On the *l*-Type Doubling and *l*-Type Resonance of Molecules in the Microwave Region*

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The *l*-type doubling and the *l*-type resonance of molecules in the micro-wave region are phenomena which one encounters quite often but in many cases they are not correctly interpreted. The present work has the purpose, to make clear the theory and also to apply it to the interpretation of the spectra of some molecules: methyl cyanide, methyl acetylene, and tertiary butyl acetylene.

INTRODUCTION

The microwave spectra of several symmetric top molecules with C_{3v}-symmetry have been studied by different authors during the last decade. In some cases it was even possible to give a detailed account of the vibration-rotation-interaction. At the same time the theory has been developed to a large extent, due to Nielsen (*1, 2*), Amat (*3*), Grenier-Besson (*4*) and Maes (*5*).

This makes possible a more refined interpretation of microwave spectra of molecules, like methyl cyanide (*6–8*), methyl acetylene (*9*), and tertiary butyl acetylene (*10, 11*). Such a refined interpretation has been given recently in the case of trifluoro-methyl-acetylene by Grenier-Besson and Amat (*12*).

The purpose of the present work is to show how these theories, which are in every case a refinement of Nielsen's theory (*1, 2*), can be applied to the analysis of the spectra mentioned above. First, we recall briefly some notations which will be used throughout this text. Second, we describe the elements of the energy matrix and compare the formula given by Grenier-Besson and Amat (*12*) with the formula used by Venkateswarlu *et al.* (*7*). Third, we interpret referring to that formalism, the rotation-vibration spectra of some symmetric tops.

I. DOUBLING AND RESONANCE

It will be useful to recall some notations [following Grenier-Besson (*4*)]. Resonances *and* doubling may be defined as follows: Suppose, we have an effect

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which can be related to a matrix element

$$\langle v_s , \xi \mid h_n' \mid v_s , \xi' \rangle, \qquad\qquad n = 1, 2 \cdots ,$$

where v_s, the vibration quantum number is diagonal. ξ, ξ' represent the rest of the quantum numbers (J, K, l), h_n' is the nth-order Hamiltonian.

(a) $$\langle \xi \mid H' \mid \xi \rangle = \langle \xi' \mid H' \mid \xi' \rangle.$$

This means that two eigenvalues (ξ, ξ') are degenerate, as is well known. If a perturbation with matrix elements $\langle \xi \mid h_n' \mid \xi' \rangle$ destroys the degeneration, it is usually called "doubling."

(b) If, on the other hand,

$$\langle \xi \mid H' \mid \xi \rangle - \langle \xi' \mid H' \mid \xi' \rangle$$

is small but not zero, the shifting caused by $\langle \xi \mid h_n' \mid \xi' \rangle$ is called "resonance." We do not deal with "accidental" resonances here but only with resonances which are due to the matrix elements we wrote.

As has been shown by Nielsen (1), Grenier-Besson (4), Maes (5), and Amat (3), one can distinguish several types, and we list three of them:

(1) $$\Delta l_t = \pm 2, \qquad \Delta K = \pm 2.$$

This leads in the case of $K = \pm 1$, $l_t = \pm 1$ to that effect which is usually called l-type doubling, or, more precisely, it leads to rotational $l(2,2)$-type doubling.

(2) Rotational resonance and doubling of $l(2,-2)$-type. As this effect only exists for molecules with a symmetry or order 4, 6 $\cdots$ but not for molecules with a symmetry of order 3, we do not describe it in detail.

(3) Rotational resonances of type $l(2,-1)$. These resonances only exist for symmetry axes of order 3, 5 $\cdots$. But they cannot give a doubling, as has been shown by Nielsen (2) and Grenier-Besson (4). We have for CH_3CN an example for this "rotational resonance."

II. THIRD-ORDER CORRECTION FOR VIBRATION-ROTATION ENERGY OF A SYMMETRIC TOP WITH C_{3v}-SYMMETRY

Having stated the various possible effects of vibration-rotation interaction, following Nielsen (2), Amat (3), Grenier-Besson (4), and Maes (5), in Part II we want to show now how it is possible to take these effects quantitatively into account. Right from the beginning we confine ourselves to molecules with C_{3v}-symmetry. Thus we shall not mention matrix elements which are different from zero only for another symmetry.

Even among the matrix elements which can be attributed to a third-order perturbation we find some which, as Maes (5) has shown, contribute very little to the energy. As a matter of fact, in the region where $J \cong K \cong 1$, we find the

TABLE I

ENERGY MATRIX FOR $J = 1$[1]

	K	$l = 1$			$l = -1$		
		-1	0	1	-1	0	1
$l = 1$	-1	$L_{-1} - \Delta$				$-2F\sqrt{2}$	
	0		L_0				$2F\sqrt{2}$
	1			$L_1 + \Delta$	P		
$l = -1$	-1			P	$L_1 + \Delta$		
	0		$-2F\sqrt{2}$			L_0	
	1		$2F\sqrt{2}$				$L_{-1} - \Delta$

[1] It should be noted, that the elements L_0, etc. have not the same value as for the $J = 3$ matrix.

following matrix elements:

Second order:	Diagonal	Off-diagonal
Hamiltonian	$\langle vlK \mid vlK \rangle$	$\langle vlK \mid v, l \pm 2, K \pm 2 \rangle$
h_2'	Energy contrib. 2, 4, 6th order	l-type doubling: 4th order
		l-type resonance: 6th order
Third order:	$\langle vlK \mid vlK \rangle$	$\langle vlK \mid v, l \pm 2, K \pm 1 \rangle$
Hamiltonian	Energy contrib. 4, 6th order	6th order
h_3'	$\langle vlK \mid vlK \pm 3 \rangle$	$\langle vlK \mid v, l \pm 2, K \pm 3 \rangle$
	Energy contrib. 10th order	10th order

First, we write the matrix for $J = 1$ [Maes (5)]. This shows us (Table I) the essential form which also directs us to the $J = 3$ matrix (Table II). It is well known that the energy in our case can (until the second-order diagonal elements only) be described by the following equation:

$$E = E_v + B_v[J(J + 1) - K^2] + C_v K^2 - K l \zeta_8 B$$
$$- D_J J^2 (J + 1)^2 - D_{JK} J(J + 1) K^2 - D_K K^4. \tag{1}$$

The following values can be taken from Nielsen's second-order perturbation (1). It goes without saying that it would be entirely misleading to use in *this* respect a correction term corresponding to that used by Venkateswarlu, Baker, and Gordy (8). This correction term represents part of the third-order correction, but cannot account for everything which is due to the third-order perturbation. We shall refer to this term later on.

Now we shall calculate the energy matrix for $J = 3$.

