

are much less, showing that the $K\beta_5$ of the metals and the $K\beta_1$ of S do not have their origin in levels in the lattice common to both atoms. In addition, in the cases of Co, Cu and Zn, the multiplicity observed by Valasek in the S lines does not have its counterpart in the corresponding line of the metals.

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The writer wishes to acknowledge his indebtedness to Dr. Joseph Valasek, who suggested the problem, and whose advice and criticism have been invaluable in the carrying out of the research; and to Mr. Christian Dane, machinist, for his careful construction of the apparatus.

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The Ultraviolet Absorption Spectrum of Ammonia

III. The Absorption Spectra of the Deuteroammonias. A Note on Rydberg Series in Ammonia

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

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The absorption spectrum of mixtures of ND_3 , ND_2H , and NDH_2 has been obtained from 2200 to 800A in a normal incidence vacuum spectrograph with a dispersion of about 8.5A/mm. The spectrum above 1675A (the end of the first electronic transition) is made up of very diffuse bands. Below 1675 all the bands are sharp. Two electronic transitions are found between 1675 and 1220A. Each electronic transition is accompanied by many vibrational transitions. Relatively long v' progressions are found for each of the molecules. Evidence for a fourth electronic

state below 1220A was found, but no analysis of the bands could be made. Only one excited state frequency appears for each molecule. This is most probably the parallel deformation frequency, which is also the only frequency found for ammonia in the ultraviolet. The numerical values of the frequencies were calculated from ammonia frequencies in corresponding excited states considering changes in mass alone, and agreed with experiment. The electronic terms for the excited states were also calculated. A discussion is given of a possible Rydberg series in ammonia.

THE absorption spectrum of ammonia has been photographed¹ in the region between 2300 and 850A, with a dispersion of 8.5A/mm. Part of the spectrum between 1620 and 1450A was recently studied² with much higher dispersion (1.3A/mm) and the rotational structure resolved and analyzed.

The present experiments were made with a sample of ND_3 gas given us by Professor H. S. Taylor of Princeton University and prepared in his laboratory. A preliminary report has been made on this work.³ The sample, received in a glass bulb provided with an inner seal, was connected to the vacuum spectrograph through two small volumes separated by stopcocks. By use of these calibrated volumes the pressure of heavy ammonia was varied from 0.014 to 0.70 mm in the spectrograph, which was cut off from the pumps during exposures. At lower pressures

no absorption could be observed, and no additional bands appeared between 0.28 and 0.70 mm pressure. The light source was the Lyman continuum operated as described previously.⁴ The exposure times were ten seconds to two minutes on Hilger Schumann plates. These plates do not give as good contrast in our experience as Eastman III-O oiled with Nujol, but they were about twenty times as fast, and we wished to avoid as far as possible exchange reactions of ND_3 in the spectrograph. Several photographs of pure NH_3 were made on each plate at corresponding pressures for visual comparisons of intensity, and as a general check on the accuracy of measurement.

The measurement of ammonia bands on these plates agreed within experimental error with previous work. All bands reported here have been measured on at least two photographs, some on as many as twelve. The accuracy of measurement is considered to be 5–15 cm^{-1} for

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

² A. B. F. Duncan and G. R. Harrison, *Phys. Rev.* **49**, 211 (1936).

³ A. B. F. Duncan, *Phys. Rev.* **47**, 886 (1935).

⁴ Noyes, Duncan and Manning, *J. Chem. Phys.* **2**, 717 (1934).

