A $^1\Pi\rightarrow{}^1\Delta$ Band of NH and the Corresponding ND Band

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A $^1\Pi\rightarrow{}^1\Delta$ band of NH at 3240A is compared with the corresponding ND band at 3235A. The rotational constants of the two bands are related within the limits of experimental errors in the way expected theoretically. It is necessary to take into account that the lowest vibrational state has half a quantum of vibrational energy. The existence of zero point vibrational energy appears also in the fact that the zero lines of the two bands are separated by 93.39 wave numbers. In agreement with the theoretical expectations the Λ-doubling in the ND band is smaller than in the NH band by a factor 3.511.

The discovery of the hydrogen isotope with mass two has opened up new possibilities for the study of the band spectra of hydrogen compounds. Whereas in all other cases the isotope effect is small, it may produce bands of an entirely different appearance if an H atom is replaced by its heavy isotope D.[2] Besides, the hydrogen isotopes present the additional very important advantage that they can be obtained in any ratio, whereas for the heavier elements one has to be satisfied with the mixture which is provided by nature (except for some very special cases as the Pb isotopes), and which very often gives a very unpleasant overlapping of the different bands.

The mass-ratio for the two hydrogen isotopes is approximately two, whereas it is very close to one for all other isotopes. This means that it is possible to study with ease also the isotope effect on finer points of the band structure as, e.g., the interaction between the electron movement and rotation. It hardly needs mentioning that the isotope effect will greatly help with the analysis of complicated spectra of hydrogen compounds and facilitate their interpretation.

We have, therefore, photographed besides the spectrum of the hydrogen molecule, the band spectra of several hydrogen compounds. The present paper presents the results on a band of very simple structure of the NH and ND molecule, respectively.

In a discharge in a mixture of nitrogen and hydrogen there is in the near ultraviolet, besides the well-known $^3\Pi\rightarrow{}^3\Sigma$ band at 3370A, a band of much simpler structure with a head at 3240A which apparently escaped until now the attention of band spectroscopists. We photographed and analyzed it some time ago but refrained from publishing the results, as a personal communication from Dr. Pearse informed us that he had found and studied the same band. In the meantime we were able to photograph the ND spectrum with the help of a drop of water which contained about 50 percent of the heavy isotope, for which we are greatly indebted to Professor G. N. Lewis. The photographs show clearly the ND bands equivalent both to the 3370 and 3240 NH bands. As the 3370 band is more complex there is a great deal of overlapping in the very closely spaced Q-branches so that photographs with purer ND samples are desirable.[3] We confine ourselves therefore in this paper to the much simpler short wave-length band. As Pearse's paper on the 3240 NH band had not appeared when this was written, we give also our results on this band[3a] as well as those of the corresponding ND band which has its head at 3235A.

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[1] National Research Fellow.

[2] We use D as symbol for the heavy hydrogen isotope because its convenience for the typist and printer without meaning to anticipate anything about the final settlement of the nomenclature.

[3] We obtained such photographs since then and hope to report also on the $^3\Pi\rightarrow{}^3\Sigma$ bands in the near future.

[3a] *Note added with proof:* Pearse's paper has appeared in the meantime (Proc. Roy. Soc. **A143**, 112, December, 1933) and his results are in good agreement with ours. His value 30, 704.13 for ν_0 is obviously a misprint.

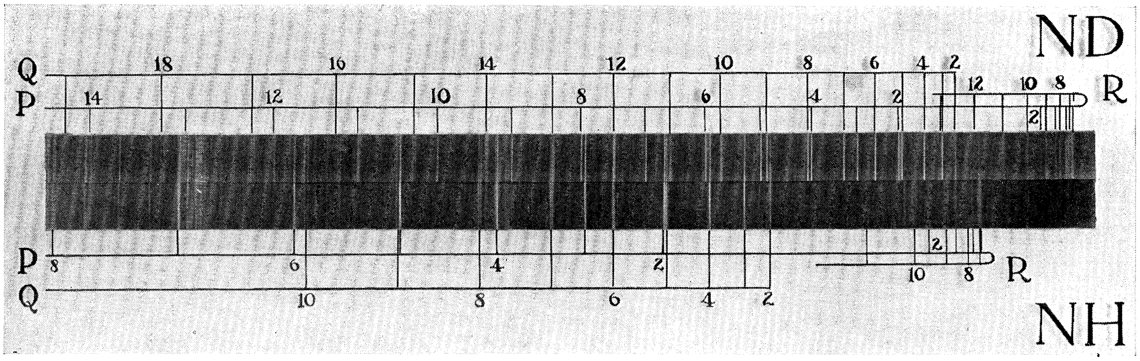

FIG. 1. Photograph of bands of NH and ND.

