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The Microwave Spectra of the Deutero-Ammonias*†

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Measurements of the inversion-rotation spectra of the deutero-ammonias have been made in the 4000-Mc/sec to 80,000-Mc/sec region. Fifty lines of NH_2D and NHD_2 have been measured and identified by means of the Stark effect. As expected, our results show that for these molecules, only simultaneous rotational and inversion transitions can be observed. Thus, corresponding to each $J_\tau \rightarrow J_{\tau'}$ transition two absorption lines can be observed, separated by either twice the rotational energy separation or twice the inversion splitting of the levels involved. From our observations the inversion splittings of the partially deuterated molecules can be calculated and are found to be in good agreement with the Dennison and Uhlenbeck inversion doubling theory. Thus, the inversion splittings for the ammonia molecules are approximately as follows: 24,000 Mc/sec for NH_3; 12,000 Mc/sec for NH_2D; 5000 Mc/sec for NHD_2; 2000 Mc/sec for ND_3. Our results are also in agreement with the structural parameters of ammonia as given by Herzberg. The sign of the nuclear quadrupole coupling constant was also measured and found to be negative, as expected. The centrifugal distortion for both rotation and inversion states has been experimentally determined.

INTRODUCTION

AMMONIA has occupied a unique position in microwave spectroscopy; and, because of its usefulness in a wide variety of spectroscopic investigations, it has perhaps the most intensively studied spectrum in the microwave region. However, most of the previous work has been confined to the inversion spectrum of NH_3, with very little effort expended to investigate the microwave spectra of the deutero-ammonias. This is somewhat surprising, since the partially deuterated ammonias can supply a considerable amount of useful and interesting information which cannot be obtained from the NH_3 microwave spectrum. Thus, since the finite NH_3 microwave absorption frequency is not due to rotational transitions, because of the symmetric top K degeneracy, but only to inversion transitions, the rotational constants cannot be obtained. Similarly, although the magnitude of the nuclear electric quadrupole coupling constant, eQq, has been obtained from the NH_3 hyperfine spectrum, its sign can be determined only by observing the NH_2D or NHD_2 spectrum. Furthermore, it should be of great interest to investigate in detail the unique microwave spectrum of these molecules in which simultaneous inversion and rotational transitions take place.

The first to investigate the microwave spectra of the deutero-ammonias was Kyhl[1] at M.I.T. in 1947. He identified a 9515-Mc/sec absorption as caused by NHD_2. More recently, Lyons[2] and a group at the National Bureau of Standards became interested in the low frequency deutero-ammonia spectrum for use in the construction of an "atomic" clock. They have reported a number of lines from 3000 Mc/sec to 17,000 Mc/sec but have given no proper interpretation of this spectrum.

ROTATIONAL ENERGY LEVELS

In this paper a description will be given of the detailed investigation of the microwave spectra of NH_2D and NHD_2. Both of these molecules are asymmetric rotors; thus, for each J rotational quantum number value there are $2J+1$ energy levels. These various levels are frequently denoted by a subscript τ which ranges from $-J$ to J and labels the levels in order of increasing energy. King, Hainer, and Cross[3] also designate these levels by means of a double subscript $K_{-1}K_1$, where $\tau=K_{-1}-K_1$. For a prolate symmetric top, K_{-1} is the quantum number for the projection of J on the principal axis of least moment of inertia, while for an oblate symmetric rotor K_1 represents the projects of J on the principal axis of greatest moment of inertia.

The rotational energy levels of a polyatomic molecule are determined by the usual three reciprocal moments of inertia, a, b, and c, where $a \geqslant b \geqslant c$. Both NH_2D and NHD_2 have a pyramidal structure with the nitrogen atom at the apex of the pyramid. For these pyramid types of molecules which have two equal atoms and one different atom on the base, one can show that the principal moments of inertia I_{zz}, I_1, and I_2 can be obtained from the following equations: (See Fig. 1).

$$\frac{I_{zz}}{mr^2}=\frac{\beta(2+\alpha)}{2+\alpha+\beta}+\frac{2\sin^2\frac{1}{2}\theta}{(2+\alpha+\beta)^2}\times[3\alpha(\alpha+2)-\beta(\beta+2)+2\alpha\beta], \tag{1a}$$

$$(I_{xx}+I_{yy})/2mr^2=(I_{zz}/2mr^2)+2\sin^2\tfrac{1}{2}\theta, \tag{1b}$$

$$\frac{I_{xx}-I_{yy}}{2mr^2}=\frac{\beta(2+\alpha)}{2(2+\alpha+\beta)}-\frac{\sin^2\frac{1}{2}\theta}{3(2+\alpha+\beta)^2}[9\alpha(\alpha+2)+5\beta(\beta+2)+2\alpha\beta(11+2\alpha+2\beta)], \tag{1c}$$

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[1] R. L. Kyhl, M.I.T. Physics Department thesis (1947).

[2] Lyons, Kessler, Rueger, and Nuckols, Phys. Rev. 81, 297, 630 (1951).

[3] King, Hainer, and Cross, J. Chem. Phys. 11, 27 (1943).

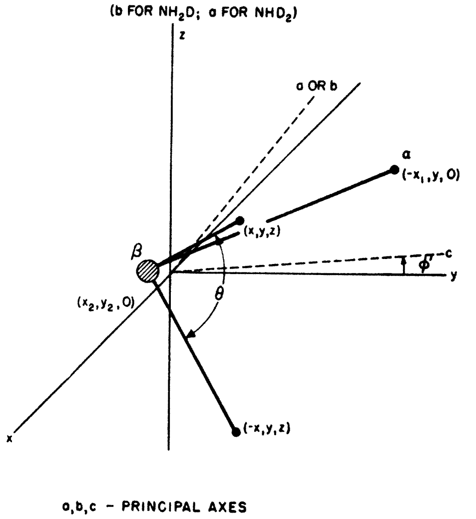

FIG. 1. Molecular geometry.

$$\frac{I_{xy}^2}{mr^2}=\frac{(1-\alpha)^2(2\beta)^2}{3(2+\alpha+\beta)^2}[\sin^2\tfrac{1}{2}\theta-(4/3)\sin^4\tfrac{1}{2}\theta], \qquad (1d)$$

$$I_{1,2}=\tfrac{1}{2}(I_{xx}+I_{yy})\pm\{[\tfrac{1}{2}(I_{xx}-I_{yy})]^2+I_{xy}^2\}^{\frac{1}{2}}, \qquad (1e)$$

$$\phi=\tan^{-1}[-(I_{xx}-I_2)/I_{xy}], \qquad (1f)$$

where α = mass ratio of the unique atom in the base of the pyramid to the mass of one of the two equal atoms, β = mass ratio of apex atom to one of the two equal atoms, r = distance from apex to corner of pyramid, θ = corner to apex to corner angle, and ϕ = angle between the geometric symmetry axis and a principal axis of inertia.

