

The Ultraviolet Absorption Spectrum of Ammonia

A. B. F. DUNCAN, *Department of Chemistry, Brown University*

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The discrete absorption spectrum of ammonia has been photographed from 2300 to 850A. The experimental results of other workers in the long wave portion of the spectrum are confirmed, and much new experimental data at shorter wavelengths found. The bands down to 1665A are all diffuse because of predissociation. Below 1665 all the bands are very sharp and show rotational fine structure which is partly resolved. True continuous absorption (in distinction to that produced by pressure broadening) does not begin

until about 1200A. At 1150A and below the continuous absorption is so strong that no more bands could be measured accurately. Sharp bands exist, however, at least as far down as 1085A, so the first ionization potential should be at least 11.3 volts. The bands are classified in four ν' progressions which fall in four different electronic states, all of the same type. All bands come from $\nu=0$ of the normal state. Only one fundamental frequency appears in the excited states.

IT is well known that the absorption spectrum of gaseous ammonia at ordinary temperatures and pressures begins at about 2200A and extends into the ultraviolet.^{1, 2} Most workers have not observed the spectrum at wavelengths shorter than 1900A, but the measurements of Leifson extend as far as 1500A. In the present work the spectrum was photographed at room temperature, with moderately high dispersion and very high resolving power from 2300 to 850A.

The vacuum grating spectrograph and light source have been described.^{3, 4} The ammonia used was obtained from the very pure liquid used for conductivity work in the laboratory of Professor C. A. Kraus. It was redistilled in vacuum and evaporated into a large storage bulb attached to the spectrograph. The spectrograph was filled by means of small calibrated volumes to pressures of 0.015 to 1 mm. No absorption was apparent at lower pressures, and higher pressures served merely to bring out weaker parts of the fine structure, of which not much use was made. Since at normal incidence only about 1000A of the spectrum could be photographed at one time, it was necessary to use two settings of the grating. We were assured that all the absorption down to 1275A was really in the first order by making one exposure through fluorite. The absorption below this wavelength seems far too strong to be due to any very short wavelength bands

(shorter wavelength than 650A) in the higher orders.

The standard lines used were 1215.68 (*H*, in absorption, narrow on most plates), 1066.662 (*Si IV*),⁵ 1338.603 (*O IV*), 1371.287 (*O V*), 1548.195 (*C IV*), 1550.768 (*C IV*)⁶ and 2066.86 (*B III*).⁷ Measurements at the two settings of the grating gave consistently a small difference in the dispersion. With a uniform but different dispersion for each setting of the grating, bands and standard lines appearing at both settings had the same values. All bands reported were found on at least two different plates. Most of the band heads were measured in at least ten different spectra.

The first four double headed bands in the near ultraviolet were measured to within 1–5 cm^{-1} . The succeeding predissociation bands were so diffuse that the centers of gravity only could be measured. For this measurement, the two limits of the absorption band were measured on several plates at a series of regularly increasing pressures. A plot was then made of the edges against pressure, and the two curves extrapolated to crossing. This value was taken as the center of gravity and the method seemed safer than extrapolating to zero pressure. Measurements by this method were reproducible to 5–20 cm^{-1} . The accuracy here rests naturally on the assumption that the

¹ S. Leifson, *Astrophys. J.* **63**, 87 (1926).

² J. K. Dixon, *Phys. Rev.* **43**, 711 (1933).

³ Noyes, Duncan and Manning, *J. Chem. Phys.* **2**, 717 (1934).

⁴ A. B. F. Duncan and J. P. Howe, *J. Chem. Phys.* **2**, 851 (1934).

⁵ B. Edlén and J. Söderqvist, *Zeits. f. Physik* **87**, 218 (1933).

⁶ B. Edlén, *Zeits. f. Physik* **85**, 85 (1933).

⁷ Corrected by Noyes, Duncan and Manning to this value by intercomparison with 1931.027 (*C III*), and N I 1745.26, 1742.74 (Bowen and Ingram, *Phys. Rev.* **28**, 444 (1926)).

same meaning is to be attached to the position of maximum absorption in all the bands. The sharp bands in the rest of the spectrum were measured with a precision usually better than 5 cm^{-1} , the precision decreasing slowly with the increasing wave number/distance ratio at shorter wavelengths.

