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Anomalous Values of Certain of the Fine Structure Lines in the Ammonia Microwave Spectrum

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The anomalous positions in the microwave spectrum of ammonia of the lines originating with the rotational levels $K=3$ are explained on the basis of a K-type splitting of these levels. The splitting is due to a fourth-order perturbation originating with the first-order correction terms to the moments of inertia, $I_{xx}^{(e)}=I_{yy}^{(e)}$, and the first-order coriolis correction terms. The Pauli exclusion principle permits only one of the two components to be present. Thus in the lower vibration state when J is even only the lower component of the levels $K=3$ is present, but when J is odd only the upper component is permitted. Similarly, for the upper vibration state when J is even only the upper component of the levels $K=3$ may exist while for J odd only the lower component may exist. Since in this spectrum $\Delta J=\Delta K=0$, the lines originating in levels where J is even will be displaced to shorter wave-lengths, while the lines originating in levels where J is odd will be displaced to longer wave-lengths. The agreement between computed shifts and measured shifts is satisfactory.

1. INTRODUCTION

RECENT measurements[1] of the microwave spectrum of ammonia gas have shown that the lines may be correlated by means of an empirical formula containing the rotational quantum numbers J and K. The simplest form of function consists of a power-series development in the variables J^2+J and K^2. It is found that such a formula will account accurately for the positions of nearly all of the lines, the exceptions being those lines originating in levels where the number K is equal to 3. (The line $J=6$, $K=6$ seems also to deviate from its predicted position. The reason for the anomaly of this single line is at present obscure.) When J is even and $K=3$, the observed line possesses a higher frequency than that predicted by the empirical formula, while when J is odd it has a lower frequency. The magnitude of the deviation increases steadily as J increases. The effect occurs in the spectrum of $N^{15}H_3$ as well as in that of $N^{14}H_3$ and the lines are displaced by nearly the same amount. It is, therefore, clearly a property of the molecule and not of the nitrogen nucleus.

The qualitative explanation of the phenomenon may be readily understood and has been discussed by us in an earlier communication.[2] It is well known that the rotational levels for which $K\neq 0$ are each double corresponding to the two wave functions (that part depending upon φ, the angle of rotation about the symmetry axis) $e^{iK\varphi}$ and $e^{-iK\varphi}$. The wave functions for the levels where K is not a multiple of 3 possess a mixed symmetry denoted by the symbol E. It has been rigorously proved that no perturbation, providing it has threefold symmetry, can ever remove the degeneracy of such a pair of levels. Since the three protons in NH_3 are identical particles, no perturbation whose origin lies within the ammonia molecule itself can split these levels apart.

When $K\neq 0$ and is a multiple of 3, the symmetry classification is quite different. One of the two originally coincident levels will be symmetrical (denoted by A_1) for an interchange of any two of the protons while the other is anti-

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[1] W. E. Good and D. K. Coles, Phys. Rev. **71**, 383 (1947); M. W. P. Strandberg, R. Kyhl, T. Wentink, Jr., and R. E. Hilliger, Phys. Rev. **71**, 639 (1947); B. Bleaney and R. P. Pinrose, Nature **157**, 339 (1946). We are also indebted to Dr. Good and Dr. Coles for the numerical results stated in this work which were sent to us in a private communication.

[2] H. H. Nielsen and D. M. Dennison, Phys. Rev. **72**, 86 (1947).

symmetric (denoted by A_2). A perturbation having the threefold symmetry is able to undegenerate the levels and split them apart. The source of a perturbation having the threefold symmetry lies in the fact that the Hamiltonian is not separable, except in zero-order approximation, into one part containing rotational coordinates only and a second part containing vibrational coordinates only. It is customary to express the Hamiltonian by means of a series expansion. All orders, with the exception of the zero-order, contain both sets of coordinates and hence constitute an interaction between vibration and rotation. Since these functions are derived from the properties of the molecule itself, they must necessarily possess threefold symmetry about the axis of the molecule.

For the lowest of the vibration states and for J odd, it will be shown that the perturbation separates the two levels where $K=3$ and that the upper member of the pair has the antisymmetrical character A_2 while the lower one is symmetrical or A_1. For the next higher vibration state (these two vibration states constitute the levels giving rise to the microwave spectrum) the situation is reversed, the upper level being A_1 and the lower A_2. From the Pauli principle and from the fact that the nuclear-spin wave functions of three protons have the symmetry characters A_1 and E, but not A_2, it is evident that the states which are A_1 as regards vibration and rotation will not exist, whereas the A_2 states will. Thus the transition $J \rightarrow J$, $K=3 \rightarrow K=3$ will consist of a single line. The displacement of this line from its expected position will be just equal to the splitting of one of the levels caused by the threefold perturbation. (It should be remarked that in the microwave spectrum of ND_3, the lines of $K=3$ will not be displaced, but will consist of doublets. In the case of NDH_2 or ND_2H every line will be doubled with the exception of those where $K=0$. This splitting occurs already in zero-order and is a consequence of the fact that these molecules are asymmetric rotators.)

2. QUALITATIVE CONSIDERATIONS

Certain qualitative features of the perturbation may be obtained easily. The perturbed energy levels will be computed in the usual manner by seeking the roots of the determinant

$$|(J, K|H|J', K') - E\delta_{JJ'}\delta_{KK'}| = 0,$$

where $(J, K|H|J', K')$ are the elements of the perturbed Hamiltonian expressed through the wave functions of the unperturbed system (i.e., the zero-order Hamiltonian). The problem is greatly simplified by three facts. (1) $(J, K|H|J', K')=0$ unless $J=J'$ (i.e., H is diagonal in J) and consequently the originally infinite determinant factors into a product of determinants each with its own value of J. (2) From the symmetry considerations given earlier $(J, K|H|J, K')=0$ unless $K-K'$ is a multiple of 3. (3) Since the only levels which can possibly be split by a threefold perturbation are those where K itself is a multiple of 3, it will not be necessary to consider any of the other levels. As an example consider the case when J is equal to 3, 4 or 5. The determinant reduces to:

$$\begin{vmatrix} A-E & b & a \\ b & B-E & b \\ a & b & A-E \end{vmatrix} = 0 \qquad (1)$$

in which the quantities A and B are, respectively, $(J, 3|H|J, 3)$ and $(J, 0|H|J, 0)$. They are large since these elements contain the zero-order terms. a and b are $(J, 3|H|J, -3)$ and $(J, 3|H|J, 0)$ and are small quantities produced by the perturbing terms.

