

where the cosmological constant Λ is taken to be zero.

If we use for the present mean density $\rho = 10^{-30}$ g cm⁻³ and for the present expansion velocity $\alpha = (d/dt) \log e^{3\sigma(t)} = 1.8 \times 10^{-17}$ sec.⁻¹, Eq. (9) is inconsistent with the real value of \Re (closed space) and also with $\Re = \infty$. The only remaining possibility is to assume an imaginary value of \Re . This gives for sufficiently late stages of expansion a constant expansion velocity, i.e., an infinite infinitely expanding space. For sufficiently early stages of expansion the Eq. (9) approaches the condition (4), and small density fluctuations in these early stages could have given rise to the condensations discussed above. Thus *in order to understand the formation of great nebulae and to satisfy the condition of continuity at the moment of their separation, it is necessary to accept the hypothesis that space is infinite and ever expanding.*

The only way to estimate the type of the curvature of our universe from direct observations is, at present, the method of Hubble and Tolman⁸ based on the changes of observed density distribution of nebulae at great distances. Their analysis indicates that the apparent den-

sity of nebular distribution increases with increasing distance, which brings them to the conclusion that our universe has positive curvature and is closed in itself. However, we must notice that these conclusions are based on the hypothesis that the absolute luminosities of nebulae, which they use for the estimate of distances, do not change with the age of the nebulae. *If, however, we suppose that the absolute luminosities of very distant nebulae are slightly higher, because we see them at an earlier stage of evolution, the observational material no longer contradicts the assumption of an opened hyperbolic space.* At the present stage of our knowledge it is, of course, difficult to predict the expected changes of nebulae with their age, but since we deal with a period comparable to the total age of nebulae small changes are quite plausible. For example a decrease of luminosity might be accounted for by the above-mentioned possibility that the nebulae are permanently losing stars possessing too large velocities to be kept back by the gravitational attraction of the nebula.

We consider it our pleasant duty to express thanks to Mr. C. G. H. Tompkins for having suggested the topic of this paper and to H. A. Bethe for valuable discussions.

⁸ E. Hubble and R. C. Tolman, *Astrophys. J.* **82**, 302 (1935).

Perpendicular Vibrations of the Ammonia Molecule

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The vibration frequency ν_2 of NH_3 is identified by means of the combination bands $\nu_2 \pm \nu_3$ at 2.2μ and 4.0μ , in each of which the spacing between component bands is about 16 cm^{-1} . From the difference band the numerical value of ν_2 is fixed at 3415 cm^{-1} . The fundamental band may be recognized in the weak and complex background of the absorption at 3μ . The coefficient ζ_2 of the vibrational angular momentum is approximately $+0.6$.

The second perpendicular fundamental band at 6μ is partially resolved, and is in good agreement with the expected pattern if ζ_4 equals -0.3 . The indicated value of ν_4 is 1628 cm^{-1} . The numerical values of ζ_2 and ζ_4 do not agree well with those predicted theoretically.

The parallel component of $2\nu_4$ is found at 3220 cm^{-1} , and two pairs of parallel combination bands, $\nu_1 + \nu_3$ at 4270 and 4303 cm^{-1} and $2\nu_4 + \nu_3$ at 4177 and 4217 cm^{-1} .

THE four atoms in the ammonia molecule, as is well known, form a pyramid with axial symmetry, and must have four different fundamental vibration frequencies. All four should be active both in infra-red and in Raman spectra. Two of these, represented by the bands at 3μ

and at 10μ , involve oscillations parallel to the axis of symmetry and are readily identified. Each gives rise to a double band with P , Q and R branches, the levels occur in pairs because of the two potential minima defining alternative equilibrium positions for the nitrogen atom. A third

band, found at 6μ , must be associated with vibrations normal to the axis, and its structure, as described below, is in accord with this view. Regarding the position of the fourth fundamental there has been considerable difference of opinion,^{1,2} and until now the experimental evidence has not been conclusive. Unpublished observations by Stinchcomb and Barker in 1929 seemed definitely to exclude as a possibility the strong band at 2.2μ because of its complexity and the relative intensities of its component lines.

