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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS
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ROTATION-VIBRATION SPECTRA

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These are preliminary lecture notes, intended only for distribution to participants.
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Introduction

1) Energy of molecules:

$$E - E_t = E_e + E_v + E_r \quad (1)$$

$$\Delta E_e \gg \Delta E_v \gg \Delta E_r \quad (2)$$

E_e : electronic energy (associated with the motion of electrons)

E_v : vibrational energy (associated with oscillations of the nuclei about their equilibrium positions)

E_r : rotational energy (associated with overall rotations of the molecule)

E_t : translation energy (associated with overall translations of the molecule). E_t is not involved in interactions of the molecule with the electromagnetic radiation. It may be overlooked

Relation (2) leads, for the diagram of energy levels of a molecule to the structure shown on fig. 1. This structure leads in turn to the three types of molecular spectra:

- electronic spectra
- rotation-vibration spectra
- rotation spectra

2) Classification of molecules

Let N be the goodness of a symmetry axis of the equilibrium configuration of the nuclei (i.e. a rotation by $\frac{2\pi}{N}$ about this axis superimposes the equilibrium configuration to itself). Table I gives the definition of the 4 classes of molecules and two characteristic properties of these classes.

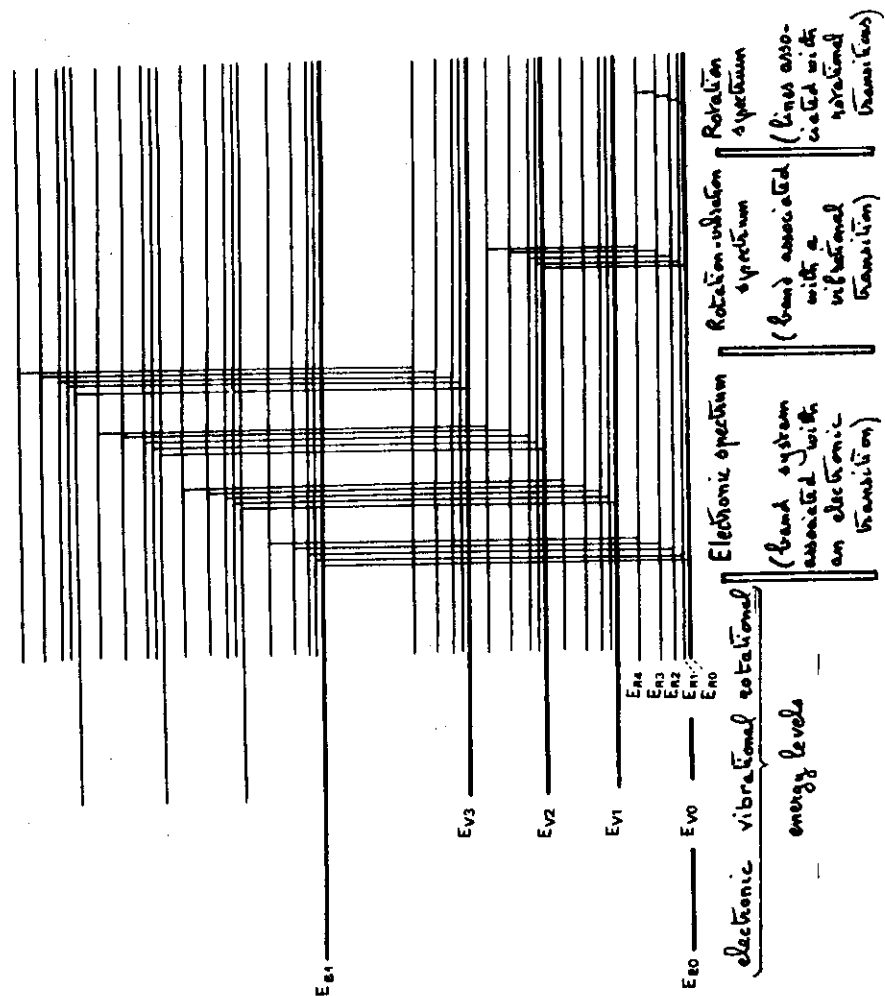


Fig. 1

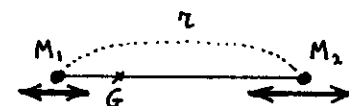
Table I

	Asymmetric Tops no axis with $N \geq 3$	Symmetric Tops 1 axis with $N \geq 3$	Spherical Tops several axes with $N \geq 3$
degree of degeneracy of normal vibrations	$d_s = 1$	$d_s = 1, 2$	$d_s = 1, 2, 3$
principal moments of inertia of the equilibrium configuration	$I_{xx}^e \neq I_{yy}^e \neq I_{zz}^e$	$I_{xx}^e = I_{yy}^e \neq I_{zz}^e$ ($I_{zz}^e = 0$ for linear mol.)	$I_{xx}^e = I_{yy}^e = I_{zz}^e$
		Linear Molecules 1 axis with $N = \infty$	

Vibration

A Diatomic molecules

- One dimensional oscillator



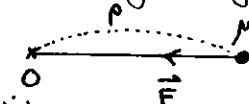
2 masses at distance r ; we assume that the center of mass G and the direction of the internuclear axis fixed. This model is equivalent to the following one:

1 mass at distance ρ of O

$$\rho = r - r_e \quad (r_e \text{ equilibrium distance of the nuclei})$$

$$\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2} \quad (\mu \text{ reduced mass})$$

$$\vec{F} = \text{force } \vec{F}(\rho)$$



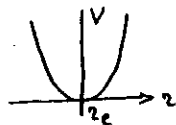
- Hamiltonian operator $H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} + V(\rho)$ potential

• Harmonic oscillator

$$V = \frac{1}{2} k p^2$$

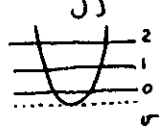
$$F = - \frac{dV}{dp} = k p$$

force constant



- Hamiltonian $H = - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial p^2} + \frac{1}{2} k p^2$

- Energy levels (eigen values of H)



$$E = h\nu \left(v + \frac{1}{2} \right) \quad v = 0, 1, 2, \dots$$

$$\nu = 2\pi \sqrt{\frac{k}{\mu}} \text{ sec}^{-1} \text{ (frequency of the classical harmonic oscillator)}$$

- Spectral terms $G(v) = \frac{E}{hc} = \omega_e \left(v + \frac{1}{2} \right)$

$$\omega_e = \frac{\nu}{c} \text{ cm}^{-1}$$

Example: for the CO molecule, $\omega_e = 2170 \text{ cm}^{-1}$

• Anharmonic oscillator

$$V = \frac{1}{2} k p^2 + k' p^3 + k'' p^4 + \dots$$

$$G(v) = \frac{E}{hc} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \dots$$

Example: CO molecule, $\omega_e = 2170 \text{ cm}^{-1}$, $\omega_e x_e = 13 \text{ cm}^{-1}$

$G(v)$ is measured from the equilibrium value

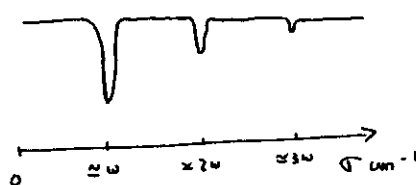
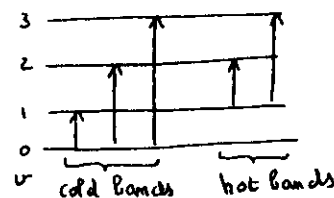
$$G_0(v) = G(v) - G(0) = \omega_0 v - \omega_0 x_0 v^2 + \dots$$

$G_0(v)$ is measured from the lower vibrational level ($v=0$)

• Vibration spectra

- Selection rules (absorption and emission)
 - a transition is allowed if the motion involves a change of the vector \vec{M} (electric dipole moment)
- Homonuclear molecules X_2 : all transitions are forbidden

- Absorption spectrum



Position of the vibration bands:

$$\sigma = \frac{E'}{hc} - \frac{E''}{hc}$$

(' refers to the upper level
' refers to the lower level)

$$\left\{ \begin{array}{l} \text{cold bands } \sigma = G_0(v') \\ \text{hot bands } \sigma = G_0(v') - G_0(v'') \end{array} \right.$$

Intensities:

for a given v'' , $\propto \Delta v$ if $\Delta v \rightarrow 1$
(influence of the transition moment)

for a given Δv , $\propto v''$ if $v'' \rightarrow \infty$
(influence of the Boltzmann factor)

B Polyatomic molecules

- Degrees of freedom: a N-atomic molecule has 3N degrees of freedom:

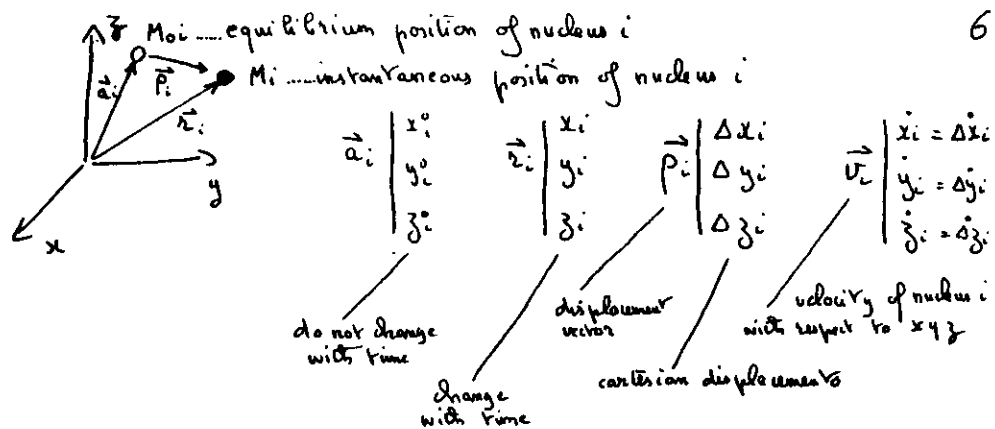
	Non-linear mol.	Linear mol.
Translations	3	3
Rotations	3	2
Deformations	$3N - 6$	$3N - 5$

• Harmonic potential

- Classical expressions of the kinetic energy T and the potential energy V:
 - masses of the nuclei

$$2T = \sum_{i=1}^N m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)$$

We consider a framework x, y, z linked to the equilibrium configuration



cartesian displacements: $\Delta x_i, \Delta y_i, \Delta z_i, \dots, \Delta z_N$
 mass-adjusted cartesian displacements: $m_i^{1/2} \Delta x_i, m_i^{1/2} \Delta y_i, m_i^{1/2} \Delta z_i, \dots, m_N^{1/2} \Delta z_N$
 $= s_1, = s_2, = s_3, \dots, = s_{3N}$

$$2T = \sum_{j=1}^{3N} \dot{s}_j^2$$

$$2V = \sum_{j,k} f_{jk} s_j s_k \quad \text{harmonic potential}$$

- Normal coordinates and normal vibrations

We perform, on the coordinates s , an orthogonal transformation chosen in such a way that, in terms of the new coordinates

Q_m , energies T and V have simpler expressions:

$$Q_m = \sum l_{mi}^{\alpha} s_j \quad \text{orthogonal transformation} \rightarrow \begin{cases} 2T = \sum_{m=1}^{3N} \dot{Q}_m^2 \\ 2V = \sum_{m=1}^{3N} \lambda_m Q_m^2 \end{cases}$$

Then we obtain for the energy:

$$E = T + V = \sum_m \frac{1}{2} \left(\dot{Q}_m^2 + \lambda_m Q_m^2 \right)$$

energy of an harmonic oscillator

α in l_{mi}^{α} $\alpha = x, y, z$ and $i = 1, 2, \dots, N$

To do so we want to diagonalize the matrix $\{f_{jk}\}$
 λ_m is an eigen-value of $\{f_{jk}\}$

$$\begin{vmatrix} f_{11} - \lambda & f_{12} & \dots & f_{1,3N} \\ f_{21} & f_{22} - \lambda & \dots & f_{2,3N} \\ \dots & \dots & \dots & \dots \\ f_{3N,1} & f_{3N,2} & \dots & f_{3N,3N} - \lambda \end{vmatrix} = 0$$

secular equation
(degree $3N$ in λ)
 $\rightarrow 3N$ roots λ_m

Among the $3N$ roots, the root $\lambda = 0$ is found six times (five times for a linear molecules). The corresponding coordinates Q_m are associated with overall displacements of the molecule (translations and rotations). We are left with $3N - 6$ coordinates associated with deformations. We shall designate them by $Q_{3\sigma}$: subscript s characterizes the distinct roots λ_s of the secular equation:

if λ_s is a simple root there is 1 coordinate Q_s ($\sigma=1$ can be omitted in $Q_{3\sigma}$) $d_s = 1$	if λ_s is a double root there are 2 coordinates Q_{s1}, Q_{s2} ($\sigma=1$ or 2) $d_s = 2$	if λ_s is a triple root there are 3 coordinates Q_{s1}, Q_{s2}, Q_{s3} ($\sigma=1, 2$ or 3) $d_s = 3$
---	---	--

d_s being the degree of degeneracy of vibration s

Then $E = \sum_s E_s \quad E_s = \frac{1}{2} \left(\sum_{\sigma} \dot{Q}_{3\sigma}^2 + \lambda_s \sum_{\sigma} Q_{3\sigma}^2 \right)$

Examples of normal vibrations (non degenerate, twofold degenerate and threefold degenerate) are given in fig. 2:

XY_2 bent symmetric	$E_x: H_2O$	$N=3 \rightarrow 3N-6=3$	} normal coordinates
XY_2 linear symmetric	$E_x: CO_2$	$N=3 \rightarrow 3N-5=4$	
XYZ linear non-symmetric	$E_x: HCN$	$N=3 \rightarrow 3N-5=4$	
XY_4 tetrahedral	$E_x: CH_4$	$N=5 \rightarrow 3N-6=9$	

For a given molecule, the possible values of d_s (degree of degeneracy of normal vibrations) is given by the symmetry properties of the equilibrium configuration (see Table I)

- Hamiltonian operator and energy levels

$$H = \sum_s H_s \quad H_s \begin{cases} \text{1 dimensional harmonic oscillator} \rightarrow E_s = hc\omega_s(v_s + \frac{1}{2}) \\ 2 \rightarrow E_s = hc\omega_s(v_s + 1) \\ 3 \rightarrow E_s = hc\omega_s(v_s + \frac{3}{2}) \end{cases}$$

$$G(\dots v_s \dots) = \frac{E}{hc} = \sum_s \omega_s \left(v_s + \frac{d_s}{2} \right)$$

Case of the 2 dimensional harmonic oscillator:

$$\text{classical energy} : E_s = \frac{1}{2} (\dot{Q}_{s1}^2 + \dot{Q}_{s2}^2 + \lambda_s (Q_{s1}^2 + Q_{s2}^2))$$

↳ hamiltonian operator \rightarrow quantized energy:

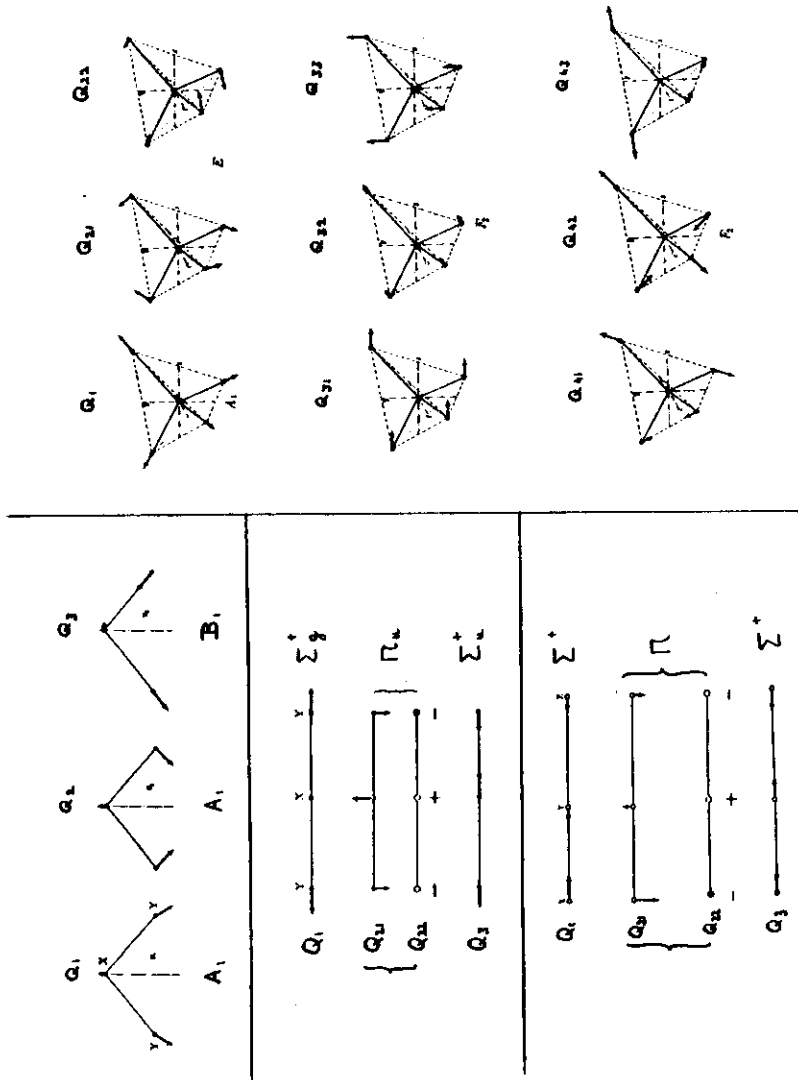
$$E_s = hc\omega_s \left(v_{s1} + \frac{1}{2} + v_{s2} + \frac{1}{2} \right) = hc\omega_s (v_s + 1)$$

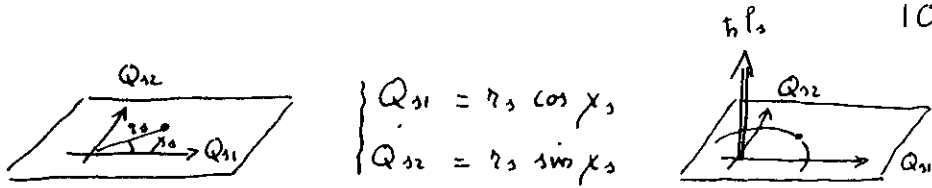
$$\text{with } v_s = v_{s1} + v_{s2}$$

While the energy levels E_s depend only upon v_s , the states $\Psi_{v_{s1} v_{s2}}(Q_{s1}, Q_{s2})$ depend upon both v_{s1} and v_{s2} . Energy levels $E(v_s)$ are degenerate. Their degree of degeneracy is $g(v_s) = v_s + 1$ (the number of states associated with a given value of the energy is equal to the number of ways of choosing v_{s1} and v_{s2} for a given value of $v_{s1} + v_{s2} = v_s$).

If instead of cartesian coordinates Q_{s1}, Q_{s2} , we use polar coordinates r_s, χ_s in the configuration space of the twofold degenerate vibration, then the state can be written as $\Psi_{v_s l_s}(r_s, \chi_s)$

Fig. 2





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the angular momentum associated with a twofold degenerate vibration is equal to $h l_3$ (in the configuration space)

• Anharmonic potential

$$2V = \sum_{s1} \lambda_s Q_{s1}^2 + \sum_{s1, s1', s1'', s1'''} h c k_{s1, s1', s1'', s1'''} Q_{s1} Q_{s1'} Q_{s1''} Q_{s1'''} + \dots$$

A perturbation computation leads to the following expression of the vibrational spectral term:

$$\frac{E}{h c} = \sum_s \omega_s \left(v_s + \frac{d_s}{2} \right) + \sum_{s1, s1'} \chi_{s1, s1'} \left(v_s + \frac{d_s}{2} \right) \left(v_{s1} + \frac{d_{s1}}{2} \right) + E^* + \dots$$

where E^* depends upon quantum numbers associated with the angular momentum of degenerate vibrations. In the case of symmetric tops (= "axially symmetric molecules") and of linear molecules, which have only non-degenerate and twofold degenerate vibrations,

$$E^* = \sum_{\substack{s1, s1' \\ \text{two fold degenerate}}} g_{s1, s1'}^v l_{s1} l_{s1'}$$

• Examples of energy diagrams, selection rules and vibrational transitions

- fig 3 gives for 3 simple molecules (H_2O , N_2O and CO_2) the definition of the symmetry species associated with the symmetry group of the equilibrium configuration, the analytical form of the vibrational spectral term $G = \frac{E}{h c}$ (see above) and the selection rules for vibrational transitions.

SYMMETRY SPECIES, ENERGY LEVELS AND SELECTION RULES		
XY_2 non linear symmetric 	XYZ linear unsymmetric (N_2O) 	XY_2 linear symmetric (CO_2)
$\Sigma^+, \Pi, \Delta, \dots$ $l_2 = 0, \pm 1, \pm 2, \dots$ Σ^+ sym. Σ^- antisym. $\left\{ \begin{array}{l} \text{reflection} / \sigma \end{array} \right.$	$\Sigma^+, \Pi, \Delta, \dots$ $l_2 = 0, \pm 1, \pm 2, \dots$ Σ^+ sym. Σ^- antisym. $\left\{ \begin{array}{l} \text{reflection} / \sigma \end{array} \right.$	$\Sigma^+, \Pi, \Delta, \dots$ $l_2 = 0, \pm 1, \pm 2, \dots$ Σ^+ sym. Σ^- antisym. $\left\{ \begin{array}{l} \text{reflection} / \sigma \end{array} \right.$
A_1, A_2, B_1, B_2 $G(v_1, v_2, v_3) = \omega_1 \left(v_1 + \frac{1}{2} \right) + \omega_2 \left(v_2 + \frac{1}{2} \right) + \omega_3 \left(v_3 + \frac{1}{2} \right) + \chi_{11} \left(v_1 + \frac{1}{2} \right)^2 + \chi_{22} \left(v_2 + \frac{1}{2} \right)^2 + \chi_{33} \left(v_3 + \frac{1}{2} \right)^2 + \chi_{12} \left(v_1 + \frac{1}{2} \right) \left(v_2 + \frac{1}{2} \right) + \chi_{13} \left(v_1 + \frac{1}{2} \right) \left(v_3 + \frac{1}{2} \right) + \chi_{23} \left(v_2 + \frac{1}{2} \right) \left(v_3 + \frac{1}{2} \right) + g_{12}^v l_2^2$	$\Sigma^+ \Sigma^- \Pi \Delta \dots$ $G(v_1, v_2, l_2, v_3) = \omega_1 \left(v_1 + \frac{1}{2} \right) + \omega_2 \left(v_2 + \frac{1}{2} \right) + \omega_3 \left(v_3 + \frac{1}{2} \right) + \chi_{11} \left(v_1 + \frac{1}{2} \right)^2 + \chi_{22} \left(v_2 + \frac{1}{2} \right)^2 + \chi_{33} \left(v_3 + \frac{1}{2} \right)^2 + \chi_{12} \left(v_1 + \frac{1}{2} \right) \left(v_2 + \frac{1}{2} \right) + \chi_{13} \left(v_1 + \frac{1}{2} \right) \left(v_3 + \frac{1}{2} \right) + \chi_{23} \left(v_2 + \frac{1}{2} \right) \left(v_3 + \frac{1}{2} \right) + g_{12}^v l_2^2$	$\Sigma^+ \Sigma^- \Pi \Delta \dots$ $G(v_1, v_2, l_2, v_3) = \omega_1 \left(v_1 + \frac{1}{2} \right) + \omega_2 \left(v_2 + \frac{1}{2} \right) + \omega_3 \left(v_3 + \frac{1}{2} \right) + \chi_{11} \left(v_1 + \frac{1}{2} \right)^2 + \chi_{22} \left(v_2 + \frac{1}{2} \right)^2 + \chi_{33} \left(v_3 + \frac{1}{2} \right)^2 + \chi_{12} \left(v_1 + \frac{1}{2} \right) \left(v_2 + \frac{1}{2} \right) + \chi_{13} \left(v_1 + \frac{1}{2} \right) \left(v_3 + \frac{1}{2} \right) + \chi_{23} \left(v_2 + \frac{1}{2} \right) \left(v_3 + \frac{1}{2} \right) + g_{12}^v l_2^2$
All transitions allowed	$\left\{ \begin{array}{l} \Delta l_2 = 0 \\ \Delta l_2 = \pm 1 \end{array} \right. \parallel$	$\left\{ \begin{array}{l} \Delta l_2 = 0 \\ \Delta l_2 = \pm 1 \end{array} \right. \parallel$
	$g \leftrightarrow u$ i.e. $\Delta v_2 + \Delta v_3$ odd	$g \leftrightarrow u$ i.e. $\Delta v_2 + \Delta v_3$ odd

fig. 3

Absorption Spectrum of N_2O

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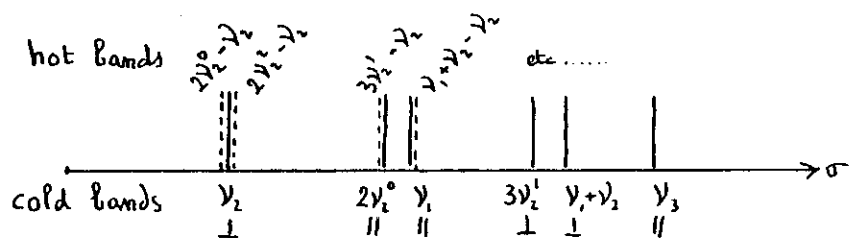
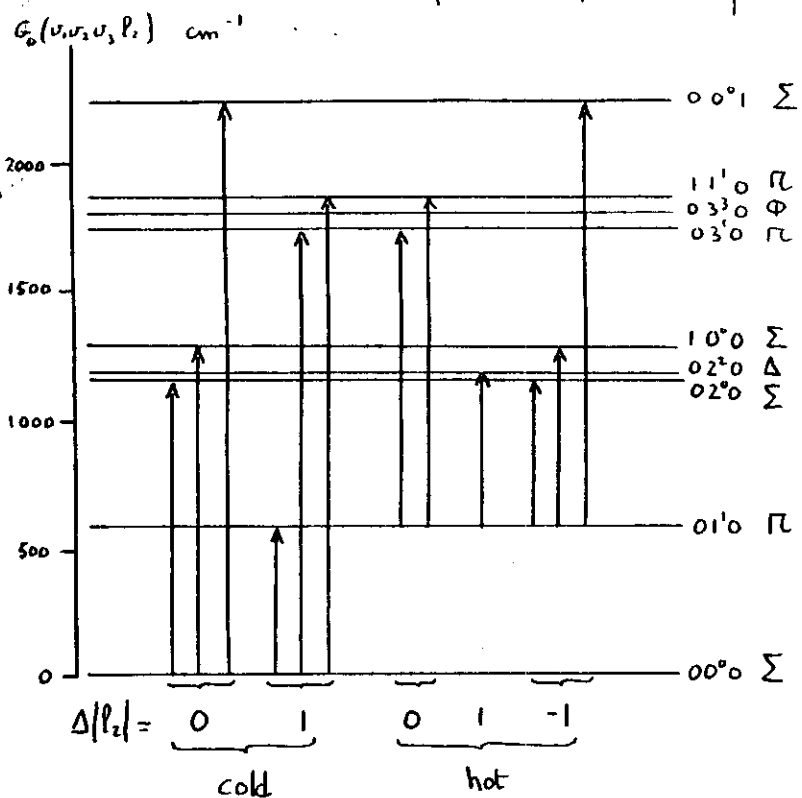


Fig. 4

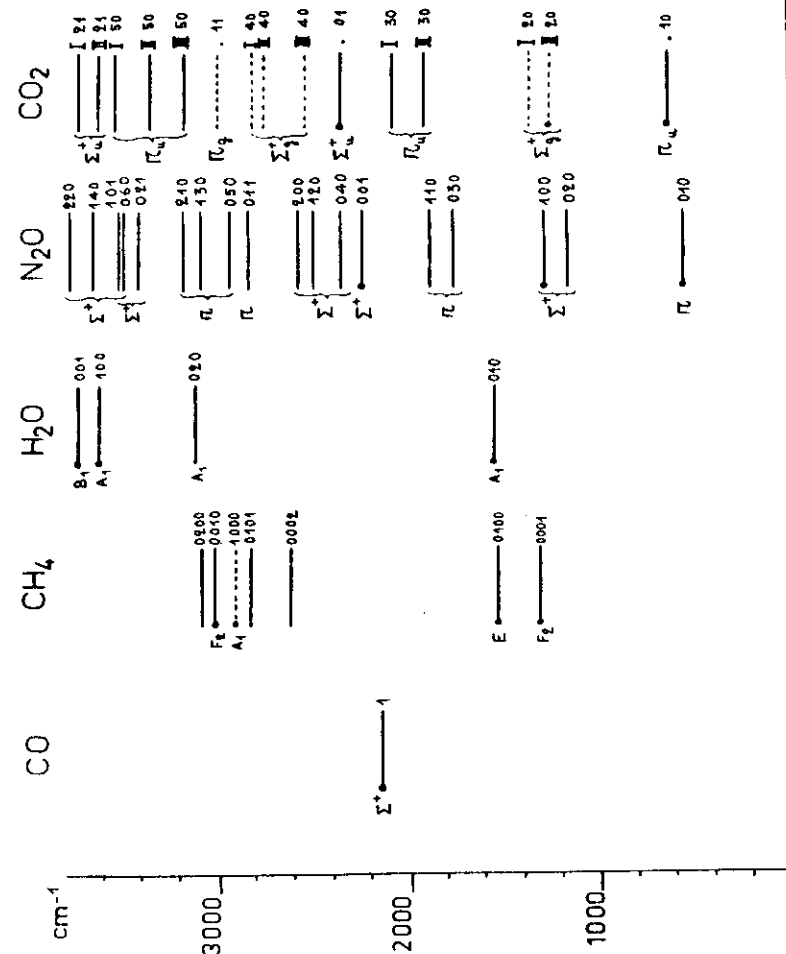


Fig 5

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- Fig. 4 gives, for N_2O , the diagram of the lowest 14 vibrational energy levels, the allowed transitions between these levels in absorption (cold bands and hot bands from the lower excited level), and a schematic picture of the spectrum showing the positions of the absorption bands [symbols ν, ν_2, ν_3 are used for the bands]

- Fig. 5 gives diagrams of vibrational energy levels for 5 molecules (CO, CH_4, H_2O, N_2O and CO_2). In this figure, \bullet — is associated with levels where 1 vibration is excited by 1 quantum (upper levels of allowed and forbidden fundamental transitions)

Remarks on Fig. 5: - for N_2O and CO_2 , ν_2 has been omitted in the symbol of the levels; only Σ and π levels are shown (compare with Fig. 4)
- the symbols used for the levels of CO_2 take Fermi Resonance into account. This will be discussed in the next paragraph.