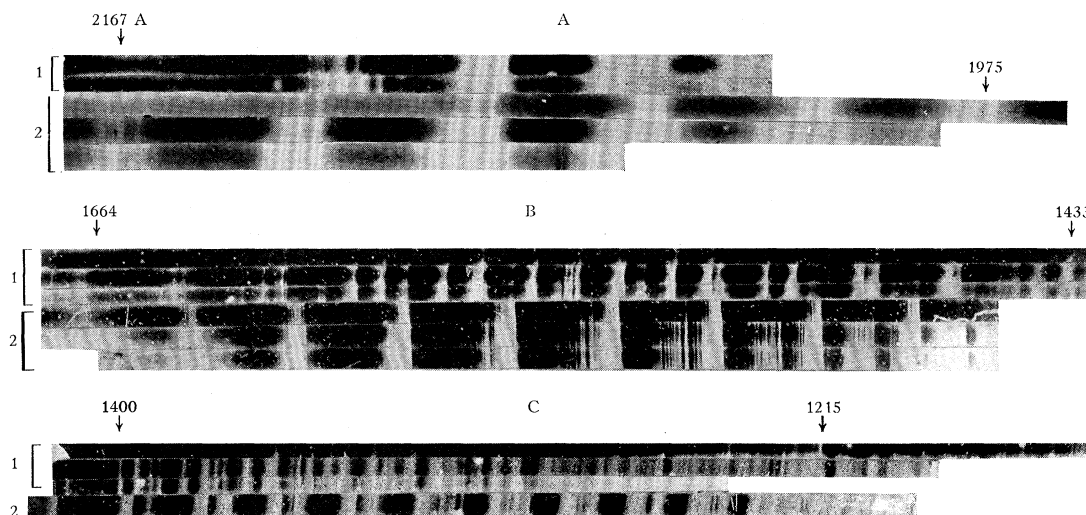


FIG. 1. A(1) ND_3 , etc. 0.3, 0.5 mm, (2) NH_3 , 0.4, 0.7, 1.0 mm; B(1) ND_3 , etc. 0.1, 0.2, 0.5 mm, (2) NH_3 , 0.2, 0.4, 0.5 mm; C(1) NH_3 , etc. 0.02, 0.04, 0.07 mm, (2) NH_3 , 0.01 mm.

sharp bands, and $20\text{--}50\text{ cm}^{-1}$ for the diffuse bands.

The general appearance of the spectra is shown in Fig. 1, which was made from enlarged reproductions (about ten diameters) of parts of representative plates. Parts of the ammonia spectrum are included for comparison.

The spectrum appears much too complicated to be due solely to ND_3 , whose spectrum should not be unlike that of NH_3 . Accordingly the presence of ND_2H and NDH_2 was suspected. This is confirmed by a detailed study of the spectrum. Whether these molecules were formed by exchange with hydrogen compounds in the spectrograph is not known, and the errors caused by contact with wax and stopcock grease cannot be avoided in any case, since we have been unable to operate the set up with an outside absorption column.

The data obtained in the region $1664\text{--}1248\text{Å}$ are the most complete and certainly the most accurate. Two electronic transitions occur in this region, called those to the second and third electronic states.

RESULTS AND DISCUSSION

The first electronic transition (2167–1675Å)

The bands here are mostly of the predissociation type. The first part of this region has been

studied by Benedict.⁵ In ammonia the bands could be arranged satisfactorily in a progression in spite of the predissociation. In the present case it would not be safe to try this, due to the presence of at least three kinds of molecules, for an observed absorption maximum may be due merely to a coincidence of the weaker parts of several bands. The bands, or rather absorption maxima are given in Table I.

The origin of the system is taken to be $46,167 \pm 30\text{ cm}^{-1}$. The maximum of intensity for the whole system is at about $51,000\text{ cm}^{-1}$. As Fig. 1 (A) shows the bands above 2100Å have some structure. $46,167$ does not reproduce well, but appears single headed on the plates. The next three bands are narrow, but weak. The next six bands have fairly sharp edges and all six appear associated in some way. Of these, the strongest is

TABLE I. Bands between 2167 and 1675Å.

| | | |
|-------|-------|-------|
| 46167 | 47932 | 54061 |
| 46479 | 48202 | 54880 |
| 46583 | 48764 | 55735 |
| 46742 | 49562 | 57357 |
| 46999 | 50496 | 57931 |
| 47039 | 51280 | 58265 |
| 47102 | 51547 | 58737 |
| 47197 | 52167 | 59108 |
| 47292 | 52582 | 59769 |
| 47402 | 53131 | 59985 |

⁵ W. S. Benedict, Phys. Rev. **47**, 641 (1935).