Raman observations upon gaseous ammonia contribute very little to this question, since scattering due to perpendicular vibrations has not been detected. The measurements of Lewis and Houston³ showed two lines in the neighborhood of 3μ , of which the one displaced by 3334 cm^{-1} is the parallel frequency ν_1 , indicated by infra-red measurements at 3337 cm^{-1} . These authors suggested that the second line, displaced by 3219 cm^{-1} , might represent the perpendicular band ν_2 . This clearly is not the case however, as the infra-red measurements show, and the line 3219 cm^{-1} must be the parallel component of the harmonic of ν_4 (1628 cm^{-1}), probably intensified somewhat by resonance interaction with ν_1 . The Raman spectrum of liquid ammonia shows three neighboring frequencies, 3216, 3304

and 3380 , corresponding exactly to the lines appearing in the liquid methyl halides⁴ where interaction of the type mentioned has been well established. In every case the highest of the three frequencies, observed only in the liquid, corresponds to a perpendicular vibration.

The similarity between NH_3 and CH_3 follows also from a mechanical treatment of the problem of vibration. Utilizing forces of the valence type, Howard⁵ has obtained a potential function involving two constants, which may be so chosen as to yield the frequencies of ν_1 (3334) and ν_4 (1626). The other two frequencies, which may then be predicted approximately, are $\nu_2=3370$ and $\nu_3=1050$. The observed value for the latter is about 950 . Since 3370 is not far from the value suggested by Raman observations on liquid NH_3 , it may be considered as a fair approximation. Three important factors were neglected in the computation, however, and it is difficult to estimate how much they may affect the result. They are anharmonicity, resonance interaction, and the double minimum.

A convincing argument supporting this approximate value of ν_2 has recently been provided by measurements upon ND_3 ,⁶ where all four of the fundamentals may be observed. If the three above-mentioned conditions are neglected, a

¹ Cl. Schaefer and F. Matossi, *Das Ultrarote Spektrum* (Berlin, Julius Springer, 1930), p. 250.

² H. Verleger, *Physik. Zeits.* **38**, 83 (1937).

³ C. M. Lewis and W. V. Houston, *Phys. Rev.* **44**, 903 (1933).

⁴ A. Adel and E. F. Barker, *J. Chem. Phys.* **2**, 627 (1934).

⁵ J. B. Howard, *J. Chem. Phys.* **3**, 207 (1935).

⁶ M. V. Migeotte and E. F. Barker, *Phys. Rev.* **50**, 418 (1936).

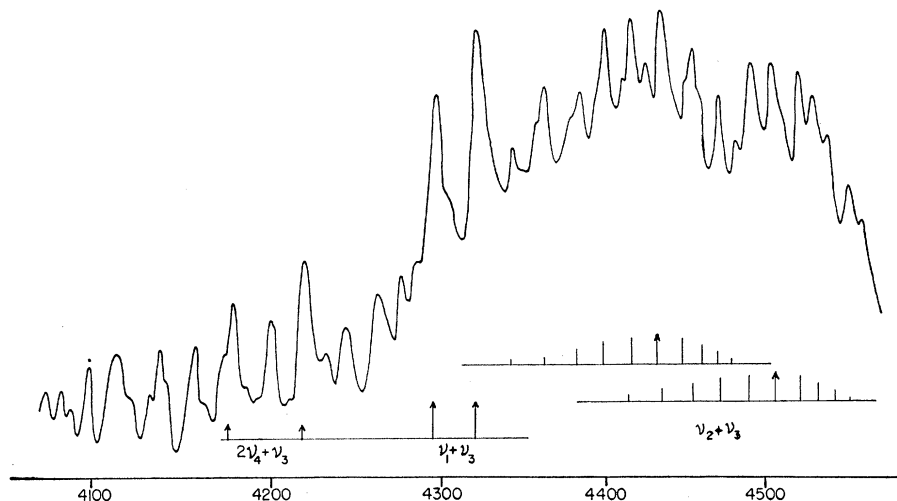


FIG. 1. The band at 2.2μ .