Parts of the spectrum will first be described separately, and then a general discussion of the entire spectrum given. It is necessary for this discussion to review the known facts about the normal state of ammonia, as revealed by Raman and infrared spectra.

THE NORMAL STATE OF AMMONIA

Studies of the infrared absorption^{8, 9, 10} and Raman spectrum of ammonia^{11, 12} show that this molecule is a regular pyramid, whose altitude is rather small (about $0.3A$). There are four fundamental vibration frequencies all of which are permitted in both types of spectra. There are some differences in the assignment of the experimental data to these frequencies, but the following interpretation seems to be that agreed on in most recent papers. In order of increasing frequency we have first $\nu_1 = 934.2, 964.3$ a non-degenerate frequency.¹³ It is associated with a parallel deformation (symmetrical bending) motion in which an equilateral triangle having an hydrogen atom at each corner, vibrates as an almost rigid unit along the symmetry axis with the nitrogen atom, which is outside the plane of the triangle. In the limiting case the H-H distance is not altered. ν_2 is the corresponding perpendicular deformation frequency and appears to be 1630 in infrared and 1580 in Raman spectra. This frequency is doubly degenerate. ν_3 represents a symmetrical stretching (parallel valency) motion, and has the value 3334 cm^{-1} . It is non-degenerate. ν_4 is the corresponding perpendicular frequency and may be considered a tipping mo-

tion of the triangle relative to the N atom. Its value must be regarded as very uncertain, but it would appear to be greater than 3000 cm^{-1} . This same designation (by subscripts) of these frequencies has not been made by all investigators, but it is the one used in all the discussion following.

THE ELECTRONIC STATES OF AMMONIA

The possible types of states^{14, 15} are A_1 , A_2 (similar to Σ^+ and Σ^- states of diatomic molecules), and E . The selection rules are different for two cases:

(1) The electric moment is parallel to the symmetry axis

$$A_1 \rightarrow A_1, \quad A_2 \rightarrow A_2.$$

(2) The electric moment is perpendicular to the symmetry axis

$$A_1 \rightarrow E, \quad A_2 \rightarrow E.$$

The normal state is most probably A_1 , therefore the excited states found are either A_1 or E , depending on the direction of the electric moment.

THE DIFFUSE BANDS (2200-1675A)

Most of these bands have been photographed by Dixon and Leifson and partly analyzed by Dixon, who studied the effect of temperature on the bands and was able to observe many bands arising from high levels of the normal state. The bands found in this research are given in Table I

TABLE I. *The diffuse bands (cm⁻¹).*

Leifson	Dixon	Duncan	Leifson	Dixon	Duncan
44247			50556	50675	50663
45246			51440	51600	51555
46157	46140	46126	52317	52407(1900A)	52501
	46200	46202	53265		53444
47003	47030	47010	54206		54411
	47090	47069	55135		55341
47869	47925	47914			56278
	47975	47962			57271
48768	48890	48803			58255
		48868			59202
49686	49790	49712			

* These first three bands are accompanied by weaker branches called satellites by Dixon. They were not investigated thoroughly in this work but were about the same number and had the same values as those found by Dixon.

⁸ D. M. Dennison and J. B. Hardy, *Phys. Rev.* **39**, 938 (1932).

⁹ D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

¹⁰ P. Lueg and K. Hedfeld, *Zeits. f. Physik* **75**, 599 (1932). References to much other work given here.

¹¹ E. Amaldi and G. Placzek, *Zeits. f. Physik* **81**, 259 (1933).

¹² C. M. Lewis and W. V. Houston, *Phys. Rev.* **44**, 903 (1933).

¹³ The very interesting explanation of this double value of the frequency is given in the above papers of Dennison.

¹⁴ R. S. Mulliken, *Phys. Rev.* **43**, 279 (1933).

¹⁵ J. E. Leonard-Jones, *Trans. Faraday Soc.* **30**, 70 (1934).

