The Millimeter Wave Spectrum of Methyl Cyanide and the l-Type Doubling*

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The millimeter wave spectrum of methyl cyanide corresponding to the transitions $J = 4 \to 5$ to $J = 11 \to 12$ from 90 kMc/sec to 225 kMc/sec has been studied. Transitions corresponding to the molecules in the ground vibrational state as well as in the excited states $v_8 = 1$ and $v_8 = 2$ are observed. The B_0, D_J, and D_{JK} obtained for the ground vibrational state are 9198.899 Mc/sec, 3.81 kc, and 176.9 kc, respectively, and for the excited state $v_8 = 1$, 9226.444 Mc/sec, 3.9 kc, and 177.7 kc, respectively. The pattern for the excited state $v_8 = 1$ is qualitatively as expected according to Nielsen's theory, but it has been found that the theory is inadequate to give a quantitative fit.

INTRODUCTION

The microwave spectrum of methyl cyanide corresponding to the lower J transitions has been worked out earlier by Ring et al. (1) by Kessler et al. (2), and recently by Jaseja (3). The present work in the millimeter region has been carried out with the idea of getting better rotational and centrifugal stretching constants of the molecule in the ground and excited vibrational states than were known earlier and also with the idea of checking whether the l-type doubling theory as known at present would hold good in the millimeter region where high J and high K values would be involved. It was also expected that the structure of the pattern obtained for molecules in the second excited state $v_8 = 2$, would show whether that vibration is of totally symmetric species or of degenerate species or of a superposition of the two species.

EXPERIMENTAL DETAILS

The details of harmonic generation and detection are essentially described by King and Gordy (4). The crystal multiplier was driven by a 2K33 Raytheon klystron. A dc bias of about 12 to 20 volts was imposed on the cat whisker with

respect to the crystal of the multiplier which is grounded. The harmonic generating crystal is a specially treated silicon crystal supplied by Mr. R. S. Ohl of the Bell Telephone Laboratories. The absorption cell used is 10 ft in length and pressures ranged from 10^{-2} to 10^{-3} mm. The observations were made at room temperature. The lines were observed on an oscilloscope using the simple crystal video detection technique, that is, the signal from the detector was taken through a type P amplifier to the oscilloscope while the usual sawtooth modulation of 60 cycles was applied to the klystron reflector. When the lines were recorded, a modulation voltage of about 1 volt at 4 kc or 2 kc was applied to the reflector of the klystron, and the signal from the detecting crystal was taken through the P amplifier and then through a 4 kc phase sensitive lock-in amplifier to the Esterline Angus dc milliameter recorder.

The frequency measurements were made by mixing the fundamental klystron frequency with the signal from a secondary frequency standard monitored by WWV Station. The standard measuring marker was superimposed on the absorption line appearing on the scope. The error in the frequency measurement of the lines around 100,000 Mc/sec is probably ± 0.25 Mc/sec and for those around 200,000 Mc/sec is probably ± 0.5 Mc/sec.

RESULTS FOR THE GROUND VIBRATIONAL STATE

The transitions from $J = 4 \rightarrow 5$ to $J = 11 \rightarrow 12$ have been observed for different values of K and the frequencies of the lines measured are listed in Table I. It has been found that some of the lines showed partially resolved hyperfine structure. Using the eQq value -4.35 Mc/sec obtained by earlier workers (2) from the low J transitions one expects for higher K and J values a doublet, the high-frequency component of which is stronger and which represents the unresolved components $F = J - 1$ to $F = J$ and $F = J + 1$ to $F = J + 2$ while the low-frequency component represents the line $F = J$ to $F = J + 1$. Where one line has been observed instead of the expected two, it has been assumed that the line observed represents the stronger high-frequency component. For low values of K in the transitions studied the hyperfine splitting expected is negligible.

Molecular constants obtained from the analysis of the lines are listed in Table III. Calculated frequencies using these constants and the eQq value of -4.35 Mc/sec are given in Table I. No attempt has been made to obtain a value for eQq precisely but the partially resolved hyperfine splitting observed for some transitions was found to be consistent with the value of eQq obtained by earlier workers (2).

All the lines listed in Table I can be represented within the experimental error by the usual forrmula for the symmetrictop molecule

$$\nu = 2B(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}K^2(J + 1) \qquad (1)$$

TABLE I

THE FREQUENCIES OF THE LINES OF THE MOLECULES CORRESPONDING TO THE GROUND VIBRATIONAL STATE[a]

