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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

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Rotation-Vibration Spectra

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Introduction

1) Energy of molecules :

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

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

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 foldness of a symetry 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.

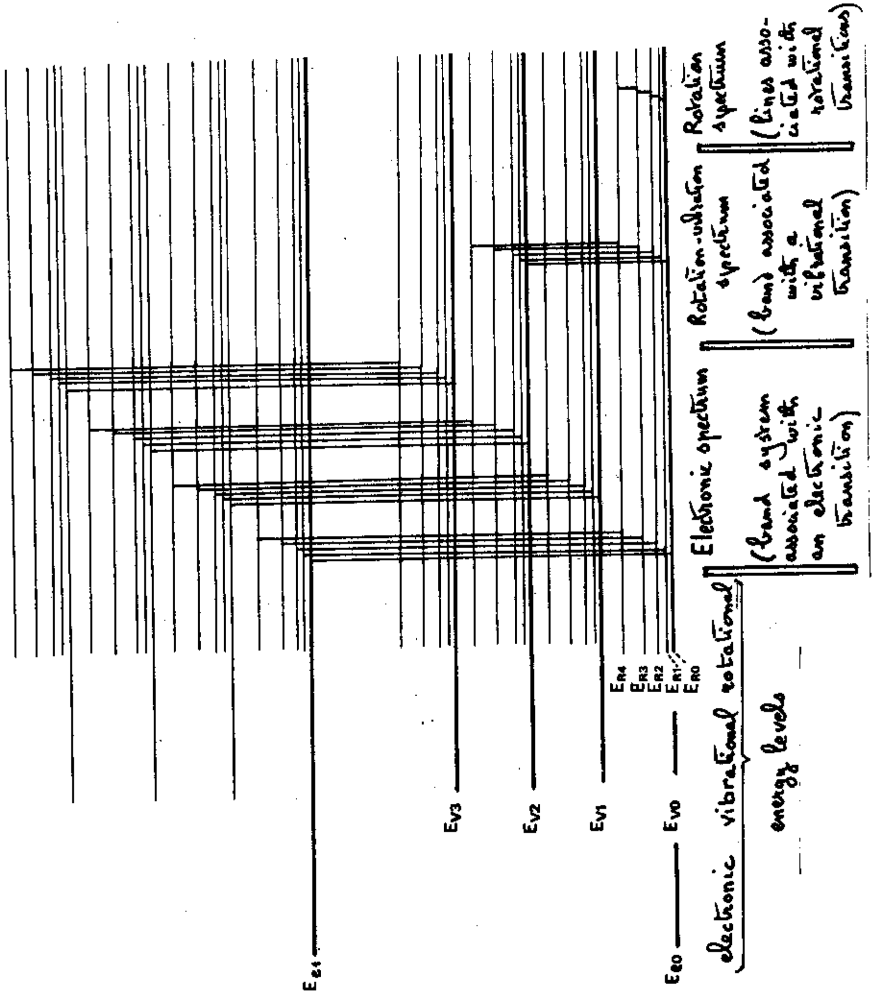


Fig. 1

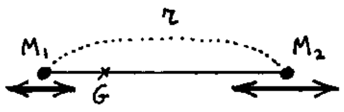
Table I

	Asymmetric Tops no axis with $N \geqslant 3$	Symmetric Tops 1 axis with $N \geqslant 3$ Linear Molecules 1 axis with $N = \infty$	Spherical Tops several axes with $N \geqslant 3$
degrees 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	$I^e_{xx} \neq I^e_{yy} \neq I^e_{zz}$	$I^e_{xx} = I^e_{yy} \neq I^e_{zz}$ ($I^e_{zz} = 0$ for linear mol.)	$I^e_{xx} = I^e_{yy} = I^e_{zz}$

Vibration

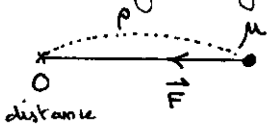
A Diatomic molecules

- 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



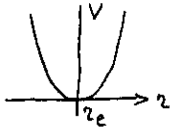
$\rho = r - r_e$ (r_e equilibrium distance of the nuclei)