TABLE II. *Band heads (complete list) (cm⁻¹).*

<i>v'</i>	Series I		Series II		Series III		Series IV	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
0	46122	46126(4) 884	60130	60136(1) 933	69748	69765(5) 904	82857	82857(6) 986
1	47008	47010(4) 904	61081	61069(3) 957	70669	70669(6) 926	83847	83843(8) 1029
2	47902	47914(5) 889	62046	62026(5) 998	71607	71595(6) 960	84871	84872(8) 1056
3	48804	48803(6) 909	63025	63024(6) 998	72564	72555(7) 989	85931	85928(9)
4	49714	49712(7) 951	64019	64017(7) 1008	73539	73544(8) 990		
5	50632	50663(7) 892	65028	65025(6) 1017	74532	74534(7) 1027		
6	51558	51555(8) 946	66051	66042(7) 1049	75543	75561(8) 1021		
7	52492	52501(10) 943	67088	67091(8) 1049	76572	76583(9) 1045		
8	53434	53444(9) 967	68140	68140(8) 1052	77619	77628(10) 1045		
9	54384	54411(8) 930	69206	69192(6) 1056	78685	78673(8) 1092		
10	55342	55341(6) 946	70287	70248(4) 1068	79768	79767(6) 1065		
11	56308	56287(6) 985	71382	71316(0)	80869	80832(8) 1052		
12	57282	57272(5) 983			81989	81884(8)		
13	58264	58255(2) 954						
14	59254	59209(0)						

together with the measurements of Leifson and Dixon (those which are due to absorption in the *cold* gas) for comparison. The last bands of the series were not found by Leifson probably because his absorbing column was too short.

The agreement of the present measurements with those of Dixon is good in the first three double headed bands. The fourth band is here found to be double headed (because of the long column used) while Dixon gives only the center. The agreement with Leifson is not very good but the general trend of differences is about the same.

It seemed best to accept Dixon's vibrational analysis with one modification. He used two frequencies to explain the upper state differences. His high difference, 2720, is almost exactly three times the lower one, 890, so that every third band falls in a 2700 *v'* progression. Only two bands (in addition to the *v''* = 0 *v'* = 0 band) were used in this progression, and attempts to fit the higher frequency bands observed in the present work into a 2700 progression required that that difference vary in a very irregular and unconvincing manner. It seems that intensities should be quite different in combination bands and in simple

overtones, and members of the 2700 progression (*n* 2700) should be quite different from bands of the type *n* 2700 + *n'* 890. This is clearly found not to be the case here, where the intensities increase in a most regular manner up to *v'* = 8 and afterwards decrease regularly to *v'* = 14. Furthermore, the upper state frequency 2720 must be interpreted as a modification of ν_3 and it is difficult to see physically why this type of frequency should be so greatly lowered. All bands observed here (long wave head used for the double headed bands) fit, within the limit of experimental error, a very simple formula

$$\nu(\text{cm}^{-1}) = 46,157 + 878(v' + \frac{1}{2}) + 4(v' + \frac{1}{2})^2 - 475, (1)$$

where 475 is used for $\omega_e(v'' + \frac{1}{2}) + x_e\omega_e(v'' + \frac{1}{2})^2$, (*v''* = 0), and accordingly all bands in this region are interpreted as members of one *v'* progression.

Dixon's interpretation of the two heads as being two rotational branches seems essentially correct, although it is doubtful whether they are *P* and *R* branches. The difference in direction of shading in these branches found by Dixon, could not be found here. All the branches in-

TABLE III. Sub-bands in series III and IV (cm⁻¹).

Heads											
					Series III						
69765(5)				254	70019(4)				722	70487(4)	
70669(6)				322	70991(5)						
71595(6)	216	71811(3)		312	71907(5)	415	72010(2)				
72555(7)	219	72774(5)		298	72853(6)						
73544(8)	207	73751(5)		310	73854(5)						
74534(7)	208	74742(3)		317	74851(7)				673	75207(4)	
75561(8)	238	75784(4)		253	75814(6)	433	75994(6)	513	76074(2)	585	76146(2)
76583(9)	219	76802(6)		278	76861(?)**	388	76971(6)	505	77088(2)	600	77183(0)
77628(10)	138	77766(5)		268	77896(8)	440	78069(8)	491	78119(0)		
78673(8)	89	78762(7)		258	78931(0)	409	79082(7)				
79767(6)	67	79834(8)*		318	80085(0)			665	80432(0)	815	80618(5)
80832(8)				278	81110(6)			645	81477(0)	765	81597(3)
81884(8)				263	82146(5)			620	82504(0)	722	82606(2)
					Series IV						
82704(1)	153	82857(6)		387	83244(3)			543	83600(4)		
83717(3)	126	83843(8)		433	84276(6)						
84749(4)	123	84872(8)		402	85274(7)						
85769(4)	159	85928(9)									
86839(5)											

Unassigned
78860 (3)
84960 (1)

* Doubtful on basis of intensity.
** Emission lines in source here.

cluding the satellites appear to be shaded to the red.

