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G. A. M. S.
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Energy Levels of Polyatomic Molecules

(Part One)

G. Amat

Laboratoire de Spectroscopie Moleculaire
Faculté des Sciences de Paris

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FINAL REPORT

(Part One)

ENERGY LEVELS OF POLYATOMIC MOLECULES

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This Final Report (Part One) deals with theoretical investigations performed from 1960 to 1966 in the "Laboratoires de Spectroscopie Moléculaire" of both Faculté des Sciences de Paris and Faculté des Sciences de Dijon. It is divided in three sections :

PART 1 - Calculation of Rotation-Vibration Energies

PART 2 - Computation of Line Frequencies

PART 3 - Analysis of Infrared and Microwave Spectra

PART I

CALCULATION OF ROTATION-VIBRATION ENERGIES

Following a suggestion made by Professor H.H.NIELSEN, and in close collaboration with him, we have started in 1954 a research on the computation of high order rotation-vibration energies of polyatomic molecules. The goal of this program was to extend to fourth order the computation previously carried out to second order by Professor NIELSEN(1). Due to significant improvements achieved in the design of infrared and microwave spectrographs, this extension had become necessary in order to analyse high resolution rotation-vibration and rotation spectra obtained in various Laboratories, chiefly located in United States.

We shall first recall the principle of this fourth order calculation of rotation-vibration energies.

In the approximation where the energy of the molecule is considered as being the sum of energies of a rigid rotor and various harmonic oscillators, the Hamiltonian can be written down as :

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(1) H.H.NIELSEN, Rev. Mod. Phys. 23, 90 (1951)

$$H_o = \frac{1}{2} \sum_{\alpha} \frac{P_\alpha^{\ 2}}{I_{\alpha\alpha}^{(e)}} + \frac{1}{2} \sum_{s\sigma} p_{s\sigma}^{2} + \frac{1}{2} \sum_{s\sigma} \lambda_s Q_{s\sigma}^{2} \qquad (1)$$

where P_α (α=x,y,z) is a component of the total angular momentum $\vec{P}$ along one of the principal inertia axis of the equilibrium configuration, $I_{\alpha\alpha}^{(e)}$ is the corresponding moment of inertia, $Q_{s\sigma}$ is one of the normal coordinates used to describe the vibration of the nuclei and $p_{s\sigma}$ is the conjugate momentum to $Q_{s\sigma}$. In this notation, the subscript s characterizes the different normal vibrations and the subscript σ characterizes the various components of a degenerate vibration.

In this approximation, the rotation-vibration energy is obtained by solving the SCHROEDINGER equation

$$H_o \ \Psi_o = E_o \ \Psi_o \qquad (2)$$

The eigenfunctions Ψ_o of the Hamiltonian H_o are defined by rotational quantum numbers J K M and vibrational quantum numbers v_s ℓ_s m_s (ℓ_s exists only for twofold and threefold degenerate vibrations, m_s exists only for threefold degenerate vibrations).

In order to compute better values of rotation-vibration energies, one needs actually to use the rigourous rotation-vibration Hamiltonian H established by DARLING and DENNISON(2). Like the Hamiltonian H_o, it depends on equilibrium moments of inertia $I_{\alpha\alpha}^{(e)}$ and force

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(2) B.T.DARLING and D.M.DENNISON, Phys.,Rev., 57, 128 (1940)

constants λ_s of the harmonic potential, but it depends also upon other molecular constants :

- force constants of the anharmonic potential

  $k_{s\sigma\, s'\sigma'\, s''\sigma''}$, $k_{s\sigma\, s'\sigma'\, s''\sigma''\, s'''\sigma'''}$ ....
- interaction constants between rotation and vibration :

  $\zeta^{\alpha}_{s\sigma\, s'\sigma'}$ (Coriolis coupling coefficients)

  $a^{\alpha\beta}_{s\sigma}$ (Coefficients of variation of moments and products of inertia with respect to normal coordinates)

It is not possible to obtain rigourous eigenvalues of the DARLING DENNISON Hamiltonian. One must use a power expansion of H with respect to normal coordinates :

$$H = H_0 + H_1 + H_2 + H_3 + H_4 + \ldots\ldots. \qquad (3)$$

where the first term on right hand side H_0 is given by equation (1).

The next step is to write down the matrix H, using as basic functions the functions ψ_0 defined by equation (2). Rotation-vibration energies E_{vr} are obtained by diagonalizing this matrix with respect to all quantum numbers J K M v_s ℓ_s m_s ....

- it can be shown that the matrix H is diagonal with respect to J and M
- in order to diagonalize with respect to the quantum numbers v_s, it is convenient to use the method of SHAFFER, NIELSEN and THOMAS(3) i.e. to perform contact transformations and to replace

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(3) W.H.SHAFFER, H.H.NIELSEN and L.H.THOMAS, Phys. Rev. 56,1051 (1939)

the Hamiltonian H with a transformed Hamiltonian :

$$H' = T\,H\,T^{-1} = H_o + h'_1 + h'_2 + h'_3 + h'_4 + \ldots\ldots\ldots \qquad (4)$$

$$H^{+} = \mathcal{C}\,H'\,\mathcal{C}^{-1} = H_o + h'_1 + h_2 + \overset{+}{h}_3 + \overset{+}{h}_4 + \ldots\ldots\ldots \qquad (5)$$

operators T and $\mathcal{C}$ being chosen in such a manner that $H_o + h'_1$, and $H_o + h'_1 + \overset{+}{h}_2$ will be diagonal with respect to quantum numbers v_s. It can then be shown that the matrix elements of $\overset{+}{H}$ off diagonal with respect to quantum numbers v_s contribute to the energy only in the sixth order.

- E_{vr} will be obtained by diagonalizing $\overset{+}{H}$ with respect to K ℓ_s and m_s, i.e. by solving for the roots of the secular equation :

$$\det.\left[(K\,\ell_s\,m_s\ldots|\overset{+}{H}|K'\ell'_s m'_s\ldots) - E_{vr}\,\delta_{KK'}\,\delta_{\ell_s\ell_{s'}}\,\delta_{m_s m_{s'}}\,\ldots\right]=0 \quad (6)$$

As a consequence, a computation of rotation-vibration energies requires the following steps

1) Expansion of the Hamiltonian and contact transformations.
   This is described in the following references:

[1] M.GOLDSMITH, G.AMAT and H.H.NIELSEN, J. Chem. Phys.,24, 1178, 1956.

[2] G.AMAT, M.GOLDSMITH and H.H.NIELSEN, J. Chem. Phys., 27, 838, 1957

[3] G.AMAT and H.H.NIELSEN, J. Chem. Phys.,27, 845, 1957

[4] G.AMAT and H.H.NIELSEN, " " " 29, 665, 1958

[5] G.AMAT and H.H.NIELSEN, " " " 36,1859, 1962

The case where accidental resonances occur needs special consideration. This problem has been studied on three papers :

[6] M.L.GRENIER-BESSON, G.AMAT and H.H.NIELSEN, J. Chem. Phys. 36, 3454, 1962

[7] M.L.GRENIER-BESSON, G.AMAT, Technical Note, Nr 3 Contract NR 61 (052) - 369 March 1962

[8] S.MAES, J. Phys. Rad. 27,37 , 1966

These papers correspond respectively to three cases of accidental resonances (Fermi type $\omega \simeq 2\,\omega'$, Fermi type $\omega \simeq \omega' + \omega''$, Coriolis type $\omega \simeq \omega'$).

2) Study of molecular constants in relation with the symmetry of the molecule.

It is very important to know for a molecule of a given symmetry which are the non-vanishing interaction coefficients and what are possibly the relations between these non-vanishing coefficients. This problem has been studied in the following papers :

[9] G.AMAT and L.HENRY, Cahiers de Physique. 95, 273, 1958

[10] L.HENRY and G.AMAT, " " ,118, 230, 1960

[11] L.HENRY and G.AMAT, J. Mol. Spectroscopy, 5, 319, 1960

[12] L.HENRY and G.AMAT, J. Mol. Spectroscopy,15, 168, 1965

The first two papers deal with the rotation-vibration interaction coefficients $a^{\alpha\beta}_{s\sigma}$, $\zeta^{\alpha}_{s\sigma\,s'\sigma'}$ The third and the fourth ones deal respectively with the cubic and quartic anharmonic coefficients $k_{s\sigma\,s'\sigma'\,s''\sigma''}$ and $k_{s\sigma\,s'\sigma'\,s''\sigma''\,s'''\sigma'''}$.

A general survey of these problems can also be found in the reference :

[13] L.HENRY, Annales de Physique (to be published).

3) Computation of matrix elements of H^{+}

In order to write down the secular equation (6), it is necessary to compute the matrix elements of h_2^{+}, h_3^{+} and h_4^{+}. They are given in the following papers :

[14] H.H.NIELSEN, Review of Modern Physics, 23, 90, 1951
[15] M.L.GRENIER-BESSON, J. Phys. Rad., 21, 555, 1960
[16] G.AMAT and L.HENRY, J. Phys. Rad., 21, 728, 1960
[17] M.L.GRENIER-BESSON, J. Phys. Rad., 25, 757, 1964
[18] S.MAES, Thesis Paris 1960
[19] S.K.KURTZ, Thesis Ohio State University, 1960

They refer respectively to the matrix elements of h_2^{+} (diagonal [14] and off diagonal [15] [16][17])of h_3^{+} [18]and of h_4^{+} [19]

4) The tetrahedral XY_4 and octahedral XY_6 molecules which are spherical rotors and have threefold degenerate vibrations require a special treatment. This problem has been studied in the reference :

[20] J.MORET-BAILLY, Cahiers de Physique, 15, 237, 1961

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The research described above had been started before the beginning of contract NR - 61 (052) - 369. This contract has enabled us to complete this program under the best conditions of efficiency ; actually the work done with its support corresponds to the material published in references [7] [8] [12] [13] [17] [20] .

As an illustration, we shall give in Chapter I the results obtained in our study of the properties of quartic coefficients $k_{s\sigma\ s'\sigma'\ s''\sigma''\ s'''\sigma'''}$ in the anharmonic potential [12].

CHAPTER I

The Quartic Anharmonic Potential Function of Polyatomic Molecules

The potential function of a polyatomic molecule can generally be expanded in a power series with respect to normal coordinates:

$$V = V_0 + V_1 + V_2 + \cdots , \tag{1}$$

where the first three terms V_0, V_1, and V_2 are, respectively, the harmonic, the cubic anharmonic, and the quartic anharmonic potentials. We studied V_1 in Ref. *1*; the present paper deals with the third term of the expansion:

$$V_2 = hc \sum_{s\sigma \leqq s'\sigma' \leqq s''\sigma'' \leqq s'''\sigma'''} k_{s\sigma s'\sigma' s''\sigma'' s'''\sigma'''} q_{s\sigma} q_{s'\sigma'} q_{s''\sigma''} q_{s'''\sigma'''} \tag{2}$$

We shall consider in this study axially symmetric, linear, and asymmetric molecules but not spherically symmetric molecules.[1]

I. AXIALLY SYMMETRIC MOLECULES

If we designate nondegenerate coordinates with subscripts n, n' $\cdots$ and two-fold degenerate coordinates with subscripts t_1, t_2, t_1', t_2', $\cdots$, V_2 can be written as

$$V_2 = V_{21} + V_{22} + V_{23} + V_{24} \tag{3}$$

---

[1] The anharmonic potential function is given for XY_4 tetrahedral and XY_6 octahedral molecules in Refs. *2* and *3*.

with

$$
\begin{aligned}
V_{21} &= hc \sum_{\substack{nn'n''n''' \\ n \leqq n' \leqq n'' \leqq n'''}} k_{nn'n''n'''} q_n q_{n'} q_{n''} q_{n'''} \,, \\
V_{22} &= hc \sum_{\substack{t\sigma t'\sigma' nn' \\ t\sigma \leqq t'\sigma' ;\, n \leqq n'}} k_{t\sigma t'\sigma' nn'} q_{t\sigma} q_{t'\sigma'} q_n q_{n'} \,, \\
V_{23} &= hc \sum_{\substack{t\sigma t'\sigma' t''\sigma'' n \\ t\sigma \leqq t'\sigma' \leqq t''\sigma''}} k_{t\sigma t'\sigma' t''\sigma'' n} q_{t\sigma} q_{t'\sigma'} q_{t''\sigma''} q_n \,, \\
V_{24} &= hc \sum_{\substack{t\sigma t'\sigma' t''\sigma'' t'''\sigma''' \\ t\sigma \leqq t'\sigma' \leqq t''\sigma'' \leqq t'''\sigma'''}} k_{t\sigma t'\sigma' t''\sigma'' t'''\sigma'''} q_{t\sigma} q_{t'\sigma'} q_{t''\sigma''} q_{t'''\sigma'''} \,.
\end{aligned}
\tag{4}
$$

The nonvanishing coefficients k appearing in V_{21}, V_{22}, V_{23}, and V_{24} are given in Tables I, II, III, and IV a–e, respectively. The notation used for the nomenclature of the groups and for the symmetry species is the same as the one used in Ref. *1*. N is the foldness of the z axis; groups I are nonabelian [C_{Nv}, D_N, D_{Nh}, D_{Nd}(N odd), $D_{(N/2)d}$($\frac{1}{2}N$ even)] while groups II are abelian [C_N, C_{Nh}, S_{2N}(N odd), S_N($\frac{1}{2}N$ even)]. The symbol m is used to characterize the various degenerate symmetry species: E_1, E_2, $\cdots$, E_m, $\cdots$. As in Ref. *1*, a standard orientation is used for the degenerate normal coordinates q_{t1}, q_{t2} [see also Ref. *4*].

It is important to point out[2] that the symbols used for symmetry species need to be completed, for certain groups, with subscripts g, u or superscripts prime, double prime. In that case, there must be an even number of coordinates characterized by u or double prime, otherwise the corresponding coefficient $k_{s\sigma s'\sigma' s''\sigma'' s'''\sigma'''}$ will vanish. Before describing the tables, it is useful to make two remarks.

(a) The operator V_2 has been split into 17 different parts corresponding to the various types of combinations of four normal vibrations, namely: $nnnn$, $nnnn'$, $nnnn'$, $nnn'n''$, $nn'n''n'''$, $ttnn$, $tt'nn$, $ttnn'$, $tt'nn'$, $tttn$, $ttt'n$, $tt't''n$, $tttt$, $tttt'$, $ttt't'$, $tt't''$, $tt't''t'''$. These 17 parts need to be considered independently.

(b) It is convenient to read the tables from the right to the left considering first the molecular group, then the symmetry species of the four particular normal vibrations under investigation in order to deduce the form of the corresponding operator and the nonvanishing coefficients k.

The nonvanishing coefficients k appearing in V_{21} are listed in Table I. The presentation of this table is similar to the presentation used in Ref. *1*. The subscript is written between brackets in $A_{(1)}$, $A_{(2)}$, $B_{(1)}$, $B_{(2)}$ in order to recall that this subscript is not defined for the groups II. In this table and in Table II we use the condition $n < n' < n'' < n'''$, assuming furthermore that the nondegenerate vibrations are labelled ($n = 1, 2, 3 \cdots$) in such a manner that the

[2] This statement holds for all the tables given in this paper.

smallest values correspond to vibrations of species A and the largest values to vibrations of species B.

Table II gives, in relation with the symmetry species of the normal coordinates, the nonvanishing coefficients appearing in[3]

$$\begin{aligned}\frac{V_{22}}{hc} = {} & \sum_{n} \Big\{ \sum_{t} k_{ttnn}(q_{t1}^2 + q_{t2}^2) \\ & + \sum_{\substack{tt' \\ t\neq t'}}{}' \, [k_{tt'nn}(q_{t1}q_{t'1} + q_{t2}q_{t'2}) + k^{*}_{tt'nn}(q_{t1}q_{t'2} - q_{t2}q_{t'1})] \Big\} q_n^{2} \\ & + \sum_{\substack{nn' \\ n<n'}} \Big\{ \sum_{t} [k_{ttnn'}(q_{t1}^2 + \theta q_{t2}^2) + 2k'_{ttnn'}q_{t1}q_{t2}] \\ & + \sum_{\substack{tt' \\ t\neq t'}} [k_{tt'nn'}(q_{t1}q_{t'1} + \theta q_{t2}q_{t'2}) + k'_{tt'nn'}(q_{t1}q_{t'2} - \theta' q_{t2}q_{t'1})] \Big\} q_n q_{n'} \, .\end{aligned} \qquad (5)$$

V_{22} (as well as V_{21}, V_{23}, and V_{24}) is a sum of quartic forms which are totally symmetric. In these forms, θ and θ' are equal to $+1$ or -1 depending upon the symmetry species of the normal coordinates.[4] The values of θ and θ' are given in Table II. To each quartic form of the coordinates which is totally symmetric corresponds a coefficient written as k_{abcd} or k'_{abcd} or k^{*}_{abcd}. To designate the two coefficients k_{abcd} and k'_{abcd} we use also the notation $k^{(j)}_{abcd}$ ($j = 0, 1$) where the index j gives the number of superscripts "prime."

For a definite combination of vibrations *abcd*, it can be seen from Table II that either k_{abcd} or k'_{abcd} can possibly be nonvanishing for molecules belonging to a group I if the vibrations have the proper symmetry species given in the table. Under the same circumstances, both k_{abcd} and k^{*}_{abcd} or both k_{abcd} and k'_{abcd} can be nonvanishing when the molecular group is a group II. More precisely, the coefficients $k^{*}_{tt'nn}$ are nonvanishing only for groups II (provided t and t' belong to species $E_m \equiv E_{m'}$; n belonging either to species A or to species B). If n, n', t, t' belong to the symmetry species ($A_{(\cdot)}$ or $B_{(\cdot)}$, $A_{(\cdot)}$ or $B_{(\cdot)}$, E_m, $E_{m'}$ respectively) required by Table II, $k_{ttnn'}$ and $k_{tt'nn'}$ will be nonvanishing

—for groups II,

—for groups I, only if n, n' belong to species s, s or a, a;

under similar conditions, $k'_{ttnn'}$ and $k'_{tt'nn'}$ will be nonvanishing

[3] The symbol $\sum'_{tt', t\neq t'}$ means that for each pair of values of the indices t, t' we write only one term in the sum, the two operators $k_{12nn}(q_{11}q_{21} + q_{12}q_{22})q_n^2$ and $k_{21nn}(q_{21}q_{11} + q_{22}q_{12})q_n^2$, for example, being identical. The other summations $\sum'$ involving two, three, or four indices which appear in Eqs. (6) and (7), are defined in the same manner.

[4] They should be written as $\theta_{ttnn'}$, or $\theta_{tt'nn'}$ and $\theta'_{tt'nn'}$. The subscripts are omitted in the tables for the sake of simplicity. The same remark holds for $\eta\eta'$ (Table III), $\alpha_1\alpha_2\alpha_3\alpha_4\alpha_6$ (Table IVa), $\beta_1 \cdots \beta_8$ (Table IVb), $\gamma_1 \cdots \gamma_9$ (Table IVc), $\delta_1 \cdots \delta_{12}$ (Table IVd), $\epsilon_1 \cdots \epsilon_{16}$ (Table IVe).

TABLE I

Nonvanishing Coefficients k Appearing in V_{21}

Nonvanishing coefficients	Symmetry species of n	n'	n''	n'''			Molecular group	
k_{nnnn}	arbitrary	—	—	—	I	II	N arbitrary[c]	*
$k_{nnn'n'}$	arbitrary	arbitrary	—	—	I	II	N arbitrary[c]	
$k_{nnnn'}$	$A_{(1)}$	$A_{(1)}$	—	—	I	II[b]	N arbitrary	*
	$A_{(2)}$	$A_{(2)}$	—	—	I		N arbitrary	
	$B_{(1)}$	$B_{(1)}$	—	—	I	II[b]	$N = 2,4 \ldots 2p \ldots$	
	$B_{(2)}$	$B_{(2)}$	—	—	I		$N = 2,4 \ldots 2p \ldots$	
$k_{nnn'n''}$	arbitrary	$A_{(1)}$	$A_{(1)}$	—	I	II[b]	N arbitrary[c]	*
		$A_{(2)}$	$A_{(2)}$	—	I		N arbitrary[c]	
		$B_{(1)}$	$B_{(1)}$	—	I	II[b]	$N = 2,4 \ldots 2p \ldots$	
		$B_{(2)}$	$B_{(2)}$	—	I		$N = 2,4 \ldots 2p \ldots$	
$k_{nn'n''n'''}$	$A_{(1)}$	$A_{(1)}$	$A_{(1)}$	$A_{(1)}$	I	II[b]	N arbitrary	*
	$A_{(2)}$	$A_{(2)}$	$A_{(2)}$	$A_{(2)}$	I		N arbitrary	
	$A_{(1)}$	$A_{(1)}$	$A_{(2)}$	$A_{(2)}$	I		N arbitrary	
	$B_{(1)}$	$B_{(1)}$	$B_{(1)}$	$B_{(1)}$	I	II[b]	$N = 2,4 \ldots 2p \ldots$	
	$B_{(2)}$	$B_{(2)}$	$B_{(2)}$	$B_{(2)}$	I		$N = 2,4 \ldots 2p \ldots$	
	$B_{(1)}$	$B_{(1)}$	$B_{(2)}$	$B_{(2)}$	I		$N = 2,4 \ldots 2p \ldots$	
	$A_{(1)}$	$A_{(1)}$	$B_{(1)}$	$B_{(1)}$	I	II[b]	$N = 2,4 \ldots 2p \ldots$	
	$A_{(1)}$	$A_{(1)}$	$B_{(2)}$	$B_{(2)}$	I		$N = 2,4 \ldots 2p \ldots$	
	$A_{(2)}$	$A_{(2)}$	$B_{(1)}$	$B_{(1)}$	I		$N = 2,4 \ldots 2p \ldots$	
	$A_{(2)}$	$A_{(2)}$	$B_{(2)}$	$B_{(2)}$	I		$N = 2,4 \ldots 2p \ldots$	
	$A_{(1)}$	$A_{(2)}$	$B_{(1)}$	$B_{(2)}$	I		$N = 2,4 \ldots 2p \ldots$	

[a] See Footnote 2.

[b] When II is written once for two, three or five rows, it means that the combinations of species written on these rows are not different from each other when the molecular group belongs to group category II.

[c] N is arbitrary when n and n' belong to species $A_{(1)}$ or $A_{(2)}$; N must be even if n (or n') belongs to species $B_{(1)}$ or $B_{(2)}$.

-for groups II,

for groups I,[5] only if n, n' belong to species s, a or a, s.

In order to illustrate the meaning of Table II, let us consider as an example the totally symmetric form which can be written with two nondegenerate vibrations n, n' and one twofold degenerate vibration t taken twice. Depending upon the

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[5] In this event the superscript prime can be omitted in k' without producing any ambiguity.

TABLE II

NONVANISHING COEFFICIENTS k APPEARING IN V_{22}

Nonvanishing coefficients	θ,	θ'	Symmetry species[a] of			Molecular group
			n	n'	tt'	
k_{ttnn}			$A_{(.)}$		m arbitrary	$N \geqq 3$ *
			$B_{(.)}$		m arbitrary	$N = 4,6 \ldots 2p \ldots$
$k_{tt'nn}k^{*}_{tt'nn}$[b]			$A_{(.)}$		$m = m'$	$N \geqq 3$ *
			$B_{(.)}$		$m = m'$	$N = 4,6 \ldots 2p \ldots$
$k_{ttnn'}$	$+1$		$A_{(s)}$ $A_{(a)}$	$A_{(s)}$ $A_{(a)}$	m arbitrary	$N \geqq 3$ *
			$B_{(s)}$ $B_{(a)}$	$B_{(s)}$ $B_{(a)}$	m arbitrary	$N = 4,6 \ldots 2p \ldots$
$k^{(j)}_{ttnn'}$[c]	-1		$A_{(.)}$	$B_{(.)}$	$m = \frac{1}{4}N$	$N = 4,8 \ldots 4p \ldots$
$k^{(j)}_{tt'nn'}$[c]	$+1$	$+1$	$A_{(.)}$	$A_{(.)}$	$m = m'$	$N \geqq 3$ *
			$B_{(.)}$	$B_{(.)}$	$m = m'$	$N = 4,6 \ldots 2p \ldots$
	-1	-1	$A_{(.)}$	$B_{(.)}$	$m + m' = \frac{1}{2}N$	$N = 4,6 \ldots 2p \ldots$

[a] See Footnote 2. $A_{(.)}$ is written for $A_{(s)}$ or $A_{(a)}$ (i.e., A_s or A_a in groups I; A in groups II); $B_{(.)}$ is written for $B_{(s)}$ or $B_{(a)}$. The symbols s and a are defined in Ref. *1*.

[b] $k^{*}_{tt'nn}$ is nonvanishing only for groups II.

[c] For groups I, $j = 0$ if n, n' belong to species s, s or a, a; $j = 1$ if n, n' belong to species s, a or a, s. For groups II, $j = 0$ and 1.

TABLE III

NONVANISHING COEFFICIENTS k APPEARING IN V_{23}

Nonvanishing coefficients	η or η'	Symmetry species[a] of		Molecular group
		n	$tt't''$	
$k^{(j)}_{tttn}$[b]		$A_{(.)}$	$3m = N$	$N = 3,6 \ldots 3p \ldots$
		$B_{(.)}$	$3m = \frac{1}{2}N$	$N = 6,12 \ldots 6p \ldots$
$k^{(j)}_{ttt'n}$[b]	$+1$	$A_{(.)}$	$m' = 2m$	$N \geqq 5$
	$+1$	$B_{(.)}$	$m' = 2m - \frac{1}{2}N$	$N = 6,8 \ldots 2p \ldots$
	-1	$A_{(.)}$	$2m + m' = N$	$N = 3;\ N \geqq 5$
	-1	$B_{(.)}$	$2m + m' = \frac{1}{2}N$	$N = 6,8 \ldots 2p \ldots$
$k^{(j)}_{tt't''n}$[b]	$+1$	$A_{(.)}$	$m'' = m + m'$	$N \geqq 5$
	$+1$	$B_{(.)}$	$m'' = m + m' - \frac{1}{2}N$	$N = 6,8 \ldots 2p \ldots$
	-1	$A_{(.)}$	$m + m' + m'' = N$	$N = 3;\ N \geqq 5$
	-1	$B_{(.)}$	$m + m' + m'' = \frac{1}{2}N$	$N = 6,8 \ldots 2p \ldots$

[a] See Footnote 2. $A_{(.)}$ is written for $A_{(s)}$ or $A_{(a)}$ (i.e., A_s or A_a in groups I; A in groups II); $B_{(.)}$ is written for $B_{(s)}$ or $B_{(a)}$.

