dot{u}_5 + u_6\dot{u}_6)\frac{u_2}{u_1}\frac{d}{dt}\left(\frac{u_2}{u_1}\right) \\ & + \frac{2\mu^2}{3m}(u_5^2 + u_6^2)\left[\frac{d}{dt}\left(\frac{u_2}{u_1}\right)\right]^2\Big\}, \end{aligned} \tag{2}$$

where $\mu = 3mM/M + 3m$ and $\rho(u_1, u_2) = [1 + (2\mu/3m)(u_2/u_1)^2]$. The symmetry of the coordinates is such that the leading terms in the Taylor expansion of the potential function about an equilibrium configuration would be

$$\begin{aligned} V = \tfrac{1}{2}\{ & 3b(u_1 - u_1^0)^2 + 2\sqrt{3}c(u_1 - u_1^0)(u_2 - u_2^0) + a(u_2 - u_2^0)^2 \\ & + 3\beta(u_3^2 + u_4^2) + 2\sqrt{3}\gamma\rho_0(u_3u_5 + u_4u_6) + \alpha\rho_0^2(u_5^2 + u_6^2) + \cdots\}, \end{aligned} \tag{3}$$

where $\rho_0 = [1 + (2\mu/3m)(u_2^0/u_1^0)^2]$, and where the force constants a, b, c, α, β, and γ, defined previously by Dennison (*10*), have been used.

It will now prove convenient to replace the coordinates u_3, u_4, u_5, and u_6 by a new set of internal coordinates Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y} defined by

$$\begin{aligned} Q_{3x} &= \cos\tau(3m)^{1/2}u_4 + \sin\tau[\mu\rho(u_1, u_2)]^{1/2}u_6, \\ Q_{4x} &= -\sin\tau(3m)^{1/2}u_4 + \cos\tau[u\rho(u_1, u_2)]^{1/2}u_6, \\ Q_{3y} &= \cos\tau(3m)^{1/2}u_3 + \sin\tau[\mu\rho(u_1, u_2)]^{1/2}u_5, \\ Q_{4y} &= -\sin\tau(3m)^{1/2}u_3 + \cos\tau[\mu\rho(u_1, u_2)]^{1/2}u_5, \end{aligned} \tag{4}$$

where

$$\cos 2\tau = \left(\frac{\beta}{m} - \frac{\alpha\rho_0}{\mu}\right)\left[\left(\frac{\beta}{m} - \frac{\alpha\rho_0}{\mu}\right)^2 + \frac{4\gamma^2\rho_0}{m\mu}\right]^{-1/2}. \tag{5}$$

The coordinates Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y} are defined in such a way that, in the vicinity of the equilibrium configurations, they become the normal coordinates describing the perpendicular vibrations. Note, however, that in general they depend on the two axially symmetric coordinates u_1 and u_2. Finally, the coordinates u_1 and u_2 are replaced by a pair of coordinates σ and ζ defined by

$$\begin{aligned} (3m)^{1/2}u_1 &= a_0 \sinh\sigma\cos\zeta, \\ (\mu)^{1/2}u_2 &= a_0\cosh\sigma\sin\zeta, \end{aligned} \tag{6}$$

where $a_0^2 = \mu(u_2^0)^2 - 3m(u_1^0)^2 + \sqrt{3}u_1^0\, u_2^0(\mu b - ma)/c$ and $\sigma \geqq 0$; $-\pi/2 \leqq \zeta \leqq \pi/2$. The constant a_0 has been chosen so that in the neighborhood of an equilibrium configuration $\delta\sigma = \sigma - \sigma_0$ and $\delta\zeta = \zeta - \zeta_0$ are proportional to the two symmetric normal coordinates of ammonia. In fact, it is easy to show that this choice of a_0 leads to the relations

$$\tfrac{1}{2}(3m\dot{u}_1^2 + \mu\dot{u}_2^2) = \tfrac{1}{2}a_0^2(\cosh^2\sigma_0 - \sin^2\zeta_0)(\delta\dot{\sigma}^2 + \delta\dot{\zeta}^2) \tag{7}$$

and

$$\begin{aligned} \tfrac{3}{2}b(u_1 - u_1^0)^2 + \sqrt{3}c(u_1 - u_1^0)(u_2 - u_2^0) + \tfrac{1}{2}a(u_2 - u_2^0)^2 \\ = \tfrac{1}{2}a_0^2(\cosh^2\sigma_0 - \sin^2\zeta_0)(\lambda_1\delta\sigma^2 + \lambda_2\delta\zeta^2), \end{aligned} \tag{8}$$

where

$$\left.\begin{matrix}\lambda_1\\ \lambda_2\end{matrix}\right\} = \frac{1}{2}\left(\frac{b}{m} + \frac{a}{\mu}\right) \pm \left[\frac{1}{4}\left(\frac{b}{m} - \frac{a}{\mu}\right)^2 + \frac{c^2}{\mu m}\right]^{1/2}.$$

In these equations σ_0 and $\pm\zeta_0$ are the equilibrium values of σ and ζ and describe the two equilibrium configurations of the molecule. The physical significance of σ and ζ is best seen by inverting Eq. (6). It will be recalled that u_2 is the height of the ammonia pyramid and u_1 is the distance from a hydrogen atom to the

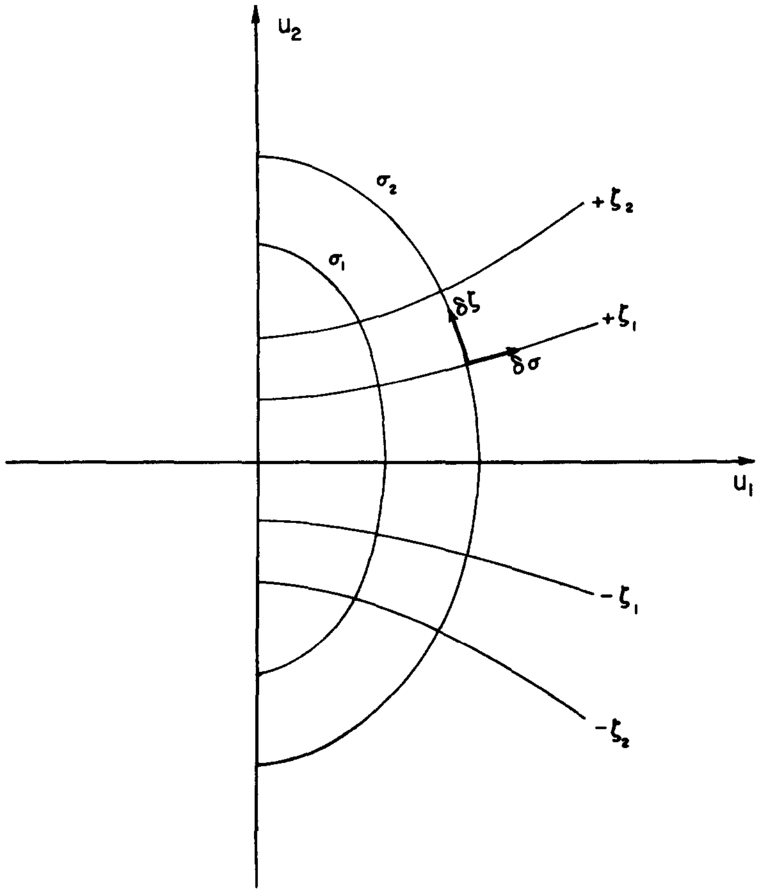

FIG. 2. The coordinates σ and ζ

center of the hydrogen triangle. One finds that the family of curves in the $u_1 - u_2$ plane with σ constant are ellipses and the family of curves with ζ constant are hyperbolas. This is illustrated in Fig. 2. The coordinate ζ may be identified as an inversion coordinate since the molecule can be inverted from one equilibrium configuration to the other by changing ζ continuously from ζ_0 to $-\zeta_0$ while keeping σ fixed at its equilibrium value σ_0.

Upon introducing the coordinates σ, ζ, Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y} into Eq. (2) one obtains for the vibrational kinetic energy

$$T_{\text{vib}} = \tfrac{1}{2}a_0^2(\cosh^2\sigma - \sin^2\zeta)(\dot{\sigma}^2 + \dot{\zeta}^2) + \tfrac{1}{2}(\dot{Q}_{3x}^2 + \dot{Q}_{3y}^2 + \dot{Q}_{4x}^2 + \dot{Q}_{4y}^2)$$
$$+ [\sin\tau\mathbf{R}_3 + \cos\tau\mathbf{R}_4]^2\cdot\left[\frac{\cosh\sigma\sinh\sigma\dot{\zeta} - \cos\zeta\sin\zeta\dot{\sigma}}{\sinh^2\sigma\cos^2\zeta + \cosh^2\sigma\sin^2\zeta}\right]^2, \tag{9}$$

where $\mathbf{R}_3$ is a vector with components Q_{3x}, Q_{3y}, and $\mathbf{R}_4$ is a vector with components Q_{4x}, Q_{4y}. So far no approximations have been made and Eq. (9) is rigorous.

