

THE MOLECULAR SPECTRUM OF AMMONIA
I. TWO TYPES OF INFRA-RED VIBRATION BANDS

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ABSTRACT

Wave-lengths and interpretation of the NH_3 absorption bands at 3.0μ and 1.9μ —The NH_3 absorption bands at 3.0μ and at 1.9μ have been sufficiently resolved by means of gratings to reveal their fine structure, which proves to be of a different character in the two cases. The 3μ band is associated with a vibration of the electric moment parallel to the symmetry axis of the molecule, yielding one zero branch and a simple rotation series. At 1.9μ there is observed a series of almost equally spaced lines showing a remarkable uniformity in intensity so that the envelope is a single broad maximum instead of the usual doublet. The band center cannot be selected by inspection. The vibration which gives rise to this band is normal to the symmetry axis. From the 3μ band the *moment of inertia* of the molecule ($I=2.83 \times 10^{-40}$) about a line normal to the symmetry axis may be determined, but this does not yield the distances between atomic nuclei. The 1.9μ band probably corresponds to one of the four fundamental frequencies. Because of its character it cannot be a harmonic nor a combination of vibrations along the axis as had previously been supposed. The 10μ and the 6μ bands probably correspond to two other fundamentals, but the selection of the fourth fundamental, and the characterization of combination bands must await further analysis to determine the nature of the vibrations involved.

THE infra-red spectrum of ammonia vapor in the region from 1μ to 15μ has been studied by Coblenz¹, Schierkolk² and Robertson and Fox³ using the best resolution available with prism spectrometers. They have observed a number of very intense vibration bands, for the most part unresolved. In the one at 6μ a single sharp zero branch was found, while the one at 10μ shows a pair of zero branches almost equally intense and lying close together. A partial resolution of the rotation series for these two bands was also possible. The bands near 1.5μ , 1.9μ , 2.2μ and 3.0μ were observed as single broad peaks with nothing to indicate the character of the vibrations with which they are associated. Spence succeeded, with the help of a grating, in resolving the 3μ band, obtaining a sharp zero branch and a rotation series rather irregularly spaced because of incomplete separation of the lines. We have re-examined this band with somewhat improved resolution, and also studied the one at 1.9μ ,⁴ using echelette gratings ruled in this laboratory. For the 3μ region two gratings having respectively 4800 and 7200 lines per inch were used, and for the 1.9μ region one having 14400 lines per inch.

¹ Coblenz, Carnegie Inst. Pub. **35**, 179 (1905).

² Schierkolk, Zeits f. Physik **29**, 277 (1924).

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

⁴ This band was the first one of its type to be observed, although since it was reported (Phys. Rev. **29**, 213, 1927; abstract 27) others have been found for a number of different symmetrical molecules.

The fine structure observed is of a different character in the two cases, and definitely assigns these bands to two different sorts of vibration.

The ammonia gas was generated by gently heating a dry mixture of ammonium chloride and calcium hydroxide, both chemically pure. The only impurity to be expected is water vapor, which was removed by passing the gas through a trap cooled to the temperature of melting ice and then through three twelve-inch drying towers. The character of the absorption, as well as the ease with which it could be reproduced, indicate satisfactory purity. A continuous stream of this dried gas was kept flowing slowly through the absorption cell, the pressure within being not more than 1 mm greater than that outside. This gave assurance that the cell was always filled and the gas undiluted through leakage or by chemical reaction.

