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The Ultraviolet Absorption Bands of Ammonia[1]

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The ultraviolet absorption bands of ammonia have been investigated in the region from 2400 to 1900A over a wide range of temperatures and pressures. The frequencies of a number of intense double-headed bands have been measured and an analysis of these bands is presented. The doublet separation is nearly constant and is equal to 70 cm^{-1}. Only two fundamental frequencies are observed in the upper state, namely, 890 and 2720 cm^{-1}. The predissociation which occurs in the excited state is discussed and accounted for by assuming that the $\nu_2'(\perp)$ type of vibration of the molecule is always unstable.

Introduction

The ultraviolet absorption bands of ammonia were investigated by Leifson[3] and shown to consist of a number of diffuse bands extending from 2260A down into the far ultraviolet. Bonhoeffer and Farkas[4] later showed that the ammonia molecule in the excited state does not fluoresce and consequently the diffuse appearance of the bands is not due to unresolved fine structure, but to predissociation. In spite of the difficulties encountered in obtaining a satisfactory analysis for the vibration bands of a polyatomic molecule, it seemed of value to investigate these ultraviolet ammonia bands more carefully than heretofore in order to see if an analysis was possible. The numerous recent investigations of the infrared spectrum of ammonia and the apparent simplicity of the bands reported by Leifson at least made the problem more attractive than would have been the case otherwise. It was obvious that the measurements of Leifson were not accurate, since he stated that only the midpoints of the bands were measured and some later work by Bates and Taylor[5] had shown that the bands possessed a double head between the ends of the bands. In the discussion that follows the cause of the predissociation is considered and an explanation of the phenomenon is given. This matter is of interest in connection with the photochemical decomposition of ammonia.

Experimental

The system necessary for carrying out the experiments consisted mainly of a trap, mercury manometer, absorption cell, suitable connecting tubing and stopcocks. An oil pump served to evacuate the apparatus. One absorption cell was all-quartz, ten inches long, with sealed-on plane ends. The second cell was two inches long, the quartz ends being cemented on with De Khotinsky cement. The longer of the two cells was used to make measurements on the heated gas, hence contained an inset tube at its middle to hold a thermocouple junction. The cell was wrapped with nichrome heating wire and well insulated with asbestos. Ammonia was secured from a small tank, in which it was stored over metallic sodium. The gas was admitted to apparatus as needed, frozen by a solid carbon dioxide alcohol mixture, pumped frequently and then admitted to the absorption cell without further purification.

The hydrogen discharge tube used as a source of light was similar to one described by Bay and Steiner[6] and ran on a current of 300 milliamperes at 8000 volts. Lenses before and after the absorption cell focussed the light on the slit of the spectrograph. Photographs were taken with a Schmidt and Haensch Universal Spectrograph,

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[1] Contribution from The Sterling Chemistry Laboratory, Yale University.

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[3] Leifson, Astrophys. J. **63**, 73 (1926).

[4] Bonhoeffer and Farkas, Zeits. f. physik. Chemie **124**, 337 (1927).

[5] Bates and Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

[6] Bay and Steiner, Zeits. f. Physik **59**, 48 (1929).

with one quartz prism. The dispersion was better than 4A per millimeter at 2200A. Below 2000A a Hilger E31 Spectrograph was employed, the dispersion amounting to about 11A per millimeter. The slit width used was 0.02 to 0.03 mm and the time of exposure usually amounted to less than fifteen minutes. An iron arc or aluminum spark served to give a comparison spectrum, the particular standard depending on the wave-length region under investigation. Eastman 33 Plates, with or without Eastman Ultraviolet Sensitizer, were used.

