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The Ultraviolet Spectrum of Ammonia

II. The Rotational Structure of Some Bands in the Schumann Region

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Seven bands of ammonia between 1620 and 1450A have been photographed in absorption with a dispersion of 1.3A/mm. These are the 0,2 — 0,8 bands of the second electronic state above the normal. Each band has one P and one R branch, and a broad intense line as a Q branch. Within the limit of observational errors, which were large in this region, the moment of inertia A' is only slightly larger than A'', and C' is about equal to C'', so that the dimensions are not greatly changed in the excited state.

A REPORT has been made recently of the absorption spectrum of ammonia in the ultraviolet between 2300 and 850A.[1] The spectrum was examined with a vacuum grating spectrograph with a dispersion of about 8.5A/mm. Some bands in the region 1700–1400A were found to possess considerable fine structure, which appeared partly resolved. Since the moments of inertia appeared to remain small in excited electronic states, almost complete resolution seemed possible at the highest dispersion available. It was hoped that an analysis of the rotational structure could be made, in spite of the large observational errors which must be present in a region where 1A is equivalent to 40–50 wave numbers.

EXPERIMENTAL

These bands were photographed with a 21-foot focus normal incidence vacuum spectrograph, a description of which has been published by one of us.[2] The grating used had 160,000 lines ruled 30,000 to the inch on speculum. The dispersion in the first order of the region used was approximately linear and averaged 1.328A/mm. The use of higher orders proved impossible, because of the fact that filters transparent to this region but opaque to the near ultraviolet and visible were unavailable.

The Lyman continuum was produced by the discharge, once a second, of an 8-mf condenser charged to 3200 volts by a transformer and UV 866 rectifier. The life of the 1-mm glass capillary (30 mm long) was about 90 minutes (5400 discharges). Exposures were 90–180 minutes on very sensitive Hilger-Schumann plates. The densities of the images were very far from being proportional to the exposure times, 270 minutes (3 capillaries) giving little if any more blackening

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[1] A. B. F. Duncan, Phys. Rev. **47**, 822 (1935).

[2] G. R. Harrison, Rev. Sci. Inst. **2**, 600 (1931); **4**, 651 (1933).

than 180 minutes. For this reason the contrast was very poor, especially at high pressures of ammonia necessary for the weak lines. Also for this reason visually estimated intensities have little meaning and are not given for these bands. Hydrogen, purified by diffusion through palladium, was pumped through the discharge tube at about 0.5 mm pressure.

Alignment of the discharge tube with the spectrograph presented unusual difficulties in this case, and the use of a long absorption column between the source and slit greatly increased these difficulties. For this reason the spectrograph itself was used as the absorbing column and the discharge was placed as close to the slit as possible. In some cases a window of lithium fluoride, transparent to 1000A was placed in front of the slit, to remove possible higher orders. This proved unnecessary, but the window served to prevent the spectrograph filling with hydrogen.

The ammonia was purified by distillation over sodium. The liquid ammonia was stored over solid ammonium nitrate which reduced its vapor pressure to about 0.5 atmosphere. Due to the high speed evacuation of the spectrograph, a continuous flow of ammonia was undesirable, since a uniform pressure could not be obtained in this way. Consequently the valve to the pump was closed during exposures, and ammonia was admitted to the desired pressure. The ammonia disappeared slowly in the spectrograph, either by absorption or reaction, or more probably through the valve into the pump, which was designed to stand pressure differences in the opposite direction. The pressure was kept constant by admitting small quantities of ammonia at intervals of 2 or 3 minutes. The pressure was measured by a McLeod gauge close to the slit, and for any one exposure probably represented a constant fraction of the true pressure in the main body of the spectrograph. The pressures of ammonia varied from 0.017 to 0.09 mm on different plates.

Seven spectra were measured and every line was measured on at least two spectra. The wave numbers reported represent the unweighted mean of two or more observations.

The plates were measured in the usual way. Emission lines in the source used as standards were C IV 1548.214, 1550.774; N I 1745.246, 1742.734.[3]

RESULTS

Lines in seven bands were measured, which are the 0,2 − 0,8 bands of the second electronic state.[1] The 0,0 and 0,1 bands did not appear at the highest pressure, and the 0,2 and 0,3 bands are very incomplete, lines near the head only appearing. The other five bands are much better developed and show two branches, with a broad central line. The heads in the *R* branches are not prominent at high dispersion, and are indeed difficult to locate at all.

The absorption lines were rather broad at the lowest pressures, often as much as 0.1 mm. For this reason an actual resolving power better than 3–5 cm^{-1} is not claimed. This is about one-tenth the theoretical at 1500A.

