

SPECTROSCOPIC EVIDENCE OF TWO TYPES
OF AMMONIA MOLECULE

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(Received February 3, 1930)

ABSTRACT

A two-fold difference exists in the equations expressing the anharmonic frequencies arising from vibratory energy changes in ammonia molecules in solution and in gaseous form. The greater coefficient of the n^2 term in the former case, indicating a more rapid approach of the energy terms toward confluence, is assumed to arise from the proximity of the molecules of the solvent. The presence of a constant term of appreciable magnitude in the solution equation is interpreted as measuring the energy required to change the molecule from an α form to a β form of greater potential energy. Chemical support for this latter interpretation is sought in some earlier measurements by Baly and Duncan on the difference in the decomposition rates of ammonia both after immediate evaporation from the liquid and after it had stood for a considerable length of time.

It becomes easier to interpret the Raman spectrum of liquid ammonia, ammonia in aqueous solution and a liquid organic derivative of ammonia, aniline, when the existence of a constant in the infra-red formula is recognized.

BADGER and Mecke¹ and the author² have independently come to the conclusion that the ammonia molecule has a fundamental absorption wavelength near 3μ . This conclusion has been arrived at in each instance by the discovery that there is an anharmonic series of absorption bands with members in the infra-red spectrum below 3μ and in the visible spectrum. The former investigators have photographed the fourth and fifth members of this series in the visible region, using long tubes of gaseous ammonia and a concave diffraction grating to secure high dispersion and resolving power. Out of the complex structure caused by rotational quantum changes they have been able to pick the lines produced by vibrational energy changes alone. They have sought the second and third members in the thermal measurements of Robertson and Fox³ and have used the frequency values of the centers of these unresolved bands. For the first member they have chosen the frequency of maximum absorption in the unresolved Q branch in the record given by Barker.⁴ They have shown that these five frequencies can be fairly well fitted to the following anharmonic formula:

$$\nu_n = 3396n - 60n^2. \quad (1)$$

The author² has used a quartz prism spectrograph to photograph the structureless absorption bands corresponding to the fourth and fifth series

¹ Badger and Mecke, *Zeits. f. Phys. Chem. B* **5**, 333 (1929).

² Ellis, *Journal Franklin Inst.* **208**, 507 (1929).

³ Robertson and Fox, *Proc. Roy. Soc.* **A120**, 128 (1928).

⁴ Barker, *Phys. Rev.* **33**, 684 (1929).

members caused by ammonia in aqueous solution. In a similar manner he has also found the weak sixth member in the visible green spectrum. Records of the second and third members have been secured by means of a registering infra-red spectrograph equipped with a thermopile. These latter he has shown retain their positions when carbon tetrachloride replaces water as a solvent. No data for the solution were then available for the first member. For reasons explained in the above reference a wave-length value of 2.916μ was assigned to the initial member of the series.

Although the former reason for selecting this value does not now seem to be well founded, the wave-length value chosen has been shown to be at least approximately correct. To show this a Hilger D 35 infra-red spectrometer equipped with a rock-salt prism was used. A 1 cm cell of ammonia in carbon tetrachloride solution was placed before the slit of the instrument and observations were made on the 3μ region. The difficulty experienced by Robertson and Fox³, namely that the wave-length determination of an absorption maximum is influenced by the variations in the refractive index of the rock-salt prism caused by temperature changes, was experienced here. When, for example, the wave-drum was set for a correct reading with the yellow sodium lines filling the thermopile slit and the instrument allowed to stand for a while with the lamp source radiating near by, the absorption band produced by a 1 mm cell of benzene shifted from its true position of 3.27μ to a value in excess of 3.4μ . Consequently, just prior to a determination of the position of the ammonia band, the reflecting mirror near the prism was so adjusted that when the galvanometer showed a minimum deflection, indicating that the maximum of absorption due to the benzene had been reached, the wave-drum indicated 3.27μ . With this procedure it was found that the ammonia solution band was not at 3.0μ , the position occupied by the gaseous ammonia band, but at 2.9μ .

The frequencies of the six members of the series observed in solution have been shown² accurately to fit the formula:

$$\nu_n = 97 + 3400n - 70n^2. \quad (2)$$

Now in spite of the assertion by Mecke⁵ that there is a good agreement between the bands observed in gaseous ammonia and in solution, a closer examination reveals a significant difference. This difference is two-fold and is revealed in Eq. (2) by the presence of the constant term 97 and by the larger coefficient of the n^2 term, 70 as compared with 60 in Eq. (1). The presence of the constant term arises from the origination of the solution series at 2.9μ rather than at 3μ . The greater coefficient of the quadratic term explains why in the higher series members the wave-lengths of the solution bands become greater than the corresponding bands in the gas. This earlier confluence of the solution series must arise from a more rapid diminution of the force coefficient of the vibrator caused by the proximity of surrounding molecules. In general, however, a less rapid approach of the series members toward confluence would be expected, because this would

⁵ Mecke, *Trans. Faraday Soc.* **25**, 942 (1929).

mean a lesser value for the heat of dissociation of the vibrator. And heats of dissociation evaluated from data obtained from the liquid state should be less than heats of dissociation evaluated from the gaseous state by an amount approximately equal to the heat of vaporization.