The spectrograms of the ammonia bands were measured on a small Leiss Comparator, which gave the position of any line with an accuracy of about 0.03 mm. The accuracy of the measurements was limited not so much by the accuracy of the instruments used as by the diffuseness of the bands. One or two plates were obtained on which the dispersion was 1A per millimeter and in these cases the bands were so diffuse that it was not possible to measure the plates. At the lower dispersion it was often necessary to mark the positions of the satellite bands (see below) before measuring the plate. The positions of the strong bands were determined with an accuracy of ± 10 cm^{-1}; where the middle of the band had to be estimated the accuracy was only 30 cm^{-1}. It was necessary to vary the ammonia pressure by relatively small increments in order to bring out all of the weak absorption bands recorded below.

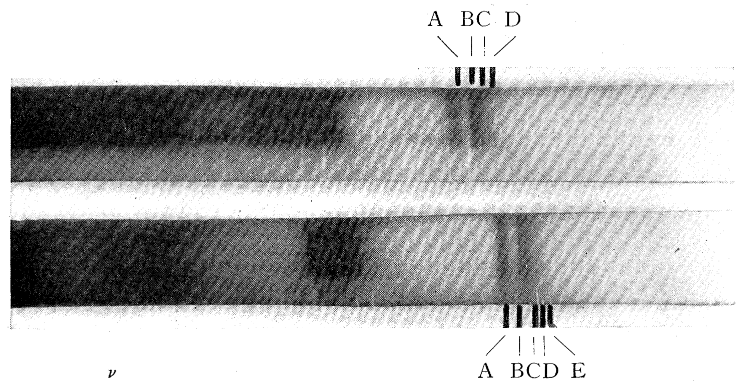

FIG. 1. The ultraviolet absorption bands of ammonia. The principal bands, *A* and *B*, and the satellite bands, *C*, *D*, *E* are marked for the regions near 45,250 and 47,060 cm^{-1}.

RESULTS

Sixteen strong ammonia bands were observed in the region from 1900 to 2400A when the temperature was varied from 25° to 600°C and the ammonia pressure from less than 0.5 mm to 2.5 atmospheres. Each of these bands is doubled and very intense as may be noted in the reproductions shown in Fig. 1. Enough plates were obtained to determine the wave-length of each band from one or more plates and the results are usually the average of measurements on four or more photographs, the greatest weight being placed on those in which the absorption was small. The wave-lengths which were found do not agree with those of Leifson and always correspond to a shorter wave-length. The reason for this is evident, because Leifson measured the center of the absorption band and this point is always to the long wave-length side of the double head. The absorption was greatest at or near the long wave side of the blue component of the doublet and at the short wave side of the red component. These positions of maximum absorption have been measured and called the heads of the band and are denoted by *A* and *B*, respectively, in Fig. 1. As the pressure increased, absorption by the red component increased rapidly towards longer wave-lengths, the blue component spread to the short wave-length side only slightly and absorption between the two heads increased until it was complete. On the long wave-length side of each red component were certain well-defined absorption maxima, which were observed clearly upon careful regulation of the ammonia pressure. Several of these are indicated in Fig. 1 by *C*, *D*, *E* and *F*. In order to illustrate these absorption maxima, a microphotometer trace of one of the bands is shown in Fig. 2. For the sake of simplicity the intense bands *A* and *B* are called the principal bands and the weak bands *C*, *D*, etc., satellite bands.

In Table I are given the frequencies of the bands measured. The principal and satellite bands have been recorded in separate parts of the table, the frequencies in wave numbers are on a vacuum basis and the effect of heat has been noted. The frequency 48,890 cm^{-1} represents the midpoint between the heads of the band and all other measurements at shorter wave-lengths are the midpoints between the ends of the bands. The double-headed bands at 46,140 and 47,030 cm^{-1} are interesting because, upon heating to 150° or 300°C, each of these bands shifted to the red and became in appearance triple-headed. In fact the original double-headed band was present, less intense, however, and a new double-head was present nearby on the long wave-length side. The band at 41,825–41,890 cm^{-1} is less intense than the one to the red and to the violet under the same conditions of temperature and pressure. The frequencies of the satellite branches at approximately 46,900 and 47,800 cm^{-1} are the average of several measurements which agreed well among themselves and consequently considerable confidence can be placed in the results. In nearly all cases the satellite bands occur in pairs, as shown in Table I.