The absorption system consisted of two separate chambers identical in all respects, the one containing ammonia and the other air which had been thoroughly dried. The ends of both were closed by mica windows cut from the same sheet and placed at an angle of approximately 30° to the light beam. Some interference due to the mica was observed but the maxima

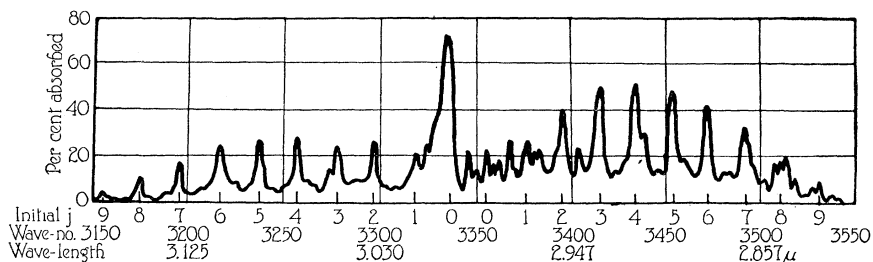


Fig. 1. Absorption pattern for the 3μ band. Vibration of electric moment parallel to symmetry axis. 2 cm cell; slit includes 1.1 wave-numbers.

were far apart and corrections for this effect—never greater than 10 percent of the total absorption—were easily made. The effective cell length was 11.5 cm for most of the observations. In the case of the 3μ band it was found desirable to use a shorter cell also. This required smaller windows so that rock-salt could be conveniently used, and the interference completely avoided.

The absorption pattern for the 3μ band is shown in Fig. 1. It consists of a fairly strong central maximum or zero branch and a rotation series of narrow lines almost equally spaced. These are indicated in the figure by numbers designating the initial rotation states. In addition to these lines there are a number of somewhat weaker ones, and considerable unresolved background, particularly on the high frequency side, suggesting the superposition of other bands of low intensity. Moreover the positive branch (high frequency side) is very much more intense than the negative branch. The observed wave-lengths and frequency differences are shown in Table I. These differences are somewhat smaller in the positive than in the negative branch, and are not as uniform as might be expected. They do not seem to follow a parabolic law as in diatomic molecules. The question of coupling

is here an interesting one which we hope to discuss later. From the spacing of these lines a fairly precise estimate may be made of the moment of inertia of the molecule about an axis normal to the line of symmetry, but this yields no direct information regarding the distances between atomic nuclei. The value is $I = 2.83 \times 10^{-40}$. Bands of this sort are to be expected for symmetrical molecules when the vibration of the electric moment is along the symmetry

TABLE I. *Wave-numbers and wave-number differences in the 3.0μ absorption bands of NH_3 .*

| Positive branch | | Negative branch | | Mean | Mean |
|--------------------|-------------|-----------------|-------------|---------|-------------|
| ν in cm^{-1} | $\Delta\nu$ | ν | $\Delta\nu$ | ν | $\Delta\nu$ |
| 3337.0 | (center) | — | — | — | — |
| 3355.7 | 18.7 | 3318.2 | 18.8 | 3337.0 | 18.75 |
| 3377.0 | 21.3 | 3296.3 | 21.9 | 36.6 | 20.18 |
| 3395.5 | 18.5 | 3277.2 | 19.1 | 36.3 | 19.71 |
| 3415.3 | 19.8 | 3256.8 | 20.4 | 36.1 | 19.81 |
| 3433.8 | 18.5 | 3236.8 | 20.0 | 35.3 | 19.70 |
| 3453.0 | 19.2 | 3216.5 | 20.3 | 34.8 | 19.71 |
| 3471.6 | 18.6 | 3195.8 | 20.7 | 33.7 | 19.70 |
| 3490.8 | 19.2 | 3175.5 | 20.3 | 33.2 | 19.71 |
| 3510.0 | 19.2 | 3156.0 | 19.5 | 33.0 | 19.67 |
| | | | | Average | 19.67 |

axis, since the frequency to be associated with any permitted change in rotation is then in first approximation independent of the angle of precession.

