THE PURE ROTATION SPECTRUM OF AMMONIA

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Abstract

New experimental means for the study of absorption spectra in the extreme infra-red are described. These have been used in extending our knowledge of the pure rotation spectra to the case of a polyatomic molecule. The absorption spectrum of ammonia has been investigated in the region between 55μ and 130μ, and a very simple structure was found. Six lines were observed which belong to a pure rotation spectrum and are apparently due to changes in the energy of rotation of the ammonia molecule about an axis normal to the line of symmetry, that is, to transitions in which the quantum number j increases by unity. Other lines due to transitions with a change also of τ, the quantum number connected with rotations about the axis of symmetry, are absent. These facts are briefly discussed in connection with the predictions of the wave mechanics with which they are shown to be in accord. The *moment of inertia* of the ammonia molecule about an axis normal to the line of symmetry is estimated to be 2.77×10^{-40} gm cm^2.

I. Introduction

THE far infra-red absorption spectra of several diatomic gases have recently been studied by Czerny[1] who has found a very simple structure which has been satisfactorily explained, and indeed had been long predicted. This is the so-called "pure rotation spectrum" which has its origin in changes in the rotational energy of the molecule in question. So far as concerns polyatomic molecules, only one rotation spectrum has been observed, that of water vapor,[2] and on account of great complexity and incomplete resolution has not as yet been satisfactorily interpreted.

The present investigation was undertaken with the object of extending our knowledge of rotation spectra to the polyatomic molecules by the study of a case capable of relatively simple interpretation. Ammonia gas seemed especially suitable for this purpose since the theoretical treatment of a molecule of this type is already at hand. It is further interesting since the ammonia vibration rotation bands have recently received considerable attention.[3]

In the course of the investigation, as well as for some time previous we have been occupied in the development of a technique for the more easy and accurate study of absorption spectra in the region between about 30μ and 150μ. As a consequence the final apparatus differs considerably from that which has been used by other investigators in this region, and embodies

[1] M. Czerny, Zeits. f. Physik **44**, 235 (1927).

[2] H. Rubens, Berlin Ber. 1921, p. 8; H. Witt, Zeits. f. Physik **28**, 236 (1924).

[3] Spence, J. O. S. A. **10**, 127 (1925); W. F. Colby and E. F. Barker, Phys. Rev. **29**, 923 (1927); E. F. Barker, Phys. Rev. **31**, 1131 (1928); R. Robertson and J. J. Fox, Proc. Roy. Soc. **A120**, 128 (1928).

several radical improvements. The particularly new features will first of all be described.

II. The Experimental Arrangement

1. *The Source of Radiation.* Previously the Wellsbach incandescent gas mantle has been the favorite source employed on account of its obvious advantages: a black-body radiation in the extreme infra-red, and a very poor emissive power in the near infra-red rays which are always a disturbing influence. On the other hand the inconveniences, namely the more or less inconstant temperature due to fluctuations in gas pressure and composition, and the evolution of a great quantity of useless heat in the neighborhood of the sensitive heat measuring device, are not inconsiderable. The very simple device of a flat electrically heated platinum strip, to which a strip cut from a Wellsbach mantle has been cemented with a trace of water glass, provides a source which is but little less advantageous than the flame heated gas mantle in respect to far infra-red emission and small intensity in the near infra-red. The temperature is readily kept constant and the filament is conveniently housed in a water jacketed case which is kept at constant temperature.

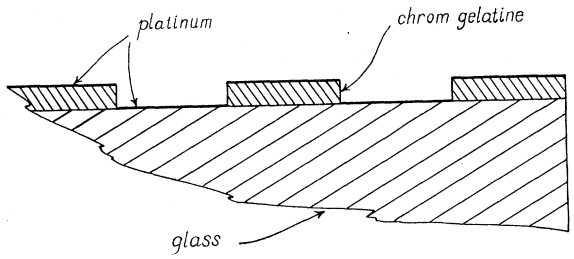

Fig. 1. Portion of a section of the laminary grating.

2. *The grating.* In a previous investigation of hydrogen chloride one of us used an echelette grating of novel construction.[4] This has the advantage of great light economy, which is of great importance in the far infra-red, but it has the drawbacks of giving higher order spectra with great intensity, and is quite unsuitable for making absolute wave-length measurements owing to the lack of a zero order spectrum or other reference. After considerable experimenting we were led to a type of reflection grating which has been described as "laminary," the construction of which may be readily understood by reference to Fig. 1. The principle is not new, and transmission gratings of a similar sort have been exhibited as curiosities, but perhaps due to the difficulties of construction for use in the optical region, seem not to have met with practical application.