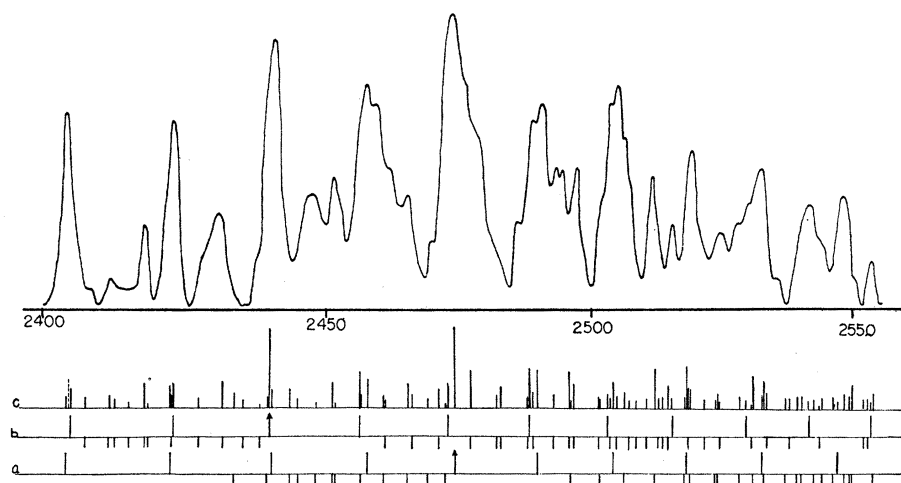


FIG. 2. The difference bands $\nu_2 - \nu_3$. a and b represent the high and low frequency components, respectively. c represents the combination, with intensities roughly indicated. For $\Delta J = 0$ marks extend upward, for $\Delta J = \pm 1$ downward.

simple numerical relation may be obtained between the values of ν_2 and ν_4 for NH_3 and for ND_3 . This yields for ν_2 (NH_3), when the other three known frequencies are introduced, a value of approximately 3400. The evidence is strong, therefore, that in NH_3 the frequencies ν_1 and ν_2 are close together, and that, since the latter has not been positively identified in the infra-red, it must be represented by a band of relatively small intensity. Hence the strong band at 2.2μ may be interpreted as a superposition of $\nu_1 + \nu_3$, $\nu_2 + \nu_3$ and $2\nu_4 + \nu_3$. A superficial examination at once indicates that the first of these cannot provide the major part of the absorption. Apparently, therefore, ν_2 combines strongly with ν_3 .

THE COMBINATION BANDS $\nu_1 + \nu_3$ AND $\nu_2 \pm \nu_3$

The 2.2μ band has been re-examined with results quite in accord with earlier (unpublished) measurements. The absorption due to 25 cm^{-1} of gas at 60 cm pressure, as observed with a grating having 4800 lines per inch, is indicated in Fig. 1. The slit includes 4 cm^{-1} , and the resolution is far from complete. Certain features may be recognized, however. At 4294 and 4319 cm^{-1} a pair of zero branches appear which must correspond to $\nu_1 + \nu_3$. The positions would be $3337 + 933 = 4270$ and $3337 + 966 = 4303$ if interaction is neglected. The change in character of the motion reduces the separation of the two ν_3 levels, as might be expected, from 33 cm^{-1} to

25 cm^{-1} , and the value of x_{13} is negative. A second pair of maxima at 4177 and 4217 cm^{-1} ($\Delta\nu = 40$) may be the zero branches of the parallel type component of $2\nu_4 + \nu_3$. The main portion of the band consists of a number of lines at intervals of approximately 16 cm^{-1} which form two distinct groups, the maxima of which occur at 4434 and 4506 . These apparently constitute the bands $\nu_2 + \nu_3$, but do not yield precise values of ν_2 since x_{23} is unknown. The very wide separation, $\Delta\nu = 72$ indicates either an amplitude of vibration of the N atom parallel to the symmetry axis

TABLE I. Lines assigned to the transitions $\Delta J = 0$ in the bands $\nu_2 - \nu_3$, ν_2 and $\nu_2 + \nu_3$.