Transition $J \to J+1$	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	Transition $J \to J+1$	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
4 → 5	0	91,987.07	91,987.08	8 → 9	0	165,568.95	165,569.07
	1	91,985.35	91,985.31		1	165,565.71	165,565.88
	2	91,980.00	91,980.00		2	165,556.18	165,556.34
	3	91,971.35**	91,971.37		3	165,540.31	165,540.42
		91,970.62*	91,970.67		4	165,517.93	165,518.12
	4	91,959.20*	91,959.26		5	165,489.39	165,489.47
		91,957.94*	91,957.91		6	165,454.34**	165,454.60
						165,454.09*	165,454.10
5 → 6	0	110,383.47	110,383.50		7	165,412.93**	165,413.28
	1	110,381.39	110,381.38		8	165,365.43**	165,365.58
	2	110,375.01	110,375.00	9 → 10	0	183,962.62	183,962.74
	3	110,364.52**	110,364.53		1	183,959.08	183,959.21
		110,364.02*	110,364.11		2	183,948.49	183,948.59
	4	110,349.68**	110,349.80		3	183,930.79	183,930.90
		110,349.00*	110,349.04		4	183,906.05	183,906.13
	5	110,330.79**	110,330.85		5	183,874.21	183,874.29
		110,329.70	110,329.65		6	183,835.34**	183,835.49
6 → 7	0	128,779.43	128,779.36		7	183,789.31**	183,789.44
	1	128,777.02	128,776.88		8	183,736.28**	183,736.42
	2	128,769.52	128,769.46	10 → 11	0	202,355.61	202,355.50
	3	128,757.03	128,757.07		1	202,351.45	202,351.61
	4	128,739.91**	128,739.89		2	202,340.10	202,339.93
		128,739.39*	128,739.42		3	202,321.54	202,320.47
	5	128,717.69**	128,717.69		4	202,293.78	202,293.24
		128,717.18*	128,717.01		5	202,257.87	202,258.21
	6	128,690.57**	128,690.57		6	202,215.87**	202,215.49
		128,689.48*	128,689.50		7	202,164.93**	202,164.92
7 → 8	0	147,174.72	147,174.58		8	202,106.80**	202,106.58
	1	147,171.95	147,171.75		9	202,040.76**	202,040.47
	2	147,163.46	147,163.26		10	201,967.02**	201,966.57
	3	147,149.28	147,149.10	11 → 12	0	220,747.24	220,747.25
	4	147,129.41	147,129.30		1	220,742.99	220,743.00
	5	147,104.07	147,103.82		2	220,730.27	220,730.27
	6	147,073.04**	147,072.93		3	220,709.08	220,709.04
		147,072.27*	147,072.22		4	220,679.32	220,679.32
	7	147,035.89**	147,036.22		5	220,641.12	220,641.11
					6	220,594.50**	220,594.47
					7	220,539.30**	220,539.31
					8	220,476.04**	220,475.65
					9	220,403.96**	220,403.51

[a] The lines marked with a double asterisk are taken to be a superposition of the hyperfine structure components $F = J - 1$ to $F = J$ and $F = J + 1$ to $F = J + 2$. The lines marked with a single asterisk are taken to be the hyperfine structure components $F = J \to F = J + 1$. For all other lines, the hyperfine splitting is expected to be small and unresolvable.
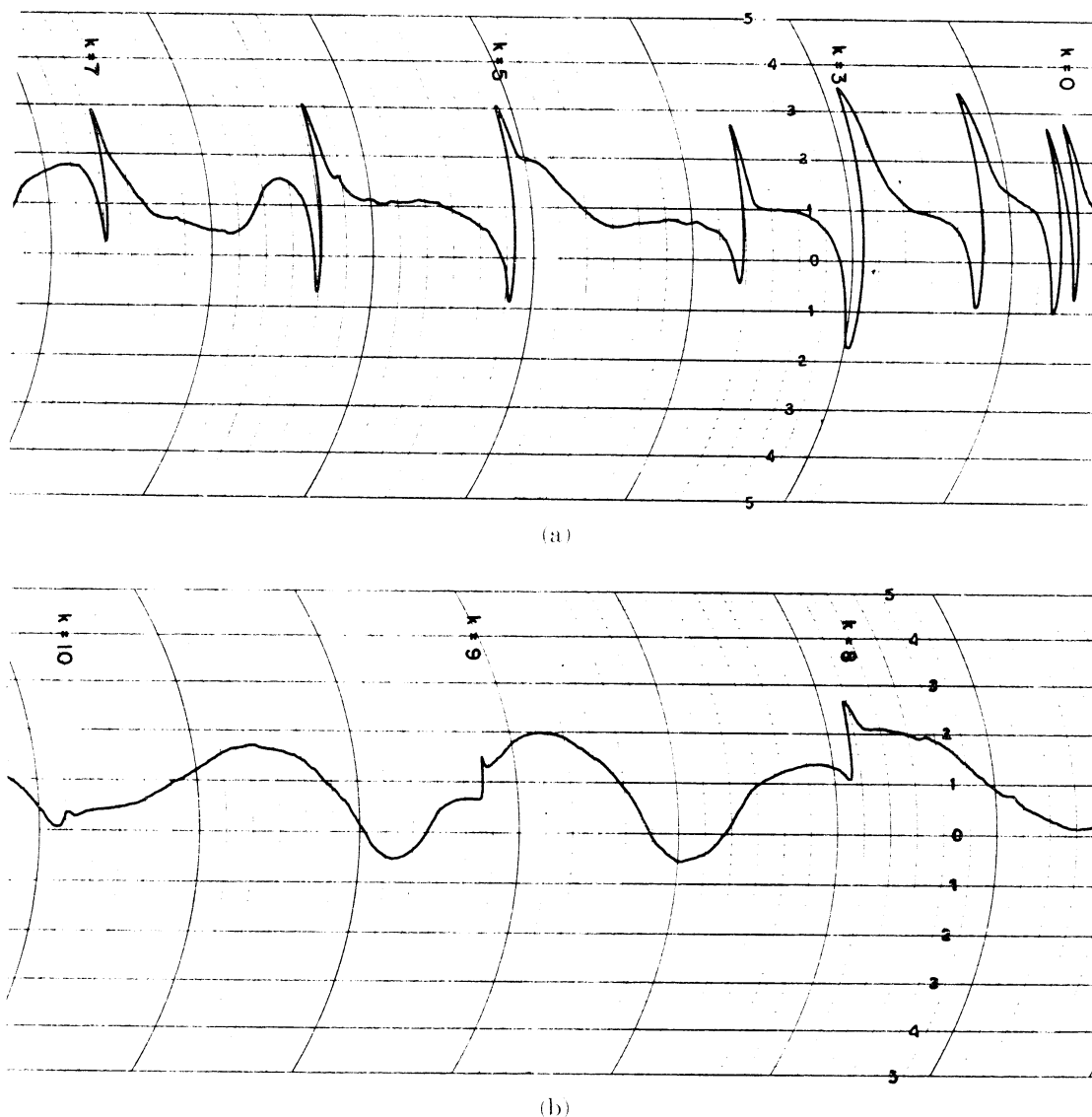
(a)