Calculation of the diagonal elements $h_0' - h_1' - h_2'$

$$L_0(J = 3, K = 0, l = \pm 1)$$
$$= E_v + 12B_v - 144D_J, \tag{2a}$$

TABLE II

I, K	$l=1$							$l=-1$						
	-3	**-2**	**-1**	**0**	**1**	**2**	**3**	**-3**	**-2**	**-1**	**0**	**1**	**2**	**3**
$I=1$, $K=-3$	$L'_{-3}-3\Delta'''$								$\langle K\|l-2,K+1\rangle$					
$I=1$, $K=-2$		$L'_{-2}-2\Delta''$								$\langle K\|l-2,K+1\rangle$				
$I=1$, $K=-1$			$L'_{-1}-\Delta'$					$\langle K\|l-2,K-2\rangle$			$\langle K\|l-2,K+1\rangle$			
$I=1$, $K=0$				L'_0					$\langle K\|l-2,K-2\rangle$			$\langle K\|l-2,K+1\rangle$		
$I=1$, $K=1$					$L'_1+\Delta'$					$\langle K\|l-2,K-2\rangle$			$\langle K\|l-2,K+1\rangle$	
$I=1$, $K=2$						$L'_2+2\Delta''$					$\langle K\|l-2,K-2\rangle$			$\langle K\|l-2,K+1\rangle$
$I=1$, $K=3$							$L'_3+3\Delta'''$					$\langle K\|l-2,K-2\rangle$		
$I=-1$, $K=-3$			$\langle K\|l+2,K+2\rangle$					$L'_{-3}-3\Delta'''$						
$I=-1$, $K=-2$	$\langle K\|l+2,K-1\rangle$			$\langle K\|l+2,K+2\rangle$					$L'_{-2}-2\Delta''$					
$I=-1$, $K=-1$		$\langle K\|l+2,K-1\rangle$			$\langle K\|l+2,K+2\rangle$					$L'_{-1}-\Delta'$				
$I=-1$, $K=0$			$\langle K\|l+2,K-1\rangle$			$\langle K\|l+2,K+2\rangle$					L'_0			
$I=-1$, $K=1$				$\langle K\|l+2,K-1\rangle$			$\langle K\|l+2,K+2\rangle$					$L'_1+\Delta'$		
$I=-1$, $K=2$					$\langle K\|l+2,K-1\rangle$								$L'_2+2\Delta''$	
$I=-1$, $K=3$						$\langle K\|l+2,K-1\rangle$								$L'_3+3\Delta'''$

$$L_1(J = 3, K = 1, l = +1)$$
$$= E_v + 11B_v + C_v - 2\zeta C - 144D_J - 12D_{JK} - D_K, \tag{2b}$$

$$L_{-1}(J = 3, K = -1, l = +1)$$
$$= E_v + 11B_v + C_v + 2\zeta C - 144D_J - 12D_{JK} - D_K, \tag{2c}$$

$$L_2(J = 3, K = 2, l = +1)$$
$$= E_v + 8B_v + 4C_v - 4\zeta C - 144D_J - 48D_{JK} - 16D_K, \tag{2d}$$

$$L_{-2}(J = 3, K = -2, l = +1)$$
$$= E_v + 8B_v + 4C_v + 4\zeta C - 144D_J - 48D_{JK} - 16D_K. \tag{2e}$$

The selection rule $\Delta K = 0$ implies that L_3 and L_{-3} which are correlated with $K = \pm 3$ are not needed for the transition $J = 2 \to 3$. We shall not deal with these levels therefore. It can easily be shown that the rest of the diagonal (namely, the elements with $l = -1$, $l' = -1$) consists of the same elements, only with reversed order. It is obvious that L_{+n} and L_{-n} differ only in the term $-2Kl\zeta_3 C$. Now, for the submatrix with $l = 1$, $l' = 1$ we have K running from -3 to $+3$ and $l = 1$, L_n running from L_{-3} to L_{+3}. For the rest of the diagonal we have

$$-2Kl\zeta C = -2K| l |\zeta C.$$

It is clear that we have the same L_n, but running from L_{+3} to L_{-3} in this part.

Now we shall deal with the off-diagonal elements $\neq 0$.

First type

$$\langle v_t l_t K| h_2' |v_t, l_t \pm 2, K \pm 2 \rangle$$
$$= q_0 \{ [J(J + 1) - K(K \pm 1)][J(J + 1) - (K \pm 1)(K \pm 2)] \tag{3}$$
$$\times (v_t \mp l)(v \pm l + 2) \}^{1/2},$$

$$\langle -1, -1 | 1, 1 \rangle = q_0 \sqrt{576}, \tag{4a}$$

$$\langle -1, 0 | 1, 2 \rangle = q_0 \sqrt{480}, \tag{4b}$$

$$\langle -1, 1 | 1, 3 \rangle = q_0 \sqrt{240} \tag{4c}$$

From the fact that the matrix represented is Hermitian, we can conclude that

$$\langle \xi'| \alpha |\xi'' \rangle = \langle \xi''| \alpha |\xi' \rangle^*$$

which in our case is reduced to

$$\langle \xi'| \alpha |\xi'' \rangle = \langle \xi''| \alpha| \xi' \rangle.$$

Obviously, the calculation is simplified further on by the symmetry with regard to the second diagonal. This also applies to the second type of off-diagonal elements.

Second type
(There are only two different elements if we disregard the sign.)

$$\langle v, l, K | h_2' | v, l \pm 2, K \mp 1 \rangle = F(2K \mp 1)\{[J(J + 1) - K(K \mp 1)] \quad (5)$$

$$(v \pm l + 2)(v \mp l)\}^{1/2},$$

$$\langle -1,-2 | 1,-3 \rangle = \langle -1,-1 | 1,-2 \rangle = -F\sqrt{120}, \quad (5a)$$

$$\langle -1,0 | 1,-1 \rangle = -F\sqrt{48}. \quad (5b)$$

To clarify the l-type doubling matrix elements

$$\langle l, K | l + 2, K + 2 \rangle,$$

we write the following part of the matrix:

$$\begin{bmatrix} \cdots & \langle -1,-3 | 1,-1 \rangle & 0 & 0 & 0 & 0 & \cdot \\ \cdots & 0 & \langle -1,-2 | 1,0 \rangle & 0 & 0 & 0 & \cdot \\ \cdots & 0 & 0 & \langle -1,-1 | 1,1 \rangle & 0 & 0 & \cdot \\ \cdots & r & 0 & 0 & \langle -1,0 | 1,2 \rangle & 0 & \cdot \\ \cdots & 0 & r & 0 & 0 & \langle -1,1 | 1,3 \rangle & \cdot \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}.$$

We have the relation $P = 4q_0$, from which we get

$$q_0\sqrt{240} = P\sqrt{15},$$

$$q_0\sqrt{480} = P\sqrt{30},$$

$$q_0\sqrt{576} = 6P.$$

Hence, the definite form of the l-type doubling elements of the $(J = 3)$ matrix is

$$\begin{bmatrix} \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdots & P\sqrt{15} & 0 & 0 & 0 & 0 & \cdot \\ \cdots & 0 & P\sqrt{30} & 0 & 0 & 0 & \cdot \\ \cdots & 0 & 0 & 6P & 0 & 0 & \cdot \\ \cdots & r & 0 & 0 & P\sqrt{30} & 0 & \cdot \\ \cdots & 0 & r & 0 & 0 & P\sqrt{15} & \cdot \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}.$$

There are still other matrix elements which should be mentioned. They may be neglected as (in the case of $J \cong K \cong 1$) they are contributing to the energy

etc. (For $\pm r$ we substitute $|r|$ and write it simply: r; where $\pm r = \langle lK \mid l \pm 2, K \mp 1 \rangle$.) This results in the factorized matrix (Table III). The matrix consists of four submatrices, as can easily be seen:

$$\begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix},$$

$A_{12} = 0$, in other words, A_{12} is a null-matrix. A_{21} plays no role in the result of the determinant.

This can be shown by induction beginning with the following simple case.

$$\begin{vmatrix} a_1 & b_1 & 0 & 0 \\ a_2 & b_2 & 0 & 0 \\ a_3 & b_3 & c_3 & d_3 \\ a_4 & b_4 & c_4 & d_4 \end{vmatrix} = \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} \times \begin{vmatrix} c_3 & d_3 \\ c_4 & d_4 \end{vmatrix}.$$

This completes the proof that the energy matrix can be factorized.

Next comes the solution of the "unperturbed problem." As is well known, in the unperturbed problem we disregard the matrix elements except the diagonal elements. The results are, therefore,

$$
\begin{aligned}
X &= L_0, \\[4pt]
X &= L_{-1}, \qquad X = L_{+1} \pm 6P, \\[4pt]
X &= L_{-2}, \qquad X = L_{+2}, \\[4pt]
(X &= L_{-3}), \qquad (X = L_{+3}).
\end{aligned}
\qquad (7)
$$

[For the explicit values see Eqs. (2a–e).]