2441 band ν	$\Delta\nu$	2473 band ν	$\Delta\nu$	3407 band ν	$\Delta\nu$	4470 band ν	$\Delta\nu$
2404.0		2405		3352		4360	
2423.0	17.0	2422.0	17	3373	21	4384	24
2440.8	17.2	2440.0	18	3389	16	4400	16
2457.7	16.9	2457.0	17	3407	18	4416	16
2473.3	15.6	2473.3	16.3	3423	16	4434	18
2488.2	14.9	2489.7	16.4	3439	16	4452	18
2502.9	14.7	2504.2	14.5	3454	15	4476	24
2516.6	13.7	2519.0	14.8			4493	17
2529.0	13.4	2532.0	13.0			4506	13
2540.1	11.1	2547	15.0			4521	15

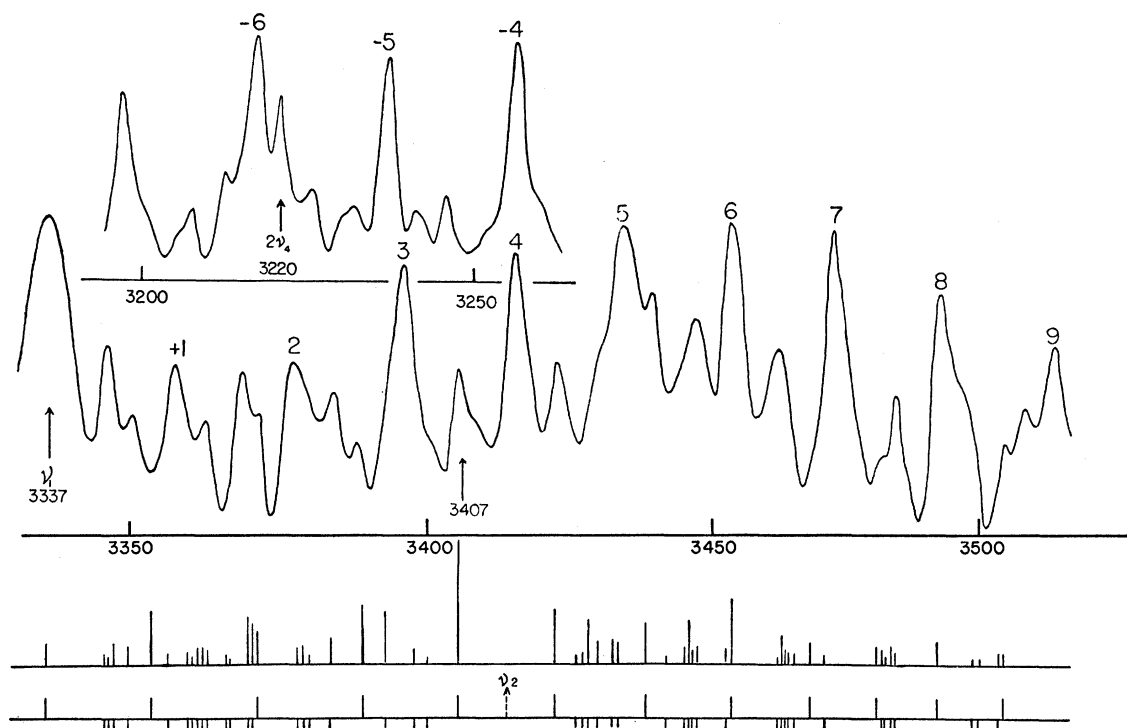


FIG. 3. A part of the 3μ band, including ν_1 and ν_2 .

which is greater than for ν_3 alone, or a decrease in the hump separating the two potential minima, or both.