We can be very brief about the experimental details. For the production of the ordinary NH bands a Pyrex tube with a horizontal part of about 50 cm length and aluminum electrodes in side tubes was used. The tube was water-cooled and took a current of about 1.5 amperes at 2000 to 6000 volts. A mixture of N_2 and H_2 streamed through the tube. (Also ammonia was used but found to have no advantages.) If the percentage of nitrogen is relatively high, the NH bands are strong, but so are the nitrogen bands which obscure many of the NH lines. For this reason it is more advantageous to use a mixture with only so little nitrogen that in the visible the spectrum is almost completely the H_2 spectrum. The NH bands appear then, though much weaker, free from the nitrogen bands. The continuous hydrogen spectrum is then bothersome. It can be much weakened by employing a condensed discharge, a means which we, however, for various reasons were unable to use.

The same remarks apply to the production of the ND spectrum. Due to the small amount of heavy hydrogen at our disposal the technique was changed in several points. The discharge tube was of the same type, but smaller, with a horizontal part of 7 mm width and 50 cm length. This horizontal part was lightly silvered on the inside as the tube was primarily used for the production of the DH and D_2 spectra. The tube was made entirely of quartz and had tantalum electrodes. The heavy water was allowed to react with sodium and the hydrogen was admitted into the discharge tube through a hot palladium tube. The portion which was bound to the sodium in the form of NaOH was recovered by heating the NaOH. If a suitable amount of nitrogen was admitted the NH and ND bands appeared easily. It was found that the nitrogen disappeared quite rapidly in the tube so that the spectrum changed from a spectrum showing predominantly the nitrogen bands to a pure hydrogen spectrum. For this reason it was necessary to repeat the admission of nitrogen from time to time, and it became rather difficult to obtain the NH bands with sufficient strength without the nitrogen bands. The nitrogen must have gone into the electrodes.

Another remarkable feature of this tube was that it made apparently no difference whether nitrogen or air was used. The appearance of the spectrum was the same in both cases and in particular there was no trace of the OH bands. This seems remarkable as it was practically impossible to eliminate the OH bands from the other tube even if great care was taken to dry the gases carefully before they were admitted. We hope to be able to clear up this point with a new tube of the same design without the inside silvering and without the palladium tube.

All the plates used for the present paper were obtained in the first order of a 6 inch, 21 foot concave grating with 30,000 lines per inch and a dispersion of 1.3A per mm.

Fig. 1 shows the bands in question. The lower part is NH only, obtained with ordinary hydrogen and contains only NH lines (besides very faintly some N_2 and OH lines). The upper part was obtained with a mixture of roughly equal parts of the light and heavy isotope. The lines which occur on the upper picture but not on the lower one are the ND lines and it is easily seen that they form a band of the same general structure as the 3240 NH band. A comparison of the two bands is the main object of this paper. (See Table I.)

The structure of each of the bands is easily recognized as that of a $^1\Pi\rightarrow{}^1\Delta$ transition. There are only three branches, which shows that the bands are singlet bands. In the P- and R-branch four lines are missing near the origin, which shows, if one takes also the position of the Q-branch into account, unambiguously that we have a $^1\Pi\rightarrow{}^1\Delta$ transition and fixes also the numbering of the lines. The fact that the R-branch is the weakest branch agrees with this.

Except for the lowest J-values all the lines show Λ-doubling. Within the limits of experimental errors the doubling is identical for $R(J-1)$, $Q(J)$, and $P(J+1)$, (see Fig. 2), and from this it follows that the doubling of the lines is entirely due to the doubling of the Π-level, and that the doubling of the Δ-level is inappreciable.