III. THE POTENTIAL ENERGY AND THE VIBRATIONAL HAMILTONIAN

The present state of development of molecular theory is not sufficiently advanced to allow an *a priori* derivation of a potential function for a molecule as complex as ammonia. The best that can be done is to choose a function with plausible physical characteristics. The function must of course satisfy the symmetry requirements and should contain a number of adjustable parameters which will be determined by comparing the results of the calculation with the experimental data.

It may be remarked that, in the six-dimensional coordinate space, there exists a path connecting the two equilibrium configurations for which the potential has the smallest set of values. It may be thought of as the lowest pass over the potential mountains standing in the way of inversion. A plausible choice for this path is that ellipse for which the coordinate ζ alone varies, all other coordinates remaining zero. The double minimum character of the potential will therefore be described through a suitable function of ζ. The usual normal vibration properties of the molecule further require the presence of terms quadratic in the remaining coordinates. It will be assumed that these always remain near their equilibrium values, so that $\delta\sigma$, Q_{3x}, Q_{3y}, Q_{4x}, and Q_{4y} are small quantities. In the subsequent discussion these small oscillation coordinates will be replaced by their dimensionless counterparts q_1, q_{3x}, q_{3y}, q_{4x}, and q_{4y}, defined by

$$\begin{aligned} \delta\sigma &= [h/4\pi^2 c\omega_1 a_0^2(\cosh^2\sigma_0 - \sin^2\zeta_0)]^{1/2} q_1 , \\ Q_{i\alpha} &= (h/4\pi^2 c\omega_i)^{142} q_{i\alpha} , \qquad i = 3, 4, \quad \alpha = x, y, \end{aligned} \tag{10}$$

where these reduce to (dimensionless) normal coordinates in the vicinity of either equilibrium configuration of the molecule.

The above considerations have therefore led to choosing a potential of the following form,

$$V/hc = V_0(\zeta)/hc + \tfrac{1}{2}c_1 q_1^2 + \tfrac{1}{2}c_3(q_{3x}^2 + q_{3y}^2) + \tfrac{1}{2}c_4(q_{4x}^2 + q_{4y}^2), \tag{11}$$

where c_1, c_3, and c_4 are constants and $V_0(\zeta)$ is a double minimum potential with minima at ζ_0 and $-\zeta_0$ and a central maximum as $\zeta = 0$.

Although the inversion splitting is an extremely sensitive function of the inversion potential, the WKB treatment of ammonia inversion given by Dennison and Uhlenbeck (*6*) suggests that there may be many mathematical functions $V_0(\zeta)$ which can account, at least approximately, for the observed splitting. Practical considerations, however, limit the form of $V_0(\zeta)$ to those functions for which energy levels and wave functions can be found with reasonable ease.

A possible candidate might be the potential proposed by Manning (7). Although the energy levels for this potential are relatively easy to find the wave functions would be somewhat cumbersome to use in a perturbation calculation. In order to obtain more manageable wave functions, the double minimum potential

$$\begin{aligned} V_0(\zeta)/hc &= -2F\cos(\zeta/L) + 2G\cos(2\zeta/L) \qquad \text{for } |\zeta| \leqq \pi L \\ &= 2(F+G) \qquad\qquad\qquad\qquad\qquad \text{for } \pi L < |\zeta| \leqq \pi/2 \end{aligned} \tag{12}$$

will be used in the present investigation. In Eq. (12), F and G are positive constants such that $F \leqq 4G$ and L is a positive constant such that $L \leqq \frac{1}{2}$. This potential has a central maximum at $\zeta = 0$ and minima at $\zeta = \pm\zeta_0$ where $\cos(\zeta_0/L) = F/4G$. It has the general form to be expected of an inversion potential in the neighborhoods of ζ_0 and $-\zeta_0$ and throughout the interval $-\zeta_0 < \zeta < \zeta_0$. For $|\zeta| \gg |\zeta_0|$ it is undoubtedly a poor approximation to the true ammonia potential, but the low-lying energy levels shouod not be affected very much by the behavior of the potential at large values of $|\zeta|$.

Interactions between the inversion coordinate and the remaining vibrational coordinates are obtained by assuming that the parameters F and G are not true constants but mild functions of the coordinates q_1, q_{3x}, q_{3y}, q_{4x}, and q_{4y}. Since these coordinates represent very small oscillations it should be possible to obtain a good approximation by expanding F and G in a Taylor series and retaining only the leading terms. In principle, L could be expanded in a Taylor series also. However, an expansion of L, F, and G would yield more unknown constants than can be determined by the available data on ammonia. Thus, in practice, one of the three parameters must be regarded as a genuine constant. The argument for choosing L as the constant can be stated as follows. The inversion splitting is expected to be a very sensitive function of the potential barrier height and the separation of the potential minima. The height of the central barrier for the potential given by Eq. (12) is $4G(1 - F/4G)^2$ and is independent of L. Furthermore, the separation of the potential minima can be shown to be very insensitive to the value of L. Thus, if one of the three parameters must be regarded as a true constant then L is probably the best choice.

The form of the expansion of F and G is restricted. First, the potential must be invariant under the symmetry operations of the molecular point group. This excludes, for example, terms linear in the $q_{3\alpha}$ and $q_{4\alpha}$. Secondly, since the coordinates q_1, $(\zeta - \zeta_0)$, q_{3x}, q_{3y}, q_{4x}, and q_{4y} are proportional to normal coordinates in the vicinity of an equilibrium configuration, the full potential must satisfy the equilibrium conditions $(\partial V/\partial q_i)_0 = 0$ and must contain no cross products in the quadratic development about an equilibrium configuration. The combination of these two requirements excludes terms linear in q_1. Finally, since F and G are assumed to be mild functions, only the first significant terms in the vibrational coordinates will be retained. Out to quadratic terms the most general form of the expansion of F and G is

$$F = F_0 + F_1 q_1^2 + F_3 r_3^2 + F_4 r_4^2 + k \cos(2\zeta_0/L)\mathbf{r}_3\cdot\mathbf{r}_4 ,$$
$$G = G_0 + G_1 q_1^2 + G_3 r_3^2 + G_4 r_4^2 + k \cos(\zeta_0/L)\mathbf{r}_3\cdot\mathbf{r}_4 , \tag{13}$$

where F_0, F_1, F_3, F_4, G_0, G_1, G_3, G_4, L, and k are true constants. Here $\mathbf{r}_3$ and $\mathbf{r}_4$ are vectors with components q_{3x}, q_{3y}, and q_{4x}, q_{4y}, respectively. As a means of keeping the ensuing computations reasonably manageable the constant k will be set equal to zero although no real physical justification can be given for doing so. Thus one obtains

$$\begin{aligned} V/hc = {} & \tfrac{1}{2}c_1 q_1^2 + \tfrac{1}{2}c_3 r_3^2 + \tfrac{1}{2}c_4 r_4^2 \\ & - 2[F_0 + F_1 q_1^2 + F_3 r_3^2 + F_4 r_4^2] \cos(\zeta/L) \\ & + 2[G_0 + G_1 q_1^2 + G_3 r_3^2 + G_4 r_4^2] \cos(2\zeta/L) \end{aligned} \tag{14}$$

as a possible approximate potential energy function for the ammonia molecule. Equation (14) is, of course, a very incomplete potential function. Cubic and quartic terms could be added. However, unless the coefficients of the cubic and quartic terms are strongly dependent on the inversion coordinate ζ, they will not make appreciable contributions to the inversion splitting. Since the purpose of this investigation is to examine the inversion splitting these extra terms will not be included.

Since q_1, q_{3x}, q_{3y}, q_{4x}, and q_{4y} reduce to dimensionless normal coordinates near the equilibrium configurations, the corresponding normal frequencies can be found by evaluating the second derivatives of V/hc at an equilibrium configuration. One finds

$$\omega_i = c_i - 4F_i \cos(\zeta_0/L) + 4G_i \cos(2\zeta_0/L) \qquad i = 1, 3, 4. \tag{15}$$

Apart from an additive constant, which can be neglected, the potential function of Eq. (14) can be rewritten as

$$\begin{aligned} V/hc = {} & \tfrac{1}{2}\omega_1 q_1^2 + \tfrac{1}{2}\omega_3 r_3^2 + \tfrac{1}{2}\omega_4 r_4^2 \\ & + [2G_0' + F_0'^2/4G_0'] - 2F_0' \cos(\zeta/L) + 2G_0' \cos(2\zeta/L) \\ & + [-2F_1(\cos(\zeta/L) - \cos(\zeta_0/L) + 2G_1(\cos(2\zeta/L) \\ & \qquad - \cos(2\zeta_0/L))](q_1^2 - \tfrac{1}{2}) \\ & + [-2F_3(\cos(\zeta/L) - \cos(\zeta_0/L)) + 2G_3(\cos(2\zeta/L) \\ & \qquad - \cos(2\zeta_0/L))](r_3^2 - 1) \\ & + [-2F_4(\cos(\zeta/L) - \cos(\zeta_0/L)) + 2G_4(\cos(2\zeta/L) \\ & \qquad - \cos(2\zeta_0/L))](r_4^2 - 1), \end{aligned} \tag{16}$$

where

$$F_0' = F_0 + \tfrac{1}{2}F_1 + F_3 + F_4 ,$$
$$G_0' = G_0 + \tfrac{1}{2}G_1 + G_3 + G_4 . \tag{17}$$

It is in this form that the potential will be used in the subsequent calculations. It should be observed that this potential has minima at $\zeta = \pm\zeta_0$ and $q_1 = r_3 = r_4 = 0$ where $\cos(\zeta_0/L) = F_0/4G_0$. These correspond to the two equilibrium configurations of the molecule.