This pair of bands consists of two sets of zero branches forming the prominent maxima, each of which is the center of a component sub-band. These are indicated diagrammatically in Fig. 1 underneath the curve. While some convergence is apparent, a numerical evaluation of the coefficients for the quadratic terms is hardly justifiable. The observed positions of the lines appear in Table I, column 7.

The difference band, $\nu_2 - \nu_3$, appears at 4μ . To observe it a four-meter cell was used, filled by displacement to a concentration of about 50 percent NH_3 . It had mica windows. The resulting absorption is presented in Fig. 2. Again the lines show intervals of about 16 cm^{-1} , but now the separation between the two component bands is exactly the ν_3 interval, i.e., 33 cm^{-1} , since in the ν_2 levels the spacing does not differ much from that of the ground state. The central maxima lie at 2440.8 and 2473.3 cm^{-1} , which indicates that the corresponding line for ν_2 occurs at 3407 cm^{-1} .

In diagram a of Fig. 2, the lines drawn upward represent the transitions $\Delta J = 0$, and those drawn downward represent $\Delta J = \pm 1$, for the band of higher frequency. Diagram b of Fig. 2 represents the lower frequency band, and the two are combined in c, where the lengths of the line segments indicate approximately the expected intensities. Because of the strong CO_2 band near 4.3μ it is not possible to extend the measurements to lower frequencies with an open spectrometer. The line at 2404 cm^{-1} is more intense than might have been expected. At exactly this position, however, one component of the difference band $\nu_1 - \nu_3$ should appear ($3337 - 933 = 2404$). The positions of the lines $\Delta J = 0$ are indicated in Table I, columns 1 and 3. In these measurements the slit included 1.5 wave numbers.

THE FUNDAMENTAL ν_2

In the earliest observations upon the 3μ band of NH_3 a lack of symmetry was noted. The high frequency side not only has a greater intensity, but also includes many lines not assignable to ν_1 . This is also clear in the measurements by

Dennison and Hardy.⁷ Without a precise knowledge of the position of ν_2 , however, a convincing analysis of the weaker and more complex band could hardly be obtained. Fig. 3 shows a part of this region at a resolution slightly less than that employed by Dennison and Hardy. The numbered lines belong to the parallel band ν_1 , while the predicted pattern for ν_2 is indicated upon the lower diagram. Lines drawn upward represent transitions for which $\Delta J=0$, and are given in column 5 of Table I. The upper diagram indicates approximate intensities.

The frequency interval between component bands depends upon the amount $\zeta h/2\pi$ of internal angular momentum associated with the degenerate vibration. If ζ were zero, this interval would be $(1/C-1/A)h/4\pi^2$, or approximately 8 cm^{-1} . In order to explain the displacements of approximately 16 cm^{-1} between component bands it is necessary to assign to ζ_2 the value $+0.6$, while that predicted by Johnston and Dennison⁸ is -0.004 . The vibration frequency itself has a value higher than that corresponding to the most intense zero branch by one-half interval, i.e., $\nu_2=3415\text{ cm}^{-1}$.

The low frequency side of this 3μ band is also complicated by the harmonic of ν_4 , consisting of a parallel and a perpendicular component. A strong maximum at 3220 cm^{-1} , near the line -6 , probably indicates the center of the parallel band, in agreement with the Raman observations already mentioned.