[b] For groups I, $j = 0$ if n belongs to species A_s or B_s; $j = 1$ if n belongs to species A_a or B_a. For groups II, $j = 0$ and 1.

molecular group and the symmetry species of nn' and t, this form (when it does not vanish) is one out of the following four:

$$W = k_{ttnn'}(q_{t1}^2 + q_{t2}^2)q_nq_{n'} ,$$

$$X = k_{ttnn'}(q_{t1}^2 - q_{t2}^2)q_nq_{n'} ,$$

$$Y = 2k'_{ttnn'}q_{t1}q_{t2}q_nq_{n'} ,$$

$$Z = k_{ttnn'}(q_{t1}^2 - q_{t2}^2)q_nq_{n'} + 2k'_{ttnn'}q_{t1}q_{t2}q_nq_{n'} .$$

W occurs, for example, when the symmetry species of n, n', t are, respectively, A_1A_1E in group C_{3v} or D_{2d}, AAE in group C_3 or C_4, BBE in group C_4, or B_2B_2E in group D_{2d}. X occurs, for example, for A_1B_1E in group D_{2d}, Y for A_1B_2E in D_{2d},[5] and Z for ABE in C_4.

TABLE IV[a]

NONVANISHING COEFFICIENTS k APPEARING IN V_{24}

a Nonvanishing coefficients $k^{(j)}_{tttt}$

IVa

	Groups I and II			Groups II		Symmetry Species of t	Molecular Group
j	α_1	α_2	α_3	α_4	α_5		
0	1	1	2			$m \neq \frac{N}{4}$	N = 3 ; N ≥ 5 *
0	1	1	0	1	-1	$m = \frac{N}{4}$	N = 4, 8 … 4p …
1	0	0	2				

b. Nonvanishing coefficients $k^{(j)}_{tt't'}$

IVb

	Groups I and II				Groups II				Symmetry Species of t t'	Molecular Groups
j	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_8		
0	1	-1	3	-3	-1	-1	3	3	$m' = 3m$	N ≥ 7
									$m' = 3m - N$	N = 5 ; N ≥ 7
0	-1	-1	3	3	-1	1	-3	3	$3m + m' = N$ ([illegible] $m = m' = \frac{N}{4}$)	N ≥ 5
0	1	1	1	1	1	-1	-1	1	$m = m' \neq \frac{N}{4}$	N = 3 ; N ≥ 5 *
0	1	1	0	0	1	-1	0	0	$m = m' = \frac{N}{4}$	N = 4, 8 … 4p.
1	0	0	1	1	0	0	1	-1		

c. Nonvanishing coefficients $k_{ttt't'}^{(j)}$

	Groups I and II					Groups II				Symmetry Species of t , t	Molecular Group
j	γ_1	γ_2	γ_3	γ_4	γ_5	γ_6	γ_7	γ_8	γ_9		
0	1	1	1	1	0					$m+m' \neq \frac{N}{2}$ $(m \neq m')$	$N \geqslant 5$
0	1	1	1	1	0	1	-1	1	-1	$m+m' = \frac{N}{2}$ $(m \neq m')$	$N = 6, 8, \ldots 2p \ldots$
1	1	1	0	0	-2						
0	1	1	1	1	0	1	-1	-1	1	$m = m' \neq \frac{N}{4}$	$N = 3$; $N \geqslant 5$ *
1	1	1	0	0	2						
0	1	1	0	0	0	1	-1	0	0	$m = m' = \frac{N}{4}$	$N = 4, 8, \ldots 4p \ldots$
1	0	0	1	1	0	0	0	1	-1		
2	0	0	0	0	2						

d. Nonvanishing coefficients $k^{(j)}_{ttt't''}$

	Groups I and II						Groups II							
j	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	Symmetry Species of $t\,t'\,t''$	Molecular Group
0	1	-1	1	-1	2	-2	-1	1	1	-1	2	2	$m'' = 2m + m'$	$N \geq 7$
													$m'' = 2m + m' - N$	$N = 5$; $N > 7$
0	-1	-1	1	1	2	2	-1	-1	1	1	-2	2	$2m + m' + m'' = N$ $\left(m \neq \frac{N}{4} ; m + m' \neq \frac{N}{2}\right)$	$N \geq 5$
0	1	1	-1	-1	2	2	-1	-1	1	1	2	-2	$m' + m'' = 2m \neq \frac{N}{2}$ $(m' \neq m'')$	$N \geq 7$
0	1	1	-1	-1	0	0	-1	-1	1	1	0	0	$m' + m'' = \frac{N}{2}$ $(m' \neq m'')$ $m = \frac{N}{4}$	$N = 8, 12 \ldots 4p \ldots$
1	0	0	0	0	1	1	0	0	0	0	1	-1		
0	1	1	1	1	0	0	1	-1	1	-1	0	0	$m \neq m' = m''$ $\left(m + m' \neq \frac{N}{2}\right)$	$N \geq 5$
0	1	1	1	1	0	0	1	-1	1	-1	0	0	$m \neq m' = m''$ $\left(m + m' = \frac{N}{2}\right)$	$N = 6, 8 \ldots 2p \ldots$
1	1	1	0	0	-1	-1	0	1	-1	0	1	-1		
0	1	1	1	1	0	0	1	-1	1	-1	0	0	$m = m' = m'' \neq \frac{N}{4}$	$N = 3$; $N \geq 5$ *
1	1	1	0	0	1	1	1	0	0	-1	-1	1		
0	1	1	0	0	0	0	1	0	0	-1	0	0	$m = m' = m'' = \frac{N}{4}$	$N = 4, 8 \ldots 4p \ldots$
1	0	0	1	1	0	0	0	1	-1	0	0	0		
2	0	0	0	0	1	1	0	0	0	0	1	-1		

e. Nonvanishing coefficients $k^{(j)}_{tt't''t'''}$

	Groups I and II								Groups II									
j	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9	ε_{10}	ε_{11}	ε_{12}	ε_{13}	ε_{14}	ε_{15}	ε_{15}	Symmetry Species of $t\,t'\,t''\,t'''$	Molecular Group
0	1	-1	1	-1	1	-1	-1	1	-1	1	1	-1	1	1	1	1	$m''' = m + m' + m''$ $m''' = m + m' + m'' - N$	$N \geq 7$ $N = 5$; $N \geq 7$
0	-1	-1	1	1	1	1	1	1	-1	-1	1	1	-1	-1	1	1	$m + m' + m'' + m''' = N$ $(m + m' \neq \frac{N}{2}$; $m + m'' \neq \frac{N}{2}$ $m + m''' \neq \frac{N}{2})$	$N \geq 5$
0	1	1	1	1	1	1	-1	-1	-1	1	-1	1	1	-1	1	-1	$m + m''' = m' + m'' \neq \frac{N}{2}$ $(m < m' \leq m'' < m''')$	$N \geq 7$
0	0	0	1	1	1	1	0	0	-1	0	0	1	0	-1	1	0	$m + m''' = m' + m'' = \frac{N}{2}$ $(m < m' \leq m'' < m''')$	$N = 8, 10 \ldots 2p \ldots$
1	1	1	0	0	0	0	-1	-1	0	-1	1	0	-1	0	0	1		
0	1	1	1	1	0	0	0	0	1	-1	1	-1	0	0	0	0	$m = m' < m'' = m'''$ $(m + m'' \neq \frac{N}{2})$	$N \geq 5$
1	0	0	0	0	1	1	-1	-1	0	0	0	0	1	-1	1	-1		
0	1	1	1	1	0	0	0	0	1	-1	1	-1	0	0	0	0	$m = m' \neq m'' = m'''$ $(m + m'' = \frac{N}{2})$	$N = 6, 8 \ldots 2p \ldots$
1	1	1	0	0	0	0	-1	-1	0	1	-1	0	1	0	0	-1		
2	0	0	0	0	1	1	-1	-1	0	0	0	0	1	-1	1	-1		
0	1	1	1	1	0	0	0	0	1	-1	1	-1	0	0	0	0	$m = m' = m'' = m''' \neq \frac{N}{4}$	$N = 3$; $N \geq 5$ *
1	1	1	0	0	1	1	0	0	1	0	0	-1	-1	0	0	1		
2	0	0	0	0	1	1	-1	-1	0	0	0	0	1	-1	1	-1		
0	1	1	0	0	0	0	0	0	0	1	-1	0	0	0	0	0	$m = m' = m'' = m''' = \frac{N}{4}$	$N = 4, 8 \ldots 4p \ldots$
1	0	0	1	1	0	0	0	0	1	0	0	-1	0	0	0	0		
2	0	0	0	0	1	1	0	0	0	0	0	0	0	1	-1	0		
3	0	0	0	0	0	0	1	1	0	0	0	0	1	0	0	-1		

Table III gives the nonvanishing coefficient k appearing in[3]

$$\begin{aligned}\frac{V_{23}}{hc} = \sum_n \Big\{ \sum_t \big[& k_{tttn}(q_{t1}^3 - 3q_{t1}q_{t2}^2) + k'_{tttn}(q_{t2}^3 - 3q_{t1}^2 q_{t2})\big] \\ & + \sum_t \sum_{\substack{t' \\ t' \neq t}} \big[k_{ttt'n}(q_{t1}^2 q_{t'1} - q_{t2}^2 q_{t'1} + 2\eta q_{t1} q_{t2} q_{t'2}) \\ & + k'_{ttt'n}(q_{t1}^2 q_{t'2} - q_{t2}^2 q_{t'2} - 2\eta' q_{t1} q_{t2} q_{t'1})\big] \\ & + \sum_{\substack{tt't'' \\ t \neq t' \neq t''}}{}' \big[k_{tt't''n}(q_{t1} q_{t'1} q_{t''1} - q_{t2} q_{t'2} q_{t''1} + \eta q_{t1} q_{t'2} q_{t''2} + \eta q_{t2} q_{t'1} q_{t''2}) \\ & + k'_{tt't''n}(q_{t1} q_{t'1} q_{t''2} - q_{t2} q_{t'2} q_{t''2} - \eta' q_{t1} q_{t'2} q_{t''1} - \eta' q_{t2} q_{t'1} q_{t''1})\big]\Big\} q_n ,\end{aligned} \tag{6}$$

where η and η' are equal to $+1$ or -1 (see Table III) and where $k_{tttn} = k_{ttt'n} = k_{tt't''n} \equiv 0$ if n belongs to species A_a or B_a while $k'_{tttn} = k'_{ttt'n} = k'_{tt't''n} \equiv 0$ if n belongs to species A_s or B_s (in groups I). The presentation of Table III is very similar to the one of Table II.

The part of the quartic potential which involves four twofold degenerate normal coordinates can be written as follows:[3, 6]

$$\begin{aligned}\frac{V_{24}}{hc} = \sum_j \Big\{ \sum_t \big[& k^{(j)}_{tttt}(\alpha_1 q_{t1}^4 + \alpha_2 q_{t2}^4 + \alpha_3 q_{t1}^2 q_{t2}^2) \\ & + k^{*}_{tttt}(\alpha_4 q_{t1}^3 q_{t2} + \alpha_5 q_{t1} q_{t2}^3)\big] \\ & + \sum_t \sum_{\substack{t' \\ t' \neq t}} \big[k^{(j)}_{tttt'}(\beta_1 q_{t1}^3 q_{t'1} + \beta_2 q_{t2}^3 q_{t'2} + \beta_3 q_{t1}^2 q_{t2} q_{t'2} + \beta_4 q_{t1} q_{t2}^2 q_{t'1}) \\ & + k^{*(j)}_{tttt'}(\beta_5 q_{t1}^3 q_{t'2} + \beta_6 q_{t2}^3 q_{t'1} + \beta_7 q_{t1}^2 q_{t2} q_{t'1} + \beta_8 q_{t1} q_{t2}^2 q_{t'2})\big] \\ & + \sum_{\substack{tt' \\ t \neq t}}{}' \big[k^{(j)}_{ttt't'}(\gamma_1 q_{t1}^2 q_{t'1}^2 + \gamma_2 q_{t2}^2 q_{t'2}^2 + \gamma_3 q_{t1}^2 q_{t'2}^2 \\ & + \gamma_4 q_{t2}^2 q_{t'1}^2 + \gamma_5 q_{t1} q_{t2} q_{t'1} q_{t'2}) \\ & + k^{*(j)}_{ttt't'}(\gamma_6 q_{t1}^2 q_{t'1} q_{t'2} + \gamma_7 q_{t2}^2 q_{t'1} q_{t'2} \\ & + \gamma_8 q_{t1} q_{t2} q_{t'1}^2 + \gamma_9 q_{t1} q_{t2} q_{t'2}^2)\big] \\ & + \sum_t \sum_{\substack{t't'' \\ t' \neq t;\, t'' \neq t \\ t' \neq t''}}{}' \big[k^{(j)}_{ttt't''} (\delta_1 q_{t1}^2 q_{t'1} q_{t''1} + \delta_2 q_{t2}^2 q_{t'2} q_{t''2} + \delta_3 q_{t1}^2 q_{t'2} q_{t''2} \\ & + \delta_4 q_{t2}^2 q_{t'1} q_{t''1} + \delta_5 q_{t1} q_{t2} q_{t'1} q_{t''2} + \delta_6 q_{t1} q_{t2} q_{t'2} q_{t''1})\end{aligned} \tag{7}$$

---

[6] In addition to the comment made in Footnote 4, it needs to be noted that, for the sake of simplicity, a superscript (j) has been omitted in the various coefficients $\alpha \cdots \epsilon$ which should actually be written as $\alpha^{(j)}_{1tttt}\alpha^{(j)}_{2tttt} \ldots \epsilon^{(j)}_{16tt't''t'''}$.

$$
\begin{aligned}
&+ k^{*(j)}_{ttt't''}(\delta_7 q_{t1}^2 q_{t'1} q_{t''2} + \delta_8 q_{t1}^2 q_{t'2} q_{t''1} + \delta_9 q_{t2}^2 q_{t'1} q_{t''2} \\
&+ \delta_{10} q_{t2}^2 q_{t'2} q_{t''1} + \delta_{11} q_{t1} q_{t2} q_{t'1} q_{t''1} + \delta_{12} q_{t1} q_{t2} q_{t'2} q_{t''2})] \\
&+ \sum_{\substack{tt't''t''' \\ t\neq t'\neq t''\neq t''}}{}' [k^{(j)}_{tt't''t'''}(\epsilon_1 q_{t1} q_{t'1} q_{t''1} q_{t'''1} + \epsilon_2 q_{t2} q_{t'2} q_{t''2} q_{t'''2} \\
&+ \epsilon_3 q_{t1} q_{t'1} q_{t''2} q_{t'''2} + \epsilon_4 q_{t2} q_{t'2} q_{t''1} q_{t'''1} + \epsilon_5 q_{t1} q_{t'2} q_{t''1} q_{t'''2} \qquad (7) \\
&+ \epsilon_6 q_{t2} q_{t'1} q_{t''2} q_{t'''1} + \epsilon_7 q_{t1} q_{t'2} q_{t''2} q_{t'''1} + \epsilon_8 q_{t2} q_{t'1} q_{t''1} q_{t'''2}) \\
&+ k^{*(j)}_{tt't''t'''}(\epsilon_9 q_{t1} q_{t'1} q_{t''1} q_{t'''2} + \epsilon_{10} q_{t1} q_{t'1} q_{t''2} q_{t'''1} \\
&+ \epsilon_{11} q_{t2} q_{t'2} q_{t''1} q_{t'''2} + \epsilon_{12} q_{t2} q_{t'2} q_{t''2} q_{t'''1} + \epsilon_{13} q_{t1} q_{t'2} q_{t''1} q_{t'''1} \\
&+ \epsilon_{14} q_{t2} q_{t'1} q_{t''1} q_{t'''1} + \epsilon_{15} q_{t1} q_{t'2} q_{t''2} q_{t'''2} + \epsilon_{16} q_{t2} q_{t'1} q_{t''2} q_{t'''2})]\}.
\end{aligned}
$$

The nonvanishing coefficients $k^{(j)}_{tttt}$, $k^{(j)}_{tttt'}$, $k^{(j)}_{ttt't'}$, $k^{(j)}_{ttt't''}$, and $k^{(j)}_{tt't''t'''}$ are given in Tables IVa, IVb, IVc, IVd, and IVe, respectively, together with the values of coefficients α, β, γ, δ, ϵ. The totally symmetric quartic forms involving $\alpha_1\alpha_2\alpha_3\beta_1\beta_2 \cdots \beta_4\gamma_1 \cdots \gamma_5\delta_1 \cdots \delta_6\epsilon_1 \cdots \epsilon_8$ may occur for a molecule belonging to a group I or II, while those involving $\alpha_4\alpha_5\beta_5\beta_6 \cdots \beta_8\gamma_6 \cdots \gamma_9\delta_7 \cdots \delta_{12}\epsilon_9 \cdots \epsilon_{16}$ occur for molecules belonging to groups II. The anharmonic coefficients are designated by k in the former case and by k^* in the later case.

The Tables IV are divided into sections by horizontal lines. The symmetry species of the degenerate vibrations are defined by conditions on the m's. It should be noted that conditions written in different horizontal sections are not compatible. Accordingly there is zero or one horizontal section to consider for each combination of four given degenerate vibrations. The same remark holds for symmetry species of degenerate and nondegenerate vibrations in Tables II and III.

It may happen, as can be seen from the tables, that more than one symmetric form can be built with four given coordinates. Any linear combination of these symmetric forms is of course also a symmetric form. One could then define other anharmonic coefficients k which would appear as linear combinations of ours. This situation is quite common for molecules belonging to groups II. It concerns only coefficients related to four degenerate coordinates when the molecule belongs to a group I.

Let us consider, for example the term in V_{21} corresponding to two degenerate vibrations t and t' (each of them being taken twice). We shall assume that the molecule belongs to a group C_{Nv} or D_N with $N = 3$ or 5, 6, 7 $\cdots$ and that t and t' belong to the same species E_m. According to Eq. (7) and Table IVc, the term under consideration can be written as

$$
\begin{aligned}
&k_{tt't'}(q_{t1}^2 q_{t'1}^2 + q_{t2}^2 q_{t'2}^2 + q_{t1}^2 q_{t'2}^2 + q_{t2}^2 q_{t'1}^2) \\
&\qquad + k'_{tt't'}(q_{t1}^2 q_{t'1}^2 + q_{t2}^2 q_{t'2}^2 + 2 q_{t1} q_{t2} q_{t'1} q_{t'2}).
\end{aligned}
$$

Actually this formula can be rewritten for example as

$$K_{tt'v'}(q_{t1}^2 q_{v'2}^2 + q_{t2}^2 q_{v'1}^2 - 2q_{t1}q_{t2}q_{v'1}q_{v'2}) + K'_{tt'v'}(q_{t1}^2 q_{v'1}^2 + q_{t2}^2 q_{v'2}^2 + 2q_{t1}q_{t2}q_{v'1}q_{v'2})$$

with

$$K_{tt'v'} = k_{tt'v'} ,$$

$$K'_{tt'v'} = k_{tt'v'} + k'_{tt'v'} .$$

Remark

In Ref. *1* we have written the cubic anharmonic potential using coefficients $k_{s\sigma s'\sigma' s''\sigma''}$ and we have given the relations which exist between these coefficients when they are nonvanishing. In the present paper we have found it more convenient to emphasize on the totally symmetric forms and to write the quartic anharmonic potential using coefficients $k^{(j)}_{ss's''s'''}$ (or $k^{*(j)}_{ss's''s'''}$). The two presentations are of course equivalent. The cubic anharmonic potential can very well be written with coefficients $k_{ss's''}$ (and possibly $k^{*}_{ss's''}$ for molecules belonging to a group II), since *one* totally symmetric form (for groups I) and possibly *two* (for groups II) can be built with three given normal vibrations. In the quartic anharmonic potential a larger number of symmetric forms can be built with four given normal vibrations when these are twofold degenerate and the presentation used in this paper proves to be more convenient than the one used in Ref. *1*.

II. ASYMMETRIC MOLECULES

The nonvanishing coefficients k for an asymmetric molecule can be obtained very easily since, for such molecules, there are only nondegenerate normal vibrations n, n', n'', n'''. The coefficients $k_{nn'n''n'''}$ will be nonvanishing if among the four coordinates $nn'n''n'''$ there are zero, two or four characterized by symbols B, 2, u or double prime. These results can be found in Table I if N is taken equal to 1 (groups C_1, C_s, C_i) or to 2 (groups C_2, C_{2h}, C_{2v}, D_2, D_{2h}).[7, 8]

III. LINEAR MOLECULES

In Tables I, II, and IV the rows marked with stars indicate the anharmonic coefficients which are nonvanishing for a linear molecule. For the symmetry species of the nondegenerate vibrations $nn'n''n'''$, one has to replace $A_{(1)}$ or $A_{(g)}$ by $\sum^+$ while the degenerate vibrations belong to species $\prod$. The symbols $\sum^+$ and $\prod$ have to be completed with a subscript g or u if the group of the molecule is $D_{\infty h}$. Here again, a nonvanishing coefficient k may involve zero, two, or four vibrations u.

---

[7] The group S_2 is identical to C_i.

[8] For groups D_2 and D_{2h} the common nomenclature of symmetry species is $AB_1B_2B_3$ instead of $A_1A_2B_2B_1$ used here.

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3. J. Moret-Bailly, *Cahiers Phys.* **112**, 476 (1959).
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PART 2

COMPUTATION OF LINE FREQUENCIES

The results obtained for the rotation-vibration energies of polyatomic molecules and described in Part 1 have been used to compute the frequencies of lines in rotation and rotation-vibration spectra.

Rotation Spectra

The rotation spectrum of axially symmetric molecules in an excited state $v_t = 1$ (t beeing a twofold degenerate vibration) has been studied in two papers :

- M.L. GRENIER-BESSON and G.AMAT, J. Molecular Spectroscopy, 8, 22, 1962
- P. KUPECEK, J. Phys. Rad., 25, 831, 1964

refering respectively to molecules with a threefold symmetry axis and to molecules with a fourfold symmetry axis. In Chapter II, we shall give the results obtained for molecules belonging to a symmetry group C_{3v}.

Rotation-Vibration Spectra

Our work on the computation of rotation-vibration lines in the spectra of linear and axially symmetric molecules is in the process of being published as a Monograph by the National Bureau of Standards.

The case of spherical tops (tetrahedral XY_4 and octahedral XY_6 molecules) requires special attention due to the high symmetry of the force field. Two papers have been published on the threefold degenerate fundamental bands of such molecules :

- J.MORET-BAILLY, Cahiers de Physique, 15, 237, 1961
- J.MORET-BAILLY, J.Molecular Spectroscopy, 15, 344, 1965

We shall study this problem in Chapter III hereafter.

CHAPTER II

Rotation Spectrum of Molecules with C_{3v} Symmetry in an Excited Vibrational State v_t 1

I. INTRODUCTION

The rotational transitions $J \rightarrow J + 1$ of a molecule with axial symmetry in an excited vibrational state $v_t = 1$, $l_t = \pm 1$ were calculated for the first time in 1950 by Nielsen (*1*). The formula obtained made it possible to interpret the transition $J = 1 \rightarrow 2$ of the excited vibrational state $v_8 = 1$ observed in the microwave spectrum of methyl cyanide and methyl isocyanide by Kessler *et al.* (*2*). Nielsen introduced into the energy matrix, on the one hand, the matrix element $(v_t, l_t, K \mid h_2' \mid v_t, l_t \pm 2, K \pm 2)$ of the second-order transformed Hamiltonian, responsible for l-type doubling and l-type resonance "2,2" and, on the other, *certain* diagonal elements of the third-order transformed Hamiltonian.

Gordy and his co-workers (*3*, *4*) extended Nielsen's formulation to the case of transitions corresponding to higher values of J. They thus interpreted the transition $J = 2 \rightarrow 3$ of methyl acetylene and the transitions $J = 4 \rightarrow 5$ and $J = 8 \rightarrow 9$ of trifluoromethyl acetylene in the excited state $v_{10} = 1$.

Nielsen's theory was satisfactory for accounting the general aspects of the rotation spectrum of molecules with a threefold axis belonging to the group C_{3v}. However, some of the frequencies calculated in accordance with this theory differed significantly from the observed frequencies; moreover, for certain coefficients, $\zeta^z_{t_1t_2}$ and D_{JK} in particular, it led to values in disagreement with those obtained by other methods (study of rotational transitions at the lowest vibrational level and analysis of the rotation-vibration bands observed in the infrared). These difficulties suggested that the matrix used for the energy was not complete.

A systematic inventory of the matrix elements having become possible as a result of the general calculation of rotation-vibration energy by Amat *et al.* (*5*), Maes (*6*) reconsidered the interpretation of the transition $J = 1 \rightarrow 2$ in the excited state $v_8 = 1$ of the methyl cyanide and methyl isocyanide molecule. To represent the energy, he employed a matrix containing *all* the diagonal elements of the third-order transformed Hamiltonian, and also the elements of l-type resonance "2, −1" calculated by Grenier-Besson (*7*). This new formulation led to reasonable values for the Coriolis coupling coefficients ζ_{8182} of the methyl cyanide and methyl isocyanide molecule. Experience has shown, however, that more accurate determinations of the ζ coefficients and other molecular constants are obtained more safely from transitions corresponding to higher values of J, in view of the availability of the measurements of a large number of lines for the computation.

II. FREQUENCY OF LINES FOR A TRANSITION $J \rightarrow J + 1$

The object of the present article is to generalize Maes's results so as to obtain a formula expressing the frequency of the lines for an arbitrary rotational transition $J \rightarrow J + 1$ of a molecule with C_{3v} symmetry in an excited vibrational state $v_t = 1$. However, the matrix employed for the energy is rigorously valid only insofar as the rotational quantum number J is not too large and also when there is no accidentally strong resonance (see below, (b)). In writing this matrix account has been taken of the symmetry properties of the molecule (*8*) and the order of magnitude of the contributions of the various matrix elements to the rotation-vibration energy (*9*).