(b)

Fig. 1. (a) The recorded spectrum for the transition $J = 10 \rightarrow 11$ from $K = 0$ to $K = 7$. The line with $K = 0$ is at 202,355.61 Mc/sec and the one with $K = 7$ is at 202,164.93 Mc/sec. (b) The recorded spectrum for the transition $J = 10 \rightarrow 11$ from $K = 8$ to $K = 10$. The line with $K = 8$ is at 202,106.80 Mc/sec and the one with $K = 10$ is at 201,967.02 Mc/sec.

to which the additional term for the hyperfine splitting is added or subtracted whenever the splitting is expected to be significant.

A recorded spectrum of the transition $J = 10 \rightarrow 11$ is shown in Figs. 1 (a) and (b).

RESULTS FOR THE EXCITED STATE $\nu_8 = 1$

The methyl cyanide molecule belongs to the point group C_{3v} and has eight fundamental vibrations of which four are totally symmetric and four are doubly

TABLE II

THE OBSERVED FREQUENCIES AND THE ASSIGNMENTS OF THE LINES CORRESPONDING
TO THE MOLECULES IN THE EXCITED STATE $v_8 = 1$

J	Transition K	l	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	J	Transition K	l	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
4 → 5	±1	±1	92,353.67	92,353.45	7 → 8	±4	±1	147,595.40	147,595.47
			92,175.46	92,175.71		±2	∓1	147,589.93	147,590.28
	±2	±1	92,264.23	92,264.03		±5	±1	147,575.44	147,575.67
	0	∓1	92,261.53	92,261.58		±3	∓1	147,569.86	147,570.27
	±3	±1	92,258.59	92,258.49		±6	±1	147,550.12	147,550.32
	±1	∓1	92,256.53	92,256.46		±4	∓1	147,543.84	147,544.46
	±4	±1	92,250.14	92,249.72		±7	±1	147,519.34	147,519.32
	±2	∓1	92,247.42	92,247.46		±5	∓1	147,512.50	147,512.89
	±3	∓1	92,234.88	92,234.84	8 → 9	±1	±1	166,228.53	166,228.36
	±4	∓1	92,218.88	92,218.63				165,908.28	165,908.41
5 → 6	±1	±1	110,823.16	110,823.12		±2	±1	166,071.30	166,071.29
			110,609.77	110,609.82		0	∓1	166,059.13	166,059.10
	±2	±1	110,716.32	110,716.32		±3	±1	166,059.13	166,059.36
	0	∓1	110,712.17	110,712.35		±1	∓1	166,051.73	166,051.82
	±3	±1	110,709.40	110,709.42		±4	±1	166,042.93	166,042.91
	±1	∓1	110,706.25	110,706.47		±2	∓1	166,036.03	166,036.29
	±4	±1	110,698.62	110,698.80		±5	±1	166,020.50	166,020.53
	±2	∓1	110,697.07	110,695.76		±3	∓1	166,013.38	166,013.89
	±5	±1	110,684.52	110,684.05		±6	±1	165,992.06	165,991.96
	±3	∓1	110,680.36	110,680.65		±4	∓1	165,983.98	165,984.89
	±4	∓1	110,660.88	110,661.26		±7	±1	165,957.03	165,957.07
	±5	∓1	110,637.22	110,637.50		±5	∓1	165,948.85	165,949.41
7 → 8	±1	±1	147,760.38	147,760.67	9 → 10	±1	±1	184,695.21	184,695.17
			147,476.07	147,476.27				184,339.70	184,339.72
	±2	±1	147,620.13	147,619.99		±2	±1	184,522.32	184,522.14
	±0	∓1	147,611.01	147,611.25		0	±1	184,505.64	184,505.68
	±3	±1	147,609.76	147,609.91		±3	±1	184,508.45	184,508.17
	±1	∓1	147,603.96	147,604.26		±1	∓1	184,498.20	184,498.33