THE SHARP BANDS (1675-1150A)

It is possible to arrange all the remaining bands heads into three progressions which obey the following series formulas. The progressions are referred to as series II, III and IV. The arrangement was made not merely on the basis of constant differences, but also intensities, appearance of the bands by direct examination of plates and enlargements, and variation of the appearance with pressure were considered. The same bands would have been picked out as belonging to the progressions if differences had not been obtained until after the arrangement had been made. The series formulas, in the same form as Eq. (1) follow:

$$\nu = 60,135 + 936.28(v' + \frac{1}{2}) + 7.22(v' + \frac{1}{2})^2 - 475, (2)$$

$$\nu = 69,769 + 902.56(v' + \frac{1}{2}) + 9.04(v' + \frac{1}{2})^2 - 475, (3)$$

$$\nu = 82,851 + 954.2 (v' + \frac{1}{2}) + 17.2(v' + \frac{1}{2})^2 - 475. (4)$$

The bands observed are given in Table II with their intensities (on a scale of ten). Values calculated from the above formulas are included for comparison.

Series II consists of very sharp bands which have their intensity maxima at a short wave-

length head. There is definite shading to the red of the most intense portions. As many as twenty or thirty "lines" (or groups of intense lines very close together) may be measured in some of the bands, but it is very doubtful that much resolution of the true rotational lines has been accomplished. The "lines" will therefore not be listed, but merely the most intense heads. The last two members of the series would fit the formula better if higher powers of $(v' + \frac{1}{2})$ were considered, and we would expect that the interaction of vibration and rotation would be considerable here. Leifson photographed five of the bands in this series, but regarded them as diffuse. The reason for this is not apparent for they are certainly very sharp here. Leifson's values¹⁶ for the "centers" agree however fairly well with the heads reported here.

The next progression, series III, slightly overlaps series II and its bands have a somewhat different appearance. Series IV is very similar to series III and the following remarks apply to both series. Each band appears to be multiple headed, the number of heads ranging from two to six. Two heads are always much stronger than the others and of the two, the long wave one is

¹⁶ The values are 61,957, 62,932, 63,938, 64,977, 66,006 cm⁻¹ and correspond to $v' = 3, 4, 5, 6$ and 7 of this series.

somewhat the stronger, and is considered the "head" of the band and is the one listed in Table II. This head has the same significance as the heads in series II. The other absorption maxima are separated from the main head by approximately constant differences in any one series. These branches which look like separate bands are all shaded to the red. It does not appear possible to explain these branches as being due to independent vibrational transitions, for the differences involved are much too small even for difference frequencies. Electronic multiplets should be excluded because of the character of the excited states, but in any case the multiplicity cannot be as large and as variable as would be required here.

In Table III are given all the measurements of intense absorption in series III and IV (with intensities on a scale of ten in parentheses). The other absorption maxima accompanying each head and considered the other more intense rotational branches are given in the same horizontal row as the head. The differences *from the head* are indicated in italics.

Toward the end of series IV the continuous absorption begins to get rather strong. It is for this reason that series IV is so short. Additional bands can be seen on the plates and on enlargements, but could not be measured accurately and are not reported. No additional progressions could be found. Series IV really seems to extend as far as $1085\text{\AA} = 92,165 \text{ cm}^{-1} = 11.36 \text{ e.v.}$ It would appear that the first ionization potential should be at least as great as this, but not necessarily much greater. The value usually given by more direct measurement is 11.3 e.v.