Although the laminary grating has not received a complete theoretical treatment, certain interesting properties are evident from qualitative con-

[4] R. M. Badger, J. O. S. A. **15**, 370 (1927).

siderations. First of all, for a wave-length such that $2d=\lambda/2$, $3\lambda/2$, $5\lambda/2$, etc., where d is the thickness of the laminae, light will not be reflected in the zero order but will appear principally in the two first order spectra. Where $2d=\lambda$, 2λ, 3λ, etc., the light will appear almost entirely in the zero order. Consequently if such a grating be illuminated by white light the first order spectrum will appear as a series of bright bands. The intensity maximum of the last band on the long wave-length side will appear at $\lambda=4d$, and beyond this the intensity slowly diminishes. The absence of second order spectra may be arranged by making the laminae and spaces between them of equal width, but in the regions of the intensity maxima of the first order spectra, is doubly assured by the fact that the wave-lengths which would here appear in the second order are principally reflected in the zero order. Third order spectra can usually be eliminated by the use of filters. It is readily seen that in the regions of the intensity maxima the laminary grating is about half as economical of light as the echelette.

The construction of a grating of this type at first offered some practical difficulties, but very satisfactory results have been obtained by means of a bichromated gelatine photographic process, as follows. A suitable plate of thick glass, having one surface plane, is first coated with a uniformly thick film of gelatine containing potassium bichromate. This may be accomplished in several ways but following simple method will serve. The glass plate is warmed and carefully placed in a horizontal position in a dessicator, a measured quantity of a warm 5 percent solution of gelatine containing enough potassium bichromate to give it a pale yellow color, is then poured upon the surface of the glass. The liquid should be as well distributed over the surface as possible, and in the interval before the gelatine sets will flow into a film of nearly uniform thickness. The dessicator is closed at once, partially evacuated, and protected from light until the film has dried, which should take place in a few hours.

The plate so prepared is backed with black paper and is exposed to sunlight with the film covered by a negative in the form of a transmission grating having opaque strips slightly narrower than the transparent ones. This transmission grating is best prepared by ruling on a silvered glass plate. The exposure time is about three minutes in bright sunlight, but must be determined by trial. The gelatine strips exposed to light become insolubilized, while the unexposed portions are readily removed by treatment with hot water of about 40–45°C. The action is facilitated by pouring onto the surface from a height of about 15 cm, though too violent treatment is to be avoided as the insolubilized gelatine may also be removed. After a rapid and uniform drying the grating is completed by the addition of a sputtered platinum film.

The grating space is of course determined by the negative used in printing, but the thickness of the laminae depends upon several factors and several attempts with varying quantities of gelatine solution may be required before a satisfactory grating results.

3. *The thermocouple.* The radiation sensitive device used was a vacuum thermoelement of very small mass, with wires of bismuth and of bismuth-tin alloy drawn by the Taylor process.[5] The method of construction was similar to that described by Pettit.[6] The thermocouple arrangement has been previously described[4] but the essential features are as follows. The couple is built symmetrically with respect to its two junctions, on each of which one half of the emergence slit of the spectrometer is focussed, greatly reduced in size, by means of a concave mirror. The rays from the upper slit half fall on one junction, and those from the lower half on the other. With a radiation source as described, and filters in the optical path consisting of a smoked quartz plate, radiations from two different portions of the spectrum reach the thermocouple. In the first place the desired radiations between about 30μ and 160μ which are spread into a spectrum by the grating, and secondly, though much weaker, radiations in the near infra-red out to about 3μ, which due to their great intensity in the black-body radiation pass even a thick soot filter in appreciable intensity and due to imperfections in the grating fall on the thermocouple at any grating setting. But since the thermocouple is symmetrical no galvanometer deflection is produced when equal amounts of radiation fall on each junction. Now if a shutter is used which is transparent to the near infra-red but opaque to the long waves, such as thin glass or rock salt, and this alternately covers lower and upper slit halves, the galvanometer deflections produced are a measure of the intensity of the far infra-red rays, as the effect of the shorter rays cancels out.

4. *The spectrometer and absorption cell and auxiliary apparatus.* The vacuum spectrometer, absorption cell, and auxiliary apparatus are shown in plan and elevation in Fig. 2. The enclosing case is constructed of heavy seamless brass tubing, soldered at the joints with care to avoid pin holes. The removable end plates and cover to the grating chamber are sealed by rubber gaskets.