To solve the "perturbed problem" requires an answer to the question how the matrix can be reduced further. If we take a submatrix of the factorized $J = 3$ matrix, it is immediately evident that the reduction is a procedure similar to the reduction of the $J = 1$ matrix (Table I). We further write the unitary matrices which can be used for reducing by a similarity transformation. The unitary matrix $\mathbf{U}$ transforms the submatrix $\mathbf{A}$ as follows:

where $$\mathbf{U}\mathbf{A}\mathbf{U}^{-1} = \mathbf{A}^*,$$

$$\mathbf{U} = \begin{Vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{Vmatrix},$$

$$\mathbf{A} = \begin{Vmatrix} a_{11} & 0 & 0 & 0 & 0 & a_{16} & 0 \\ 0 & a_{22} & 0 & 0 & a_{25} & 0 & 0 \\ 0 & 0 & a_{33} & a_{34} & 0 & 0 & a_{37} \\ 0 & 0 & a_{43} & a_{44} & 0 & a_{46} & 0 \\ 0 & a_{52} & 0 & 0 & a_{55} & 0 & 0 \\ 0 & 0 & 0 & a_{64} & 0 & a_{66} & 0 \\ 0 & 0 & a_{73} & 0 & 0 & 0 & a_{77} \end{Vmatrix},$$

$$\mathbf{A^*} = \begin{Vmatrix} a_{11} & 0 & 0 & a_{16} & & & & \\ 0 & a_{22} & a_{25} & 0 & & & & \\ 0 & a_{52} & a_{55} & 0 & & & & \\ a_{61} & 0 & 0 & a_{66} & 0 & a_{64} & 0 \\ & & & 0 & a_{33} & a_{34} & a_{37} \\ & & & a_{46} & a_{43} & a_{44} & 0 \\ & & & 0 & a_{73} & 0 & a_{77} \end{Vmatrix},$$

$\mathbf{A^*}$ explicitly written:

$L_{-3} - 3\Delta'''$	0	0	$\mid F \mid \sqrt{120}$			
0	$L_{-2} - 2\Delta''$	$\mid F \mid \sqrt{120}$	0			
0	$\mid F \mid \sqrt{120}$	$L_1 + \Delta' + 6P$	0			
$\mid F \mid \sqrt{120}$	0	0	$L_2 + 2\Delta''$	0	$P\sqrt{30}$	0
			0	$L_{-1} - \Delta'$	$\mid F \mid \sqrt{48}$	$P\sqrt{15}$
			$P\sqrt{30}$	$\mid F \mid \sqrt{48}$	L_0	0
			0	$P\sqrt{15}$	0	$L_3 + 3\Delta'''$

To calculate the secular determinant, some evident changes of rows and columns are made:

$L_{-2} - 2\Delta''$	$\mid F \mid \sqrt{120}$					
$\mid F \mid \sqrt{120}$	$L_1 + \Delta' + 6P$					
		$L_2 + 2\Delta''$	0	$P\sqrt{30}$	0	0
		0	$L_{-1} - \Delta'$	$\mid F \mid \sqrt{48}$	0	$\mid F \mid \sqrt{120}$
		$P\sqrt{30}$	$\mid F \mid \sqrt{48}$	L_0	$P\sqrt{15}$	0
		0	0	$P\sqrt{15}$	$L_3 + 3\Delta'''$	0
		0	$\mid F \mid \sqrt{120}$	0	0	$L_{-3} - 3\Delta'''$

From this form of $\mathbf{A^*}$ we write the secular determinant.

The secular determinant for $J = 3$ is

$$\det \parallel A^*_{ik} \parallel = \{(L_{-2} - 2\Delta'' - X - \Delta X)(L_1 + \Delta' \pm 6P - X - \Delta X)$$

$$- 120\,F^2\} \times \{(L_2 + 2\Delta'' - X - \Delta X)[(L_{-1} - \Delta' - X - \Delta X)$$

TABLE III

FACTORIZED MATRIX ($J = 3$)

Block I:

$$\begin{pmatrix}
L_3-3\Delta''' & |F|\sqrt{120} & & & & & \\
|F|\sqrt{120} & L'_2-2\Delta'' & |F|\sqrt{48} & & & & \\
 & |F|\sqrt{48} & L_1-\Delta & |F|\sqrt{48} & P\sqrt{15} & & \\
 & & |F|\sqrt{48} & L'_0 & |F|\sqrt{120} & P\sqrt{30} & \\
 & P\sqrt{15} & & |F|\sqrt{120} & L'_1+\Delta'+6P & |F|\sqrt{120} & \\
 & & P\sqrt{30} & & |F|\sqrt{120} & L'_2+2\Delta'' & P\sqrt{30} \\
 & & & & & P\sqrt{15} & L'_3+3\Delta'''
\end{pmatrix}$$

Block II:

$$\begin{pmatrix}
L'_3-3\Delta''' & -|F|\sqrt{120} & & & & & \\
-|F|\sqrt{120} & L'_2-2\Delta'' & -|F|\sqrt{120} & & & & \\
 & -|F|\sqrt{120} & L'_1-\Delta' & -|F|\sqrt{48} & -P\sqrt{15} & & \\
 & & -|F|\sqrt{48} & L'_0 & -|F|\sqrt{120} & -P\sqrt{30} & \\
 & -P\sqrt{15} & & -|F|\sqrt{120} & L'_1+\Delta'-6P & -|F|\sqrt{120} & \\
 & & -P\sqrt{30} & & -|F|\sqrt{120} & L'_2+\Delta'' & -P\sqrt{15} \\
 & & & & & -P\sqrt{15} & L'_3+\Delta'''
\end{pmatrix}$$

$$\times (L_0 - X - \Delta X) \times (L_3 + 3\Delta''' - X - \Delta X) - 15P^2) - 48F^2\,(L_3$$

$$+ 3\,\Delta''' - X - \Delta X)\,(L_0 - X - \Delta X) - 15P^2)] - 30P^2[(L_{-1} - \Delta' - X$$

$$- \Delta X)\,(L_3 + 3\Delta''' - X - \Delta X)\,(L_{-3} - 3\Delta''' - X - \Delta X) + 120F^2(L_3$$

$$+ 3\Delta''' - X - \Delta X)]\} = 0.$$

The energy levels due to h_0', $+h_i + h_2' + h_3'$ for $J = 3$ in terms of microwave-spectroscopic parameters.

(The third-order terms Δ', etc. are written explicitly below.)