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

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

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

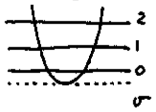
- Harmonic oscillator $\quad V = \frac{1}{2} k \rho^2$



$F = -\frac{dV}{d\rho} = k\rho$ — k force constant

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

– Energy levels (eigen values of H)



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

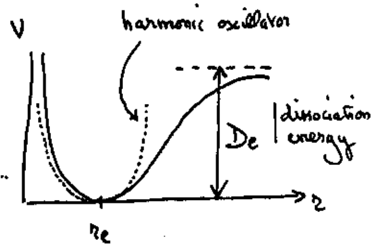
$\nu = 2\pi\sqrt{\frac{k}{\mu}}$ sec^{-1} (frequency of the classical harmonic oscillator)

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

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

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

- Anharmonic oscillator



$V = \frac{1}{2}k\rho^2 + k'\rho^3 + k''\rho^4 + \ldots$

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

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

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

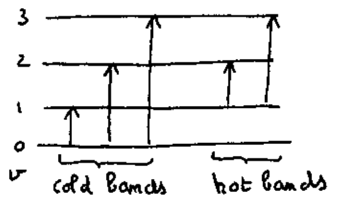
$G_0(v) = G(v) - G(0) = \omega_0 v - \omega_0 x_0 v^2 + \ldots$

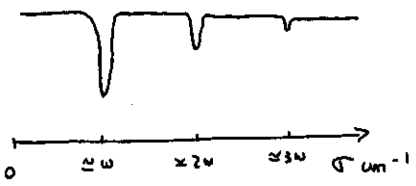
$G_0(v)$ is measured from the lower vibrational level ($v = 0$)

- 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
Heteronuclear molecules XY: all transitions are allowed

- Absorption spectrum





Position of the vibration bands:

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

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

$$\begin{cases} \text{cold bands} & \sigma = G_0(v') \\ \text{hot bands} & \sigma = G_0(v') - G_0(v'') \end{cases}$$

Intensities:

for a given v'', $I \searrow$ if $\Delta v \nearrow$
(influence of the transition moment)

for a given Δv, $I \searrow$ if $v'' \nearrow$
(influence of the Boltzmann factor)

B Polyatomic molecules

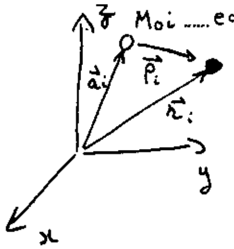
- Degrees of freedom: a N-atomic molecule has 3N degrees of freedom:

	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:

$$2T = \sum_{i=1}^{N} \overset{\text{masses of the nuclei}}{m_i} \left(v_{x_i}^2 + v_{y_i}^2 + v_{z_i}^2 \right)$$

We consider a frame-work x y z linked to the equilibrium configuration



M_{oi} ……equilibrium position of nucleus i

M_i ……instantaneous position of nucleus i

$$\vec{a}_i \left| \begin{matrix} x_i^0 \\ y_i^0 \\ z_i^0 \end{matrix} \right. \qquad \vec{r}_i \left| \begin{matrix} x_i \\ y_i \\ z_i \end{matrix} \right. \qquad \vec{\rho}_i \left| \begin{matrix} \Delta x_i \\ \Delta y_i \\ \Delta z_i \end{matrix} \right. \qquad \vec{v}_i \left| \begin{matrix} \dot{x}_i = \Delta\dot{x}_i \\ \dot{y}_i = \Delta\dot{y}_i \\ \dot{z}_i = \Delta\dot{z}_i \end{matrix} \right.$$

do not change with time

change with time

displacement vector

cartesian displacements

velocity of nucleus i with respect to x y z

cartesian displacements: $\Delta x_1 \quad \Delta y_1 \quad \Delta z_1 \quad \dots \quad \Delta z_N$

mass-adjusted cartesian displacements: $m_1^{1/2}\Delta x_1 = s_1 \quad m_1^{1/2}\Delta y_1 = s_2 \quad m_1^{1/2}\Delta z_1 = s_3 \quad \dots \quad m_N^{1/2}\Delta z_N = s_{3N}$

$$\boxed{\begin{aligned} 2T &= \sum_{j=1}^{3N} \dot{s}_j^2 \\ 2V &= \sum_{jk} f_{jk} s_j s_k \end{aligned}} \quad \text{harmonic potential}$$