The frequency of the transition $J \rightarrow J + 1$ for a molecule with C_{3v} symmetry in the excited vibrational state $v_t = 1$ is given by the equation:

$$\nu = 2B^*(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)(Kl-1)^2 + 2\rho^*(J+1)(Kl-1) + \begin{cases} \pm 4q_J(J+1) & \text{if } Kl = +1 \\ \text{or} & \\ -\dfrac{4q_J^2(J+1)^3}{(B_v - C_v + C_v\zeta)(Kl-1)} & \text{if } Kl \neq +1, \end{cases} \tag{1}$$

where

$$B^* = B_v - D_{JK} + \eta_{lJ} + \frac{12r^2}{B_v - C_v - 2C_v\zeta}, \tag{2}$$

$$\rho^* = \eta_{lJ} - 2D_{JK} + \frac{2q_J^2}{B_v - C_v + C_v\zeta} + \frac{8r^2}{B_v - C_v - 2C_v\zeta}. \tag{3}$$

In the above equations, B_v and C_v designate the constants of inertia; D_J and D_{JK}, the coefficients of centrifugal distortion; ζ, the Coriolis coupling coefficient $\zeta^{z}_{t_1 t_2}$; q_J, the constant of *l*-type doubling "2,2", r, the constant of *l*-type resonance "2, −1"; and η_{lJ}, the coefficient of the term in $Kl\, J(J+1)$ in the third-order energy (see Ref. *6*).[1]

The equation that follows from the earlier theory (*1*, *3*, *4*) may be obtained by substituting in Eq. (1):

$$\eta_{lJ} = 2(2D_J + D_{JK})\zeta,$$

$$r = 0$$

equations which are in fact false.

In regard to the validity of Eq. (1), two remarks must be made:

(a) *In writing the matrix* of the energy, only those matrix elements that may make a sixth-order contribution have been retained, in accordance with the discussion in Ref. *9*. The order of magnitude of the various matrix elements depends in fact upon the value of the rotational quantum numbers, and we have assumed that J and K are small ($J \cong K \cong 1$). For larger values of the rotational quantum numbers ($J \cong K \cong 30$ and, especially, $J \cong 30$, $K \cong 1$), additional matrix elements may contribute to the energy. The values J or $K \cong 30$ beyond which new terms must be added to the equations varies from one molecule to another.

(b) *In solving the secular equation*, a perturbation method has been used to calculate the contributions of the elements of *l*-type resonances "2,2" and "2, −1". This technique is valid only insofar as the nondiagonal elements are small in relation to the differences between the corresponding diagonal elements, which implies the following two inequalities:

$$\tfrac{1}{2}\,|\,q_J\,|\,J(J+1) \ll |\,B_v - C_v + C_v\zeta\,|,$$

$$|\,r\,|\sqrt{J(J+1)} \ll |\,B_v - C_v - 2C_v\zeta\,|.$$

It may happen that, as a result of particular values of the molecular constants, one or the other of these inequalities no longer holds beyond a certain value of J (see Ref. *9*: "accidentally strong resonance"). In this case, the contribution of the nondiagonal matrix elements cannot be calculated by a perturbation method, and it is necessary to proceed to a numerical solution of the secular equation.

---

[1] As Nielsen (*10*) has shown, the *l*-type doubling constant varies with J:

$$q_J = q_0 - \mu\, J(J+1)$$

The constants q_0 and r are identical with the coefficients F' and E' of Ref. 7.

III. APPLICATION TO THE INTERPRETATION OF THE MICROWAVE SPECTRUM OF TRIFLUOROMETHYL ACETYLENE

With the aim of verifying the above formulation, we have studied the rotational transitions $J = 4 \rightarrow 5$ and $J = 8 \rightarrow 9$ of the excited vibrational level $v_{10} = 1$ of trifluoromethyl acetylene. As stated above, these transitions have been observed in the microwave region by Anderson *et al.* (*4*) and interpreted in the light of Nielsen's theory. The agreement between theoretical and observed frequencies was not completely satisfactory.

In the excited vibrational state $v_t = 1$, the $2(J + 1)$ lines belonging to the transition $J \rightarrow J + 1$ are arranged in the following fashion: $2\,J$ lines are grouped together in the middle of the interval separating the two extreme lines. These two lines, which are rather far from the central group, correspond to $Kl - 1 = 0$

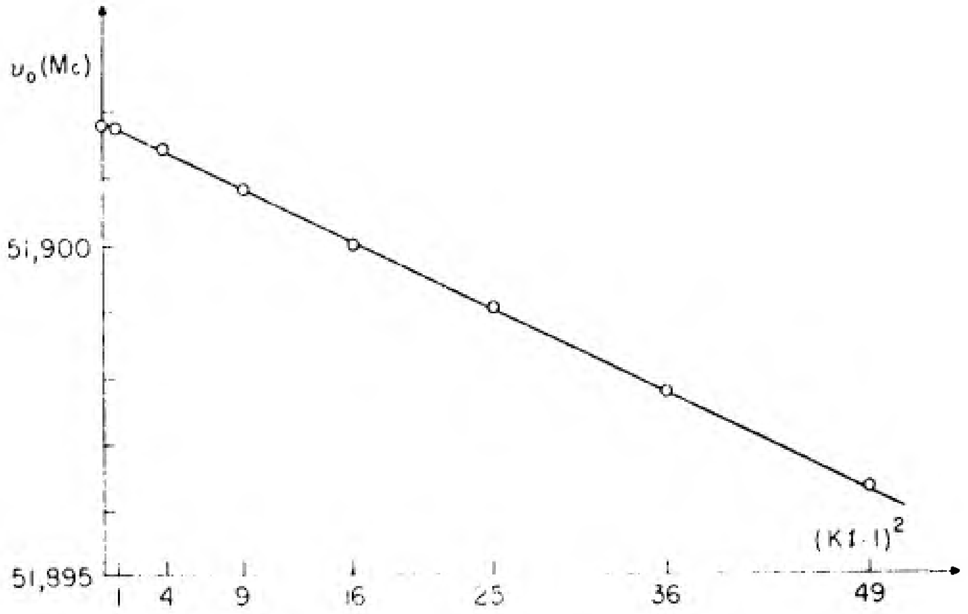

FIG. 1. Transition $J = 8 \rightarrow 9$. The slope is equal to $-18\ D_{JK}$

TABLE I

MOLECULE $CF_3 - C \equiv CH$

	Our results	Results of A,T,S,G	
	$v_t = 1$	$v_t = 1$	$v_t = 0$
B_v^+	2883.45_0 Mc	2883.46 Mc	(B_0 = 2877.948 Mc)
$B_v - C_v + C_v\zeta$	455 ± 10 Mc	458 Mc	
D_{JK}	0.00625 Mc	0.0070 Mc	0.0063 Mc
D_J	0.00022 Mc	0.0002 Mc	0.00024 Mc
ρ	0.025_4 Mc		
$q^{(J=4)}$	0.90_3 Mc	0.90_5 Mc	
$q^{(J=8)}$	0.90_7 Mc		
ζ	0.574 ± 0.005	1.5	

and are affected by l-type doubling. The lines of the central group correspond to $Kl - 1 \neq 0$. In interpreting them, it is convenient to distinguish $J - 1$ doublets, for which $| Kl - 1 | = 1, 2, \cdots, J - 1$, and two singlets, corresponding to $Kl - 1 = -J, -(J + 1)$.

The difference and half-sum of the frequencies of the lines $Kl - 1 = 0$ immediately give q_J and $\nu_0{}^J = 2B^*(J + 1) - 4D_J(J + 1)^3$: the half-sums of the components of the central group give $J - 1$ equations depending only on D_{JK} and $\nu_0{}^J$.

The frequencies of the two singlets and the differences between the components of the doublets of the central group give $J + 1$ equations which (q_J being known) depend only on ρ^* and $(B_v - C_v + C_v\zeta)$.

This method applied to the transition $J = 8 \rightarrow 9$ allows us to determine the five constants $q_{(J=8)}$, $\nu_0^{(J=8)}$, D_{JK}, ρ^* and $(B_v - C_v + C_v\zeta)$ from 18 experimental frequencies.

From the curve of Fig. 1, it is seen that the plot of the half-sums of the frequencies of the components of the doublets versus, $(Kl - 1)^2$, gives a straight line. Intersection of the straight line with the vertical axis and its slope are, respectively, $\nu_0^{(J=8)}$ and-18 D_{JK}.

The same method applied to the transition $J = 4 \rightarrow 5$ yields values of $\nu_0^{(J=4)}$ and 10 D_{JK}; we thus know two values of $\nu_0{}^J$, from which we may deduce B^* and D_J.

TABLE II

Transition	Observed (Mc)	Calculated by us	Calculated (A,T,S,G)	No.
$J = 8 \rightarrow 9$				
$l = \pm 1 \quad K = 0$	51,906.64	51,906.64	51,906.69	1
$l = \pm 1 \quad K = \mp 1$	51,903.42	51,903.39	51,903.55	2
$l = \pm 1 \quad K = \pm 1$	51,869.14	51,869.14	51,869.10	3
	51,934.48	51,934.48	51,934.20	4
$l = \pm 1 \quad K = \mp 2$	51,901.68	51,901.66	51,901.87	5
$l = \pm 1 \quad K = \pm 2$	51,896.86	51,896.74	51,896.89	6
$l = \pm 1 \quad K = \mp 3$	51,899.99	51,900.14	51,900.36	7
$l = \pm 1 \quad K = \pm 3$	51,899.44	51,899.33	51,899.26	8
$l = \pm 1 \quad K = \mp 4$	51,898.61	51,898.57	51,898.77	9
$l = \pm 1 \quad K = \pm 4$	51,899.99	51,899.95	51,899.68	10
$l = \pm 1 \quad K = \mp 5$	51,896.86	51,896.87	51,896.06	11
$l = \pm 1 \quad K = \pm 5$	51,899.99	51,899.90	51,899.42	12
$l = \pm 1 \quad K = \mp 6$	51,894.95	51,894.99	51,895.04	13
$l = \pm 1 \quad K = \pm 6$	51,899.44	51,899.45	51,898.74	14
$l = \pm 1 \quad K = \mp 7$	51,892.88	51,892.94	51,892.71	15
$l = \pm 1 \quad K = \pm 7$	51,898.61	51,898.69	51,897.72	16
$l = \pm 1 \quad K = \mp 8$	51,890.62	51,890.64	51,890.42	17
$l = \pm 1 \quad K = \pm 8$	51,897.63	51,897.66	51,896.39	18

If we put

$$B_v^* = B_v^+ - D_{JK} + \rho$$

$$\rho^* = \rho - 2D_{JK} + \frac{2q_J^2}{B_v - C_v + C_v\zeta},$$

we can calculate B_v^+ and ρ, constants which can be simply expressed in terms of the molecular parameters.

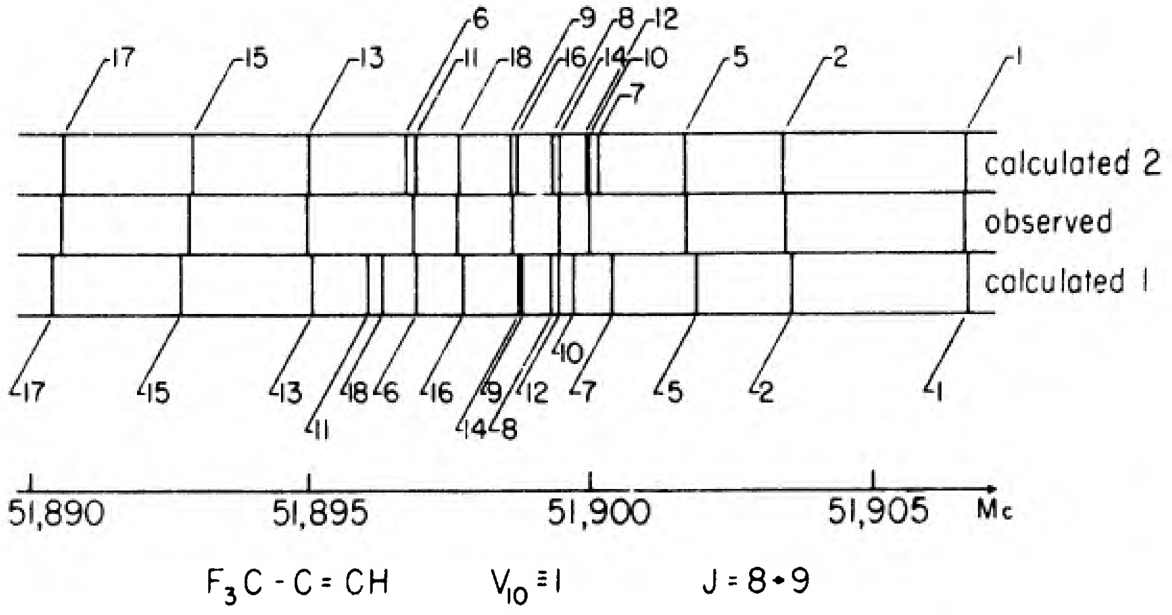

FIG. 2. The numbers 1 and 2 refer to frequencies calculated by Anderson *et al.* and by us, respectively.

TABLE III

Transition	Observed (Mc)	Calculated by us	Calculated (A,T,S,G)	No.
$J = 4 \to 5$				
$l = \pm 1$ $K = 0$	28,835.26	28,835.26	28,835.31	1
$l = \pm 1$ $K = \mp 1$	28,834.45	28,834.46	28,834.65	2
$l = \pm 1$ $K = \pm 1$	28,816.48	28,816.52	28,816.52	3
	28,852.61	28,852.65	28,852.72	4
$l = \pm 1$ $K = \mp 2$	28,833.81	28,833.83	28,833.94	5
$l = \pm 1$ $K = \pm 2$		28,833.79	28,833.78	6
$l = \pm 1$ $K = \mp 3$	28,833.22	28,833.15	28,833.19	7
$l = \pm 1$ $K = \pm 3$	28,834.20	28,834.21	28,834.12	8
$l = \pm 1$ $K = \mp 4$	28,832 ± 1	28,832.38	28,832.48	9
$l = \pm 1$ $K = \pm 4$	28,834.20	28,834.22	28,834.03	10

$$B_v^+ = B_v + \frac{4r^2}{B_v - C_v - 2C_v\zeta} \cong B_v ,$$

$$\rho = \eta_{tJ} + \frac{8r^2}{B_v - C_v - 2C_v\zeta} .$$

If the equilibrium configuration of the molecule is known, the inertia constant C_e can be calculated. Using B_v^+ and C_e as approximate values of B_v and C_v , it is then possible to obtain ζ with excellent accuracy from the value of

$$(B_v - C_v + C_v\zeta)$$

determined above.

Table I gives our results together with those previously obtained by Anderson *et al*. This table suggests the following remarks:

(1) The value 6.25 kc given for D_{JK} is that obtained from the transition $J = 8 \rightarrow 9$ (Fig. 1). If we use the transition $J = 4 \rightarrow 5$, we obtain the value 6.2_2 for this constant. Since this result is much less accurate than the preceding one, it cannot be affirmed that the slight difference between these two values is due to a variation of D_{JK} with J. The result obtained for D_{JK} in the excited state $v_t = 1$, viz., 6.25 kc, does not differ greatly from the value for this constant obtained by Anderson *et al.* in the fundamental state $v_t = 0(D_{JK} = 6.3$ kc). The value of $D_{JK} = 6.25$ kc is more satisfactory than the value 7.0 kc given by Anderson *et al.* for the state $v_t = 1$.

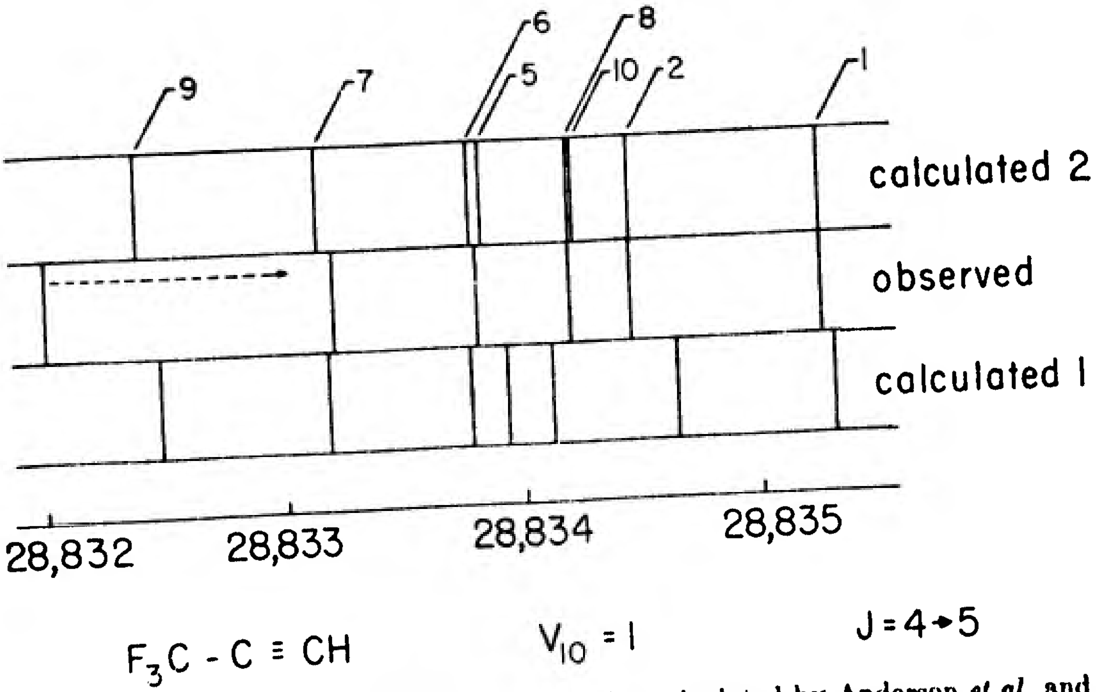

FIG. 3. The numbers 1 and 2 refer to frequencies calculated by Anderson *et al.* and by us, respectively. The precision on the line No. 9 in the observed spectrum is very poor (±1 Mc).

(2) Further experimental results would be necessary to determine with certainty the variation of q with J. The data utilized are not precise enough to justify the assertion that the difference of 4 kc observed between the values of $q^{(J=8)}$ and $q^{(J=4)}$ is significant.

(3) The two quantities $(B_v - C_v + C_v\zeta)$ and ρ^* may be determined by using either the transition $J = 4 \rightarrow 5$ or the transition $J = 8 \rightarrow 9$. Since these transitions furnish 10 and 18 experimental frequencies, respectively, the values determined from the latter are much more exact than those determined from the former. The values of $(B_v - C_v + C_v\zeta)$ and ρ^* given in Table I were obtained from the 18 experimental data of the transition $J = 8 \rightarrow 9$.

(4) In calculating the coefficient ζ, the value $C_v = 5700 \pm 50$ Mc has been used for the constant of inertia C_v. Precision on ζ is very good, and the value obtained, $\zeta = 0.574$, seems more likely than that given by Anderson *et al.* ($\zeta = 1.5$), which is incompatible both with the value of $(B_v - C_v + C_v\zeta)$ obtained by the same authors and with the requirement $0 < |\zeta| < 1$.

Having thus determined (Table I, column 2) the constants that occur in Eq. (1), we have calculated the theoretical frequencies of the lines of the transition $J = 8 \rightarrow 9$ and obtained the results presented in Table II. They are in very good agreement with the observed frequencies. Figure 2 shows the experimental lines, the lines calculated by us and those calculated with Nielsen's equation by Anderson *et al.* This comparison exhibits the progress that Eq. (1) introduces in the interpretation of the spectrum. The same constants have been used to calculate the lines of the transition $J = 4 \rightarrow 5$. Table III and Fig. 3 show that the agreement is still very good. To avoid crowding, only the lines of the central group $(Kl - 1 \neq 0)$ are represented in Figs. 2 and 3.

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CHAPTER III

Calculation of The Frequencies of the Lines in a Threefold Degenerate Fundamental Band of a Spherical Top Molecule

I. QUANTUM NUMBERS

The vibration-rotation energy levels are characterized by the following quantum numbers: (a) a vibrational quantum number v_1 for the nondegenerate vibration; (b) two vibrational quantum numbers v_2 and ℓ_2 for the twofold degenerate vibration; (c) three vibrational quantum numbers v_s , ℓ_s and m_s $(s > 2)$ for each threefold degenerate vibration; (d) three rotational quantum numbers J, K, and M.

Suppose here that the value of the vibrational quantum numbers is zero except possibly for three of them $(v_s \ell_s m_s)$, corresponding to one threefold degenerate vibration characterized by a definite value of the subscript s. These nonvanishing quantum numbers are designated as v, ℓ, m, omitting the subscript.

As the energy of a free molecule does not depend on the quantum number m, it is necessary to consider only the five quantum numbers v, l, m, J, and K The quantum number v, will have the value $v = 0$ in the ground state and the value $v = 1$ in the excited state. In the first case, ℓ and m are zero; in the second case, they have the values $\ell = 1$ and $m = 0 \pm 1$; J is a non-negative integer, and K has integral values such that $-J \leqq K \leqq J$.

Quantum numbers ℓ and J give the lengths of the vibrational angular momentum **l** and of the total angular momentum **P**. The symbols m and K quantize the projections of **l** and **P** on an axis bound to the molecule.

But m and K are not good quantum numbers, and are replaced by a set of new quantum indices, namely,

(i) a rotational quantum number R related to the length of the pure rotational angular momentum $\mathbf{R} = \mathbf{P} - \mathbf{l}$. R is a positive integer (or zero) such that $(J - \ell) \leqq R \leqq J + \ell$;

(ii) a quantum index C which is one of the symbols of the irreducible representations of the molecular group: for the XY_4 molecules (T_d group),

$$C = A_1, A_2, E, F_1, F_2;$$

for the XY_6 molecules (O_h group),

$$C = A_{1u}, A_{1g}, A_{2u}, A_{2g}, E_u, E_g, F_{1u}, F_{1g}, F_{2u}, F_{2g}.$$

(iii) a quantum index σ with two possible values $\sigma = 1, 2$ when $C = E$ (or E_gE_u) and three possible values $\sigma = 1, 2, 3$ when $C = F_1F_2$ (or $F_{1g}F_{1u}F_{2u}F_{2g}$). Different values of σ correspond to various components of degenerate basis. As the energy does not depend on the quantum index σ we shall always omit it.

(iv) a quantum index n ($n = 0, 1, 2 \cdots$) that is used to characterize different states belonging to the same species, i.e., states that have the same values of v, ℓ, J, R, C, and σ. In fact, we shall designate these different states by symbols $C, C', C'', \cdots$, etc. (for instance $A_1, A_1', A_1'', \cdots$), where the number of primes is equal to n.

Often, for the sake of brevity, we shall replace the two symbols (C, n) by a single letter p.

II. SELECTION RULES IN THE INFRARED

The selection rules for electric dipole absorption or emission between two states a and b are:

$$R_a = R_b \qquad C_a = C_b \qquad n_a = n_b \tag{1}$$

but the rule $R_a = R_b$ is not rigorous, and there are weak lines corresponding to

$$R_a \neq R_b; \qquad C_a = C_b \tag{2}$$

without any rule for n_a and n_b.

III. ENERGY LEVELS

A) Ground State

In the ground state, the Hamiltonian matrix is diagonal in the representation defined above. Since $\ell = 0$, the quantum numbers R and J are identical. The energy is given by the formula

$$\begin{aligned} E^0_{(R,p)} &= \alpha^0 + \beta^0 R(R+1) + \gamma^0 R^2(R+1)^2 + \pi^0 R^3(R+1)^3 \\ &+ [(2R-3)(2R-2)\cdots(2R+5)]^{1/2}[\epsilon^0 + \rho^0 R(R+1)](-1)^R F^{(4RR)}_{A_1pp} \\ &+ [(2R-5)(2R-4)\cdots(2R+7)]^{1/2}\xi^0(-1)^R F^{(6RR)}_{A_1pp}. \end{aligned} \tag{3}$$

In this formula appear (a) molecular constants α^0, β^0, $\cdots$ (their order of magnitude will be given in the following section), (b) the quantum number R, (c) Clebsch-Gordan coefficients $F^{(4RR)}_{A_1pp}$ or $F^{(6RR)}_{A_1pp}$ adapted to the cubic symmetry. A table of numerical values of these coefficients has been calculated (*1*).

B. EXCITED STATE

The Hamiltonian matrix is not diagonal in the representation used here, and the energy levels are obtained by a perturbation calculation.