The values of r and θ for ammonia have been determined from the infrared data of NH_3 and ND_3 and are given by Herzberg[4] as follows: $r(N-H)=1.014\times10^{-8}$ cm and $\theta=H-N-H$ angle $=106.78°$. These values, although not fully accurate for the partially deuterated molecules, because of different zero-point vibrations, should still permit good preliminary calculations.

The rigid rotor energy value of the J_τ level can be expressed by

$$W(J_{1\tau})=\tfrac{1}{2}(a+c)J(J+1)+\tfrac{1}{2}(a-c)E_\tau^J(\kappa), \qquad (2)$$

where $E_\tau^J(\kappa)$ is a function of the asymmetry parameter which is defined by $\kappa=(2b-a-c)/(a-c)$ and can vary from -1 to $+1$. Values of the reduced energies $E_\tau^J(\kappa)$ are given by King, Hainer, and Cross for values of J from 0 to 12 in intervals of κ of 0.1. For intermediate values of κ, five-point lagrangian interpolation is required to obtain sufficient accuracy.

SELECTION RULES

The pure rotational selection rules on J for these molecules are $\Delta J=0, \pm1$, while the selection rules on the change in the subscripts $K_{-1}K_1$ depend upon the orientation of the dipole moment with respect to the principal axes of inertia. For NH_2D and NHD_2 the dipole moment is only about 10° from the c axis (axis of largest moment of inertia); thus, only c-type transitions will give the intense lines. These transitions require that the K_1 subscript shall not change during the transition.

However, since these ammonia molecules can also undergo inversion, an additional over-all species selection rule must also be considered. This selection rule can be determined from a consideration of the matrix elements of the electric dipole moment, referred to a fixed coordinate system. By considering the symmetry properties of the rotational and inversion wave functions it will be shown that a rotational transition cannot take place without a simultaneous inversion transition, and, similarly, that an inversion transition must be accompanied by a rotational transition. Thus, let us consider the space-fixed Z component of the matrix element of μ_g, the molecule-fixed g component of the dipole moment. This matrix element is given by

$$|\mu_{oj}|_Z=\int\psi_{ro}{}^*\psi_{io}{}^*\langle\mu_g\rangle_{\mathrm{nev}}\Phi_{gZ}\psi_{rj}\psi_{ij}dv$$

$$=\int\psi_{ro}{}^*\Phi_{gZ}\psi_{rj}dv_r\int\psi_{io}{}^*\langle\mu_g\rangle_{\mathrm{nev}}\psi_{ij}dv_i, \qquad (3)$$

where ψ_r is the rotational wave function, ψ_i is the inversion wave function, and the subscripts o and j indicate the initial and final states, respectively. Also, Φ_{gZ} is the direction cosine between the g and Z axes and $\langle\mu_g\rangle_{\mathrm{nev}}$ is the dipole moment averaged over the nuclear, electronic, and vibrational wave functions.

In order that the integral

$$\int\psi_{io}{}^*\langle\mu_g\rangle_{\mathrm{nev}}\psi_{ij}dv_i=\langle\mu_g\rangle_{\mathrm{nevi}} \qquad (4)$$

(which is the average value of the dipole moment as seen by the rotating molecule) should have a non-zero value, the integrand must not change sign upon reflection in a plane perpendicular to the g axis. Since μ_r is a linear function of the coordinates, it does change sign. Therefore, ψ_{io} and ψ_{ij} must have different symmetry properties for this reflection. For the ammonia molecules, a reflection in a plane perpendicular to the dipole moment is equivalent to an inversion, so that the initial and final inversion wave functions must have opposite symmetry properties for inversion. We have thus shown that an inversion transition must take place during a rotational transition to make $|\mu_{oj}|_Z$ different from zero.

The dipole matrix element can now be written as

$$|\mu_{oj}|_Z=\langle\mu_g\rangle_{\mathrm{nevi}}\int\psi_{ro}{}^*\Phi_{gZ}\psi_{rj}dv_r. \qquad (5)$$

Therefore, the dipole moment matrix element is now in

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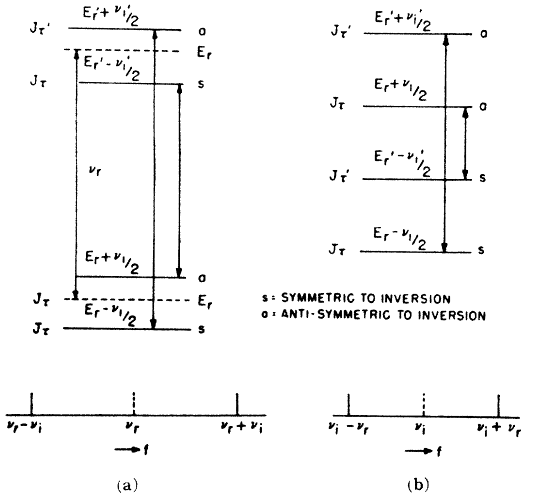
[4] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945).

the same form as that for a normal rotational transition, and is subject to the normal rotational selection rules. We have therefore shown that the dipole matrix element will be different from zero only if both rotational and inversion transitions take place, subject to the usual rotational selection rules and to the restriction that the symmetry to inversion must change during the transition. The above argument is, of course, also valid for NH_3; but, because of the K degeneracy of the symmetric rotor energy levels, there is no observable energy change between a K^+ level to a K^- level. With an asymmetric molecule, this K degeneracy is removed so that the inversion transition is affected by an observable amount by the simultaneous rotational transition. The above selection rules are equivalent to the over-all species selection rule $+\leftrightarrow-$ given by Herzberg.[4]

The resulting inversion-rotation energy level diagram is given in Fig. 2, which shows that for a given $J_\tau\rightarrow J_{\tau'}$ transition, instead of one absorption line two lines result because of the inversion splitting. The separation between the two absorption frequencies will be equal to the sum of the inversion splittings of the two levels involved, if the pure rotational separation frequency ν_r is larger than the inversion splitting, as shown in Fig. 2(a). On the other hand, if the inversion splitting is larger than the pure rotational energy difference, then the separation between the resulting two absorption lines is equal to twice the pure rotational frequency, as shown in Fig. 2(b). Thus, one can determine the pure rotational frequency ν_r and the pure inversion frequency ν_i by measuring the two absorption lines corresponding to a $J_\tau\rightarrow J_{\tau'}$ transition.



