NOVEMBER 1, 1932 PHYSICAL REVIEW VOLUME 42

The Molecular Scattering of Light from Ammonia Solutions. The Fine Structure of a Vibrational Raman Band

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(Received September 2, 1932)

The Raman band of the ammonia molecule corresponding to the infrared absorption at 3 μ has been partially resolved into its fine structure. The experiments have been made not with gaseous or liquid ammonia but with aqueous solutions of relatively high concentration. The lines have been assigned to *Q*, *P*, *R*, *PP*, and *RR* branches, corresponding to changes in rotational quantum number $\Delta k=0$, ± 1, and ± 2. The moment of inertia about a line normal to the axis of symmetry calculated from the spacing of the lines is $I=2.82\times 10^{-40}$ g cm^2. As far as the present, somewhat incomplete results may be taken to indicate the structure of the NH_3 molecule is largely uninfluenced by the force fields of the solvent molecules.

A NUMBER of investigators have utilized the study of the Raman effect to indicate the changes taking place when an inorganic electrolyte is dissolved in water. The purpose of these studies has usually been to investigate the eventual possibility of obtaining a quantitative measure of the degree of dissociation of the dissolved electrolyte into ions. On the other hand the use of solvents to make it practical to work with simpler substances which do not dissociate upon solution has not met with general favor, it being assumed that perturbations arising from the mutual interaction of solvent and solute molecules will cause difficulties. Also in the case of pure liquids it has been stated[1] that similar interaction produces a lack of sharpness in the rotational states, so that rotational transitions give rise to continuous Raman spectra instead of sharply defined lines. In addition there are presented in this article data whose intent are to show a well-defined difference in the vibrational Raman shifts between gaseous and liquid ammonia.[2] Our experience with solutions in water has led us to believe such views to be unfortunate, at least in the case of the particular system we are about to describe, ammonia plus water. A very incomplete report of the work has already been published as a preliminary communication to the Editor of this Journal.[3]

The molecular scattering of light from gaseous ammonia has been studied by Wood,[4] by Dickinson, Dillon and Rasetti[1] and, more recently and com-

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[1] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

[2] Experimental error cannot account for the difference in Raman shift in the case of the liquid, $\Delta\nu=3298$, and that for the gas, $\Delta\nu=3334$. However, the "somewhat weaker" shift reported for the liquid, $\Delta\nu=3215$, may be the strong vibration-rotation line, $\Delta\nu=3216$, in our Table I. If this is true, liquid ammonia and the aqueous solution give the same result in this case.

[3] Hollaender and Williams, Phys. Rev. **37**, 1367 (1931).

[4] Wood, Phil. Mag. **7**, 744 (1929).

pletely, by Amaldi and Placzek.[5] There are here reported a vibrational line corresponding to $\Delta\nu = 3311$, and rotational lines which could be measured on both sides of the mercury exciting line $\lambda 2536$. The experiments with liquid ammonia[6,7,1] have revealed the presence of the frequency differences $\Delta\nu = 3311$, $\Delta\nu = 1580$ and $\Delta\nu = 1070$, corresponding to three of the four fundamental frequencies of the pyramidal formula usually assumed for ammonia. Other weaker lines present in these spectra have either been described as having been caused by the association of single ammonia molecules to form double and triple molecules or have not been mentioned at all.