It has been shown by Shaffer[3] that for a molecule of the ammonia type, the first contributions which can be made to a and b are of third order. It will appear later from the analysis that in the case of a, the first non-vanishing contribution comes from the fourth-order perturbation.

The roots of the secular determinant may be designated as E_3^+, E_3^- and E_0. E_3^+ and E_3^- are very close together and differ only slightly from A, while E_0 is nearly equal to B. An elementary study of the determinant shows that E_3^+-A or $E_3^- - A$ will depend upon a to the first power but only upon b^2 as well as upon higher powers of a and b. Since b is already at least a third-order term, its influence upon E_3^+ and E_3^- will be, at best, only of sixth order. It may therefore

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

be neglected.[4] In that case the determinant becomes very simple and the two roots are,

$$E_3^+ = A + a, \quad E_3^- = A - a. \tag{2}$$

The stabilized wave functions (those parts depending upon φ) for E_3^+ and E_3^- are, respectively, $\psi_3^+ = (e^{3i\varphi} + e^{-3i\varphi})$ and $\psi_3^- = (e^{3i\varphi} - e^{-3i\varphi})$. The symmetry properties of these wave functions may be readily obtained by performing a transformation in which two of the hydrogen nuclei are interchanged.[5] It is found that when J is an even integer ψ_3^+ is symmetrical (has the character A_1) and ψ_3^- is antisymmetrical, or A_2. If J is odd, the symmetries are interchanged and ψ_3^+ is A_2 while ψ_3^- is A_1.

It has already been pointed out that the wave functions of the protons have characters A_1 and E, but not A_2. The total wave function must be antisymmetric or A_2. Thus for the lower of the pair of vibrational states giving rise to the inversion frequency and for J even, only the state defined by the wave function ψ_3^- exists. For the higher of the two vibrational levels only ψ_3^+ exists. The observed absorption line will therefore be displaced towards *higher* frequencies by the amount $2a$. The analysis will show that a is a positive quantity and is a function of J. In a similar fashion one can show that when J is odd the observed line will be displaced towards *lower* frequencies. These qualitative results are in complete agreement with the experimental observations.

3. ANALYSIS OF THE SPLITTING OF LEVELS WHERE $K=3$

The problem of the vibration-rotation energies of the pyramidal XY_3 molecule has been studied by Shaffer[3] who expanded the quantum-mechanical Hamiltonian to include second-order terms and evaluated relations for the energies to this approximation. As has been mentioned, Shaffer demonstrated that to second order the energy matrix contained elements only along the principal diagonal. This is equivalent to stating that to this order the molecule remains a symmetric rotator and that none of the degeneracies in K are removed. It is therefore necessary in our case to investigate the energies to approximations beyond the second. We have, moreover, seen that no degeneracies in K except for those states where K is an integer equal to a multiple of 3 can be removed by any perturbation which lies within the molecule itself. It is only necessary to consider, therefore, the elements $(K = \pm 3 | K = \mp 3)$ to the energy in a given approximation. It has been pointed out that elements of the kind $(K = \pm 3 | K = 0)$ may be neglected, since they can only introduce exceedingly high order terms. Since the expansion of the quantum-mechanical Hamiltonian contains the angular-momentum operators at most quadratically in any approximation the elements $(K = \pm 3 | K = \mp 3)$ cannot arise before in third order of approximation. It is readily shown that these will be equal in nth order to:

$$\begin{aligned}
&(\tau, K=\pm 3|H^{(n)}|\tau, K=\mp 3)\\
&=\sum_{\tau'}\sum_{\tau''}\cdots\sum_{\tau^{(n-1)}} \frac{(\tau, K=\pm 3|H^{(1)}|\tau', K')(\tau'K'|H^{(1)}|\tau''K'')\cdots(\tau^{(n-1)}K^{(n-1)}|H^{(1)}|\tau, K=\mp 3)}{(hc)^{n-1}\omega(\tau,\tau')\omega(\tau,\tau'')\cdots\omega(\tau,\tau^{(n-1)})}\\
&+\sum_{\tau'}\sum_{\tau''}\cdots\sum_{\tau^{(n-2)}} \frac{(\tau, K=\pm 3|H^{(2)}|\tau', K')(\tau'K'|H^{(1)}|\tau'', K'')\cdots(\tau^{(n-2)}K^{(n-2)}|H^{(1)}|\tau, K=\mp 3)}{(hc)^{n-2}\omega(\tau,\tau')\omega(\tau,\tau'')\cdots\omega(\tau,\tau^{(n-2)})}\\
&+\sum_{\tau'}\sum_{\tau''}\cdots\sum_{\tau^{(n-2)}} \frac{(\tau, K=\pm 3|H^{(1)}|\tau', K')(\tau', K'|H^{(2)}|\tau'', K'')\cdots(\tau^{(n-2)}K^{(n-2)}|H^{(1)}|\tau, K=\mp 3)}{(hc)^{n-2}\omega(\tau,\tau')\omega(\tau,\tau'')\cdots\omega(\tau,\tau^{(n-2)})}+\cdots\\
&+\sum_{\tau'}\sum_{\tau''}\cdots\sum_{\tau^{(n-2)}} \frac{(\tau, K=\pm 3|H^{(1)}|\tau', K')(\tau', K'|H^{(1)}|\tau'', K'')\cdots(\tau^{(n-2)}K^{(n-2)}|H^{(2)}|\tau, K=\mp 3)}{(hc)^{n-2}\omega(\tau,\tau')\omega(\tau,\tau'')\cdots\omega(\tau,\tau^{(n-2)})}+\cdots,
\end{aligned} \tag{3}$$

where τ is made to embrace all the vibration quantum numbers.