The bands are both $0\rightarrow 0$ vibrational transitions. That is made probable by the fact that no other vibrational transitions of the system are observed and confirmed by the isotope effect.

We come now to a comparison of the two bands. The rotational energy of a diatomic molecule is given by the well-known expression

$$W_r/h=BJ(J+1)-DJ^2(J+1)^2 +FJ^3(J+1)^3-\cdots, \quad (1)$$

in which, if I is the moment of inertia and ω the frequency of the internuclear vibrations

$$B=h/8\pi^2I; \qquad D=4B^3/\omega^2; \qquad F=3D^2/B. \quad (2)$$

All the constants are in general functions of the vibrational quantum number v.

Assuming the validity of a formula of the type (1) the constants were calculated from the first eight differences

$$R(J-1)-Q(J-1)=Q(J)-P(J) =F'(J)-F'(J-1)$$

$$R(J-1)-Q(J)=Q(J-1)-P(J) =F''(J)-F''(J-1)$$

respectively, and

$$F(J)-F(J-1)=2BJ-4DJ^3+2F(3J^5+J^3). \quad (3)$$

TABLE I. The wave numbers and intensities of the bands. There are a few coincidences which are indicated in the column "Remarks." If a weak line is covered by a strong one, its wave number is not given, as it would be meaningless. The ND lines were measured on plates which showed the NH band with about the same strength, whereas the NH lines could be measured on plates free from ND, so that in this case the coincidence with a ND line does not affect the measurement. In such cases the coinciding lines are put between brackets.

J	P-branch	I	Remarks	Q-branch	I	Remarks	R-branch	I	Remarks
				NH band at 3240A					
2	30 685.39	4		30 741.93	3		308 26.69	1	
3	643.45	4		728.10	4		40.85	2b	
4	597.07	4b		709.71	5		49.90 50.36	1c 1c	
5	545.97 46.22	3c 3c		686.25 86.72	3c 3c		54.08 54.77	2 1	R6
6	490.35 90.88	3c 3c		658.20 58.92	3 3	(ND Q 12) (ND Q 12)	53.15 54.08	1 2	 R5
7	430.39 31.03	2d 2	λ3370R	625.20 26.10	3 3	 (ND Q 13)	46.96 48.16	1 1	
8	365.51 66.42	2 2		587.25 88.43	3 3		35.32 36.79	1 1	
9	296.09 97.35	1 2	 λ3370R	544.14 45.74	2 2c	 close to $P5$	18.05 19.86	1 1	
10				495.77 97.58	1 1		307 94.87 94.14	0 0	
11							65.83 68.49	0 0	
				ND band at 3235A					
2	30 811.28	4	(R14)	30 841.82	3		308 87.52	1	
3	788.86	5		834.61	4		95.56	2	
4	764.06	5		825.01	5		309 01.05	2	
5	736.92	5		812.99	6		04.10	2c	
6	707.40	5		798.51	6		04.57	2c	
7	675.46	5		781.59	5b		02.45	2b	
8	641.25	4b		761.96 62.25	3c 3c		308 97.58 97.95	1c 1c	
9	604.58	4b		739.95 40.34	3 3		90.16 90.60	1 1	
10	565.28 65.64	3c 3c		715.37 15.94	2 2		80.00 80.56	1 1	
11	523.68 24.20	2 2		688.23 88.81	2 2		67.04 67.81	1 1	
12	479.57 80.29	1 1				NH Q6 NH Q6	51.36 52.20	1 1	
13	433.08 33.86	1 2	Traces of head of 3285 N_2 band	626.01 26.73	3 2	NH Q7	32.78 33.68	0 0	
14	383.96 84.92	2 1	other line superimposed	590.85 91.67	2*d* 2*d*	Traces of head of 3268 N_2 band	12.16	0	P_2
15				552.66 53.79	1 1		307 86.57 87.87	0 0	
16				511.80 13.05	1 1				
17				467.88 69.41	1 1				
18				420.94 22.53	1 1				
19				370.97 72.72	0 0				

This is permissible on account of the fact that the Λ-doubling for the Δ-level is negligible. It appears that the observations can be represented within the limits of experimental errors by (3) and the constants obtained in this way are collected in Table II. In calculating the constants for NH it is necessary to take the term $FJ^3(J^3+1)$ in (1) into account. The error which is made when this term is neglected is, however, negligible for ND.