- indicates the upper level of a forbidden transition from the ground state (in the case of CH_4 , the transition ν_2 , i.e. $0100 \leftarrow 0000$ is forbidden by the selection rules; it is nevertheless observed because it shares intensity with ν_4 as a consequence of a Coriolis resonance between 0100 and 0001)

Fermi Resonance

For a linear triatomic molecule, it is in principle possible, from 10 independent vibrational levels, to compute the 10 parameters ($3 \omega_e + 6 \omega_{ex} + 1 g_{ex}$) appearing in the spectral term G (see Eq. 3) and then, using G , to compute all the energy levels of the molecule. In the case of CO_2 ,

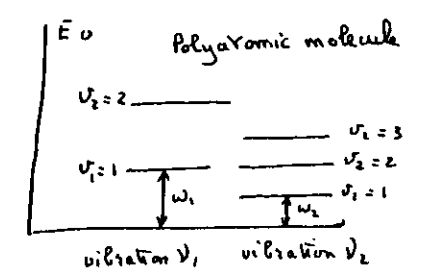
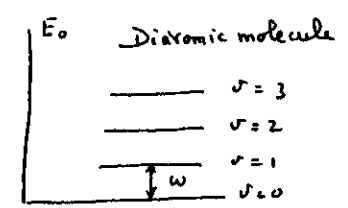
this has proved to be impossible. The explanation was given by Fermi in 1931. The spectral term G has been obtained through a second order non degenerate calculation. In such a calculation, the second order correction to the energy arising from the first order hamiltonian is given by:

$$H = H_0 + H_1 + H_2 + \dots$$

$$E = E_0 + E_1 + E_2 + \dots$$

$$E_2(n) = \langle n | H_2 | n \rangle + \sum_{n'' \neq n} \frac{\langle n | H_1 | n'' \rangle \langle n'' | H_1 | n \rangle}{E_0(n) - E_0(n')}$$

This assumes that the differences $E_0(n) - E_0(n'')$ are of zeroth order (same order as $E_0(n)$). It is so for the vibrational levels of a diatomic molecule; it is not necessarily so for a polyatomic molecule. In the case of CO_2 , it happens that $\omega_1 \approx 2\omega_2$, then the two levels



$\nu_1=1, \nu_2=0$ and $\nu_1=0, \nu_2=2$ correspond to values of E_0 which are about the same. In the last equation above, there will be, in the summation $\sum_{n''}$, one term with a very small denominator; if the corresponding numerator does not vanish, this term will be very large and it cannot be considered as a second order correction. This situation is known as a "resonance", namely the Fermi-resonance in the case

In order to have a resonance, two conditions must be fulfilled:

- 1) Two levels must have about the same energy in the zeroth order
- 2) There must be a non-vanishing coupling matrix element between these two levels

In the case of Fermi-resonance, the coupling matrix element must be of the type $\langle v_1 v_2 l_2 v_3 | H_1 | v_1+1, v_2-2, l_2 v_3 \rangle$

Actually there are such non vanishing matrix elements arising from the operator $hc k_{122} Q_1 (Q_{21}^2 + Q_{22}^2)$ in the cubic part of the anharmonic potential.

The difficulty comes from the fact that a non-degenerate perturbation treatment has been used, while the two levels 10^0 and 02^0 are quasi-degenerate.

We must consider polyads of resonating levels:

$$\begin{array}{l} \Sigma \text{ diads } \left\{ \begin{array}{l} 10^0 \\ 02^0 \end{array} \right\} \left\{ \begin{array}{l} 10^0 \\ 02^0 \end{array} \right\} \dots \\ \Pi \text{ diads } \left\{ \begin{array}{l} 11^0 \\ 03^0 \end{array} \right\} \left\{ \begin{array}{l} 11^0 \\ 03^0 \end{array} \right\} \dots \\ \Delta \text{ diads } \left\{ \begin{array}{l} 12^0 \\ 04^0 \end{array} \right\} \left\{ \begin{array}{l} 12^0 \\ 04^0 \end{array} \right\} \dots \end{array} \quad \begin{array}{l} \Sigma \text{ triads } \left\{ \begin{array}{l} 20^0 \\ 12^0 \\ 04^0 \end{array} \right\} \left\{ \begin{array}{l} 20^0 \\ 12^0 \\ 04^0 \end{array} \right\} \dots \\ \Pi \text{ triads } \left\{ \begin{array}{l} 21^0 \\ 13^0 \\ 05^0 \end{array} \right\} \left\{ \begin{array}{l} 21^0 \\ 13^0 \\ 05^0 \end{array} \right\} \dots \\ \text{etc.} \dots \end{array}$$

(levels $0 v_2 l_2 v_3$ with $l_2 = v_2$ are not involved in Fermi resonance). A Fermi polyad is defined by constant values of $2v_1 + v_2$, of v_3 and of l_2 . For each polyad, the energy levels are obtained by solving secular equations

Examples:

$$\begin{vmatrix} E_{10^0} - X & -hc \frac{k_{122}}{\sqrt{2}} \\ -hc \frac{k_{122}}{\sqrt{2}} & E_{02^0} - X \end{vmatrix} = 0$$

$$\begin{vmatrix} E_{11^0} - X & -hc k_{122} \\ -hc k_{122} & E_{03^0} - X \end{vmatrix} = 0$$

$$\begin{vmatrix} E_{20^0} - X & -hc k_{122} & 0 \\ -hc k_{122} & E_{12^0} - X & -hc \sqrt{2} k_{122} \\ 0 & -hc \sqrt{2} k_{122} & E_{04^0} - X \end{vmatrix} = 0$$

In these equations, $E_{v_1 v_2 l_2 v_3}$ is given by the formula shown in fig 3 ($G(v_1 v_2 l_2 v_3) = \frac{1}{hc} E_{v_1 v_2 l_2 v_3}$); the general formula for the coupling matrix element is:

$$\langle v_1 v_2 l_2 v_3 | H_1 | v_1-1, v_2+2, l_2 v_3 \rangle = -hc \frac{k_{122}}{\sqrt{2}} \frac{[(v_1+2)! l_2^2]^{1/2}}{2} v_1^{1/2}$$

The energy levels will be obtained by solving for the roots of the secular equations above; they will be written X_I, X_{II} for a diad X_I, X_{II}, X_{III} for a triad and so on, with $X_I > X_{II} > X_{III} > \dots$

It can be seen that the symbols 10^0 and 02^0 are not adequate for the first Σ diad, because the actual states are mixtures of these two uncoupled states.

The three secular equations given above will then lead to energy levels for which the following symbols are more adequate:

$$\Sigma \text{ diad } \begin{array}{l} \text{---} (10^0, 02^0)_I \\ \text{---} (10^0, 02^0)_{II} \end{array} \quad \text{or in short } \begin{array}{l} I 2^0 \\ II 2^0 \end{array}$$

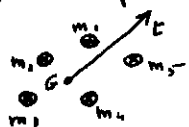
$$\Pi \text{ diad } \begin{array}{l} \text{---} (11^0, 03^0)_I \\ \text{---} (11^0, 03^0)_{II} \end{array} \quad \begin{array}{l} I 3^0 \\ II 3^0 \end{array}$$

$$\Sigma \text{ triad } \left\{ \begin{array}{l} (20^0 \dots 04^0)_I \text{ or in short } I 4^0 \\ (20^0 \dots 04^0)_{II} \quad II 4^0 \\ (20^0 \dots 04^0)_{III} \quad III 4^0 \end{array} \right.$$

In the shortened notation, the last numbers v_1, v_2, v_3 define the Fermi-polyad, while the first number: I, II, ... designate individual levels in a given Fermi-polyad, the order I, II, III, ... being the order of decreasing energies.

Rotation

• Principal axes of inertia



Consider a distribution of masses (for example the set of nuclei in a molecule). Let t be an axis through the center of mass of the distribution. If we compute the moment

of inertia of the distribution with respect to axis t and consider all directions for t around G , it can be shown that there are in general 3 directions for which the moment of inertia is maximum or minimum.

These are called principal directions of inertia; the corresponding moments are the principal moments of inertia. We shall use a reference system x, y, z , linked to the equilibrium configuration of the molecule and rotating with it, x, y, z being along the principal directions of inertia of the equilibrium configuration. $I_{xx}^e, I_{yy}^e, I_{zz}^e$ will designate the principal moments of inertia of the equilibrium configuration; Table I shows the relations existing among them for the various

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- Hamiltonian for the rigid rotator
We assume that the nuclei stay in their equilibrium positions, then

$$H = \frac{P_x^2}{2I_{xx}^e} + \frac{P_y^2}{2I_{yy}^e} + \frac{P_z^2}{2I_{zz}^e}$$

where P_x, P_y and P_z are the components of the angular momentum \vec{P} along the principal directions of inertia

- Rotation energy for the rigid rotator

- Symmetric tops $I_{xx}^e = I_{yy}^e$

$$H = \frac{P_x^2 + P_y^2}{2I_{xx}^e} + \frac{P_z^2}{2I_{zz}^e} = \frac{P^2 - P_z^2}{2I_{xx}^e} + \frac{P_z^2}{2I_{zz}^e}$$

the eigen values of P^2 and P_z are respectively $\hbar^2 J(J+1)$ and $\hbar K$ with

$$J = 0, 1, 2, \dots$$

$$K = 0, \pm 1, \pm 2, \dots \pm J$$

therefore

$$\frac{E}{\hbar c} = B_x [J(J+1) - K^2] + B_z K^2$$

with

$$B_x = \frac{h}{8\pi^2 c I_{xx}^e}$$

$$B_z = \frac{h}{8\pi^2 c I_{zz}^e}$$

B_x and B_z are the "rotational constants"

- Spherical tops $I_{xx}^e = I_{yy}^e = I_{zz}^e$

$$\frac{E}{\hbar c} = B_x J(J+1)$$

- Linear molecules $I_{xx}^e = I_{yy}^e$ $I_{zz}^e = 0$

the angular momentum for the rotation is, in the case of a linear molecule, perpendicular to the molecular axis: $P_z = 0$, then $K = 0$

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It can be shown that

$$\frac{E}{hc} = B_x J(J+1)$$

- Asymmetric tops: no explicit formula can be given for the rotational energy levels.

For the pure rotational problem, the total angular momentum is identical to the angular momentum associated with the rotation: $\vec{P} = \vec{P}_R$

In the cases of symmetric tops (also called axially symmetric molecules), spherical tops and linear molecules, the rotation energy can be written as

$$\frac{E_R}{hc} = B_x (P_R^\perp)^2 + B_z (P_R^z)^2$$

where P_R^\perp and P_R^z are respectively the components of \vec{P}_R along an axis perpendicular to z and along the z axis (z is the molecular axis for a linear molecule, the symmetry axis with $N \geq 3$ for a symmetric top and any axis for a spherical top)

- Rotation - Vibration energy (first order approximation)

It can be shown that the formula written above for the rotational spectral term still holds when the interaction between rotation and vibration is taken into account, but we have now

$$\vec{P} = \vec{P}_R + \vec{P}_v$$

\vec{P}_v being the angular momentum associated with the vibration. As shown on Fig. 6, the quantum numbers J and K are defined in relation with the total angular momentum \vec{P} , but it is P_R

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which comes in the formula giving the rotational spectral term. The rotation-vibration spectral term is equal to $\frac{E_v}{hc} + \frac{E_R}{hc}$ where $\frac{E_v}{hc} = G$ is the vibrational term defined previously.

Fig. 6 gives, for rotation and for rotation-vibration, the definition of rotational quantum numbers, the formula for the rotational spectral term and the coupling schemes for \vec{P}_R and \vec{P}_v . In the first order approximation, one can use for the vibrational angular momentum \vec{P}_v the contribution arising only from degenerate vibrations. In the case of linear and axially symmetric molecules, there are only twofold degenerate vibrations and the expression to be used for the eigen values of P_v is very simple. It is given on Fig. 7 (J_s written in short for J_{s1s2} is a Coriolis coupling coefficient; its exact definition will be given later).

Fig. 7 gives, for axially symmetric and linear molecules, the explicit expression of the rotational spectral term, the rotational energy diagrams and the selection rules. Examples of the rotational structure of the corresponding infrared bands (rotation-vibration spectrum) are given on Fig. 8.

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ASYMMETRIC MOL.	SPHERICAL TOPS	AXIALLY SYM. MOL.	LINEAR MOL.
ROTATION	<p> $J = 0, 1, 2, \dots$ $K = 0, \pm 1, \pm 2, \dots \pm J$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1)$ </p>	<p> $J = 0, 1, 2, \dots$ $K = 0$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1)$ </p>	<p> $J = 0, 1, 2, \dots$ $K = 0$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1)$ </p>
VIBRATION - ROTATION	<p> $J = 0, 1, 2, \dots$ $K = 0, \pm 1, \pm 2, \dots \pm J$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1) + (B_y - B_x) K^2$ </p>	<p> $J = 0, 1, 2, \dots$ $K = 0$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1) + (B_y - B_x) K^2$ </p>	<p> $J = 0, 1, 2, \dots$ $K = 0$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1)$ </p>
VIBRATION - ROTATION	<p> $J = 0, 1, 2, \dots$ $K = 0, \pm 1, \pm 2, \dots \pm J$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1) + (B_y - B_x) K^2$ </p>	<p> $J = 0, 1, 2, \dots$ $K = 0$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1) + (B_y - B_x) K^2$ </p>	<p> $J = 0, 1, 2, \dots$ $K = 0$ </p> <p> $\frac{E_R}{hc} = B_x J(J+1)$ </p>

Fig. 6

Axially Symmetric Molecules

$$P_v = \sum \hbar J_z p_z$$

$$-1 \leq J_z \leq 1$$

$$P_v = \hbar J \ell$$

1 degenerate vibration

Linear Molecules

$$P_v = \sum \hbar p_z$$

$$P_v = \hbar \ell$$

$$K = \ell$$

$$\frac{E_R}{hc} = B_x [J(J+1) - K^2] + B_y [K - \ell]^2$$

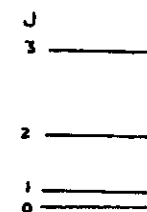
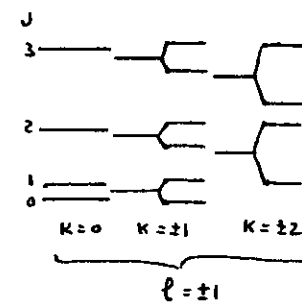
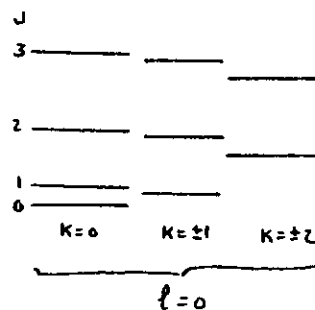
$$\frac{E_R}{hc} = B_x [J(J+1) - \ell^2]$$

$$\frac{E_R}{hc} = B_x J(J+1) + (B_y - B_x) K^2 - 2B_y J K \ell$$

($-B_y J^2 \ell^2$ is written with $\frac{E_v}{hc}$)

$$\frac{E_R}{hc} = B_x J(J+1)$$

($-B_x \ell^2$ is written with $\frac{E_v}{hc}$)



Selection Rules (threefold axis)

$$\Delta \ell = 0, \pm 3, \pm 6, \dots$$

$$\Delta K = 0$$

$$\Delta J = \begin{cases} 0, \pm 1 & (\text{if } K \neq 0) \\ \pm 1 & (\text{if } K = 0) \end{cases}$$

$$\Delta \ell = \pm 1, \pm 2, \pm 4, \dots$$

$$\Delta K = \pm 1$$

$$\Delta J = 0, \pm 1$$

$$\Delta K - \Delta \ell = 0, \pm 3, \pm 6, \dots$$

Selection Rules:

$$\Delta \ell = 0$$

$$\Delta J = \begin{cases} 0, \pm 1 & (\text{if } \ell \neq 0) \\ \pm 1 & (\text{if } \ell = 0) \end{cases}$$

$$\Delta \ell = \pm 1$$

$$\Delta J = 0, \pm 1$$

LINEAR MOLECULES

// BAND ($\Sigma \leftarrow \Sigma$)

\perp BAND ($\Pi \leftarrow \Sigma$)



AXIALLY SYM. MOL.