Carrelli, Pringsheim and Rosen[8] were the first to study solutions of ammonia in water, reporting frequency shifts of $\Delta\nu = 3314$ and $\Delta\nu = 3385$. The next work, as far as we are aware, is contained in the preliminary note referred to above,[3] in which it could be stated "that all the lines which have been reported from gaseous and liquid ammonia have now been found in the concentrated solution (16 normal) as well." There was also included here the microphotographic record of one of the plates which had been exposed in a small Steinheil glass spectrograph. This record shows not only the presence of the vibrational band corresponding to the infrared absorption at $3\,\mu$[9] but also unmistakable evidence of a fine structure due to its combination with the rotation spectrum of the ammonia molecule. The dispersion of the instrument was such that the position of the vibration-rotation lines could not be determined with a sufficient degree of accuracy to assign the proper rotational quantum numbers, so that further experiments with an instrument having a much greater dispersion were necessary. The work to be reported here was done with a Steinheil GH glass spectrograph. Satisfactory exposures were made with ammonia solutions varying in concentration from four normal to sixteen normal, but publication of the results had been postponed in the hope that exposures and microphotographic records suitable for reproduction might be included. It has just now come to our attention that in an article published last month Langseth,[10] working with ammonia solutions of like concentration, has also been able to resolve the Raman band corresponding to the infrared absorption band at $3\,\mu$. The positions of the lines in the two researches agree very well with each other except that we have as yet been unable to find sufficient positive evidence for the combination frequency differences which would make possible the calculation of the moment of inertia characteristic of the rotation about the axis of symmetry. The moment of inertia calculated for the rotation about an axis at right angles to the line of symmetry is almost identical in the two experiments. Under these circumstances it is felt that immediate submission of our present results is advisable even though they are incomplete in certain respects.

[5] Amaldi and Placzek, Naturwiss. **20,** 521 (1932).
[6] Daure, Trans. Farad. Soc. **25,** 825 (1929).
[7] Bhagavantam, Ind. Jour. Phys. **5,** 35 (1930).
[8] Carrelli, Pringsheim and Rosen, Zeits. f. Physik **51,** 511 (1928).
[9] Stinchcomb and Barker, Phys. Rev. **33,** 305 (1929).
[10] Langseth, Zeits. f. Physik **77,** 60 (1932).

APPARATUS AND TECHNIC

The experimental arrangement was similar to that described by Kohlrausch[11] in his recent book. The ammonia gas, taken from a commercial cylinder, was thoroughly washed before it was passed into conductance water to form the solution. The solution to be investigated was placed in a long tube, illuminated along its length with a commercial mercury arc, and the spectrum of the scattered light which passed through a plane window in the end of the tube was recorded by using the spectrograph mentioned above. The tubes were cooled by means of a jacket through which a continuous stream of cold water was pumped. A comparison spectrum from a copper arc was recorded on each plate. The mercury lamps were cooled by an electric fan. The Raman lines reported were all excited by Hg 4047. The filter technic used was essentially that described by Wood. In the calculation of the frequency differences the frequency of this line was taken as 24,705 cm^{-1}.

The plates were photometered with a Moll recording microphotometer. The frequencies of the Raman lines were obtained by interpolation on a calibration curve prepared from the microphotometric record of the copper spectrum. All lines reported were observed on several of the plates taken, with different concentrations of ammonia and different times of exposure. The intensity of the lines, while difficult to establish in any quantitative way, always became weaker as the concentration of the solution was decreased, indicating that the excitation of the water bands was not a source of difficulty and that the structure observed was actually characteristic of the ammonia molecule.

EXPERIMENTAL RESULTS

The results of the experimental determinations are summarized in Table I. The columns of this table give, from left to right; the frequency of the excited line in reciprocal centimeters, the corresponding frequency difference between exciting and excited line, the assignment of rotational quantum number for the transition $\Delta k \pm 1$, and the assignment of rotational quantum number for the transition $\Delta k = \pm 2$. In a number of cases the microphotometric record shows the head of the line to be somewhat broadened rather than sharp, therefore the exact positions of the weaker lines will be somewhat in doubt. Nevertheless, it is believed that most of them have been located to within ± 3 cm^{-1}. It is interesting to note that the transitions $\Delta k = +1$ and $\Delta k = -1$ are required to account for the positions of some of the observed Raman lines. As Placzek[12] has pointed out this is to be expected in the case of a nonlinear molecule like ammonia. A graphical analysis of the k-structure assigned shows no irregularity or inconsistency.

In Table II there are compared the frequency differences of the several levels for ammonia found by Badger and Cartwright from their study of the infrared rotation bands, by Amaldi and Placzek from the Raman effect for

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[11] Kohlrausch, *Der Smekal-Raman Effekt*, Springer, Berlin, 1931.