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[4] Although our example was for $J=3$, 4 or 5 in order not to introduce the complication of K equalling higher multiples of 3, it is evident that the argument may be extended to include any value of J.

[5] The total wave function is a product of the vibrational wave function ψ_v and a rotational wave function containing the quantum numbers J, K, and M. Since the symmetry cannot depend upon the magnetic quantum number M it

Shaffer made use of a method whereby the quantum-mechanical Hamiltonian is transformed by a contact transformation such that the first order transformed Hamiltonian, $H^{(1)\prime}$, will contain no terms to second order except the coriolis terms arising from the twofold degenerate oscillations. He does not, therefore, state explicitly the quantum-mechanical Hamiltonian before transformation, but gives only the first- and second-order transformed Hamiltonians. Since these are good only to second order it becomes necessary here to expand the quantum-mechanical Hamiltonian to the second order of approximation. This may be accomplished by using the method of Howard and Wilson,[6] or what is actually simpler, the method of Nielsen[7] for the general polatomic molecule.

Retaining the notation of Shaffer except in minor respects we obtain

$$\begin{aligned} H^{(0)}=(\hbar/2)\{\sum_{i=1,\,3}\lambda_i^{\frac{1}{2}}(p_i{}^2/\hbar^2+q_i{}^2)+\sum_{k=2,\,4}\lambda_k^{\frac{1}{2}}(p_{k,\,1}{}^2/\hbar^2+p_{k,\,2}{}^2/\hbar^2+q_{k,\,1}{}^2+q_{k,\,2}{}^2)\} \\ +(1/2)\{(P_x{}^2+P_y{}^2)/I_{xx}{}^{(e)}+(P_z{}^2/I_{zz}{}^{(e)})\}, \end{aligned} \tag{4a}$$

$$\begin{aligned} H^{(1)}=\cdots-\{&\sum_{i=1,\,2}\sum_{k=2,\,4}\xi_{ik}[(\omega_i/\omega_k)^{\frac{1}{2}}q_{k,\,2}p_i-(\omega_k/\omega_i)^{\frac{1}{2}}q_ip_{k,\,2}]+\xi_{24}[(\omega_2/\omega_4)^{\frac{1}{2}}(q_{4,\,2}p_{2,\,1}+q_{4,\,1}p_{2,\,2}) \\ &-(\omega_4/\omega_2)^{\frac{1}{2}}(q_{2,\,1}p_{4,\,2}+q_{2,\,2}p_{4,\,1})]\}(P_x/I_{xx}{}^{(e)})+\{\sum_{i=1,\,3}\sum_{k=2,\,4}\xi_{ik}[(\omega_i/\omega_k)^{\frac{1}{2}}q_{k,\,1}p_i-(\omega_k/\omega_i)^{\frac{1}{2}}q_ip_{k,\,1}] \\ &-\xi_{2,\,4}[(\omega_2/\omega_4)^{\frac{1}{2}}(q_{4,\,1}p_{2,\,1}-q_{4,\,2}p_{2,\,2})-(\omega_4/\omega_2)^{\frac{1}{2}}(q_{2,\,1}p_{4,\,1}-q_{2,\,2}p_{4,\,2})]\}(P_y/I_{xx}{}^{(e)}) \\ &-\tfrac{1}{2}\sum_{i=1,\,3}(\hbar^2/\lambda_i)^{\frac{1}{4}}\{2[(I_{xx}{}^{(e)}-\tfrac{1}{2}I_{zz}{}^{(e)})^{\frac{1}{2}}\alpha_i-\tfrac{1}{2}\beta_i(I_{zz}{}^{(e)})^{\frac{1}{2}}](P_x{}^2+P_y{}^2)/(I_{xx}{}^{(e)})^2\}q_i \\ &+\tfrac{1}{2}\sum_{k=2,\,4}(\hbar^2/\lambda_k)^{\frac{1}{4}}\{(I_{zz}{}^{(e)})^{\frac{1}{2}}\delta_k(P_x{}^2-P_y{}^2)/(I_{xx}{}^{(e)})^2\}q_{k,\,1} \\ &-\tfrac{1}{2}\sum_{k=2,\,4}(\hbar^2/\lambda_k)^{\frac{1}{4}}\{(I_{zz}{}^{(e)})^{\frac{1}{2}}\delta_k(P_xP_y+P_yP_x)/(I_{xx}{}^{(e)})^2\}q_{k,\,2} \\ &+\tfrac{1}{2}\sum_{k=2,\,4}(\hbar^2/\lambda_k)^{\frac{1}{4}}\{(2I_{zz}{}^{(e)})^{\frac{1}{2}}(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\delta_{k'}(P_yP_z+P_zP_y)/(I_{xx}{}^{(e)})(I_{zz}{}^{(e)})\}q_{k,\,2} \\ &+\tfrac{1}{2}\sum_{k=2,\,4}(\hbar^2/\lambda_k)^{\frac{1}{4}}\{(2I_{zz}{}^{(e)})^{\frac{1}{2}}(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\delta_{k'}(P_zP_x+P_xP_z)/(I_{xx}{}^{(e)})(I_{zz}{}^{(e)})\}q_{k,\,1}+V_1, \end{aligned} \tag{4b}$$