// BAND \rightarrow

\perp BAND \downarrow

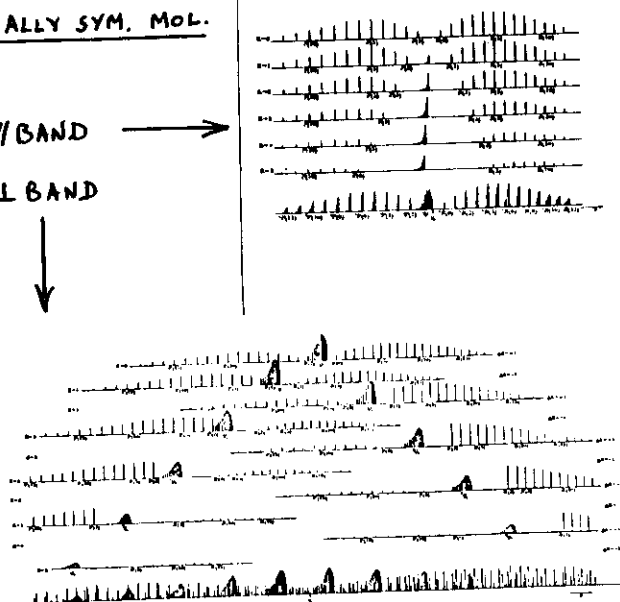


Fig. 8

Missing rotational levels

In the energy diagram of CO_2 , levels with odd J values are missing in the ground vibrational state.

As a consequence, one line out of 2 is missing in the P and R branches of $\Sigma - \Sigma$ transitions.

To show it, let us consider the total Schroedinger wave function of the molecule.

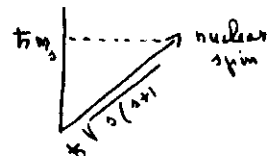
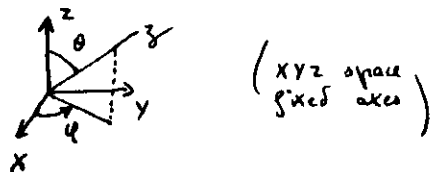
$$\Phi_{a \dots} (x_N \dots s_N \dots x_e \dots s_e)$$

it is a function of all position coordinates $x_N \dots x_e$ and spin coordinates $s_N \dots s_e$ of nuclei and electrons. The quantum numbers $a \dots$ characterize the state associated with the wave function under consideration. This wave function can be written with a good approximation as the product of an electronic and a nuclear wave function. The nuclear wave function can be written as the product of a wave function depending upon position coordinates (itself separable in translation, rotation and vibration terms) and a spin wave function (separable into terms associated with the various nuclei)

$$\Phi_{a \dots} (x_N \dots s_N \dots x_e \dots s_e) \approx \Psi_e (x_e \dots s_e) \Psi_n (x_N \dots s_N)$$

$$\Psi_e (x_e \dots s_e) \Psi_e (xyz) \Psi_2 (\theta \phi) \Psi_{\nu} (Q_{\nu}) \quad \Psi_n (x_N \dots) \Psi_n (s_N \dots) \quad \prod_i \Psi_{J_i} (i)$$

In this formula, Π_i is a product over nuclear spin functions associated with individual nuclei; XYZ are the coordinates of the center of mass, θ, φ are the angles defining the orientation of the molecular axis z , Ω_m is a normal coordinate; m_s is the spin projection quantum number.



In the molecule CO_2 (with ^{12}C and ^{16}O) all nuclear spins s are zero, then all quantum numbers m_s are zero

$$\Pi_i \Psi_{m_s}(i) = \Psi_0(o_1) \Psi_0(c) \Psi_0(o_2)$$

We want now to exchange the two oxygen nuclei o_1 and o_2 .

The total wave function Φ is either symmetric or antisymmetric with respect to the exchange of two identical particles

(electrons or nuclei). It is antisymmetric when the two particles are fermions (spin $\frac{1}{2}, \frac{3}{2}, \dots$), this would be the case for the exchange of two electrons (spin $\frac{1}{2}$). Φ is

symmetric when the two particles are bosons (spin $0, 1, \dots$),

this is the case for the two nuclei of ^{16}O (spin zero).

When we permute the two oxygen nuclei,

- Φ is symmetric

- Ψ_e is symmetric, because the permutation has no effect on a state of translation of the whole molecule

- $\Pi_i \Psi_{m_s}(i)$ is symmetric, because $\Psi_0(o_2) \Psi_0(c) \Psi_0(o_1) = \Psi_0(o_1) \Psi_0(c) \Psi_0(o_2)$

- Ψ_0 is symmetric, because the ground electronic state of CO_2 is Σ_g^+ : we can exchange the two oxygen nuclei by performing a rotation by π about an axis u perpendicular

to z . Let us call $C_y(\pi)$ this rotation:

$C_y(\pi) = i \cdot \sigma_{x_3}$ (product of a reflection at the xz plane and of an inversion at the center of the equilibrium configuration). Σ_g^+ and Σ_u^- are symmetric with respect to $C_y(\pi)$; Σ_g^- and Σ_u^+ are antisymmetric with respect to $C_y(\pi)$

(even recall that $+$ - are respectively symmetric and antisymmetric with respect to σ_{x_3} and that g, u are respectively symmetric and antisymmetric with respect to i)

Remark: for the exchange of the two oxygen nuclei in O_2 molecule, Ψ_e would be antisymmetric because the ground electronic state of O_2 is Σ_g^-

- Ψ_v is symmetric for the same reason as above because the ground vibrational state of CO_2 is Σ_g^+ .

Remark: Ψ_v is antisymmetric for a Σ_u^+ excited vibrational state as 00^1

- From all what has been said, it results that Ψ_e must be symmetric. Rotating by π about the y axis is the same as replacing θ and φ by $\pi - \theta$ and $\varphi + \pi$. It can then be shown that

$$\Psi_e(\pi - \theta, \varphi + \pi) = (-1)^J \Psi_e(\theta, \varphi)$$

Ψ_e is symmetric only if J is even.

Levels with odd values of J are missing in the ground vibrational state of the ground electronic state of CO_2 .

The Rotation-Vibration Hamiltonian

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In this section the following symbols are used

- P_α component of the total angular momentum on axes x, y, z linked to the equilibrium configuration
- Q_{sr} normal coordinate $Q_{sr} = \sum_i l_{i, sr}^x m_i^{1/2} \Delta x_i$
- p_{sr}^{\oplus} conjugate momentum of Q_{sr}
- $\Delta x_i = x_i - x_i^0$ cartesian displacement of nucleus i ($\alpha = x, y, z$)
- x_i ($= x_i, y_i, z_i$) instantaneous coordinate of nucleus i
- x_i^0 (or y_i^0 or z_i^0) equilibrium coordinate of nucleus i
- P_α component of the internal angular momentum

$$P_\alpha = \sum_{sr} A_{sr}^x p_{sr}^{\oplus}$$

$$A_{sr}^x = \sum_i \sum_{s'r'} (l_{i, sr'}^\beta l_{i, sr}^\gamma - l_{i, sr}^\beta l_{i, sr'}^\gamma) Q_{s'r'} \quad \alpha \neq \beta \neq \gamma$$

$$P_\alpha = \sum_{sr, s'r'} J_{sr, s'r'}^\alpha Q_{sr} p_{s'r'}^{\oplus}$$

$$J_{sr, s'r'}^\alpha = \sum_i (l_{i, sr}^\beta l_{i, s'r'}^\gamma - l_{i, s'r'}^\beta l_{i, sr}^\gamma)$$

"Coriolis coupling coefficient" $\left\{ \begin{array}{l} J_{sr, sr}^\alpha = 0 \\ J_{s'r', sr}^\alpha = -J_{sr, s'r'}^\alpha \end{array} \right. \quad -1 \leq J_{sr, s'r'}^\alpha \leq 1$

- V potential function

Hamiltonians $\left\{ \begin{array}{l} \text{classical } H_0, H_I, H_{II} \text{ (approximate)}, H_{III} \text{ (exact)} \\ \text{quantum } H_{WH}, H_{DB} \text{ (both exact and equivalent)} \end{array} \right. \quad 29$

"Rigid rotator - Harmonic oscillators" Approximation

$$H_0 = H_{0R} + H_{0V} = \frac{1}{2} \sum_\alpha \frac{P_\alpha^2}{I_{\alpha\alpha}^e} + \frac{1}{2} \sum_{sr} p_{sr}^{\oplus 2} + \frac{1}{2} \sum_{sr} \lambda_{sr} Q_{sr}^2$$

Influence of anharmonicity

$$H_I = \frac{1}{2} \sum_\alpha \frac{P_\alpha^2}{I_{\alpha\alpha}^e} + \frac{1}{2} \sum_{sr} p_{sr}^{\oplus 2} + V$$

$$V = \frac{1}{2} \sum_{sr} \lambda_{sr} Q_{sr}^2 + hc \sum_{sr, s'r', s''} k_{sr, s'r', s''} Q_{sr} Q_{s'r'} Q_{s''} + \dots$$

Influence of non-rigidity

$$H_{II} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta}^I P_\alpha P_\beta + \frac{1}{2} \sum_{sr} p_{sr}^{\oplus 2} + V$$

$$\{\mu_{\alpha\beta}^I\} = \{I_{\alpha\beta}^e\}^{-1}$$

$$I_{\alpha\alpha} = I_{\alpha\alpha}^e + \sum_{sr} a_{sr}^{\alpha\alpha} Q_{sr} + \sum_{sr, s'r'} A_{sr, s'r'}^{\alpha\alpha} Q_{sr} Q_{s'r'}$$

$$(\alpha \neq \beta) \quad I_{\alpha\beta} = \sum_{sr} a_{sr}^{\alpha\beta} Q_{sr} + \sum_{sr, s'r'} A_{sr, s'r'}^{\alpha\beta} Q_{sr} Q_{s'r'}$$

$$(\alpha \neq \beta \neq \gamma) \quad \left\{ \begin{array}{l} a_{sr}^{\alpha\alpha} = 2 \sum_i m_i^{-1/2} (\beta_i^0 l_{i, sr}^\beta + \gamma_i^0 l_{i, sr}^\gamma) \\ a_{sr}^{\alpha\beta} = - \sum_i m_i^{-1/2} (\alpha_i^0 l_{i, sr}^\beta + \beta_i^0 l_{i, sr}^\alpha) \end{array} \right.$$

Influence of interaction between rotation and vibration

$$H_{III} = \frac{1}{2} \sum_{\alpha\beta} (P_\alpha - P_\alpha) \mu_{\alpha\beta} (P_\beta - P_\beta) + \frac{1}{2} \sum_{sr} p_{sr}^{\oplus 2} + V$$

the order of the three factors is not important in classical mechanics; it is important in quantum mechanics because H_{II} does not commute with P_α and P_β (see next page)

$$p_\alpha = \sum_{sr} J_{sr}^{\alpha} Q_{sr} \quad \text{intrinsic angular momentum}$$

$$\{M_{\alpha\beta}\} = \{I'_{\alpha\beta}\}^{-1}$$

$$\left. \begin{array}{l} \alpha \neq \beta \\ \alpha, \beta = 1, 2, 3 \end{array} \right\} I'_{\alpha\beta} = I'_{\alpha\beta} + \sum_{sr} a_{sr}^{\alpha\beta} Q_{sr} + \sum_{sr, s', r'} A_{sr, s', r'}^{\alpha\beta} Q_{sr} Q_{s'r'}$$

non vanishing only if $\alpha = \beta$

$$A_{sr, s', r'}^{\alpha\beta} + A_{s'r, s, r'}^{\alpha\beta} = \sum_s \frac{a_{sr}^{\alpha\beta} a_{s'r}^{\beta\gamma} + a_{s'r}^{\alpha\gamma} a_{sr}^{\beta\gamma}}{4 I_{sr}'} \quad \left. \begin{array}{l} \alpha = \beta \\ \alpha \neq \beta \end{array} \right\}$$

Influence of quantum-mechanical effects

- non commutativity of operators:

$$H_{WH} = \frac{1}{2} \sum_{\alpha\beta} (P_\alpha - p_\alpha) \mu_{\alpha\beta}^{-\frac{1}{2}} (P_\beta - p_\beta) \mu_{\alpha\beta}^{\frac{1}{2}} + \frac{1}{2} \sum_{sr} p_{sr}^{\oplus} \mu^{-\frac{1}{2}} p_{sr}^{\ominus} \mu^{\frac{1}{2}} + V$$

(Wilson-Hammett Hamiltonian) $\mu = |\mu_{\alpha\beta}|$

- choice of a convenient volume element in the configuration space

$$H_{DD} = \frac{1}{2} \mu^{\frac{1}{2}} \sum_{\alpha\beta} (P_\alpha - p_\alpha) \mu_{\alpha\beta}^{-\frac{1}{2}} (P_\beta - p_\beta) \mu_{\alpha\beta}^{\frac{1}{2}} + \frac{1}{2} \mu^{\frac{1}{2}} \sum_{sr} p_{sr}^{\oplus} \mu^{-\frac{1}{2}} p_{sr}^{\ominus} \mu^{\frac{1}{2}} + V$$

(Darling-Dennison Hamiltonian)

$$H_{DD} = H_{WH} + \Lambda(\dots Q_{sr} \dots)$$

$$\Lambda(\dots Q_{sr} \dots) = -\frac{\hbar^2}{8} \sum_{\alpha} \mu_{\alpha\alpha}$$

Remarks:

- 1) Molecular parameters $\lambda_0, K_{sr, s', r'}, K_{sr, s', r', s'', r''}, \dots$
 $I_{\alpha\alpha}^e, a_{sr}^{\alpha\beta}, J_{sr}^{\alpha\beta}$

- 2) Particular case of linear molecules:
 $\vec{P}_\alpha (= \vec{P} - \vec{P}_\beta)$ is perpendicular to $z \rightarrow P_\beta - p_\beta = 0$ (Sayre's relation)
in $\sum_{\alpha\beta}$, $\alpha\beta = x, y$ no terms with subscript z in the Hamiltonian