(a) (b)

FIG. 2. Rotation-inversion energy levels: (a) $\nu_r>\nu_i$, (b) $\nu_i>\nu_r$.

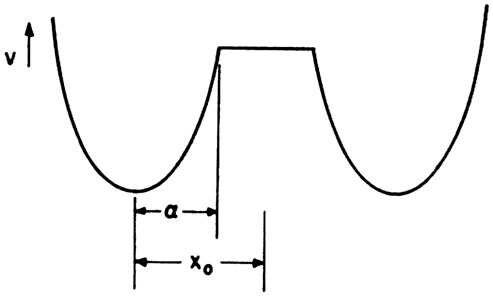


FIG. 3. Dennison and Uhlenbeck's potential well.

INVERSION DOUBLING THEORY

The theoretical study of inversion doubling in ammonia has been carried out in detail by a large number of investigators. For our purposes, the Dennison and Uhlenbeck[5] treatment of this problem is the simplest, and still gives surprisingly accurate results. As is well known, ammonia has a double minimum potential because of its pyramidal structure which permits two equivalent positions of equilibrium for the nitrogen atom, one on either side of the plane of the hydrogen atoms. Dennison and Uhlenbeck treated this problem of a particle in a two-minima potential field by means of the WKB method and showed that each level is split into two, corresponding to the two wave functions, $\psi_{\text{symmetrical}}$ and $\psi_{\text{antisymmetrical}}$. In order to evaluate Δ, the inversion splitting, Dennison and Uhlenbeck chose a particular potential curve consisting of two equal parabolas connected by a straight line, as shown in Fig. 3. The splitting is then evaluated explicitly as a function of the length of the joining line $2(x_0-\alpha)$ and the distance between the two minima $2x_0$. Thus, one obtains

$$\Delta_0/\nu_1=(2\alpha/\pi^{\frac{1}{2}})\exp[-\alpha^2-2(x_0-\alpha)(\alpha^2-1)^{\frac{1}{2}}], \tag{6a}$$

$$\Delta_1/\nu_1=[(4\alpha^3-4\alpha)/\pi^{\frac{1}{2}}]\times\exp[-\alpha^2-2(x_0-\alpha)(\alpha^2-3)^{\frac{1}{2}}], \tag{6b}$$

$$x_0=(4\pi^2\mu\nu_1/h)^{\frac{1}{2}}q;\quad V=\alpha^2h\nu_1/2, \tag{6c}$$

where Δ_0 = line splitting of ground state, Δ_1 = line splitting of excited state, q = height of ammonia pyramid $=0.38\times10^{-8}$ cm, μ = reduced mass, V = height of potential hill, and α and x_0 are dimensionless parameters adjusting the height of the potential barrier and the position of the minimum of the potential well to the observed data.

Since Δ_0 and ν_1 are known for NH_3, one can calculate x_0 and V, the potential height. This latter is calculated to be 1793.36 cm^{-1} and should remain the same for the deuterated ammonias as well, since the isotopic change should not affect the electronic structure. In calculating the reduced mass for NH_2D and NHD_2, one can make use of the fact that the vibrational frequency is inversely proportional to the square root of the reduced mass at least to the first order. One thus obtains Table I, which gives the calculated and observed values. In this table the observed values of Δ_0 are those calculated for the $J=0$ level, as indicated later.

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

Table I. Calculated and observed inversion values.

	NH_3		NH_2D		NHD_2		ND_3	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Δ_0 cm^{-1}	0.7935	0.7935	0.402	0.406	0.172	0.1705	0.068	
Δ_1 cm^{-1}	30.4	35.84	15.5	19.7	6.8	9.84	2.8	3.4
ν_1 cm^{-1}		950.16		884		813		747.3
x_0	3.173		3.2896		3.4302		3.5778	
α	1.9429		2.0143		2.1004		2.1908	
μ Amu	2.47		2.87		3.385		4.20	

A comparison of the calculated and observed values of the inversion splitting in the ground state of NH_2D and NHD_2 indicates that the Dennison and Uhlenbeck theory is surprisingly accurate (the agreement is better than 1 percent) even for the unsymmetrical molecule in which the motion of the nitrogen atom is not precisely along the axis of the pyramid. Furthermore, when one considers that the potential energy depends somewhat upon the distance between the hydrogen atoms, as well as being a function of the displacement of the nitrogen atom from its equilibrium position, one can marvel at the agreement obtained by using the simple one-dimensional potential function. These calculations also predict that the ND_3 inversion frequencies should occur near 0.068 cm^{-1}.

The limitations of the above theory become apparent, however, when one compares the calculated and observed values of Δ_1, the inversion splitting in the excited parallel vibrational state. As can be seen from Table I here the agreement is only fair, with the calculated values for all four of the ammonia molecules being too low by approximately 20 percent. This discrepancy is not excessive, considering the simple theory used, and was not pursued further, since our main interest is in the ground-state splitting.

Table IIa. Calculated and observed inversion splittings for NH_2D (Mc/sec).

Transition	Calculated ν_i	Observed ν_i
$2_{02}\rightarrow 2_{12}$	12,099	12,096.44
$3_{03}\rightarrow 3_{13}$	12,114	12,117.37
$4_{04}\rightarrow 4_{14}$	12,184	12,190*
$5_{05}\rightarrow 5_{15}$	12,306	12,307.40
$6_{06}\rightarrow 6_{16}$	12,475	12,473.47
$7_{07}\rightarrow 7_{17}$	12,692	12,685*
$8_{08}\rightarrow 8_{18}$	12,955	12,952.02
$9_{09}\rightarrow 9_{19}$	13,267	13,269.12
$10_{0,10}\rightarrow 10_{1,10}$	13,625	13,640*
$11_{0,11}\rightarrow 11_{1,11}$	14,030	14,070*
$7_{16}\rightarrow 7_{26}$	11,148	
$8_{17}\rightarrow 8_{27}$	11,186	
$10_{19}\rightarrow 10_{29}$	11,400	
$9_{27}\rightarrow 9_{37}$	10,167	

* Probable value; see text.

