

THE MOLECULAR SPECTRUM OF AMMONIA

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PRELIMINARY REPORT

A number of years ago it was found that hydrogen chloride showed a double branched absorption band at a wavelength of approximately 45,000 A. U. This wavelength is found in the near infra-red spectrum. The bands were accounted for by Bjerrum (Nernst Festschrift, 1911) assuming that the diatomic molecule rotated about a line at right angles to the line joining the atomic centers and that the atomic centers vibrated along the line joining them. Such a system of molecules will absorb energy from a beam of radiation passing through them corresponding to the frequency of rotation and also the frequency of the combined frequencies of rotation and vibration. The double branched band will have frequencies corresponding to $f_v \pm f_r$, where f_v is the frequency of vibration of the molecule and f_r is the frequency of rotation.

Later experiments revealed the fact that the double branched band was not simple but made up of a number of fine bands. Bjerrum modified his theory involving the quantum theory. His theory was not altogether satisfactory, and later Lenz (Verh. d. D. Phys. Ges. 31, 632, 1919) following the idea of the stationary state of Bohr in his atomic theory arrived at a more satisfactory expression for the wavelength of these bands. The Lenz theory assumes that the molecules exist in a series of stationary states in regard to rotation and vibration, and that energy is emitted or absorbed during a transition between stationary states. Lenz's expression for the frequency of the emitted or absorbed radiation is

$$f = nf_0 + \frac{h}{8\pi^2 I} \pm \frac{mh}{4\pi^2 I}$$

where f and f_0 are the frequencies of the absorbed radiation and the atomic vibration frequency respectively, h is the Planck constant, I the moment of inertia of the molecule and m and n are small integers characterizing

the stationary states of rotation and vibration respectively.

The interpretation of the above expression is interesting. When the molecule is in the state characterized by the quantum numbers $n = m = 0$, it has no energy of vibration and of rotation. When a change occurs during absorption of energy such that $n = m = 1$, the frequency of the absorbed radiation is given by

$$f = f_0 + \frac{h}{8\pi^2 I}$$

So far this so called zero branch of the curve has never been observed, as far as the writer is aware. If the molecule is in the stationary state characterized by $n = 0$, and $m = 1$, then a transition to $n = 1$, and $m = 2$ gives rise to an absorbed radiation of frequency

$$f = f_0 + \frac{h}{8\pi^2 I} \pm \frac{h}{4\pi^2 I}$$

This expression indicates two bands, one on each side of the above zero branch. If now we allow the change from $n = 0$ to $n = 1$, and $m = 2$ to $m = 3$, and so on, we have a series of equidistant bands which approximate the experimental values fairly well. Experimentally these bands are not equidistant. The above theory was developed assuming an independence of m and n , or that the moment of inertia of the molecule is independent of the angular velocity. By making the necessary modifications with this point in mind an extremely satisfactory theory is developed which accounts for the facts very well.

The above theory was developed for the diatomic molecule. No theory exists for the polyatomic molecule. However, double branched absorption bands with the fine structure have been observed for polyatomic molecules. Their characteristics are, in the main, similar to those of the diatomic molecule.

In an investigation to bring to light other examples of these double branched absorption bands it was found that ammonia gas showed a serrated double band with a zero branch at 30,000 A. U. The investigation was carried on with an infra-red grating spectrometer, using a

radiometer as the receiving instrument. The grating was one of 2500 lines per inch and had a ruled surface 2 x 2 inches. A cell 10 cm. long with mica windows was so arranged before the slit of the spectrometer that it could be moved in or out of the beam of light brought to focus on the slit. Such an arrangement made it possible to determine the per cent absorption. The bands as observed for ammonia are not equally spaced, the wavelength interval between them increasing from about 140 A. U. on the short wave side of the band to 200 A. U. on the long wave side. In addition to the system of narrow bands a deep band was found at 299,000 A. U. which corresponds to the transition of $n = m = 0$ to $n = m = 1$ as indicated above. This appears to be the first substance found to show the zero branch of the double absorption band. Eight of the narrow bands were found on each side the zero branch. Inasmuch as the grating used in the investigation was a 2500 line per inch grating it did not have sufficient resolving power to make accurate quantitative determinations possible. It is planned to examine these bands under larger resolving power.

The frequency difference between the narrow bands is given from the expression of Lenz as

$$df = \frac{h}{4\pi^2 I}$$

From this expression it is possible to get an estimate of the moment of inertia of the ammonia molecule. Substituting wavelengths in the expression and solving for I we have

$$I = \frac{h\lambda^2}{4\pi^2 c d\lambda}$$

where c is the velocity of light, λ the wavelength of a band and $d\lambda$ the difference of wavelengths between two bands. Making the substitutions, we find 2.8×10^{-40} gm. cm² as the moment of inertia of the ammonia molecule.

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