Expansion of the Hamiltonian

$$H_{III} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} P_\alpha P_\beta - \frac{1}{2} \sum_{\alpha\beta} (p_\alpha \mu_{\alpha\beta} P_\beta + p_\beta \mu_{\alpha\beta} P_\alpha) + \frac{1}{2} \sum_{\alpha\beta} p_\alpha \mu_{\alpha\beta} p_\beta + \frac{1}{2} \sum_{sr} p_{sr}^{\oplus 2} + V$$

$$\{I'_{\alpha\beta}\} = \begin{Bmatrix} I'_{xx} & I'_{xy} & I'_{xz} \\ I'_{yx} & I'_{yy} & I'_{yz} \\ I'_{zx} & I'_{zy} & I'_{zz} \end{Bmatrix} \quad \{M_{\alpha\beta}\} = \{I'_{\alpha\beta}\}^{-1}$$

$$\mu_{\alpha\alpha} = (I'_{\beta\beta} I'_{\gamma\gamma} - I'^2_{\beta\gamma}) / \Delta$$

$$\mu_{\alpha\beta} = (I'_{\alpha\gamma} I'_{\beta\gamma} - I'_{\alpha\beta} I'_{\gamma\gamma}) / \Delta \quad \alpha + \beta + \gamma \quad \Delta = |I'_{\alpha\beta}|$$

$$\mu_{\alpha\alpha} = \frac{1}{I_{\alpha\alpha}^e} - \sum_{sr} \frac{a_{sr}^{\alpha\alpha}}{(I_{\alpha\alpha}^e)^2} Q_{sr} + \dots$$

$$\mu_{\alpha\beta} = - \sum_{sr} \frac{a_{sr}^{\alpha\beta}}{I_{\alpha\alpha}^e I_{\beta\beta}^e} Q_{sr} + \dots$$

$$H_{III} = H_0 + H_1 + \dots$$

$$H_0 = \frac{1}{2} \sum_{\alpha} \frac{P_\alpha^2}{I_{\alpha\alpha}^e} + \frac{1}{2} \sum_{sr} p_{sr}^{\oplus 2} + \frac{1}{2} \sum_{sr} \lambda_0 Q_{sr}^2$$

$$H_1 = -\frac{1}{2} \sum_{\alpha\beta} \sum_{sr} \frac{a_{sr}^{\alpha\beta}}{I_{\alpha\alpha}^e I_{\beta\beta}^e} Q_{sr} P_\alpha P_\beta - \sum_{\alpha} \frac{1}{I_{\alpha\alpha}^e} p_\alpha P_\alpha$$

$$+ \hbar c \sum_{sr, s', r', s'', r''} K_{sr, s', r', s'', r''} Q_{sr} Q_{s'r'} Q_{s''r''}$$

Remark: we use H_{III} because $\Lambda(\dots Q_{sr} \dots)$ does not contribute in the lowest orders

First order corrections to the rotation-vibration energy 32

These corrections will come from diagonal matrix elements of H_1 . Only the second term in H_1 , being of even degree with respect to the vibrational operators ($Q_{00}, \dots, p_{00}^2, \dots$) has matrix elements diagonal with respect to the quantum numbers v_s . This term is responsible for the Coriolis correction discussed in the last section for axially symmetric molecules (see fig 7):

$$\langle n | \frac{H_1}{hc} | n \rangle = \langle n | - \sum_{\alpha} \frac{1}{hc I_{\alpha\alpha}} h \times P_{\alpha} | n \rangle = -2B_3 \sum K l$$

(n designates the whole set of quantum numbers)

First order resonances

- Suppose that, in a molecule, two vibration frequencies happen to have about the same value $\omega_1 \approx \omega_2$; then the two states $|v_1=1, v_2=0\rangle$ and $|v_1=0, v_2=1\rangle$ have about the same energy in zeroth order; there is furthermore a non-vanishing coupling element

$$\langle 10 | - \sum_{\alpha} \frac{h \times P_{\alpha}}{hc I_{\alpha\alpha}} | 01 \rangle$$

originating from the second term in H_1 (provided the vibrations 1 and 2 have the proper symmetry species). We have a resonance known as "Coriolis resonance".

Coriolis resonance occurs between v_1 and v_3 of H_2O (i.e. between states 100 and 001); Coriolis resonance occurs between v_2 and v_4 of CH_4 (i.e. between states ... and ...).

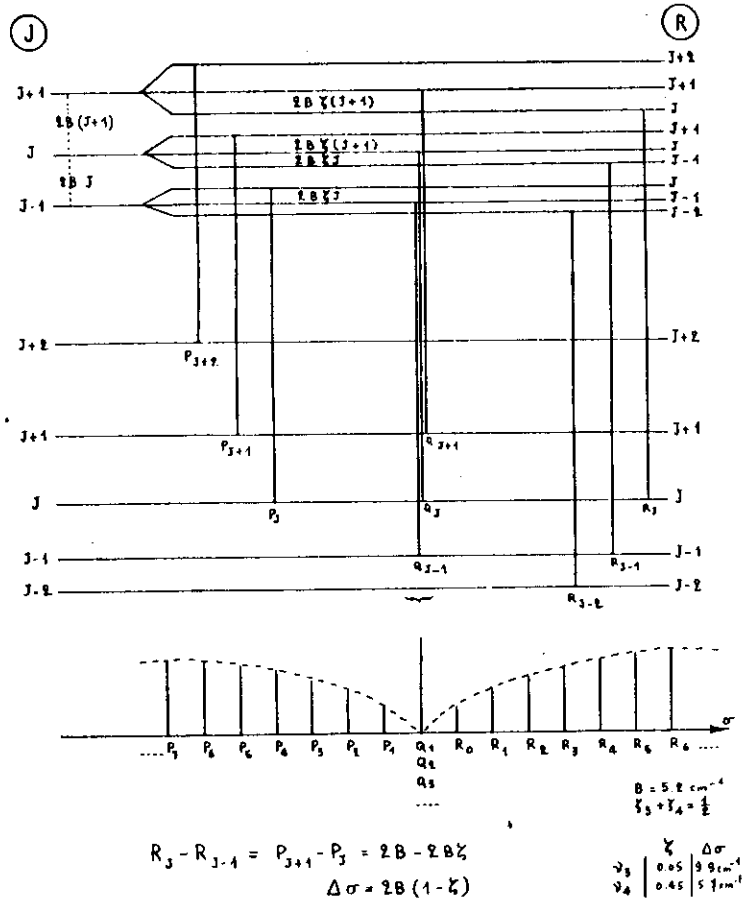
- in the same way, if $\omega_1 \approx \omega_2 + \omega_3$, an "anharmonic resonance" may occur, the coupling matrix element arising from the third term in H_1 :

$$\langle v_1, v_2, v_3 | h c h_{102030} Q_{10} Q_{20} Q_{30} | v_1-1, v_2+1, v_3+1 \rangle$$

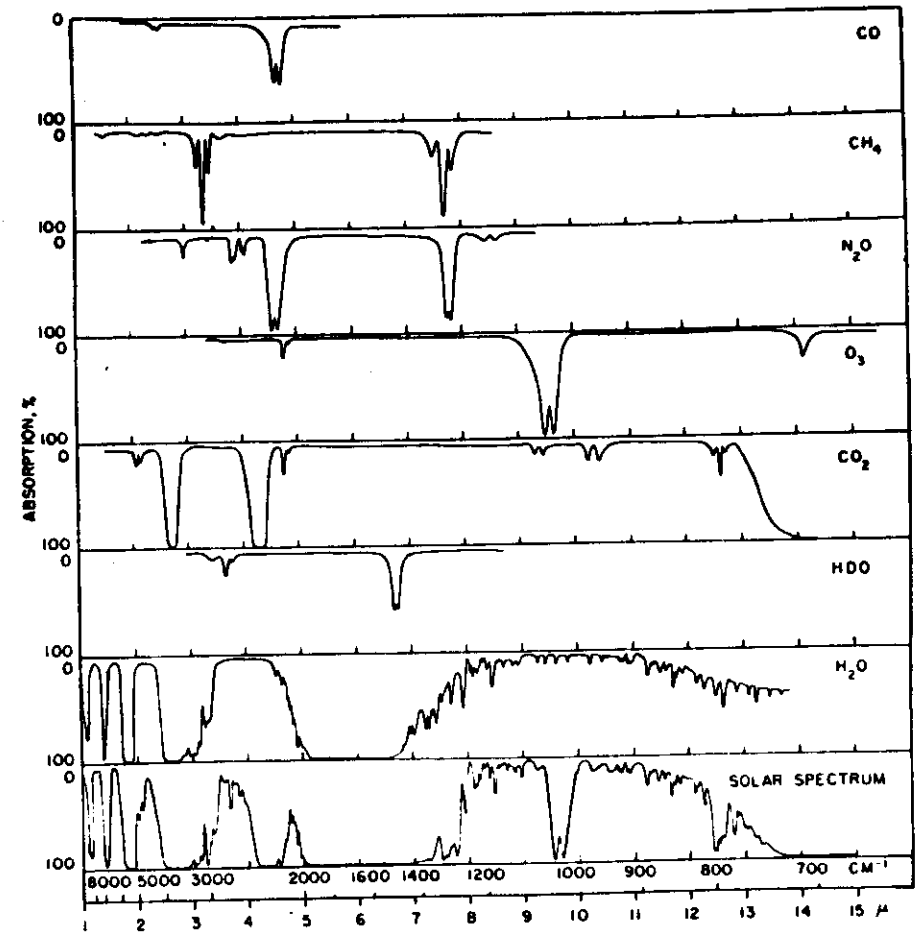
Fermi resonance in CO_2 is a particular case of such a resonance ($\omega_1 \approx 2\omega_2$).

The vibration diagrams in fig 2 and the structures of rotation-vibration bands in fig 8 are taken from the book by G. Herzberg: Molecular Spectra and Molecular Structure. Vol II (Van Nostrand, 1945)

①

BANDS ν_3 AND ν_4 OF METHANE

②

Fig. 16-1. The Near-Infrared spectra of Solar Irradiation and of CO, CH₄, N₂O, O₃, CO₂, HDO and H₂O

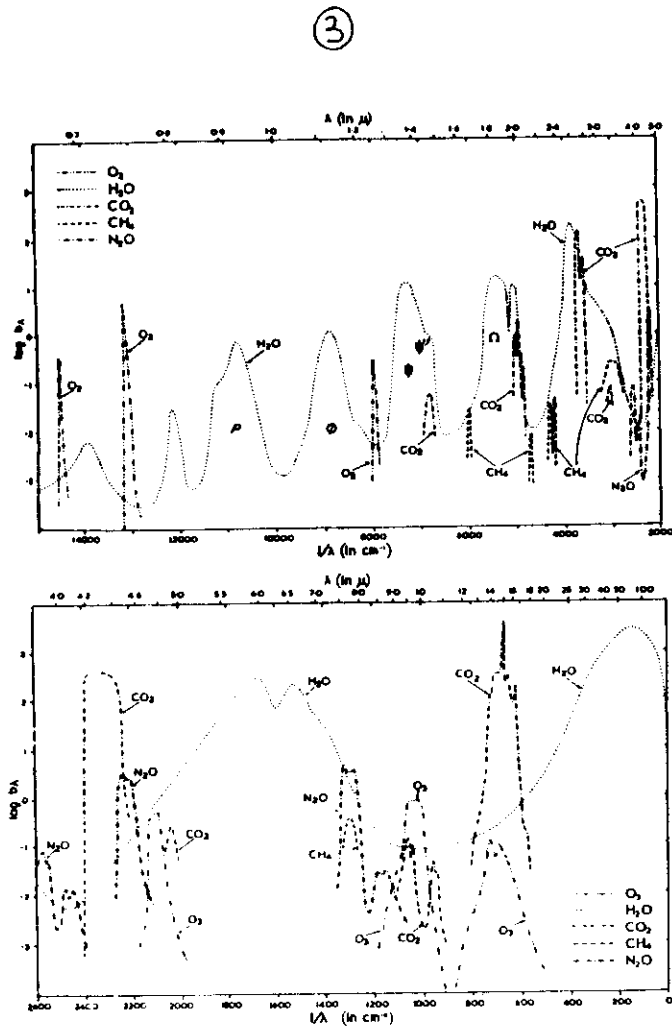
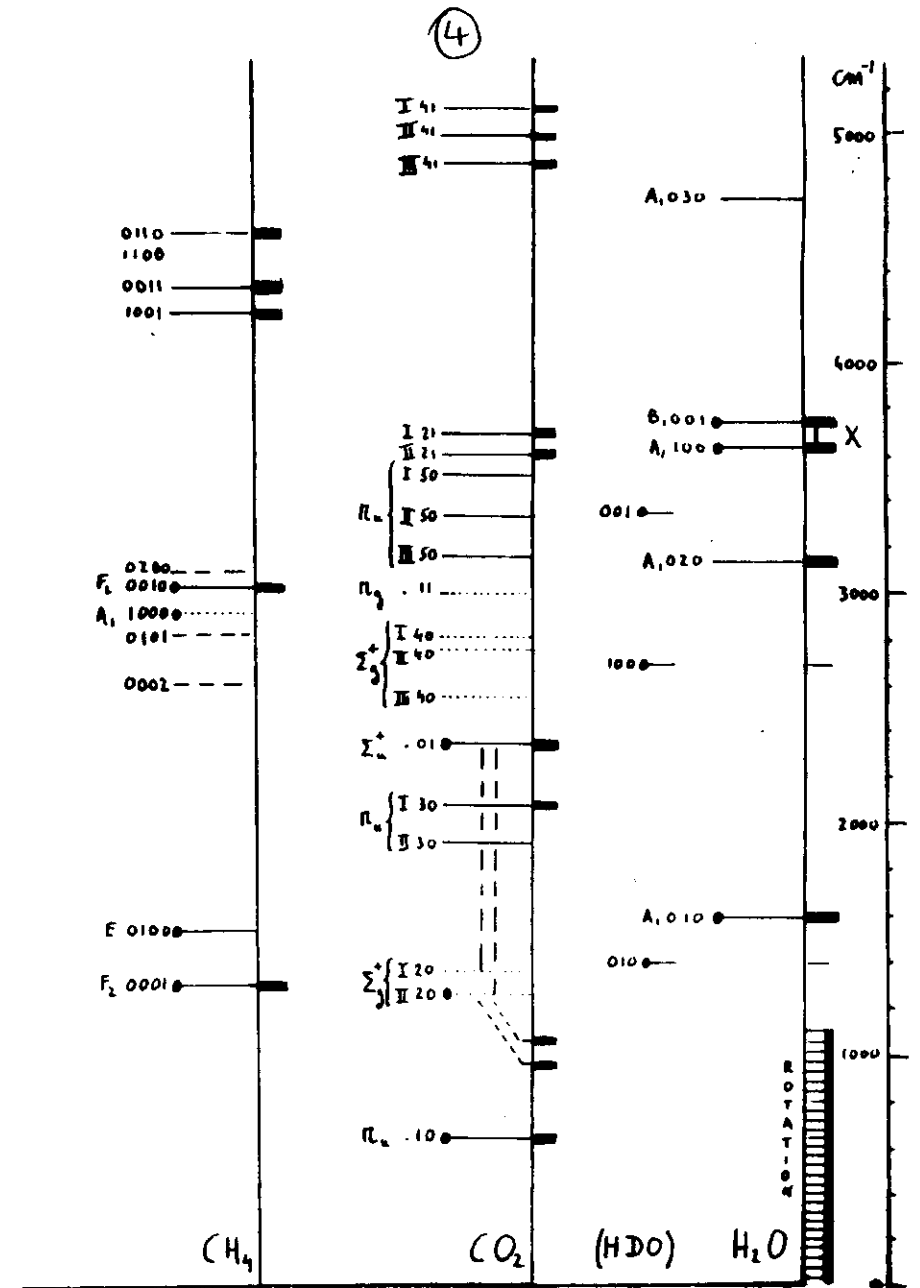
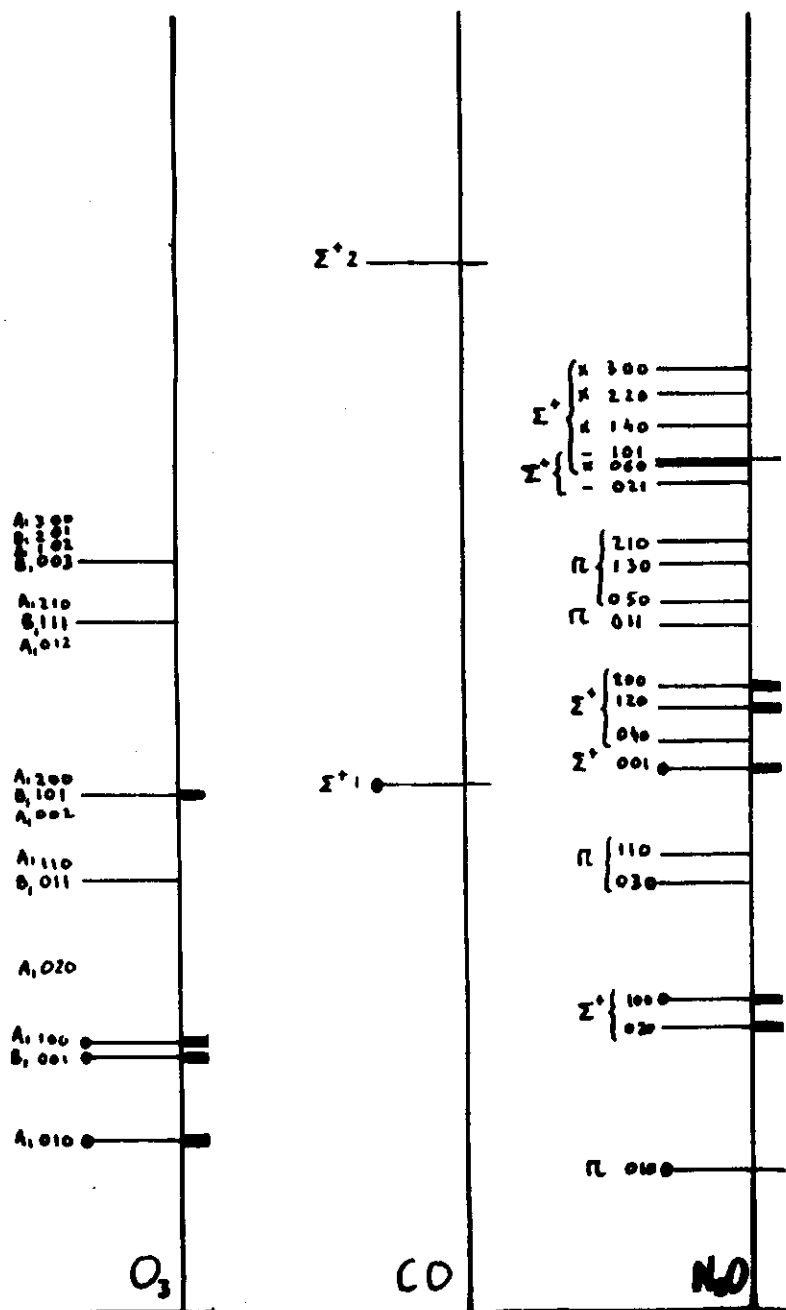