Having arrived at expressions for the kinetic and potential energies, one can set up the vibrational Hamiltonian for the molecule. Equation (9), which is a rigorous expression for the kinetic energy, is somewhat more general than is needed. Examination of this equation reveals that the term involving

$$[\sin \tau \mathbf{R}_3 + \cos \tau \mathbf{R}_4]^2$$

gives contributions to the inversion splitting of the order of $B_n^- - B_n^+$, namely of the order of 0.005 cm^{-1} for states with $n_2 = 0$, and of the order of 0.2 cm^{-1} for states with $n_2 = 1$ (see Table I). This term will be neglected in the treatment of the inversion-vibration splitting since this is of the order of 0.8 cm^{-1} in states with $n_2 = 0$ and 35 cm^{-1} in states with $n_2 = 1$. A further simplification arises from the assumption that σ never differs very much from σ_0. Thus, the vibrational kinetic energy can be approximated by

$$T_{\text{vib}} = \tfrac{1}{2}a_0^2(\cosh^2 \sigma_0 - \sin^2 \zeta)(\delta\dot{\sigma}^2 + \dot{\zeta}^2) + \tfrac{1}{2}(\dot{Q}_{3x}^2 + \dot{Q}_{3y}^2 + \dot{Q}_{4x}^2 + \dot{Q}_{4y}^2). \tag{18}$$

With the introduction of the dimensionless coordinates defined by Eq. (10) and a dimensionless inversion coordinate

$$x = \zeta/L \qquad (x_0 = \zeta_0/L), \tag{19}$$

the quantum mechanical vibrational Hamiltonian becomes

$$H_{\text{vib}} = H_{\text{vib}}^{(0)} + H_{\text{vib}}^{(1)} , \tag{20}$$

where

$$\begin{aligned} H_{\text{vib}}^{(0)}/kc = {} & \frac{\omega_1}{2}\left(-\frac{\partial^2}{\partial q_1^2} + q_1^2\right) + \frac{\omega_3}{2}\left(-\frac{\partial^2}{\partial q_{3x}^2} - \frac{\partial^2}{\partial q_{3y}^2} + r_3^2\right) \\ & + \frac{\omega_4}{2}\left(-\frac{\partial^2}{\partial q_{4x}^2} - \frac{\partial^2}{\partial q_{4y}^2} + r_4^2\right) \\ & + \left(-D\frac{\partial^2}{\partial x^2} + 2G_0' + \frac{F_0'^2}{4G_0'} - 2F_0' \cos x + 2G_0' \cos 2x\right) \end{aligned} \tag{21}$$

and

$$H_{\text{vib}}^{(1)}/hc = h_1(x)(q_1^2 - \tfrac{1}{2}) + h_3(x)(r_3^2 - 1) + h_4(x)(r_4^2 - 1)$$
$$- D\left[f_1(x)\frac{\partial^2}{\partial x^2} + f_2(x)\frac{\partial}{\partial x}\right] - \frac{\omega_1}{2} f_1(x)\left(\frac{\partial^2}{\partial q_1^2} + \frac{1}{2}\right), \tag{22}$$

where

$$h_i(x) = -2F_i(\cos x - \cos x_0) + 2G_i(\cos 2x - \cos 2x_0) \quad i = 1, 3, 4 \tag{23}$$

and

$$D = h/[8\pi^2 c a_0^2(\cosh^2\sigma_0 - \sin^2\zeta_0)L^2], \tag{24}$$

$$f_1(x) = \frac{\sin^2(Lx) - \sin^2\zeta_0}{\cosh^2\sigma_0 - \sin^2(Lx)},$$
$$f_2(x) = \frac{2L(\cosh^2\sigma_0 - \sin^2\zeta_0)\sin(Lx)\cos(Lx)}{[\cosh^2\sigma_0 - \sin^2(Lx)]^2}. \tag{25}$$

The transcription to quantum mechanics has been made in such a way that the volume element in configuration space is simply $dq_1\, dx\, dq_{3x}\, dq_{3y}\, dq_{4x}\, dq_{4y}$. It will be noted that $H_{\text{vib}}^{(0)}$ is completely separable in the various coordinates and that the inversion splitting, to this approximation, depends only upon x. $H_{\text{vib}}^{(1)}$ on the other hand, contains the interaction terms between the inversion and the other vibrational coordinates. In the calculations to follow, $H_{\text{vib}}^{(1)}$ will be treated through perturbation methods. This appears justified since the change in energy levels (as opposed to the change in inversion splitting) caused by the interactions is small compared to the values of the levels themselves.

IV. VIBRATIONAL ENERGIES OF NH_3 IN LOWEST APPROXIMATION

Consider the Schrödinger equation for the unperturbed Hamiltonian

$$H_{\text{vib}}^{(0)}\Psi_{\text{vib}}^{(0)} = E_{\text{vib}}^{(0)}\Psi_{\text{vib}}^{(0)}.$$

As just remarked, this equation is separable and gives

$$E_{\text{vib}}^{(0)}/hc = E_{n_2\pm} + \omega_1(n_1 + \tfrac{1}{2}) + \omega_3(n_3 + 1) + \omega_4(n_4 + 1), \tag{26}$$

$$\Psi_{\text{vib}}^{(0)} = \psi_{n_2\pm}(x)\psi_{n_1}(q_1)\psi_{n_3 l_3}(q_{3x}, q_{3y})\psi_{n_4 l_4}(q_{4x}, q_{4y}), \tag{27}$$

where ψ_{n_1} is a one-dimensional harmonic oscillator wave function while $\psi_{n_3 l_3}$ and $\psi_{n_4 l_4}$ are two-dimensional isotropic harmonic oscillator wave functions. $E_{n_2\pm}$ and $\psi_{n_2\pm}$ are eigenvalues and eigenfunctions of the one-dimensional equation which describes the inversion.

$$H_2\psi(x) = E\psi(x), \tag{28}$$

where

$$H_2 = -D(\partial^2/\partial x^2) + [2G_0' + (F_0'^2/4G_0')] - 2F_0' \cos x + 2G_0' \cos 2x \qquad \text{for } -\pi \leqq x \leqq \pi,$$

$$H_2 = -D(\partial^2/\partial x^2) + [2G_0' + (F_0'^2/4G_0')] + 2(F_0' + G_0') \qquad \text{for } \pi < |x| < \pi/2L.$$

It does not appear possible to obtain exact solutions of equation (28) in terms of known functions. However, for $E \ll V(\pi)$ eigenvalues and eigenfunctions may be calculated numerically to any desired order of approximation. The proper procedure would be to obtain solutions in the interval $-\pi \leqq x \leqq +\pi$ and join them to the exponential solutions in the intervals $\pi < |x| \leqq \pi/2L$. However, for the levels of interest in the present investigation $\psi(x)$ becomes vanishingly small as $|x| \rightarrow \pi$ so that the solutions in the intervals $\pi < |x| \leqq \pi/2L$ can be neglected entirely.[2] Consequently, only solutions in the interval $-\pi \leqq x \leqq +\pi$ need be considered.

Since the operator H_2 is unchanged when x is replaced by $-x$, the eigenfunctions must be either even or odd functions of x. The form of H_2 suggests that $\psi(x)$ should be expanded in a Fourier series in the interval $-\pi \leqq x \leqq +\pi$. As a computational procedure only the first N terms of the Fourier expansions will be retained. Thus, the even functions become

$$\psi_+ = \frac{a_0}{\sqrt{2\pi}} + \sum_{k=1}^{N-1} \frac{a_k}{\sqrt{\pi}} \cos kx \tag{29a}$$

and the odd functions

$$\psi_- = \sum_{k=1}^{N} \frac{b_k}{\sqrt{\pi}} \sin kx. \tag{29b}$$

Regarding these wave functions as N-parameter variational wave functions one obtains, by minimizing the usual variational integral with respect to the a_i or b_i, the two matrix equations

$$\begin{aligned} \sum_{k=0}^{N-1} [(H_2)_{jk}^{+} - E_+\delta_{jk}]a_k &= 0, \\ \sum_{k=1}^{N} [(H_2)_{jk}^{-} - E_-\delta_{jk}]b_k &= 0, \end{aligned} \tag{30}$$

[2] For the 0^+ level, for example, the function $\psi(x)$ has a value of approximately 0.00005 at $x = \pi$ compared with a value of 0.94 at the maximum of the wave function.