[12] Placzek, *Molekülstruktur*, Leipziger Vorträge, Hirzel, 1931; Amaldi and Placzek, Naturwiss. **20**, 521 (1932).

TABLE I. *Raman spectrum from aqueous ammonia solution showing fine structure of vibrational transition band corresponding to infrared absorption at 3μ.*

ν in cm^{-1}	$\Delta\nu$ (4047A) in cm^{-1}	Transition $\Delta k = \pm 1$	Transition $\Delta k = \pm 2$
21096	3609	14→15	6→8
21125	3580	13→14	
21161	3544	11→12	
21215	3490	8→9	3→5
21230	3475	7→8	
21254	3451	6→7	2→4
21280	3425	5→6	
21296	3409	4→5	1→3
21315	3390	3→4	
21332	3373	2→3	0→2
21356	3349	1→2	
21394	3311	—	—
21430	3275	2→1	
21450	3255	3→2	2→0
21469	3236	4→3	
21489	3216	5→4	3→1
21510	3195	6→5	
21532	3173	7→6	4→2
21567	3138	9→8	5→3
21586	3119	10→9	
21607	3098	11→10	6→4
21631	3074	12→11	
21656	3049	13→12	7→5
21685	3020	15→14	8→6
21709	2996	16→15	
21743	2962	18→17	

the gas, and by us from our work with aqueous solutions. The agreement, while it cannot be claimed to be excellent, is satisfactory when one considers the difficulties associated with the proper location of the lines and with a possible slight deformation of the ammonia molecule when dissolved to such high concentration.

TABLE II. *Comparison between Raman and infrared spectrum of ammonia.*

Concentrated water solution at 10°C Raman effect*			Gas under pressure Raman effect†			Rotation spectrum infrared absorption‡		
$\Delta k = \pm 2$	$\Delta k = \pm 1$	Frequency	$\Delta k = \pm 2$	$\Delta k = \pm 1$	Frequency	$\Delta k = \pm 1$	Frequency observed	Frequency calculated
	1←→2	41		1←→2	—	1←→2	—	—
0←→2	2←→3	59	0←→2	2←→3	—	2←→3	—	59.1
	3←→4	77		3←→4	79.5	3←→4	79.8	79.5
1←→3	4←→5	97	1←→3	4←→5	99.5	4←→5	99.1	99.2
	5←→6	115		5←→6	119.5	5←→6	118.6	118.6
2←→4	6←→7	139	2←→4	6←→7	140.2	6←→7	—	138.0
	7——→8	164		7←→8	159.6	7←→8	156.8	157.1
3←→5	8←→9	176	3←→5	8←→9	179.0	8←→9	176.1	175.9
	9←10	192		9←→10	199.0	9←→10	—	194.5
4←6	10←11	213	4←→6	10←→11	219.0	10←→11	—	—

* Present experiments.

† Amaldi and Placzek, Naturwiss. **20**, 521 (1932).

‡ Badger and Cartwright, Phys. Rev. **33**, 692 (1929).

In the microphotometric record mentioned above[3] the fine structure corresponding to the *R* and *RR* branches was less distinct than that on the low wave-length side of the line corresponding to no change in rotation. There is included as Fig. 1 a portion of a microphotograph which shows the resolution of the high wave-length side of the band to greater advantage. Another record, Fig. 2, taken from a plate for which a considerably higher dispersion was used, gives the general structure of the band and permits an estimate of the relative intensities of the lines to be made.

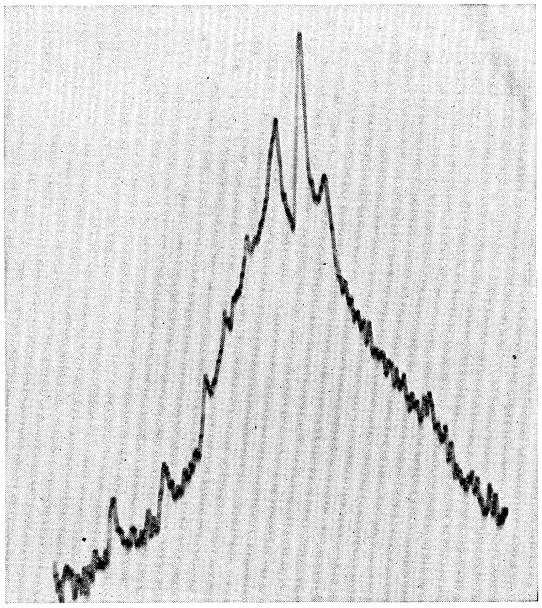

Fig. 1.