$K = 0$

$$L_0' = E_v + 12B_v - 144D_J$$

$l = \pm 1$
$$+ \frac{15\,P^2}{2(B_v - C_v + \zeta C)} - \frac{48\,F^2}{B_v - C_v - 2\zeta C}\,, \tag{8a}$$

$K = l$

$$L_1' = E_v + 11\,B_v + C_v - 2\zeta C - 144\,D_J - 12D_{JK}$$

$l = \pm 1$
$$\pm 6P + \frac{120\,F^2}{B_v - C_v - 2\zeta C} + \Delta'\,, \tag{8b}$$

$K = -l$

$$L_{-1}' = E_v + 11\,B_v + C_v + 2\zeta C - 144\,D_J - 12\,D_{JK}$$

$-l = \pm 1$
$$+ \frac{15\,P^2}{8(B_v - C_v + \zeta C)} - \frac{48\,F^2}{B_v - C_v - 2\zeta C} - \Delta'\,, \tag{8c}$$

$K = \pm 2$

$$L_2' = E_v + 8\,B_v + 4\,C_v - 4\zeta C - 144\,D_J - 48\,D_{JK}$$

$l = \pm 1$
$$+ \frac{6\,P^2}{B_v - C_v + \zeta C} + \frac{120\,F^2}{B_v - C_v - 2\zeta C} + 2\Delta''\,, \tag{8d}$$

$K = \pm 2$

$$L_{-2}' = E_v + 8\,B_v + 4\zeta C - 144\,D_J - 48\,D_{JK}$$

$l = \mp 1$
$$- \frac{120\,F^2}{B_v \mid C_v - 2\zeta C} - 2\,\Delta''\,. \tag{8e}$$

L_3 and L_{-3} are not needed explicitly due to the selection rule $\Delta K = 0$. The third-order rotation-vibration-energy terms from the diagonal are in general

given by the following formula (5):

$$\Delta E \, l_8 \, K \left[\eta_{8,J} \, J(J+1) + \eta_{8,K} \, K^2 + \eta_8 + 2\eta_{8,8} + \sum_{\substack{s \\ (s \neq 8)}} \eta_{8,s} \frac{g_s}{2} \right]. \qquad (9)$$

For $J = 3$ they are, if $|\, l \,| = 1$,

$$\Delta L_0 = 0,$$

$$\Delta L_1' = \left[12\eta_{8,2} + \eta_{8,-1} + \eta_8 + 2\eta_{8,8} + \sum_s \eta_{8,s} \frac{g_s}{2} \right] = \Delta',$$

$$\Delta L_{-1}' = - \left[12\eta_{8,3} + \eta_{8,1} + \eta_8 + 2\eta_{8,8} + \sum_s \eta_{8,s} \frac{g_s}{2} \right] = - \Delta',$$

$$\Delta L_2' = 2 \left[12\eta_{8,3} + 4\eta_{8,-2} + \eta_8 + 2\eta_{8,8} + \sum_s \eta_{8,s} \frac{g_s}{2} \right] = 2\Delta'',$$

$$\Delta L_{-2}' = -2 \left[12\eta_{8,3} + 4\eta_{8,2} + \eta_8 + 2\eta_{8,8} + \sum_s \eta_{8,s} \frac{g_s}{2} \right] = -2\Delta''.$$

For practical reasons, however, it is useful, not to take the energy levels, but rather their differences. We shall have to deal now with the formulas which represent these differences.

(a) There are essentially three formulas for nonrigid symmetric tops: We obtain a frequency formula from Nielsen's work regarding the second-order perturbation. It is used by Venkateswarlu, Baker, and Gordy (8) to describe CH_3CN rotation-vibration interaction.

$$\nu = 2B_v(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2$$
$$+ 4(D_J + D_{JK})(J+1)Kl\zeta_8 + \Delta P(J, K, l), \qquad (10)$$

where

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

and

$$\Delta P(J, K, l) = \frac{(J+1)\,[(J+1)^2 - (K+1)^2]}{K \pm 1} \times \frac{q^2}{4[C(1 - \zeta) - B_v]} \qquad (11)$$
$$\text{for } K \neq l = \pm 1.$$

C, B_v, D_J, and D_{JK} are the well-known constants; q and ζ_8 refer to l-type doubling and coriolis doubling, respectively.

Nonetheless, it is necessary to introduce a semiempirical correction term which in some cases even gets an order of magnitude comparable with the split-

ting described by Nielsen's theory. We shall treat this problem in more detail in Part III.

(b) A more refined treatment (also of second order) has been devised by Grenier-Besson (*4*). It stresses that there is an influence of the off-diagonal elements on the energy levels.

(c) Grenier-Besson and Amat give a formula (*12*) which is an extension of Maes' third-order perturbation calculation. We use this third-order perturbation throughout the text.

The formula runs as follows:

$$\begin{aligned} = {}& 2B^*(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)(Kl-1)^2 \\ & + 2\rho^*(J+1)(Kl-1) \pm 4q_J(J+1) \\ & - 4q_J{}^2(J+1)^3/(B_v - C_v + C_v\zeta)(Kl-1) \end{aligned}$$

(12)

$$\text{(for } Kl = +1)\quad \text{(for } Kl \neq +1).$$

Here B_v and C_v designate the same constants of inertia. The constants D_J, D_{JK}, and ζ_8 have the same meaning as above. q_J is the constant of $l2,2$-type doubling, r the constant of $l2,-1$-resonance, η_{tJ} the coefficient of the term in $KlJ(J+1)$. These constants are related to B^* and ρ^* as has been shown by Amat (*12*):

$$B^* = B_v{}^+ - D_{JK} + \rho,\tag{13a}$$

$$\rho^* = \rho - 2D_{JK} + 2q_J{}^2/(B_v - C_v + C_v\zeta),\tag{13b}$$

and

$$B_v{}^+ = B_v + 4r^2/(B_v - C_v - 2C_v\zeta) \cong B_v,\tag{14a}$$

$$\rho = \eta_{tJ} + 8r^2/(B_v - C_v - 2C_v\zeta).\tag{14b}$$

If we note that $r = F$, and $P = 4q_J$, it can be seen that every term of Eq. (12) is related to the third-order perturbation described above, or is related to lower order perturbations plus the unperturbed state. To compare the two formulas (Venkateswarlu, Baker, and Gordy (*8*) and Grenier-Besson and Amat (*12*) we write them as follows:

Grenier-Besson and Amat (*12*)	Venkateswarlu *et al.* (*8*)
$2B_v(J+1)$	$2B_v(J+1)$
$-4D_J(J+1)^3$	$-4D_J(J+1)^3$
$-2D_{JK}(J+1) - 2D_{JK}(J+1)K^2$ $\quad + 4D_{JK}(J+1)Kl$	$-2D_{JK}(J+1)K^2$
$-2D_{JK}(J+1) - 4D_{JK}(J+1)Kl$ $\quad + 4D_{JK}(J+1)$	

$2\eta_{tJ}(J + 1) + 2\eta_{tJ}(J + 1)Kl$
$$- 2\eta_{tJ}(J + 1)$$

$4(2D_J + D_{JK})(J + 1)Kl\zeta_8$ [which bases on a false equation (11)]

$$\frac{24 \, r^2}{B_v - C_v - 2C_v\zeta_8} (J + 1)$$

(In this formula there is no term corresponding to r^2)

$$\frac{16 \, r^2}{B_v - C_v - 2C_v\zeta_8} (Kl - 1)(J + 1)$$

(In this formula there is no term corresponding to r^2)

$$+ \frac{4 \, q^2}{B_v - C_v + C_v\zeta_8} (J + 1)(Kl - 1)$$

$$- \frac{q^2(J + 1)[(J + 1)^2 - (Kl - 1)^2]}{(B_v - C_v + C\zeta_8)(Kl - 1)}$$

$$- \frac{4 \, q^2}{(B_v - C_v + C_v\zeta_8)(Kl - 1)} (J + 1)^3$$

(for $Kl \equiv +1$)

No correction term needed.

Correction term: $+4\epsilon\zeta_8 Kl(J + 1)$

Result: The comparison of these two formulas shows (apart from many terms which are identical for both):

(a) Terms which are not included at all in Venkateswarlu, Baker, and Gordy, but in Grenier-Besson and Amat (those with r^2) (12).

(b) Terms which are comparable only to some approximation (η_{tJ}).

(c) On the other hand, we have from Venkateswarlu, Baker, and Gordy (8) a correction term which allows us to predict the experimental frequencies:

$$4\epsilon\zeta_8 Kl(J + 1).$$

We shall deal with this correction term in more detail in Part III in the case of CH_3CN.