Fig. 1 is included to show the difference in the locations of the fifth members of the series in solution and in the gas. The figure shows the solution band approximately symmetrically located between two neon comparison lines, 0.6507μ and 0.6533μ . It has been given the value of 0.652μ . The value given by Mecke and Badger for the analogous gaseous band is 0.647μ , which lies completely outside of the region of absorption in the solution.

The constant term in Eq. (2) has been interpreted⁵ as representing the amount of energy, in wave-number units, required to change the molecule in solution over to a new form before vibration takes place. A chemical investigation carried out a number of years ago by Baly and Duncan⁶ seems to have some bearing upon this subject. These authors showed that

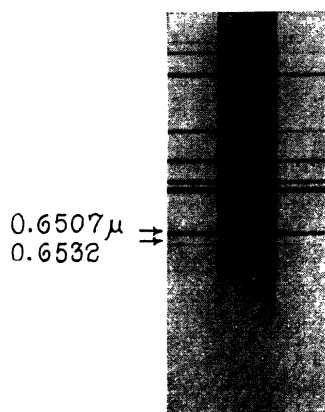


Fig. 1. The 0.652μ absorption band of ammonia in aqueous solution.

ammonia gas which had been slowly evaporated from the liquid or which had stood for some time in contact with the liquid had a certain constant rate of decomposition. The decomposition was effected by thermal energy supplied at a known rate by a heated platinum wire and the decomposition rate was determined from pressure changes in the gas. But when the experiment was repeated upon gas which had been suddenly evaporated from the liquid they found that the decomposition rate was much less than in the previous instance. Furthermore, this rate gradually increased with time. These facts led the investigators to postulate two forms of ammonia molecules, which they designated inactive and active forms, but which we shall designate as α and β forms respectively for reasons which will be apparent presently. The molecules are in the α form when the substance is in the liquid state or in the gaseous state immediately following sudden vaporization. The β form makes up predominantly, or exclusively, the gas which has stood

⁶ Baly and Duncan, Jour. Chem. Soc. 121, 1008 (1922).

for a considerable length of time. According to these investigators, the decomposition rate of inactive (α) ammonia is lessened because of the use of a portion of the energy supplied by the wire to activate the molecules.

Tronstad⁷ has pointed out that the experimental procedure of Baly and Duncan was similar to that of Bonhoeffer and Harteck in their study of ortho and para hydrogen. He furthermore has stated that Baly and Duncan have not proved the existence of two chemically different types of ammonia molecules, but that their results can be explained equally well on the basis of two forms with different heat conductivities and specific heats. The two types would then be analogous respectively to para and ortho hydrogen.

From considerations of the experimental results of Baly and Duncan it may be concluded that the 97 cm^{-1} term of Eq. (2) represents an energy of "activation." (The assumption is made here that ammonia in solution exists in the α state.) However, in the light of Tronstad's criticism it must be recognized that this activating process may be one in which geometrical and physical changes occur rather than chemical changes.

From the quantitative measurements of Baly and Duncan it would seem that the modified interpretation of Tronstad is the more tenable. Baly and Duncan have shown that in some instances the amount of decomposition is doubled when the β form is used in place of the α form. Under their interpretation then half of the energy supplied by the hot platinum wire must go into energy of activation. Now the energy required to decompose one molecule of NH_3 into NH_2 and H requires some $30,000\text{--}40,000\text{ cm}^{-1}$ ² which is 300 or 400 times as great as the 97 cm^{-1} energy of activation. But Baly and Duncan state that from 0.5 to 4 percent of the molecules are decomposed during the 20 seconds of observation; and under the assumption that this percentage of molecules decomposes, say into NH_2 and H, there would be required many more molecules than the total number available, to take up the energy of activation.

Following Tronstad's assumption of a greater heat conductivity characterizing the α molecules, the difficulty met with in the discussion of the above paragraph does not enter, for more of the heat than previously could escape to the surrounding constant temperature water bath.