TABLE II—Continued

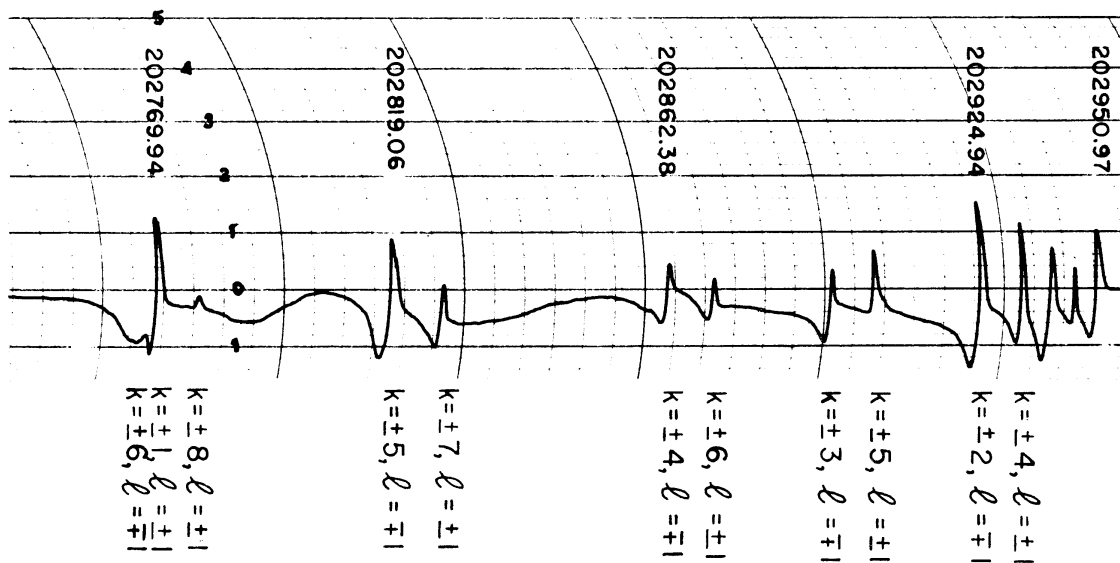| J	Transition K	Transition l	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	J	Transition K	Transition l	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
9 → 10	±4	±1	184,489.56	184,489.66	10 → 11	±7	±1	202,830.05	202,830.11
	±2	∓1	184,481.06	184,481.30		±5	∓5	202,819.06	202,819.63
	±5	±1	184,464.84	184,464.67		±8	±1	202,779.70	202,779.64
	±3	∓1	184,456.00	184,456.53		±6	∓1	202,768.06	202,768.47
	±6	±1	184,433.11	184,432.84		±9	±1	202,721.62	202,721.40
	±4	∓1	184,424.19	184,424.40		±7	∓1	202,709.07	202,709.43
	±7	±1	184,394.55	184,394.01		±10	±1	202,655.71	202,655.39
	±5	∓1	184,384.64	184,385.03		±8	∓1	202,642.27	202,642.51
10 → 11	±1	±1	203,161.23	203,161.53	11 → 12	±1	±1	221,625.91	221,626.02
			202,769.94	202,770.08				221,200.23	221,199.42
	±2	±1	202,972.63	202,972.53		±2	±1	221,422.37	221,422.45
	0	∓1	202,950.97	202,950.87		0	∓1	221,394.15	221,394.51
	±3	±1	202,956.31	202,956.28		±3	±1	221,403.82	221,403.60
	±1	∓1	202,943.39	202,943.68		±1	∓1	221,387.30	221,387.73
	±4	±1	202,935.67	202,935.61		±4	±1	221,380.74	221,380.70
	±2	∓1	202,924.94	202,925.23		±2	∓1	221,367.67	221,368.02
	±5	±1	202,907.98	202,907.97		±5	±1	221,350.37	221,350.38
	±3	∓1	202,897.68	202,898.15		±3	∓1	221,338.22	221,338.59
	±6	±1	202,872.91	202,872.87		±6	±1	221,311.95	221,311.97
	±4	∓1	202,862.38	202,862.88		±4	∓1	221,299.88	221,300.22
						±7	±1	221,265.54	221,265.26
						±5	∓1	221,252.93	221,253.12

degenerate (5, 6). Of these the lowest fundamental $\nu_8(e)$ which is degenerate lies (7, 8) at 361 cm^{-1}. The Boltzman factor for this frequency as well as that for its over tone would be appreciable, and therefore one can expect at room temperature an appreciable number of molecules in excited states $r_8 = 1$ and $r_8 = 2$. The number of molecules in the state $r_8 = 2$ will of course be much smaller than those in $r_8 = 1$ which in turn will again be smaller than those in the ground vibrational state $r_8 = 0$. The frequencies of the lines corresponding to the molecules in the excited state $r_8 = 1$ are listed in Table II. The recorded spectrum for the transition $J = 10 \rightarrow 11$ with $r_8 = 1$ is shown in Figs. 2 (a), (b), and (c).

