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TECHNICAL REPORT NO. 188

FEBRUARY 19, 1951

RESEARCH LABORATORY OF ELECTRONICS
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

The research reported in this document was made possible through support extended the Massachusetts Institute of Technology, Research Laboratory of Electronics, jointly by the Army Signal Corps, the Navy Department (Office of Naval Research) and the Air Force (Air Materiel Command), under Signal Corps Contract No. W36-039-sc-32037, Project No. 102B; Department of the Army Project No. 3-99-10-022.

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Abstract

Extension of the investigation of the deutero-ammonias down to the 4,000 Mc/sec region produced many inversion-rotation spectrum lines of ND_2H. This search was conducted to complete the investigation carried on by Weiss (1) in the frequency range from 6,500-80,000 Mc/sec. Selection rules, molecular constants, and equations employed by Weiss were found to be reliable with the exception of the need for a slight modification of the constants developed for the Sheng, Barker, and Dennison (2) type inversion equation.

Frequencies in this region may serve other purposes than that of investigating the ND_2H molecule. The lines are of sufficient intensity to provide a good frequency check in this region. Inasmuch as a mixture of the ammonias is easily prepared and the combined spectrum covers the whole microwave region, the deutero-ammonias are exceptionally useful for this purpose. With the use of this energy region for commercial microwave relay systems these frequencies may have value for stabilization purposes. Frequencies in this region are already being considered by the National Bureau of Standards for use in an "atomic clock", a clock controlled by constant absorption frequencies.

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General Theory

The deutero-ammonias have absorption frequencies in a lower energy region than ammonia because of their asymmetry and the consequent allowed $\Delta J = 0$ transitions. The change in energy level in a rotational transition for an asymmetric rotor in the case of $\Delta J = 0$ is

$$\Delta W(J,\tau) = \frac{a-c}{2}\left[E^J_{\tau_2}(\kappa) - E^J_{\tau_1}(\kappa)\right] = \nu_{12} \quad .$$

In this report Weiss's values for $(a-c)/2$ and κ are used and prove to be valid. These values are

$$\frac{a-c}{2} = 55,200 \pm 100 \text{ Mc/sec}$$

$$\kappa = -0.1385 \pm 0.002 \quad .$$

The dipole moment lies close to the c axis; therefore all intense absorption lines follow the symmetry properties for this case. This results in the selection rule $\Delta K_1 = 0$ for the case of the deutero-ammonias.

Pure rotational transitions are not observed however, for inversion of the ammonia molecule and rotational transition must occur simultaneously. This fact can be proven theoretically (1), and results have substantiated the validity of the rule.

The equation for the inversion splitting of the ammonia molecule is

$$\nu_i = \Delta_o - E\left[J(J+1) - K^2\right] + FK^2 \quad .$$

Δ_o is the splitting for the ground state; E and F are constants. This equation is not exact and would require higher-order terms for greater accuracy. At transitions of high J levels the discrepancy caused by the lack of these terms is more noticeable. The equation is adaptable to the case of the deutero-ammonias with the substitution of $<P_c^2>$, the averaged squared angular momentum about the c axis, for K^2. The value of $<P_c^2>$ for the two rotational levels involved in a transition will differ slightly but is averaged for ease of calculation with little effect in final determinations. Splitting is assumed to be even about the energy levels, the antisymmetric level being one-half the inversion frequency above the normal energy level.

With the inversion going to opposite symmetry in a transition the total energy shift in a rotation-inversion transition always has two values: the rotation shift plus the inversion splitting and the rotation shift minus the inversion splitting in the case of the rotational transition exceeding the inversion splitting, and inversion splitting plus and minus the rotational transition in the other case. All lines found in this investigation are of this second type. The spectrum is that of ND_2H in the region of its ground state inversion frequency, 5,111 Mc/sec.

The inversion frequency equation was found to be

$$\nu_i = 5,111 - 26 \left[J(J+1) - \langle P_c^2 \rangle \right] = 8.1 \langle P_c^2 \rangle \quad .$$

This equation gave calculated values which checked well with values observed by us. It was also found that values calculated with this equation checked with the values observed by Weiss in the higher energy region.

Calculations of rotational distortion produced by the nonrigidity of the molecule were made with the Lawrance (3) type equation. The equation as extended for the case of ND_2H by Weiss is

$$\begin{aligned} d\nu = &- 0.296618 \left[\left(\frac{dE_2}{d\mathcal{K}}\right)^2 - \left(\frac{dE_1}{d\mathcal{K}}\right)^2 \right] - 16.56467 \left[\frac{dE_2}{d\mathcal{K}} E_2 - \frac{dE_1}{d\mathcal{K}} E_1 \right] \\ &+ 2.33861\, J(J+1) \left[\frac{dE_2}{d\mathcal{K}} - \frac{dE_1}{d\mathcal{K}} \right] - 65.6743 \left[E_2^2 - E_1^2 \right] \\ &+ 11.44885\, J(J+1) \left[E_2 - E_1 \right] \quad . \end{aligned}$$

This equation gave reasonable results for those values which we were able to check. The effect of distortion for all lines observed was slight.

Results

The spectrum lines of ND_2H which were observed and identified are listed in Table 1. Intensity calculations were made with the assumption of a half-width of 29.2 Mc/sec at a pressure of 1 mm Hg. Lines were paired for all transitions found, except in the case of the $5_{05} \rightarrow 5_{15}$ line, where the lower frequency line lies in the 3800 Mc/sec region, below the lower limit of the tube used. Corresponding inversion splittings are listed in Table 2. The $5_{05} \rightarrow 5_{15}$ inversion is not a truly observed splitting, having been calculated from rigid rotor and distortion determinations using the one line observed. Values of inversion splittings calculated with the equation are also listed for comparison. Table 3 contains the lines observed by Weiss, and Table 4 lists the inversion splittings and the values calculated with the revised equation. The $4_{04} \rightarrow 4_{14}$ line is also not a truly observed splitting.