INVERSION AS A FUNCTION OF ROTATIONAL LEVEL

The Dennison and Uhlenbeck theory outlined above does not, however, take into account the variation of the inversion splitting with rotational levels. For NH_3, this variation was treated by Sheng, Barker, and Dennison,[6] who based their analysis upon the centrifugal force distortion of the ammonia potential function. Their equation for the inversion frequency is

$$\nu_i = \Delta_0 - A[J(J+1) - K^2] + BK^2, \tag{7}$$

where Δ_0, A, and B are all positive numbers and J and K are the usual rotational quantum numbers. This equation has been found to be quite accurate for NH_3 although higher order terms have since been introduced for greater accuracy. The form of this equation should also be valid for the deuterated molecules although K^2 must now be redefined, since it is no longer a good quantum number for asymmetric rotors. For K, the angular momentum along the symmetry axis for a symmetric top, one can substitute P_c which is the angular momentum along the c axis. For NH_2D and NHD_2, the c axis is about 10 degrees from the symmetry axis.

One can calculate $\langle P_c^2\rangle$, the average squared momentum about the c axis, from the following equations, as given by Bragg and Golden:[7]

$$\langle P_b^2\rangle = dE(\kappa)/d\kappa, \tag{8a}$$

$$2\langle P_a^2\rangle = J(J+1) + E(\kappa) - (1+\kappa)\langle P_b^2\rangle, \tag{8b}$$

$$\langle P_c^2\rangle = J(J+1) - \langle P_a^2\rangle - \langle P_b^2\rangle. \tag{8c}$$

From calculations it is seen that $\langle P_c^2\rangle$ is nearly the same for the J_τ level as it is for the $J_{\tau'}$ level; hence, an average value for $\langle P_c^2\rangle$ was used in calculating ν_i for the various $J_\tau\rightarrow J_{\tau'}$ transitions. Furthermore, it should be mentioned that $\langle P_c^2\rangle$ is approximately equal to the square of the second subscript in the King, Hainer, and Cross[3] $J_{K_{-1}K_1}$ notation.

Table II lists the "observed" (calculated from the two observed lines) inversion splittings for six lines for each of the molecules NH_2D and NHD_2. Since only a single line was observed for the other transitions listed, no accurate determination of the splitting could be

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[6] Sheng, Barker, and Dennison, Phys. Rev. **60**, 786 (1941).

[7] J. K. Bragg and S. Golden, Phys. Rev. **75**, 735 (1949).

made. However, in some cases a fairly accurate calculation can be made of the pure rotational separation of the two levels involved by using the centrifugal distortion theory. In these cases, the inversion frequency can be calculated by taking the difference between the calculated rotational frequency and the observed absorption frequency. Values so obtained are marked by an asterisk.

Table II also lists the inversion frequency calculated from the previous equation relating ν_i to J and $\langle P_c^2\rangle$. The values of Δ_0, A, and B were calculated by a least squares process to fit the "observed" inversion frequencies, resulting in the following equations for ν_i:

for NH_2D,

$$\nu_i=12{,}181.6-76.7-[J(J+1)-\langle P_c^2\rangle]+23.6\langle P_c^2\rangle; \quad \text{(9a)}$$

for NHD_2,[7a]

$$\nu_i=5110.9-26[J(J+1)-\langle P_c^2\rangle]+8.1\langle P_c^2\rangle; \quad \text{(9b)}$$

for NH_3,

$$\begin{aligned}\nu_i=23{,}785.75-151.450[J(J+1)-K^2]&\\+59.892K^2+0.49569(J^2+J-K^2)^2&\\-0.37674K^2(J^2+J-K^2)+0.06554K^2.& \quad \text{(9c)}\end{aligned}$$

By comparing the values for the inversion frequencies, as calculated from the above equations with the "observed" values, one can see that there is close agreement. The discrepancies, which vary from a few Mc/sec to about 25 Mc/sec, can be partially attributed to the fact that the value of the inversion splitting of the two rotational levels involved in the observed transitions are not identical. Furthermore, higher order terms were neglected; and these can be of importance for the high J transitions, as seen from the equation for NH_3.

In the above equations for ν_i, the values for Δ_0, the extrapolated inversion splitting for $J=0$, have previously been discussed and shown to agree very well with calculations based on the Dennison and Uhlenbeck[5] theory. Theoretical calculations for A and B, on the other hand, involve a very complicated numerical integration which was not carried through for the deuterated molecules. Significant empirical relations for determining the scaling factor for A and B, in going from the light to heavier molecules, could not be obtained.

EXPERIMENTAL RESULTS

A total of 35 NH_2D and NHD_2 lines, whose Stark components permitted positive identification, were measured and identified in the frequency region 7000 Mc/sec to 80,000 Mc/sec. These line frequencies, together with their intensities, are listed in Tables III and IV. It is to be noted that for each of the two molecules six pairs of lines were observed for $J_\tau \rightarrow J_{\tau'}$ transitions, whereas only a single line was measured for each of the other transitions listed. Although a number of other lines were observed and measured, they are not listed, because no positive identification could be made, usually because of interference of strong nearby lines. The 13,923.95-Mc/sec line listed in Table IV is tentatively assigned the $9_{27}\rightarrow 9_{37}$ transition in NHD_2 because of definite Stark evidence. However, the measured frequency is several hundred megacycles from the calculated value. Therefore, no definite assignment can be given for this line until a further experimental search is made for the other $9_{27}\rightarrow 9_{37}$ NHD_2 line in the 5000-Mc/sec region.

TABLE IIb. Calculated and observed inversion splittings for NHD_2 (Mc/sec).

Transition	Calculated ν_i	Observed ν_i
$1_{01}\rightarrow 1_{11}$	5093	5083.11
$2_{02}\rightarrow 2_{12}$	5086	5089.11
$3_{03}\rightarrow 3_{13}$	5095	5098.99
$4_{04}\rightarrow 4_{14}$	5122	5126*
$5_{14}\rightarrow 5_{24}$	4822	4824.49
$6_{15}\rightarrow 6_{25}$	4809	4795.59
$8_{26}\rightarrow 8_{36}$	4325	4355.35

* Probable value; see text.