As has been shown by Maes (5) the expression $4(2D_J + D_{JK})(J + 1)Kl\zeta_8$ can only be compared to a very limited extent with the expression containing the factor η_{tJ}. Furthermore, it can be shown that there are other differences between the comparable terms. These differences may be partly explained by the fact that the following commutators have been neglected in Nielsen's theory (5).

$$[p_a p_\alpha , q_b] \quad \text{and} \quad [p_a , q_b p_\alpha],$$

where

$$i\hbar[p_a p_\alpha , q_b] = p_a p_\alpha q_b - q_b p_a p_\alpha \neq 0$$

by the well-known definition of the Poisson-brackets (13). p_a is an internal (vibrational) angular momentum and p_α its projection on an axis α of the molecule. q_b can be regarded as a conjugate coordinate. This suggests that relatively important operators are still neglected. We shall see that from a quite different viewpoint in Part III, namely, in the drastic correction term for CH_3CN, not to mention the $\langle K \mid K \pm 3 \rangle$ elements.

To make the application of the formula of Grenier-Besson and Amat (*12*) more obvious, we state the splitting which can be calculated by that formula:

K	l	$Kl-1$	$\Delta\nu = \nu' - \nu''$
± 2	± 1	1	
0	∓ 1	-1	$2(J+1)\rho^* \times 2 - \dfrac{4q^2(J+1)^3 \times 2}{B_v - C_v + C\zeta}$
± 3	± 1	2	
± 1	∓ 1	-2	$2(J+1)\rho^* \times 4 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 2}$
± 4	± 1	3	
± 2	∓ 1	-3	$2(J+1)\rho^* \times 6 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 3}$
± 5	± 1	4	
± 3	∓ 1	-4	$2(J+1)\rho^* \times 8 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 4}$
± 6	± 1	5	
± 4	∓ 1	-5	$2(J+1)\rho^* \times 10 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 5}$
± 7	± 1	6	
± 5	∓ 1	-6	$2(J+1)\rho^* \times 12 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 6}$
± 8	± 1	7	
± 6	∓ 1	-7	$2(J+1)\rho^* \times 14 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 7}$
± 9	± 1	8	
± 7	∓ 1	-8	$2(J+1)\rho^* \times 16 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 8}$
± 10	± 1	9	
± 8	∓ 1	-9	$2(J+1)\rho^* \times 18 - \dfrac{4q^2(J+1)^3 \times 2}{(B_v - C_v + C\zeta) \times 9}$

III. APPLICATION OF PART II TO SOME MOLECULES

In this part we shall apply the formalism of Part II for the interpretation of microwave absorption spectra. We confine the calculations to vibrations with $v = 1, l = \pm 1$.

Let us take *methyl cyanide* (CH_3CN) as our first example. We shall first calculate the spectrum for $J = 1 \rightarrow 2$. Kessler *et al.* (*6*) who measured this transition for the first time, have reported three lines (compared to four in the transition of CH_3NC and other similar molecules). However, it is not difficult to show that these measurements can be explained very well by the third-order perturbation based on the following equations (*5*):

$$(K = l = \pm 1)$$

$$\nu_1 = 4B_v + 2P - 32D_J - 4D_{JK} + [48F^2/(B_v - C_v - 2\zeta C)] + 4\eta_{8,J}, \quad (15a)$$

$(K = l = \pm 1)$

$$\nu_2 = 4B_v - 2P - 32D_J - 4D_{JK} \tag{15b}$$
$$+ [48F^2/(B_v - C_v - 2\zeta C)] + 4\eta_{8,J},$$

$(K = -l = \pm 1)$
$$\nu_3 = 4B_v - 32D_J - 4D_{JK} \tag{15c}$$
$$- [16F^2/(B_v - C_v - 2\zeta C)] + 4\eta_{8,J},$$

$(K = 0, l = \pm 1)$
$$\nu_4 = 4B_v - 32D_J$$
$$+ [3P^2/2(B_v - C_v + \zeta C)] + [16F^2/(B_v - C_v - 2\zeta C)]. \tag{15d}$$

Now it even seems that for $\nu_3 = \nu_4$ (for CH_3CN) the interpretation is simplified because, compared with CH_3NC, it is easier to make an assignment.

For CH_3NC two possibilities remain. On the other hand, it may be questioned whether there are *really* only three lines. This was indeed the question which was put forward first by Amat (*14*). We reason as follows:

A transition $(J \rightarrow J + 1)$ has two extreme lines (corresponding to $Kl - 1 = 0$), and the lines of the central group [consisting of $J - 1 = 0$ doublets

$$(Kl - 1 \neq 0)$$

and two singlets $Kl - 1 = -J$, $Kl - 1 = -(J + 1)$]. This has been proved by Amat (*12*). This means for $J = 1 \rightarrow 2$ that the central group just consists of two singlets. It does not seem probable to find only *one* instead of two singlets, as might have been the case with a not resolved doublet.

Now the point is that Sheridan (*14*), following Amat's consideration (*14*) found the second line of the central group, which had been missing so far. Now it is possible to make a self-consistent interpretation of the *four* lines. The values do not differ very much from Maes' calculation with three lines (*5*). But then we shall also make calculations with the other possible assignment of the singlets. Which assignment is to be preferred, however, will be seen only after inspecting the higher transitions.

The calculation differs from Maes' calculation (*5*) only insofar as we have different values. The frequencies measured are [ν_1, ν_4, ν_2 Kessler *et al.* (*6*), ν_3 Sheridan only (*14*)], divided into a doublet (ν_1, ν_2) and two singlets (ν_3, ν_4):

$Kl - 1 = 0$	$\nu_1 = 36\ 942.00$ Mc/sec,
$Kl - 1 = 0$	$\nu_2 = 36\ 870.85$ Mc/sec,
Singlet	$\nu_3 = 36\ 905.50$ Mc/sec $(K = -l = \pm 1)$,
Singlet	$\nu_4 = 36\ 903.31$ Mc/sec $(K = 0, l = \pm 1)$.

Kessler *et al.* (6) and Sheridan (14) report values which are equal in the limits of experimental error (except ν_3). The following constants will be used:

$$B_0 = 9198.70 \pm 0.2 \text{ Mc/sec } (6),$$

$$\alpha_8 = -22.5 \pm 10 \text{ Mc/sec } (6)$$

$$B_v = 9221.2 \pm 10 \text{ Mc/sec } (6)$$

$$D_{JK} = 0.178 \pm 0.01 \text{ Mc/sec } (6)$$

Another value has been reported also but we shall not use it. From the structure of CH_3CN we get $C = 158\,400$ Mc/sec, where $C_v = C \pm 1\%$, which is entirely within the limits of error. Therefore it makes no difference whether we use C_v or C. In addition to that, we shall use the difference

$$C_v - B_v = 149\,179 \text{ Mc/sec.} \tag{16a}$$

From Eqs. (15a and b) it is obvious that

$$\tfrac{1}{4}(\nu_1 - \nu_2) = P = 17.79 \text{ Mc/sec.} \tag{16b}$$

Moreover, we get

$$\nu_4 - \nu_3 = 4D_{JK} + [3P^2/(2B_v - 2C_v + 2\zeta C)]$$
$$+ [32F^2/(B_v - C_v - 2\zeta C)] + 4\eta_{8,J} = -2.19 \pm 0.01 \text{ Mc/sec} \tag{17}$$

from Eqs. (15c and d). Here we get for the first time a difference from the calculation with $\nu_4 = \nu_3$. This difference, however, has only a small influence on the results. We get from Eqs. (15b and c)

$$\nu_3 - \nu_2 = 2P - [64F^2/(B_v - C_v - 2\zeta C)] - 8\eta_{8,J}$$
$$= 34.65 \pm 0.02 \text{ Mc/sec} \tag{18}$$

and

$$\tfrac{1}{2}(\nu_3 - \nu_2) = 17.325 \text{ Mc/sec,}$$

which, in connection with

$$\tfrac{1}{2}(\nu_3 + \nu_2) = 36\,888.175 \text{ Mc/sec,}$$

leads to the following equation:

$$\nu_4 - \tfrac{1}{2}(\nu_3 + \nu_2) = P + 4D_{JK} + 3P^2/(2B_v - 2C_v + 2\zeta C)$$
$$= 15.135 \text{ Mc/sec} \pm 0.02 \text{ Mc/sec.} \tag{19}$$