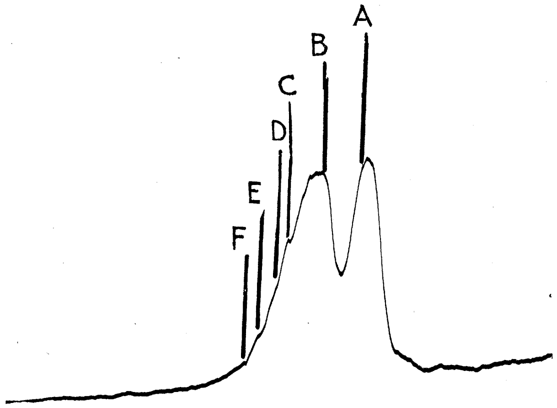

FIG. 2. Microphotometer trace showing the ammonia absorption band at 2124A. *A* and *B* are the principal bands; *C–F* the week satellite bands.

TABLE I. *Ultraviolet absorption bands of ammonia.* (A plus sign in parenthesis after the frequency indicates that an increase in temperature increased the intensity of the band in question.)

cm^{-1}	Assignment	cm^{-1}	Assignment
	A. Principal Ammonia Bands		
41140 (+) 41220 (+)	$\nu_4''\rightarrow\nu_1'(0)$	46140 46200	(origin) $\nu_1''(0)\rightarrow\nu_1'(0)$
41825 (+) 41890 (+)	$\nu_1''+2\nu_2''\rightarrow\nu_1'(0)$	46980 (+) 47060 (+)	$\nu_1''\rightarrow 2\nu_1'$
42680 (+) 42760 (+)	$\nu_1''+2\nu_2''\rightarrow\nu_1'$	47030 47090	$\nu_1''(0)\rightarrow\nu_1'$
42810 (+) 42890 (+)	$\nu_3''\rightarrow\nu_1'(0)$	47925 47975	$\nu_1''(0)\rightarrow 2\nu_1'$
43760 (+) 43830 (+)	$\nu_1''+\nu_2''\rightarrow\nu_1'(0)$	48890	$\nu_1''(0)\rightarrow\nu_3'$
		49790	$\nu_1''(0)\rightarrow\nu_1'+\nu_3'$
44540 (+) 44610 (+)	$\nu_2''\rightarrow\nu_1'(0)$	50675	$\nu_1''(0)\rightarrow 2\nu_1'+\nu_3'$
45220 (+) 45280 (+)	$\nu_1''\rightarrow\nu_1'(0)$	51600	$\nu_1''(0)\rightarrow 2\nu_3'$
		52470	$\nu_1''(0)\rightarrow\nu_1'+2\nu_3'$
46040 (+) 46120 (+)	$\nu_1''\rightarrow\nu_1'$		
	B. Satellite Ammonia Bands		
42590	$\nu_1''+2\nu_2''\rightarrow\nu_1'$	46020 46080	
43560 (+) 43640 (+)	$\nu_1''+2\nu_2''\rightarrow\nu_3'$	46875 46910	
43660 (+) 43710 (+)	$\nu_1''+\nu_2''\rightarrow\nu_1'(0)$	46940 46990	
44445 (+) 44500 (+)	$\nu_2''\rightarrow\nu_1'(0)$	47730 47780 47815	
45100 (+) 45160 (+)	$2\nu_1''\rightarrow\nu_1'$	47860	