TABLE II

EIGENVALUES AND EIGENVECTORS OF H_2^+ (12 × 12 TRUNCATION)

n_2^+	0^+	1^+	2^+	3^+	4^+
$E_{n_2^+}$ (cm^{-1})	514.55	1451.71	2131.65	2899.49	3925.35
a_0	0.647154	0.125510	0.437270	−0.131256	0.224109
a_1	0.362054	0.495878	0.307225	0.225158	−0.131521
a_2	−0.447480	0.603562	0.177672	0.357973	−0.113213
a_3	−0.467819	−0.073639	0.575400	−0.048483	0.371143
a_4	−0.022430	−0.531707	0.485977	0.269292	0.000916
a_5	0.160871	−0.252730	−0.102389	0.733106	−0.014177
a_6	0.062313	0.097022	−0.304725	0.353268	0.637748
a_7	−0.020628	0.110248	−0.089206	−0.172564	0.578506
a_8	−0.017838	0.009066	0.055148	−0.188563	−0.005545
a_9	−0.000387	−0.019376	0.034769	−0.014796	−0.192113
a_{10}	0.002506	−0.005476	−0.002021	0.034106	−0.054597
a_{11}	0.000494	0.001508	−0.005404	0.010167	0.020004

where

$$(H_2)^{\pm}_{jk} = \int_{-\pi}^{\pi} u_j^{\pm} H_2 \, u_k^{\pm} \, dx,$$

$$u_0^+ = 1/\sqrt{2\pi}, \qquad u_k^+ = (1/\sqrt{\pi}) \cos kx, \qquad u_k^- = (1/\sqrt{\pi}) \sin kx.$$

Very good approximations to the low-lying eigenvalues and the corresponding eigenfunctions can be obtained by finding the eigenvalues and the eigenvectors of the two $N \times N$ matrices H_2^+ and H_2^-, provided only that N is sufficiently large. The actual diagonalization was performed with the aid of the IBM 704 digital computer of The University of Michigan Computing Center.

By trial and error it was found that a value of N equal to 12 was sufficiently large since an increase in N beyond this value leads to insignificant changes in those eigenvalues and eigenfunctions which correspond to the presently observed levels in the ammonia spectrum. At least two cycles of computation are required to determine the constants D, F_0', and G_0'. Although the decomposition of the vibrational Hamiltonian into $H_{\text{vib}}^{(0)}$ and $H_{\text{vib}}^{(1)}$ was made in a way that minimizes the contribution of $H_{\text{vib}}^{(1)}$ to the levels $(0, n_2^{\pm}, 0^0, 0^0)$, this contribution is not negligible. A tentative choice of D, F_0', and G_0' is made by neglecting $H_{\text{vib}}^{(1)}$ altogether and choosing the three potential constants so that the best possible fit to the observed levels $(0, n_2^{\pm}, 0^0, 0^0)$ is obtained. Using the resulting eigenfunctions, the approximate contribution due to $H_{\text{vib}}^{(1)}$ is calculated. Then the values of D, F_0', and G_0' are adjusted to compensate for the contributions of $H_{\text{vib}}^{(1)}$ to the levels $(0, n_2^{\pm}, 0^0, 0^0)$. The best values that have been found in this

TABLE III

EIGENVALUES AND EIGENVECTORS OF H_2^- (12 × 12 TRUNCATION)

n_2^-	0^-	1^-	2^-	3^-	4^-
$E_{n_2}^-$ (cm^{-1})	515.49	1487.20	2401.77	3387.16	4482.53
b_1	0.771718	−0.122245	0.368526	−0.240582	0.254615
b_2	0.523913	0.481142	0.004443	0.298187	−0.266783
b_3	−0.148653	0.760754	0.107159	0.188733	0.088427
b_4	−0.310924	0.174758	0.695448	−0.110052	0.307827
b_5	−0.072999	−0.313068	0.539354	0.448221	−0.151417
b_6	0.066367	−0.206113	−0.085132	0.717284	0.214791
b_7	0.037308	0.021520	−0.254207	0.178893	0.728610
b_8	−0.003985	0.056222	−0.064203	−0.205890	0.352643
b_9	−0.007251	0.009731	0.040722	−0.122294	−0.129749
b_{10}	−0.000800	−0.007187	0.021746	0.011743	−0.140729
b_{11}	0.000775	−0.002637	−0.001966	0.024031	−0.009218
b_{12}	0.000206	0.000383	−0.003106	0.003291	0.020130

TABLE IV

ENERGY DIFFERENCES FOR THE LEVELS $(0, n_2^\pm, 0^0, 0^0)$ ($N \times N$ TRUNCATION)

Level	Energy difference (cm^{-1})			
		Calculated		
$n_2^\pm$	$N = 12$	$N = 16$	$N = 20$	Observed
0^+	0.00	0.00	0.00	0.00
0^-	0.94	0.94	0.94	0.793
1^+	937.16	937.16	937.16	932.51
1^-	972.65	972.65	972.65	968.32
2^+	1617.10	1617.09	1617.09	1597.42
2^-	1887.22	1887.22	1887.22	1882.16
3^+	2384.94	2384.85	2384.85	2383.46
3^-	2872.61	2872.55	2872.55	2895.48
4^+	3410.80	3409.30	3409.30	—
4^-	3967.98	3967.67	3967.67	—

way are $D = 64.93$ cm^{-1}, $F_0' = 1894.61$ cm^{-1}, and $G_0' = 1288.68$ cm^{-1}. Eigenvalues and eigenvectors of the matrices H_2^+ and H_2^- have been computed using these values for the potential constants. The results, for N equal to 12, are presented in Tables II and III. The calculated energy differences $E_{n_2}^{\pm} - E_0^+$ for N equal to 12, 16, and 20, are given in Table IV along with the observed differences for the levels $(0, n_2^\pm, 0^0, 0^0)$. However, comparison between theory and experiment should be made only after the contributions of $H_{vib}^{(1)}$ have been computed and incorporated in the calculated values.

V. INVERSION-VIBRATION INTERACTIONS

Having obtained zeroth order energies and wave functions it is now possible to compute the contributions due to the perturbation $H_{vib}^{(1)}$. This calculation is done in two steps. First, perturbation theory is used to express the energy corrections as functions of the interaction constants F_i and $G_i (i = 1, 3, 4)$. The second step is to choose numerical values of the interaction constants in such a way that a good overall description of the vibration-inversion splitting is obtained.

In the matrix elements of $H_{vib}^{(1)}$ the integrals over the harmonic oscillator wave functions are well known. The integrals over the double minimum wavefunctions must, however, be evaluated numerically. The matrix of $H_{vib}^{(1)}$ is diagonal in the quantum numbers l_3 and l_4 and moreover has no matrix elements connecting + states with − states. Since there are no matrix elements connecting states of the same unperturbed energy, nondegenerate first- and second-order perturbation theory can be used to calculate the energy corrections.

In order to achieve the desired goal of expressing the energy corrections as functions of the interaction constants alone it is necessary to know the numerical values of the normal frequencies ω_1, ω_3, and ω_4. Furthermore, in order to do the numerical integrations over the inversion coordinate x one must assign numerical values to the five parameters a_0, ζ_0, σ_0, L, and x_0. The most recent estimates of the normal frequencies and equilibrium moments of inertia of NH_3 and ND_3 have been made by Benedict and Plyler (*2*) and their values for ω_1, ω_3, and ω_4 were used in the present calculations. The equilibrium dimensions u_1^0 and u_2^0 were obtained from their estimates of the equilibrium moments of inertia. The constant a_0 can be calculated once the quadratic force constants a, b, and c for the symmetric vibrations are known. These are calculated from the normal frequencies $(\omega_1)_{NH_3}$, $(\omega_1)_{ND_3}$, and $(\omega_2)_{NH_3}$. For the first two of these frequencies the values given by Benedict and Plyler were used. The normal frequency $(\omega_2)_{NH_3}$ can be calculated from the potential energy function given by Eqs. (14) or (16). One finds

$$(\omega_2)^2 = 16DG_0[1 - (F_0/4G_0)^2]. \tag{31}$$

The constants F_0 and G_0 are as yet unknown. However, from the known constants $F_0' = F_0 + (\frac{1}{2})F_1 + F_3 + F_4$ and $G_0' = G_0 + (\frac{1}{2})G_1 + G_3 + G_4$ an approximate value for $(\omega_2)_{NH_3}$ can be found, assuming the F_1, F_3, and F_4 are much smaller than F_0, and that G_1, G_3, and G_4 are much smaller than G_0. In the final cycle of the calculation an improved value of $(\omega_2)_{NH_3}$ derived from the constants F_0 and G_0 will be used. The energies, including contributions due to $H_{vib}^{(1)}$, are given by

$$E_{\text{vib}} = E_{\text{vib}}^{(0)} + E_{\text{vib}}^{(1)},$$

where $E_{\text{vib}}^{(1)}$ is the zeroth order energy given by Eq. (26) and $E_{\text{vib}}^{(1)}$ is a function of the six interaction constants F_i and $G_i (i = 1, 3, 4)$.