$$\begin{aligned} H^{(2)}=\cdots\tfrac{1}{2}\{&\sum_{k=2,\,4}(\hbar^4/\lambda_k{}^2)^{\frac{1}{4}}(3\delta_k{}^2I_{zz}{}^{(e)}/4I_{xx}{}^{(e)})(q_{k,\,1}{}^2+q_{k,\,2}{}^2)+3\sum_{i=1,\,3}(\hbar^4/\lambda_i{}^2)^{\frac{1}{4}}[(1-(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}})\alpha_i \\ &-(\beta_i/\sqrt{2})(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}]^2q_i{}^2\}(P_x{}^2+P_y{}^2)/(I_{xx}{}^{(e)})^2-\tfrac{1}{2}\{\textstyle\sum_k(\hbar^4/\lambda_k{}^2)^{\frac{1}{4}}[\delta_k{}^2-3(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\delta_{k'}{}^2 \\ &+4(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^2\delta_{k'}{}^2-(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^2\delta_{k'}{}^4-(1+(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^2)\delta_k\delta_{k'}-\delta_k{}^4](q_{k,\,1}{}^2+q_{k,\,2}{}^2) \\ &-3\textstyle\sum_i(\hbar^4/\lambda_k{}^2)^{\frac{1}{4}}\alpha_iq_i{}^2\}(P_z/I_{zz}{}^{(e)})^2+\tfrac{1}{2}\textstyle\sum_k(\hbar^4/\lambda_k{}^2)^{\frac{1}{2}}\{2\delta_{k'}{}^2(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})q_{k,\,1}{}^2 \\ &-[\delta_{k'}{}^2(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})-(\xi_{k,\,1}{}^2+\xi_{k,\,3}{}^2)]q_{k,\,2}{}^2\}(P_x/I_{xx}{}^{(e)})^2+\tfrac{1}{2}\textstyle\sum_k(\hbar^4/\lambda_k{}^2)^{\frac{1}{2}} \\ &\times\{2\delta_{k'}{}^2(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})q_{k,\,2}{}^2-[\delta_{k'}{}^2(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})-(\xi_{k,\,1}{}^2+\xi_{k,\,3}{}^2)]q_{k,\,1}{}^2\}(P_y/I_{xx}{}^{(e)})^2 \\ &-\tfrac{1}{2}\sum_{k=2,\,4}(\hbar^4/\lambda_k{}^2)^{\frac{1}{2}}\{2\delta_{k'}{}^2(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})+[\delta_{k'}{}^2(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})-(\xi_{k,\,1}{}^2+\xi_{k,\,3}{}^2)]\} \\ &\times q_{k,\,1}q_{k,\,2}(P_xP_y+P_yP_x)/(I_{xx}{}^{(e)})^2+V_2+\cdots. \end{aligned} \tag{4c}$$

To test the relation H against computational errors, we may specialize it for the case of the planar XY_3 model by letting the height of the pyramid go to zero, i.e., then $I_{zz}{}^{(e)}=2I_{xx}{}^{(e)}$. Inspection reveals that (4) reduces to the relations (14) in the work of Silver and Shaffer.[8]

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will be convenient to chose $M=0$. In that case, one has $\Psi=\psi_v\ \sin^3\theta F(\cos\theta)f(\varphi)$. When J is even, $F(\cos\theta)$ is an odd function of $\cos\theta$ while for J odd it is even. For the level $E_3{}^+$, $f(\varphi)=\cos 3\varphi$ while for $E_3{}^-$, $f(\varphi)=\sin 3\varphi$. The process of interchanging two of the protons may be accomplished through the following steps. (1) Invert the molecule. For the lowest of the vibrational levels $\psi_v\rightarrow\psi_v$ while for the higher one $\psi_v\rightarrow-\psi_v$. (2) Let $\theta\rightarrow\pi-\theta$. Clearly $F\rightarrow-F$ when J is even and $F\rightarrow F$ when J is odd. (3) Let $\varphi\rightarrow\pi-\varphi$. In this process $\cos 3\varphi\rightarrow-\cos 3\varphi$, but $\sin 3\varphi\rightarrow\sin 3\varphi$. (4) Let $\psi\rightarrow\pi+\psi$. The angle ψ is the third Eulerian angle and does not appear in the wave functions since M has been set equal to zero.

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

[7] H. H. Nielsen, Phys. Rev. **60**, 794 (1941).

[8] S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

It is convenient to replace the coordinates $q_{k,1}$ and $q_{k,2}$ by $r_k \cos\chi_k$ and $r_k \sin\chi_k$, respectively, and the conjugate momenta, $p_{k,1}$ and $p_{k,2}$, by their equivalents $(\cos\chi_k p_{r_k} - (\sin\chi_k/r_k)p_{\chi_k})$ and $(\sin\chi_k p_{r_k} + (\cos\chi_k/r_k)p_{\chi_k})$ where $p_{r_k} = -i\hbar\partial/\partial r_k$ and $p_{\chi_k} = -i\hbar\partial/\partial\chi_k$. When this is accomplished the relations become:

$$\begin{aligned} H_0 = (\hbar/2)\{ &\sum_{i=1,3} \lambda_i^{\frac{1}{2}}(p_i^2/\hbar^2+q_i^2) + \sum_{k=2,4} \lambda_k^{\frac{1}{2}}[((1/r_k)p_{r_k}r_kp_{r_k})/\hbar^2+(p_{\chi_k}^2/r_k^2)+r_k^2]\} \\ &+(1/2)\{(P_x^2+P_y^2)/I_{xx}^{(e)}+(P_z^2/I_{zz}^{(e)})\}, \end{aligned} \tag{5a}$$