- 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*:

$$\underbrace{\boxed{Q_m = \sum l_{mi}^{\alpha} s_j}}_{\text{orthogonal transformation}} \longrightarrow \boxed{\begin{aligned} 2T &= \sum_{m=1}^{3N} \dot{Q}_m^2 \\ 2V &= \sum_{m=1}^{3N} \lambda_m Q_m^2 \end{aligned}}$$

Then we obtain for the energy:

$$E = T + V = \sum_m \underbrace{\frac{1}{2}\left(\dot{Q}_m^2 + \lambda_m Q_m^2 \right)}_{\text{energy of an harmonic oscillator}}$$

* in l_{mi}^{α}, $\alpha = x, y, z$ and $(\alpha, i) \equiv j$

To do so we want to diagonalize the matrix $\{f_{jk}\}$

λ_m is an eigen-value of $\{f_{jk}\}$

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

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

Among the 3N roots, the root $\lambda = 0$ is found six times (five times for a linear molecule). 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 $Q_{s\sigma}$: subscripts s characterize the distinct roots λ_s of the secular equation :

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

d_s being the degree of degeneracy of vibration s

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

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

XY_2	bent symmetric	Ex : H_2O	$N=3 \longrightarrow 3N-6=3$
XY_2	linear symmetric	Ex : CO_2	$N=3 \longrightarrow 3N-5=4$
XYZ	linear non-symmetric	Ex : HCN	$N=3 \longrightarrow 3N-5=4$
XY_4	tetrahedral	Ex : CH_4	$N=5 \longrightarrow 3N-6=9$

} normal coordinates

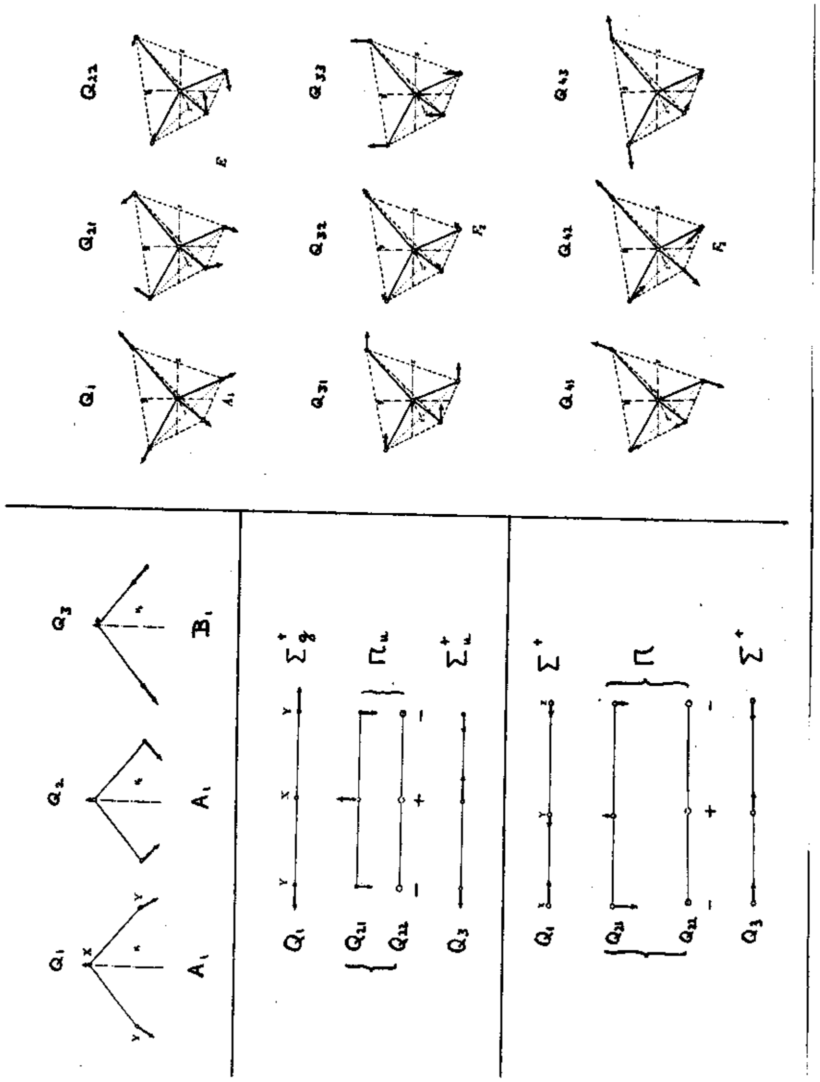


Fig. 2

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

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

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

Case of the 2 dimensional harmonic oscillator:

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

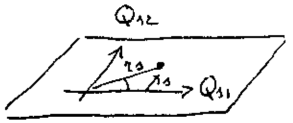
↳ hamiltonian operator ⟶ quantized energy:

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

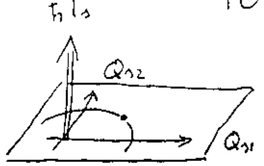
While the energy levels E_s depend only upon v_s, the states $\Psi_{v_{s1}\,v_{s2}}(Q_{s1}\ Q_{s2})$ depend upon both v_{s1} and v_{s2}. Energy levels $E(v_s)$ are degenerate. Their degree of degeneracy is $g(v_s) = v_s + 1$ (the number of states associated with a given value of the energy is equal to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

with $|l_s| = v_s,\ v_s - 2,\ v_s - 4 \dots\dots 0$ or 1



$$\begin{cases} Q_{s1} = r_s \cos \chi_s \\ Q_{s2} = r_s \sin \chi_s \end{cases}$$



the angular momentum associated with a twofold degenerate vibration is equal to $\hbar l_s$ (in the configuration space)

- Anharmonic potential

$$2V = \sum_{s\sigma} \lambda_s Q_{s\sigma}^2 + \sum_{s\sigma\, s'\sigma'\, s''\sigma''} hc\,k_{s\sigma\, s'\sigma'\, s''\sigma''}\, Q_{s\sigma}\, Q_{s'\sigma'}\, Q_{s''\sigma''}$$
$$+ \sum_{s\sigma\, s'\sigma'\, s''\sigma''\, s'''\sigma'''} hc\,k_{s\sigma\, s'\sigma'\, s''\sigma''\, s'''\sigma'''}\, Q_{s\sigma}\, Q_{s'\sigma'}\, Q_{s''\sigma''}\, Q_{s'''\sigma'''} + \dots$$

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

$$\frac{E}{hc} = \sum_s \omega_s\left(v_s + \frac{d_s}{2}\right) + \sum_{\substack{ss' \\ s\leq s'}} x_{ss'}\left(v_s + \frac{d_s}{2}\right)\left(v_{s'} + \frac{d_{s'}}{2}\right) + E^* + \dots$$

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,

$$E^* = \sum_{\substack{s\,s' \\ \text{twofold degenerate} \\ s \leq s'}} g^v_{ss'}\, l_s\, l_{s'}$$

- 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 $G = \frac{E}{hc}$ (see above) and the selection rules for emission and absorption.