CENTRIFUGAL DISTORTION AND STRUCTURAL PARAMETERS

From the above observed data, one should be able to calculate the rotational and structural constants $(a-c)$ and κ for NH_2D and NHD_2. However, to do so, account must be taken of the fact that centrifugal distortion

TABLE III. List of observed NH_2D lines.

Transition	Frequency Mc/sec	Intensity 10^{-6} cm^{-1}
$2_{02}\rightarrow 2_{12}$	49,962.85±0.10	685
$2_{02}\rightarrow 2_{12}$	74,155.73±0.15	594
$3_{03}\rightarrow 3_{13}$	18,807.74±0.05	157
$3_{03}\rightarrow 3_{13}$	43,042.48±0.10	275
$4_{04}\rightarrow 4_{14}$	25,023.88±0.05	108
$5_{05}\rightarrow 5_{15}$	7562.06±0.05	30.2
$5_{05}\rightarrow 5_{15}$	17,052.74±0.05	51.4
$6_{06}\rightarrow 6_{16}$	10,842.62±0.05	57.6
$6_{06}\rightarrow 6_{16}$	14,104.32±0.05	32.5
$7_{07}\rightarrow 7_{17}$	12,154.57±0.05	61.8
$8_{08}\rightarrow 8_{18}$	12,784.10±0.05	41.2
$8_{08}\rightarrow 8_{18}$	13,119.94±0.05	14.5
$9_{09}\rightarrow 9_{19}$	13,217.78±0.05	43.3
$9_{09}\rightarrow 9_{19}$	13,320.46±0.05	14.7
$10_{0,10}\rightarrow 10_{1,10}$	13,626.80±0.05	45.5
$11_{0,11}\rightarrow 11_{1,11}$	14,069.73±0.05	48.9
$7_{16}\rightarrow 7_{26}$	29,186.99±0.05	193
$8_{17}\rightarrow 8_{27}$	18,254.38±0.05	47.6
$10_{19}\rightarrow 10_{29}$	12,399.24±0.05	22.5
$9_{27}\rightarrow 9_{37}$	33,909.34±0.05	87.1

[7a] The accuracy of this equation has been improved by the low frequency measurements of K. Sawyer in this laboratory. See the Appendix.

TABLE IV. List of observed NHD_2 lines.

Transition	Frequency Mc/sec	Intensity 10^{-6} cm^{-1}
$1_{01}\rightarrow 1_{11}$	57,674.76±0.15	396.0
$1_{01}\rightarrow 1_{11}$	67,841.52±0.15	273.0
$2_{02}\rightarrow 2_{12}$	28,560.90±0.05	86.3
$2_{02}\rightarrow 2_{12}$	38,739.13±0.10	343.0
$3_{03}\rightarrow 3_{13}$	8283.92±0.05	20.1
$3_{03}\rightarrow 3_{13}$	18,481.91±0.05	50.1
$4_{04}\rightarrow 4_{14}$	9517.55±0.05	30.0
$5_{14}\rightarrow 5_{24}$	28,677.86±0.05	15.0
$5_{14}\rightarrow 5_{24}$	38,326.84±0.10	13.4
$6_{15}\rightarrow 6_{25}$	7801.38±0.05	5.51
$6_{15}\rightarrow 6_{25}$	17,392.56±0.05	55.0
$8_{26}\rightarrow 8_{36}$	20,608.77±0.05	17.4
$8_{26}\rightarrow 8_{36}$	29,319.47±0.05	71.0
$9_{27}\rightarrow 9_{37}$*	13,923.95±0.05	6.24

* Tentative assignment.

will change the rotational absorption frequencies from the values calculated on a rigid rotor basis. To accomplish this, use was made of the centrifugal distortion theory developed by Lawrance and Strandberg.[8] According to their work, the effect of centrifugal distortion on the energy of a given state can be expressed, to the first order, as

$$dW = P_a^2 da + P_b^2 db + P_c^2 dc. \qquad (10)$$

By expressing P_a^2, P_b^2, and P_c^2 in terms of J, κ, and $E(\kappa)$, as given previously, and by postulating that

$$\tfrac{1}{4} da = A_a P_a^2 + A_b P_b^2 + A_c P_c^2 \qquad (11)$$

with similar expressions for db and dc, they obtained the following equation for dW:

$$dW = L(dE/d\kappa)^2 + M(dE/d\kappa)E + N(dE/d\kappa)J(J+1) + QE^2 + REJ(J+1) + SJ^2(J+1)^2, \qquad (12)$$

where the E's are the reduced energies. The frequency correction, owing to centrifugal distortion, can now be obtained by subtracting dW_1, the correction to one energy level, from dW_2, the correction to the other level involved in the transition. For $\Delta J = 0$ transitions, the frequency correction becomes

$$\begin{aligned} d\nu_{12} = {} & L[(dE_2/d\kappa)^2 - (dE_1/d\kappa)^2] \\ & + M[(dE_2/d\kappa)E_2 - (dE_1/d\kappa)E_1] \\ & + NJ(J+1)[(dE_2/d\kappa) - (dE_1/d\kappa)] \\ & + Q[E_2^2 - E_1^2] + RJ(J+1)[E_2 - E_1]. \qquad (13) \end{aligned}$$

This equation was applied to the spectrum of formaldehyde, which is nearly a symmetric top. Therefore, E and $(dE/d\kappa)$ could be approximated with good accuracy by means of rather simple expressions. In our case, no similar accurate approximations could be made; thus, our calculations involve the complete equation as given above.

The evaluation of the structural parameters and of the centrifugal distortion constants can now be undertaken. We shall first discuss the NH_2D molecule. A first approximation to $(a-c)/2$ and to κ was made by assuming zero centrifugal distortion for the $J=2$, and 3 transitions. Since the rigid rotor frequencies can be obtained in closed form in terms of $(a-c)/2$ and κ, one can easily solve for these parameters. These values were then changed slightly, to give an amount of centrifugal distortion which would best fit the distortion equation given above. The constants for this equation were evaluated by means of a least-squares process to fit the six $J_\tau \rightarrow J_{\tau'}$ transitions for which both rotation-inversion lines were observed. It is to be noted that in all of these transitions the K_{+1} subscript is the same as the J-value.