Taking into account that $P = 17.79$ Mc/sec and $4D_{JK} = 0.712$ Mc/sec, we get from Eqs. (15d) and (19) the following result:

$$475.025/3.377 = C_v - B_v - \zeta C. \tag{20a}$$

Remembering the value for $C_v - B_v$ (8) this is

$$C_v - B_v - \zeta C = 140.6 \text{ Mc/sec.} \tag{20b}$$

Therefore,

$$\zeta_8 = 0.9409, \tag{20c}$$

which is in good agreement with the values from the infrared (8). Moreover,

$$B_v - C_v - 2\zeta C = -447.129 \text{ Mc/sec.}$$

From Eq. (17) we get

$$4\eta_{8J} = 1.57 + 32F^2/447\ 121. \tag{21}$$

As F^2 is not known, this gives only a limit for η_{8J}

$$\eta_{8J} > 0.393.$$

Now we take into account the absolute frequencies:

$$\nu_4 = 4B_v - 32D_J + [3P^2/(2B_v - 2C_v + 2\zeta_8 C)] \\ + [16F^2/(B_v - C_v - 2\zeta_8 C)]. \tag{22}$$

As D_J is small compared with all other quantities, we may neglect it. If we take the value for B_v mentioned above we shall have the difficulty that $16F^2/447\ 121$ turns out to be -20.88 Mc/sec. Therefore we take the value $B_v = 9226.44$ Mc/sec (8) which is more reliable. With these values we get

$$4B_v = 36\ 905.76 \text{ Mc/sec,}$$

$$-\nu_4 = -36\ 903.31 \text{ Mc/sec.}$$

The difference, together with Eq. (17) results in the following equation:

$$16F^2/447\ 121 = -1.12 \text{ Mc/sec.} \tag{23}$$

This is no longer an incompatible result compared with -20.88 Mc/sec. It rather speaks for the precision of the value B_v of Venkateswarlu *et al.* (8). This value is also compatible with

$$\alpha_8 < -27.7,$$

namely,

$$\alpha_8 = -27.5,$$

based on

$$B_v = B_0 - \sum_s \alpha_s(v_s + \tfrac{1}{2}g_s).$$

Although one cannot give very precise values for α_8, it nevertheless fits remarkably well into our assumptions.

Now it remains to test whether the order of magnitude is reasonable.

$$B_v \gg P \gg D_{JK} \cong P^2/(4C_v - 4B_v + 4C)$$

$$\cong \eta_{8,J} + 8F^2/(B_v - C_v - 2\zeta C), \quad (24\text{a})$$

$$9.226.44 \gg 17.79 \gg 0.178 \cong 0.33 \cong 0.39. \quad (24\text{b})$$

As Maes (*5*) has shown, the elements

$$\langle K| \, {}^{\alpha}h_3' \, |l \pm 2, K \mp 1 \rangle$$

are of the same order of magnitude as the elements

$$\langle K| \, {}^{\alpha\beta\gamma}h_3' \, |K \rangle$$

in the range $J \cong K \cong 1$ (third-order contribution). They are even equal in the limits of experimental error, so that it is impossible to separate their influence. On the other hand, for very high J and $K(\cong 30)$ this is no longer necessarily true.

This is not the only assignment which is possible. It will be remembered that the singlets can also be assigned in another way whereas the *l*-type doublets $(Kl - 1 = 0)$ remain. Therefore, our next calculation is based on the following assumptions:[1]

$Kl - 1 = 0 \qquad \nu_1 = 36\ 942.00$ Mc/sec,

$Kl - 1 = 0 \qquad \nu_2 = 36\ 870.85$ Mc/sec,

Singlet $\qquad \nu_3 = 36\ 903.31$ Mc/sec $(K = -l = \pm 1)$,

Singlet $\qquad \nu_4 = 36\ 905.50$ Mc/sec $(K = 0, l = \pm 1)$.

The constants B_0, α_8, B_v, D_{JK}, $C \cong C_v$ are the same as before,

$$\tfrac{1}{4}(\nu_1 - \nu_2) = P = 17.79 \text{ Mc/sec (as before)}, \quad (25)$$

$$\nu_4 - \nu_3 = 4D_{JK} + [3P^2/(2B_v - 2C_v + 2\zeta C)]$$
$$+ [32F^2/(B_v - C_v - 2\zeta C)] + 4\eta_{8,J} = +2.19 \text{ Mc/sec.} \quad (26)$$

For the other differences we get the following values:

$$\nu_3 - \nu_2 = 2P - [64F^2/(B_v - C_v - 2\zeta C)] - 8\eta_{8,J}$$
$$= 32.46 \text{ Mc/sec,} \quad (27)$$

$$\tfrac{1}{2}(\nu_3 + \nu_2) = 36\ 887.08 \text{ Mc/sec,} \quad (28)$$

$$\nu_4 - \tfrac{1}{2}(\nu_3 + \nu_2) = 18.420 \text{ Mc/sec.} \quad (29)$$

[1] The process of calculating is exactly the same as for the other assignment.

If we take into account the values $P = 17.79$ and $4D_{JK} = 0.712$ we get with the relation

$$C_v - B_v - \zeta C = \frac{3}{2} \frac{P^2}{P + 4D_{JK} - \left(\nu_4 - \dfrac{\nu_3 + \nu_2}{2}\right)} \tag{30}$$

the following result:

$$474.725/0.082 = 5789.3 \text{ Mc/sec} = C_v - B_v - \zeta C. \tag{31}$$

We shall come back to this result later. If we refer to the values of B_v and C_v, this result now contains also a value for ζ_8 :

$$\zeta_8 = 0.905.$$

This value is not so good compared with $\zeta_8 = 0.9409$. But the values for the higher transitions imply strongly that this value is nevertheless to be preferred. From

$$4\eta_{8J} = 1.56 + 32F^2/435\,883, \tag{32}$$

we can give the limit $\eta_{8J} > 0.39$ as well as the relation

$$0.18 = 16F^2/447\,121. \tag{33}$$

Now we shall deal with some aspects of the higher transitions. The transitions from $J = 4 \rightarrow 5$ to $J = 11 \rightarrow 12$ have been measured by Venkateswarlu et al. (8). We make some preliminary remarks:

(a) The correction term of Eq. (10): $8\epsilon\zeta K(J + 1)$ is of the same order of magnitude as the splitting. For example, for $J = 5 \rightarrow 6$ and $K = 1$ the splitting is

$$\Delta\nu_{K,K-2} = 3.97 \text{ Mc/sec.}$$

The correction term for these quantum numbers is

$$8\epsilon\zeta K(J + 1) = 1.43 \text{ Mc/sec.}$$

For higher K the correction term even becomes larger than the splitting itself.

(b) It sometimes occurs that it is no longer possible to divide the lines into an l-type doublet with extreme frequency values and the central group on the other hand. For example, for $J = 10 \rightarrow 11$ the frequency observed for $K = 10$ is 202 655.71 Mc/sec. On the other hand, the frequency for $Kl - 1 = 0$ is 202 769.94 Mc/sec. Although the latter frequency is supposed to be the lowest of that group, this is evidently not the case.