DISCUSSION

It is apparent that the principal bands consist of a series of double-headed bands, the average separation of the components remaining practically constant and equal to about 70 cm^{-1}. It can be assumed that the doubling is caused by an electronic doublet in the excited state of the molecule. The component bands of such a doublet should be very similar in structure, but, since it is observed that one component shades to the red and the other to the violet, the explanation is probably incorrect. Furthermore, ammonia possesses an even number of extranuclear electrons and hence the multiplicity should be odd and not even. The doubling of the infrared bands of ammonia at 10μ and 3μ has been observed and Dennison[7] has shown that these phenomena are due to the symmetry properties of the ammonia molecule, one form being symmetrical and the other antisymmetrical with regard to their wave functions. The components of the infrared bands are then exactly the same except for a small constant frequency difference between the rotational lines of the same quantum number. Dennison and Hardy[8] pointed out that the frequency difference should become greater for higher vibrational quantum numbers. If an analogous line of reasoning is followed in connection with the electronic bands, it is seen that the facts do not agree with the expectations, since the doublet separation remains constant and the components are not similar in appearance. The best explanation of the doubling is one in which each band is assumed to consist of a P and an R branch, the latter doubling back to the red. This explains why the absorption in the short wave component spread to the violet only slightly and the fact that the absorption in the other component increased rapidly to the red as the ammonia pressure was increased. At high pressures and temperatures the R branch was developed at higher rotational quantum numbers and hence absorbed completely in between the origins of the two branches. Even though the rotational structure is diffuse as a result of predissociation, the effects produced by the branches should be the same as in the case of discrete states. The reason for the large separation of the origins of the P and R branches is not apparent and this difficulty constitutes an objection to the explanation of the doubling.

For the reasons given below the origin of the electronic system is chosen as 46,140 cm^{-1} for the P branch and 46,200 cm^{-1} for the R branch. The subsequent discussion of the analysis of the vibration bands is limited to a discussion of the origins of the P branches, since the origin of each R branch is displaced 70 cm^{-1} from the origin of the corresponding P branch. The intensity of the 46,140 cm^{-1} band decreased and all bands to the red were increased in intensity upon heating the ammonia. This is an indication that the former is located at or to the short wave-length side of the origin. Furthermore, the bands at 45,220 and 44,540 cm^{-1} are separated from the origin by 920 and 1600 cm^{-1}, respectively, and represent transitions from the first two vibrational levels in the lower state to the ground level in the excited state. Infrared data[9] give these frequencies as 933 and 1630 cm^{-1}. No other choice of an origin gives an agreement as satisfactory as the above nor explains the heating experiments and intensities of the bands as well. Bearing in mind that the first two vibration levels observed in the upper state lie 895 and 1785 cm^{-1} above the zero level, the bands to the red of the origin are given the assignments shown in Table I.

The analysis is satisfactory except with regard to several bands. The transition $\nu_1''+\nu_2''\rightarrow\nu_1'(0)$ should be displaced 2500 cm^{-1} from the origin, while the observed value is only 2380 cm^{-1}. Robertson and Fox[10] gave 2500 cm^{-1} as the infrared frequency because it represented the position of maximum absorption in the band, but the absorption at 2380 cm^{-1} was also considerable. The fact that the band results from a combination of a perpendicular and a parallel vibration of the molecule shows that the band is complex and hence it is not possible to predict from which level in the ground state will arise the strongest transition to the upper electronic state. The assignment $\nu_1''+\nu_2''\rightarrow\nu_1'(0)$ to the band at 43,760 cm^{-1} is probably correct for this reason. The satellite branches at 43,660 and 43,710 cm^{-1} are then associated with the same transition, but a smaller probability of transition. The same kind of difficulty arises in connection with the bands at 41,140 and 41,825 cm^{-1}. In each case the observed displacement from the origin is less than the infrared frequency and, as before, the infrared frequency represents the position of maximum absorption. For example,

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[7] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[8] Dennison and Hardy, Phys. Rev. **39**, 938 (1932).

[9] Weizel, Handbuch der Experimental Physik; **1**, p. 416 (1931).