TABLE II. Bands of second electronic transition.

| ν | NDH ₂ | | ND ₂ H | | ND ₃ | |
|-------|------------------|-------|-------------------|-------|-----------------|----------|
| | calc. | obs. | calc. | obs. | calc. | obs. |
| 0 | 60113 | 60133 | 60083 | 60081 | 60071 | 60081 |
| 1 | 60992 | 60974 | 60892 | 60911 | 60795 | 60792 |
| 2 | 61883 | 61869 | 61710 | 61690 | 61525 | 61516 |
| 3 | 62788 | 62788 | 62538 | 62533 | 62263 | 62255 |
| 4 | 63706 | 63715 | 63375 | 63368 | 63007 | 63005 |
| 5 | 64636 | 64641 | 64221 | 64223 | 63757 | (63765)* |
| 6 | 65580 | 65586 | 65076 | 65080 | 64515 | 64521 |
| 7 | 66536 | 66533 | 65941 | 65947 | 65279 | 65287 |
| 8 | 67506 | 67513 | 66815 | 66821 | 66049 | 66047 |
| 9 | 68488 | 68481 | 67698 | 67699 | 66827 | (66821) |
| 10 | | | 68590 | 68582 | 67611 | (—) |
| 11 | | | 69492 | 69486 | 68401 | 68411 |
| 12 | | | | | 69199 | 69187 |
| 13 | | | | | 70003 | 70027 |
| 14 | | | | | 70814 | 70850 |

* Obscured by NDH₂ 63,715.

47,197. All the bands following have no structure at the lowest pressure, and the centers are given.

The second electronic transition (1664–1412)

All the bands belonging to this transition are sharp, and at the low dispersion used show heads on the ultraviolet side. In spite of the somewhat complicated appearance of the spectrum it was possible to pick out by inspection two upper state progressions on the basis of appearance and intensities of the bands. They fit the following formulas, obtained from a least squares solution:

$$\nu_{\text{NDH}_2} = 60,133 + 872n + 6.48n^2, \quad (n=0, 1, 2, 3 \dots), \quad (1)$$

$$\nu_{\text{ND}_2\text{H}} = 60,083 + 804n + 4.64n^2 \quad (n=0, 1, 2, \dots). \quad (2)$$

All the remaining bands then fitted into a third series represented by

$$\nu_{\text{ND}_3} = 60,071 + 721n + 3.33n^2, \quad (3)$$

except one weak band, 64,003, which is probably due to NH₃ since a strong band in the spectrum of the latter is at 64,017. Here this band has about 0.01 the intensity of neighboring bands. The bands represented by these formulas are considered due to the molecules NDH₂, ND₂H and ND₃. The observed frequencies together with those calculated by Eqs. (1)–(3) are given in Table II.

It is evident that only one frequency appears for each molecule, which in each case corresponds to the lowest fundamental frequency of the

molecule. The normal state values of these frequencies are known from recent work⁶ to be (taking the mean of the double frequencies) 746.5 (ND₃), 813 (ND₂H), 884 (NDH₂) and 950 (NH₃). If we assume simple ratios between normal state and excited state frequencies such as

$$\omega''_{\text{ND}_3}/\omega''_{\text{NH}_3} = \omega'_{\text{ND}_3}/\omega'_{\text{NH}_3}$$

we may estimate the excited state frequencies for the heavy ammonias from the previously found frequencies of NH₃. The results for this electronic state are given in Table III.

This calculation gives us some confidence both in regard to the assignment of the bands and in the simple dependence of the frequencies on the masses alone, implied in the above calculation. It follows that the excitation of an electron in these four molecules has at least no large specific effect on the frequencies of vibration. Such a calculation should be based on infinitesimal frequencies rather than on those observed which are of finite amplitude. The agreement in spite of this fact must be due to the fact that the anharmonic corrections are all of the same order of magnitude.