(c) As is well known the center of gravity of the doublets should be a function of K^2, if we take the center of the $Kl - 1 = 0$ lines as origin. But if the centers of these lines vary with K^2 the first differences should be linear functions

of K and the second differences should be constant. A brief look at these second differences shows that they are evidently not constant. For $J = 5 \to 6$ we have, for example, the following second differences:

$$4.20 \text{ Mc/sec} \quad 3.50 \text{ Mc/sec} \quad 5.42 \text{ Mc/sec.}$$

Remarks (b) and (c) have the immediately evident consequence that some values of the measured frequencies (8) should not get the same treatment as the majority of the values. For example: for $J = 11 \to 12$ the first of a series of second differences is 7.890, whereas the other values are 8.655, 8.555, 8.470, and 8.300 (Mc/sec). The frequencies connected with the first of these differences will evidently not give the same results as frequencies connected with 8.655, etc. Therefore we shall drop these values, and also the ones in connection with (b).

The l-type doubling constant P from seven transitions is $P = 17.782$ Mc/sec which is in excellent agreement with $P = 17.79$ Mc/sec from $J = 1 \to 2$.

Now it is possible to calculate the constant ρ^* [see Grenier-Besson and Amat (12)], and $B_v - C_v + \zeta C$. Instead of using the latter constant it is more convenient to use $1/(B_v - C_v + \zeta C)$, which we call y. We shall explain the method to calculate these constants for two transitions. The splitting for $J = 8 \to 9 K = 5$ and 3 gives the following value:

$$\Delta \nu = 7.12 \text{ Mc/sec.}$$

On the other hand

$$7.12 = 2(J + 1)\rho^* \times 8 - 4q^2(J + 1)^3 \times 2/(B_v - C_v + C\zeta) \times 4.$$

If we take the appropriate numerical values, this leads to the equation

$$\Delta \nu = 7.12 = 144\rho^* - 28\ 807y. \tag{34}$$

In the same way we get for $J = 9 \to 10$, $K = 6$ and 4 the following equation:

$$8.92 = 2(J + 1)\rho^* \times 10 - 4q^2(J + 1)^3 \times 2/(B_v - C_v + C\zeta) \times 5.$$

The numerical values give for this equation

$$8.92 = 200\rho^* - 31\ 612.8\ y. \tag{35}$$

From these two equations we get as results

$$-y = 0.0001154 \quad \text{(which corresponds to } 1/y = 8665 \text{ Mc/sec)}$$

and $\rho^* = 0.024$ Mc/sec. If we take many transitions into account we eventually get the following values:

$$y = -0.000118 \quad \text{(which corresponds to } 1/y = 8475 \text{ Mc/sec)} \quad \text{and}$$

$$\rho^* = 0.023 \text{ Mc/sec.}$$

In conclusion, these results show that it is much more consistent to make for $J = 1 \rightarrow 2$ the second assignment. y is for $J = 1 \rightarrow 2$ as well as for the higher transitions of the same order of magnitude if we make for $J = 1 \rightarrow 2$ the second assignment. Even if the value of ζ_8 is not so good at first sight, it should be remembered that 0.905 may still be within the limits of ζ used by Venkateswarlu et al. (8), namely, from 0.92 to 0.97. It should also be remembered that nothing is known precisely of the elements $\langle K \mid K \pm 3 \rangle$.

Our second example is *methyl acetylene*. $J = 1 \rightarrow 2$ and $2 \rightarrow 3$ transitions have been recorded by Trambarulo and Gordy (9). First we shall deal with the rotation-vibration interaction when the molecule makes a $C\equiv C—H$ bending vibration ($v_9 = 1$). It has been recorded (9) that no reasonable assignment of the lines was possible. It can be shown, however, that such an assignment is possible. $2(J + 1) = 6$ lines have been reported which shows that the transition is complete. We tentatively assign the following frequencies to the $Kl - 1 = 0$ group:

$$\nu = 51\ 280.45\ \text{Mc/sec} \quad \text{and} \quad \nu = 51\ 334.81\ \text{Mc/sec}.$$

In the same way we assign the following four frequencies to the central group $(Kl - 1 \neq 0)$:

$$\nu = 51\ 296.33\ \text{Mc/sec}$$
these may be singlets;
$$\nu = 51\ 304.05\ \text{Mc/sec}$$

$$\nu = 51\ 305.93\ \text{Mc/sec}$$
this may be a doublet.
$$\nu = 51\ 307.47\ \text{Mc/sec}$$

It will be shown that these assignments allow a consistent interpretation. The difference and half-sum of the frequencies of the lines $Kl - 1 = 0$ immediately give

$$q_J = 2.265\ \text{Mc/sec} \quad (l\text{-type doubling constant}),$$

$$B^* = 8551.22\ \text{Mc/sec}.$$

With regard to the $2J(=4)$ lines of the central group we have two singlets correlated to

$$Kl - 1 = -2 \quad \text{and} \quad Kl - 1 = -3$$

and $J - 1$ doublets, i.e., *one* doublet, corresponding to $\mid Kl - 1 \mid = 1$. The frequencies of the two singlets and the difference of the doublet give three equations, namely:

singlet:

$$\nu = 2B^*(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)4 - 2\rho^*(J + 1)2$$
$$+ 4q^2(J + 1)^3/(B_v - C_v + C_v\zeta)2, \tag{36}$$

singlet:

$$= 2B^*(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)9 - 2\rho^*(J + 1)3$$
$$+ 4q^2(J + 1)^3/(B_v - C_v + C_v\zeta)3, \quad (37)$$

separation

of doublet: $\Delta\nu = 4\rho^*(J + 1) + 8q^2(J + 1)^3/(B_v - C_v + C_v\zeta).$ (38)

These equations are simultaneously consistent if we take the following values:

$$\zeta_9 = 0.947, \quad (C_v - B_v - C\zeta_9) = 32.77 \text{ Mc/sec}, \quad \rho^* = 1.17 \text{ Mc/sec}. \quad (39)$$

With these values it is possible to explain the six frequencies with the above-mentioned assignment consistently. Moreover, the difference between the $Kl - 1 = 0$ doublet and the $|Kl - 1| = 1$ doublet should be equal to $6D_{JK}$. This difference is 0.860 Mc/sec, whereas $6D_{JK}$ is 0.918 Mc/sec. It is true that there remains still a difference. But this difference falls entirely into the experimental uncertainty and therefore we shall not deal with it. This completes the proof that our tentative assignment is correct.

Methyl acetylene gives also another excited vibrational state: $v_{10} = 1$. This is due to the C—C≡C-bond bending vibration. $J = 2 \rightarrow 3$ gives $2(J + 1) = 6$ lines which have been reported by Trambarulo and Gordy (9). The following two frequencies are the $Kl - 1 = 0$ group [and are not, as has been reported (9), related with $\begin{Bmatrix} K = \pm 1 \\ l = \mp 1 \end{Bmatrix}$ which evidently could not give $Kl - 1 = 0$].

$$\nu = 51\ 369.12 \text{ Mc/sec},$$

$$\nu = 51\ 469.85 \text{ Mc/sec} \ (9).$$

The central group is the $Kl - 1 \neq 1$-group:

$$\nu_1 = 51\ 410.51$$
$$\nu_2 = 51\ 415.35 \quad \text{singlets,}$$

$$\left.\begin{array}{l} \nu_3 = 51\ 418.23 \\ \nu_4 = 51\ 418.75 \end{array}\right\} \quad \text{doublet.}$$

Now we have again one doublet ($|Kl - 1| = 1 = J - 1$) and two singlets in the central group. It will be shown that this is a consistent assumption. It can be seen immediately that

$$\Delta\nu = 24q_J = 100.73 \text{ Mc/sec}$$

gives the *l*-type doubling constant q_J :

$$q_J = 4.197 \text{ Mc/sec}.$$

From $\nu_0{}^J = 51\ 419.485$ Mc/sec, taking into account the value of $D_J = 0.003$

Mc/sec,

$$4D_J(J + 1)^3 = 0.324 \text{ Mc/sec},$$

we get

$$2B^*(J + 1) = 51\ 419.161 \text{ Mc/sec}$$

and therefore

$$B^* = 8569.86 \text{ Mc/sec}.$$

This may be compared with $B_v = 8569.764$ Mc/sec, as reported by Trambarulo and Gordy (9).