TABLE II. *Constants of the bands.*

	NH	ND	Ratio
B_a'	14.154	7.639	1.8529
B_b'	14.171	7.640	1.8555
B''	16.446	8.836	1.8614
D'	2.44×10^{-3}	6.54×10^{-4}	3.72
D''	1.74×10^{-3}	5.05×10^{-4}	3.45
			Difference
ν_0	307 55.61	308 49.00	93.39

If we distinguish the constants of the heavy isotope by a – above the symbol, and if we call, as is customary, the ratio of the reduced masses $\rho^2=\bar{\mu}/\mu$ we have the following relations

$$\omega=\rho\bar{\omega},\qquad B=\rho^2\bar{B},\qquad D=\rho^4\bar{D},\qquad F=\rho^6\bar{D},\tag{4}$$

if we assume that the only difference in the nonrotating molecules is the difference in the masses of the H and D atoms.

As the term $BJ(J+1)$ is by far the largest part of the rotational energy the effect of the substitution of an H nucleus by a D nucleus is that the rotational energies and therefore also the distance of the band lines from the origin of the band shrink by a factor ρ^2, and that this is approximately the case is immediately apparent from Fig. 1. But Fig. 1 shows also that this simple shrinking by a factor ρ^2 cannot be the complete change. For, if this were so, the relative position, except for the factor ρ^2, of all the lines should be exactly the same in both bands. A look at the position of the line $R(2)$ with respect to $R(9)$ and $R(10)$, e.g., shows immediately that this is not the case and the reason for this is that, for a given J, the centrifugal distortion is relatively bigger in NH than in ND which is expressed in that the coefficient D in (1) is multiplied by a higher power of ρ than B.

The last column of Table II gives the ratio of the constants for the two bands. If we take the value 2.01363 of Bainbridge[4] for the mass of the D atom we obtain the following values for the powers of ρ:

$$\rho=1.3684,\quad \rho^2=1.8726,\quad \rho^3=2.5625,\quad \rho^4=3.5113.$$

For D′ and D″ the agreement between the values of the ratios in Table II and the above value of ρ^4 is satisfactory, as the accuracy of the D values cannot be very great. The discrepancy between the B-ratios and ρ^2 is, however, too big to be attributed to experimental errors. In order to make sure of this we made some special calculations which showed that by no adjustment of the constants which is compatible with the observations is it possible to get ρ^2 as the ratio for the B-values.

We find the explanation for this apparent discrepancy, if we realize that the relations (4) hold only if the constants are the constants of the nonvibrating and nonrotating molecule. The constants in Table II are the constants for the nonrotating molecule in its lowest vibrational state. This lowest vibrational state has still half a quantum of vibrational energy, and in order that (4) is applicable we have to extrapolate the constants to the vibrationless state. This correction is important only for B and we have

$$B=B_e[1-\alpha(v+1/2)],$$

in which B_e is the B value for the vibrationless molecule and v the vibrational quantum number.[5] ($v=0$ for our case.) As we have only one vibrational state, the value of α is not known, and therefore it is not possible to calculate B_e. We can, however, calculate the value of α which will make $\bar{B}/B=\rho^2\cdot$ α is multiplied by ρ if H is substituted for D, and therefore we have, if R is the ratio of the *observed* B-values,

$$\alpha=2\rho(\rho^2-R)/(\rho^3-R)$$

for NH, and

$$\bar{\alpha}=2(\rho^2-R)/(\rho^3-R)$$

for ND. The values found in this way are for NH: 0.076 for Π_a, 0.066 for Π_b, and 0.044 for Δ. For ND they are 0.055, 0.048, and 0.032, respectively. These values have the right order of magnitude. We are making efforts to find some

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[4] K. T. Bainbridge, Phys. Rev. **44**, 57 (1933).