[10] Robertson and Fox, Proc. Roy. Soc. (London) **A120**, 161 (1928).

Robertson and Fox[10] give three strong absorption maxima in the infrared at 4504, 4420 and 4320 cm^{-1}, the second of which is slightly stronger than the other two. The band at 41,825 cm^{-1} is displaced from the origin by 4315 cm^{-1}, which agrees with the smallest of the three infrared frequencies but not the other two. Further investigation of the infrared bands may make it clear as to which levels in the ground state are favored as initial states in the electronic bands.

The frequencies in the excited state which are necessary to account for the bands to the short wave-length side of the origin are 890 and 2720 cm^{-1}. The assignments are given in Table I. The wave number differences between successive bands alternates between about 890 and 920 cm^{-1} and hence it is necessary to have two frequencies in order to account for the observed results. Leifson's data show irregularities in the differences which are similar to those observed here. The satellite bands to the short wave side of the origin may arise from the same transitions assigned to the nearby principal bands, but in view of the uncertainty the assignments have not been given in Table I. The bands in the excited state show little, if any, convergence, hence an approximation of the heat of dissociation is not possible.

The fact that only two frequencies appear in the excited state is significant and suggests that one, and possibly two, of the types of vibration in the upper state are unstable. If one considers the mechanical picture of the possible types of vibration of the ammonia molecule,[7] it is seen that the ν_2' vibration should be least stable. This consists of a vibration of the nitrogen atom perpendicular to the axis of symmetry and the oscillation of two of the hydrogen atoms in a direction opposite but parallel to that of the third hydrogen atom. Recent studies of the photochemical decomposition of ammonia and related problems,[11] give a mechanism for the decomposition which requires a primary dissociation into NH_2 and H after the absorption of light. The ν_2' frequency accounts for this dissociation, since one of the hydrogen atoms is unique and dissociation should yield NH_2 and H. Since the frequencies in excited states are usually less than those in the ground states, the frequencies 890 and 2720 cm^{-1} correspond to ν_1'' and ν_3'', respectively, of the ground state. Predissociation is then of the type which is called vibrational predissociation by Herzberg.[12] The energy present in ν_1', ν_3' or a combination of these two passes into the vibration ν_2' and dissociation follows, since the latter is assumed to be unstable. This transfer of energy from one type of vibration to another is assumed to take place in many molecules as will be seen from a perusal of the recent literature on the subject of unimolecular chemical reactions. The type of predissociation suggested for the ammonia molecule accounts for the observation that the absorption bands are diffuse over the entire region investigated.

It is a pleasure to acknowledge and thank Professor W. W. Watson of the Physics Department for his constant interest and help during the course of this investigation.

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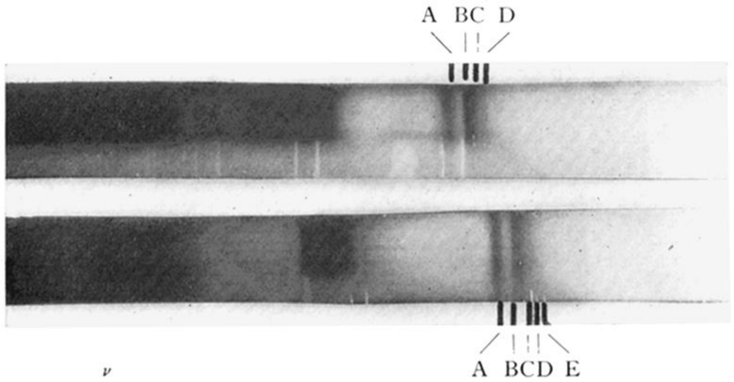
[11] Wiig and Kistiakowsky, J. Am. Chem. Soc. **54**, 1806 (1932); Dixon, ibid. **54**, 4262 (1932).

[12] Herzberg, Ergebn. d. exakt. Naturwiss. **10**, 207 (1931).



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