Moreover, we may regard as centers of the doublets the frequencies

$$\nu_0^J = 51\ 419.485 \text{ Mc/sec},$$

$$\tfrac{1}{2}(\nu_3 + \nu_4) = 51\ 418.490 \text{ Mc/sec}.$$

This leads to the following difference:

$$\nu_0^J - \tfrac{1}{2}(\nu_3 + \nu_4) = 0.995 \text{ Mc/sec} = 6D_{JK}.$$

This is a value which again fits in the range of experimental error compared with

$$6D_{JK} = 0.918 \text{ Mc/sec}$$

from measurements in the ground state (9). It may be stressed that no other assignment of the lines of this group fits even to a rough approximation into these theoretical relations. Thus it is quite clear that $|Kl - 1| = 1$ is the correct assignment for the doublet ν_3, ν_4. The two singlets ($Kl - 1 = -2$ and $Kl - 1 = -3$) give in this case the following equations:

for $Kl - 1 = -2$

$$\nu_1 - \nu_0^J = -1.224 - 12z + 95.121y = -8.975 \text{ Mc/sec}, \qquad (40a)$$

for $Kl - 1 = -3$

$$\nu_2 - \nu_0^J = -4.135 \text{ Mc/sec} = -2.754 - 18z + 634.13y. \qquad (40b)$$

(Note that $z = \rho^*$ and $y = 1/(B_v - C_v + C_v\zeta_{10}.)$ From these equations we get

$$y = 0.020846.$$

This corresponds to

$$C_v - B_v - C\zeta_{10} = 47.971 \text{ Mc/sec}.$$

This constant is in the order of magnitude comparable with the corresponding value for $v_9[y = 0.0249$ Eq. (39)]. On the other hand, we have $B_v = 8569.8$

Mc/sec and $C_v \cong C = 160\ 572$ Mc/sec (from the structure). We get

$$\zeta_{10} = 152\ 050/160\ 572 = 0.947.$$

That ζ_{10} is rather near to ζ_9 may be due to a great extent to C, B_v which are the same for both cases. Having eliminated y we now get z:

$$-7.751 = -12z + 1.9829,$$
$$z = 0.8112 = \rho^*. \tag{42}$$

The same result for z we can also get from another equation (corresponding to another line).

To examine the constants we found we shall calculate on the established assignment the four lines for the transition $J = 1 \rightarrow 2$ again. (We could do the same for $v_9 = 1$, but there we have no experimental results, so it would be useless in this case.) For $J = 1 \rightarrow 2$ we have one doublet and two singlets

$$(Kl - 1 = -1, \quad \text{and} \quad Kl - 1 = -2).$$

If we take the following values (9):

$$B^* = 8569.86 \text{ Mc/sec} \quad [\text{Eq. (13a)}],$$

$$D_J = 0.003 \text{ Mc/sec},$$

$$D_{JK} = 0.153 \text{ Mc/sec},$$

and the following frequencies (9) (excited vib. state $v_{10} = 1$):

$$\nu_1 = 34\ 246.30 \text{ Mc/sec},$$

$$\nu_2 = 34\ 277.05 \text{ Mc/sec},$$

$$\nu_3 = 34\ 278.98 \text{ Mc/sec},$$

$$\nu_4 = 34\ 313.21 \text{ Mc/sec},$$

then we can calculate from ν_1 and $\nu_4 q_J$ (the *l*-type doubling constant):

$$q_J = 4.1818 \text{ Mc/sec} \quad (\text{from } J = 1 \rightarrow 2),$$

$$q_J = 4.197 \text{ Mc/sec} \quad (\text{from } J = 2 \rightarrow 3).$$

Moreover, we assume that $\rho^* = 0.8112$ [from Eq. (42)], and that $y = 0.020846$ [from Eq. (41)]. To find y, we may either use B^* from the transition $J = 2 \rightarrow 3$ ($B^* = 8569.86$ Mc/sec) or B^* from the transition $J = 1 \rightarrow 2(B^* = 8569.83$ Mc/sec). That the B^* values are equally applicable speaks for the quality of the measurements. The value ζ mainly depends on B_v, C_v, C and little on the frequencies ν. Therefore, what practically remains to test is ρ^*. We do this in the following equations, which are based on differences of frequencies between the

singlets and the middle on the l-type doublet ($\nu_0^J = 34{,}279.34$ Mc/sec) respectively, taking into account D_J.

To $Kl - 1 = -2$ corresponds the following equation ($\nu_0^J - \nu_2$):

$$-2.58 = -2.448 - 8\rho^* + 5.875. \tag{43}$$

Here we get $\rho^* = 0.751$ Mc/sec. This value is in good agreement with 0.811 Mc/sec from $J = 2 \to 3$. Now the only alternative is to correlate $Kl - 1 = -1$ with ν_2

$$-2.58 = -0.612 - 4\rho^* + 11.75. \tag{44}$$

Here we get $\rho^* = 3.43$ Mc/sec. If we compare the results

from $J = 1 \to 2$
$\rho^* = 3.43$ Mc/sec   Eq. (44),

$\rho^* = 0.751$ Mc/sec   Eq. (43) (This value also confirms

our assignment for $J = 2 \to 3$)

from $J = 2 \to 3$ $\rho^* = 0.811$ Mc/sec   Eq. (42),

it is immediately clear which assignment is the right one, namely, the assignment with the correlation

$$\nu_2 \leftrightarrow Kl - 1 = -2, \quad \text{and} \quad (\nu_1, \nu_4) \leftrightarrow Kl - 1 = 0.$$

$$\nu_3 \leftrightarrow Kl - 1 = -1,$$

This concludes the study of the vibration-rotation interactions of methyl acetylene.

l-type doubling as a means to assign unidentified lines

For $(CH_3)_3C-C\equiv CH$ it has been reported (*15, 10*) that the lines $l_\tau(+)$ corresponding to $l_\tau(-)$ and $l_\beta(-)$ corresponding to $l_\beta(+)$ could not be resolved. The values

$$\tau_e = 21\ 453.5\ \text{Mc/sec} \quad \text{and} \quad l_\tau(-) = 21\ 446.0\ \text{Mc/sec}$$

are excited vibrational satellites of $(CH_3)_3C-C\equiv CH$. Now we propose to find the not yet identified vibrational satellite $l_\tau(+)$, using the symmetry of the l-type doubling. The line

$$l_\tau(+) = 21\ 461.2\ \text{Mc/sec}$$

has been measured by Winnewisser (*16*). The same applies to the l-type doublet $l_\beta(+)$ and $l_\beta(-)$. The values are

$$\beta_e = 21\ 486.4\ \text{Mc/sec},$$

$$l_\beta(+) = 21\ 499.7\ \text{Mc/sec},$$

$$l_\beta(-) = 21\ 473.0\ \text{Mc/sec}.$$

The line $l_\beta(-)$ has been measured by Winnewisser (*16*).

In these two cases we can only make tentative assignments which have to be confirmed by further investigations. But nevertheless it seems possible to use the symmetry properties of the *l*-type doubling which was shown very clearly for the $J = 1 \rightarrow 2$ transition of the same molecule (*16*).

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