In a first approximation, the off-diagonal matrix elements can be neglected; so the energy is given by the diagonal matrix elements of the Hamiltonian:

$$\begin{aligned}
W_{J=R+1,R,p} = {} & \alpha + 2\lambda + 6\delta + (\beta + 2\lambda + 10\delta + 2\chi)(R+1) \\
& + (\beta + 4\delta + 4\chi + \gamma)(R+1)^2 + (2\gamma + 2\chi + 14\psi + \pi) \\
& \qquad (R+1)^3 \\
& + (\gamma + 4\psi + 3\pi)(R+1)^4 + 3\pi(R+1)^5 + \pi(R+1)^6 \\
& + [\varphi + 20\epsilon - 8\mu + (18\epsilon - 4\mu + \sigma - 90\tau)(R+1) \\
& + (4\epsilon + \sigma - 20\tau)(R+1)^2 + 22\rho(R+1)^3 + 4\rho(R+1)^4] \qquad (4) \\
& \times \frac{[(2R-3)(2R-2)\cdots(2R+5)]^{1/2}}{(2R+2)(2R+3)} (-1)^R F^{(4RR)}_{A_1pp} \\
& + [\eta + 26\xi(R+1) + 4\xi(R+1)^2] \\
& \times \frac{[(2R-5)(2R-4)\cdots(2R+7)]^{1/2}}{(2R+2)(2R+3)} (-1)^R F^{(6RR)}_{A_1pp},
\end{aligned}$$

$$\begin{aligned}
W_{J=R,R,p} = {} & \alpha + 2\lambda + 6\delta + (\beta - 8\delta + 2\chi)R(R+1) + (\gamma - 8\psi)R^2(R+1)^2 \\
& + \pi R^3(R+1)^3 \\
& + [16\mu - 40\epsilon - 2\varphi + (-2\sigma + 40\tau + 4\epsilon)R(R-1) \\
& \qquad + 4\rho R^2(R+1)^2] \\
& \times \frac{[(2R-3)(2R-2)\cdots(2R+5)]^{1/2}}{2R(2R+2)} (-1)^R F^{(4RR)}_{A_1pp} \qquad (5) \\
& + [-2\eta + 4\xi R(R+1)] \frac{[(2R-5)(2R-4)\cdots(2R+7)]^{1/2}}{2R(2R+2)} \\
& \qquad (-1^R)\, F^{(6RR)}_{A_1pp},
\end{aligned}$$

$$
\begin{aligned}
W_{J=R-1,R,p} = {} & \alpha + 2\lambda + 6\delta - (\beta + 2\lambda + 10\delta + 2\chi)R \\
& + (\beta + 4\delta + 4\chi + \gamma)R^2 - (2\gamma + 2\chi + 14\psi + \pi)R^3 \\
& + (\gamma + 4\psi + 3\pi)R^4 - 3\pi R^5 + \pi R^6 \\
& + [\varphi + 20\epsilon - 8\mu - (18\epsilon - 4\mu + \sigma - 90\tau)R \\
& + (4\epsilon + \sigma - 20\tau)R^2 - 22\rho R^3 + 4\rho R^4] \\
& \times \frac{[(2R-3)(2R-2)\cdots(2R+5)]^{1/2}}{(2R-1)(2R)} (-1)^R F^{(4\,R\,R)}_{A_1 p\,p} \\
& + [\eta - 24\xi R + 4\xi R^2] \frac{[(2R-5)(2R-4)\cdots(2R+7)]^{1/2}}{(2R-1)(2R)} \\
& \cdot (-1)^R F^{(6\,R\,R)}_{A_1 p\,p} .
\end{aligned} \tag{6}
$$

In these formulas, the meaning of the letters is the same as in formula (3). The approximation which is obtained is poor, and so, there is no point in taking into account the small terms written in Eqs. (4)-(6). With the orders of magnitude given in the following section, one sees that it is sufficient to calculate, in place of $W_{J,R,p}$ the simplified expressions

$$
\begin{aligned}
W^0_{J=R+1,R,p} = {} & \alpha + 2\lambda + 6\delta + (\beta + 2\lambda + 10\delta + 2\chi)(R+1) \\
& + (\beta + 4\delta + 4\chi + \gamma)(R+1)^2 \\
& + [\varphi + 20\epsilon - 8\mu + (18\epsilon - 4\mu + \sigma - 90\tau)(R+1) \\
& + (4\epsilon + \sigma - 20\tau)(R+1)^2] \\
& \times \frac{[(2R-3)(2R-2)\cdots(2R+5)]^{1/2}}{(2R+2)(2R+3)} (-1)^R F^{(4\,R\,R)}_{A_1 p\,p}
\end{aligned} \tag{7}
$$

or

$$
\begin{aligned}
W^0_{J=R,R,p} = {} & \alpha + 2\lambda + 6\delta + (\beta - 8\delta + 2\chi)R(R+1) \\
& + [16\mu - 40\epsilon - 2\varphi + (-2\sigma + 40\tau + 4\epsilon)R(R+1)] \\
& \times \frac{[(2R-3)(2R-2)\cdots(2R+5)]^{1/2}}{2R(2R+2)} (-1)^R F^{(4\,R\,R)}_{A_1 p\,p}
\end{aligned} \tag{8}
$$

or

$$
\begin{aligned}
W^0_{J=R-1,R,p} = {} & \alpha + 2\lambda + 6\delta - (\beta + 2\lambda + 10\delta + 2\chi)R \\
& + (\beta + 4\delta + 4\chi + \gamma)R^2 \\
& + [\varphi + 20\epsilon - 8\mu - (18\epsilon - 4\mu + \sigma - 90\tau)R + (4\epsilon + \sigma \\
& - 20\tau)R^2] \\
& \times \frac{[(2R-3)(2R-2)\cdots(2R+5)]^{1/2}}{(2R-1)(2R)} (-1)^R F^{(4\,R\,R)}_{A_1 p\,p} .
\end{aligned} \tag{9}
$$

It is easily seen that the same approximation could be obtained in the ground state putting $\pi^0 = \rho^0 = \xi^0 = 0$ in Eq. (3).

A second approximation is given by a second-order perturbation calculation:

$$W^1_{J,R,p} = W'_{J,R,p} + \sum_{R \neq R'} \frac{W'_{J,R,p;J,R',p'}\, W'_{J,R',p';J,R,p}}{W'^0_{J,R,p} - W'^0_{J,R',p'}}. \tag{10}$$

The products $W'_{J,R,p;J,R',p'} W'_{J,R',p';J,R,p}$ of the off-diagonal matrix elements have the following values:

for $R = J - 1; \quad R' = J + 1,$

$$\frac{5}{2}\left[(12\epsilon - 6\mu + \varphi)^2 - 4\nu^2(2J+1)^2\right] \times \frac{(2J-3)(2J-2)\cdots(2J+5)}{(2J+1)^2(2J)(2J+2)} \left[F\begin{pmatrix}4 & J+1 & J-1\\ A_1 & p' & p\end{pmatrix}\right]^2; \tag{11}$$

for $R = J - 1; \quad R' = J,$

$$-\frac{5}{2}\left\{[\varphi + 20\epsilon - 8\mu + (8\epsilon - 8\mu)J]^2 - 4\nu^2 J^2\right\} \times \frac{(2J-4)(2J-3)\cdots(2J+4)}{4J^2(2J+1)(2J+2)} \left[F\begin{pmatrix}4 & J & J-1\\ A_1 & p' & p\end{pmatrix}\right]^2; \tag{12}$$

for $R = J; \quad R' = J + 1,$

$$-\frac{5}{2}\left\{[\varphi - 12\epsilon + 6\mu + J(8\epsilon - 2\mu)]^2 - \nu^2(2J+2)^2\right\} \times \frac{(2J-2)(2J-1)\cdots(2J+6)}{(2J+2)^2(2J)(2J+1)} \left[F\begin{pmatrix}4 & J+1 & J\\ A_1 & p' & p\end{pmatrix}\right]^2. \tag{13}$$

If p and p' in the expressions (11)-(13) are exchanged, the three expressions obtained correspond, respectively, to:

$$R = J + 1; \quad R' = J - 1,$$
$$R = J; \quad R' = J - 1,$$
$$R = J + 1; \quad R' = J.$$

A third approximation comes from a third-order perturbation calculation

$$W'^2_{J,R,p} = W'_{J,R,p} + \sum_{R \neq R'} \frac{W'_{J,R,p;J,R',p'}\, W'_{J,R',p';J,R,p}}{W'^1_{J,R,p} - W'^1_{J,R',p'}} + \sum_{\substack{R \neq R'\\ R \neq R''\\ R' \neq R''}} \frac{W'_{J,R,p;J,R',p'}\, W_{J,R',p';J,R'',p''}\, W'_{J,R'',p'';J,R,p}}{(W'^1_{J,R,p} - W'^1_{J,R',p'})(W^1_{J,R,p} - W'^1_{J,R'',p''})}, \tag{14}$$

where the product $W_{J,R,p;J,R',p'}W_{J,R',p';J,R'',p''}W_{J,R'',p'';J,R,p}$ of three off-diagonal matrix elements is, for $R = J - 1$; $R' = J$; $R'' = J + 1$:

$$
\begin{aligned}
&W_{J,J-1,p;J,J,p'}\,W_{J,J,p';J,J+1,p''}\,W_{J,J+1,p'';J,J-1,p} \\
&\qquad = -\left(\frac{5}{2}\right)^{3/2}(12\epsilon+\varphi)[4\epsilon(2J+5)+\varphi-2J(\mu+\nu)] \\
&\qquad \times [4\epsilon(2J+3)-\varphi+2J(\nu-\mu)] \\
&\times \frac{(2J-4)^{1/2}(2J-3)[(2J-2)(2J-1)\cdots(2J+4)]^{3/2}\times(2J+5)(2J+6)^{1/2}}{[2J(2J+1)(2J+2)]^2} \qquad (15) \\
&\times(-1)^J F\begin{pmatrix}4 & J-1 & J+1\\ A_1 & p & p''\end{pmatrix} F\begin{pmatrix}4 & J & J-1\\ A_1 & p' & p\end{pmatrix} \\
&\qquad\qquad\qquad\qquad \times F\begin{pmatrix}4 & J & J+1\\ A_1 & p' & p''\end{pmatrix}.
\end{aligned}
$$

This formula is not changed by any permutation of the three systems of indices $(J, J-1, p)$, (J, J, p'), and $(J, J+1, p'')$ on the left side.

IV. ORDERS OF MAGNITUDE

The calculations are done by successive approximations. In the beginning, it is convenient to neglect the smallest matrix elements. So, we shall give the orders of magnitude of the various terms in formulas (4) to (15). The values of the orders of magnitude given by Nielsen and Amat are used here (*2*). They have defined an index of magnitude corresponding to the various terms of the expansion for the energy

$$E = E^0 + E^1 + \cdots .$$

A large value of the index of magnitude corresponds to a small value of the energy; an increase by one unit in the index of magnitude means roughly a decrease in the energy by a factor of about $1/30$.

The frequency of a line is proportional to the transition energy (difference between the energies of the two levels involved in the transition).

Equations (10) or (14) give the energy levels as functions of diagonal matrix elements and products of off-diagonal matrix elements. The latter are given by formulas (11), (12), (13), and (15), and the former by formulas (3), (4), (5), and (6). All these formulas contain sums of terms on the right-hand-side of the various equations. In each one of these terms, a coefficient expressed by a letter (or a product of such coefficients) is multiplied by a function of rotational quantum numbers R and J.

In Table I, one finds:

(a) the indices of magnitude of the various coefficients α^0, β^0, $\cdots$ α, β, $\cdots$;

TABLE 1

ORDERS OF MAGNITUDE

		Smallest order of magnitude of:																		
					the contribution to energy level;						the contribution to energy of transition;					
	Coefficient which is a factor of the term	the coefficient	the term		Diagonal term		2nd order perturbation		3rd order perturbation		Diagonal term		2nd order perturbation		3rd order perturbation	
			$R \simeq 1$	$R \simeq 30$	$R \simeq 1$	$R \simeq 30$	$R \simeq 1$	$R \simeq 30$	$R \simeq 1$	$R \simeq 30$	$R \simeq 1$	$R \simeq 30$	$R \simeq 1$	$R \simeq 30$	$R \simeq 1$	$R \simeq 30$
α	α^0	0	0	0	0	0					0	0				
β	β^0	2	2	0	2	0					2	1				
γ	γ^0	6	6	2	6	2					6	3				
ϵ	ϵ^0	6	6	2	6	2	8	3	10	4	6	3	8	3	10	4
$\pi\rho\xi$	$\pi^0\rho^0\xi^0$	10	10	4	10	4					10	5				
	λ	2	2	1	2	1					2	1				
	δ	4	4	2	4	2					4	2				
	φ	4	4	2	4	2	6	3	8	4	4	2	6	3	8	4
	χ	6	6	3	6	3					6	3				
	ν	6	6	3			10	5	10	5			10	5	10	5
	μ	6	6	3	6	3	8	4	10	5	6	3	8	4	10	5
	$\xi\psi\tau\eta\sigma$	10	10	4	10	4					10	4				

(b) the indices of magnitude of the corresponding terms appearing in formulas (3)–(6). These indices depend on the value of the rotational quantum number R. Two special cases: $R \simeq 1$ and $R \simeq 30$ have been considered;

(c) the indices of magnitude of contributions to the energy levels. Equations (10) and (14) show that the same coefficient can give a contribution to the energy either through a diagonal matrix element or through an off-diagonal matrix element. In the first case, the indices of magnitude are the same for the energy and the matrix element; they are generally different in the second case;

(d) the indices of magnitude of the transition energies. If a term is the same in the lower state (ground state) and in the upper state (excited state) of a transition, the transition energy does not depend on this term. This fact shows that the index of magnitude of a contribution to a transition energy can be larger than the index of magnitude of the contribution to energy levels. Except for α and α^0 the index of magnitude of a difference of two coefficients that differ only by the superscript zero (for instance π and π^0) is larger by two units than the index of magnitude of any one of these coefficients (for instance, $\pi - \pi^0$ has the index 12, π having the index 10).

V. PRACTICAL CALCULATION

First Approximation

If the off-diagonal matrix elements and fourth- or higher order diagonal contributions are neglected, the transition energies are given below for lines belonging to P, Q, and R branches:

for the P branch ($v = 0, R, J = R \rightarrow v = 1, R, J = R - 1$),

$$\begin{aligned}(P_R{}^p)_{\text{diag}} \simeq \alpha - \alpha^0 + 2\lambda - (\beta + \beta^0 + 2\lambda + 10\delta)R \\ + (\beta - \beta^0 + 4\delta)R^2 - (4\gamma + 2\chi)R^3 \\ + [\varphi + (4\mu - 16\epsilon)R] \frac{[(2R-3)\cdots(2R+5)]^{1/2}}{(2R-1)(2R)} (-1)^R F^{(4\ R\ R)}_{A_1\,p\ p};\end{aligned} \tag{16}$$

for the Q branch ($v = 0, R, J = R \rightarrow v = 1, R, J = R$),

$$\begin{aligned}(Q_R{}^p)_{\text{diag}} \simeq \alpha - \alpha^0 + 2\lambda + 6\delta + (\beta - \beta^0 - 8\delta + 2\chi)R(R+1) \\ + [16\mu - 40\epsilon - 2\varphi] \frac{[(2R-3)\cdots(2R+5)]^{1/2}}{2R(2R+2)} (-1)^R F^{(4\ R\ R)}_{A_1\,p\ p};\end{aligned} \tag{17}$$

for the R branch ($v = 0, R, J = R \rightarrow v = 1, R, J = R + 1$),

$$\begin{aligned}(R_R{}^p)_{\text{diag}} \simeq \alpha - \alpha^0 + 2\lambda + (\beta + \beta^0 + 2\lambda + 10\delta)(R+1) \\ + (\beta - \beta^0 + 4\delta)(R+1)^2 + (4\gamma + 2\chi)(R+1)^3 \\ + [\varphi - (4\mu - 16\epsilon)(R+1)] \frac{[(2R-3)\cdots(2R+5)]^{1/2}}{(2R+2)(2R+3)} (-1)^R F^{(4\ R\ R)}_{A_1\,p\ p}\end{aligned} \tag{18}$$

The true problem is not to calculate the frequencies or the energies of the transitions, but knowing these, to obtain the values of the molecular constants.[1] It may be seen that it is very easy to obtain the independent constants of formulas (16)–(18).

For a given value of the quantum number R, $(P_R{}^p)_{\text{diag}}$, $(Q_R{}^p)_{\text{diag}}$, and $(R_R{}^p)_{\text{diag}}$ are linear functions of $X = (-1)^R F^{(4\ R\ R)}_{A_1\, p\ p}$:

$$(P_R{}^p)_{\text{diag}} = a_R X + b_R\,, \tag{19}$$

$$(Q_R{}^p)_{\text{diag}} = e_R X + f_R\,, \tag{20}$$

$$(R_R{}^p)_{\text{diag}} = c_R X + d_R\,. \tag{21}$$

By plotting the experimental values $P_R{}^p$, $Q_R{}^p$, and $R_R{}^p$ of the transition energies versus X we obtain curves (Γ) which are approximately straight lines, and we can deduce from them starting values for a_R, b_R, $\cdots$.

From Eqs. (16), (17)–(21), we obtain

$$\begin{aligned} &d_{R-1} + b_R \\ &\quad = 2(\alpha - \alpha^0 + 2\lambda) + 2(\beta - \beta^0 + 4\delta)R^2, \end{aligned} \tag{22}$$

$$\begin{aligned} &(1/R)(d_{R-1} - b_R) \\ &\quad = 2(\beta + \beta^0 + 2\lambda + 10\delta) + 2(4\gamma + 2\chi)R^2, \end{aligned} \tag{23}$$

$$f_R = \alpha - \alpha^0 + 2\lambda + 6\delta + (\beta - \beta^0 - 8\delta + 2\chi)R(R + 1), \tag{24}$$

$$\begin{aligned} &\{2R(2R - 1)/[(2R - 3)\cdots(2R + 5)]^{1/2}\}a_R \\ &\quad = \varphi + (4\mu - 16\epsilon)R, \end{aligned} \tag{25}$$

$$\begin{aligned} &\{2R(2R + 2)/[(2R - 3)\cdots(2R + 5)]^{1/2}\}e_R \\ &\quad = 16\mu - 40\epsilon - 2\varphi, \end{aligned} \tag{26}$$

$$\begin{aligned} &\{(2R + 2)(2R + 3)/[(2R - 3)\cdots(2R + 5)]^{1/2}\}c_{R-1} \\ &\quad = \varphi - (4\mu - 16\epsilon)R. \end{aligned} \tag{27}$$

These functions are linear in R, R^2, or $R(R + 1)$. Experimental curves can be drawn, using the starting values of a_R, b_R, $\cdots$, and so the following combinations of molecular constants are obtained:

$$\alpha - \alpha^0 + 2\lambda,\ \delta,\ \beta - \beta^0,\ \beta + \beta^0 + 2\lambda,\ \chi,\ \gamma,\ \varphi,\ \mu,\ \epsilon.$$

To have the values of β, β^0, and λ it is necessary to use other experimental results; this can be done by observation of weak lines obeying the selection rule (2) (4). [For these lines, it is very easy to establish, from Eqs. (3)–(6), formulas similar to (16), (17), or (18).]

[1] For the general theory, see Reference 3.

SECOND AND FOLLOWING APPROXIMATIONS

Having these approximate values of molecular constants, and neglecting ν, we can use formulas (10) to (13) to obtain experimental approximate values of off-diagonal contributions in a second-order perturbation calculation. Subtracting these from the experimental values of energy levels, we obtain "corrected energy levels" which obey formulas (4)–(6) with a better accuracy than true energy levels. So, we are able to construct (Γ) curves with a better precision than in the first approximation, and obtain better molecular constants.

Performing the computation once more, we can take into account third-order perturbations [formulas (14) and (15)].

Then, trial values of the constants that were neglected will be used, if necessary.

VI. CONCLUSION

The constants we use have no obvious physical significance. So, we shall compare them with the constants that are used in more simple formulas: In a first approximation, the energy level E in the excited state is

$$E = E_v + hc[B_v J(J + 1) + D_v J^2(J + 1)^2 + a], \tag{28}$$

with

$$a = 2(B\zeta)_v(J + 1) \quad \text{for} \quad J = R + 1,$$

$$a = 0 \quad \text{for} \quad J = R,$$

and

$$a = -2(B\zeta)_v J \quad \text{for} \quad J = R - 1.$$

We have the approximate relations:

$$\alpha^0 = E_{v=0} \quad \text{(vibrational energy in the ground state)}, \tag{29}$$

$$\alpha = E_{v=1} \quad \text{(vibrational energy in the excited state)}, \tag{30}$$

$$(1/hc)(\alpha - \alpha^0 + 2\lambda + 6\delta) = \nu_0 \quad \text{(center of the vibration-rotation band)}, \tag{31}$$

$$\beta/hc = B_v \quad \text{and} \quad \beta^0/hc = B_{v=0} \quad \text{(inertia constants)}, \tag{32}$$

$$\lambda/hc = -(B\zeta)_v, \quad \zeta \text{ being the Coriolis coupling constant}, \tag{33}$$

$$-\gamma/hc = D_v \quad \text{(centrifugal distortion constant)}. \tag{34}$$

χ is connected with the variation of ζ with rotational quantum numbers.

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PART 3

ANALYSIS OF INFRARED AND MICROWAVE SPECTRA

The theoretical results presented in Part 2 have been used in order to explain anomalies met in the analysis of actual rotation and rotation-vibration spectra.

The various problems dealt with are listed hereafter together with the references of papers where they were first published :

1) - Microwave spectra

1a) Interpretation of the rotation spectrum of trifluoromethyl acetylene in the excited vibrational state $v_{10} = 1$.

- M.L.GRENIER-BESSON and G.AMAT (Technical note NR.2 Contract NR.61 (052)-369 January 1961 and J. of Mol. Spectr. 8, 22, 1962)

1b) The anomalous rotation spectrum of fluoroform in the vibrational state $v_6 = 1$.

- S.MAES and G.AMAT (Can. J. of Phys. 43, 321, 1965. In French).

The first topic (1a) has been described in Part 2 of the present Report as an illustration of our general study of rotation spectra of molecules with C_{3v} symmetry in an excited vibrational state.

2) - Infrared spectra

2a) Anomalous rotational structure of level 03^11 in the rotation-vibration spectrum of $C^{13}O_2^{16}$.

- M.H.ANDRADE e SILVA and G.AMAT (Technical note NR.1 Contract NR.61 (052)-369 January 1961 and J. of Mol. Spectr. 9, 354, 1962).

2b) Rotational structure of the fundamental band ν_6 of methyl cyanide.

- G.AMAT and H.H.NIELSEN (Molecular orbital in chemistry, physics and biology. Academic Press, 1964, p.293).

2c) General discussion of Fermi resonance in Carbon dioxyde with a new assignment of vibrational levels.

- G.AMAT and M.PIMBERT (J. of Mol. Spectr. 16, 278, 1965).

2d) Study of the fundamental ν_4 in methane.

- J.MORET-BAILLY (Thesis. Cah. Phys. 130, 237, 1961. In French)

The first three topics above (2a-2b-2c) will be treated in the present section of the Report as Chapters IV, V, and VI, respectively.

CHAPTER IV

Anomalous Rotational Structure of Level 03^11 in the Rotation-Vibration Spectrum of $C^{13}O_2^{16}$

INTRODUCTION

Courtoy (*1*), in studying the hot band 01^10-03^11 in the vibration-rotation spectrum of the $C^{13}O_2^{16}$ molecule, has observed that the level 03^11 is affected by a rotational perturbation. He has shown that, among the different rotational sublevels of 03^11, only those that correspond to an even J are affected; in other words, in the P and R branches of the band in question the lines corresponding to an even J'' occupy normal positions, while those corresponding to an odd J'' occupy anomalous positions. Courtoy suggests that the perturbation is due to a resonance between the level 03^11 and the level 30^00 which has nearly the same energy. In the first part of this paper, we propose to study from a theoretical point of view the *strong* resonance which takes place between these two levels. We shall see however that the off-diagonal matrix elements involved in this effect are also responsible for *weak* perturbations in other rotation-vibration levels of the molecule. These perturbations will be studied in the second part.

I. LEVELS 30^00 AND 03^11

If the perturbation of the level 03^11 appears indeed to be due to the proximity of the level 30^00, it nevertheless seems impossible to explain the "Courtoy resonance" by a direct interaction between the two levels. For a resonance between two levels A and B to have an observable effect two conditions are necessary: (a) the nonperturbed levels E_A and E_B must have nearly the same energy, and (b) the matrix element of coupling $(A \mid H \mid B)$ must be sufficiently large. Now in the present case the simplest vibrational operator with nonvanishing matrix elements of the form $(03^11 \mid H \mid 30^00)$ is $r_1^3 r_2^3 r_3$, where $r_s (s = 1, 2, 3)$ designates either a normal coordinate $q_{s\sigma}$ or its conjugate momentum $p_{s\sigma}$. In addition, the resonance taking place between a Σ state and a Π state, the coupling matrix element is off diagonal in l. Then, the Sayvetz's relation ($P_z = p_z$, i.e.: $K = l$) shows that the responsible operator must contain at least one P_α (projection of the total angular momentum on an axis bound to the equilibrium configuration). It follows that if we consider a direct interaction between the two levels 03^11 and 30^00 the simplest operator that could be responsible for the coupling is of the form $r_1^3 r_2^3 r_3 P_\alpha$. But such an operator does not appear before the sixth-order terms in the expansion of the Hamiltonian; its matrix elements are consequently much too small to account for an effect of the magnitude observed by Courtoy.

Up to this point we have taken no account of Fermi resonance. Now the level 03^11 is coupled with 11^11 (Π diad), while the level 30^00 is coupled with 22^00, 14^00 and 06^00 (Σ^+ tetrad). It follows, taking Fermi resonance into account, that a matrix element corresponding to an interaction between any level of the Π diad and any level of the Σ^+ tetrad may contribute to the Courtoy resonance just as well as the element $(03^11 \mid H \mid 30^00)$ considered above. We are thus led to consider the influence of the following eight matrix elements:

$$\begin{array}{lll}
c_{13} = (11^11 \mid H' \mid 30^00) & \quad & \text{(3rd order)} \\
c_{14} = (11^11 \mid H' \mid 22^00) & & \text{(2nd order)} \\
c_{15} = (11^11 \mid H' \mid 14^00) & & \text{(3rd order)} \\
c_{16} = (11^11 \mid H' \mid 06^00) & & \text{(6th order)} \\
c_{23} = (03^11 \mid H' \mid 30^00) & & \text{(6th order)} \\
c_{24} = (03^11 \mid H' \mid 22^00) & & \text{(3rd order)} \\
c_{25} = (03^11 \mid H' \mid 14^00) & & \text{(2nd order)} \\
c_{26} = (03^11 \mid H' \mid 06^00) & & \text{(3rd order),}
\end{array}$$

the order of magnitude of each element being indicated in parentheses. In the matrix elements c_{ij} the index $i = 1, 2$ corresponds to a level of the Π diad, and the index $j = 3, 4, 5, 6$ to a level of the Σ^+ tetrad, where these levels are numbered in decreasing order of v_1 for each polyad. All the above matrix elements are calculated by using the eigenfunctions ψ^0 of the operator H_0 as basic functions:

$$c_{ij} = \int_\tau \bar{\psi}_i^0 H' \psi_j^0 \, d\tau, \tag{1}$$

where H' designates the transformed Hamiltonian $H' = THT^{-1}$ (of which, in the absence of resonance, the matrix elements, nondiagonal in v_s, make only a fourth-order contribution[1]).

---

[1] The contact transformation $H' = THT^{-1}$ has been defined for the general case by Shaffer *et al.* (*2*) and by Herman and Shaffer (*3*). Actually, the operator H' that we employ here differs slightly from that employed in the general case, in order to take account of Fermi resonance (*4, 5*).

Taking Fermi resonance into account, the matrix element of coupling between the levels 03^11 and 30^00 is given by

$$\gamma = \int_\tau \bar{\psi}_2 H' \psi_3 \, d\tau, \tag{2}$$

where the perturbed wave functions ψ are linear combinations of the non-perturbed functions ψ^0:

$$\begin{aligned} \psi_2 &= \sum_{i=1}^{2} a_{2i} \psi_i^0, \\ \psi_3 &= \sum_{j=3}^{6} a_{3j} \psi_j^0, \end{aligned} \tag{3}$$

whence

$$\gamma = \sum_{ij} \bar{a}_{2i} a_{3j} c_{ij} \, . \tag{4}$$

As Fermi resonance is strong in the case of the CO_2 molecule, the coefficients $a_{k\ell}$ are all of the same order of magnitude. Consequently in Eq. (4) we may neglect the c_{ij} elements of the third and sixth order and, retaining only those of the second order, write:

$$\gamma = \bar{a}_{21} a_{34} c_{14} + \bar{a}_{22} a_{35} c_{25} \, . \tag{5}$$

Taking the degeneracy in ℓ of the Π levels ($\ell = \pm 1$) into account, we have then four matrix elements c_{ij} to calculate:

$$\left(11^{+1}1 \left| \frac{H'}{hc} \right| 22^00\right), \left(11^{-1}1 \left| \frac{H'}{hc} \right| 22^00\right), \left(03^{+1}1 \left| \frac{H'}{hc} \right| 14^00\right), \left(03^{-1}1 \left| \frac{H'}{hc} \right| 14^00\right). \tag{6}$$

These four matrix elements are of the form.

$$\left(v_1, v_2, v_3, \ell_2 \left| \frac{H'}{hc} \right| v_1 + 1, v_2 + 1, v_3 - 1, \ell_2 + \epsilon\right) \tag{7}$$

with $\epsilon = \pm 1$. The transformed second-order Hamiltonian h_2' has, as we have observed, matrix elements of this type. They come from the operator

$$\sum_{\alpha = x,y} \sum_{\sigma = 1,2} \Big[{}_{(F)(2)}^{\;\;\;\;\alpha}Y^{\gamma 1,2\sigma,3} \, p_1 p_{2\sigma} p_3 + \sum_a {}_{(F)(2)}Y^{\gamma a}_{a'a''} \, \tfrac{1}{2}(q_{a'} q_{a''} p_a + p_a q_{a'} q_{a''}) \Big] P_\alpha , \tag{8}$$

with $a, a', a'' \equiv 1, 2\sigma, 3$ or $2\sigma, 1, 3$ or $3, 1, 2\sigma$.