$$\begin{aligned} H_1 = \cdots\{ &\sum_{\substack{i=1,3\\k=2,4}} (i\xi_{ik}/2)e^{i\chi_k}[(\omega_i/\omega_k)^{\frac{1}{2}}r_kp_i-(\omega_k/\omega_i)^{\frac{1}{2}}q_i(p_{r_k}+ip_{\chi_k}/r_k)] \\ &-(i\xi_{2,4}/2)e^{-i(\chi_2+\chi_4)}[(\omega_2/\omega_4)^{\frac{1}{2}}r_4(p_{r_2}-ip_{\chi_2}/r_2)-(\omega_4/\omega_2)^{\frac{1}{2}}r_2(p_{r_4}-ip_{\chi_4}/r_4)]\}(P_x-iP_y)/I_{xx}^{(e)} \\ &-\{\sum_{\substack{i=1,3\\k=2,4}} (i\xi_{ik}/2)e^{-i\chi_k}[(\omega_i/\omega_k)^{\frac{1}{2}}r_kp_i-(\omega_k/\omega_i)^{\frac{1}{2}}q_i(p_{r_k}-ip_{\chi_k}/r_k)]+(i\xi_{2,4}/2)e^{i(\chi_2+\chi_4)} \\ &\times[(\omega_2/\omega_4)^{\frac{1}{2}}r_4(p_{r_2}+ip_{\chi_2}/r_2)-(\omega_4/\omega_2)^{\frac{1}{2}}r_2(p_{r_4}+ip_{\chi_4}/r_4)]\}(P_x+iP_y)/I_{xx}^{(e)} \\ &-(\hbar^{\frac{1}{2}}/2)\{\sum_{i=1,3} 2[(I_{xx}^{(e)}-\tfrac{1}{2}I_{zz}^{(e)})\alpha_i-\tfrac{1}{2}\beta(I_{zz}^{(e)})^{\frac{1}{2}}](q_i/\lambda_i^{\frac{1}{4}})\}(P_x^2+P_y^2)/(I_{xx}^{(e)})^2 \\ &+(\hbar^{\frac{1}{2}}/4)(I_{zz}^{(e)})^{\frac{1}{2}}\{\sum_{k=2,4} (\delta_k/\lambda_k^{\frac{1}{4}})r_ke^{i\chi_k}(P_x+iP_y)^2/(I_{xx}^{(e)})^2+\sum_{k=2,4} (\delta_k/\lambda_k^{\frac{1}{4}})r_ke^{-i\chi_k}(P_x-iP_y)^2/(I_{xx}^{(e)})^2\} \\ &+(\hbar^{\frac{1}{2}}/4)(2I_{xx}^{(e)})^{\frac{1}{2}}(1-I_{zz}^{(e)}/2I_{xx}^{(e)})\{(\gamma_k/\lambda_k^{\frac{1}{4}})r_ke^{i\chi_k}[(P_x-iP_y)P_z+P_z(P_x-iP_y)]/(I_{xx}^{(e)})(I_{zz}^{(e)})\} \\ &+(\hbar^{\frac{1}{2}}/4)(2I_{xx}^{(e)})^{\frac{1}{2}}(1-I_{zz}^{(e)}/2I_{xx}^{(e)})\{(\gamma_k/\lambda_k^{\frac{1}{4}})r_ke^{-i\chi_k} \\ &\times[(P_x+iP_y)P_z+P_z(P_x+iP_y)]/(I_{xx}^{(e)})(I_{zz}^{(e)})\}^{9}+V_1+\cdots, \end{aligned} \tag{5b}$$

$$\begin{aligned} H_2 = \cdots(&\sum_{i=1,3} a_iq_i^2+\sum_{k=2,4} a_kr_k^2)(P_x^2+P_y^2)/(I_{xx}^{(e)})^2+(\sum_{i=1,3} b_iq_i^2+\sum_{k=2,4} b_kr_k^2(P_z/I_{zz}^{(e)})^2 \\ &+\tfrac{1}{4}\sum_{k=2,4} (\hbar^4/\lambda_k^2)^{\frac{1}{4}}r_k^2e^{2i\chi_k}[(3\gamma_k^2/4)(1-I_{zz}^{(e)}/2I_{xx}^{(e)})][(P_x+iP_y)^2/(I_{xx}^{(e)})^2] \\ &+\tfrac{1}{4}\sum_{k=2,4} (\hbar^4/\lambda_k^2)^{\frac{1}{4}}r_k^2e^{-2i\chi_k}[(3\gamma_k^2/4)(1-I_{zz}^{(e)}/2I_{xx}^{(e)})][(P_x-iP_y)^2/(I_{xx}^{(e)})^2]+V_2+\cdots, \end{aligned} \tag{5c}$$

In the foregoing relations the constants α_1 and β_1 take the values α and β, respectively, defined by Eqs. (10) in reference (3), while α_3 and β_3 take the values β and $-\alpha$, respectively. Similarly, δ_2 and γ_2 assume the values δ and γ in Shaffer's notation and δ_4 and γ_4 take the values $-\gamma$ and δ, respectively. The subscripts k and k' take the values 2 and 4, but $k \neq k'$. The quantities a_i, b_i, etc., are constants which we shall not state explicitly since they do not enter the final result.