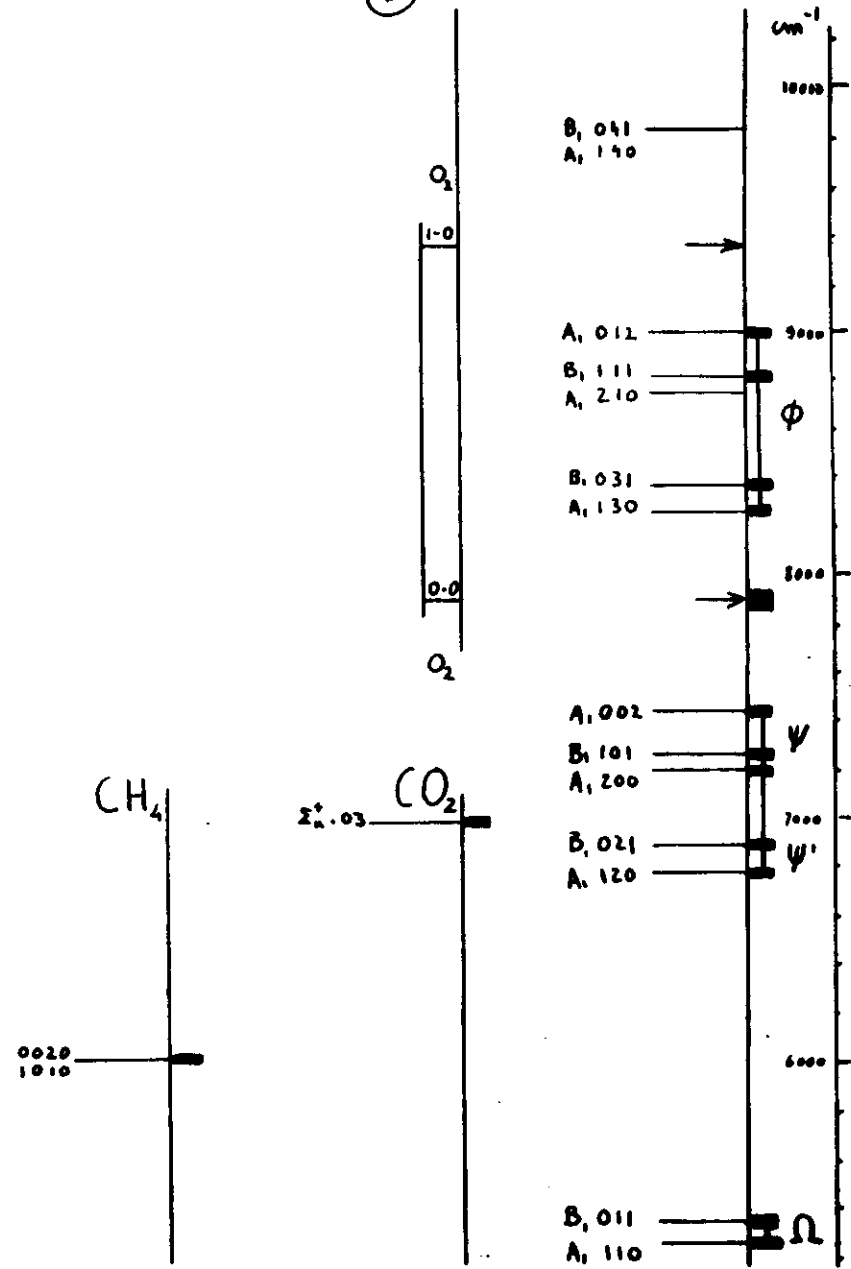
Figure -17-

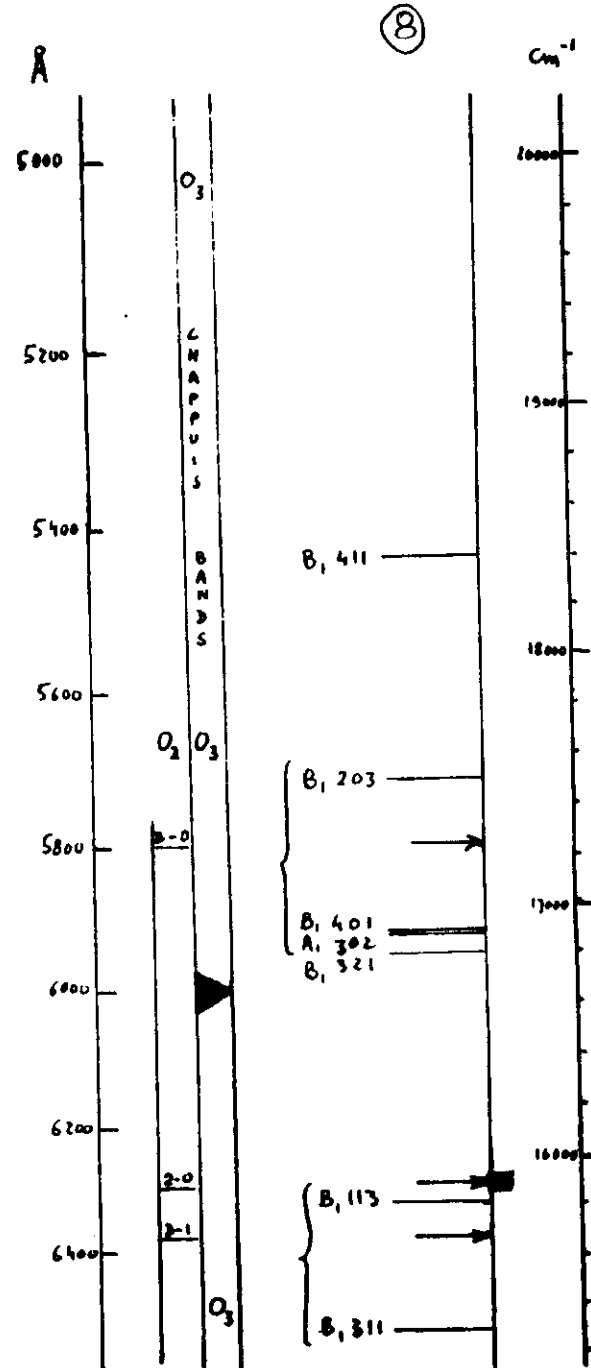
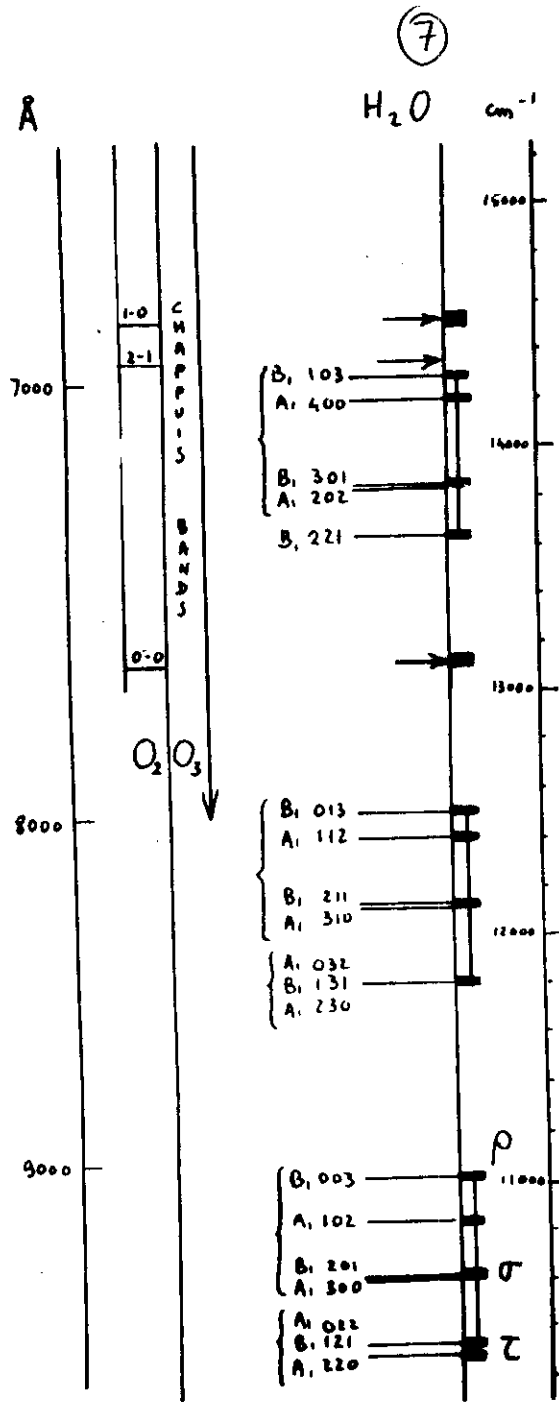


(5)



(6)





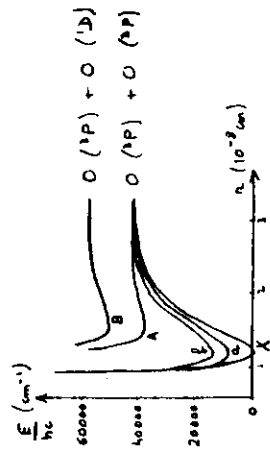
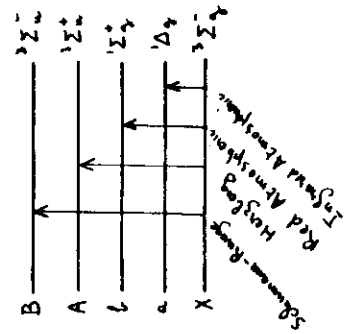
(9)

Atmospheric Molecules	Rotational constants (cm ⁻¹)	Spacing of lines in rotational structure of rotation-vibration bands (cm ⁻¹)
Diatomic		
(N ₂)	(B ≈ 2.0)	(1)
(O ₂)	(B ≈ 1.43)	(1)
CO	B ≈ 1.92	2B ≈ 3.8
Linear		
CO ₂	B ≈ 0.39	4B ≈ 1.6
N ₂ O	B ≈ 0.42	2B ≈ 0.8
Spherical top		
CH ₄	B ≈ 5.25	2B(1-3) ≈ $\begin{cases} 9.9 \text{ for } \nu_3 \\ 5.7 \text{ for } \nu_4 \end{cases}$ (2)
Asymmetric tops		
H ₂ O	A ≈ 27.8 B ≈ 14.6 C ≈ 9.3	(1)
O ₃	A ≈ 3.50 B ≈ 0.44 C ≈ 0.39	(F) $2\left(\frac{B+C}{2}\right) \approx 0.8$

- (1) no rotation-vibration spectrum
- (2) one line (out of two) missing due to spin zero of nucleus ¹⁶O
- (3) taking first order Coriolis interaction into account
- (4) no regularity in rotational structure
- (5) close to axially symmetric top (B ≈ C)

See Note on "Introducing Molecular Spectroscopy"

Electronic transitions of O₂



(10)