It can easily be shown that

$$\left(v_1\, v_2\, v_3\, \ell_2 \left| \frac{h_2'}{hc} \right| v_1 + 1, v_2 + 1, v_3 - 1, \ell_2 + \epsilon\right) \qquad (9)$$
$$= Z\{[J(J+1) - \ell_2(\ell_2+\epsilon)](v_1+1)(v_2+\epsilon\ell_2+2)v_3\}^{1/2}$$

with

$$Z = \frac{1}{8\sqrt{2}\,\pi c}\,[\hbar^3\,{}_{(F)(2)}^{\;\;\;\;\;\;\;y}Y^{1,21,3} + \hbar\,{}_{(F)(2)}^{\;\;\;\;\;\;\;y}Y^{21}_{1,3} + \hbar\,{}_{(F)(2)}^{\;\;\;\;\;\;\;y}Y^{1}_{21,3} - \hbar\,{}_{(F)(2)}^{\;\;\;\;\;\;\;y}Y^{3}_{1,21}], \qquad (10)$$

where ${}_{(F)(2)}Y$ designates a coefficient that has been corrected to take account of Fermi resonance. The matrix elements (9) usually contribute to the energy only in the fourth order of magnitude. Due to accidental resonance they can, for the molecule $C^{13}O_2^{16}$, possibly contribute in the second order. We shall then write them in the energy matrix.

Equation (9) shows that the matrix elements (6) originating from the operator (8) are equal. Their common value is

$$c = 2Z\sqrt{J(J+1)}. \qquad (11)$$

THE ENERGY MATRIX

Figure 1 gives the matrix that represents the transformed Hamiltonian H', using the eigenfunctions ψ^0 of H_0 as basic functions.

We have included in this matrix all the levels that are coupled, either directly or indirectly, with the levels 30^00 and 03^11, with matrix elements of coupling belonging to the first or second order. The coupling matrix elements can be either diagonal in v_s (ℓ-type doubling or ℓ-type resonance) or off diagonal in v_s (accidental resonances). In the latter case they can originate from the Fermi operator $hc\,k_{122}q_1(q_{21}^2 + q_{22}^2)$ or from the second-order Coriolis operator given by Eq. (8). In Fig. 1 diagonal elements are designated by E, ℓ-type resonance elements by L, elements responsible for ℓ-type doubling by $\mathcal{L}$, Fermi resonance elements by F and Coriolis resonance elements by c. The levels affected by Courtoy resonance are indicated by arrows in the upper part of Fig. 1.

The matrix of Fig. 2 is obtained from the preceding one by replacing the basic functions by symmetric and antisymmetric linear combinations:

$$\psi_\ell{}^0(\text{sym.}) = (1/\sqrt{2})(\psi^0_{+\ell} + \psi^0_{-\ell})$$
$$\psi_\ell{}^0(\text{antisym.}) = (1/\sqrt{2})(\psi^0_{+\ell} - \psi^0_{-\ell}). \qquad (12)$$

It is important to notice that in the "symmetric" matrix two levels (03^11 and 30^00) have about the same energy. We shall show that they are coupled through a strong resonance. On the other hand, in the "antisymmetric" matrix, one cannot find any level close to the level 03^11. Consequently, the level 03^11 anti-

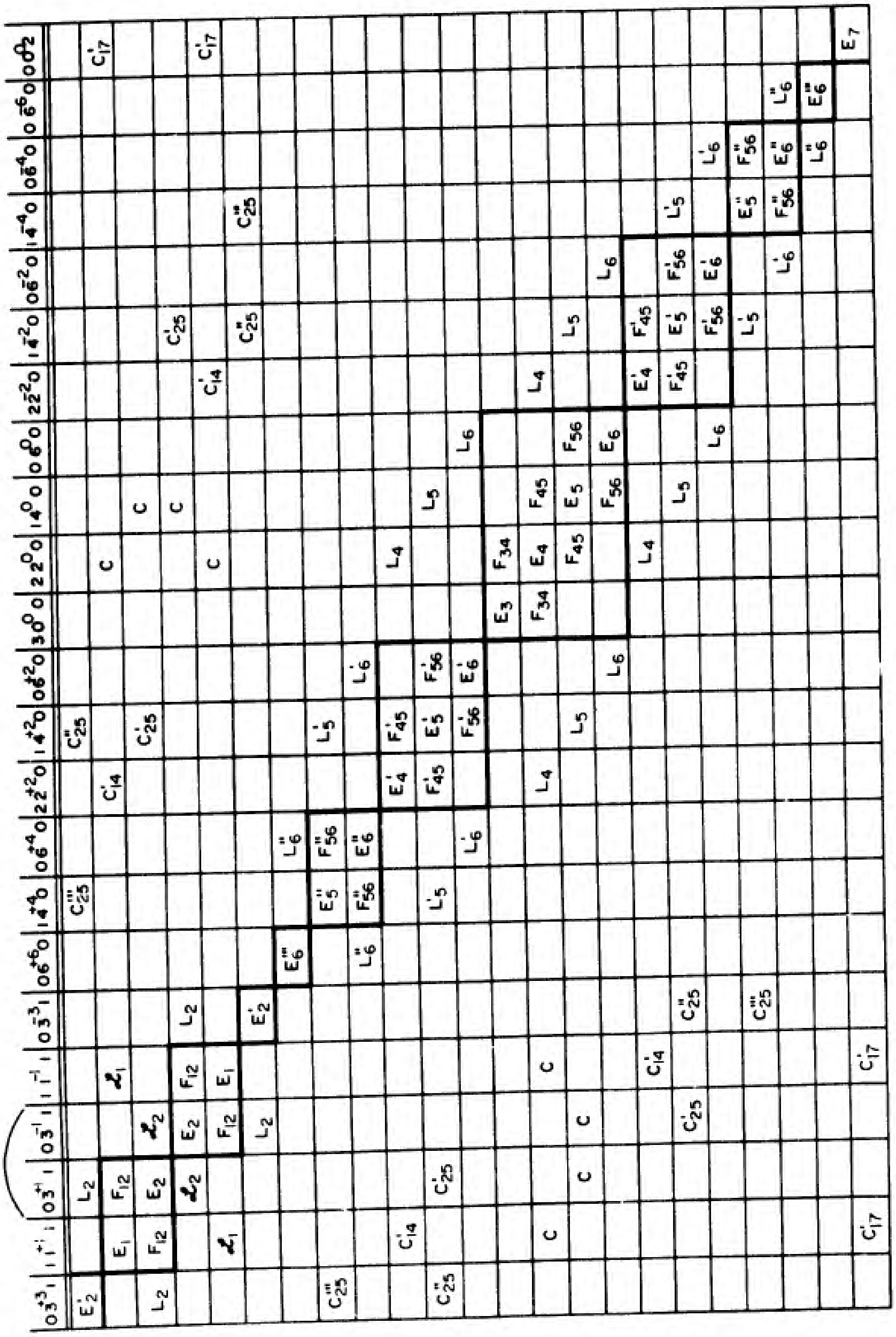
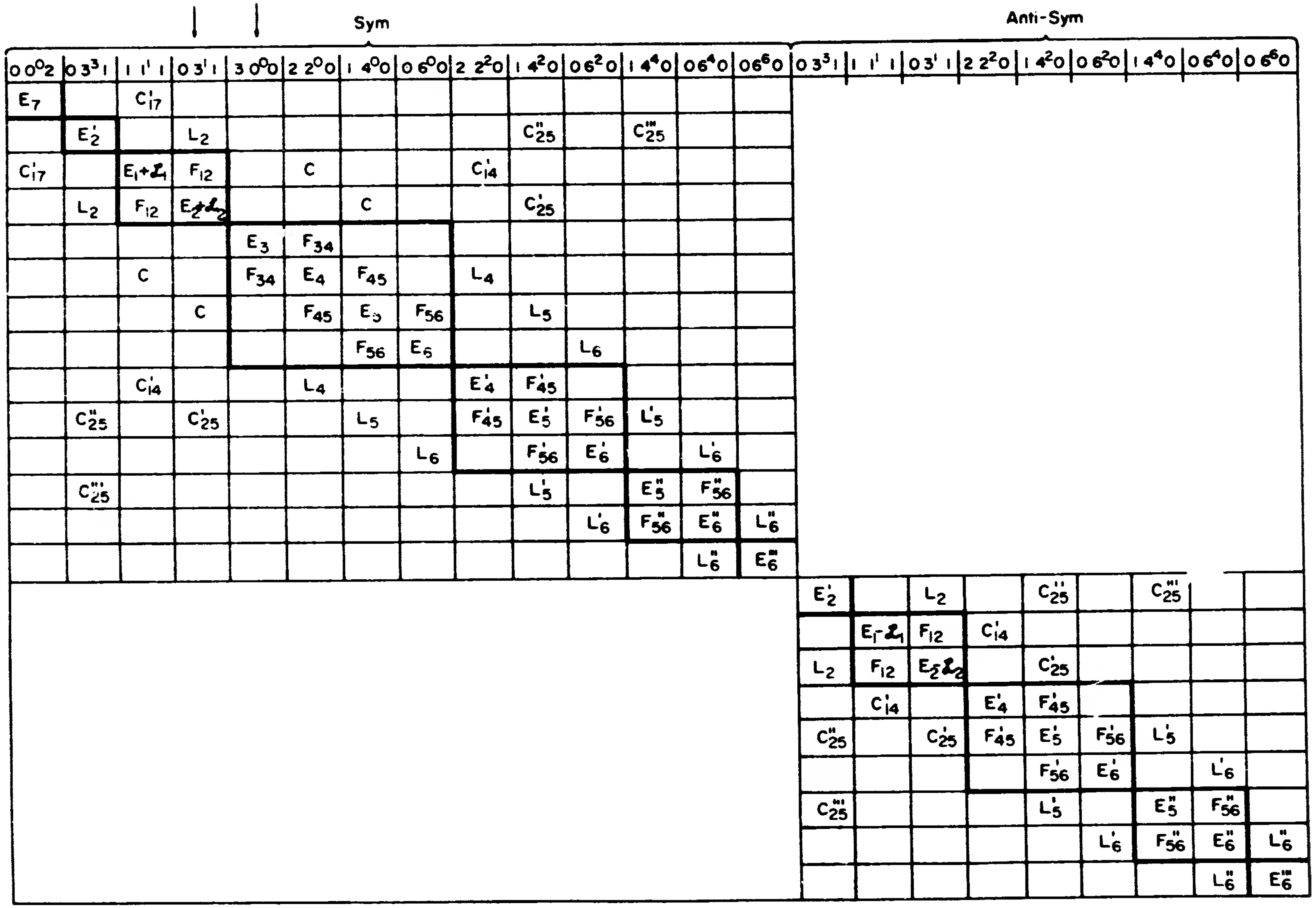

03+3 1
11+1 1
03+1 1
03-1 1
11-1 1
03-3 1
06+6 0
14+4 0
06+4 0
22+2 0
14+2 0
06+2 0
30 0 0
22 0 0
14 0 0
06 0 0
22-2 0
14-2 0
06-2 0
14-4 0
06-4 0
06-6 0
00 0 2

FIG. 1



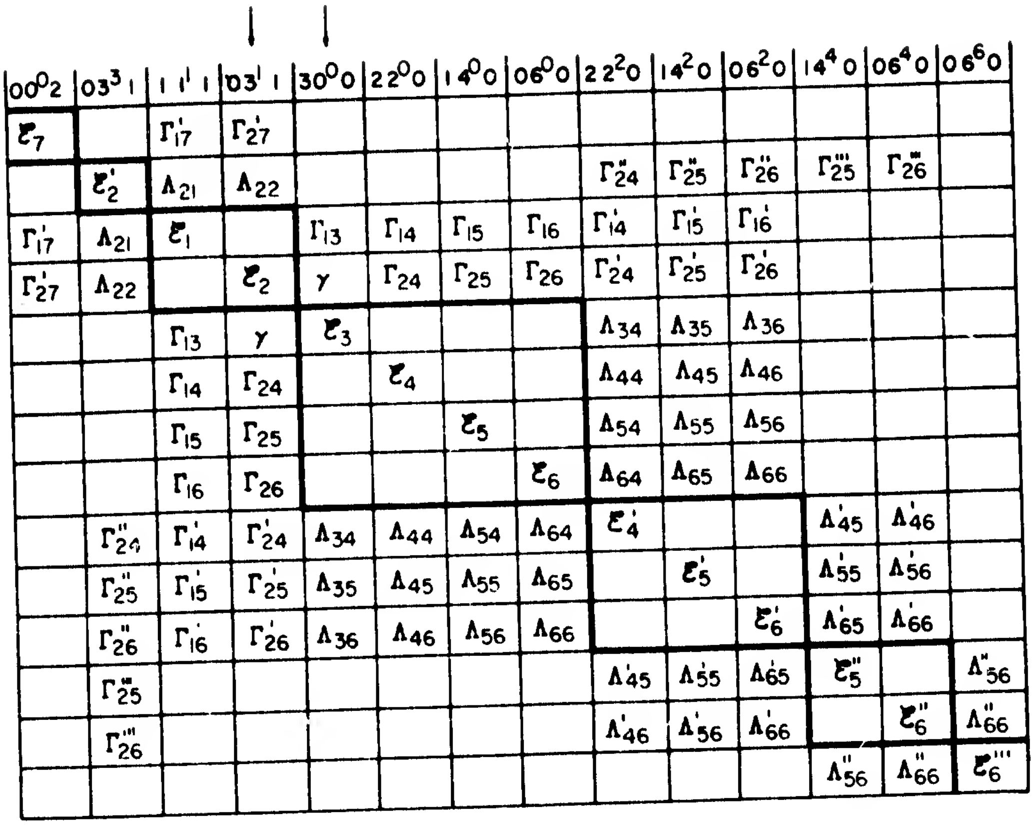
Sym

$0\,0^0\,2$	$0\,3^3\,1$	$1\,1^1\,1$	$0\,3^1\,1$	$3\,0^0\,0$	$2\,2^0\,0$	$1\,4^0\,0$	$0\,6^0\,0$	$2\,2^2\,0$	$1\,4^2\,0$	$0\,6^2\,0$	$1\,4^4\,0$	$0\,6^4\,0$	$0\,6^6\,0$
E_7		C'_{17}											
	E'_2		L_2						C''_{25}		C'''_{25}		
C'_{17}		$E_1+\mathcal{L}_1$	F_{12}		C			C'_{14}					
	L_2	F_{12}	$E_2+\mathcal{L}_2$			C			C'_{25}				
				E_3	F_{34}								
		C		F_{34}	E_4	F_{45}		L_4					
			C		F_{45}	E_5	F_{56}		L_5				
						F_{56}	E_6			L_6			
		C'_{14}			L_4			E'_4	F'_{45}				
	C''_{25}		C'_{25}			L_5		F'_{45}	E'_5	F'_{56}	L'_5		
							L_6		F'_{56}	E'_6		L'_6	
	C'''_{25}								L'_5		E''_5	F''_{56}	
										L'_6	F''_{56}	E''_6	L''_6
												L''_6	E'''_6

Anti-Sym

$0\,3^3\,1$	$1\,1^1\,1$	$0\,3^1\,1$	$2\,2^2\,0$	$1\,4^2\,0$	$0\,6^2\,0$	$1\,4^4\,0$	$0\,6^4\,0$	$0\,6^6\,0$
E'_2		L_2		C''_{25}		C'''_{25}		
	$E_1-\mathcal{L}_1$	F_{12}	C'_{14}					
L_2	F_{12}	$E_2-\mathcal{L}_2$		C'_{25}				
	C'_{14}		E'_4	F'_{45}				
C''_{25}		C'_{25}	F'_{45}	E'_5	F'_{56}	L'_5		
				F'_{56}	E'_6		L'_6	
C'''_{25}				L'_5		E''_5	F''_{56}	
					L'_6	F''_{56}	E''_6	L''_6
							L''_6	E'''_6

FIG. 2



00^02	03^31	11^11	03^11	30^00	22^00	14^00	06^00	22^20	14^20	06^20	14^40	06^40	06^60
$\mathcal{E}_7$		Γ'_{17}	Γ'_{27}										
	$\mathcal{E}'_2$	Λ_{21}	Λ_{22}					Γ''_{24}	Γ''_{25}	Γ''_{26}	Γ'''_{25}	Γ'''_{26}	
Γ'_{17}	Λ_{21}	$\mathcal{E}_1$		Γ_{13}	Γ_{14}	Γ_{15}	Γ_{16}	Γ'_{14}	Γ'_{15}	Γ'_{16}			
Γ'_{27}	Λ_{22}		$\mathcal{E}_2$	γ	Γ_{24}	Γ_{25}	Γ_{26}	Γ'_{24}	Γ'_{25}	Γ'_{26}			
		Γ_{13}	γ	$\mathcal{E}_3$				Λ_{34}	Λ_{35}	Λ_{36}			
		Γ_{14}	Γ_{24}		$\mathcal{E}_4$			Λ_{44}	Λ_{45}	Λ_{46}			
		Γ_{15}	Γ_{25}			$\mathcal{E}_5$		Λ_{54}	Λ_{55}	Λ_{56}			
		Γ_{16}	Γ_{26}				$\mathcal{E}_6$	Λ_{64}	Λ_{65}	Λ_{66}			
	Γ''_{24}	Γ'_{14}	Γ'_{24}	Λ_{34}	Λ_{44}	Λ_{54}	Λ_{64}	$\mathcal{E}'_4$			Λ'_{45}	Λ'_{46}	
	Γ''_{25}	Γ'_{15}	Γ'_{25}	Λ_{35}	Λ_{45}	Λ_{55}	Λ_{65}		$\mathcal{E}'_5$		Λ'_{55}	Λ'_{56}	
	Γ''_{26}	Γ'_{16}	Γ'_{26}	Λ_{36}	Λ_{46}	Λ_{56}	Λ_{66}			$\mathcal{E}'_6$	Λ'_{65}	Λ'_{66}	
	Γ'''_{25}							Λ'_{45}	Λ'_{55}	Λ'_{65}	$\mathcal{E}''_5$		Λ''_{56}
	Γ'''_{26}							Λ'_{46}	Λ'_{56}	Λ'_{66}		$\mathcal{E}''_6$	Λ''_{66}
											Λ''_{56}	Λ''_{66}	$\mathcal{E}'''_6$

FIG. 3

symmetric will not be displaced by the resonance as the level 03^11 symmetric is. This result is in agreement with Courtoy's observation. In what follows we shall consider the matrix obtained by retaining only the symmetric levels in the matrix of Fig. 2.

The matrix of Fig. 3 is obtained by diagonalizing the Fermi submatrices, that is to say, by substituting linear combinations of the type (3) for the basic functions (12) in each Fermi-resonance polyad. The matrix elements c must then be replaced by new matrix elements (linear combinations of the c's), which are designated by Γ or γ in the matrix of Fig. 3. Likewise, the elements c', c'', c''', L, L', L'' must be replaced by linear combinations which we have respectively designated by Γ', Γ'', Γ''', Λ, Λ', Λ''.

The element γ couples two levels whose energies are very close to one another. We thus have to deal with a near-degenerate problem, the solution of which requires that we first diagonalize the sub-matrix:

$$\begin{Bmatrix} \mathcal{E}_2 & \gamma \\ \gamma & \mathcal{E}_3 \end{Bmatrix}. \tag{13}$$

We then obtain the matrix of Fig. 4, in which[2]

$$\begin{matrix} \mathcal{E}_+ \\ \mathcal{E}_- \end{matrix} = \frac{\mathcal{E}_2 + \mathcal{E}_3}{2} \pm \sqrt{\left(\frac{\mathcal{E}_2 - \mathcal{E}_3}{2}\right)^2 + \gamma^2}. \tag{14}$$

---

[2] For low values of J, $\mathcal{E}_+$ and $\mathcal{E}_-$ correspond to the perturbed levels 03^11 and 30^00, respectively, for high values of J, $\mathcal{E}_+$ and $\mathcal{E}_-$ correspond to the perturbed levels 30^00 and 03^11, respectively.

			03^11 30^00										
00^02	03^31	11^11	+	−	22^00	14^00	06^00	22^20	14^20	06^20	14^40	06^40	06^60
$\mathcal{E}_7$		Γ'_{17}	Γ^*_{+7}	Γ^*_{-7}									
	$\mathcal{E}'_2$	Λ_{21}	Λ^*_{+2}	Λ^*_{-2}				Γ''_{24}	Γ''_{25}	Γ''_{26}	Γ'''_{25}	Γ'''_{26}	
Γ'_{17}	Λ_{21}	$\mathcal{E}_1$	Γ^*_{+1}	Γ^*_{-1}	Γ_{14}	Γ_{15}	Γ_{16}	Γ'_{14}	Γ'_{15}	Γ'_{16}			
Γ^*_{+7}	Λ^*_{+2}	Γ^*_{+1}	$\mathcal{E}_+$		Γ^*_{+4}	Γ^*_{+5}	Γ^*_{+6}	Λ^*_{+4}	Λ^*_{+5}	Λ^*_{+6}			
Γ^*_{-7}	Λ^*_{-2}	Γ^*_{-1}		$\mathcal{E}_-$	Γ^*_{-4}	Γ^*_{-5}	Γ^*_{-6}	Λ^*_{-4}	Λ^*_{-5}	Λ^*_{-6}			
		Γ_{14}	Γ^*_{+4}	Γ^*_{-4}	$\mathcal{E}_4$			Λ_{44}	Λ_{45}	Λ_{46}			
		Γ_{15}	Γ^*_{+5}	Γ^*_{-5}		$\mathcal{E}_5$		Λ_{54}	Λ_{55}	Λ_{56}			
		Γ_{16}	Γ^*_{+6}	Γ^*_{-6}			$\mathcal{E}_6$	Λ_{64}	Λ_{65}	Λ_{66}			
	Γ''_{24}	Γ'_{14}	Λ^*_{+4}	Λ^*_{-4}	Λ_{44}	Λ_{54}	Λ_{64}	$\mathcal{E}'_4$			Λ'_{45}	Λ'_{46}	
	Γ''_{25}	Γ'_{15}	Λ^*_{+5}	Λ^*_{-5}	Λ_{45}	Λ_{55}	Λ_{65}		$\mathcal{E}'_5$		Λ'_{55}	Λ'_{56}	
	Γ''_{26}	Γ'_{16}	Λ^*_{+6}	Λ^*_{-6}	Λ_{46}	Λ_{56}	Λ_{66}			$\mathcal{E}'_6$	Λ'_{65}	Λ'_{66}	
	Γ'''_{25}							Λ'_{45}	Λ'_{55}	Λ'_{65}	$\mathcal{E}''_5$		Λ''_{56}
	Γ'''_{26}							Λ'_{46}	Λ'_{56}	Λ'_{66}		$\mathcal{E}''_6$	Λ''_{66}
											Λ''_{56}	Λ''_{66}	$\mathcal{E}'''_6$

FIG. 4

Γ^* designates linear combinations of the elements Γ and Λ^* designates linear combinations of the elements Λ and Γ.

The elements Λ^* and Γ^* couple levels whose energies differ sufficiently for these matrix elements to be studied by means of a perturbation method.

It follows that the perturbed energy of the levels $(30^00, 03^11)$ is given by the equation

$$E_\pm = \left(\frac{\mathcal{E}_2 + \mathcal{E}_3}{2}\right) \pm \sqrt{\left(\frac{\mathcal{E}_2 - \mathcal{E}_3}{2}\right)^2 + \gamma^2} + \sum_k \frac{(\Gamma^*_{\pm k})^2}{\mathcal{E}_\pm - \mathcal{E}_k} + \sum_k \frac{(\Lambda^*_{\pm k})^2}{\mathcal{E}_\pm - \mathcal{E}_k}, \tag{15}$$

in which, by virtue of Eqs. (5) and (11),

$$\gamma = N\sqrt{J(J+1)}, \tag{16}$$

where

$$N = 2Z(a_{21}a_{34} + a_{22}a_{35}) \tag{17}$$

(the coefficients a_{2i} and a_{3j} are all real).

Discussion of Eq. (15)

An examination of Eq. (15) will allow us to replace it by a simpler formula for practical use.

(a) Note, first of all, that when we are far from resonance the radical can be expanded in a series. The first two terms in Eq. (15) can be written as

$$\begin{Bmatrix} \mathcal{E}_2 \\ \mathcal{E}_3 \end{Bmatrix} \pm \frac{\gamma^2}{\mathcal{E}_2 - \mathcal{E}_3}.$$

The difference $\mathcal{E}_2 - \mathcal{E}_3$ is of the form $\Delta\nu_0 + \Delta BJ(J+1) - \Delta DJ^2(J+1)^2$. For the largest values of J observed in the spectrum the term $\Delta BJ(J+1)$ is larger than $\Delta\nu_0$ and $\Delta DJ^2(J+1)^2$. It follows that, as γ^2 is equal to $N^2J(J+1)$, the ratio $\gamma^2/(\mathcal{E}_2 - \mathcal{E}_3)$ varies little with respect to J. This term accounts for the practically constant gap observed in Fig. 1 of Ref. *12* between the unbroken-line curve and the dotted-line curve.

(b) The $\Gamma^*_{\pm k}$'s are of the same order of magnitude as γ; the $\mathcal{E}_\pm - \mathcal{E}_k$ are much larger than $\mathcal{E}_2 - \mathcal{E}_3$; hence $\gamma^2/(\mathcal{E}_2 - \mathcal{E}_3)$ is large compared to the third term of the right side of Eq. (15). Consequently this third term is negligible compared to the second when we are far from resonance. This result is still more valid in the neighborhood of resonance.