It is readily verified that $H^{(1)}$ will have non-vanishing matrix components of the kind

$$\begin{gathered} (v_i, v_k, l_k, v_{k'}, l_{k'}, K \mid v_i\pm 1, v_k\pm 1, l_k\pm 1, v_{k'}, l_{k'}, K\pm 1), \\ (v_i, v_k, l_k, v_{k'}, l_{k'}, K \mid v_i, v_k\pm 1, l_k\pm 1, v_{k'}\pm 1, l_k\pm 1, K\mp 1), \\ (v_i, v_k, l_k, v_{k'}, l_{k'}, K \mid v_i, v_k\pm 1, l_k\pm 1, v_{k'}, l_{k'}, K\mp 2), \end{gathered}$$

and

$$(v_i, v_k, l_k, v_{k'}, l_{k'}, K \mid v_i', v_{k'}', l_{k}', v_{k'}', l_{k'}', K)$$

where l_k is a quantum number characterizing the angular momentum associated with the degenerate vibration ω_k and has the values v_k, $v_k - 2$, $\cdots 1$ or 0. The last type of matrix component stated above originates with the potential energy terms V_1 which is given by Shaffer, but is not stated explicitly here. Except for the first two terms, which are diagonal in K and therefore of no interest here, the

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[9] The last two terms in Eq. (5b) may be neglected from here on. They have matrix components of the same kind as the first term in (5b) but are of the order $(B_e/\omega_k)^{\frac{1}{2}}$ times these. The factor $(B_e/\omega_k)^{\frac{1}{2}}$ is, of course, small.

non-vanishing matrix components of H_2 are the following:

$$(v_i, v_k, l_k, v_{k'}, l_{k'}, K|v_i, v_k\pm 2, l_k\pm 2, v_{k'}, l_{k'}, K\pm 2),$$
$$(v_i, v_k, l_k, v_{k'}, l_{k'}, K|v_i, v_k, l_k\pm 2, v_{k'}, l_{k'}, K\pm 2)$$

and $(v_i, v_k, l_k, v_{k'}, l_{k'}, K|v_i', v_k', l_k, v_{k'}', l_{k'}, K)$, the last of these originating with the quartic terms of the potential-energy function.

We are interested in making the computations indicated here only for the normal-vibration state, i.e., where the vibration quantum numbers v_i, v_k, l_k are all equal to zero. To make the calculation for states beyond the normal state would be so laborious as to be hardly practicable and it is doubtful, moreover, that the analysis presented here would be valid in higher states. If the relation (3) is specialized for the case where $n=3$ (i.e., third approximation) it is readily seen that only the first term may yield matrix elements of the kind $(v_i, v_k, l_k, v_{k'}, l_{k'}, K=\pm 3|H^{(3)}|v_i', v_k', l_k', v_{k'}', l_{k'}', K=\mp 3)$ and these must originate with the third type of matrix components of $H^{(1)}$, i.e., the elements $(v_i, v_k, l_k, v_{k'}, l_{k'}, K|H^{(1)}|v_i, v_k\pm 1, l_k\pm 1, v_{k'}, l_{k'}, K\mp 2)$. It is clear, however, that with $v_i=v_k=l_k=0$ the quantum numbers v_i', v_k', l_k' cannot all be equal to zero. There are, therefore, no $(K=\pm 3|H^{(3)}|K=\mp 3)$ elements of third order of magnitude.

Turning now to fourth order we specialize the relation (3) for the case $n=4$. In this case elements of the type $(v_i, v_k, l_k, v_{k'}, l_{k'}, K=\pm 3|H^{(4)}|v_i', v_k', l_k', v_{k'}', l_{k'}', K=\mp 3)$ can originate from all the terms in the expansion. It is quickly verified, however, that none but the first terms are significant here. The latter terms are "cross product" terms between $H^{(1)}$ and $H^{(2)}$ which to give elements $(\cdots K=\pm 3|H^{(4)}|\cdots K=\mp 3)$ must arise with the matrix elements $(\cdots K|H^{(1)}|\cdots K\pm 2)$ and $(\cdots K|H^{(2)}|\cdots K\pm 2)$. It will be seen from the character of these, however, that if $v_i=v_k=l_k=0$ the quantum numbers v_i', v_k' and l_k' cannot all be equal to zero. They do not, therefore, contribute to the energy in fourth order.

There are essentially only two different kinds of contributions of the first type which are caused by "cross product" terms of $H^{(1)}$. There may be $(v_i, v_k, l_k, v_{k'}, l_{k'}, K=\pm 3|H^{(4)}|v_i', v_k', l_k', v_{k'}', l_{k'}', K=\mp 3)$ elements from $(\cdots K|H^{(1)}|\cdots K\pm 2)$ occurring three times and $(\cdots K|H^{(1)}|\cdots K)$ occurring one time. Inspection reveals that if v_i, v_k, l_k, etc., are equal to zero, then, as before, the values of v_i', v_k', l_k', etc. cannot all be equal to zero. Such contributions may therefore be neglected for the normal state. The only remaining types of contributions originate from $(v_i, v_k, l_k, v_{k'}, l_{k'}, K|H^{(1)}|v_i, v_k', l_k\mp 1, v_{k'}, l_{k'}, K\pm 2)$ elements occurring twice with $(v_i, v_k, l_k, v_{k'}, l_{k'}, K|H^{(1)}|v_i\pm 1, v_k'', l_k\pm 1, v_{k'}, l_{k'}K\pm 1)$ elements also occurring twice and from $(v_i, v_k, l_k, v_{k'}, l_{k'}K|H^{(1)}|v_i, v_k', l_k\mp 1, v_{k'}, l_{k'}, K\pm 2)$ elements and $(v_i, v_k, l_k, v_{k'}, l_{k'}K|H^{(1)}|v_i, v_k, l_k, v_{k'}', l_{k'}\mp 1, K\pm 2)$ elements each occurring once with the elements $(v_i, v_k, l_k, v_{k'}, l_{k'}, K|H^{(1)}|v_i\pm 1, v_k', l_k\pm 1, v_{k'}, l_{k'}, K\pm 1)$ and $(v_i, v_k, l_k, v_{k'}, l_k, K|H^{(1)}|v_i\pm 1, v_k, l_k, v_{k'}', l_{k'}\pm 1, K\pm 1)$ each occurring once. These present a possibility since in the one type of element l_k and K vary in the same sense while in the other type they vary in the opposite sense. Thus the original and final K values may be $K=\pm 3$ and $K=\mp 3$, respectively, while v_i, v_k, l_k, etc., and v_i', v_k', l_k', etc., are all equal to zero. Typical examples of such products which go to make up the sum of terms constituting (3) are these $(0, 0, 0, 0, 0, K=3|H^{(1)}|0, 1, 1, 0, 0, K=1)$ $(0, 1, 1, 0, 0, K=1|H^{(1)}|0, 2, 2, 0, 0, K=-1)(0, 2, 2, 0, 0, K=-1|H^{(1)}|1, 1, 1, 0, 0, K=-2)$ $(1, 1, 1, 0, 0, K=-2|H^{(1)}|0, 0, 0, 0, 0, K=-3)$ and $(0, 0, 0, 0, 0, K=3|H^{(1)}|0, 1, 1, 0, 0, K=1)$ $(0, 1, 1, 0, 0, K=1|H^{(1)}|0, 1, 1, 1, 1, K=-1)(0, 1, 1, 1, 1, K=-1|H^{(1)}|1, 1, 1, 0, 0, K=-3)$ $(1, 1, 1, 0, 0, K=-2|H^{(1)}|0, 0, 0, 0, 0, K=-3)$. We have thus the rather surprising result that to this approximation the splitting is independent of the anharmonic constants in the potential energy.