It should be pointed out that Barker,⁸ following Hund, has postulated two forms of ammonia molecule in his interpretation of the doubleness of another fundamental infra-red band of ammonia at 10.5μ . The difference in potential energy between the two types, however, is only 27 cm^{-1} . The approximate equality in intensity of the two components of this double band lead to the conclusion that the two kinds of molecules postulated must exist in the gaseous state with approximately equal abundance. Mecke⁹ also believes that his visible bands which are harmonics of the 3μ fundamental also exhibit a double structure, one set being much weaker than the other. But the frequency difference which he finds is even lower than Barker's 27 cm^{-1} .

⁷ Tronstad, *Zeits. f. Phys. Chem. B* **5**, 333 (1929).

⁸ Barker, *Phys. Rev.* **33**, 684 (1929).

⁹ Mecke, *Phys. Zeits.* **30**, 907 (1929).

The Raman spectrum of ammonia exhibits one, two or three lines corresponding to the 3μ region, the exact locations and number of components depending upon the phase in which the substance exists and upon the individual investigators. Wood¹⁰ and Dickinson, Dillon and Rasetti¹¹ have shown that the Raman frequency corresponding to a rotationless vibrational energy change in the gaseous molecule is 3330 and 3334 cm^{-1} respectively, in good agreement with the 3336 cm^{-1} value obtained by putting n equal to 1 in Eq. (1). The latter investigators¹¹ have shown that liquid ammonia yields two frequencies, 3298 and 3214 cm^{-1} . Daure,¹² however, found in addition to these two frequencies, a third one at 3380 cm^{-1} . His record shows that all three components have approximately equal intensities.

Carrelli, Pringsheim and Rosen¹³ found two frequencies, 3385 and 3312 cm^{-1} , when they used an aqueous solution of ammonia. These authors recognized, however, the possibility that one of these components may have been due to the water solvent.

If the three components found by Daure in the liquid all originate in ammonia molecules, they might be explained by assuming the existence of both the α and β forms of molecule in the liquid state. The components corresponding to greatest, intermediate and least frequency changes could then be correlated with the following energy changes respectively:— α , $0 \rightarrow \beta$, 1; α , $0 \rightarrow \alpha$, 1 or β , $0 \rightarrow \beta$, 1; and β , $0 \rightarrow \alpha$, 1. Here α , 0 designates a vibrationless α type of molecule, β , 1 a β type of molecule vibrating in quantum state 1, etc. The 80 and 90 cm^{-1} frequency differences between the components are comparable to the 97 cm^{-1} term of Eq. (2). However, the failure of Dickinson, Dillon and Rasetti completely to corroborate the findings of Daure raises the question as to whether impurities may have been present in the latter's experiment. Water would be the most likely impurity and water yields at least two Raman bands with frequencies comparable to those given.

Spectroscopically, aniline, $\text{C}_6\text{H}_5 \cdot \text{NH}_2$, which is a derivative of ammonia, behaves in a manner similar to its parent substance. The writer has justified his earlier correction¹⁴ to Bell's¹⁵ 2.8μ value for the fundamental N-H band, for he has studied the 3μ region for aniline with the Hilger D35 infra-red spectrometer and has found the band to have its maximum of absorption at 2.9μ . There is a remarkably close agreement between the members of the anharmonic series originating at 2.9μ for aniline and for ammonia in solution. Consequently, a constant term must be included in the aniline series, a fact which has hitherto¹⁴ been overlooked.

Again, the Raman effect in aniline according to Bonino¹⁶ shows a single frequency shift corresponding to a 3.0μ wave-length, rather than to 2.9μ . Thus once more the difference between the Raman frequency and the fundamental infra-red frequency is of the order of 97 cm^{-1} .

¹⁰ Wood, *Phil. Mag.* **7**, 774 (1929).

¹¹ Dickinson, Dillon and Rasetti, *Phys. Rev.* **34**, 582 (1929).

¹² Daure, Thesis, Masson et Cie, Paris, (1929).

¹³ Carrelli, Pringsheim and Rosen, *Zeits. f. Phys. Chem. B* **5**, 333 (1929).

¹⁴ Ellis, *Phys. Rev.* **33**, 27 (1929).

¹⁵ Bell, *Jour. Amer. Chem. Soc.* **47**, 2192 (1925).

¹⁶ Bonino, *Gazz. chim. Ital.* **59**, 668 (1929).

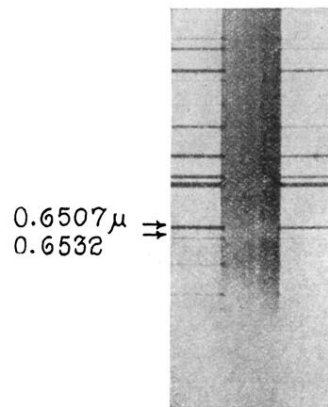


Fig. 1. The 0.652μ absorption band of ammonia in aqueous solution.