The absorption chamber has an optical path of 77 cm, which begins at a slit in the wall separating it from the chamber containing the radiation source, and ends at the initial slit of the spectrometer. These slits are covered with plates of crystal quartz, which form the windows of the absorption cell, and the arrangement has the advantage that the windows are of very small area and may be made very thin if necessary and yet stand considerable pressure differences. The path contains two mirrors, the first a concave one which focusses an image of the hot filament on the spectrometer slit. The other is plane and merely deviates the beam through about 90°. It fits in a frame so designed that an exchange of mirrors may be made without disturbing the optical adjustment. The system is focussed using an ordinary optical mirror which is then replaced by a steel plate having a slightly rough surface. This scatters the short waves in all directions but still reflects the long waves perfectly, and serves to supplement the soot filter which is deposited on one window of the absorption cell.

[5] G. F. Taylor, Phys. Rev. **23**, 655 (1924).

[6] E. Pettit, Publications of the Mount Wilson Observatory.

The absorption cell is provided with an independent evacuation system, a manometer, and a McLeod gauge designed for reading pressures up to several millimeters of mercury. In the investigations the ammonia gas was admitted directly from a small pressure tank containing a pure preparation obtained from the Fixed Nitrogen Research Laboratory in Washington, D. C.

The spectrometer is similar to several which have been used in infra-red work and the essential features are evident in the figure. The focussing and collimating mirror is of 50 cm focal length and 10 cm diameter. The plane reflecting grating used in the investigation has a 1 mm spacing. The initial

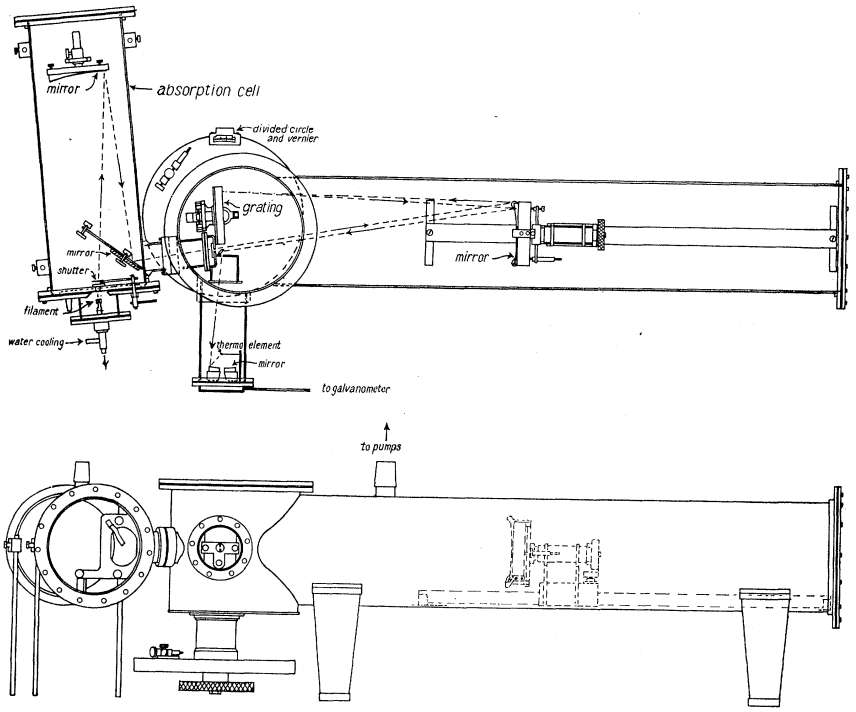

Fig. 2. The vacuum spectrometer and absorption cell in plan and elevation.

and emergence slits are fixed and of 1.25 mm width. The spectrometer is enclosed in a vacuum tight case which also houses the thermocouple. The grating is mounted on a vertical spindle which passes through the base of the grating chamber in a vacuum tight cone. During observations a vacuum of considerably better than 0.001 mm was maintained to secure the maximum thermocouple sensitivity.

The galvanometer employed with the thermoelement was of the moving coil type and had a resistance of about 15 ohms and a sensitivity of about 1 mm deflection, at a scale distance of one meter, per 2.4×10^{-9} ampere. The galvanometer was enclosed in an air tight case with a metal sheath, and

the leads to the thermoelement passed through a copper tube shield. A thermoelement of the type used is very sensitive in detecting short electromagnetic waves which originate from various devices in use in the laboratory, but the above precautions entirely eliminated disturbances. The galvanometer was read by a device which is not new but the merits of which do not seem to have met general appreciation. A galvanometer lamp with vertical filament was used, but instead of focussing the light reflected from the galvanometer mirror on a scale, the image of the lamp was observed in a magnifying eyepiece which could be moved horizontally across the path of the beam by means of a micrometer screw. Lamp and table carrying the eyepiece were mounted on a solid pedestal three meters from the galvanometer, and a simple lens over a window in the galvanometer house caused a life sized image of the lamp to be focussed in the plane of the eyepiece. This image may be very diffuse due to the small size and imperfections of the galvanometer mirror, but may be centered on a cross hair in the eyepiece with surprising accuracy. Galvanometer deflections are thus read by measurement of the displacements of the eyepiece, using a scale with which the micrometer screw is provided.