In order to describe the method by which the interaction constants are determined it is convenient to introduce the notation

$$\Delta E(n_1 n_2 n_3^{l_3} n_4^{l_4}) = E(n_1 n_2^- n_3^{l_3} n_4^{l_4}) - E(n_1 n_2^+ n_3^{l_3} n_4^{l_4}),$$

$$\bar{E}(n_1 n_2 n_3^{l_3} n_4^{l_4}) = \tfrac{1}{2}[E(n_1 n_2^- n_3^{l_3} n_4^{l_4}) + E(n_1 n_2^+ n_3^{l_3} n_4^{l_4})].$$

Thus, ΔE is the splitting of the pair of levels $(n_1, n_2^{\pm}, n_3^{l_3}, n_4^{l_4})$ and $\bar{E}$ is their mean position. For simplicity, the splittings $\Delta E(0, n_2, 0^0, 0^0)$ will be denoted by Δ_{n_2}. The constants F_3 and G_3 can be determined from the observed shift in splitting $\Delta E(0\ 0\ 1^1\ 0^0) - \Delta_0$ and the observed anharmonicity $\bar{E}(0\ 1\ 1^1\ 0^0) - [\bar{E}(0\ 1\ 0^0\ 0^0) + \bar{E}(0\ 0\ 1^1\ 0^0)]$ since these two quantities turn out to be independent of F_1, G_1, F_4, and G_4. The observed numbers yield

$$F_3 = -175.0\ \text{cm}^{-1}, \qquad G_3 = 14.0\ \text{cm}^{-1}.$$

Similarly, the shift in splitting $\Delta E(0\ 0\ 0^0\ 1^1) - \Delta_0$ and the anharmonicity $\bar{E}(0\ 1\ 0^0\ 1^1) - [\bar{E}(0\ 1\ 0^0\ 0^0) + \bar{E}(0\ 0\ 0^0\ 1^1)]$ yield a pair of equations involving F_4 and G_4 alone which give

$$F_4 = 29.7\ \text{cm}^{-1}, \qquad G_4 = -13.8\ \text{cm}^{-1}.$$

The question naturally arises why the two observed shifts in splitting

$$\Delta E(0\ 0\ 1^1\ 0^0) - \Delta_0 \quad \text{and} \quad \Delta E(0\ 1\ 1^1\ 0^0) - \Delta_1$$

were not used to determine F_3 and G_3. Unfortunately one finds that the two equations for F_3 and G_3 obtained in this way are almost constant multiples of each other and consequently, with an interaction of the form postulated above, the two observed splittings with $n_3 = 1$ are not, effectively, independent pieces of information. Two pieces of information of a distinctly different nature are needed and the observed anharmonicity and one of the observed splittings satisfy this requirement.

The determination of F_1 and G_1 is subject to a much greater uncertainty than is the case for F_3, G_3, F_4, and G_4. Three pairs of levels,

$$(1, 0^{\pm}, 0^0, 0^0), \qquad (1, 1^{\pm}, 0^0, 0^0), \qquad \text{and} \qquad (1, 0^{\pm}, 0^0, 1^1),$$

involving the excitation of the q_1 mode have been observed in the spectrum of NH_3. Unfortunately,

$$E_{\text{vib}}(1, 0^{\pm}, 0^0, 0^0) \qquad \text{and} \qquad E_{\text{vib}}(0, 0^{\pm}, 0^0, 2^0)$$

differ only by about 120 cm^{-1}, and these levels may be in Fermi resonance with each other through a cubic potential term of the form $K_{144} q_1 r_4^2$ which has been neglected in the potential function used in this investigation. Similarly, the levels $(1, 1^{\pm}, 0^0, 0^0)$ may be in resonance with $(0, 1^{\pm}, 0^0, 2^0)$ and $(1, 0^{\pm}, 0^0, 1^1)$ may be in resonance with $(0, 0^{\pm}, 0^0, 3^1)$. (The levels $(0, 0^{\pm}, 0^0, 3^1)$ and $(0, 1^{\pm}, 0^0, 2^0)$ have not yet been observed in the ammonia spectrum.) In general, one would expect the Fermi resonance to have some effect on the splittings of the levels involved. Similarly, the observed anharmonicity

$$\bar{E}(1\ 1\ 0^0\ 0^0) - [\bar{E}(0\ 1\ 0^0\ 0^0) + \bar{E}(1\ 0\ 0^0\ 0^0)]$$

can be expected to involve a contribution due to the Fermi resonance. No matter whether the observed numbers or estimated values of the unperturbed numbers, corrected for Fermi resonance, are used, one has the problem of choosing F_1 and G_1 such that

$$\Delta E(\ 1\ 0\ 0^0\ 0^0) > \Delta_0\,,$$

$$\Delta E(1\ 1\ 0^0\ 0^0) < \Delta_1\,.$$

It appears that no values of F_1 and G_1 exist, unless third and higher order perturbations give significant contributions, which will satisfy these inequalities. One can fit the splitting of the levels $(1\ 0^{\pm}, 0^0, 0^0)$, in which case the predicted splitting of the levels $(1, 1^{\pm}, 0^0, 0^0)$ is much too large or one can fit the splitting of the levels $(1, 1^{\pm}, 0^0, 0^0)$, in which case the calculated splitting of the levels $(1, 0^{\pm}, 0^0, 0^0)$ will be too small. In order to obtain a rough estimate of the values of F_1 and G_1 the second alternative was chosen. Although the choice is quite arbitrary it might be hoped that the Fermi resonance has a smaller percentage influence on the splitting of the levels $(1, 1^{\pm}, 0^0, 0^0)$ than on the splitting of the levels $(1, 0^{\pm}, 0^0, 0^0)$. The values of F_1 and G_1 obtained in this way are

$$F_1 = -144.0 \text{ cm}^{-1}, \qquad G_1 = 25.6 \text{ cm}^{-1}.$$

It should be understood that the numbers for F_1 and G_1 may be badly in error. In fact, the dilemma cited above casts doubt upon the validity of the interaction function between q_1 and x which has been postulated.

Since F_0' and G_0' are known, the values of the interaction constants can be used, with the aid of Eq. (17), to calculate F_0 and G_0. Equation (31) then yields an improved value for the normal frequency ω_2 for NH_3, which in turn can be used to obtain corrected estimates of the force constants a, b, and c. Improved estimates of the parameters a_0, ζ_0, σ_0, L, and x_0 then can be made. The best values obtained for these parameters are presented in Table V. As a final step, the corrections to the energy levels due to $H_{\text{vib}}^{(1)}$ have been recalculated.

It should be noticed that the magnitudes of the interaction constants F_i and G_i are sufficiently small to justify the use of perturbation theory. That this would be so was not obvious at the beginning of the calculation. Another point of interest is that $H_{\text{vib}}^{(1)}$ contributes a correction to the levels $(0, n_2^{\pm}, 0^0, 0^0)$.

TABLE V

PARAMETERS FOR NH_3

$\omega_1 = 3516.98 \text{ cm}^{-1}$	$(3m)^{1/2}u_1^0 = 2.101 \times 10^{-20} \text{ cm} \times \text{g}^{1/2}$
$\omega_3 = 3590.51 \text{ cm}^{-1}$	$(\mu)^{1/2}u_2^0 = 0.7757 \times 10^{-20} \text{ cm} \times \text{g}^{1/2}$
$\omega_4 = 1689.11 \text{ cm}^{-1}$	
$F_0' = 1894.61 \text{ cm}^{-1}$	$G_4 = -13.8 \text{ cm}^{-1}$
$G_0' = 1288.68 \text{ cm}^{-1}$	$x_0 = 1.1441$
$D = 64.93 \text{ cm}^{-1}$	$\sinh \sigma_0 = 1.1133$
$F_0 = 2111.91 \text{ cm}^{-1}$	$\sin \zeta_0 = 0.2648$
$G_0 = 1275.68 \text{ cm}^{-1}$	$L = 0.2342$
$F_1 = -144.0 \text{ cm}^{-1}$	$a_0 = 1.9574 \times 10^{-20} \text{ cm} \times \text{g}^{1/2}$
$G_1 = 25.6 \text{ cm}^{-1}$	$\omega_2 = 1047.98 \text{ cm}^{-1}$
$F_3 = -175.0 \text{ cm}^{-1}$	$a = 2.2712 \times 10^5$ dyne/cm
$G_3 = 14.0 \text{ cm}^{-1}$	$b = 7.0770 \times 10^5$ dyne/cm
$F_4 = 29.7 \text{ cm}^{-1}$	$c = 2.0624 \times 10^5$ dyne/cm