Rotational energy levels of a symmetric top molecule in a doubly degenerate vibrational state are known to be split (5) into two because of Coriolis interaction (5). The splitting is given by $4A_v Kl\zeta$ where A_v is the rotational constant in the vibrational state, ζ is the Coriolis interaction constant, l is the quantum number of the vibrational angular momentum and K is the rotational quantum number of the level. The quantum number l takes the values $r, r - 2 \cdots 0$ where r is the quantum number of the degenerate vibration. The vibrational angular momentum about the figure axis because of the Coriolis interaction is $l\zeta(h/2\pi)$. This will add or subtract to the pure rotational angular momentum along the figure axis. For the CH₃CN molecule the quantum number l takes the values ± 1 when $r_8 = 1$ and 0 or ± 2 when $r_8 = 2$. The cases $l = \pm 1$ and $l = \pm 2$ represent doubly degenerate vibrational species while the case $l = 0$ represents a totally symmetric vibrational species. If the ζ for a particular degenerate vibration is positive, the rotational level having a positive value of Kl will be lower than that having a negative value. Herzberg (5) designates the level with a negative value of Kl as $-l$ and the other as $+l$. When $|K| = 3p + 1$ where p is an integer including zero, the level with positive value of Kl represents two coinciding levels of species A and the level with a negative value of Kl represents a doubly degenerate level of species E. When $|K| = 3p + 2$ the situation would be the reverse. In the case $|K| = 3p$ (and not zero) each of the two
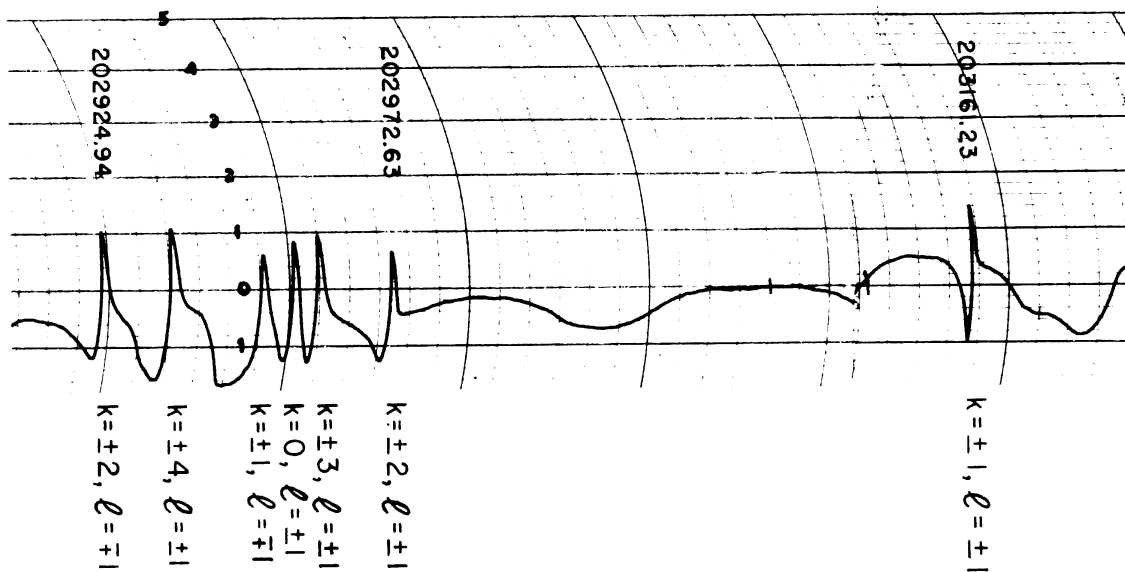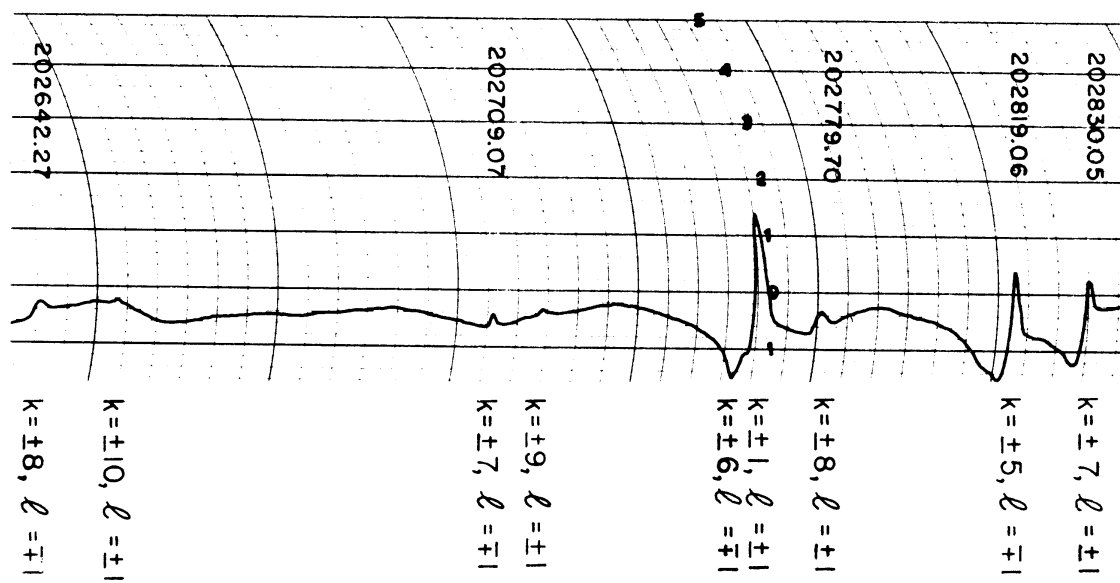