When some care was taken to keep the temperature of the room constant the drift of the galvanometer during readings was very inconsiderable, amounting usually to less than 1 cm per hour. The sensitivity of the thermocouple galvanometer system together is rather difficult to estimate. When the grating was set at about 85μ the deflection produced by the continuous background of the source (with evacuated absorption cell) was of the order of 1.5 mm. Readings could be reproduced within an error of about 0.05 mm. The principal limit on the accuracy of reading was slight mechanical disturbances of the galvanometer.

5. *The experimental procedure.* It does not seem necessary to describe in detail the experimental procedure. The absorption lines were first roughly located, and then each was studied separately. The intensity distribution in the background radiation in the neighborhood of the line was first investigated with evacuated cell. Ammonia gas was then admitted and the measurements repeated. Observations were made in both of the first order spectra.

III. The Experimental Results

The results of the investigation are shown in Fig. 3, which is a plot of the apparent percentage absorption of ammonia against wave-length. The absorption spectrum consists of one series of lines separated by approximately equal frequency intervals. A careful search between these lines failed to discover others in appreciable intensity. The absorption lines seem to be quite narrow and the apparent width as seen in the plot would seem to be accounted for by the limited resolving power of the spectrometer.

The absorption curves plotted were made with a pressure of 3 cm ammonia in the absorption chamber except in the case of the line numbered 6 which was observed at pressures of 1.9 and 3.9 cm. The line numbered 7, as

indicated by the dotted curve, was not experimentally located as it fell near one of the minima of reflection of the grating and also near a disturbance in the continuous background. This was observed by one of us in a previous investigation of hydrogen chloride, and since it is independent of the source

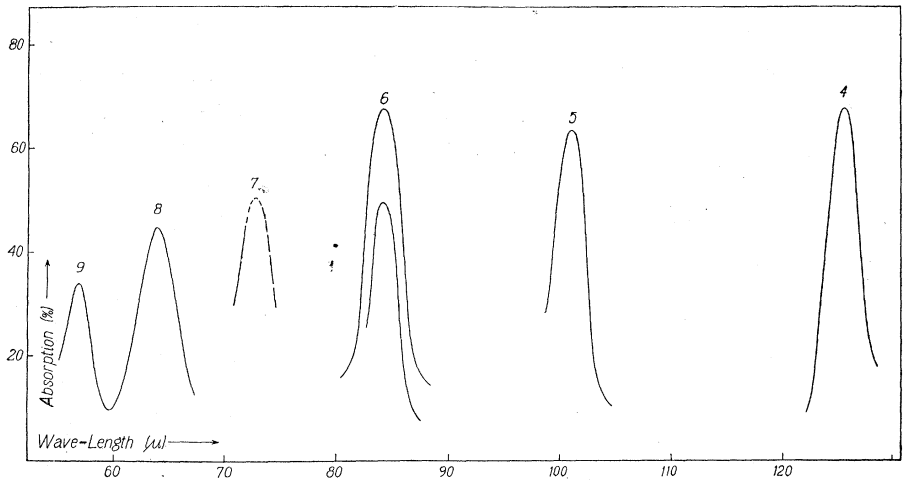

Fig. 3. The absorption spectrum of ammonia. The absorption measurements were made with a path length of 77 cm and an ammonia pressure of 3 cm except line number 6 which was measured at pressures of 1.9 and 2.9 cm respectively.

of radiation used, and of the blackening material on the thermocouple, seems to be due to an absorption in the quartz windows.[7]

Within experimental error the wave numbers of the absorption lines may be expressed by means of the following formula:

$$\nu = 19.957m - 0.0050826m^3. \tag{1}$$

The accuracy of the fit may be judged from the following table:

TABLE I. *Observed and calculated values of the frequencies.*

m	ν obs.	ν calc.	Δ
4	79.79	79.504	−0.286
5	99.06	99.150	0.090
6	118.60	118.645	0.045
7	—	137.960	—
8	156.80	157.054	0.254
9	176.10	175.908	−0.192

V. DISCUSSION OF THE RESULTS

The case of the symmetrical rotator has been treated on the basis of the wave mechanics by Reiche and Rademacher,[8] who have found that the

[7] Czerny has communicated to us that he has found a strong absorption of quartz in this region.