THE FUNDAMENTAL ν_4

The most intense absorption in the ammonia spectrum occurs in the region of 6μ . When examined at moderate dispersion it has the appearance of a parallel band with an intense central maximum.⁹ Higher resolution shows, however, that this is not a typical zero branch, but consists rather of a group of strong lines at intervals of four or five wave numbers, with intensities decreasing rapidly in both directions from the center. This is exactly the situation predicted by Dennison for the perpendicular

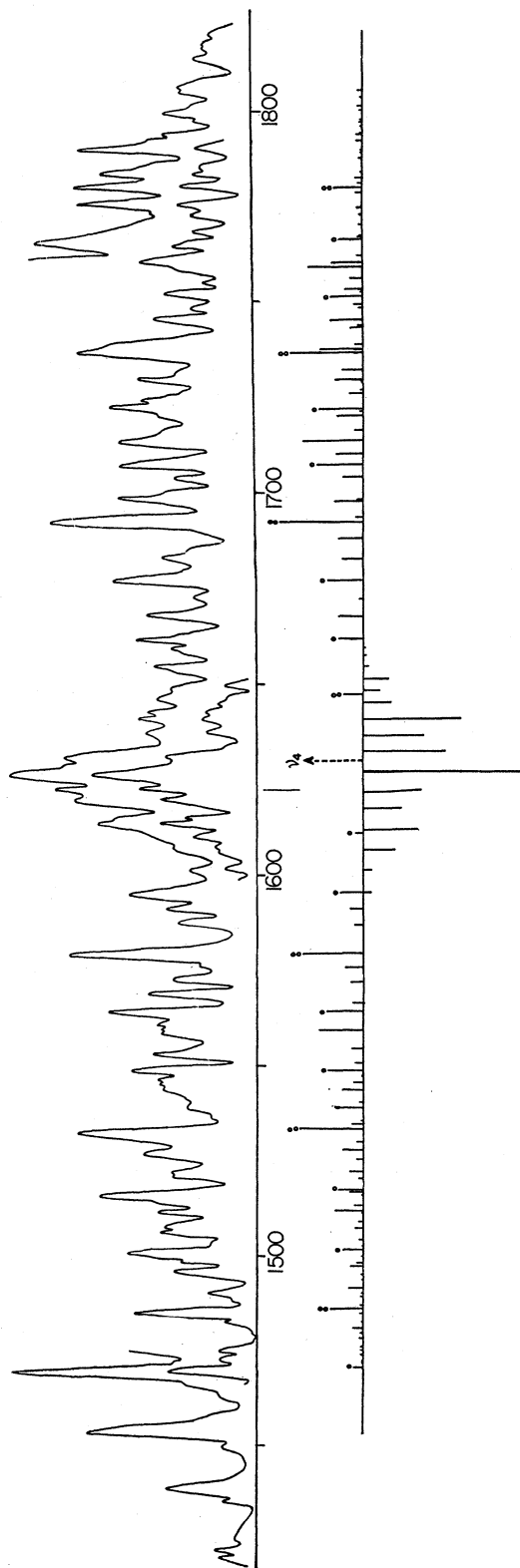


FIG. 4. The band ν_4 at 6μ , as observed and as predicted.

⁷ D. M. Dennison and J. D. Hardy, Phys. Rev. **39**, 938 (1932).

⁸ M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

⁹ R. Robertson and J. J. Fox, Proc. Roy. Soc. **A120**, 161 (1928).

band ν_4 . Moreover, the lateral portions of the band show definite indications of alternating intensities, which must be associated with changes in the angular momentum about the axis of symmetry. In the observed absorption pattern, which appears in Fig. 4, resolution is obviously incomplete, although the slits included only slightly over one wave number. The absorption due to atmospheric water vapor renders observations in this region somewhat difficult and a few minor details may be subject to later revision. The principal lines, however, stand out clearly and may be identified with confidence.