(a)

Fig. 2. (a) The recorded spectrum of the transition $J = 10 \rightarrow 11$ with $r_8 = 1$. This shows the lines in the region 203,161.23–202,924.94 Mc/sec. (b) The recorded spectrum of the transition $J = 10 \rightarrow 11$ with $r_8 = 1$. This shows the lines in the region 202,950.97–202,768.06 Mc/sec. (c) The recorded spectrum of the transition $J = 10 \rightarrow 11$ with $r_8 = 1$. This shows the lines in the region 202,830.05–202,642.27 Mc/sec. [See page 222 for (b) and (c).]

Spectrum values: 202950.97, 202924.94, 202862.38, 202819.06, 202769.94

Scale marks: 5, 4, 3, 2, 1, 0, 1

Labels:
$k=\pm 4, \ell=\pm 1$
$k=\pm 2, \ell=\mp 1$
$k=\pm 5, \ell=\pm 1$
$k=\pm 3, \ell=\mp 1$
$k=\pm 6, \ell=\pm 1$
$k=\pm 4, \ell=\mp 1$
$k=\pm 7, \ell=\pm 1$
$k=\pm 5, \ell=\mp 1$
$k=\pm 8, \ell=\pm 1$
$k=\pm 6, \ell=\mp 1$
$k=\pm 7, \ell=\pm 1$

(b)

Spectrum values: 202830.05, 202819.06, 202779.70, 202709.07, 202642.27

Scale marks: 5, 4, 3, 2, 1, 0, 1

Labels:
$k=\pm 7, \ell=\pm 1$
$k=\pm 5, \ell=\mp 1$
$k=\pm 8, \ell=\pm 1$
$k=\pm 6, \ell=\mp 1$
$k=\pm 1, \ell=\pm 1$
$k=\pm 9, \ell=\pm 1$
$k=\pm 7, \ell=\mp 1$
$k=\pm 10, \ell=\pm 1$
$k=\pm 8, \ell=\mp 1$

(c)

FIG. 2—Continued

levels, the one with positive value of Kl and the other with the negative value of Kl, represents separately a degenerate level of species E. According to Wilson (9) the degeneracy of the levels of species E persists even if all interactions are taken into account, whereas the pairs of the coinciding levels of species A may split. This splitting has been designated by Herzberg as K-type doubling. Nielsen

(10) has shown that this splitting for $v_8 = 1$ is appreciable for the levels with $K = 1$ only and is negligible for the levels having other values of K. The doubling of the levels in general, that is, the splitting of all the K levels into doublets as well as the further splitting of A species of the $K = 1$ levels, is called l-type doubling by Nielsen (11).

According to the Nielsen theory the frequencies of the rotational transitions, for the case $v_8 = 1$ are given by (3, 12)

$$\nu = 2B_r(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)K^2$$
$$+ 4(2D_J + D_{JK})(J + 1)Kl\zeta + \Delta P_{J,K,l}, \quad (2)$$

where

$$\Delta P_{J,K,l} = \pm(J + 1)q \quad \text{for} \quad K = l = \pm 1$$

and

$$\Delta P_{(J,K,l)} = \pm \frac{(J + 1)[(J + 1)^2 - (K \mp 1)^2]}{K \mp 1} \times \frac{q^2}{4[A(1 - \zeta) - B]}$$

for $K \neq l = \pm 1$.

In this equation the upper signs correspond to the cases where K and l have the same sign while the lower signs correspond to those where K and l are of different signs.

This equation predicts that lines with K having a positive value of Kl and those with $K-2$ having a negative value of Kl will form doublets. According to Eq. (2) the frequencies of the centers of such doublets are:

$$\nu = 2B_r(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1) - 2D_{JK}\bar{K}^2(J + 1)$$
$$+ 4(2D_J + D_{JK})(J + 1)\zeta, \quad (3)$$

while the center of the doublet corresponding to $K = l = \pm 1$ is:

$$\nu = 2B_r(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)$$
$$+ 4(2D_J + D_{JK})(J + 1)\zeta. \quad (4)$$

The centers of the doublets represented by Eq. (3) are thus expected to be situated at a distance of $2D_{JK}\bar{K}^2$ from the center of the doublet represented by Eq. (4). The $\bar{K}$ represents the average of the K and $K-2$ values of the lines that form the doublet. The D_{JK} and the D_J values obtained in the usual graphical manner with the help of the above relations for the excited states under consideration are included in Table III. Although the positions of the observed doublets are as expected from Nielsen's theory, the separations of the lines in the individual doublets are not. According to Eq. (2) the doublet separations

TABLE III

THE ROTATIONAL AND CENTRIFUGAL STRETCHING CONSTANTS OBTAINED FOR THE
GROUND VIBRATIONAL STATE AND FOR THE EXCITED STATES $\nu_s(e)$ AND $2\nu_8(A)$