The frequencies of the pure electronic transitions in the isotopic molecules are of some interest, but to be rigorous we must know the zero point energies for both states. Since only one of the four (six in the case of ND₂H and NDH₂) frequencies appears in the excited states for each molecule, this energy cannot be determined. If the assumption is made that the absent vibration frequencies are unchanged in the excited states, the zero point energies due to them cancel and we may write Eqs. (1)–(3) in the form

$$\nu = \nu_e + \omega_1'(v' + \frac{1}{2}) + x_1'\omega_1'(v' + \frac{1}{2})^2 - \omega_1''/2 - x_1''\omega_1''/4$$

TABLE III. Estimated and observed excited state frequencies for the heavy ammonias.

| M | Ratio $\omega''_M/\omega''_{\text{NH}_3}$ | $\omega'_{\text{calc.}}$ | $\omega'_{\text{obs.}}$ |
|-------------------|---|--------------------------|-------------------------|
| NH ₃ | 1 | | 936 |
| ND ₃ | 0.78579 | 736 | 721 |
| ND ₂ H | 0.85579 | 801 | 804 |
| NDH ₂ | 0.93053 | 871 | 872 |

⁶ E. F. Barker and M. Migeotte, Phys. Rev. **47**, 702 (1935).

TABLE IV. Bands of third electronic transition.

| v | NDH ₂ | | ND ₂ H | | ND ₃ | |
|-----|------------------|-----------|-------------------|-------|-----------------|-----------|
| | calc. | obs. | calc. | obs. | calc. | obs. |
| 0 | 69768 | 69786 | 69764 | 69786 | 69791 | 69786 |
| 1 | 70614 | 70609 | 70546 | 70528 | 70485 | (-) |
| 2 | 71480 | 71466 | 71344 | 71345 | 71192 | 71201 |
| 3 | 72364 | 72337 | 72156 | 72152 | 71915 | 71918 |
| 4 | 73268 | 73252 | 72982 | 72976 | 72653 | 72656 |
| 5 | 74190 | 74201 | 73824 | 73811 | 73406 | 73379 |
| 6 | 75132 | 75167 | 74680 | 74682 | 74174 | (74201)* |
| 7 | 76092 | 76110 | 75550 | 75548 | 74957 | 74923 |
| 8 | 77071 | 77052 | 76435 | 76449 | 75755 | 75776 |
| 9 | 78070 | 78059 | 77335 | 77327 | 76568 | 76555 |
| 10 | 79087 | 79064 | | | 77332 | (77327)** |
| 11 | 80123 | 80112 | | | | |
| 12 | 81179 | 81223 (?) | | | | |

* Used also for NDH₂.
 ** Used also for ND₂H.

x_1'' is not known but $x_1''\omega_1''/4$ is probably small. The equations are then

$$\nu_{\text{NH}_3} = 60,135 + 936(v' + \frac{1}{2}) + 7.22(v' + \frac{1}{2})^2 - 475, \quad (4)$$

$$\nu_{\text{NDH}_2} = 60,117 + 866(v' + \frac{1}{2}) + 6.48(v' + \frac{1}{2})^2 - 442, \quad (5)$$

$$\nu_{\text{ND}_2\text{H}} = 60,087 + 800(v' + \frac{1}{2}) + 4.64(v' + \frac{1}{2})^2 - 407, \quad (6)$$

$$\nu_{\text{ND}_3} = 60,083 + 717(v' + \frac{1}{2}) + 3.33(v' + \frac{1}{2})^2 - 373. \quad (7)$$

This gives a spread of 52 cm⁻¹ in the electronic terms of the four molecules which may probably be attributed mainly to error in the assumption made above in regard to the zero point energies.

The maxima of intensity in the progressions occurs for ND₂H and NDH₂ at $v'=6$ and for ND₃ at $v'=6$ or 7. The intensities of corresponding bands of ND₂H and NDH₂ appear very nearly equal. The bands of ND₃ appear to have about $\frac{2}{3}$ the intensity of the others. Whether this is due to the composition of the sample would have to be determined by measuring the absorption coefficients of pure isotopic samples.

The third electronic transition (1433-1248A)

Bands belonging to this transition are also sharp and are more crowded together since the vibrational frequencies are smaller. The electronic transition as a whole is much stronger than the one preceding. The intensity is about equal to that of the first electronic transition as judged by the values of the pressure at which corresponding bands first appear. The same is

TABLE V. Bands below 1220A. In the bands marked V the red edge was measured. In the other cases the ultraviolet edge was measured.

| | | |
|---------|---------|-------|
| 82017 ? | 83764 | 85732 |
| 82111 ? | 83980 | 86272 |
| 82361 | 84078 | 86613 |
| 82806 | 84391 V | 86798 |
| 83186 | 84838 V | 87483 |
| 83480 V | 85406 | |

true of the corresponding transitions of ammonia.