DISCUSSION

We may now survey the ammonia spectrum as a whole. The four progressions may all be interpreted as v' progressions all coming from $v=0$ in the normal state. The four progressions must be in four different electronic states since the differences between the first members are far too large to be vibrational differences and are of the order of magnitude of electronic term differences. According to the electronic selection rules, and the experimental fact that only parallel vibra-

tions are found in the excited electronic states, all these states must be of the same type as the normal state (either A_1 or A_2 , but more probably A_1). The fact that the four 0,0 bands do not form a Rydberg series does not present a very serious argument against the excited states being all of the same type.¹⁷

These four progressions involve only the frequency ν_1 . This fact introduces such a great simplification in the discussion that it seemed very important to verify it as well as possible. Accordingly the appearance and intensities were disregarded (since consideration of these requires the above progressions, with *only* the frequency ν_1), and an extensive search made for other approximately constant differences made from a complete table of differences. It was of course possible to find pairs of bands in series III and IV (if all the absorption maxima in Table III were considered as equally probable band heads) which could be attributed to modifications of ν_2 and ν_3 , but only pairs could be found, and no two pairs seemed to have any connection by numbers which could be considered as even greatly modified normal frequencies. Normal state differences should have almost exactly the values of the normal Raman and infrared frequencies, or be exact multiples of these, and no differences at all fulfilled this requirement. So we must conclude that the use of frequencies¹⁸ other than ν_1 results in progressions which are too short to be convincing, are very great in number and cannot be further classified, and that the most elementary intensity rules are violated.

The four progressions are sufficiently long and the data exact enough to obtain what should be fairly reliable values for the first anharmonic constants in the series formulas. These are analogous to the $x_e\omega_e$ constant of diatomic molecules. The most noteworthy fact about them are

¹⁷ R. S. Mulliken, J. Chem. Phys. 1, 494 (1933).

¹⁸ The objection may be made following Dixon's discussion that the other frequencies exist in the excited states, and are unstable, and that after light absorption of ν_1 , ammonia goes over into one of the other frequencies and dissociates. It would appear that this would lead to a continuous or at least a predissociation spectrum in all the states, neither of which is observed except in part of the first state. The cause of the predissociation in this state may be found elsewhere, probably in an additional repulsive level with which the normal state does not combine optically.

that they are all negative¹⁹ and increase with increasing electronic excitation. The constant seems to change sign after the fourteenth member of series I and after the tenth member of series II, but there are too few bands and these have too low intensities to determine a new slope of the $E(v'+1) - E(v')/n$ curves. No determination of the spectroscopic heat of dissociation is therefore possible here.

It was first thought that series II was a continuation of series I, since the last member of series I is separated from the first member of series II by 927 cm^{-1} . The predissociation would then cease abruptly at $v=14$ in the combined series. The main reason for rejecting this idea was because of the quite different slopes of the first difference/ n curves for the bands in series I and II making it impossible to find a formula to fit the combined series. The problem of finding an explanation for the two intensity maxima in the combined series also could not be solved.

Another general experimental fact which seems rather important concerns the intensities in the progressions. The maximum of intensity in series I occurs at $v=7-9$, in series II at $v=7$ in series III at $v=8$ and in series IV at about the same value, although the continuous absorption is too strong here to get a reliable estimate. Application of the Franck-Condon principle here indicates that " r_e " is changed considerably in all the excited states relative to the normal state,

but at least the first three electronic excited states, and probably the fourth have a similar " r_e ". This quantity is to be regarded as depending on the height of the pyramid and at least one other dimension of the molecule, as the N-H or H-H distance.

With the rotational structure of the bands completely resolved in the excited states, and a satisfactory interpretation of this made, the dimensions of the molecule could be exactly calculated in these states from the changes in A and C . Differences in A and B might even be discovered. It would seem impossible to ever accomplish this in series I because of the predissociation. It would be impossible with present instruments in series III and IV because of the large wave number/distance ratio. Series II could be studied more completely from this standpoint with instruments of greater dispersion (our resolving power was most probably limited by the plates used). A discussion of rotational structure will be postponed until this is done.

The continuous absorption at the end of series IV suggests that decomposition would be produced directly by light absorption there, and we might expect from the character of the vibration that all three hydrogens would be split off simultaneously. It is to be noted that the energy becomes just large enough to do this in this part of the spectrum. Absorption to the second and higher excited states could be followed by return of the molecule to the first excited state, and it could decompose there due to the predissociation in that state. This process should be accompanied by fluorescence in the near ultraviolet and visible. This prediction will be tested experimentally.

¹⁹ This is common in polyatomic molecules which have been studied from this standpoint. J. H. Clements, Phys. Rev. **47**, 224 (1935), H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931).