Vibrational state	B in Mc/sec	D_J in kc/sec	D_{JK} in kc/sec
Ground vib. state	9198.89$_9$	3.8	176.9
$\nu_s(e)$	9226.44$_1$	3.9$_0$	177.7
$2\nu_s(A)$	(9254.12$_5$)	(3.0)	(143)

should be:

$$\Delta\nu = 8(J + 1)\bar{K}[2\zeta DJ - (1 - \zeta)D_{JK}]$$
$$+ 2\frac{(J + 1)\{(J + 1)^2 - \bar{K}^2\}}{\bar{K}} \times \frac{q^2}{4\{(1 - \zeta)A_r - B_r\}}. \tag{5}$$

However, to get agreement with the observations, it was found necessary to add
to the formula a term of the type $8\epsilon\zeta K(J + 1)$ which is equivalent to adding
$4\epsilon K l\zeta(J + 1)$ to Eq. (2) when ϵ is a small fraction of the order of 0.034. It has
been thus found that all the lines observed could be well fitted by using the
formula

$$\nu = 18452.89(J + 1) - 0.0156(J + 1)^3 - 0.3554(J + 1)K^2$$
$$+ 4 \times 0.193(J + 1) \times Kl + \Delta P, \tag{6}$$

where

$$\Delta P = \pm 17.775(J + 1) \text{ for } K = l = \pm 1$$

and

$$\Delta P = \pm\frac{(J + 1)\{(J + 1)^2 - (K \mp 1)^2\}}{4K \mp 1)} \times 0.0308.$$

A comparison of Eq. (6) with Eq. (2) shows that $q^2/|A(1 - \zeta) - B| = 0.0308$.
This yields a value of 0.878 for ζ if the values $A = 158,400$ Mc/sec and $B = 9,226.44$ Mc/sec and $q = 17.775$ Mc/sec are used. This ζ value is consider-
ably lower than the ζ values estimated by earlier workers from infrared data
$(6, 8, 13)$.*

Recently Amat (14) has made considerable modifications to Nielsen's treat-
ment by taking higher order vibration-rotation interactions into account. He

* The information (obtained from Dr. K. N. Rao to whom the authors are thankful)
saying that the attempts made at Ohio State University to resolve the ν_s band did not suc-
ceed so far suggests that the ζ_s value may probably be around 0.92 to 0.97 while the present
value obtained is 0.878. A future improvement of the theory of l-type doubling will prob-
ably be able to remove this discrepancy.

finds that the coefficient of ζ in Eqs. (2) to (5) is not simply $(2D_J + D_{JK})$, but contains additional molecular constants. Further the apparent rotational constant B_v is shifted in a manner that varies with the vibrational state. The first effect would account for the ϵ term needed to fit Eq. (5) to the observations; the second is suggested by the slight change in the rotation-vibration constant α_8 in going from state $v_8 = 1$ to $v_8 = 2$ in Table III. However, these changes do not account for the low value of ζ obtained by us, and it appears that much further work is required, particularly for the state $v_8 = 2$ in which no detailed qualitative fit to Nielsen's theory seems possible.

ALTERNATION OF INTENSITIES

The statistical weights for the different K levels of the ground vibrational state are as calculated by Wilson (15). The expected alternation of intensities as "strong, weak, weak, strong" was observed, the lines with $K = 3p$ being more intense than the others. The statistical weights of the levels with the different K and l values for the $v_8 = 1$ state were calculated by extension of Wilson's procedure and the results are listed in Table IV. It can be seen that the doublets corresponding to $[K = \pm(3p + 1), l = \pm 1]$, $[K = \pm(3p - 1), l = \mp 1]$ where

TABLE IV

THE STATISTICAL WEIGHTS OF THE ROTATIONAL LEVELS IN THE DOUBLY DEGENERATE VIBRATIONAL STATE v_8. THE WEIGHTS LISTED ARE IN GENERAL TO BE MULTIPLIED BY $(2J + 1)$ AND $(2I + 1)$ WHERE I REPRESENTS SPIN OF THE NITROGEN NUCLEUS

$\pm K$	l	Species of	Statistical weights
0	± 1	A	4
1	± 1	A,A	4,4
1	∓ 1	E	4
2	± 1	E	4
2	∓ 1	$2A$	8
3	± 1	E	4
3	∓ 1	E	4
4	± 1	$2A$	8
4	∓ 1	E	4
5	± 1	E	4
5	∓ 1	$2A$	8
6	± 1	E	4
6	∓ 1	E	4
7	± 1	$2A$	8
7	∓ 1	E	4
8	± 1	E	4
8	∓ 1	$2A$	8
9	± 1	E	4
9	∓ 1	E	4
10	± 1	$2A$	8
10	∓ 1	E	4