(c) The fourth term in the right side of Eq. (15) depends on J in a very complex manner. Nevertheless when we are far from resonance the wave functions corresponding to $\mathcal{E}_-$ and $\mathcal{E}_+$ are very close to those that correspond to $\mathcal{E}_2$ and $\mathcal{E}_3$. It follows that the elements from Fig. 4 can be replaced by the corresponding elements from the Fig. 3. More precisely, the elements $\Lambda^*_{\pm k}$ can be replaced[3] by Λ_{2k} or Λ_{3k}. In these conditions, the contribution of the last term of Eq. (15) lies in $\delta''_\ell J^2(J+1)^2$. It represents the influence of the ℓ-type resonance on the centrifugal distortion constant D. For computing the coefficient δ''_ℓ it is convenient to use the formula given in Ref. 10[4] instead of Eq. (15).

The last term of Eq. (15) makes no important contribution to the energy except for large values of J, that is to say, far from resonance. We shall not therefore explicitly calculate its contribution to the energy in the neighborhood of resonance.

To summarize, Eq. (15) may be replaced by the following:

$$E_\pm = \frac{\mathcal{E}_2^* + \mathcal{E}_3^*}{2} \pm \sqrt{\left(\frac{\mathcal{E}_2^* - \mathcal{E}_3^*}{2}\right)^2 + \gamma^2}, \tag{18}$$

where $\mathcal{E}_2^*$ and $\mathcal{E}_3^*$ are computed taking into account the two contributions to "anomalous D constants" in conformity with the formulas given in Ref. *10*, and where $\gamma = N\sqrt{J(J+1)}$.

---

[3] The elements Γ'_{2k} will be neglected for the reason given in Paragraph (b) above.

[4] Given the manner in which we have performed our calculations $\mathcal{E}_2$ and $\mathcal{E}_3$ contain the term $\delta''_{an}J^2(J+1)^2$, but not the term $\delta''_\ell J^2(J+1)^2$. These two terms correspond to the two contributions to the "anomalous D constants" described in Ref. *10*:

$$D_{\text{eff}} = D - \delta''_{an} - \delta_\ell .$$

NUMERICAL CALCULATION OF N

The numerical value of the constant N can be computed by means of Eq. (17), in which the coefficients Z and a_{2i}, a_{3j} are defined by Eqs. (10) and (3), respectively. Expressed as a function of the molecular parameters,[5] Z is given by the equation

$$Z = -\frac{1}{8\sqrt{2}\pi c}\left\{\frac{hc}{I_e}\left[\frac{5}{4}k_{122}\varphi_2 + k_{133}\varphi_3\right] - \frac{\hbar^{3/2}a_1}{I_e^2\lambda_1^{1/4}}\frac{\lambda_2^{1/2}+\lambda_3^{1/2}}{(\lambda_2\lambda_3)^{1/4}}\right\}, \qquad (19)$$

where

$$\varphi_2 = \frac{1}{2(2\lambda_2^{1/2}+\lambda_1^{1/2})}\left[\frac{\lambda_2^{1/2}-\lambda_3^{1/2}}{(\lambda_2\lambda_3)^{1/4}}\right] + \frac{1}{2\lambda_1^{1/2}}\left[\frac{\lambda_2^{1/2}+\lambda_3^{1/2}}{(\lambda_2\lambda_3)^{1/4}}\right] + \frac{2(\lambda_2\lambda_3)^{1/4}}{\lambda_3-\lambda_1},$$

$$\varphi_3 = -\frac{2\lambda_2^{1/4}\lambda_3^{3/4}}{\lambda_1^{1/2}(4\lambda_3-\lambda_1)} + \frac{\lambda_3^{3/4}}{\lambda_2^{1/4}(4\lambda_3-\lambda_1)} - (\lambda_2\lambda_3)^{1/4}\left(\frac{1}{4\lambda_3-\lambda_1} - \frac{2}{\lambda_2-\lambda_3}\right) - \frac{\lambda_3^{1/4}(2\lambda_3-\lambda_1)}{\lambda_1^{1/2}\lambda_2^{1/4}(4\lambda_3-\lambda_1)}.$$

We have computed[6] the numerical value of the constant N, by using for the molecular parameters, the values given by Courtoy. This leads to:

$$|N| = 0,011 \text{ cm}^{-1} \qquad (20)$$

---

[5] The relations between the ${}_{(P)(2)}Y$ and the usual coefficients ${}_{(2)}Y$ are given in Ref. *5*; the coefficients ${}_{(2)}Y$ are given in terms of the molecular parameters in Refs. *6* and *7*. Finally, we recall (*8*, *9*) that for a linear and symmetric triatomic molecule XY_2 the only interaction coefficients $k_{s\sigma s'\sigma' s''\sigma''}$, $a_{s\sigma}^{\alpha\beta}$, $\zeta_{s\sigma s'\sigma'}$ different from zero are

$$\begin{array}{ll} k_{111} & a_1(=a_1^{xx}=a_1^{yy}) = 2\,I_e^{1/2} \\ k_{133} & \zeta_{22,3}^{x} = \zeta_{3,21}^{y} = 1 \\ k_{122}(=k_{1,21,21}=k_{1,22,22}) & \zeta_{21,22}^{z} = 1 \end{array}$$

Remarks: (1) The above values correspond to a clearly defined choice of the sign of the normal coordinate q_1 : q_1 is positive when the distance between the two oxygen nuclei is larger than the equilibrium distance.

(2) By virtue of Sayvetz's equation ($P_z = p_z$), $\zeta_{21,22}^{z}$ does not figure in the calculations.

[6] Since this first computation it has appeared to us that the molecular parameters of CO_2 should be revised (See Ref 11 and Chapter VI hereafter). A new computation of N is in progress using the revised values.

Courtoy and Triaille have shown (*12*) that Eqs. (18) and (16) lead to computed energy levels in good agreement with experimental values provided we put

$$|N| = 0.014 \text{ cm}^{-1}. \tag{21}$$

In Fig. 1 of Ref. *12*, the circles represent experimental points and the dotted-line curve[7] the theoretical values obtained by using Eqs. (16), (18), and (21).

Considering the uncertainty of the various molecular parameters used in calculation, the theoretical value (20) that we have obtained is in excellent agreement with the value (21) determined by Courtoy on the basis of his experimental results.

II. OTHER LEVELS

As we have just seen, the matrix elements (9) of the operator (8), which usually contribute to the energy only in the fourth order of approximation, contribute in the second order for the levels 30^00 and 03^11. In the usual perturbation calculation, the effect of the second contact transformation (*13*) is to suppress the operator (8) in the second order and to replace it by an operator having diagonal matrix elements on the fourth order. This procedure cannot be used here: we need to keep in the second-order Hamiltonian an operator having the same matrix elements (9) as (8), its other matrix elements being however zero. This result can be obtained by a slight change in the S function of the second contact transformation (*4*, *5*). In other words, since we wish to keep in the second-order Hamiltonian matrix the elements (9) involved in the strong resonance of levels 30^00 and 03^11, we cannot avoid keeping them everywhere in this matrix. Theoretically, the influence of matrix elements (9) has then to be taken into account in the computation of every energy level of the molecule which can be done by a perturbation method for every level but 30^00 and 03^11. It can be seen that the main effect produced by these matrix elements is a term in $J(J+1)$, i.e., a change in the inertia constants B. This correction has been studied in detail by Courtoy and Triaille (*12*).

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[7] The unbroken-line curves correspond to ε_2^* and ε_3^*, that is to say, values calculated without taking account of the elements c.

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CHAPTER V

Rotational Structure of the Fundamental Band ν_6 of Methyl Cyanide

I. Introduction

The infrared absorption spectrum of methyl cyanide has been previously studied by Venkateswarlu (1950, 1952) and by Thompson and Williams (1952) then with a higher resolving power by Parker *et al.* (1957), by Dick and Meister (1960), by Yarger (1960), and by Nakagawa and Shimanouchi (1962).

The fundamental ν_6 is a perpendicular band observed in the region between 1300 and 1600 cm^{-1}. It is the most intense of all the observed bands of the methyl cyanide spectrum and it corresponds to an antisymmetric deformation of the C–C–H angles. The rotational structure shows nearly equally spaced sharp Q branches but examination of the spectrum indicates that this regular pattern is distorted by perturbations, at least in two regions. The first perturbation is a maximum in the region of 1490 cm^{-1} and its most evident effect is a doubling of the two branches described as $^{R}Q_1$ and $^{R}Q_2$ (Parker *et al.*, 1957; Nakagawa and Shimanouchi, 1962). We shall explain this perturbation by a resonance between ν_6 and the combination band $\nu_7 + \nu_8$ (Fermi-type resonance, i.e., diagonal in K). A second perturbation can be observed in the region of 1390 cm^{-1}; its effect is a considerable broadening of the Q branches which can be explained by a resonance between ν_6, and the parallel fundamental ν_3 (Coriolis-type resonance which is off-diagonal in K).

II. The (ν_6, $\nu_7 + \nu_8$) Resonance

The perturbation of the rotational structure in the region of 1490 cm^{-1} was first pointed out by Parker *et al.* They observed that two Q branches near the center of the band occur as "twins," namely $^RQ_1$ (split into two lines, 60 and 58) and $^RQ_2$ (split into two lines, 50 and 52). They furthermore observed that "a plot of the lines in this region versus a running number K results in two progressions, one ending abruptly with 52, and the other ending with 58" and "that the two sections exhibit different curvatures" (Parker *et al.* (1957), Fig. 3). The authors suggest that the perturbation could be related to an unexplained interaction between ν_6 and ν_3. However, neglecting the irregularities observed, they draw (see their Fig. 3) the best straight line that fits their data and obtain from this treatment the value $\zeta_6 = -0.39$.

Actually the curve shown (Parker *et al.* (1957), Fig. 3) becomes much easier to understand if one adds one unit to the K values assigned to the lines of the second progression (the one which corresponds to larger wave numbers and ends at line 58) without changing the K assignment for the lines belonging to the first progression. This results in a translation of the second progression by 1 unit toward the right and the two progressions now look like the two branches of a hyperbola, which is the usual pattern for the lines of two bands of which the upper levels interact through a vibrational (Fermi-type) resonance. This is furthermore supported by the fact that the two progressions actually do not end abruptly with lines 52 and 58. As Yarger has already pointed out, less intense lines can be found in the spectrum that continue the two progressions beyond lines 52 and 58.

Figure 1 shows the two progressions. The spectrum is the one given by Nakagawa and Shimanouchi (1962); both identification numbers used by Parker *et al.* (1957) (PNF) and by Yarger (1960) (Y) are listed. It can be seen that all the most intense lines can be included in one or the other of the two progressions.

Figure 2 shows the plot of the lines belonging to the two progressions versus a running number K. Since there is some uncertainty on the position of the band origins, we do not give definite K values on Fig. 2 but rather a new set of identification symbols *abc* . . . *wx*, the same symbol being used for two resonating lines belonging to the first and the second progressions. These identification symbols are also reproduced in Fig. 1.

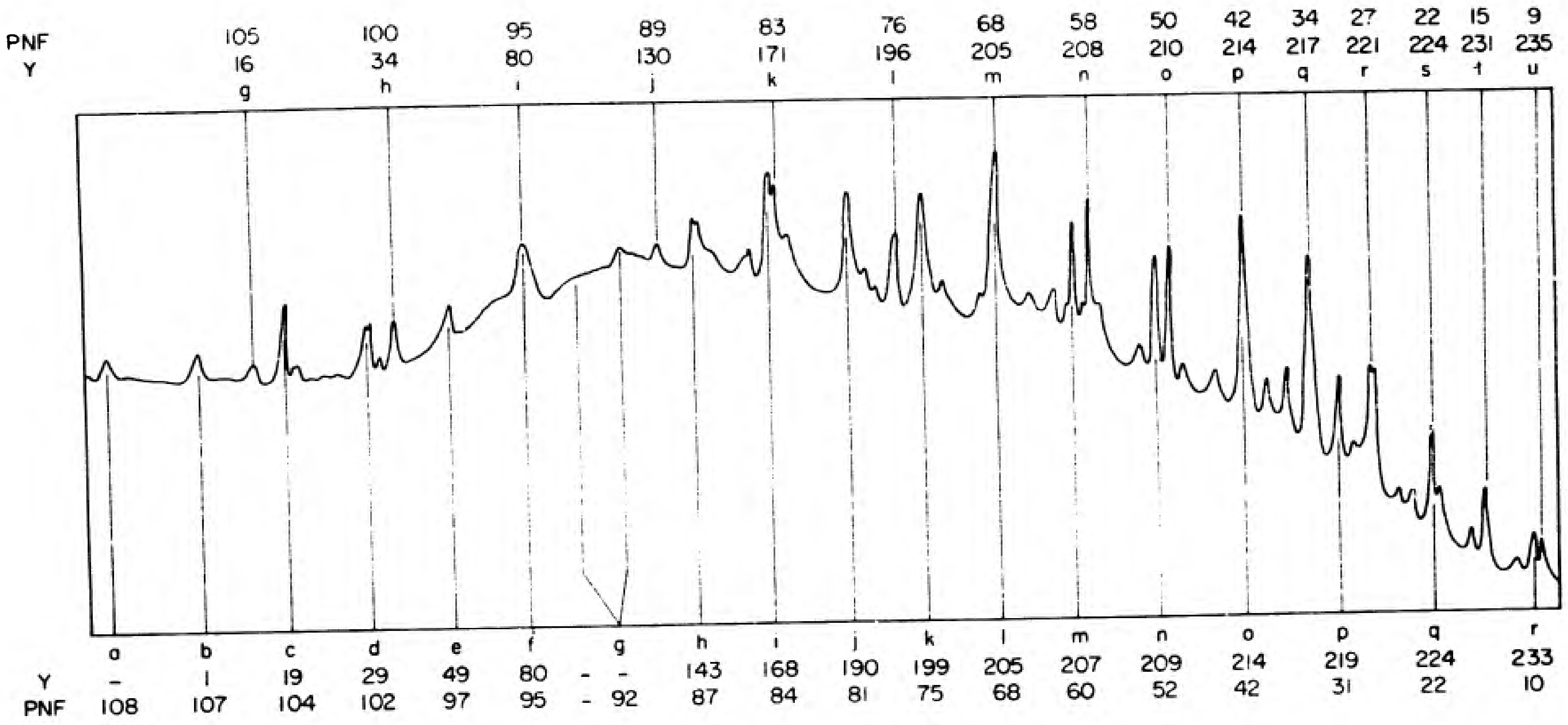

FIG. 1. Identification of the lines in the bands ν_6 and $\nu_7 + \nu_8$ of methyl cyanide.

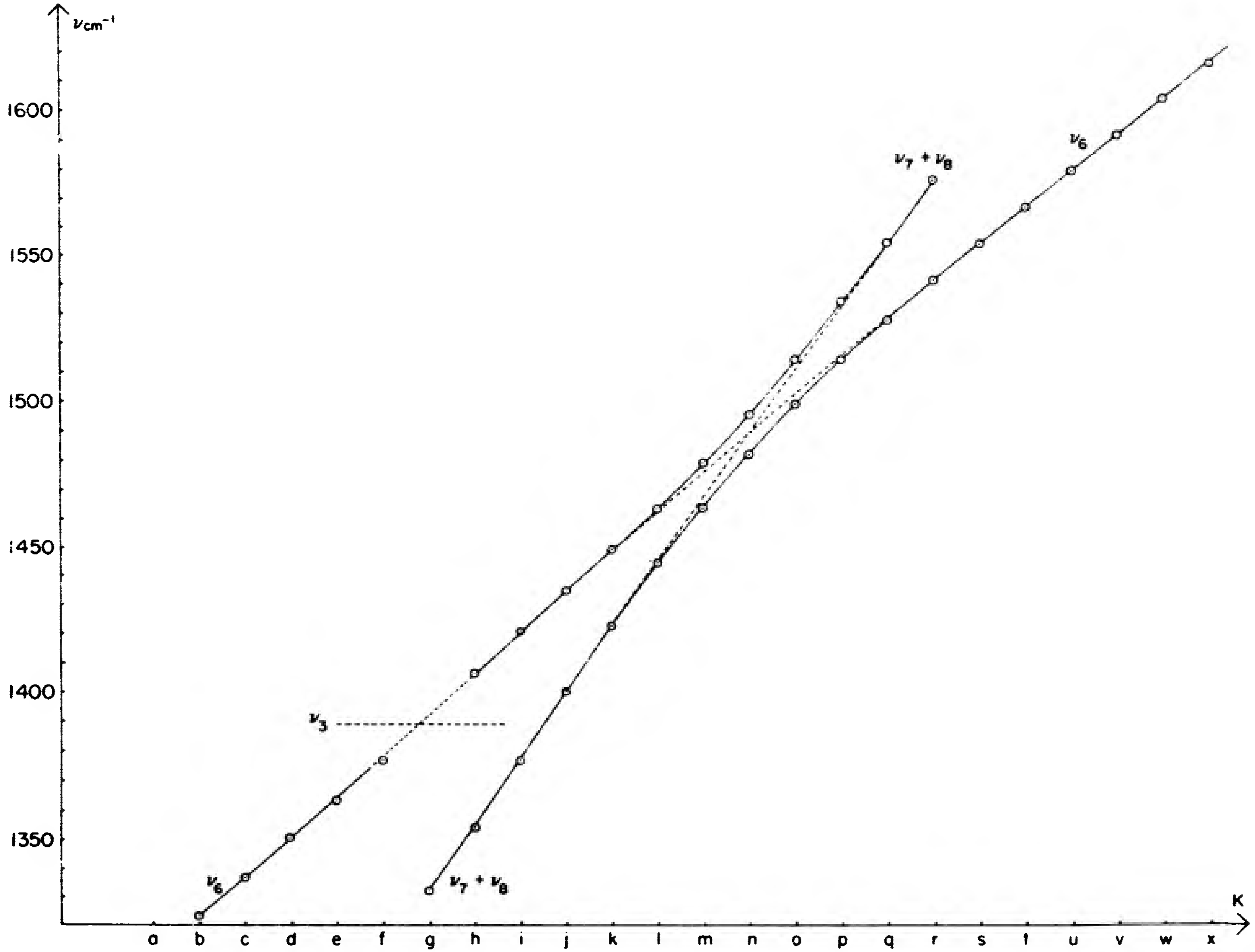

FIG. 2. Wave numbers of lines in ν_6 and $\nu_7 + \nu_8$ plotted against values of *K*.

The next step is to find the level which interacts with the upper level of the ν_6 transition. The only cold bands expected in this region of the spectrum are ν_3, $\nu_7 + \nu_8$, and $4\nu_8$. The parallel band ν_3 can immediately be ruled out: The upper levels of ν_3 and ν_6 belonging to species A_1 and E, respectively, can only interact through matrix elements off-diagonal in K. The largest among these is the first-order Coriolis matrix element from K to $K \pm 1$. Since it is proportional to $[J(J+1) - K(K \pm 1)]^{1/2}$, the perturbation would be J-dependent, which means that the J structure of the Q branches would be spread out by the resonance. No sharp Q branches would be observed any longer in the resonance region. We shall see that such an effect is indeed observed close to $1390\ \mathrm{cm}^{-1}$: The Q structure of the band ν_6 disappears precisely in the region where Parker, Nielsen, and Flechter have located the center of the band ν_3 from its envelope which can be observed on their spectrum. On the other hand, both $\nu_7 + \nu_8$ and $4\nu_8$ can interact with ν_6 through a vibrational Fermi-type resonance diagonal in K. However, the coupling between the upper levels of ν_6 and $4\nu_8$ is of third-order importance; it would probably give rise to a very small perturbation observed in one single Q branch of ν_6. The kind of perturbation described by Fig. 2 is more likely due to the first-order Fermi-type resonance (ν_6, $\nu_7 + \nu_8$). We shall obtain a confirmation of this hypothesis later by measuring the slopes of the asymptotes on the hyperbola of Fig. 2.

The major part of the operator responsible for the coupling between the upper levels of ν_6 and $\nu_7 + \nu_8$ is that portion of the cubic potential which contains the terms $q_{6\sigma} q_{7\sigma'} q_{8\sigma''}$. It can be seen from Henry and Amat (1960) that this operator is in fact

$$\mathscr{H} = hck_{678}(q_{61}q_{71}q_{81} - q_{61}q_{72}q_{82} - q_{62}q_{71}q_{82} - q_{62}q_{72}q_{81}) \qquad (1)$$

By direct computation or by using symmetry consideration (Amat, 1960), one finds that the only nonvanishing matrix elements of $\mathscr{H}$ are those conforming to the rule $\Delta l_6 + \Delta l_7 + \Delta l_8 = \pm 3$. Then if we consider the set of quantum numbers $v_6\, l_6\, v_7\, l_7\, v_8\, l_8$ the coupling matrix element originating from $\mathscr{H}$ will be

$$hc\alpha_0 = (1 \mp 1000\ |\mathscr{H}|\ 00\ 1 \pm 1\ \ 1 \pm 1) = \pm \frac{hck_{678}}{2} \qquad (2)$$

Actually other operators with a smaller order of magnitude will also contribute to the coupling. The second-order transformed Hamiltonian h_2' contains operators $q_a q_b p_c P_z$ and $p_a p_b p_c P_z$ where [illegible] and c refer to the vibrations 6, 7, and 8 (or any permutation of these). These operators have matrix elements, similar to those of $\mathscr{H}$, which can be written as $\alpha_1 K$ where α_1 is much smaller than α_0. Finally the coupling matrix element can be expressed as

$$hc\alpha = hc\alpha_0 + hc\alpha_1 K + \cdots \qquad (3)$$

where the second term can be neglected for small values of K.

Let E_6 and E_{78} be respectively the unperturbed energy levels corresponding to the values $1 \mp 1\ 00\ 00$ and $00\ 1 \pm 1\ 1 \pm 1$ of the quantum numbers $v_6 l_6 v_7 l_7 v_8 l_8$. The perturbed energy for the same levels is given by the secular equation

$$\begin{vmatrix} E_6 - \varepsilon & hc\alpha \\ hc\alpha & E_{78} - \varepsilon \end{vmatrix} = 0 \tag{4}$$

whence

$$\varepsilon = \tfrac{1}{2}(E_6 + E_{78}) + (\delta/2)[(E_6 - E_{78})^2 + 4h^2c^2\alpha^2]^{1/2} \tag{5}$$

where δ can be either $+1$ or -1. If now we consider instead of the energies E the wave numbers ν of the Q branches

$$\nu = \frac{\varepsilon(JK') - E_0(JK'')}{hc} \tag{6}$$

where $K' = K'' + 1$ or $K'' - 1$ and where E_0 is the energy of the ground state, we find that the perturbed ν and unperturbed ν_6, ν_{78} in wave numbers are related by the equation

$$\nu = \tfrac{1}{2}(\nu_6 + \nu_{78}) + (\delta/2)[(\nu_6 - \nu_{78})^2 + 4\alpha^2]^{1/2} \tag{7}$$

where account has been taken of Eqs. (2) and (3). In this equation the unperturbed wave numbers can be written as:

$$\begin{aligned} \nu_6 &= \nu_6{}^0 + 2[A_6'(1 - \zeta_6) - B_6']K \\ &\quad + (A_6' - A_0 - B_6' + B_0)K^2 + (B_6' - B_0)J(J + 1) \\ \nu_{78} &= \nu^0_{78} + 2[A'_{78}(1 + \zeta_7 + \zeta_8) - B'_{78}]K \\ &\quad + (A'_{78} - A_0 - B'_{78} + B_0)K^2 + (B'_{78} - B_0)J(J + 1) \end{aligned} \tag{8}$$

where ν_0 is an unperturbed band center; A' and B', A_0 and B_0 are inertia constants of the excited and the ground state, respectively.

Before comparing the Eq. (7) with the experimental curve of Fig. 2 it is necessary to make a choice for the band origins. This choice is not an obvious one since the intensity alternation which characterizes the molecules with a threefold axis is obliterated here by the perturbations and the overlapping of lines belonging to the two progressions. We came to the conclusion that the most reasonable choice was to identify ${}^RQ_0$ with line l in both progressions, ${}^RQ_1$ with line m, ${}^PQ_1$ with line k, and so on. This choice agrees with the one made by Thompson and Williams (1952), Parker *et al.* (1957), Yarger (1960), and Nakagawa and Shimanouchi (1962). It should be pointed out, however, that there is some uncertainty about this choice.

The comparison of Eq. (7) with the experimental curve of Fig. 2 leads to the following conclusions:

(a) Since $B_0 = 0.31\ \mathrm{cm}^{-1}$ and $A_0 = 5.28\ \mathrm{cm}^{-1}$ in methyl cyanide, it is reasonable to neglect $B' - B_0$ in the third term of Eqs. (8). The curvature of the asymptotes can then be used to compute A'_{78} and A_6'. The asymptote associated with ν_{78} is the one with the larger slope, while the asymptote associated with ν_6 is the one with the smaller slope. We have obtained the value $A_6' \simeq 5.23$, while for reasons which will become apparent later the value of A'_{78} is more uncertain.

(b) The coefficient of the terms linear in K in Eqs. (8), i.e., the slope of the asymptotes in the vicinity of the band origins, gives the values:

$$\begin{aligned} \zeta_7 + \zeta_8 &= 1.2 \\ \zeta_6 &= -0.35 \end{aligned} \tag{9}$$

The value obtained here for $\zeta_7 + \zeta_8$ is in fairly good agreement with the best known values of ζ_7 and ζ_8 [$\zeta_7 = 0.42$ from infrared data (Parker *et al.*, 1957) and $\zeta_8 = 0.88$ from microwave investigations (Venkateswarlu, 1961)]. This agreement supports the interpretation we propose here that the perturbation is due to a resonance between ν_6 and $\nu_7 + \nu_8$.

(c) The determination of the asymptotes of the hyperbola permits the evaluation of the unperturbed band origins $\nu_6{}^0$ and ν^0_{78}. These quantities can be used in the vibrational analysis.

$$\begin{aligned} \nu_6{}^0 &= \frac{1}{hc}(E_6^{\mathrm{vib}} - E_0^{\mathrm{vib}}) + A_6'(1 - 2\zeta_6) - B_6' \\ \nu^0_{78} &= \frac{1}{hc}(E_{78}^{\mathrm{vib}} - E_0^{\mathrm{vib}}) + A'_{78}(1 + 2\zeta_7 + 2\zeta_8) - B'_{78} \end{aligned} \tag{10}$$

where

$$\begin{aligned} &\frac{1}{hc}(E_6^{\mathrm{vib}} - E_0^{\mathrm{vib}}) = \omega_6{}^0 + x_{66} + x_{l_6 l_6} \\ &\frac{1}{hc}(E_{78}^{\mathrm{vib}} - E_0^{\mathrm{vib}}) \simeq \omega_7{}^0 + \omega_8{}^0 + x_{77} + x_{88} + x_{78} + x_{l_7 l_7} + x_{l_8 l_8} + x_{l_7 l_8} \end{aligned} \tag{11}$$

We have found for the values of $\nu_6{}^0$ and ν^0_{78} the following:

$$\begin{aligned} \nu_6{}^0 &= 1462\ \mathrm{cm}^{-1} \\ \nu^0_{78} &\simeq 1445\ \mathrm{cm}^{-1} \end{aligned} \tag{12}$$

This value of $\nu_6{}^0$ is to be compared with 1454.2 from Parker *et al.* (1957) and 1453.53 from Nakagawa and Shimanouchi (1962), where the K assignment of the ${}^RQ_0$ line is the same in all cases, no account having been taken of the resonance in the case of the latter two references.