Since the major contributions to the energy corrections of the lower states come from matrix elements of $H_{\text{vib}}^{(1)}$ with $\Delta n_2 = 0, \pm 1$, and since it is estimated that contributions of matrix elements with $n_2 \geqq 4$ are less important for these states than the effects of third or higher order perburbation terms, only matrix elements $(n_2|\, H_{\text{vib}}^{(1)}\, |n_2')$ with n_2, $n_2' < 4$ have been retained for simplicity, and the corrections for states, $n_2 = 3$, have not been included. The corrected energies for the levels $(0, n_2^{\pm}, 0^0, 0^0)$ for $n_2 = 0$, 1, and 2 are given in Table VI. In this table two sets of calculated energy values are given. For the first of these the simple form of the inversion potential, assumed up to now in this investigation, has been used for the zeroth order calculation. The corrected energies should be compared with the unperturbed energies given in Table IV. It is seen that the inclusion of the corrections due to $H_{\text{vib}}^{(1)}$ improves the agreement between calculated and observed energies. However, the ground state splitting remains too large even after the correction has been applied. With the simple form of the inversion potential used so far it does not seem possible to decrease the ground state splitting and still retain a very good overall description of the remaining $(0, n_2^{\pm}, 0^0, 0^0)$ levels. However, only a very slight modification of the inversion potential function is needed to give an excellent fit between the observed and predicted levels. In one possible generalization the simple form of the potential function used so far can be regarded as consisting of the leading and dominant terms in a Fourier expansion of the true potential function. Better approximations might then be obtained by including $\cos 3x$, $\cos 4x$, or higher terms. It is found that it is possible to fit both the observed $n_2 = 0$ and $n_2 = 1$ levels with the inclusion of a small negative $\cos 4x$ term, that is with the following modified form of the effective inversion potential function

$$V_0'(x) = 2G_0' + F_0'^2/4G_0' - 2F_0' \cos x + 2G_0' \cos 2x - 2\mu_0 \cos 4x. \quad (28m)$$

TABLE VI
CORRECTED ENERGY LEVELS $E_{vib}(0, n_2^{\pm}, 0^0, 0^0)$

Level	*Calculated* (cm^{-1}) Simple form of inversion potential	*Observed* (cm^{-1})	*Calculated* (cm^{-1}) Modified form of inversion potential
0 0^+ 0^0 0^0	0.00	0.00	0.00
0 0^- 0^0 0^0	0.88	0.793	0.79
0 1^+ 0^0 0^0	933.20	932.51	932.52
0 1^- 0^0 0^0	968.29	968.32	968.33
0 2^+ 0^0 0^0	1606.70	1597.42	1588.24
0 2^- 0^0 0^0	1877.78	1882.16	1868.25
Splitting	*Calculated* (cm^{-1}) Simple form of inversion potential	*Observed* (cm^{-1})	*Calculated* (cm^{-1}) Modified form of inversion potential
Δ_0	0.88	0.793	0.79
Δ_1	35.09	35.81	35.81
Δ_2	271.08	284.56	280.01

The calculated energy values given in the last column of Table VI (which also include the corrections due to $H_{vib}^{(1)}$) were obtained with the following values of the parmeters: $\mu_0 = 21.80$ cm^{-1}, $F_0' = 1{,}888.81$ cm^{-1}, $G_0' = 1{,}287.65$ cm^{-1}, and $D = 64.71$ cm^{-1}. Comparison with Table V shows that the inclusion of the small cos $4x$ term necessitates a slight adjustment of the dominant potential parameters. With the addition of still further small correction terms it would be possible to improve the fit of the higher inversion states. No such refinements however will be made since the main purpose of the present investigation is to account for the dependence of the inversion splittings on the vibrational and rotational quantum numbers. For all subsequent calculations therefore only the simple form of the effective inversion potential (without the cos $4x$ term) will be used.

The calculated inversion splitting, as a function of the vibrational quantum numbers, for levels with n_2 equal to 0 or 1 is given by

$$\begin{aligned}\Delta E(n_1\ 0\ n_3^{l_3}\ n_4^{l_4}) = \Delta_0 &- 0.56n_1 - 0.73n_3 + 0.22n_4 \\ &+ 0.27n_1^2 + 0.28n_3^2 + 0.03n_4^2 - 0.17n_3n_4 \\ &+ 0.78n_1n_3 - 0.18n_1n_4 - 0.0003l_3^2 - 0.0007l_4^2\end{aligned} \tag{32}$$

and

$$\begin{aligned}\Delta E(n_1\ 1\ n_3^{l_3}\ n_4^{l_4}) = \Delta_1 &- 16.44n_1 - 22.63n_3 + 6.75n_4 \\ &+ 5.95n_1^2 + 6.21n_3^2 + 0.54n_4^2 - 3.69n_3n_4 \\ &+ 12.16n_1n_3 - 3.60n_1n_4 - 0.005l_3^2 - 0.002l_4^2\end{aligned} \tag{33}$$

An inspection of these equations suggests that, regarded as power series developments in the quantum numbers, they may not be rapidly convergent. Cubic and quartic terms would have been obtained through third and higher order perturbation corrections but this lies outside the scope of the present paper.

The calculated splittings for levels with $n_1 = 0$ are compared with the observed splittings in Table VII. These numbers were obtained from Eqs. (32) and (33) by setting Δ_0 and Δ_1 equal to their observed values 0.793 and 35.81 cm^{-1}, respectively. The numbers in Table VII are sensitive functions of F_3, G_3, F_4, and G_4 but are essentially independent of F_1 and G_1. It is seen that the calculated and observed results agree reasonably well with the exception of the splitting of the levels $(0, 0^{\pm}, 0^0, 2^0)$. It was pointed out above that this pair of levels may be in Fermi resonance with the pair $(1, 0^{\pm}, 0^0, 0^0)$ and consequently a good agreement is perhaps not to be expected. Apart from the exception just mentioned, eleven data have been accounted for with four interaction constants. No doubt a still better agreement could be obtained by introducing further parameters in the potential function and by carrying out the perturbation calculation to higher orders. The fact that the calculated numbers do not reproduce exactly the data used to determine the interaction constants

TABLE VII

INVERSION-VIBRATION INTERACTIONS: DEGENERATE VIBRATIONS

Level	Inversion splitting: Calculated (cm^{-1})	Inversion splitting: Observed (cm^{-1})
001^10^0	0.34	0.35[a]
002^00^0	0.46	—
002^20^0	0.46	0.43
000^01^1	1.04	1.04[b, c]
000^02^0	1.34	2.24
000^02^2	1.33	1.42
001^11^1	0.42	0.57
011^10^0	19.39	18.49
010^01^1	43.10	45.4
011^11^1	23.00	23.68

Anharmonicity	Calculated (cm^{-1})	Observed (cm^{-1})
$\bar{E}(011^10^0) - [\bar{E}(010^00^0) + \bar{E}(001^10^0)]$	32.32	31.98[a]
$\bar{E}(010^01^1) - [\bar{E}(010^00^0) + \bar{E}(000^01^1)]$	−15.28	−14.9[b,d]
$\bar{E}(011^11^1) - [\bar{E}(010^00^0) + \bar{E}(001^11^1)]$	19.18	21.24

[a] Used to fit F_3 and G_3.

[b] Used to fit F_4 and G_4.

[c] A more recent value is 1.01 cm^{-1}—see Ref. *5*.

[d] In view of Ref. *5*, −16.88 cm^{-1} is probably better.

is due primarily to the fact that these constants were obtained using approximate values of the parameters a_0 , ζ_0 , σ_0 , L, and x_0 , whereas the numbers given in Table VII were calculated using improved values for these parameters. Table VIII summarizes the results for the splittings of states in which the symmetric q_1 vibration has been excited. The agreement is seen to be relatively poor. The anharmonicity used to determine F_1 and G_1 should be the one corrected for Fermi resonance, namely, 20.18 cm^{-1} + $C_{FR}(100^00^0)$ − $C_{FR}(110^00^0)$, where C_{FR} is the correction due to Fermi resonance. Benedict *et al.* (4) have estimated that $C_{FR}(100^00^0)$ is 13.5 cm^{-1}. Since the levels $(0, 1^{\pm}, 0^0, 2^0)$ have not been observed it is difficult to make a reasonable estimate of $C_{FR}(110^00^0)$. For the purpose of determining F_1 and G_1 a somewhat arbitrary estimate of 10 cm^{-1} was made for the overall contribution of the Fermi resonance to the anharmonicity.

It might be thought that the discrepancy between the computed and observed splitting for the pair of levels $(1, 0^{\pm}, 0^0, 0^0)$ can be attributed entirely to a Fermi resonance with the pair $(0, 0^{\pm}, 0^0, 2^0)$. The effects of Fermi resonance, however, cannot be the only source of the error since it can be shown (*11*) that the sum of the splittings for the states $(1, 0^{\pm}, 0^0, 0^0)$ and $(0, 0^{\pm}, 0^0, 2^0)$ is unchanged by the resonance whereas the predicted splittings (Tables VII and VIII) are too small in both cases. The trouble may lie in the simple form assumed for the interaction between q_1 and x. Further experimental information about states such as $(2, 0^{\pm}, 0^0, 0^0)$ or $(1, 2^{\pm}, 0^0, 0^0)$ might help to clear up this difficulty.