The general pattern of this band is indicated in Fig. 5, where each horizontal row represents one component, corresponding to a certain change in the axial momentum K . Initial values of K are indicated at the left. The number of missing lines near each band center increases with K , since $J \geq K$. Transitions starting from levels where K is divisible by three yield bands of double weight. The first lines on either side of the band centers for which ΔJ and ΔK have the same sign are marked with small circles, and those of double weight with pairs of small circles. The same symbols appear in Fig. 4, which makes the correlation relatively simple. Line intensities are not indicated in Fig. 5, but a certain amount of convergence has been introduced empirically, to give a proper distribution of the more prominent lines. The band centers must converge, and also the individual lines in the component bands. Since relatively few of

TABLE II. Wave numbers and assignments of lines in the band ν_4 . Columns headed J and K indicate quantum numbers of the initial state; the appended sign designates + or - transitions.

J	K	ν	J	K	ν
0 ₀	0+	1626.4	1+	1+	1661.7
2-	2-	1594.9	1+	0+	1667.4
2-	1-	1591.1	2+	2+	1676.6
2-	0+	1587.3	3+	3+	1691.8
3-	3-	1579.8	2+	3+	1698.7
6-	6-	1532.8	4+	4+	1707.0
7-	7-	1516.2	3+	4+	1713.3
8-	8-	1501.0	5+	5+	1722.2
9-	9-	1485.3	6+	6+	1736.6
10-	10-	1470.0	7+	6+	1760.0
11-	11-	1454.0	9+	9+	1779.5

these lines can be identified with certainty, and the positions of the various zero branches are not fixed with great precision, no attempt has been made to evaluate the quadratic coefficients. The wave numbers for some of the lines are listed in Table II. Since the most intense zero branch occurs at 1626 cm^{-1} , one-half space from the band center, the value of ν_4 is 1628 cm^{-1} . From the observed band spacing it follows that ζ_4 is approximately -0.3 , instead of -0.17 as predicted.

The experimental values of ζ_2 and ζ_4 are not only very different from those theoretically expected; they are also inconsistent with the prediction requiring their sum to equal $(C/2A) - 1$. This suggests that some revision is necessary, either in the interpretation of the data, or in the mechanical treatment of the interaction between vibration and rotation.

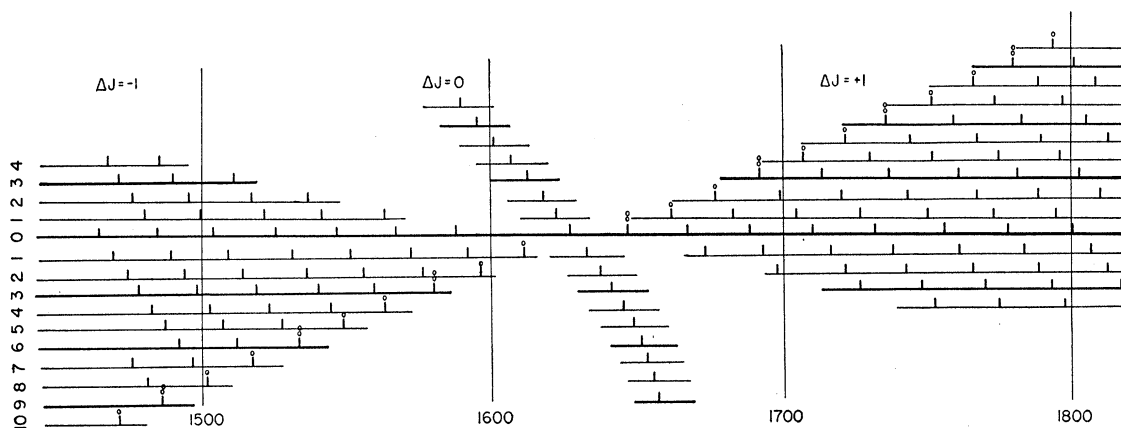


FIG. 5. Analysis of the band ν_4 . Initial values of K indicated at the left. $\Delta K = +1$ for horizontal rows 0 and above. $\Delta K = -1$ for horizontal rows below 0.