Three progressions are also found here, belonging to the three molecules NDH₂, ND₂H, and ND₃. A few of the strongest ammonia bands also appear weakly in this region. All the bands not positively identified with NH₃ fit one of these three formulas:

$$\nu_{\text{NDH}_2} = 69,786 + 837n + 9.50n^2, \quad (8)$$

$$\nu_{\text{ND}_2\text{H}} = 69,764 + 775n + 7.32n^2, \quad (9)$$

$$\nu_{\text{ND}_3} = 69,791 + 686n + 7.50n^2. \quad (10)$$

The observed bands are given in Table IV, where the agreement with the above formulas may be seen. The frequencies for this state were calculated from the normal state ratios in Table III and are 840, 772 and 709 for NDH₂, ND₂H and ND₃, which are to be compared to the values in Eqs. (8)-(10). Here again the agreement is good for NDH₂ and ND₂H. The above equations may be written in the form of Eqs. (4)-(7) in order to compare the pure electronic terms. With NH₃ for comparison they are:

$$\nu_{\text{NH}_3} = 69,769 + 902.5(v' + \frac{1}{2}) + 9.04(v' + \frac{1}{2})^2 - 475, \quad (11)$$

$$\nu_{\text{NDH}_2} = 69,794 + 827.5(v' + \frac{1}{2}) + 9.50(v' + \frac{1}{2})^2 - 442, \quad (12)$$

$$\nu_{\text{ND}_2\text{H}} = 69,785 + 768.0(v' + \frac{1}{2}) + 7.32(v' + \frac{1}{2})^2 - 407, \quad (13)$$

$$\nu_{\text{ND}_3} = 69,823 + 678.5(v' + \frac{1}{2}) + 7.50(v' + \frac{1}{2})^2 - 373. \quad (14)$$

There is here again a spread of 54 cm⁻¹ between the terms of NH₃ and ND₃, but the order of the terms is reversed, i.e., $\nu_e(\text{ND}_3) > \nu_e(\text{NH}_3)$.

The maximum of intensity in any one progression is rather difficult to determine due to some overlapping of the bands, but appears to occur at $v'=5-7$ for all the molecules. The

bands of NDH_2 are noticeably stronger than those of ND_2H in this region, and the latter are stronger than those of ND_3 , though the difference between the latter two is not very great. The intensity decreases rapidly on the ultraviolet side of the maximum for all three molecules though the NDH_2 bands could be followed to $80,122 \text{ cm}^{-1}$.

In the region $78,000\text{--}82,000 \text{ cm}^{-1}$ emission lines in the source are troublesome and often reversed. This probably explains the failure to observe additional bands in this particular region. No way of removing these lines is possible with this source, since they are due to C, and to Si and O from the glass.

The spectrum below 1220A

A list of these bands is given in Table V. Three (marked *V*) are different from all other bands of this spectrum in being shaded to the ultraviolet. The emission lines here are not troublesome but the bands overlap considerably. This is thought to be due to the beginning of a fourth excited electronic state corresponding to the ammonia state with origin $82,857 \text{ cm}^{-1}$. Since strong continuous absorption begins just below $87,000$ the existence of progressions could not be established because of too few members. Obviously higher dispersion is needed to resolve the structure in this region. The existence of a discrete band at $87,483 \text{ cm}^{-1}$ shows that the ionization potential is probably larger than a value calculated from this figure.

A NOTE ON RYDBERG SERIES IN AMMONIA

The analysis of the spectra of the heavy ammonias has confirmed all our previous analysis of the spectrum of NH_3 . In particular a doubt previously expressed⁷ about the independent existence of the second electronic state has been removed. However, if the electron in all these states is a nearly nonbonding $[za_1]$ electron,⁸ these electronic states should fit into a Rydberg

series. The writer tried without success to fit the *electronic* terms of the four states into a series, the values used being 46,157, 60,135, 69,769 and 82,857. No two of these values will fit even approximately into a series which converges at the correct ionization potential, taken as 11.3 ev.