We have already pointed out that there is some uncertainty on the assignment of the ${}^RQ_0$ line, so that the values we give for the band origins $\nu_6{}^0$ and ν_{78}^0 could possibly be revised after further experimental investigation. In that event the values obtained for ζ_6 and $\zeta_7 + \zeta_8$ could be slightly modified.

(d) In Fig. 3, the half-differences $\Delta/2$ between spectral terms of resonating levels belonging to the two progressions are plotted against K. The experimental points lie on a hyperbola as expected from Eq. (6):

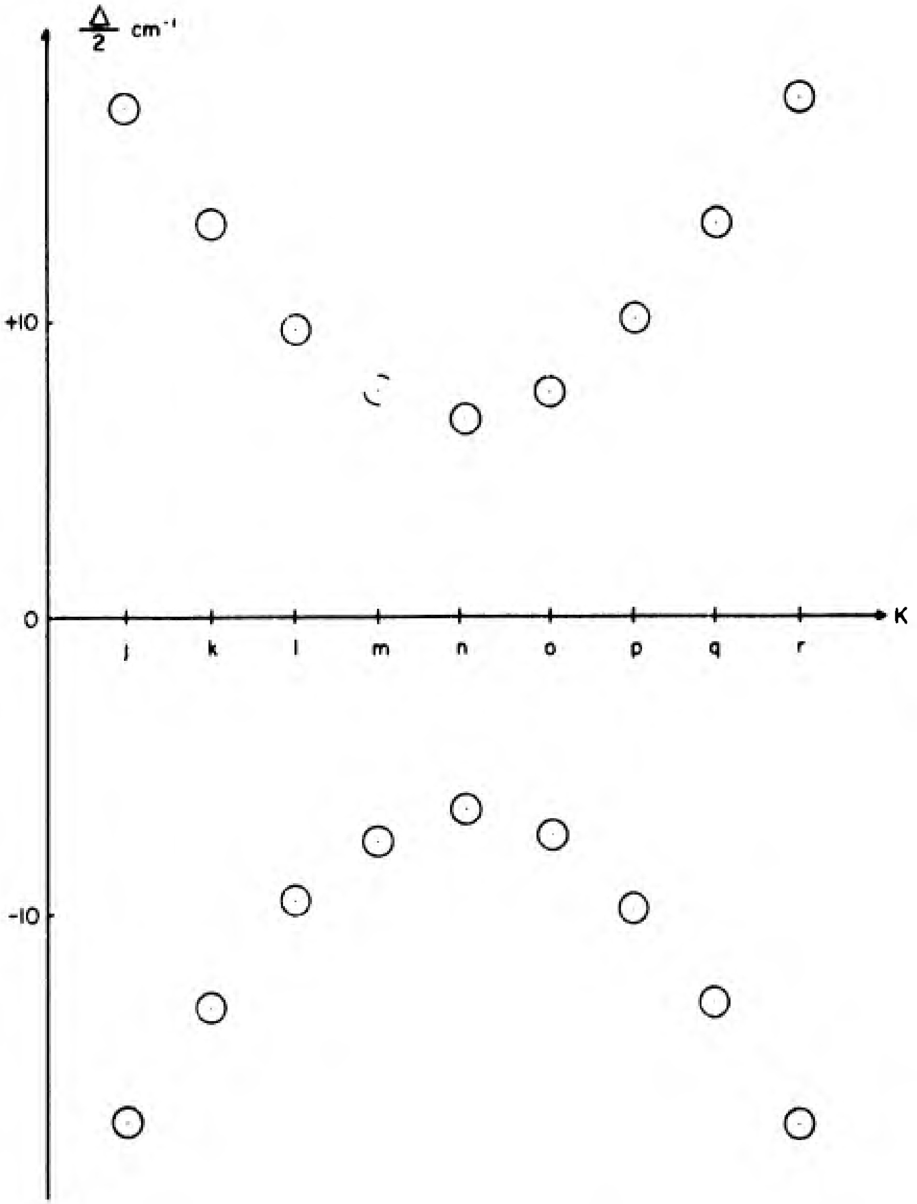

FIG. 3. Differences between resonating levels in ν_6 and $\nu_7 + \nu_8$ plotted against K.

$$\frac{\Delta}{2} = \pm\left[\left(\frac{\nu_6 - \nu_{78}}{2}\right)^2 + (k_{678} + 2\alpha_1 K)^2\right] \tag{13}$$

The comparison of this equation with the observed data permits obtaining the value of the cubic force constant k_{678}:

$$k_{678} = 13.2\ \mathrm{cm}^{-1} \tag{14}$$

On the other hand, by using the half-difference $\Delta/2$ between spectral terms of resonating levels and the half-sum of these spectral terms, which is not perturbed by the resonance, it is possible to compute the unperturbed frequencies ν_6 and ν_{78} from lines in the resonance region. For $\nu_6{}^0$ and ν_{78}^0 this procedure leads to values which agree with the values of Eq. (12) within 1.5 wave number, while the values obtained for ζ_6 and $\zeta_7 + \zeta_8$ are -0.37 and 1.1, respectively, which are in fairly good agreement with the values of Eq. (9). It can be seen, however, that this agreement is not excellent, and neither is the agreement between the value of $\zeta_7 + \zeta_8$ obtained here and the values of ζ_7 and ζ_8 derived from other studies. Various reasons reduce the accuracy on the numerical values which can be obtained from the spectrum:

(1) There is some uncertainty on the frequency of a number of lines due to the overlapping of the two progressions and due to the background corresponding to unresolved *P* and *R* lines.

(2) The *Q* branches being unresolved, the *J* value corresponding to the maximum of absorption in the profile is not known. This gives rise to a systematic error in the determination of ν_0 through the last term of Eq. (8). If the value of *J* for which the maximum occurs varies with *K*, further errors can be expected.

(3) The rotational perturbation which will be discussed in the next section considerably broadens some of the *Q* branches in ν_6.

(4) It is possible that the frequencies ν_{78} given by Eq. (8) are furthermore perturbed by a resonance between $\nu_7 + \nu_8$ and $4\nu_8$. This resonance would be of the same kind as the one between ν_7 and $3\nu_8$, which is the only possible interpretation of the perturbation in the rotational structure of ν_7 reported by Yarger (1960).

(5) As it has been already pointed out, there is some uncertainty on the identification of the branch ${}^RQ_0$ in both progressions.

(6) Finally, the accuracy on $\nu_7 + \nu_8$ is certainly smaller than on ν_6, for the *Q* branches are not observed for very high *K* values in the former band, which has a weaker intensity than the latter far from the resonance region. On this last point, some further experimental studies of the wings of the bands with higher gas pressures would be very useful.

III. The (ν_6, ν_3) Resonance

As we have already mentioned, the perturbation in the region of 1390 cm^{-1} can be explained by a resonance between the upper levels of ν_6

and ν_3. The coupling operator is now the first-order Coriolis operator:

$$\mathscr{H}' = -\frac{\zeta^x_{3,62}}{I^e_{xx}}\left[\left(\frac{\omega_6}{\omega_3}\right)^{1/2} q_3(p_{62}P_x - p_{61}P_y) - \left(\frac{\omega_3}{\omega_6}\right)^{1/2} p_3(q_{62}P_x - q_{61}P_y)\right] \tag{15}$$

If we consider the set of quantum numbers $v_6\, l_6\, v_3\, K$, the coupling matrix element is

$$(1 \mp 1\ 0\ K\ |\mathscr{H}'|\ 00\ 1\ K \pm 1)$$

$$= hc\zeta^x_{3,62}B^{xx}_e \frac{\omega_3 + \omega_6}{(2\omega_3\omega_6)^{1/2}}\,[J(J+1) - K(K \pm 1)]^{1/2} \tag{16}$$

This matrix element is J-dependent and so also will be the perturbation. When the resonance is strong, we shall not observe sharp Q branches but their J structure will be spread out.

Figure 4 shows, for a given value of J, the relative position of the unperturbed upper levels in bands ν_6 and ν_3; the values of l_6 and K are given for these levels as well as the identification of unperturbed absorption lines which would end up at these levels. It has been assumed that the $J = K = 0$ level in the upper state of ν_3 lies at 1389 cm^{-1} in accordance with the estimation of Parker *et al.* (1957). It can be seen from Fig. 4 that ${}^PQ_5$, and to a smaller extent ${}^PQ_6$, are the most strongly perturbed Q branches of ν_6. This is in excellent agreement with the observations, for these two branches are considerably spread out. The perturbation is weaker for ${}^PQ_7$, ${}^PQ_8$. It can be expected from Fig. 4 that the various lines of these branches will be displaced toward smaller wave numbers with an increasing displacement for increasing J values. This will result in a shading of these branches toward smaller wave numbers. For the same reason a shading toward large wave numbers is expected in the branches ${}^PQ_4$ ${}^PQ_3$. These expectations are well borne out.

IV. Conclusion

The study of the band ν_6 gives a very clear illustration of the two kinds of perturbations due to accidental resonances which can be encountered in rotation-vibration spectra: Fermi-type vibrational resonances where the matrix element of the coupling is diagonal in K and does not depend upon rotational quantum numbers; Coriolis-type rotational resonances where the matrix element of the coupling depends upon rotational quantum numbers (this matrix element can be either diagonal or off-diagonal in K, the latter being the one observed here).

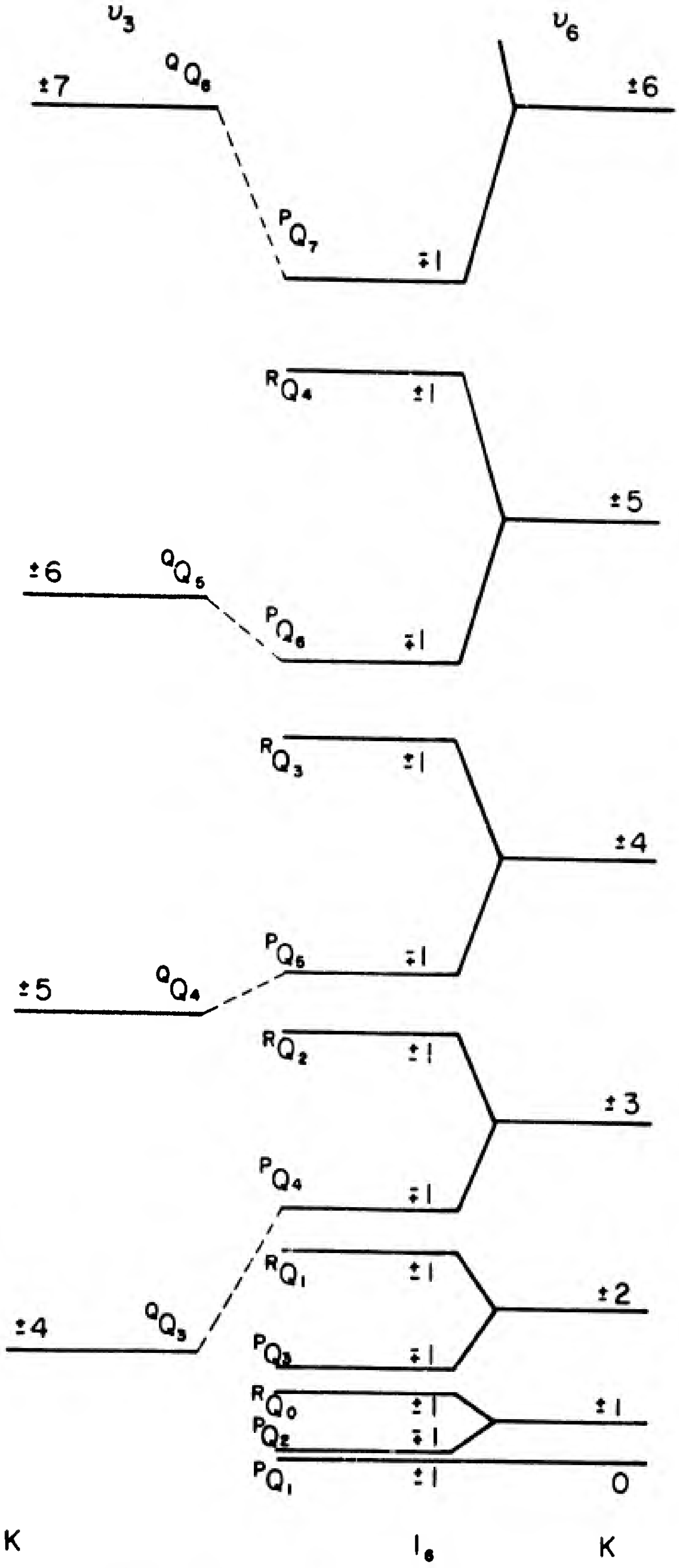

FIG. 4. Energy diagram for the excited levels in ν_3 and ν_6.

Microwave studies[2] have led, for the Coriolis coupling coefficient ζ_8, to the value 0.88, which is smaller than the value 0.93 previously obtained from the ζ sum rule

$$\zeta_5 + \zeta_6 + \zeta_7 + \zeta_8 = 1 + \frac{B}{2A} \simeq 1.03 \tag{17}$$

and from the values of ζ_5, ζ_6, and ζ_7 derived from infrared spectra, so that the ζ sum rule seemed not to be verified any longer.

The present study of the band ν_6 suggests that the value[3] of ζ_6 is larger than had been believed (-0.35 instead of -0.39). The ζ sum rule is fairly well verified by the best ζ values currently obtained ($\zeta_5 = 0.07$; $\zeta_6 = -0.35$; $\zeta_7 = 0.42$; $\zeta_8 = 0.88$).

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[2] The transition $J = 1 \rightarrow 2$ in the excited state $v_8 = 1$ of methyl cyanide was first studied by Kessler *et al.* (1950). The theory (Nielsen, 1950; Maes, 1960), permitted one to derive from these data the value $\zeta_8 = 0.94$ which was in good agreement with the value $\zeta_8 = 0.93$ previously obtained from the ζ sum rule and from the values of the other ζ's known from infrared spectra.

Transitions with higher J values were studied by Venkateswarlu *et al.* (1961). The theory (Grenier-Besson and Amat, 1962), for these transitions leads to the value $\zeta = 0.88$. Grenier Besson and Amat have then pointed out that this later value is also in agreement with the data of the $J = 1 \rightarrow 2$ transition if one assumes that a strong line has, for some reason, not been recorded in the spectrum by Kessler *et al.* (1950). Sheridan and Turner (1962) have since shown that this assumption is borne out by experiments, so that the value $\zeta_8 = 0.88$ agrees with all microwave data.

[3] *Note added on proof.* The value we obtain for ζ_6 is in good agreement with the one calculated by J. L. Duncan in his recent study of the force field of methyl cyanide (to be published in *Spectrochemica Acta*). We thank Dr. Duncan for the kind communication of his manuscript prior to publication.

CHAPTER VI

General Discussion of Fermi Resonance in Carbon Dioxyde with a New Assignment of Vibrational Levels

INTRODUCTION

Courtoy (*1, 2*) has determined, for the carbon dioxide molecule, spectroscopic constants which permit the computation of all the rotation-vibration energy levels of $C^{12}O_2^{16}$ and of the various other isotopic species ($C^{13}O_2^{16}$, $C^{12}O^{16}O^{18}$, etc.). The agreement between observed and calculated energy levels is excellent; but, two difficulties are met as far as the internal consistency of the spectroscopic constants is concerned.

(1) The relations for isotopic substitution are well satisfied by the constants ω_s, $x'_{ss'}$, $\cdots$ obtained for the different isotopic molecules, with one major exception, namely, the one of the Fermi coupling coefficient W_e. The values of the relative variation $(W_e^* - W_e)/W_e$ of this coefficient in isotopic substitutions are as follows (*2, 3*).

	$(W_e^* - W_e)/W_e$	
	Obs (%)	Calc (%)
$C^{13}O_2^{16}$	-10	-3
$C^{12}O^{16}O^{18}$	$+2.3$	-2.2
$C^{12}O_2^{18}$	$+4.4$	-4.4

As can be seen from this tabulation the best values of W_e^* determined for each molecule from observed data, do not agree with the values calculated from W_e of $C^{12}O^{16}$ using the theoretical formulas for isotopic substitution.

(2) The coefficient k_{122} appearing in the cubic part of the anharmonic potential

expanded with respect to normal coordinates can be obtained very easily from W_e, since

$$W_e = -k_{122}/\sqrt{2}, \tag{1}$$

which gives a reasonable value of k_{122}. On the other hand, this same coefficient can, in theory, be derived from the values of the anharmonicity constants x_{22} and $x_{l_2 l_2}$ [whose definition will be recalled in Eqs. (3) and (4)], since[1]

$$x_{22} + 3x_{l_2 l_2} = -\tfrac{1}{2}k_{122}^2[1/\omega_1 - 1/2(2\omega_2 + \omega_1)]. \tag{2}$$

Actually the best values (*1*, *2*) of x_{22} and $x_{l_2 l_2}$ lead to an imaginary value for k_{122}.

The starting point of the study reported here has been an attempt to overcome these two difficulties.

A. VIBRATIONAL ANALYSIS

(a) The vibration energy of levels which are not perturbed by Fermi resonance (i.e., levels with $v_2 = |l_2|$) is given to second order by the formula

$$E_v^0 = \sum_s \omega_s^0 v_s + \sum_{\substack{ss' \\ s \leqq s'}} x_{ss'} v_s v_{s'} + g_{22} l_2^2, \tag{3}$$

where s and s' designate one of the normal vibrations 1, 2, or 3 and where

$$g_{22} = x_{l_2 l_2} - B. \tag{4}$$

Although Eq. (3) cannot be used for levels perturbed by Fermi resonance, it holds for the sum of the energies of all the levels belonging to a given Fermi polyad. By using two singlet Σ states, two singlet Π states, one singlet Δ state, and the sums of the levels of two diads Σ, of one diad Π, of one triad Σ, as those listed in Fig. 1, it is possible to obtain six of the ten constants appearing on the right side of Eq. (3) and three linear combinations of the remaining four constants. It can be shown that taking into consideration additional Fermi polyads would lead to linear combinations of the nine quantities "framed" in Fig. 1 without bringing the tenth independent information necessary for a complete knowledge of the constants appearing in Eq. (3). Any new linear combination of ω_1^0, x_{12}, x_{22}, and g_{22} can be chosen for the unknown parameter. We shall actually consider $x_{12} - 4x_{22}$ as being this unknown parameter which needs to be computed in order to know the ten constants ω_s^0, x_{ss}, and g_{22}.

(b) For this purpose we need to take Fermi resonance explicitly into account; in addition to the diagonal elements (3), we introduce in the energy matrix the Fermi coupling off-diagonal elements:

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[1] Let us recall (*4*) that

$$x_{22} = \tfrac{3}{2}k_{2222} - k_{122}^2\,[1/2\omega_1 + 1/8(2\omega_2 + \omega_1)],$$

$$x_{l_2 l_2} = -\tfrac{1}{2}k_{2222} + k_{122}^2/8(2\omega_2 + \omega_1).$$

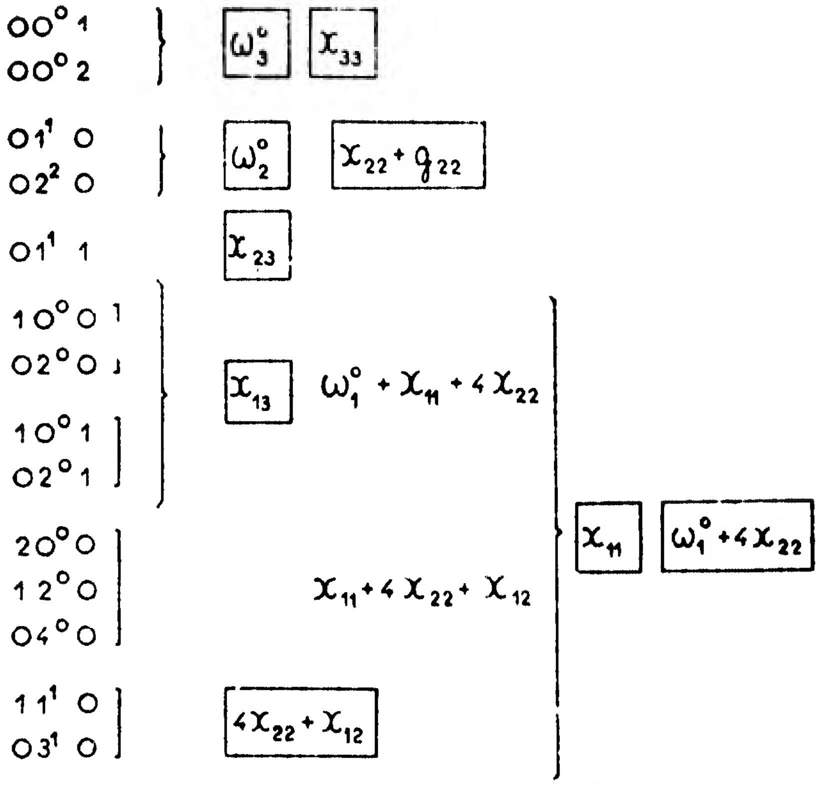

Fig. 1. Determination of vibrational constants from energy levels or sums of energy levels not perturbed by Fermi resonance.

$$W = \langle v_1 v_2 l_2 v_3 |\, H/hc\, | v_1 - 1,\, v_2 + 2,\, l_2 v_3 \rangle. \tag{5}$$

Up to second order, they can be written

$$W = W_s(\tfrac{1}{2})[(v_2 + 2)^2 - l_2^2]^{1/2} v^{1/2}, \tag{6}$$

with W_s given by Eq. (1).

Let us now designate by 1 and 2 the two levels 10^0v_3 and 02^0v_3 of a Σ diad, by Δ the difference $E_1 - E_2$ between the vibrational energies of these two levels, computed taking Fermi resonance into account, and by Δ_0 the difference $E_1^0 - E_2^0$ between the unperturbed vibrational energies of the same levels given by Eq. (3). Δ which is known from the spectra is related to the unknown quantities Δ_0 and W as written below:

$$\Delta^2 = \Delta_0^2 + 4W^2. \tag{7}$$

For a Σ diad,

$$W = W_s = -k_{122}/\sqrt{2}. \tag{8}$$

On the other hand, the difference

$$\Delta_0 = \omega_1^0 - 2\omega_2^0 + x_{11} - 4x_{22} + (x_{13} - 2x_{23})v_3 \tag{9}$$

can be expressed in terms of the known constants framed in Fig. 1 and of the unknown parameter $x_{12} - 4x_{22}$; then Δ_0 appears as a known linear function of this parameter. Therefore the curve representing Eq. (7) considered as a relation between k_{122} and $(x_{12} - 4x_{22})$ is an ellipse. Equation (7) holds also for Π, Δ, $\cdots$ diads; in the case of a Π diad,[2] for example:

$$W = W_e\sqrt{2} = -k_{122}\,, \tag{10}$$

$$\Delta_0 = \omega_1{}^0 - 2\omega_2{}^0 + x_{11} + x_{12} - 8x_{22} + (x_{13} - 2x_{23})v_3\,. \tag{11}$$

Let us now draw on the same diagram ellipses corresponding to the various diads Σ, Π, $\cdots$ for all the values of v_3 for which these diads have been observed. (Ellipses can also be drawn for the triads but it is much less practical.) The intersection of the various ellipses should give in principle the value of both $(x_{12} - 4x_{22})$ and k_{122}. These ellipses are drawn on Fig. 2 and 3 for $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$, respectively (curves marked Σ, Π, Δ); it can be seen from these figures that this procedure is very disappointing, because the ellipses do not give a well-defined intersection point. There is instead a wide region where the curves run almost parallel and very close to each other. (It is reasonable to think that they would appear almost superimposed on each other in this same region if the higher order terms listed in the "Remark" below would be taken into account.) Instead of a determination of both $(x_{12} - 4x_{22})$ and k_{122} we obtain only a relation between these two parameters. This shows that there are an infinity[3] of sets of vibrational constants $\omega_s{}^0 x_{ss'} g_{22} k_{122}$ which will enable one to compute the correct values of vibrational energy levels. In other words the fact that a set of vibrational constants permits the computation of energy levels in good agreement with experimental values does not necessarily mean that these constants are the right ones. We shall describe in Sec. B and C two possible ways of selecting the right set of vibrational constants.

Remark

The second-order vibrational analysis described in the present section is only a first approximation. In order to obtain a very good fit with experimental data, the calculation must be carried to fourth order, which means that additional terms must be included in the energy matrix:

(1) Terms of degree three with respect to vibrational quantum numbers v_s and l_2 need to be written[4] at the right end of formula (3). The coefficients of these terms are traditionally designated by y with three subscripts.

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[2] For a Π diad, we define Δ_0 as follows:

$$\Delta_0 = E_1{}^0 - E_2{}^0 = E^0{}_{1^1v_3)} - E^0_{(03^1v_3)}\,.$$

[3] In all these sets six out of the eleven constants, namely, $\omega_2{}^0$ $\omega_3{}^0$ x_{11} x_{33} x_{13} and x_{23} keep, of course, the same values (see Fig. 1).

[4] Consequently such terms will obviously also appear at the right end of Eqs. (9) and (11).