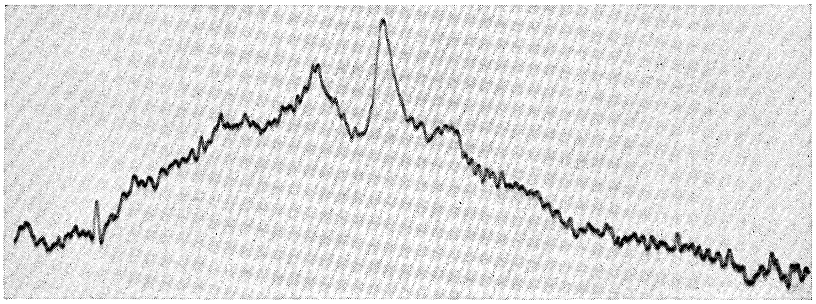

Fig. 2.

DISCUSSION

The structure of the ammonia molecule is now known to resemble a regular pyramid in form. This is definitely indicated both by potential energy calculations[13] and by observations of the molecular spectra. In neither case have the mathematical analyses and experimental results been sufficiently refined to enable the assignment of universally acceptable dimensions to the model. However, there is now agreement that the 3μ band in the near infrared is associated with a vibration of the electric moment parallel to the symmetry axis, and that it has been successfully resolved into one zero branch and a simple rotation series.[9] From this band the moment of inertia of the molecule about a line normal to the symmetry axis has been obtained. Values lying between $I=2.77\times 10^{-40}$ and $I=2.83\times 10^{-40}$ have been reported by a number of investigators of the infrared spectra, so that the agreement here is excellent.

This absorption band has now been resolved by means of the Raman effect, the spacing of the lines corresponding well with that reported by Stinchcomb and Barker. From this spacing it is possible to calculate the moment of inertia.

As indicated in Table I the Raman lines have been assigned to an R branch, $\Delta k=+1$; to an RR branch, $\Delta k=+2$; to a P branch, $\Delta k=-1$; and to a PP branch, $\Delta k=-2$. The frequencies of the lines can be quite exactly expressed by means of the following formulae:

$$\Delta k = +1, \quad \nu = 3311 + 2B(k+1) \quad \text{where } 2B = 19.7 \text{ cm}^{-1},$$
$$\Delta k = +2, \quad \nu = 3311 + 2B(2k+3) \quad \text{where } 2B = 19.8 \text{ cm}^{-1},$$
$$\Delta k = -1, \quad \nu = 3311 - 2B(k) \quad \text{where } 2B = 19.4 \text{ cm}^{-1},$$
$$\Delta k = -2, \quad \nu = 3311 - 2B(2k-1) \quad \text{where } 2B = 19.4 \text{ cm}^{-1}.$$

The values for the constant $2B$ vary but little within each series, in addition the values determined for each series show only slight differences from each other. Taking 19.6 cm^{-1} as an average the moment of inertia may be calculated from the well-known formula, $B=h/8\pi^2cI$, with the result that, $I=2.82\times 10^{-40}$ g cm^2. This value is almost identical with that given by Stinchcomb and Barker.[9] It is evident that the dissolved ammonia molecules have not been deformed to any appreciable extent by the continual bombardment and electrical force fields of the solvent molecules otherwise the moment of inertia could have been expected to deviate somewhat from this value.