[8] F. Reiche and H. Rademacher, Zeits. f. Physik **39**, 444 (1928).

rotational energy or "eigenwert" may have the values given by the following equation:

$$W=\frac{h^2}{B\pi^2}\left[\frac{1}{A}j(j+1)+\left(\frac{1}{C}-\frac{1}{A}\right)\tau^2\right]. \tag{2}$$

Here C is the moment of inertia about the axis of symmetry, A the moment of inertia about an axis perpendicular to the first, and j and τ are integers.

The particular case of a rotating molecule having three similar atoms and a fourth dissimilar has been considered by Hund.[9] Considering rotations and vibrations separately he finds for the lowest vibrational state two possibilities, one in which the eigenfunction is symmetric in the three similar particles, the other in which it is antisymmetric. For the eigenfunctions describing the rotations alone the following possibilities are found. All

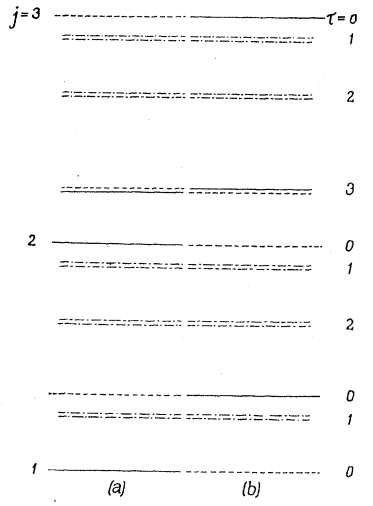

Fig. 4. Symmetry character of the rotation terms of the ammonia molecule when the vibrational state is (*a*) symmetric, (*b*) antisymmetric.
———— symmetric term
– – – – – – – – antisymmetric term
— — — — — — term of degenerate symmetry

functions where τ is not divisible by three have degenerate symmetry character. Where $\tau>0$, but is divisible by three, there are an equal number of symmetric and antisymmetric eigenfunctions. And where $\tau=0$ the function might be either symmetric or antisymmetric depending on whether it is even or odd in the coordinate h, which is the distance of the plane of the three similar atoms to the fourth. Considering together rotations and vibrations in the lowest oscillatory state the symmetry possibilities are given in Fig. 4, which is adapted from Hund.

[9] F. Hund, Zeits. f. Physik **43**, 805 (1927).

As to the possible energy transitions, only terms having the same symmetry should combine. Hund derives further that $\Delta\tau = 0$ occurs when a vibrational state combines with another of reciprocal character, and $\Delta\tau = \pm 1$ occurs when one degenerate vibrational state combines with another symmetric, antisymmetric, or degenerate state. Evidently then, any transition where $\Delta\tau \neq 0$ is excluded in the pure rotation spectrum on account of the limitation on the nature of the oscillational eigenfunctions in the lowest energy state. The change in j is restricted as usual to ± 1.

These considerations are in agreement with experiment as far as one can see. The ammonia rotation spectrum consists of a single set of lines which is apparently due to transitions with constant τ and j increasing by unity. Each of these lines, however, should be a multiplet with a number of components corresponding to the possible number of values of τ. These components should be appreciably separated due to the stretching of the molecule with increasing speed of rotation about the symmetry axis. Since $\tau \leqq j$, one should expect the unresolved lines to broaden with increasing j. This is, however, not evident in Fig. 3 although the stretching of the molecule as it rotates about the other axis is evident from the rather large correction term in Eq. (1).

As to the existence and relative prevalence of the various types of eigenfunction it is not possible to draw any certain conclusion without resolving the multiplets. A further complication is suggested by Barker[3] who mentions that in interpreting the rotation oscillation bands one must consider also the possibility of dissimilarity of the three hydrogen atoms due to a difference in the orientation of a spin. In this case the possibility of eigenfunctions of degenerate symmetry will be further increased.

With the use of the constants of Eq. (1) it is possible to calculate a moment of inertia for the ammonia in its lowest rotational state. One finds that $A = 2.77 \times 10^{-40}$ gm cm^2. Barker[2] states that from the structure of the ammonia band at 2μ he concludes that the distance h from the nitrogen atoms to the plane of the hydrogen atoms is equal to from 1/10 to 1/16 d, the distance between hydrogen atoms. Assuming the former relation one may obtain for d the value 1.78×10^{-8} cm.

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