Using, however, the maxima of intensity in the four states we have the values 52,501, 65,025, 77,628, and 84,872. It can now be shown that the first, third and fourth of these fit reasonably well in a Rydberg series which converges at about 11.5 ev. The equation for the series is

$$\nu = 93,380 - R/(n - 0.362)^2 \quad n = 2, 3, 4$$

and the calculated values are 52,480, 77,611, and 85,088. The differences between these values are 25,131 and 7477 cm^{-1} which may be compared with the differences 20,349 and 6190 between 3s, 4s, and 5s in the normal nitrogen atom. This analogy is not stressed however, and may even be wrong.

If this series has a reality, a difficulty is raised concerning the second electronic state, which does not fit into the series. It cannot be regarded as a continuation of the first electronic transition with origin at $46,157 \text{ cm}^{-1}$. The bands are definitely parallel (from the rotational analysis) and so the selection rules (electronic times vibration) give for this state A_1 if the normal state is taken as 1A_1 . The transition $A_1 \rightarrow E$ is not consistent with definitely parallel bands. The first electronic transition has been considered by Mulliken to be to an 1A_1 state and if the series is real the third and fourth are also to 1A_1 states. So we have apparently an extra A_1 not related to the other excited 1A_1 states. Possibly the transition is to a 3A_1 state corresponding to the 1A_1 state with origin 69,769, following a suggestion of Mulliken.⁸ The transition is much weaker than 69,765 as might be expected from a transition involving a change of multiplicity.

The writer expresses his gratitude to Professor H. S. Taylor for the sample of heavy ammonia, and to the Warren fund of the American Academy of Arts and Sciences for financial aid during the progress of this work.

⁷ Reference 1, page 827.

⁸ R. S. Mulliken, *J. Chem. Phys.* **3**, 506 (1935).

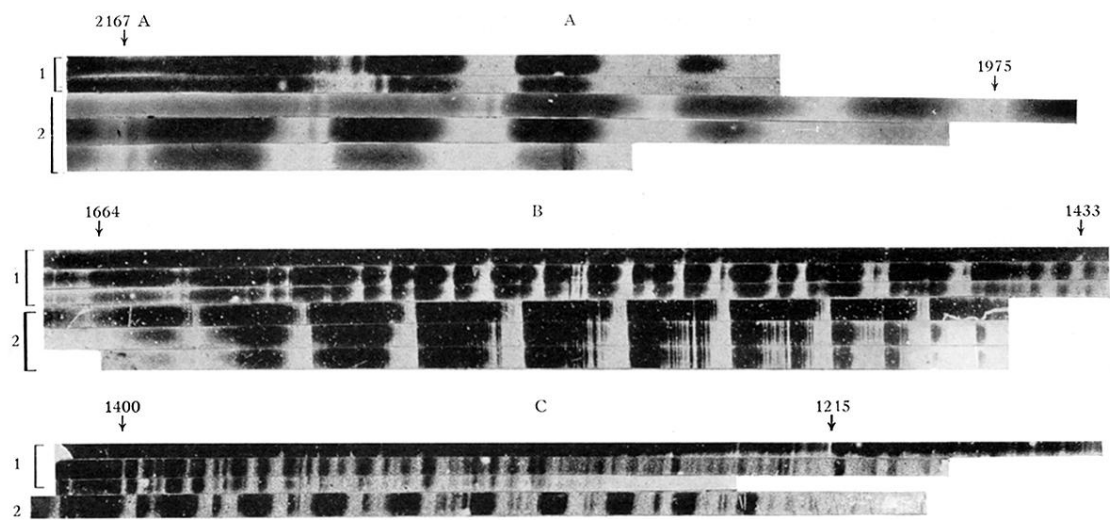


FIG. 1. A(1) ND₃, etc. 0.3, 0.5 mm, (2) NH₃, 0.4, 0.7, 1.0 mm; B(1) ND₃, etc. 0.1, 0.2, 0.5 mm, (2) NH₃, 0.2, 0.4, 0.5 mm; C(1) NH₃, etc. 0.02, 0.04, 0.07 mm, (2) NH₃, 0.01 mm.