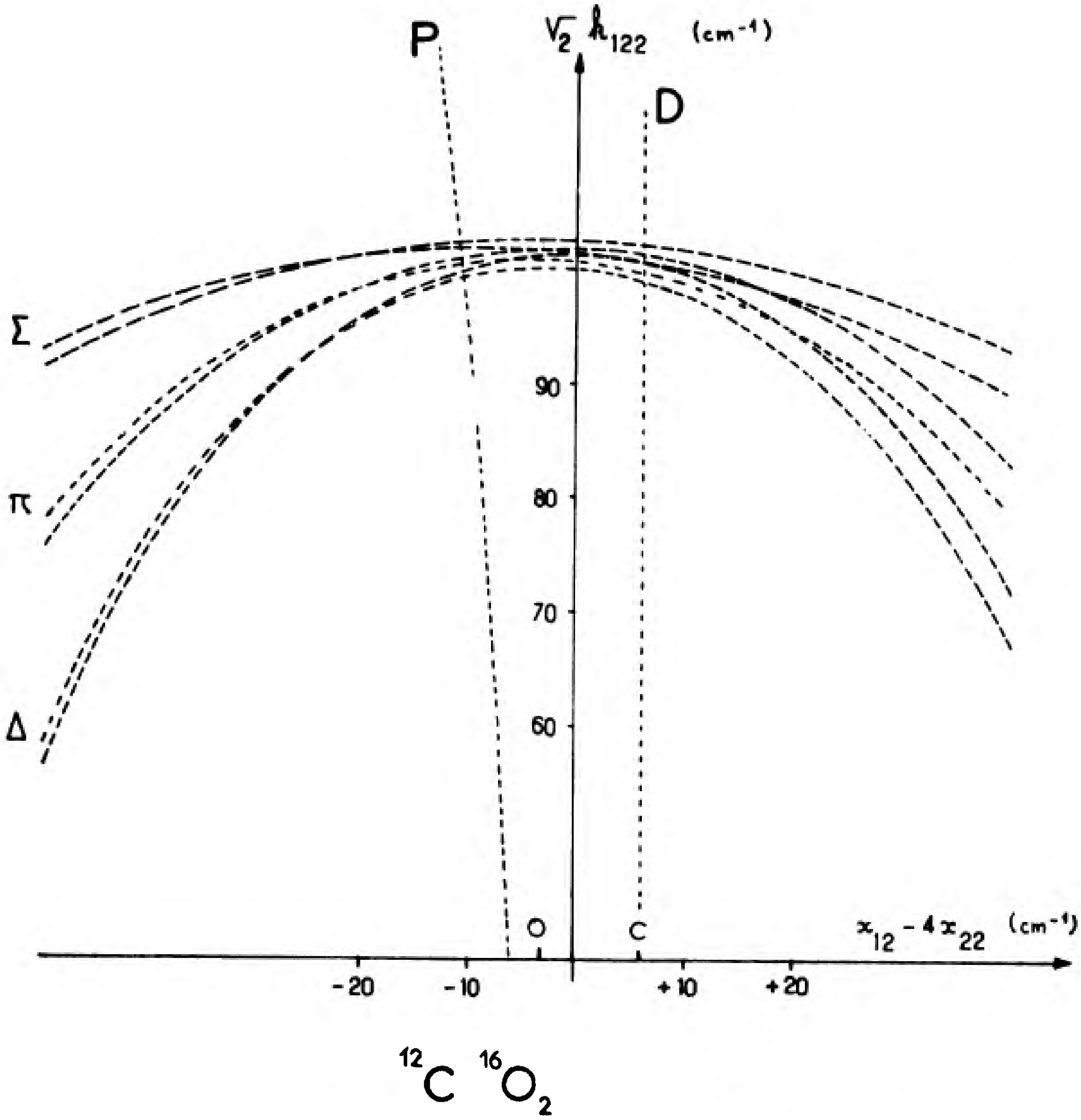

FIG. 2. Determination of $(x_{12} - 4x_{22})$ and k_{122} for $C^{12}O_2^{16}$

(2) In formula (6), W_e must be replaced by (*5*, *6*):

$$W_v = W_e + \lambda_1 v_1 + \lambda_2(v_2 + 2) + \lambda_3(v_3 + \tfrac{1}{2}). \qquad (12)$$

(3) In triads, tetrads, $\cdots$ new resonance matrix elements must be included in the secular determinants:

$$\left\langle v_1\, v_2\, l_2\, v_3 \left| \frac{{}_{(P)}h_4\dagger}{hc} \right| v_1 - 2,\, v_2 + 4,\, l_2\, v_3 \right\rangle$$
$$= u\{[(v_2 + 2)^2 - l_2^2][(v_2 + 4)^2 - l_2^2]v_1(v_1 - 1)\}^{1/2}. \qquad (13)$$

(For the definition of operator ${}_{(P)}h_4\dagger$, see Ref. *7*). It is probably worthwhile to point out that, while the first two kinds of terms [(1) and (2) above] have been

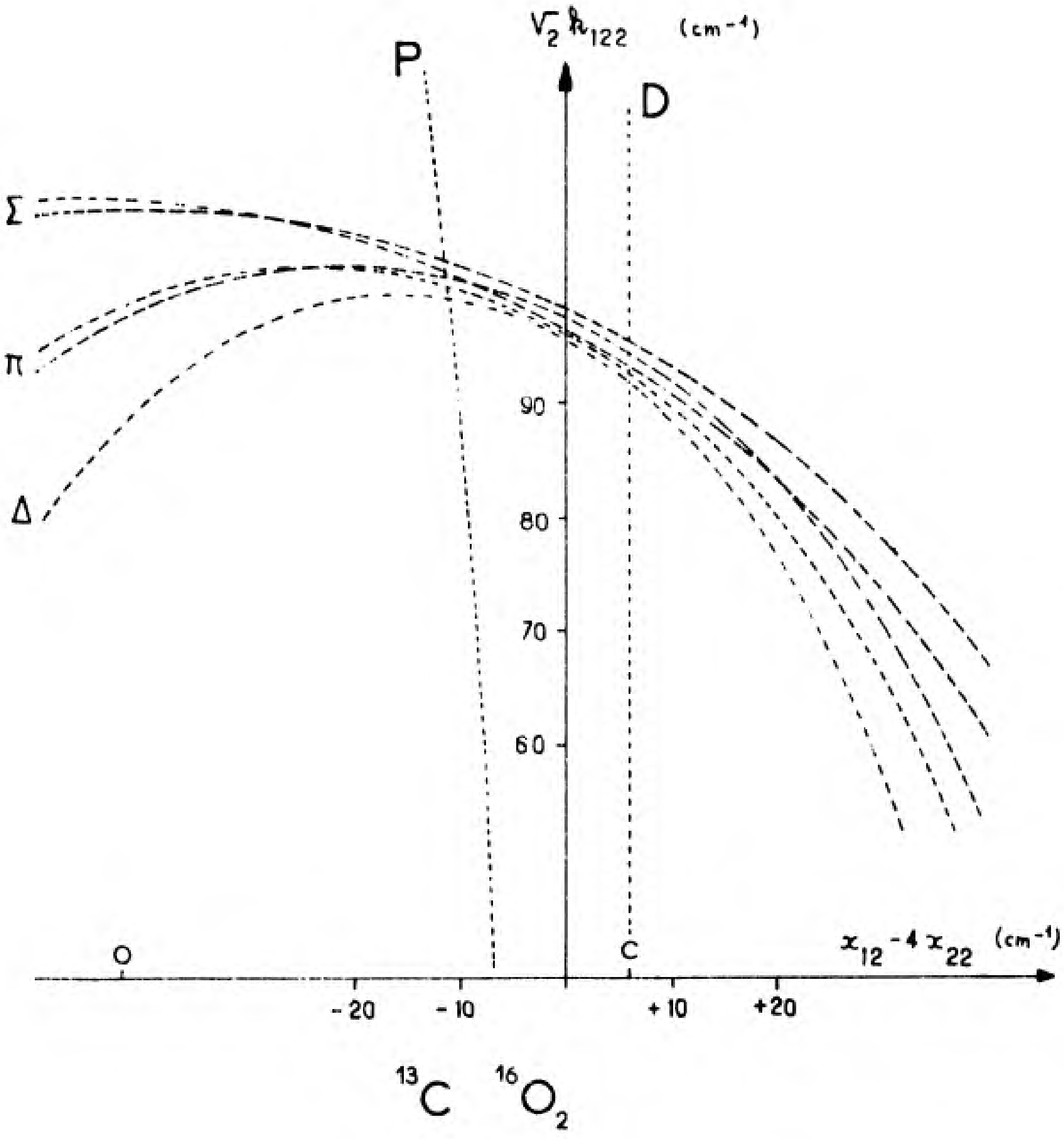

Fig. 3. Determination of $(x_{12} - 4x_{22})$ and k_{122} for $C^{13}O_2^{16}$

taken into account in the best vibrational analysis (*1*, *2*) of CO_2, the third kind [(3) above] has not been considered to the best of our knowledge.

B. Utilization of Rotational Constants

Due to Fermi resonance, the inertia constants B are linear combinations of unperturbed constants B^0 with[5]

$$B^0(v_1v_2^{l_2}v_3) = B_0^0 - \alpha_1v_1 - \alpha_2v_2 - \alpha_3v_3 . \tag{14}$$

For the Σ diad 10^00, 02^00, we can write, using for levels 1 and 2 the convention

---

[5] In the case of Π levels, formula (14) holds for the half sum of the constants B^0 corresponding to the two sublevels of the l-type doublet.

made in Section *A*:

$$B_1^0 = B^0_{(10^00)} = B_0^0 - \alpha_1, \tag{15}$$

$$B_2^0 = B^0_{(02^00)} = B_0^0 - 2\alpha_2. \tag{16}$$

If the Fermi coupling would be an exact resonance with degeneracy of the unperturbed levels ($E_1^0 = E_2^0$, i.e., $\Delta_0 = 0$), the mixing of the states 1 and 2 would be complete and the rotational constants B would be equal for the two perturbed states as shown in Fig. 4a:

$$B = \tfrac{1}{2}B_1^0 + \tfrac{1}{2}B_2^0. \tag{17}$$

(In the case of exact resonance there is no possibility of designating the perturbed levels as 1 or 2.) In fact the resonance is not exact ($\Delta_0 \neq 0$); the situation is then the one shown in Fig. 4b. The mixing of states 10^00 and 02^00 being not complete we can without ambiguity call 1 and 2 the perturbed states which contain the largest fraction of 10^00 and 02^00, respectively.

B_1 and B_2 are linear combinations of B_1^0 and B_2^0 and it can be shown (*8*, *9*, *2*) that

$$(B_1 - B_2)/(B_1^0 - B_2^0) = (E_1^0 - E_2^0)/(E_1 - E_2) \tag{18}$$

or

$$\Delta B = (\Delta_0/\Delta)\Delta B_0 \tag{19}$$

with

$$\begin{aligned} \Delta B &= B_1 - B_2, \\ \Delta B_0 &= B_1^0 - B_2^0. \end{aligned} \tag{20}$$

An important implication of the situation described on Fig. 4b is that

$$\begin{aligned} &\text{if} \quad E_1^0 > E_2^0 \quad \text{then} \quad E_1 > E_2 \\ &\text{if} \quad E_1^0 < E_2^0 \quad \text{then} \quad E_1 < E_2 \end{aligned} \tag{21}$$

and

$$\begin{aligned} &\text{if} \quad B_1^0 > B_2^0 \quad \text{then} \quad B_1 > B_2 \\ &\text{if} \quad B_1^0 < B_2^0 \quad \text{then} \quad B_1 < B_2. \end{aligned} \tag{22}$$

Application to the labelling of the states for CO_2

For the Σ diads of $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$ experience shows definitely that, if one considers two bands in which the upper levels are members of the same diad, the spacing of the lines is smaller in the band with the higher frequency. In other words, the level with the larger vibrational energy has the smaller B constant. Then

$$\begin{aligned} &\text{either} \quad E_1 > E_2 \quad \text{and} \quad B_1 < B_2 \\ &\text{or} \qquad E_1 < E_2 \quad \text{and} \quad B_1 > B_2 . \end{aligned} \tag{23}$$

Experience definitely shows also that, in Σ diads of $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$,

$$B_1^0 < B_2^0. \tag{24}$$

Indeed if one measures the inertia constants B in levels 00^00, 01^10, 02^00, 10^00, the first two levels are not perturbed by Fermi resonance and the last two levels belong to the same diad; therefore:

$$\begin{aligned} B_{(00^00)} &= B_0^0, \\ B_{(01^10)} &= B_0^0 - \alpha_2 , \\ B_{(10^00)} + B_{(02^00)} &= B_1^0 + B_2^0 \\ &= 2B_0^0 - \alpha_1 - 2\alpha_2 . \end{aligned} \tag{25}$$

It is easy to obtain first B_0^0, α_1, and α_2 from the four experimental values, then to compute B_1^0 and B_2^0 by using Eqs. (15), (16), and, as a consequence, to establish relation (24).

Now if we use the relations (24), (22), (23), and (21) (in this order), we come to the conclusion that

$$E^0_{(10^00)} > E^0_{(02^00)} \tag{26}$$

and that the labelling shown on Fig. 4b is correct.

Application to the determination of vibrational constants

Since Δ and ΔB are known directly from the spectrum and since ΔB_0 can be obtained as we have just described. Eq. (19) gives Δ_0 from which the value of the unknown parameter $x_{12} - 4x_{22}$ can be obtained.

This value is shown by point C on the horizontal axis in Fig. 2 and 3. The intersection of the vertical straight line D with the ellipses permits then to obtain a value of k_{122}. The arguments given in the present section were used by Courtoy in his fourth-order determination of vibrational constants of CO_2 (*1*, *2*) and his method is essentially equivalent to the one described here. As we have said his constants permit the computation of energy levels in excellent agreement with experimental values but they lead to the two inconsistencies pointed out in the Introduction.

C. UTILIZATION OF RELATIONS BETWEEN VIBRATIONAL CONSTANTS

Since the discrepancies are due to the fact that certain theoretical relations are not verified by the vibrational constants, it seems suitable to take these relations into account from the beginning in the analysis.

(1) Let us consider relation (2). The left side

$$x_{22} + 3x_{l_2l_2} = x_{22} + 3g_{22} + 3B \tag{27}$$

can be expressed in terms of the inertia constant B, of the known quantities framed in Fig. 1 and of the unknown parameter $x_{12} - 4x_{22}$. It can furthermore be shown that ω_1 and ω_2 appearing on the right side of Eq. (2) depend only upon the known quantities framed in Fig. 1, so that Eq. (2) considered as a relation between $(x_{12} - 4x_{22})$ and k_{122} is the equation of a known parabola (curve P on Fig. 2 and 3). The intersection of this parabola with the ellipses drawn in Sec. A gives values of $x_{12} - 4x_{22}$ and k_{122}. It can be seen that these values are different from those obtained in Sec. B, leading then to a different set of vibrational constants which is expected to give as good agreement between observed and calculated levels as the first one with the additional advantage that Eq. (2) will be verified.

The fact that the straight line D has no intersection with the parabola P on Fig. 2 and 3 explains why using Eq. (2) to compute k_{122} from the values of x_{22} and $x_{l_2l_2}$ obtained in Sec. B leads to imaginary values of κ_{122}.

(2) If the method of paragraph (1) above is used for $C^{12}O_2^{16}$ and independently for $C^{13}O_2^{16}$ it is found that k_{122} and k^*_{122} obtained, respectively, for these two molecules have the good theoretical ratio expected for this isotopic substitution:

$$k^*_{122}/k_{122} = \omega_2{}^*/\omega_2 = \omega_3{}^*/\omega_3 . \tag{28}$$

This can be seen on Fig. 2 and 3 where $\sqrt{2}k_{122}$ has been used as ordinate on both diagrams [relation (28) making possible a transformation from k^*_{122} to k_{122} before drawing Fig. 3]: The intersection of P with the ellipses has about the same ordinate on both Fig. 2 and 3. The fact that the intersection of D with the ellipses does not correspond to the same ordinate on Fig. 2 and 3 explains why the values obtained for the constants k_{122} and k^*_{122} by the method of Sec. B do not give the right ratio for the isotopic substitution from C^{12} to C^{13}.

To summarize, the vibrational constants obtained in Section B give the correct inertia constants but do not satisfy the equation (2) and do not give the right ratio for k_{122} in isotopic substitutions, while the vibrational constants obtained in the present section satisfy the equation (2) and give the right ratio for k_{122} in the isotopic substitution from C^{12} to C^{13} but do not seem to give the correct inertia constants. We shall see in Sec. D however that, in the case of a strong Fermi resonance, the formulas used thus far in the computation of effective inertia constants require modification, which will then permit one to overcome this difficulty.

(3) We have already pointed out that Δ_0 is a known linear function of $x_{12} - 4x_{22}$. The point 0 on the horizontal axes in Fig. 2 and 3 indicates the value of $x_{12} - 4x_{22}$ for which Δ_0 vanishes. One sees that in the case of $C^{12}O_2^{16}$, the new value of $x_{12} - 4x_{22}$ (abscissa of the intersection of P with the ellipses) gives a

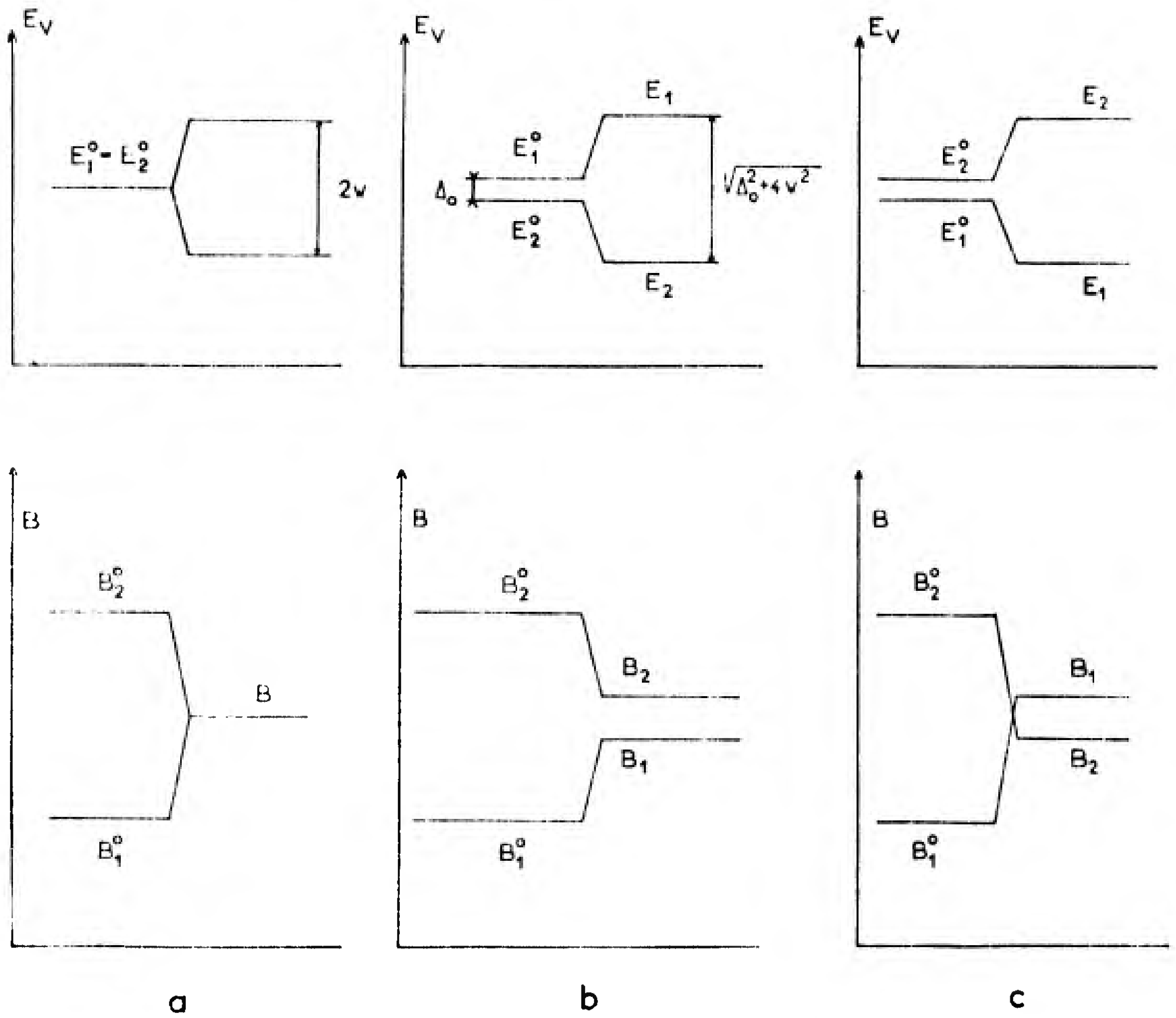

FIG. 4. Influence of Fermi resonance on vibrational energies E_v and inertia constants B. In each diagram the unperturbed values (with superscripts 0) are shown on the left and the perturbed values are shown on the right. a. exact resonance $E_1{}^0 = E_2{}^0$, b. case where $E_1{}^0 > E_2{}^0$, c. case where $E_1{}^0 < E_2{}^0$.

negative value for Δ_0 so that in this scheme

$$E'^{0}_{(10^00)} < E'^{0}_{(02^00)} , \tag{29}$$

which means that the current assignment of ν_1 and $2\nu_2$ should be reversed. If we come back to the discussion of Sec. B, the propositions (21), (23), and (24) cannot be questioned so that the only possibility is to admit that the proposition (22) does not hold, giving then the picture shown on Fig. 4c. The theory to be developed in the next section has to explain this crossing of the inertia constants when going from the unperturbed to the perturbed values. In the case of $C^{13}O_2^{16}$, the position of the point 0 in Fig. 3 shows that we still have the situation corresponding to relation (26), i.e., to Fig. 4b.

Remark

The arguments developed in Sec. B and C are not the only ones which can be used in order to find the correct assignment of ν_1 and $2\nu_2$ and to obtain the right vibrational constants:

(1) In the earlier studies on Fermi resonance *(10)*, the relative intensity of the two Raman bands ν_1 and $2\nu_2$ was used in support of the hypothesis (26) for $C^{12}O_2^{16}$. We must admit that this observation is in apparent contradiction with the conclusions obtained in the present section. However, we are inclined not to consider this argument as a decisive one because the theory of intensities of Raman transitions is rather uncertain, especially when Fermi resonance occurs.

(2) There is a relation between α_2 and k_{122}. However, the accuracy of α_2 being rather low, it seems more reliable to use Eq. (2) in order to determine k_{122} and then to check that the value obtained is compatible with the observed value of α_2.

D. COMPUTATION OF INERTIA CONSTANTS IN THE CASE OF A STRONG FERMI RESONANCE

It can be seen on Fig. 4 that, as an effect of Fermi resonance, $\Delta B \ll \Delta B_0$. While $\Delta B_0 J(J+1)$ belongs to second order, $\Delta BJ(J+1)$ will belong to a higher order, so that a correct computation of the inertia constants B in the case of Fermi resonance could, even in the lowest approximation, involve operators belonging to terms with an order of magnitude higher than the second in the expansion of the Hamiltonian.

Beside the third- and fourth-order vibrational corrections listed in the Remark at the end of Section A, various fourth-order (diagonal) rotational corrections can be taken into account. One of them will change slightly the computed B values: it consists in adding terms $\gamma_{ss'} v_s v_{s'}$ at the right end of Eq. (14). This fourth-order correction has been taken into account in previous analysis; but it is one or two orders of magnitude smaller than the effect we are looking for.

However Maes *(6)* has pointed out that third-order off-diagonal contributions should also be taken into consideration; they come about from the fact that the matrix element (5) varies with J so that a term $+\delta J(J+1)$ must be written on the right end of Eq. (12). This effect has so far never been taken into account. It can easily be seen that it introduces an additional term in relation (19), which for a Σ diad[6] becomes, up to third order,[7]

$$\Delta B = (\Delta_0/\Delta)\Delta B_0 + (4W_e/\Delta)\delta. \tag{30}$$

ΔB_0 and δ are, respectively, the coefficients of terms in $J(J+1)$ coming from second-order and third-order Hamiltonians; if Δ_0 and $4W_e$ have about the same order of magnitude, the second term on the right side of Eq. (30) is much smaller than the first one; then Eq. (19) holds with a very good approximation. If, on

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[6] The general formula for any diad $(v_1 v_2^{l_2} v_3)(v_1 - 1, v_2 + 2^{l_2}, v_3)$ is

$$\Delta B = (\Delta_0/\Delta)\Delta B_0 + (W_e/\Delta)\delta[(v_2+2)^2 - l_2^2]v_1 .$$

[7] Equation (30) can still be used on a higher approximation, provided the fourth-order terms mentioned above are included in Δ_0 and ΔB_0, and provided W_e is replaced by W_r.

the other hand, Δ_0 is one order of magnitude smaller than W_e, as it happens for CO_2, the two terms on the right side of Eq. (30) have the same order of magnitude. If the second one is larger in absolute value than the first one and opposite in sign, then ΔB and ΔB_0 will have opposite signs which corresponds to the situation shown in Fig. 4c with a crossing of the values of the inertia constants when going from the unperturbed to the perturbed case.

Effective values in agreement with the experimental ones can be computed for the inertia constants B of the various diads of $C^{12}O_2^{16}$ by using the vibrational constants obtained in Sec. C and by assuming

$$\delta \simeq 2\ 10^{-4}\ \text{cm}^{-1}, \tag{31}$$

which is a very reasonable order of magnitude for such a constant.

The considerations above overcome the main difficulty encountered in the approach described in Sec. C. This approach leads then to conclusions which appear to be much more satisfactory than those obtained in Sec. B.

CONCLUSION

From a general viewpoint, the three following considerations seem to be important:

(1) The fact that a set of vibrational constants permits the computation of energy levels in good agreement with experimental values does not mean necessarily that these constants are the right ones.

(2) The theoretical relations existing between the vibrational constants must be used from the beginning in the vibrational analysis in order to obtain the correct set of vibrational constants.

(3) The variation of the Fermi coupling element with J must be taken into account in the computation of rotational constants, principally when the Fermi resonance is very strong.

When the considerations above are applied to carbon dioxide, they suggest that the traditional assignment of ν_1 and $2\nu_2$ should be reversed in the case of $C^{12}O_2^{16}$. However it is only when vibrational energies, effective rotational constants B and D, and intensities have been recomputed on this new basis for all the observed levels and shown to agree with experimental values that the scheme proposed in Sec. C of this paper will possibly appear to be the right one.

Preliminary results obtained in collaboration with Courtoy show that it could very well be so.

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13. ABSTRACT

The rotation-vibration energies of polyatomic molecules have been computed to the fourth order of approximation. These energies are used to obtain the frequencies of lines in rotation and rotation-vibration spectra. Such very accurate calculations are necessary in order to explain many effects observed in very high resolution spectra. The following topics are emphasized in the present Report :

- The quartic anharmonic potential function
- The rotation spectrum of axially symmetric molecules in an excited vibrational state
- The rotation-vibration spectra of spherical top molecules
- Anomalous rotational structure of level $03^{1}1$ in the rotation-vibration spectrum of $C^{13}O^{16}_{2}$
- Rotational structure of the fundamental ν_6 of methyl cyanide
- A general discussion of Fermi resonance in CO_2 with a new assignment of vibrational levels.