The agreement between observed and calculated values is good at the lower values of J. Above J = 11 the calculated value rapidly falls below the observed value. The attempt was not made to secure better agreement for these transitions at the expense of the other levels. The disagreement is evidence of the need for higher-order terms for greater accuracy. At the higher energy levels the neglect of such terms would have a more pronounced effect, as was observed.

In the case of the high J transitions the change in energy level was so slight that the lines found were close doublets. Above J = 11 measurement was possible at only one point, that of maximum intensity. Measurements could be made with reasonable exactness at these points but an additional allowance for deviation was made because of the realization that the observed absorption was the sum of two lines. For all transitions above J = 7 the centrifugal distortion was so slight that the five-place tables (4) of energy levels caused errors in excess of the distortion. Table 5 gives calculated rigid rotor and observed transitions for as many of the lines as was possible with the tables. The observed distortion, along with the distortion calculated with the Lawrance equation, fitted with Weiss's constants, for the $6_{06} \rightarrow 6_{16}$ and $7_{07} \rightarrow 7_{17}$ lines are also listed. The calculated distortion for the $5_{05} \rightarrow 5_{15}$ line is that used in calculating the "observed" inversion frequency.

Table 1

Observed ND_2H Lines

Transition	Frequency Mc/sec	Intensity $10^{-6}cm^{-1}$
$5_{05} \rightarrow 5_{15}$	6,461.09 ± 0.05	8.4
$6_{06} \rightarrow 6_{16}$	5,581.08 ± 0.05	12.2
$6_{06} \rightarrow 6_{16}$	4,860.20 ± 0.05	4.6
$7_{07} \rightarrow 7_{17}$	5,392.07 ± 0.05	4.7
$7_{07} \rightarrow 7_{17}$	5,197.56 ± 0.05	8.8
$8_{08} \rightarrow 8_{18}$	5,414.15 ± 0.05	8.9
$8_{08} \rightarrow 8_{18}$	5,364.03 ± 0.05	4.4
$9_{09} \rightarrow 9_{19}$	5,507.75 ± 0.05	3.6
$9_{09} \rightarrow 9_{19}$	5,494.98 ± 0.05	7.1
$10_{0,10} \rightarrow 10_{1,10}$	5,635.18 ± 0.05	6.0
$10_{0,10} \rightarrow 10_{1,10}$	5,631.97 ± 0.05	3.0
$11_{0,11} \rightarrow 11_{1,11}$	5,787.16 ± 0.05	2.3
$11_{0,11} \rightarrow 11_{1,11}$	5,786.44 ± 0.05	4.6
$12_{0,12} \rightarrow 12_{1,12}$	5,962.30 ± 0.20	3.4
$13_{0,13} \rightarrow 13_{1,13}$	6,161.86 ± 0.20	1.7
$14_{0,14} \rightarrow 14_{1,14}$	6,387.23 ± 0.20	

Table 2

Inversion Splittings for ND_2H (Mc/sec)

Transition	Calculated	Observed
$5_{05} \rightarrow 5_{15}$	5,156	5,145*
$6_{06} \rightarrow 6_{16}$	5,226	5,220.64
$7_{07} \rightarrow 7_{17}$	5,301	5,294.81
$8_{08} \rightarrow 8_{18}$	5,396	5,389.09
$9_{09} \rightarrow 9_{19}$	5,504	5,501.35
$10_{0,10} \rightarrow 10_{1,10}$	5,628	5,633.57
$11_{0,11} \rightarrow 11_{1,11}$	5,771	5,786.80
$12_{0,12} \rightarrow 12_{1,12}$	5,932	5,962.30
$13_{0,13} \rightarrow 13_{1,13}$	6,102	6,161.86
$14_{0,14} \rightarrow 14_{1,14}$	6,291	6,387.23

*Value calculated from only one line

Table 3

ND_2H Lines Observed by Weiss

Transition	Frequency Mc/sec	Intensity $cm^{-1} \times 10^6$
$1_{01} \rightarrow 1_{11}$	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
$3_{03} \rightarrow 3_{13}$	8,283.92 ± 0.05	20.1
$3_{03} \rightarrow 3_{13}$	18,481.91 ± 0.05	50.1
$4_{04} \rightarrow 4_{14}$	9,517.55 ± 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
$6_{15} \rightarrow 6_{25}$	7,801.38 ± 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

Table 4

Inversion Splittings of ND_2H by Weiss

Transition	Calculated	Observed
$1_{01} \rightarrow 1_{11}$	5,093	5,083.11
$2_{02} \rightarrow 2_{12}$	5,086	5,089.11
$3_{03} \rightarrow 3_{13}$	5,095	5,098.99
$4_{04} \rightarrow 4_{14}$	5,122	5,126*
$5_{14} \rightarrow 5_{24}$	4,822	4,824.49
$6_{15} \rightarrow 6_{25}$	4,809	4,795.59
$8_{26} \rightarrow 8_{36}$	4,325	4,355.35

$$\nu_i = 5{,}111 - 26 \left[J(J+1) - P_c^2\right] + 8.1\, P_c^2$$

*Value calculated from only one line

Table 5

Rotational Transitions (Mc/sec)

Transition	Frequency		Distortion	
	Rigid Rotor	Observed	Observed	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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