There has been much discussion with respect to a shift in the characteristic frequency differences given by an ion such as $CO_3^=$ or $SO_4^=$ when it is dissolved in water. Embirikos[14] could detect shifts of approximately 10 cm^{-1} in sulphate solutions when the concentration was changed from one normal to two normal. Even larger shifts were observed by Woodward[15] in the case of lines associated with the $SO_4^=$ ion in his studies of sulphuric acid solutions. These systems differ from the type considered in this article because the scattering is caused by a doubly charged ion instead of by a neutral mole-

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[13] Debye, *Polar Molecules*, Chemical Catalog Co., New York, 1929.

[14] Embirikos, Zeits. f. Physik **65**, 266 (1930).

[15] Woodward, Phys. Zeits. **32**, 212 (1931).

cule. The ability of an ion to segregate and orient water molecules about it is well known.

Ammonia gas when dissolved in a large excess of water will first neutralize the acid H_3O^+ and then begin to remove protons from the water itself according to the reactions,

$$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O,$$

and

$$H_2O + NH_3 \rightarrow \underset{\displaystyle NH_4OH}{\underset{\uparrow\downarrow}{NH_4^+}} + OH^-.$$

But as the concentration of the gas is increased greater and greater amounts of ammonia molecules which have not reacted in a chemical way must be present. In such cases the concentration of the ammonia molecules may become so great that observations of the light scattered by them may be made with relative ease. It might be well to mention that the concentration as determined by ordinary analytical methods includes both the NH_3 and the NH_4OH formed.

One might reasonably expect similar experiments in which hydrochloric acid gas was dissolved in water to be successful. Undissociated hydrochloric acid molecules are known to exist in aqueous solutions of concentration as low as one normal, and it is possible to obtain solutions containing more than ten times this amount of hydrochloric acid. However, Woodward[15] and others have reported failure to find any Raman lines using a solution saturated with the gas. The concentration of the undissociated HCl molecules should be sufficient for the purpose. In spite of such experiences, it is to be hoped that there may be accomplished the resolution of the other bands of ammonia and the similar treatment of the spectra of many other simpler gaseous substances using the solution method to obtain a sufficient molecular concentration.

It is a pleasure to acknowledge the material assistance of Professor J. G. Winans of this University in connection with the interpretation of the results.

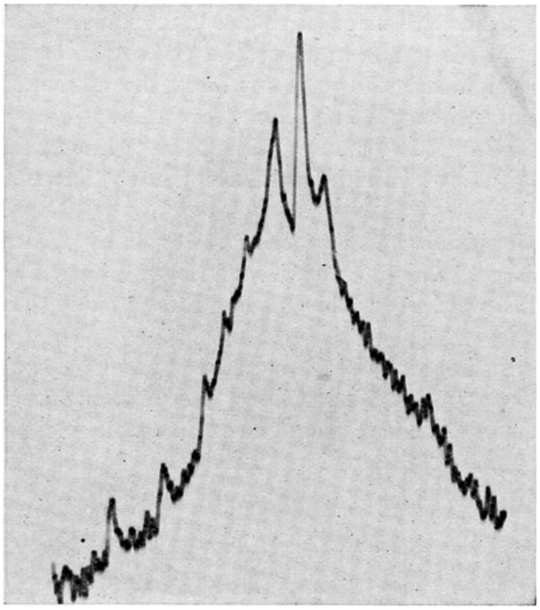

Fig. 1.

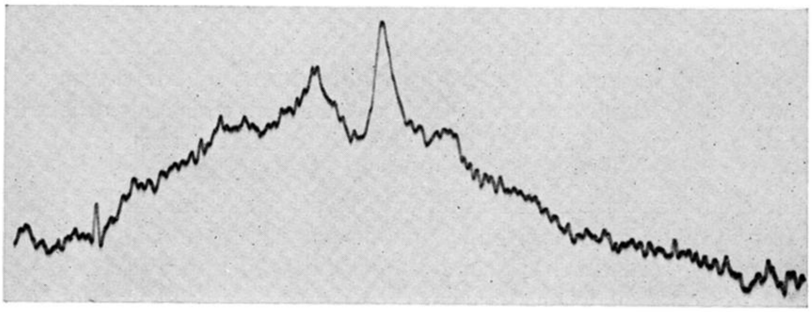

Fig. 2.