The final choice for the rotational constants is $(a-c)/2 = 74{,}350 \pm 150$ Mc/sec and $\kappa = -0.315 \pm 0.002$ for the NH_2D molecule. These are not equilibrium values but are effective values including zero-point vibration. With a knowledge of $(a-c)$ and κ and with the aid of the equations it is possible to determine the effective values of θ, the corner-to-apex-to-corner angle of the ammonia pyramid, and r, the nitrogen-to-hydrogen distance. For NH_2D the following values were obtained: $\theta = 107.3° \pm 0.2°$ and $r = (1.008 \pm 0.004)$A.

For NHD_2, a procedure similar to that used for NH_2D resulted in the following choice for the rotational constants of this molecule: $\tfrac{1}{2}(a-c) = 55{,}200 \pm 100$ Mc/sec and $\kappa = -0.1385 \pm 0.002$. This corresponds to an effective value for θ of $107° \pm 2°$ and for r of (1.016 ± 0.008)A. Considering that zero-point vibration will cause the effective values of θ and r to differ slightly for the different isotopic ammonias, these values are in good agreement with the following average NH_3 and ND_3 values given by Herzberg: $\theta = 106.78°$ and $r = 1.014$A.

Tables V and VI list the centrifugal distortion as observed and as calculated from a "best-fit" equation, and a comparison indicates that there is fairly good agreement. The rigid rotor frequencies listed in these tables were calculated, using 5-point lagrangian interpolation in the King, Hainer, and Cross tables. This type of interpolation gives an accuracy to the fifth decimal place, which is equivalent in our case to a frequency accuracy of about one Mc/sec. In Table VI, listing the NHD_2 centrifugal distortion, it is to be noted that for several transitions, centrifugal distortion tends to raise the transition frequency rather than lower it, as is more usual. This does not violate any stability principle, since each energy level is lowered by the centrifugal distortion with the lower energy level involved in the transition being affected more than the upper energy level, thus resulting in an increase in the transition energy.

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[8] R. B. Lawrance and M. W. P. Strandberg, Phys. Rev. **83**, 363 (1951).

ABSORPTION COEFFICIENTS

For pressure broadened microwave spectrum lines the method of Van Vleck and Weisskopf can be used to calculate the absorption coefficients. One can show that with the usual simplifying assumptions permissible for microwave lines, the expression for the absorption coefficient α for our asymmetric molecules, measured at the peak of resonance, is given by

$$\alpha=\frac{8\pi^2}{3ckT}\frac{n}{\Delta\nu}\frac{\nu^2\mu^2\lambda\exp[-W_i/kT]}{(kT/h)^{\frac{3}{2}}(\pi/abc)^{\frac{1}{2}}}g, \tag{14}$$

where α = power absorption coefficient in cm^{-1}, n = no. of molecules of absorbing gas per cm^3, $\Delta\nu$ = half-width of absorption line at half-intensity and taken to be 29 Mc/sec for a pressure of 1 mm of Hg at room temperature, W_i = energy of lower state involved in the transition, ν = frequency of absorption line, μ = dipole moment, λ = line strength calculated by Cross, Hainer, and King, and g = statistical weight factor due to nuclear spin. All other symbols have their usual meanings.

The statistical weight factor due to nuclear spin can be determined from the following considerations. For the NH_2D molecule, an inversion followed by a rotation about the a axis (see Fig. 1) is equivalent to an interchange of the two hydrogen atoms. Since these are Fermi particles, the parity of the over-all wave function must change for the above operation. Therefore, for those states in which the inversion and the rotation about the a axis (frequently denoted by $C_2{}^a$) are both symmetric or both antisymmetric (i.e., for lower inversion state and K_{-1} even or upper inversion state and K_{-1} odd), only the antisymmetric spin wave function will occur so that the over-all wave function will be antisymmetric. Similarly, for the lower inversion state and K_{-1} odd or upper inversion state and K_{-1} even, only the symmetric spin wave function will occur. One can now determine the ratio of the statistical weights of the symmetrical to antisymmetrical spin states by the same argument used for calculating the alternation of intensities for homonuclear diatomic molecules. This ratio is found to be $(I+1):I$, where I is the nuclear spin. Therefore, for NH_2D the nuclear weight factor g is $\frac{3}{4}$ or $\frac{1}{4}$ for symmetric or antisymmetric spin states, respectively.

TABLE V. Centrifugal distortion correction for NH_2D; $\frac{1}{2}(a-c)=74{,}350$; $\kappa=-0.315$.

Transition	Rigid rotor ν Mc/sec	Observed ν Mc/sec	Observed $\Delta\nu$ Mc/sec	Best fit $\Delta\nu$ Mc/sec
$2_{02}\rightarrow 2_{12}$	62,150.95	62,059.29	91.7	91.9
$3_{03}\rightarrow 3_{13}$	31,178.52	30,925.11	253.4	253.4
$4_{04}\rightarrow 4_{14}$	13,054.85			225.7
$5_{05}\rightarrow 5_{15}$	4879.07	4745.34	133.4	133.4
$6_{06}\rightarrow 6_{16}$	1699.19	1630.85	68.3	68.7
$7_{07}\rightarrow 7_{17}$	564.23			33.9
$8_{08}\rightarrow 8_{18}$	181.19	167.92	13.3	12.4
$9_{09}\rightarrow 9_{19}$	56.43	51.34	5.1	5.7
$10_{0,10}\rightarrow 10_{1,10}$	27.48			5.4
$11_{0,11}\rightarrow 11_{1,11}$	5.32			3.9

Distortion equation:

$$\begin{aligned}\Delta\nu=&-4.083[(dE_2/d\kappa)^2-(dE_1/d\kappa)^2]\\&+43.43[(dE_2/d\kappa)E_2-(dE_1/d\kappa)E_1]\\&+47.25[(dE_2/d\kappa)-dE_1/d\kappa]J(J+1)\\&=241.1[E_2{}^2-E_1{}^2]-264.7[E_2-E_1]J(J+1)\end{aligned}$$

TABLE VI. Centrifugal distortion correction for NHD_2; $\frac{1}{2}(a-c)=55{,}200$; $\kappa=-0.1385$.