The actual evaluation of the matrix elements $(0, 0, 0, 0, 0, K=\pm 3|H^{(1)}|0, 0, 0, 0, 0, K=\mp 3)$ is a very tedious and laborious task. This is particularly true since, while the matrix elements of $e^{+i\chi r}$ have been given by Shaffer,[10] the corresponding elements of $e^{\pm i\chi}(p_r\pm ip_\chi/r)$ have not been investigated. The matrix elements required in this calculation have all been evaluated here in the usual

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[10] W. H. Shaffer, Rev. Mod. Phys. 16, 245 (1944).

quantum-mechanical manner, i.e.,

$$(v_k, l_k | v_k', l_k') = \int \bar{\Psi}_{v_k, l_k} f(r_k, p_{r_k}, \chi_k, p_{x_k}) \Psi_{v_k', l_k'} d\tau$$

where the functions Ψ_{v_k, l_k} used are the ones given by Dennison.[11] These have already been normalized.

No attempt will be made here to set down the details of this calculation. We shall point out only that in the sum of terms which comprise (3) there are twenty components where $(v_i, v_k, l_k, v_{k'}, l_{k'}, K | H^{(1)} | v_i, v_k', l_k \mp 1, v_{k'}, l_{k'}, K \pm 2)$ occur together with the elements $(v_i, v_k, l_k, v_{k'}, l_{k'}, K | H^{(1)} | v_i \pm 1, v_k', l_k \pm 1, v_k', l_k', K \pm 1)$, ten components for each value of K, and of the components where the elements $(v_i, v_k, l_k, v_{k'}, l_{k'}, K | H^{(1)} | v_i, v_k', l_k \mp 1, v_{k'}, l_{k'}, K \pm 2)$ and $(v_i, v_k, l_k, v_{k'}, l_{k'}, K | H^{(1)} | v_i, v_k, l_k, v_{k'}', l_{k'} \mp 1, K \pm 2)$ occur together with the elements $(v_i, v_k, l_k, v_{k'}, l_{k'}, K | H^{(1)} | v_i \pm 1, v_k', l_k \pm 1, v_{k'}, l_{k'}, K \pm 1)$ and $(v_i, v_k, l_k, v_{k'}, l_{k'} K | H^{(1)} | v_i \pm 1, v_k, l_k, v_{k'}', l_{k'} \pm 1, K \pm 1)$, each occurring once, there are twenty-four. When a common denominator for all these components is found and they are all added together the following surprisingly simple relation for the elements which lie off of the principal diagonal of the energy matrix is obtained:[12]

$$\begin{aligned}(0, 0, 0, 0, 0, K = \pm 3 | H^{(4)} | 0, 0, 0, 0, 0, K = \mp 3) = \sum_{i=1,3} (I_{zz}^{(e)}/I_{xx}^{(e)})(h^2/8\pi^2 I_{xx}^{(e)}) \\ \times [(B_e/\omega_2)^2 \delta \xi_{i2} + (B_e/\omega_4)^2 \gamma \xi_{i4}]^2 [J(J+1)][J(J+1)-2][J(J+1)-6]. \quad (6)\end{aligned}$$

For the purpose of computation (6) is more conveniently written in the form:

$$\begin{aligned}(0, 0, 0, 0, 0, K = \pm 3 | H^{(4)} | 0, 0, 0, 0, 0, K = \mp 3) = (I_{zz}^{(e)}/2I_{xx}^{(e)})(1 + I_{zz}^{(e)}/2I_{xx}^{(e)})(h^2/8\pi^2 I_{xx}^{(e)}) \\ \times [(B_e/\omega_2)^2 + (B_e/\omega_4)^2]^2 \{(n_2^2/\mu_2 m)/[(4n_2^2/\mu_2 m) + (n_1/\mu_2 - n_3/m)^2]\} \\ \times \{[J(J+1)][J(J+1)-2][J(J+1)-6]\}. \quad (6')\end{aligned}$$

The actual energy values of the molecule will, therefore, be the same as those given by Shaffer[3] for all states except those where $|K| = 3$. In all cases save these the energies are given by the elements along the principal diagonal and for the cases where $|K| = 3$ the elements may be so arranged as to form a little box with two rows and two columns each. These sub-matrices may then be diagonalized independently and the energies will be found to be:

$$E(|K| = 3) = E(s) \pm \epsilon \quad (7)$$

$E(s)$ being the values for the energy states where $K = 3$ given by Shaffer[3] and ϵ has the values (6′). The actual separation in cm^{-1} between the component levels will evidently be:

$$\begin{aligned}\Delta\nu = (2\epsilon/hc) = (I_{zz}^{(e)}/I_{xx}^{(e)})(1 + I_{zz}^{(e)}/2I_{xx}^{(e)}) B_e [(B_e/\omega_2)^2 + (B_e/\omega_4)^2]^2 \{(n_2^2/\mu_2 m)/[(4n_2^2/\mu_2 m) \\ + (n_1/\mu_2 - n_3/m)^2]\} \{[J(J+1)][J(J+1)-2][J(J+1)-6]. \quad (8)\end{aligned}$$

It has been shown in the introduction that (8) is actually the amount by which the measured lines will be displaced.