The band at 1.9μ , illustrated in Fig. 2, is obviously of a different sort and must arise from a vibration of the electric moment along a line normal to the symmetry axis. Instead of a single band with an intense central absorption peak this yields a whole family of bands whose zero branches

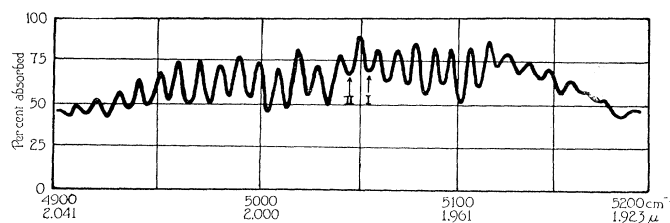


Fig. 2. Absorption pattern for the 1.9μ band. Vibration of electric moment normal to symmetry axis. 11.5 cm cell; slit includes 2.0 wave-numbers.

are separated by an approximately constant frequency difference, in this case about 10 cm^{-1} . There results a characteristic intensity distribution with no well-marked center and with an envelope forming a single maximum instead of the symmetrical doublet so often observed. We have tentatively selected as the central frequency, i.e. the frequency of the vibration from which this band arises, the value 5054 cm^{-1} , marked *I* in the figure, and numbered the lines to the right and left from this point. The reason for adopting this frequency in preference to the value 5045 cm^{-1} , marked *II*,

will be discussed in a subsequent paper. The positions of the lines as observed and the frequency differences between them are shown in Table II.

TABLE II. *Wave-numbers and wave-number differences in the 1.9 μ absorption band of NH₃.*

| High frequency side | | | | Low frequency side | | | |
|---------------------------|-------------|--------|-------------|--------------------|-------------|--------|-------------|
| ν in cm ⁻¹ | $\Delta\nu$ | ν | $\Delta\nu$ | ν | $\Delta\nu$ | ν | $\Delta\nu$ |
| 5058.7 | 8.6 | 5137.7 | 11.7 | 5050.1 | 9.9 | 4970.1 | 10.5 |
| 5069.4 | 10.7 | 5148.6 | 10.9 | 5040.2 | 11.1 | 4959.6 | 9.0 |
| 5079.1 | 9.7 | 5158.7 | 10.1 | 5029.1 | 9.7 | 4950.6 | 10.4 |
| 5088.7 | 9.6 | 5168.8 | 10.1 | 5019.4 | 10.0 | 4940.2 | 9.6 |
| 5098.0 | 9.3 | 5179.1 | 10.3 | 5009.4 | 9.8 | 4930.6 | 10.2 |
| 5107.8 | 9.8 | | | 4999.6 | 9.9 | 4920.4 | 9.8 |
| 5117.1 | 9.3 | | | 4989.7 | 9.6 | 4910.6 | 10.9 |
| 5126.0 | 8.9 | | | 4980.1 | 10.0 | 4899.7 | — |

Mean $\Delta\nu$ 9.98

Other bands in the ammonia spectrum are now under investigation and will be reported later. It should be emphasized that until the character of the various vibrations appearing in the spectrum of any molecule is known, an attempt to decide which are fundamental and which combination bands is hazardous. Following Schierkolk's measurements which mapped the whole ammonia spectrum Hettner⁵ proposed an interpretation of all the strong bands in terms of the two frequencies ν_1 and ν_2 , corresponding to 10 μ and 6 μ , as fundamentals. He believed the bands at 3 μ and at 1.9 μ to be harmonics, with frequencies 2 ν_2 and 3 ν_2 respectively. Hund⁶ employed three fundamental frequencies including that of the band at 2.2 μ , while Dennison⁷ selected four fundamental frequencies, adding that of the 3 μ band also. Robertson and Fox³ have suggested a still different classification. All these writers, however, agree in describing the 1.9 μ band, either as an overtone of one or as a combination of two vibrations parallel to the symmetry axis. Our analysis shows conclusively that neither of these possibilities can be correct. We are apparently forced to the conclusion that this is one of the fundamental vibrations. Analysis of the band at 2.2 μ , on the other hand, has progressed far enough to suggest that it probably is not. To discuss in detail the mechanical problem of the vibrations in this system will hardly be profitable until the four fundamental frequencies have been definitely determined by observations taken with adequate dispersion.

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December 1, 1928.

⁵ Hettner, Zeits. f. Physik **31**, 273 (1925).

⁶ Hund, Zeits. f. Physik **31**, 81 (1925).

⁷ Dennison, Phil. Mag. **1**, 195 (1926).