VI. VIBRATIONAL ENERGIES OF ND_3 IN LOWEST APPROXIMATION

As a test of the validity of the inversion potential chosen for the ammonia molecule it will be interesting to calculate the set of vibrational levels $(0, n_2^{\pm}, 0^0, 0^0)$ for ND_3 . As is well known, the potential functions for two isotopic species of a molecule are identical to a very high order of approximation. This

TABLE VIII

INVERSION-VIBRATION INTERACTIONS: LEVELS WITH $n_1 = 1$

	Inversion splitting	
Level	Calculated (cm^{-1})	Observed (cm^{-1})
100^00^0	0.51	0.99
101^10^0	0.84	—
100^01^1	0.58	0.86
110^00^0	25.32	25.55

Anharmonicity	Calculated (cm^{-1})	Observed (cm^{-1})
$\bar{E}(110^00^0) - [\bar{E}(010^00^0) + \bar{E}(100^00^0)]$	30.63	30.18 cm[a]

[a] Including a somewhat arbitrary correction of 10 cm^{-1} for Firmi resonance.

identity of potential function imposes the following relations between the constants of Eq. (14) and those of the corresponding formula for ND_3.

$$\begin{aligned}
(F_0)_{ND_3} &= (F_0)_{NH_3}, \qquad (G_0)_{ND_3} = (G_0)_{NH_3}, \\
(F_i)_{ND_3} &= [(\omega_i)_{ND_3}/(\omega_i)_{NH_3}](F_i)_{NH_3} \\
(G_i)_{ND_3} &= [(\omega_i)_{ND_3}/(\omega_i)_{NH_3}](G_i)_{NH_3} \qquad i = 1, 3, 4. \\
(c_i)_{ND_3} &= [(\omega_i)_{ND_3}/(\omega_i)_{NH_3}](c_i)_{NH_3}
\end{aligned} \tag{34a}$$

These relations follow at once from the fact that the ratio (ζ/L) is a mass independent, dimensionless quantity while the coordinates q_1, r_3, and r_4 are dimensionless small oscillation coordinates related to the ω's in the usual way. The transformation of the quantity D which occurs in the kinetic energy part of the Hamiltonian is accomplished through Eq. (31) and is

$$(D)_{ND_3} = [(\omega_2)_{ND_3}/(\omega_2)_{NH_3}]^2(D)_{NH_3} \tag{34b}$$

The normal frequency $(\omega_2)_{ND_3}$ can be obtained through the aid of the observed ω_1 by applying the product rule

$$\frac{(\omega_1)_{ND_3}\,(\omega_2)_{ND_3}}{(\omega_1)_{NH_3}\,(\omega_2)_{NH_3}} = \frac{m_H}{m_D}\left[\frac{M + 3m_D}{M + 3m_H}\right]^{1/2}$$

where M is the nitrogen mass, m_H the hydrogen mass, and m_D the deuterium mass.

The values of the constants for ND_3, calculated from Eq. (34), are given in Table IX along with the constants F_0' and G_0' appearing in the effective one-dimensional potential. Using these values of the constants the eigenvalues of the one-dimensional double minimum problem, Eq. (28), (simple form of the inversion potential), have been found for ND_3 according to the method described in Section IV. In this case, the 0^+ level lies 394.93 cm^{-1} above the minima of the effective one-dimensional potential. The energy differences $E_{n_2}^+ - E_0^+$ are given in Table X.

TABLE IX

CONSTANTS FOR $ND_3(cm^{-1})$

ω_1 = 2496.96	
ω_3 = 2642.18	
ω_4 = 1226.32	
ω_2 = 801.01	F_3 = −128.8
D = 37.93	G_3 = 10.3
F_0 = 2111.91	F_4 = 21.6
G_0 = 1275.68	G_4 = −10.0
F_1 = −102.2	F_0' = 1953.61
G_1 = 18.2	G_0' = 1285.08

TABLE X
ENERGY DIFFERENCES FOR THE LEVELS $(0, n_2^{\pm}, 0^0, 0^0)$ OF ND_3 ($N \times N$ TRUNCATION)

Level	Energy differences (cm^{-1})					
$n_2^{\pm}$	*Calculated simple form of inversion potential* $N = 12$	$N = 16$	$N = 20$	*Calculated modified form of inversion potential* $N = 16$	*Estimated perturbation correction*	*Observed*
0^+	0.00	0.00	0.00	0.00		0.00
0^-	0.08	0.08	0.08	0.07	−0.02	0.053
1^+	746.90	746.74	746.74	748.18	−2.0	745.7
1^-	751.20	751.18	751.18	752.61	−2.2	749.4
2^+	1359.71	1359.45	1359.45	1347.44	−5	1359
2^-	1435.70	1435.60	1435.60	1429.39	−4.5	1429
3^+	1835.47	1834.98	1834.98	1814.24		1830
3^-	2115.41	2115.08	2115.07	2101.24		2106.60
4^+	2495.39	2485.28	2485.28	2468.57		—
4^-	2873.08	2867.55	2867.55	2851.93		—

The table also gives these energy differences calculated with the modified form of the effective one-dimensional inversion potential, Eq. (28*m*). The potential constants again follow from those of NH_3 and have the values: $\mu_0 = 21.80$ cm^{-1}; $F_0' = 1947.81$ cm^{-1}; $G_0' = 1284.05$ cm^{-1}; $D = 37.80$ cm^{-1}. An exact calculation of the perturbation due to $H_{\text{vib}}^{(1)}$ has not been performed and might be difficult to interpret since there exist a number of resonances. However, on the basis of the $H_{\text{vib}}^{(1)}$ contributions for NH_3, a very rough estimate has been made of their probable values for ND_3. These appear in the next to last column under the heading *Estimated Perturbation Correction.*

VII. INVERSION-ROTATION SPLITTINGS IN NH_3

The observed infrared spectrum of ammonia shows the rotational fine structure which is characteristic of a symmetric top molecule where, however, the effective rotational constants are functions of the vibrational quantum numbers and of the symmetry (+ or −) of the inversion states. The inversion splitting may therefore be expressed as a function of the rotational quantum numbers through a formula of the form

$$\Delta_n = \Delta_n^0 + (B_n^- - B_n^+)[J(J+1) - K^2] + (C_n^- - C_n^+)K^2 + \cdots .$$

Although terms quartic in J and K are often added to this type of expression in order to obtain a more exact fit to the experimentally observed splittings, the dominant contribution comes from the quadratic terms. In the present investigation no attempt will be made to calculate these higher order terms. One of the consequences of the potential function chosen to represent the ammonia molecule is that the potential becomes exceedingly high and the wave function vanishingly small for all values of the coordinates for which the configuration departs significantly from pyramidal symmetry. For this reason the total Hamiltonian which includes both rotation and vibration may be represented to first order as the sum of the vibrational Hamiltonian already treated and a rotational Hamiltonian characterizing a symmetrical top. Thus

$$H = H_{\text{vib}} + (\tfrac{1}{2}I_{\parallel})(P_x^2 + P_y^2) + (\tfrac{1}{2}I_{\perp})P_z^2, \tag{35}$$

where $I_{\perp}$ is the moment of inertia about the symmetry axis and $I_{\parallel}$ is the moment of inertia about an axis perpendicular to the symmetry axis. As usual P_x, P_y, and P_z denote the components of the total angular momentum along the principal axes of the molecule.

From Table I it can be seen that the rotation-inversion constants $B_n^- - B_n^+$ and $C_n^- - C_n^+$ are very sensitive functions of the inversion quantum number, n_2, while their dependence on the remaining quantum numbers is much less pronounced. This fact suggested the following plan of attack. The Hamiltonian of Eq. (35) was initially simplified by including in H_{vib} and in $I_{\parallel}$ and $I_{\perp}$ only those terms which depend upon the inversion coordinate x. The inversion splittings can be calculated with some exactness using perturbation theory. Subsequently the dependence of $B_n^- - B_n^+$ and $C_n^- - C_n^+$ on the remaining coordinates will be examined.

For the purpose of computation it is convenient to rewrite Eq. (35) as

$$H = H^{(0)} + H^{(1)},$$

where

$$H^{(0)}/hc = H_{\text{vib}}^{(0)}/hc + B_e[\mathbf{J}^2 - J_z^2] + C_eJ_z^2, \tag{36}$$

$$H^{(1)}/hc = H_{\text{vib}}^{(1)}/hc + (B - B_e)[\mathbf{J}^2 - J_z^2] + (C - C_e)J_z^2, \tag{37}$$

and

$$B = h/8\pi^2cI_{\parallel}, \qquad C = h/8\pi^2cI_{\perp}. \tag{38}$$

The rotational coefficients B and C are functions of the inversion coordinate whereas $B_e = 9.965\ \text{cm}^{-1}$ and $C_e = 6.341\ \text{cm}^{-1}$ are their equilibrium values as estimated by Benedict and Plyler (*2*). For convenience, dimensionless angular momentum operators $J_\alpha = P_\alpha/\hbar(\alpha = x, y, z)$ have been introduced. $H_{\text{vib}}^{(0)}$ is given by Eq. (21) and $H_{\text{vib}}^{(1)}$ by Eq. (22).