Transition	Rigid rotor ν Mc/sec	Observed ν Mc/sec	Observed $\Delta\nu$ Mc/sec	Best fit $\Delta\nu$ Mc/sec
$1_{01}\rightarrow 1_{11}$	62,845.20	62,758.14	87.1	87.9
$2_{02}\rightarrow 2_{12}$	33,874.03	33,650.02	224.0	222.1
$3_{03}\rightarrow 3_{13}$	13,540.01	13,382.92	157.1	160.0
$4_{04}\rightarrow 4_{14}$	4454.36			63.4
$5_{14}\rightarrow 5_{24}$	33,898.32	33,502.35	396.0	396.0
$6_{15}\rightarrow 6_{25}$	12,716.15	12,596.97	119.2	118.4
$8_{26}\rightarrow 8_{36}$	24,944.05	24,964.12	−20.1	−20.0
$9_{27}\rightarrow 9_{37}$	9060.80			−181.3

Distortion equation:

$$\begin{aligned}d\nu=&-0.296618[(dE_2/d\kappa)^2-(dE_1/d\kappa)^2]\\&-16.56467[(dE_2/d\kappa)E_2-(dE_1/d\kappa)E_1]\\&+2.33861J(J+1)[(dE_2/d\kappa)-dE_1/d\kappa]\\&-65.6743[E_2{}^2-E_1{}^2]+11.44885[E_2-E_1]J(J+1)\end{aligned}$$

In the case of NHD_2 the reasoning must involve an inversion followed by a rotation about the b axis rather than about the a axis, since for this molecule it is the b axis which is the symmetry axis passing through the NDD plane. The symmetry for the operation $C_2{}^b$ (rotation about the b axis) is determined by the product $K_{-1}K_1$; and since the deuteron is a Bose particle, an inversion followed by $C_2{}^b$ must not change the parity of the over-all wave function. Therefore, the statistical weight factor for NHD_2 is determined as follows. For a lower inversion state and $C_2{}^b$ even, or for a higher inversion state and $C_2{}^b$ odd, only the symmetric states will occur, while for other combinations, only the antisymmetric spin states will occur. Thus, g for NHD_2 is $\frac{2}{3}$ or $\frac{1}{3}$ for symmetric or antisymmetric spin states, respectively.

Values for the absorption coefficients for the various observed lines are listed in Tables III and IV. Experimentally, no absolute intensity measurements were made although approximate estimates were made by relative comparison with known NH_3 lines and with the known sensitivity of the spectroscope. The correlation of these rough estimates and the calculated values are good. The relative intensities of the high and low frequency components of a given $J_\tau\rightarrow J_{\tau'}$ transition were also checked experimentally and found to agree with the calculated ratios.

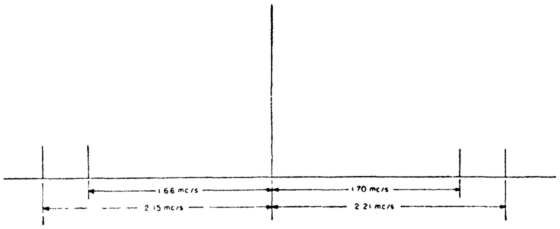

FIG. 4. Observed quadrupole structure.

SIGN OF NUCLEAR QUADRUPOLE COUPLING CONSTANT

The value of the nuclear electric quadrupole coupling constant *eqQ* has been measured for NH_3 and should be the same for the deuterated molecules, since it merely involves the nuclear quadrupole moment of the N^{14} nucleus. However, owing to the fact that the microwave spectrum of NH_3 is caused by transitions between states having the same rotational structure, the resulting quadrupole pattern is completely symmetrical and does not permit a determination of the sign of the quadrupole coupling constant.

With partially deuterated ammonia, rotational levels are not degenerate, so that a sign determination can be made with high resolution equipment. To accomplish this, the hyperfine structure of the $4_{04} \rightarrow 4_{14}$ transition of NH_2D occurring at 25,023.88 Mc/sec was investigated, using a high resolution microwave spectroscope developed by Eshbach. The theoretical asymmetry in the quadrupole pattern was calculated, using essentially the theory discussed by Loomis and Strandberg,[9] with the magnetic correction of Henderson[10] applied. Our results (Fig. 4) show that the quadrupole coupling constant is negative and is in agreement with the accepted value of -4.10 Mc/sec for *eqQ*. The sign has long been assumed negative both from considerations of the probable electronic structure of the ammonia molecule, as discussed by Townes and Dailey,[11] and from the negative value of *eqQ* for NF_3 as measured by Sheridan and Gordy.[12]

TABLE VII. Observed ND_2H lines.

Transition	Frequency Mc/sec	Intensity 10^{-6} cm^{-1}
$5_{05} \rightarrow 5_{15}$	6461.09±0.05	8.4
$6_{06} \rightarrow 6_{16}$	5581.08±0.05	12.2
$6_{06} \rightarrow 6_{16}$	4860.20±0.05	4.6
$7_{07} \rightarrow 7_{17}$	5392.07±0.05	4.7
$7_{07} \rightarrow 7_{17}$	5197.56±0.05	8.8
$8_{08} \rightarrow 8_{18}$	5414.15±0.05	8.9
$8_{08} \rightarrow 8_{18}$	5364.03±0.05	4.4
$9_{09} \rightarrow 9_{19}$	5507.75±0.05	3.6
$9_{09} \rightarrow 9_{19}$	5494.98±0.05	7.1
$10_{0,10} \rightarrow 10_{1,10}$	5635.18±0.05	6.0
$10_{0,10} \rightarrow 10_{1,10}$	5631.97±0.05	3.0
$11_{0,11} \rightarrow 11_{1,11}$	5787.16±0.05	2.3
$11_{0,11} \rightarrow 11_{1,11}$	5786.44±0.05	4.6
$12_{0,12} \rightarrow 12_{1,12}$	5962.30±0.20	3.4
		1.7
$13_{0,13} \rightarrow 13_{1,13}$	6161.86±0.20	
$14_{0,14} \rightarrow 14_{1,14}$	6387.23±0.20	

EXPERIMENTAL TECHNIQUES

The partially deuterated ammonias were synthesized by a method involving the following reaction:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3.$$

The magnesium nitride was made by heating magnesium powder in a closed Vykor crucible with a Meker burner. The top layer of white magnesium oxide was then removed and the remaining magnesium nitride was placed in an evacuated vessel. By adding a mixture of deuterated and ordinary water, various quantities of NH_3, NH_2D, NHD_2, and ND_3 were evolved. Presumably, partially deuterated ammonia could also be made by adding heavy water to ordinary ammonia.