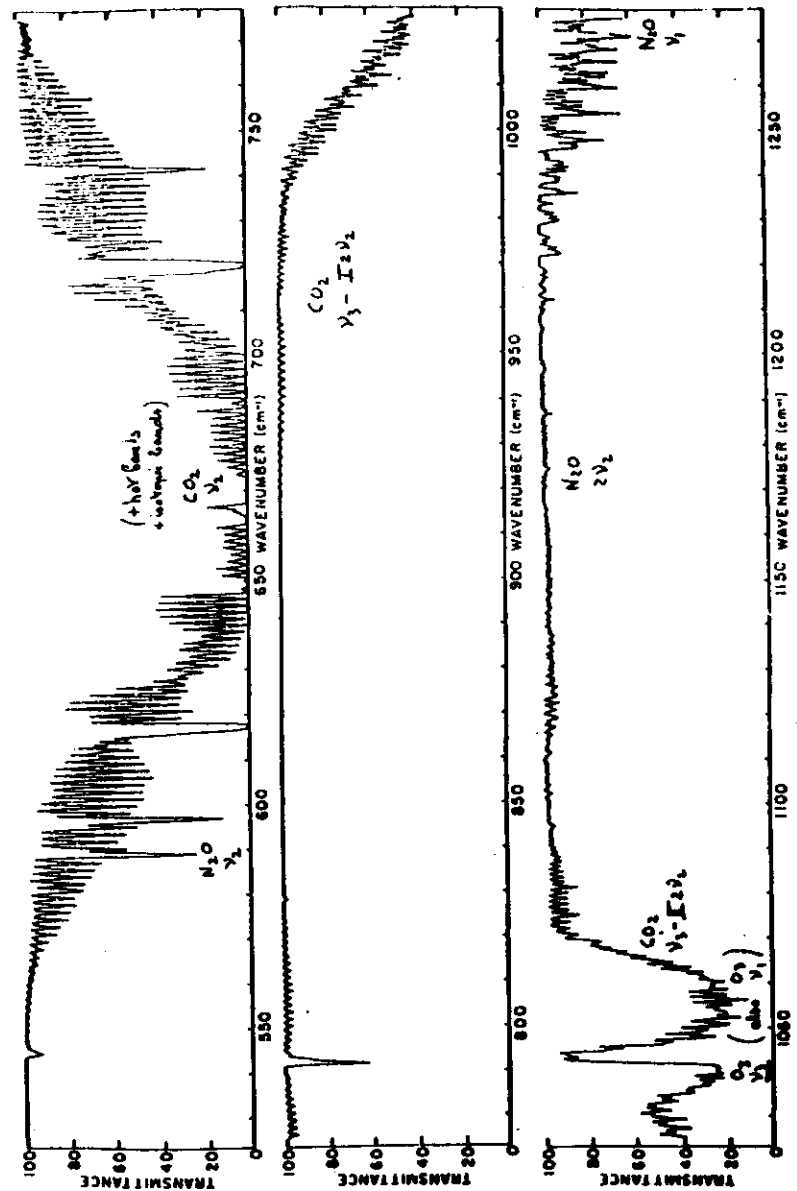


Figure 7a. Calculated spectra over much of the infrared for 40 K ft to space. Computations by Dr. T. Kyle, University of Denver.

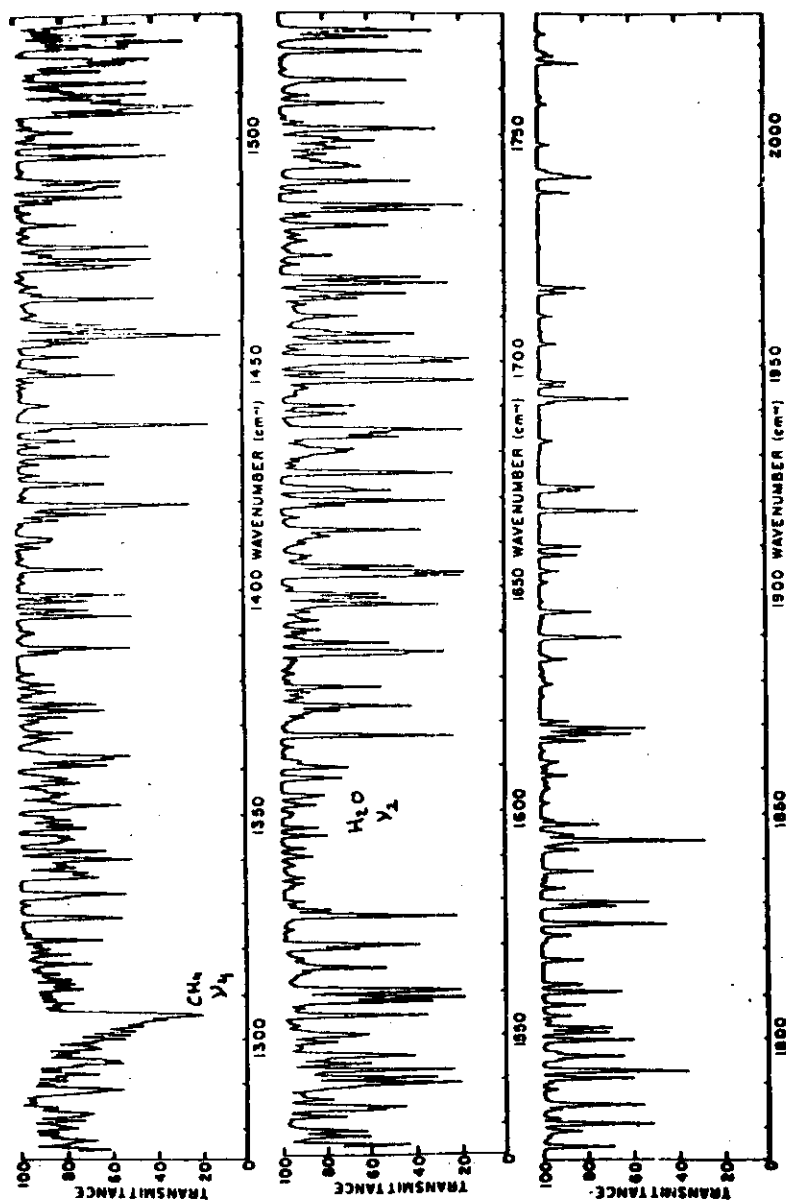


Figure 7b.

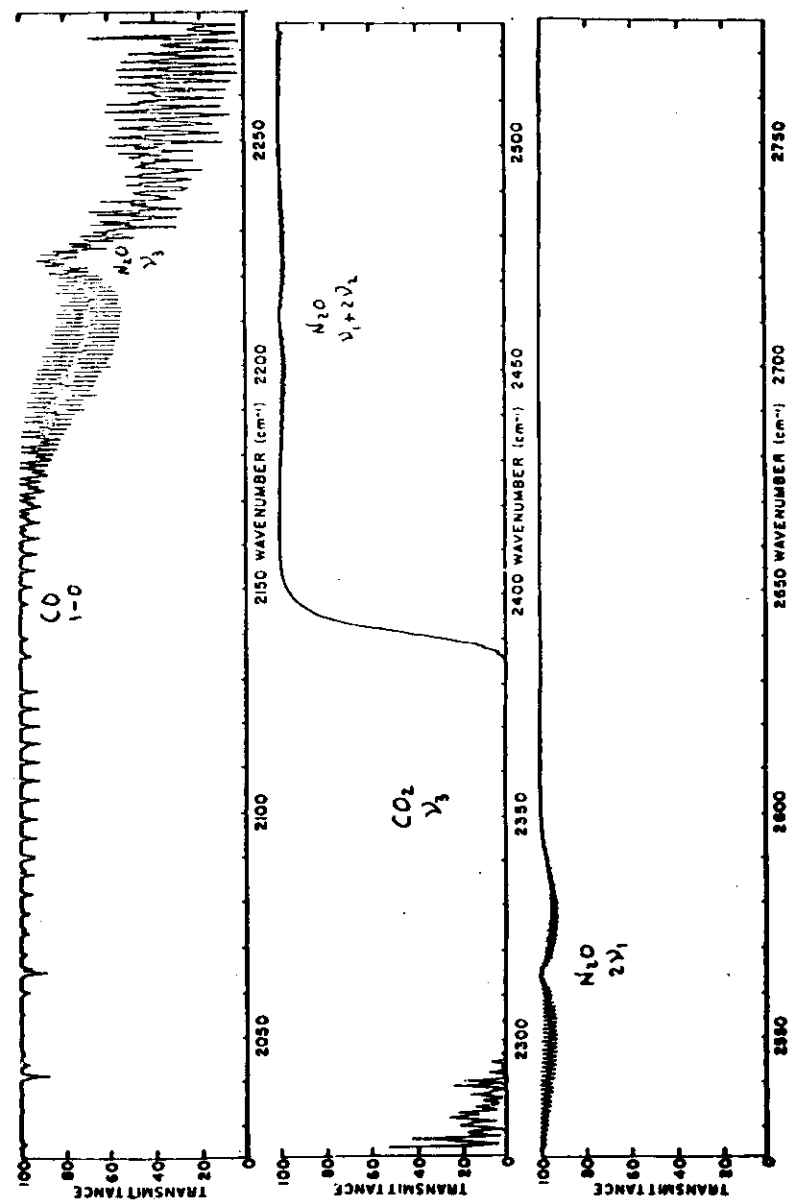


Figure 7c.

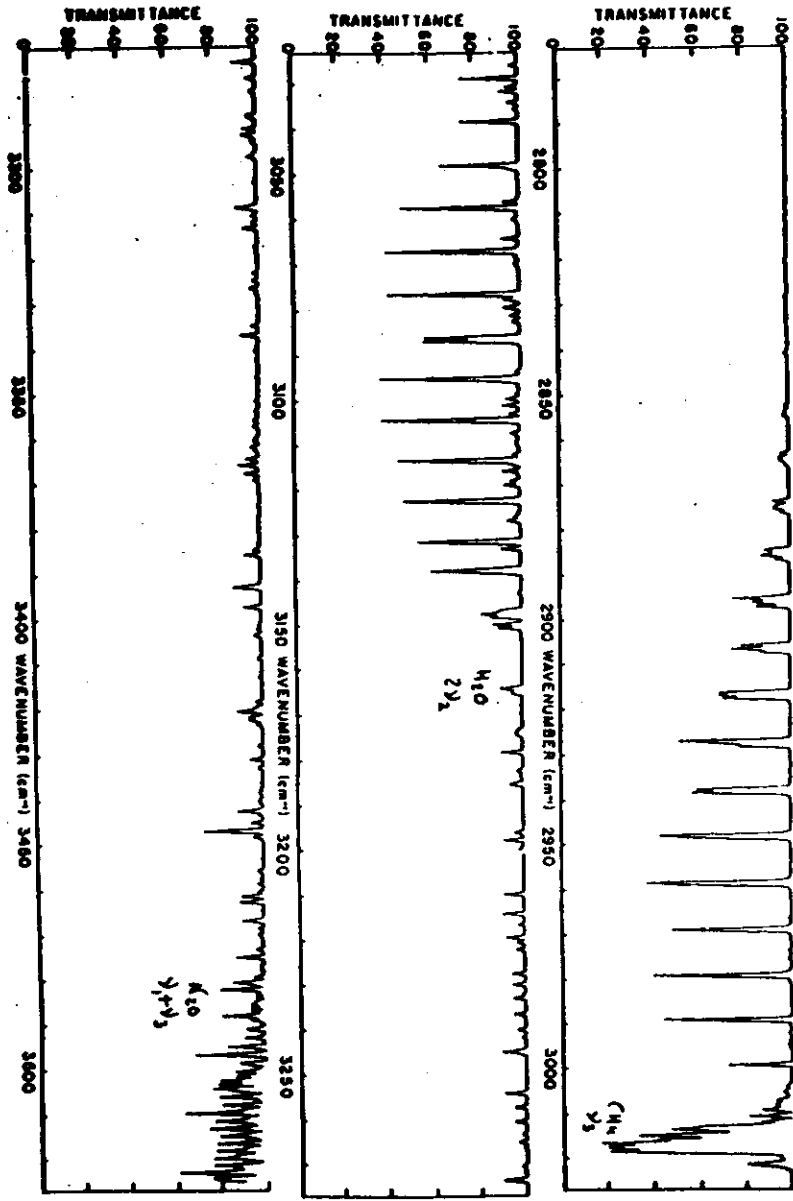


Figure 7d.

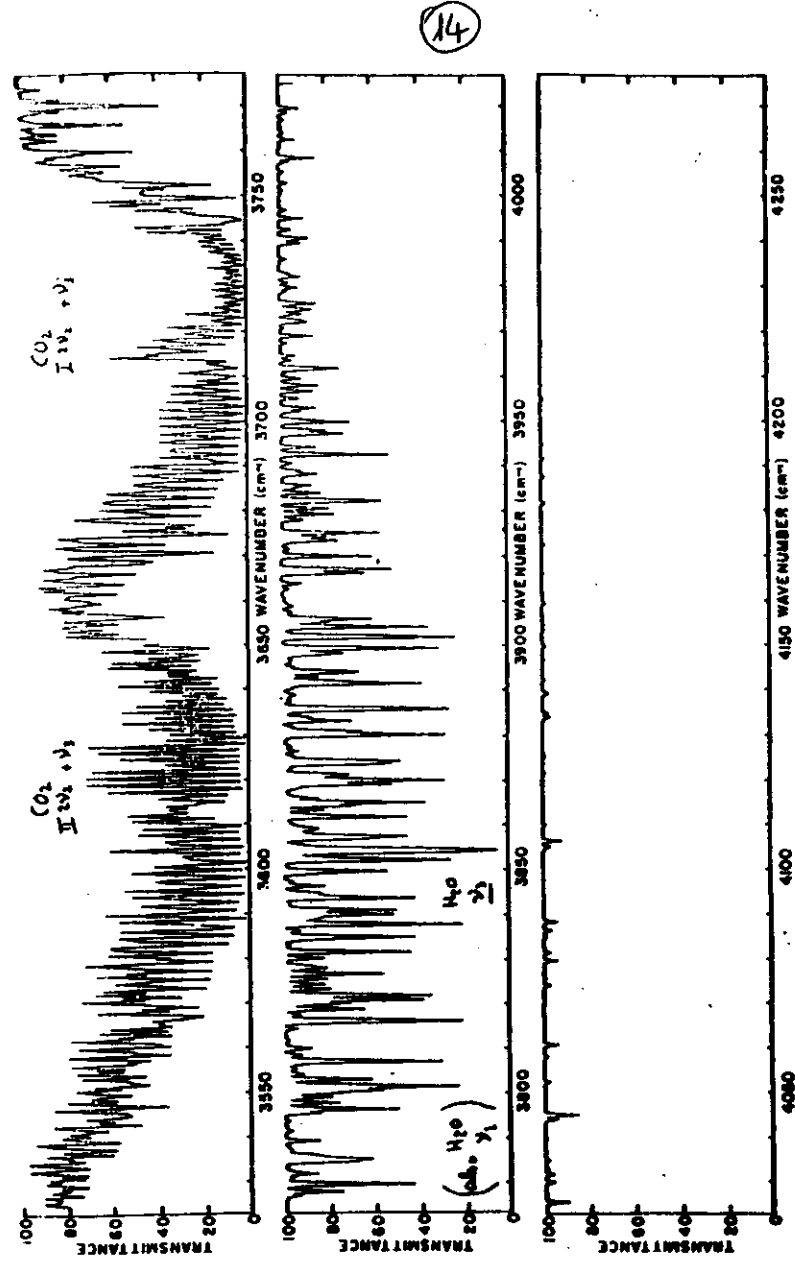


Figure 7e.