4. NUMERICAL RESULTS

The quantities which occur in the relation (8) may all be arrived at from the experimental data on the ammonia and deutero-ammonia spectra and we shall make the calculations for these two molecules where the nitrogen atom is taken to be the more abundant N^{14}. The frequencies ω_2 and

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[11] D. M. Dennison, Rev. Mod. Phys. **3**, 380 (1931).

[12] This is a special case of the $(K | K \pm 6)$ matrix elements which may be shown to be

$$[J(J+1) - K(K \pm 1)]^{\frac{1}{2}} [J(J+1) - (K \pm 1)(K \pm 2)]^{\frac{1}{2}} \cdots [J(J+1) - (K \pm 5)(K \pm 6)]^{\frac{1}{2}}.$$

TABLE I. Numerical values for rotational constants for NH_3 and ND_3.

	$I_{xx}^{(e)}\times 10^{40}$ g-cm^2	$I_{zz}^{(e)}\times 10^{40}$ g-cm^2	B_e
NH_3	2.816	4.437	9.941
ND_3	5.448	8.868	5.138

ω_4 for these molecules have been determined with considerable precision by Dennison[13] who has made corrections to the observed frequencies for the anharmonicity of the oscillational motion. His values are $\omega_2=3622$ cm^{-1} and $\omega_4=1685$ cm^{-1} for NH_3 and $\omega_2=2670$ cm^{-1} and $\omega_4=1221$ cm^{-1} for ND_3. From these he has evaluated the constants

$$k_1,\ k_2,\ k_3,\ (I_{zz}^{(e)}/2I_{xx}^{(e)})^2 n_1,\ (I_{zz}^{(e)}/2I_{xx}^{(e)})n_2,\ n_3$$

retaining Shaffer's notation. We need only the last three of these constants and for these he obtains

$$(I_{zz}^{(e)}/2I_{xx}^{(e)})^2 n_1=10.494,$$
$$(I_{zz}^{(e)}/2I_{xx}^{(e)})n_2=4.168$$

and $n_3=4.098\times 10^5$ dyne/cm.

The values for the moments of inertia and of $B_e=h/8\pi^2 I_{xx}^{(e)}c$ are known with considerable accuracy for the NH_3 and ND_3 molecules from their spectra. The values for these are set down in Table I and are those given by Herzberg.[14]

When these constants are substituted into relation (8) one obtains the values for the K-type splitting given in Table II. Here also are given, for various J values, the shifts of the lines originating in the levels where $K=3$ as measured by Good and Coles[1] as well as the shifts predicted by this theory. In Table II are also given the predicted shifts for the $K=3$ lines in ND_3.

TABLE II. Numerical values of the K-type splitting and line shifts.

	NH_3			ND_3	
J value	$\Delta\nu$ (Mc)	Calculated shifts (Mc)	Measured shifts	$\Delta\nu$ (Mc)	Calculated shifts (Mc)
3	0.26	−0.26	−0.30	0.03	0.03
4	1.80	1.80	1.76	0.24	0.24
5	7.21	−7.21	−7.17	0.95	0.95
6	21.63	21.63	22.3	2.85	2.85
7	54.27	−54.27	—	7.14	7.14

The values of the constants required in (8) to make the same calculations for the $N^{15}H_3$ and $N^{15}D_3$ molecules have not been evaluated from the experimental data. The values of ω_2 and ω_4 for these molecules can, however, be calculated from a knowledge of the constants k_1, k_2, k_3, etc. which have been evaluated. Similarly, the rotational constants for the $N^{15}H_3$ and $N^{15}D_3$ molecules have not been determined from experiment. They can, nevertheless, be calculated from geometrical considerations.[15] It may be shown, however, that the constants for the ammonia molecules with the isotope N^{15} are the same within a fraction of a percent as those for the molecules with the ordinary nitrogen atom. We shall, therefore, not here give the shifts of the lines for these molecules since within the limits to which these calculations may be regarded as accurate they will be the same as those given in Table II. This is particularly true since $(4n_2^2/\mu_2 m)\gg(n_1/\mu_2-n_3/m)^2$ for all these molecules so that the constant $(4n_2^2/\mu_2 m)/[(4n_2^2/\mu_2 m)-(n_1/\mu_2-n_3/m)^2]$ approaches unity.

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[13] D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

[14] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 437.

[15] It may be shown that $I_{xx}^{(e)}=I_{yy}^{(e)}=\mu h_0^2+\frac{1}{2}I_{zz}^{(e)}$, where h_0 is the height of the pyramid and μ is the reduced mass $3mM/(3m+M)$. The moment of inertia $I_{zz}^{(e)}$ depends only upon the masses of the hydrogen atoms and their distances from the center of gravity of the H_3 triangle. It remains the same for the $N^{14}H_3$ and the $N^{15}H_3$ molecules and for the $N^{14}D_3$ and $N^{15}D_3$ molecules. Also the pyramidal height, h_0, remains the same throughout.