[5] Usually what is called here $B_e\alpha$ is designated by α.

other vibrational transitions of the same band system from which the value of α can be calculated.[5a]

We have seen in the preceding section that the ratio of the B-values will come at least very close to its expected value ρ^2 if the constants for the nonvibrating molecule are chosen. Although in ignorance of the values for α we are not able to test now whether this value will be exactly ρ^2, it may be well to call attention to some causes which might make it deviate from this value.

There is in the first place the obvious but very unlikely effect which would occur if the internuclear distance would change by substituting D for H. We have, however, only the right to assume such a change in internuclear distance, if we are quite sure that none of the other possible causes is responsible for any deviation from the relations (4).

The expression (1) for the rotational energy together with (2) are only valid if the interaction between rotation and electronic movement can be neglected. We know that this is the case for $^1\Sigma$-levels which are far enough away from other levels with which they might interact. None of the levels involved here is a $^1\Sigma$-level. For $^1\Pi$ and $^1\Delta$ levels the interaction between rotation and electron movement has been calculated by Hill and Van Vleck[6] and the formulae of these authors apply if there are not other electronic levels near which might interact with the levels in question. The deviations from (1) are in first approximation proportional to $J(J+1)$ and the next higher term is proportional to $J^2(J+1)^2$. The formula for the rotational energy has, therefore, still the form (1) but the coefficients are no longer connected with the moment of inertia and the frequency of the nuclear vibrations by (2).

The simplest case is a $^1P\Pi$ term, i.e., a level for which the resultant angular momentum of the electron motion is one and directed along the internuclear axis. It is split up, like all levels which are not $^1\Sigma$ levels,[7] into two components (here distinguished by subscripts a and b). One of these components is exactly represented by (1) and (2), the other one has the additional terms (A is a constant)

$$(4B^2/A)J(J+1)-(16B^4/A^3)J^2(J+1)^2,$$

of which only the first one is of any significance for our case. It represents the Λ-doubling and it is multiplied by ρ^4 in going from ND to NH. Of the two B-values which are found for the Π level we see that only one can be expected to satisfy the relations (4). We cannot say in our case which of the two this is, but if the α values are known, the above fact can be used to decide about the nature of the Π level. For a $^1D\Pi$ level none of the resultant B-values will have exactly the ratio ρ^2, as both doublet components have additional terms proportional to $BJ(J+1)/A$.

In any case the Λ-doubling should be proportional to $J(J+1)$ and its transformation factor should be ρ^4. This can be tested very well with the data at our disposal. A glance at Fig. 1 shows immediately that the Λ-doubling is considerably larger for NH than for ND. That this must be the case can be seen qualitatively without any calculation if we consider the fact that the Λ-doubling is due to the interaction between electron motion and rotation and will be determined principally by the angular velocity of the rotation as the electron motion is assumed to be the same in both isotopes. As the angular velocity is proportional to J/I, for a given value of J it is larger in NH than in ND by a factor ρ^2, and therefore the Λ-doubling must be larger in the lighter isotope.

Fig. 2 gives the results of a quantitative analysis of the Λ-doubling. The upper curve represents $0.0161J(J+1)$ and the figure shows that it agrees excellently with the observed Λ-doubling for NH. The lower curve is $0.0161J(J+1)/\rho^4$ and it represents well the Λ-doubling for ND.

In a $^1\Delta$-level there are also additional terms in $J(J+1)$ and $J^2(J+1)^2$ which express the interaction between rotation and electron motion. The

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[5a] *Note added with proof:* Since the present article was written we have succeeded in photographing and analyzing the 1→0 band of NH and the 1→0 and 1→2 bands of ND. From the analysis of these bands it is possible to obtain the vibrational constants and the values of α. If these values are taken into account the agreement of the value of the B_e-ratios with the theoretical value, ρ^2, becomes satisfactory. Details about these bands will be given in a subsequent paper.

[6] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

[7] For a discussion of the properties of such terms see also G. H. Dieke, Zeits. f. Physik **57**, 71 (1929).