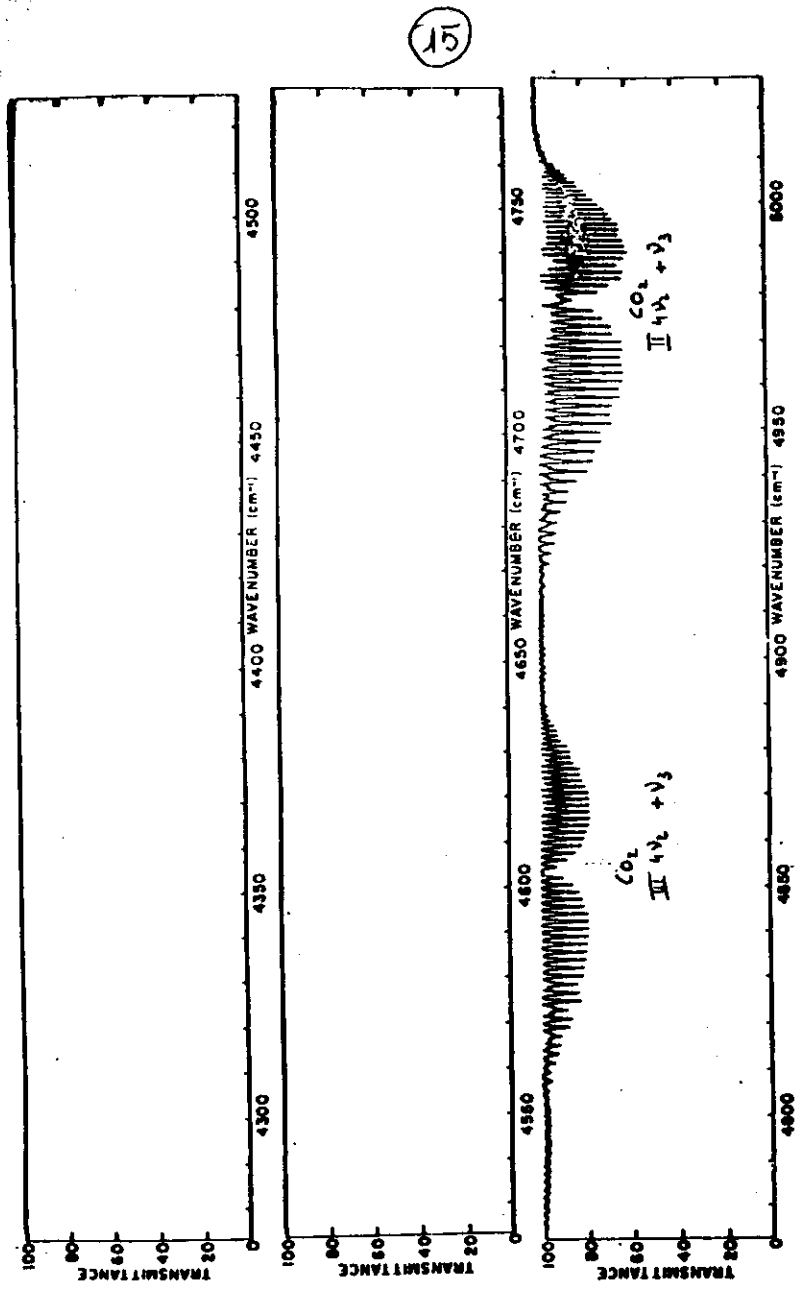


Figure 7f.

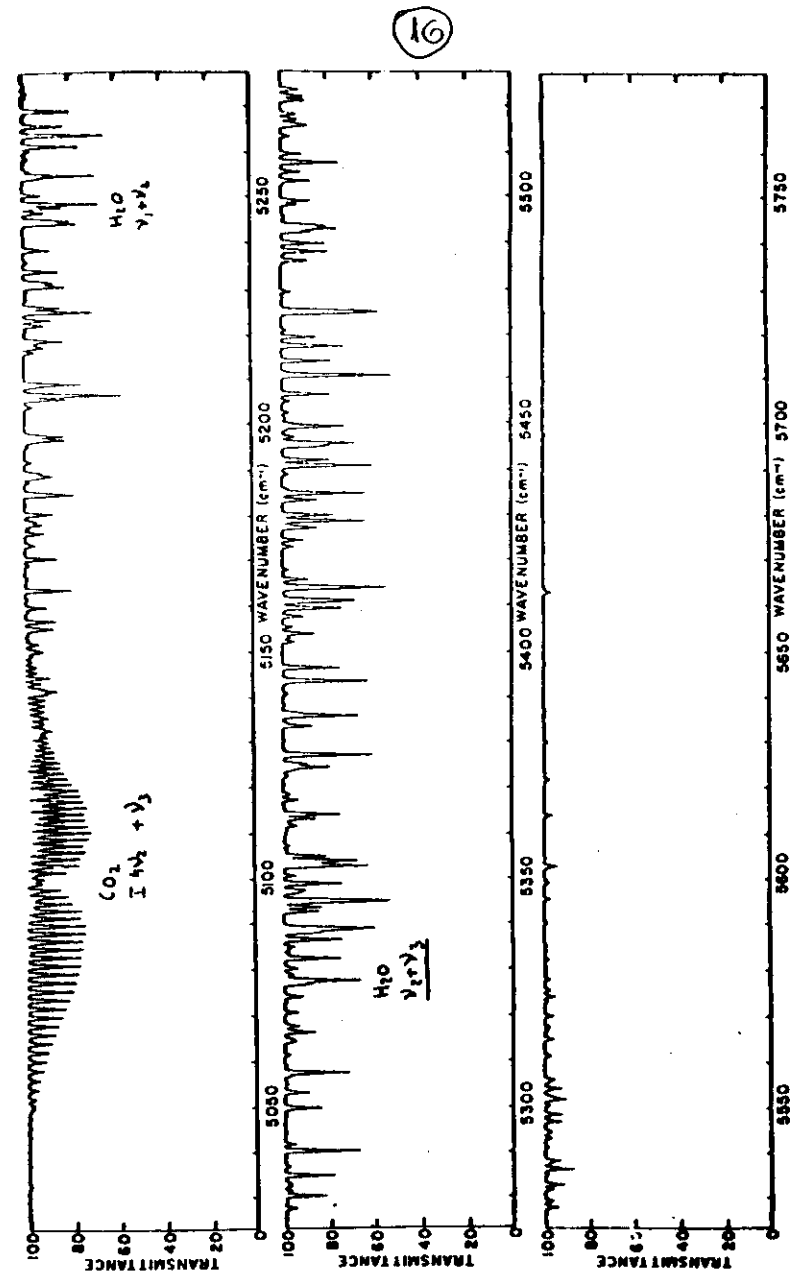


Figure 7g.

1- order correction to the rotation - vibration energy 1- (Coriolis coupling)

$$\langle v_3 \dots | H_1 | v_3 \dots \rangle = \langle v_3 \dots | H_1^* | v_3 \dots \rangle$$

operator diagonal with respect to the quantum number v_3

$$H_1^* = - \sum_{\alpha} \frac{1}{I_{\alpha}} v_{\alpha}^* P_{\alpha}$$

$$H_1^* = \sum_{\alpha \beta \gamma} \sum_{\alpha' \beta' \gamma'} Q_{\alpha \beta \gamma \alpha' \beta' \gamma'} (Q_{\alpha' \beta' \gamma'} - Q_{\alpha \beta \gamma})$$

- Linear molecules: the Hamiltonian contains no terms with subscripts - the coefficients $\sum_{\alpha \beta \gamma \alpha' \beta' \gamma'}$ and $\sum_{\alpha \beta \gamma \alpha' \beta' \gamma'}$ are equal to zero

$$H_1^* = 0 \quad E_1 = 0$$

- Symmetric top molecules (\equiv axially symmetric molecules)

$$H_1^* = H_1^* = 0$$

$$H_1^* = - \frac{v_3^* P_3}{I_3}$$

$$E_1 = - \sum_{\alpha \beta \gamma} \frac{3 v_{\alpha \beta \gamma}}{I_3} P_{\alpha} P_{\beta} P_{\gamma}$$

$$\frac{E_1}{h c} = - 2 \sum_{\alpha \beta \gamma} \frac{3 v_{\alpha \beta \gamma}}{I_3} B_{\alpha} P_{\alpha} P_{\beta} P_{\gamma}$$

E is interaction energy of diagonal vibration

- Spherical top molecules

$$H_1^* = - \frac{1}{I_3} (P_x^* P_x + P_y^* P_y + P_z^* P_z)$$

H_1^* is diagonal with respect to P_3 but not with respect to m_3 and K

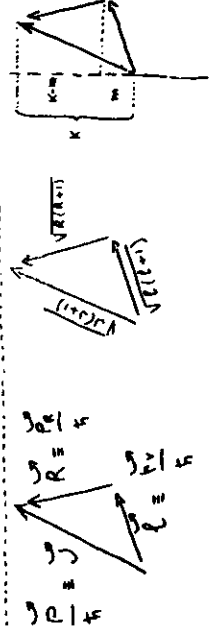


$$P_x^* = \sum_{\alpha} P_{\alpha} \cos \alpha$$

E_1 is obtained by diagonalizing H_1^* with respect to m_3 and K

4

$$\begin{aligned} \frac{E_1}{h c} &= 2 J_3 B_{\alpha} J_3 = - 2 J_3 B_{\alpha} J_3 \\ \frac{E_1}{h c} &= - 2 J_3 B_{\alpha} J_3 = - 2 J_3 B_{\alpha} J_3 \\ \frac{E_1}{h c} &= - 2 J_3 B_{\alpha} (J_3 - 1) = - 2 J_3 B_{\alpha} J_3 \end{aligned}$$



$$J = R + L, R + L - 1, \dots, |R - L|$$

$$\frac{H_1^*}{h c} = - \frac{P_x^* P_x}{h c I_x} = - 2 J_3 B_{\alpha} (J_3 - 1)$$

un coupled representation

$$|J K L m\rangle$$

(J_3, L_3) is not diagonal

$$J_3 = L_3 + R_3$$

$$(R_3, L_3) = (J_3 - L_3)(J_3 - L_3)$$

$$= (J_3 - L_3) + (L_3 - L_3) - 2 J_3 L_3$$

$$(J_3, L_3) = \frac{1}{2} (J_3 - L_3) + (L_3 - L_3) - R_3 L_3$$

$$= \frac{1}{2} [J(J+1) + L(L+1) - R(R+1)]$$

$$\frac{L}{1} \left\{ \begin{matrix} R(R+1) \\ (J+1)(J+2) \\ J(J+1) \\ J(J-1) \end{matrix} \right.$$

one obtains for $\frac{E_1}{h c}$ the same results as above

Operator	non-vanishing matrix element
$P_{\alpha z}$	$\langle v_3 l_3 m_3 P_{\alpha z} v_3 l_3 m_3 \pm 1 \rangle$
$P_{\alpha y}$	$\langle v_3 l_3 m_3 P_{\alpha y} v_3 l_3 m_3 \pm 1 \rangle$
$P_{\alpha x}$	$\langle v_3 l_3 m_3 P_{\alpha x} v_3 l_3 m_3 \pm 1 \rangle$
$P_{\alpha z}$	$\langle J K M P_{\alpha z} J K M \pm 1 \rangle$
$P_{\alpha y}$	$\langle J K M P_{\alpha y} J K M \pm 1 \rangle$
$P_{\alpha x}$	$\langle J K M P_{\alpha x} J K M \pm 1 \rangle$
H_1^*	$\langle \dots K m_3 H_1^* \dots K m_3 \rangle$

H_1^* is diagonal with respect to $K - m_3$

$|\dots K m_3\rangle$ is coupled only with $|\dots K \pm 1, m_3 \pm 1\rangle$ and $|\dots K - 1, m_3 - 1\rangle$ let us assume that only one Coriolis vibration is properly excited

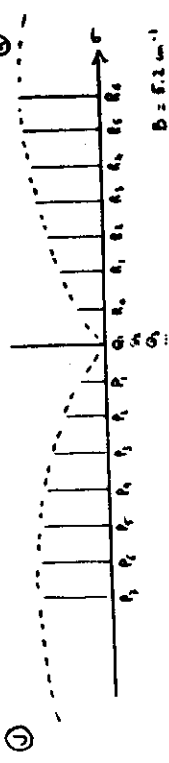
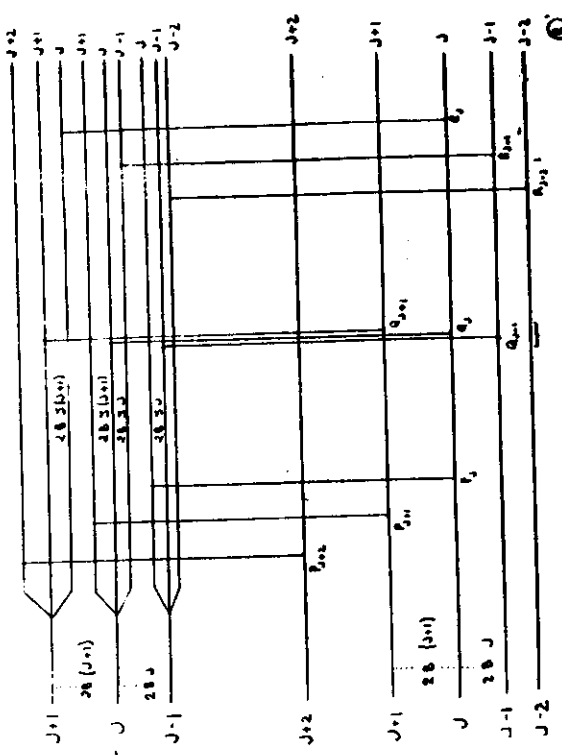
$$\langle \dots K m_3 | H_1^* | \dots K m_3 \rangle = - 2 \sum_{\alpha} B_{\alpha} m_{\alpha} K$$

$$\langle \dots K m_3 | H_1^* | \dots K \pm 1, m_3 \pm 1 \rangle = \pm \sqrt{l(l \pm 1) m_3(m_3 \pm 1)} \sqrt{(J \pm K)(J \pm K \pm 1)} \sum_{\alpha} B_{\alpha}$$

Particular case: $v_3 = 1 \rightarrow l_3 = 1 \rightarrow m_3 = +1, 0, -1$

$$\begin{aligned} & \begin{vmatrix} -K-1-E & [\frac{1}{2}(J-K)(J-K+1)]^{\frac{1}{2}} & 0 \\ [\frac{1}{2}(J-K)(J-K+1)]^{\frac{1}{2}} & -E & -[\frac{1}{2}(J-K)(J-K+1)]^{\frac{1}{2}} \\ 0 & -[\frac{1}{2}(J-K)(J-K+1)]^{\frac{1}{2}} & K-1-E \end{vmatrix} = 0 \\ & \uparrow \quad \uparrow \quad \uparrow \\ & m_3 = +1 \quad m_3 = 0 \quad m_3 = -1 \\ & K+1 \quad K \quad K-1 \end{aligned}$$

4



$$B = 5.2 \text{ cm}^{-1}$$

$$\frac{B}{J_3 + \frac{1}{2}} = \frac{5.2}{J_3 + \frac{1}{2}}$$

$$R_{J-1} - R_{J+1} = P_{J-1} - P_{J+1} = 2B - 2B J$$

$$\Delta F = 2B(1 - J)$$

$$P \Delta J = 1 \quad Q \Delta J = 0 \quad R \Delta J = 1$$

Bands ν_3 and ν_4 of methane