TABLE V

FREQUENCIES OF THE OBSERVED LINES CORRESPONDING TO THE MOLECULES IN THE EXCITED STATE $\nu_8 = 2$

J	K	Relative intensity	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)	J	K	Relative intensity	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
4 → 5	1	1	92,538.7	92,538.3	7 → 8		4	148,032.5	
	2	2	92,533.0	92,534.0		4	3	148,022.7	148,023.2
	3	3	92,526.9	92,526.9			1	148,019.2	
		2	92,525.1			5	4	148,004.9	148,002.7
		4	92,524.2			6	3	147,977.5	147,977.5
		2	92,519.6				2	147,973.5	
		1	92,510.7			7	3	147,947.9	147,947.7
5 → 6		1	111,049.4				2	147,939.1	
	0	1	111,047.4	111,046.9			2	147,921.1	
	1	2	111,046.0	111,045.2			1	147,910.6	
	2	1	111,040.9	111,040.0	10 → 11		3	203,583.3	
		2	111,039.1			0	3	203,574.3	203,574.8
	3	1	111,030.8	111,031.5		1	2	203,572.6	203,571.6
		2	111,028.8				2	203,564.4	
		2	111,021.5			2	1	203,563.1	203,562.2
		4	111,009.3				7	203,553.8	
		1	110,987.8			3	8	203,544.4	203,546.5
		1	110,975.7				4	203,533.9	
7 → 8		3	148,082.0				3	203,529.3	
		2	148,064.0				1	203,517.7	
	0	4	148,060.0	148,059.9			1	203,514.6	
	1	2	148,058.7	148,057.6			7	203,485.0	
		3	148,052.0			6	1	230,461.2	203,461.5
	2	4	148,050.4	148,050.7			4	203,449.5	
	3	7	148,038.6	148,039.3			4	203,441.2	
		4	148,035.3				2	203,413.7	
							2	203,409.5	
							1	203,303.5	
							0	(203,300)	

$p = 1, 2$ etc. will be stronger than the other doublets. Thus the doublets with $\bar{K} = 3, 6, 9$, etc. are expected to be stronger than those with $\bar{K} = 2, 4, 5, 7, 8$, etc. apart from the regular intensity factor which decreases with increasing K. The observed alternation of intensities among the doublets studied is according to this expectation.

RESULTS FOR THE EXCITED STATE $\nu_8 = 2$

The frequencies of the observed lines for the molecules in the excited state $\nu_8 = 2$ corresponding to the transitions $J = 4 \rightarrow 5, 5 \rightarrow 6, 7 \rightarrow 8$, and $10 \rightarrow 11$,
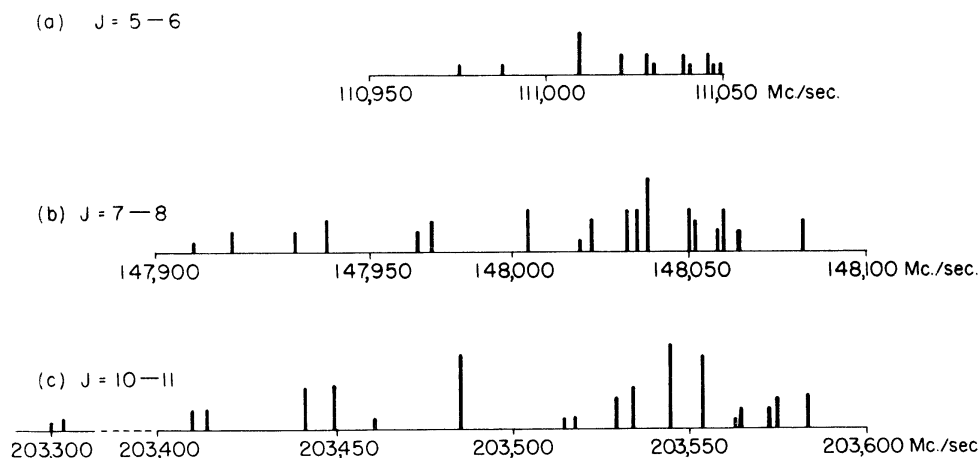
Fig. 3. A rough schematic representation of the spectral patterns observed for the transitions (a) $J = 5 \to 6$, (b) $J = 7 \to 8$, and (c) $J = 10 \to 11$ all with $v_8 = 2$.

are listed in Table V. The observed spectral patterns for the last three of those transitions are schematically shown in Fig. 3.

Some of the molecules in the overtone vibration $2v_8$ are expected to be in the vibrational state of species E with $l = \pm 2$ while others will be in the vibrational state of species A with $l = 0$. The observed lines appear to represent a mixture of both the species. It has not been possible as yet to assign uniquely the K and l values of all the different lines. However, it was possible to represent some of the lines by the equation

$$\nu = 18508.25(J + 1) - 0.12(J + 1)^3 - 0.286K^2(J + 1), \qquad (7)$$

and such lines probably belong to the molecules in the vibrational state $2v_8$ (A). The assignment of the K values for such lines and the corresponding calculated frequencies are included in Table V. The unassigned lines probably belong to the molecules in the vibration state $2v_8$ (E).

A comparison of Eq. (1) with Eq. (7) shows that $B = 9254.125$ Mc/sec, $D_{JK} = 143$ kc, and $D_J = 3$ kc. If the assignment of the lines is correct, the D_{JK} and D_J values thus come out to be smaller than those for the ground state while the D_{JK} and D_J values for the $v_8(e)$ state come out to be larger than those for the ground state. No definite conclusions can however be drawn unless the D_{JK} and D_J values are also obtained for the state $2v_8(E)$ which is possible only after the complete assignment of all the observed lines is made. Till then the present assignments shown in Table V can only be taken as tentative.

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