The lines observed appear in Table I. The lines of λ1612 and λ1587 could not be numbered but they appear to form the *R* branches of these bands. The lines of λ1562, 1537, 1514, 1490, and 1467 (wave-lengths of heads) are numbered. This numbering will be discussed later.

EXPECTED STRUCTURE OF THE BANDS

In its excited states ammonia is either a regular pyramid or a plane. In the latter case we have the special relation $2A' = C'$, while the general relation for a pyramid is $A' - C'/2 = \mu h^2$. Here C is the moment of inertia about the symmetry axis and A the moment around an axis in a plane through the center of mass perpendicular to the axis of symmetry, h the height of the pyramid and μ the reduced mass. The rotational energy levels are those of the symmetrical top in both cases. Our measurements are not sufficiently accurate to detect any but large deviations from the symmetrical top case, and these do not appear to be present.

The rotational levels of the symmetrical top have been discussed in detail by Dennison, and by Dieke and Kistiakowsky.[4, 5] The latter

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[3] J. C. Boyce and C. A. Rieke, Phys. Rev. **47**, 654 (1935).

[4] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[5] G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).

authors have discussed particularly selection rules and intensities in perpendicular bands, deviations from the symmetrical top, and have applied the theory to certain bands of formaldehyde. The theory for parallel bands (to which type these ammonia bands belong) is much more simple and will be briefly stated here.

The general form of the rotational energy is

$$W_{\text{rot}}=\frac{h^2}{8\pi^2}\left[\frac{J(J+1)}{A}+\left(\frac{1}{C}-\frac{1}{A}\right)K^2\right].$$

The selection rules are $\Delta J=0,\ \pm 1$; $\Delta K=0$. The branches to be expected are qP, pQ, and qR.[5] The appearance of the bands will depend on the relative magnitudes of A' and A'', C' and C'', and on the absolute value of K. Several cases may be considered.

(I) $K=0$; $A'=A''$.	a single P and R branch; a single line for the Q branch.
(II) $K=0$; $A'\neq A''$.	a single P, Q and R branch.
(III) $K\neq 0$; $A'=A''$; $C'=C''$.	same as (I), since the separate P branches, Q branches and R branches coincide.
(IV) $K\neq 0$; $A'\neq A''$; $C'\neq C''$.	(general case) a separate P, Q and R branch for each value of K.

The separations of the branches may have any values in case IV. The separation of the Q branches for the same value of J but two different values of K will be given by

$$\Delta\nu(\text{cm}^{-1})=\frac{h}{8\pi^2 c}(K_2^2-K_1^2)\left[\frac{1}{C'}-\frac{1}{A'}-\frac{1}{C''}+\frac{1}{A''}\right]. \quad (2)$$

TABLE I. *Observed lines.*

λ1612 *R branch ?*	λ1587 *R branch ?*
62037	62964
61991	933
61962	908
61932	898
905	882
878	861
845	840
820	818
	761
	741

	λ1562		λ1537	
J	*P(J)*	*R(J)*	*P(J)*	*R(J)*
0	63763		64778	
1	—		759	64815
2	—		—	—
3	710	63804	720	848
4	683	—	695	877
5	659	835	—	—
6	649	865	662	914
7	626	887	637	—
8	599		615	957
9	—		—	
10	568		576	
11	—		551	
12	528		—	
13	516		513	
14	470		489	
15	448		469	
16	437		—	
17	416		437	
18	—		—	
19	392		399	
20	—		386	
21	352		365	
22			335	
23				
24				
25				
26				

	λ1514		λ1490	
J	*P(J)*	*R(J)*	*P(J)*	*R(J)*
0	65709		66665	
1	—	65745	—	
2	—	—	—	66732
3	641	782	610	—
4	634	818	582	762
5	609	829	557	794
6	590	—	—	800
7	—	871	522	829
8	559	—	—	837
9	525	906	485	862
10	—	935	—	895
11	490	944	441	—
12	—	961	—	930
13	448		405	954
14	418		380	975
15	402		—	—
16	—		345	67000
17	372		—	
18	355		304	
19	324		278	
20	299		264	
21	281		—	
22	270		231	
23	242		—	
24	—		174	
25	217			

	λ1467	
J	*P(J)*	*R(J)*
0	67650	—
1	—	—
2	—	—
3	595	—
4	—	—
5	553	—
6	537	—
7	511	—
8	479	67832
9	67465	—
10	—	67870
11	427	894
12	—	909
13	384	923
14		939
15		965
16		989

In this general case, for each value of K we have a sub-band which is entirely analogous to a complete three-branch band of a diatomic molecule. These sub-bands would be separated from one another only if A' and C' had very different values, since A'' is about 1/2 of C'' (from infrared measurements).[6]

Obviously, if C' and C'', as well as A' and C'' are nearly but not exactly equal, case IV goes over into case I, with the result that the individual lines are more or less broad, because of the near coincidence of lines with the same J but different K values. This is equivalent to saying that the sub-bands almost coincide.