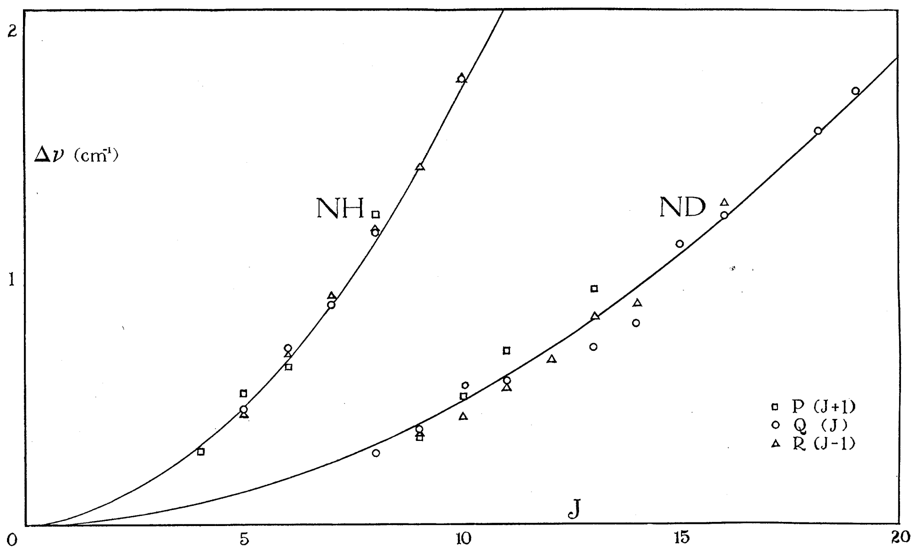

FIG. 2. Λ-doubling of the $^1\Pi$-level.

essential difference from a $^1\Pi$-term is that the terms in $J(J+1)$ have the same sign and magnitude for both doublet components so that therefore the Λ-doubling is much smaller and roughly proportional to $J^2(J+1)^2$. In our $^1\Delta$-term it is too small to be noticed. But even if the Λ-doubling is unnoticeable the term in $J(J+1)$ may be appreciable so that the observed B ratios may be different from ρ^2. There are no data which would allow an estimate of how big this difference is in our case.

The zero lines of the two bands are 307 55.61 for NH and 308 49.00 for ND. The shift of 93.39 wave numbers is due to the zero point vibrational energy of half a quantum which was also responsible for the apparent discrepancy between the observed B-ratios and the expected value ρ^2. If we neglect the anharmonic terms in the vibrational energy we have

$$\nu_0=\nu_e-1/2(\omega''-\omega').$$

From which it follows that the shift is

$$[(\rho-1)/2\rho](\omega''-\omega')=93.39$$

or

$$\omega''-\omega'=694 \text{ cm}^{-1}.$$

If the transition were not a 0→0 but, e.g., a 0→1 transition we would have

$$3\omega''-\omega'=694,$$

which would give $\omega''<347$ which is much too small a value.

We wish to thank Professor G. N. Lewis and Dr. R. T. Macdonald for the heavy water which made this investigation possible.

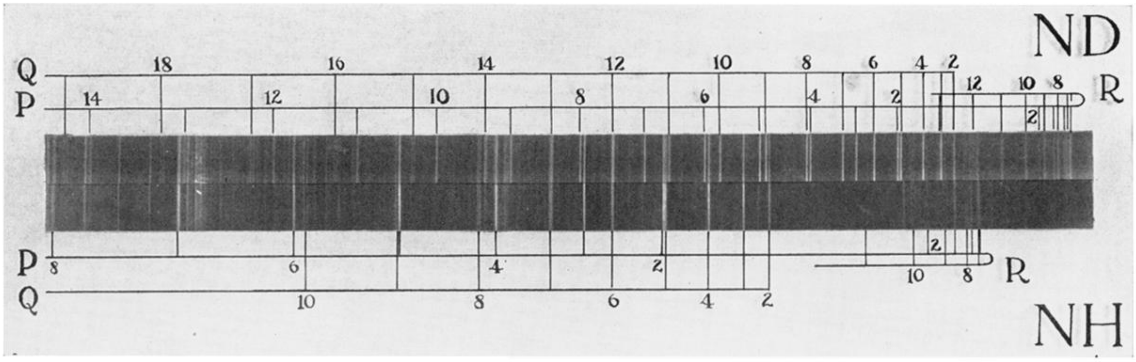

FIG. 1. Photograph of bands of NH and ND.