If the degenerate frequencies are not excited the rotational constants are given by

$$\begin{aligned} B - B_e &= B_e\left[\frac{\sin^2\zeta_0 - \sin^2(Lx)}{\cosh^2\sigma_0 - 1)/(\cosh^2\sigma_0 + 1) + \sin^2(Lx)}\right], \\ C - C_e &= C_e\left[\frac{\cos^2\zeta_0 - \cos^2(Lx)}{\cos^2(Lx)}\right], \end{aligned} \tag{39}$$

where $x = \zeta/L$ is the inversion coordinate and σ_0 is the equilibrium value of the coordinate σ.

The zeroth order Schrödinger equation has solutions

$$\Psi^{(0)} = \Psi_{\text{vib}}^{(0)} \psi_{JKM}, \tag{40}$$

$$E^{(0)} = E_{\text{vib}}^{(0)} + B_e[J(J+1) - K^2] + C_e K^2, \tag{41}$$

where ψ_{JKM} is a symmetric top wave function, $\Psi_{\text{vib}}^{(0)}$ is the wave function given by Eq. (27), and $E_{\text{vib}}^{(0)}$ the energy given by Eq. (26). Since the calculation of the vibration-rotation energies will be restricted to terms at most quadratic in the rotational quantum numbers J and K, the corrected energies are found to have the form

$$E = E_{\text{vib}} + B(n_1 n_2^{\pm} n_3 n_4)[J(J+1) - K^2] + C(n_1 n_2^{\pm} n_3 n_4)K^2, \tag{42}$$

where E_{vib} is the vibrational energy calculated previously.

The quantities of interest in this investigation are the differences of the rotational constants of the $(+)$ and $(-)$ levels, namely,

$$B_n^- - B_n^+ = B(n_1 n_2^- n_3 n_4) - B(n_1 n_2^+ n_3 n_4),$$

$$C_n^- - C_n^+ = C(n_1 n_2^- n_3 n_4) - C(n_1 n_2^+ n_3 n_4).$$

The calculated values of $B_n^- - B_n^+$ and $C_n^- - C_n^+$, for the levels $(0, n_2^{\pm}, 0^0, 0^0, J, K)$ are compared with the observed values in Table XI. The numbers in Table XI are differences of the diagonal matrix elements of $B - B_e$ and $C - C_e$ when only the inversion coordinate x is considered. As stated, it is believed that these represent the major contributions to the rotational part of the inversion splitting. A comparison with the observations tends to verify this conclusion since the agreement is relatively good. In particular it is gratifying to see that the increase as n_2 takes on the values 0, 1, 2 and the decrease for $n_2 = 3$ is correctly predicted. Although the agreement is quite good it is far from perfect as might be expected from the approximate nature of the calculation. It may be remarked that Sheng *et al.* (*8*) and Hadley and Dennison (*9*) made similar calculations for $n_2 = 0$ and 1 using essentially the same techniques. A compari-

TABLE XI

INVERSION-ROTATION SPLITTING IN THE LEVLES $(0\ n_2^{\pm}\ 0^0\ 0^0\ J\ K)$

$n_2^{\pm}$	$(B^- - B^+)_{\text{calc}}$[a]	$(B^+ - B^+)_{\text{obs}}$	$(C^- - C^+)_{\text{calc}}$[a]	$(C^- - C^+)_{\text{obs}}$
$0^{\pm}$	−0.0055 (cm^{-1})	−0.005054 (cm^{-1})	0.0015 (cm^{-1})	0.001998 (cm^{-1})
$1^{\pm}$	−0.17	−0.1817	0.049	0.0721
$2^{\pm}$	−0.57	−0.535	0.17	0.231
$3^{\pm}$	−0.25	−0.3041	0.095	0.1034

[a] Major contributions only, as given by the simple Hamiltonian (35).

son shows their results to be in substantial agreement with ours revealing the same type of deviations from the experimental data.

Although the differences of the rotational constants depend mainly on the inversion quantum number, n_2, it is clear that they are also functions of the vibrational quantum numers n_1, n_3, and n_4. In order to discuss this dependence it is convenient to write

$$B(n_1n_2^-n_3n_4) - B(n_1n_2^+n_3n_4) = B(0n_2^-00) - B(0n_2^+00) + \Delta B(n_1n_2n_3n_4)$$

and

$$C(n_1n_2^-n_3n_4) - C(n_1n_2^+n_3n_4) = C(0n_2^-00) - C(0n_2^+00) + \Delta C(n_1n_2n_3n_4).$$

In the present approximation, ΔB and ΔC arise from cross terms between off-diagonal matrix elements of $H_{\text{vib}}^{(1)}$ and off-diagonal matrix elements of $B - B_e$ and $C - C_e$. The calculated values of ΔB and ΔC for levels with $n_2 = 1$ are compared with the observed values in Table XII. It is seen from this table that the changes in $B_n^- - B_n^+$ and $C_n^- - C_n^+$, for levels with $n_2 = 1$, as a function of n_1, n_3, and n_4, are given surprisingly well by the simple Hamiltonian expressed by Eq. (35). In all cases the signs of ΔB and ΔC are correct and, with the exception of the level $(0, 1^{\pm}, 0^0, 1^1)$, the calculated magnitudes agree rather well with the observed numbers. The corresponding numbers for levels with $n_2 = 0$ are shown in Table XIII. The calculated values of ΔB and ΔC for the levels $(1, 0^{\pm}, 0^0, 0^0)$ undoubtedly should be disregarded since they are strongly dependent on the potential constants F_1 and G_1 which were found earlier to be inadequate for describing the inversion-vibration splitting of the pure vibra-

TABLE XII

DEPENDENCE OF $(B^- - B^+)$ AND $(C^- - C^+)$ ON n_1, n_3, AND n_4 WHEN $n_2 = 1$

Level	$\Delta B_{\text{calc}}(\text{cm}^{-1})$[a]	$\Delta B_{\text{obs}}(\text{cm}^{-1})$	$\Delta C_{\text{calc}}(\text{cm}^{-1})$[a]	$\Delta C_{\text{obs}}(\text{cm}^{-1})$
$1\ 1^{\pm}\ 0^0\ 0^0$	0.067	0.0552	−0.019	−0.0251
$0\ 1^{\pm}\ 1^1\ 0^0$	0.091	0.0833	−0.025	−0.0292
$0\ 1^{\pm}\ 0^0\ 1^1$	−0.027	−0.009	0.008	0.025
$0\ 1^{\pm}\ 1^1\ 1^1$	0.064	0.052	−0.018	−0.018

[a] Major contributions only, as given by the simple Hamiltonian (35).

TABLE XIII

DEPENDENCE OF $(B^- - B^+)$ AND $(C^- - C^+)$ ON n_1, n_3, AND n_4 WHEN $n_2 = 0$

Level	$\Delta B_{\text{calc}}(\text{cm}^{-1})$*	$\Delta B_{\text{obs}}(\text{cm}^{-1})$	$\Delta C_{\text{calc}}(\text{cm}^{-1})$*	$\Delta C_{\text{obs}}(\text{cm}^{-1})$
$1\ 0^{\pm}\ 0^0\ 0^0$	0.0049	−0.007	−0.0019	0.001
$0\ 0^{\pm}\ 1^1\ 0^0$	0.0041	0.0015	−0.0011	−0.0013
$0\ 0^{\pm}\ 0^0\ 1^1$	−0.0012	0.099	0.0003	0.009

[a] Major contributions only, as given by the simple Hamiltonian (35).

tional levels $(1, 0^{\pm}, 0^0, 0^0)$. For the levels $(0, 0^{\pm}, 1^1, 0^0)$ the calculated and observed values of ΔC agree well while the corresponding values of ΔB agree in sign and only roughly in magnitude. The calculated and observed numbers for the levels $(0, 0^{\pm}, 0^0, 1^1)$ are not in good agreement and indeed even the sign of ΔB is not given correctly.

A complete agreement between the calculated and observed rotation-inversion constants should not be expected on the basis of a Hamiltonian as incomplete as Eq. (35). The fact that the agreement is as good as it is appears to verify the assumption that Eq. (35) does indeed contain the dominant terms. An attempt was made to introduce corrections to Eq. (35) for the purpose of examining the next order of approximation. Details of this attempt are given elsewhere (*11*).[3] Unfortunately a number of difficulties appeared which prevented any substantial progress being made. In the first place the additional terms which are quite complex in form, contribute mainly through off-diagonal elements and thus second order perturbation theory must be employed. There were found to exist a number of near resonances among the interacting levels which appear to limit the validity of nondegenerate perturbation theory. While the numerical values for these correction terms did not substantially improve the agreement between the calculated and observed rotation-inversion constants, the theory did predict that the fine structure of the resonance perturbed levels $(0, 0^{\pm}, 0^0, 1^1)$ and $(0, 1^{\pm}, 0^0, 1^1)$ should exhibit marked perturbations of the rotation lines. Experimentally (*3–5*) it is found that the rotation-inversion pattern for these bands is indeed highly irregular and can not well be expressed by a power series in the rotational quantum numbers. It seems probable that further progress may require important modifications of the inversion potential function as well as refinements in the method of calculation.

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[3] In Ref. (*11*) an attempt has been made to generalize the complete vibration-rotation Hamiltonian to include the effects of the inversion, and all contributions to the inversion-rotation constants of order B^2/ω have been examined.