DISCUSSION OF THE RESULTS

We next see how far the observed structure of the bands is in agreement with the structure expected on the basis of the preceding theory. It is at once apparent that the observed structure is much more simple than case IV would predict. Calculations of the relative intensities of the sub-bands show that the intensities of sub-bands $K=3n(n=0,1,2\cdots)$ have an intensity only slightly higher than the sub-bands for which K has the value $3n\pm 1$, so that there seems no reason why all sub-bands (at least with low values of K) do not appear. Since only one sub-band is observed for each vibrational transition, we must conclude that case IV has practically degenerated into case I. This happens, as we have seen, when A' is equal to A'', and C' to C''.

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[6] P. Lueg and K. Hedfeld, Zeits. f. Physik **75**, 599 (1932).

There is additional evidence that $A' \cong A''$. The formula for each qP and qR branch, considered separately, must depend on J, A' and A'' but not on C', C'' and K, and have the following form:

$$qP = \nu_0 - 2B(J) + C(J^2),$$

$$qR = \nu_0 + 2B(J+1) + C(J+1)^2,$$

where ν_0 = the electronic + vibrational term

$$2B = \frac{h}{8\pi^2 c}\left(\frac{1}{A'} + \frac{1}{A''}\right) \quad \text{and} \quad C = \frac{h}{8\pi^2 c}\left(\frac{1}{A'} - \frac{1}{A''}\right).$$

The branch lines have a linear rather than a quadratic dependence on J even at high J values, which points to the fact that C is very small. The average interval between lines should be then very nearly equal to $2B$. Since A'' is well known from infrared data, A' may be determined from the above relation, and comes out very close to A''.

If $A' \cong A''$ in a diatomic molecule, the head is formed at high values of J and the interval between head and origin varies considerably with the vibrational quantum number.[7] This is exactly what is found to be the case here.

There is unfortunately no independent confirmation that $C' \cong C''$ but this assumption appears to be necessary to explain the entire absence of other sub-bands.

All the bands studied come from the normal (nonvibrating) state of the molecule and combination differences can be formed which involve constants of this lower state only. These constants are well known from work in the infrared. For example, $R(J-1) - P(J+1) = 4B''(J+1/2)$, where $B'' = 9.94$ cm^{-1}. From this relation a table of differences for successive values of J may be constructed, and a search made for successive pairs of lines separated by the theoretical differences. When this is done it is immediately evident that many lines are missing. This is not surprising when the difficulty of finding weak lines is considered. For this reason the numbering of the lines had to be made in the following way.

We may be certain of the origins of five of the seven bands. This gives, of course the positions of the $Q_0(=P_0)$ lines. If we assume that $A' = A''$ and $2B' = 20$, for simplicity of calculation, we can calculate the position of every line in these bands. Then every line found experimentally must coincide (within the limit of error) with a calculated line. This method is possible only when the intervals between lines are much greater than the experimental error.

These calculations will not be reproduced here but the general results only given. A total of 109 lines (exclusive of the Q_0 lines) were measured. From the number of blank spaces, this turns out to be a little more than 75 percent of all the lines expected. Of the measured lines 60 percent fall within 5 cm^{-1} of a calculated line and 82 percent within 8 cm^{-1}. There is no trend of differences between observed and calculated even at high J values. This should certainly be observed if the difference between A' and A'' were larger than the experimental error. The missing lines appear to be scattered entirely at random in the bands and thus no theory of their absence can be given.

From this discussion we may be reasonably sure that A' is not far different from A'', and C' is probably nearly equal to C''. However A' must be somewhat larger than A'' since a head, however indefinite, is formed in the R branch. If C' were exactly equal to C'', the pyramid would be slightly higher in the excited state. A variation undetectable in our measurements could, however, keep the height the same or make the pyramid slightly flatter. Much more accurate measurements would be necessary to determine unambiguously the dimensions in the excited states.

One of us (A. B. F. D.) expresses his appreciation to the Warren Fund of the American Academy of Arts and Sciences for financial aid during the progress of this work.

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[7] W. Jevons, *Report on Band-Spectra of Diatomic Molecules* (University Press, Cambridge, 1932).