TABLE VIII. Inversion splittings for ND_2H (Mc/sec).

Transition	Calculated	Observed
$5_{05} \rightarrow 5_{15}$	5156	5145*
$6_{06} \rightarrow 6_{16}$	5226	5220.64
$7_{07} \rightarrow 7_{17}$	5301	5294.81
$8_{08} \rightarrow 8_{18}$	5396	5389.09
$9_{09} \rightarrow 9_{19}$	5504	5501.35
$10_{0,10} \rightarrow 10_{1,10}$	5628	5633.57
$11_{0,11} \rightarrow 11_{1,11}$	5771	5786.80
$12_{0,12} \rightarrow 12_{1,12}$	5932	5962.30
$13_{0,13} \rightarrow 13_{1,13}$	6102	6161.86
$14_{0,14} \rightarrow 14_{1,14}$	6291	6387.23

* Value calculated from only one line.

The Stark modulation spectroscope used in this investigation is the result of development of the entire microwave spectroscopy group at the Research Laboratory of Electronics and has been described by Weiss *et al.*[13] The high resolution spectroscope used to measure the quadrupole hyperfine structure was built by Eshbach and is to be described in a forthcoming paper. Recently, a low frequency spectroscope has been constructed to investigate the ammonia spectrum, between 3000 Mc/sec and 7000 Mc/sec. Sawyer has undertaken this investigation, and his results are reported in the Appendix.

APPENDIX

K. SAWYER

The absorption transitions of ND_2H which were observed below 6500 Mc/sec and identified are listed in Table VII. Intensity

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[9] C. C. Loomis and M. W. P. Strandberg, Phys. Rev. **81**, 798 (1951).

[10] R. S. Henderson, Phys. Rev. **24**, 107, 626 (1948).

[11] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

[12] J. Sheridan and W. Gordy, Phys. Rev. **79**, 513 (1950).

[13] Weiss, Strandberg, Lawrance, and Loomis, Phys. Rev. **78**, 202 (1950).

calculations are made with an assumed line half-width of 29.2 Mc/sec at 1 mm Hg. The transitions are paired for all transitions found, except in the case of the $5_{05}-5_{15}$ line, where the lower frequency component lies in the 3800-Mc/sec region. Corresponding inversion splittings are listed in Table VIII. The $5_{05}-5_{15}$ inversion is not truly an observed splitting, since it is calculated from the position of the pure rotation transition.

The agreement between observed and calculated values is good at low values of J. Above $J=11$ the calculated value rapidly falls below the observed value, indicating the need of higher order terms.

In the case of high J transitions, the rotational transition frequency is so slight that the lines are close doublets. Above $J=11$ measurements were made at the maximum intensity of the unresolved doublet. For all transitions above $J=7$, the centrifugal distortion is so slight that the five-place tables of the reduced energy caused errors in excess of the distortion. Table IX gives the calculated and observed rotational energy differences. The centrifugal distortion was calculated, using equation for Table VI above.

TABLE IX. Rotational transitions (Mc/sec).

Transition	Frequency Rigid rotor	Frequency Observed	Distortion Observed	Distortion Calculated
$5_{05}\rightarrow 5_{15}$	1314.31			−2.40
$6_{06}\rightarrow 6_{16}$	361.56	360.44	1.12	0.70
$7_{07}\rightarrow 7_{17}$	95.50	97.25	−1.75	−2.56
$8_{08}\rightarrow 8_{18}$	24.29	25.06	−0.77	
$9_{09}\rightarrow 9_{19}$	6.07	6.37	−0.30	
$10_{0,10}\rightarrow 10_{1,10}$	1.66	1.60	0.06	
$11_{0,11}\rightarrow 11_{1,11}$		0.36		

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Centrifugal Distortion in Asymmetric Molecules. II. HDS

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A perturbation method for relating the theory of centrifugal distortion in asymmetric top molecules to observed microwave Q branch, *a* or *c* type transitions, is presented. The formula for the distortion correction is expressed in terms of the total angular momentum, J, the symmetry axis momentum of the nearest symmetric top, K, and five distortion constants. The formula yields a satisfactory fit to the observed spectrum of HDS ($\kappa\simeq-0.5$). The electric dipole moment is determined as 1.02±0.02 debye. The inertia defect and distortion constants are calculated. The effective structure for the HDS molecule so determined is in agreement with infrared determinations.

INTRODUCTION

THE vibration-rotation energies of polyatomic molecules have been derived to a second order of approximation for special cases by a number of authors. In general, the method followed has been equivalent to that of Wilson and Howard.[1] This work may be summarized by stating that the rotational term values of a molecule depend upon these quantities: the equilibrium structure of the molecule, the normal frequencies of vibration, and the nonvanishing coefficients of the anharmonic (cubic) terms in the expression for the binding potential energy of the molecule. Nielsen[2] has calculated the matrix elements for the rotational energy including, to second order, vibration-rotation energies.

Unfortunately the correction of centrifugal distortion in asymmetric top rotational term values is, in general, an inconvenient process. The explicit diagonalization of the reduced energy matrix may be accomplished for only a relatively few low J terms, when the asymmetry coefficient and the six centrifugal distortion coefficients are included as unknowns. Since the experimental data are best used to evaluate the centrifugal distortion coefficients, the diagonalization of the reduced energy matrix for each trial value of these coefficients is awkward for comparison with experiment.

A method of arriving at an explicit form of the formula for centrifugal distortion correction terms to the rigid rotor frequencies has been demonstrated.[3] This paper will discuss a method of determining centrifugal distortion correction factors in terms of the general centrifugal distortion matrix elements.

I. THEORY

The method used here is that of determining the centrifugal distortion correction in terms of rigid rotor frequencies specifically for Q branch "*a*" type or "*c*" type transitions. This dependence may be determined explicitly in terms of quantum or pseudo-quantum numbers and the rigid rotor absorption frequency, by a modified application of conventional perturbation theory.

To review briefly, the reduced energy matrix is diagonal in J and M; the nonvanishing elements in K (i.e., P_z) are $(K|H|K)$, $(K|H|K\pm2)$, and $(K|H|K\pm4)$.

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

[3] R. B. Lawrance and M. W. P. Strandberg, Phys. Rev. 83, 363 (1951).