SYMMETRY SPECIES, ENERGY LEVELS AND SELECTION RULES

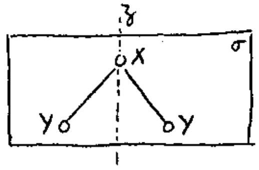
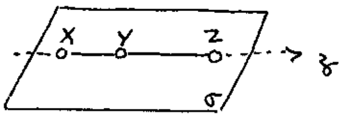
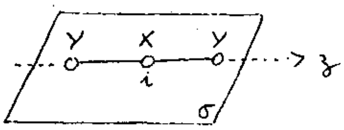
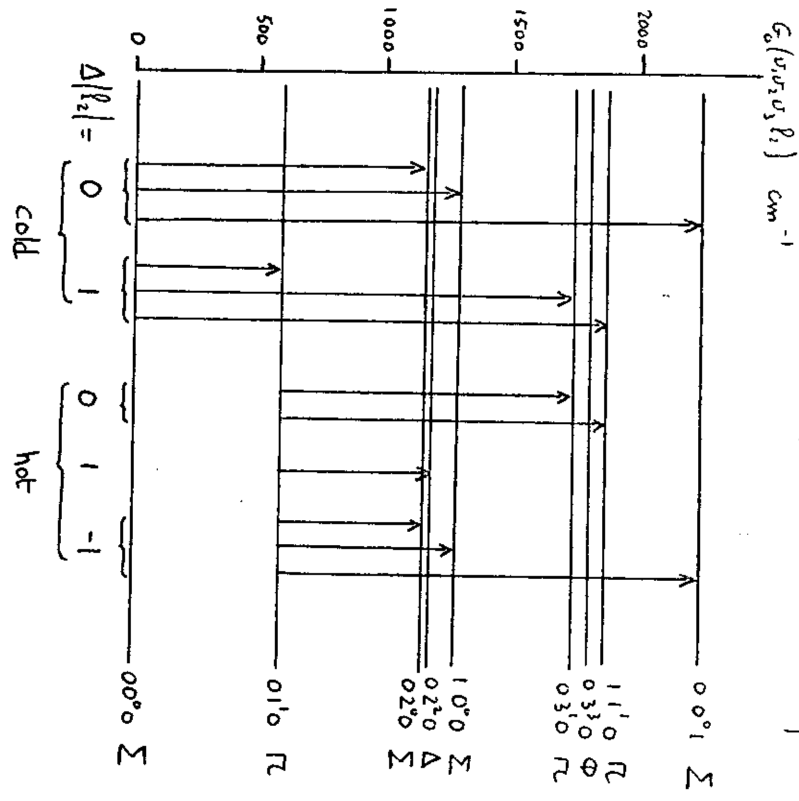
XY_2 non linear symmetric (H_2O)	XYZ linear unsymmetric (N_2O)	XY_2 linear symmetric (CO_2)
		
A sym. B antisym. } rotation (π) / z 1 sym. 2 antisym } reflection / σ	$\Sigma, \Pi, \Delta, \ldots$ $l_2 = 0, \pm 1, \pm 2 \ldots$ Σ^+ sym. Σ^- antisym. } reflection/σ 	$\Sigma, \Pi, \Delta, \ldots$ $l_2 = 0, \pm 1, \pm 2, \ldots$ Σ^+ sym. Σ^- anti sym. } reflection / σ g sym u anti sym } inversion / i
$A_1 A_2 B_1 B_2$	$\Sigma^+ \; \Sigma^- \; \Pi \; \Delta \ldots$	$\Sigma_g^+ \Sigma_u^+ \Sigma_g^- \Sigma_u^- \Pi_g \Pi_u \Delta_g \Delta_u \ldots$
$G(v_1 v_2 v_3) = \omega_1(v_1+\frac{1}{2}) + \omega_2(v_2+\frac{1}{2}) + \omega_3(v_3+\frac{1}{2}) + x_{11}(v_1+\frac{1}{2})^2 + x_{22}(v_2+\frac{1}{2})^2 + x_{33}(v_3+\frac{1}{2})^2 + x_{12}(v_1+\frac{1}{2})(v_2+\frac{1}{2}) + x_{23}(v_2+\frac{1}{2})(v_3+\frac{1}{2}) + x_{13}(v_1+\frac{1}{2})(v_3+\frac{1}{2})$	$G(v_1 v_2 l_2 v_3) = \omega_1(v_1+\frac{1}{2}) + \omega_2(v_2+1) + \omega_3(v_3+\frac{1}{2}) + x_{11}(v_1+\frac{1}{2})^2 + x_{22}(v_2+1)^2 + x_{33}(v_3+\frac{1}{2})^2 + x_{12}(v_1+\frac{1}{2})(v_2+1) + x_{23}(v_2+1)(v_3+\frac{1}{2}) + x_{13}(v_1+\frac{1}{2})(v_3+\frac{1}{2}) + g_{22}^v l_2^2$	
All transitions allowed	$\Delta l_2 = 0$ ∥ $\Delta l_2 = \pm 1$ ⊥ Allowed transitions	$\Delta l_2 = 0$ ∥ $\Delta l_2 = \pm 1$ ⊥ $g \longleftrightarrow u$ i.e. $\Delta v_2 + \Delta v_3$ odd

fig. 3

Absorption Spectrum of N_2O



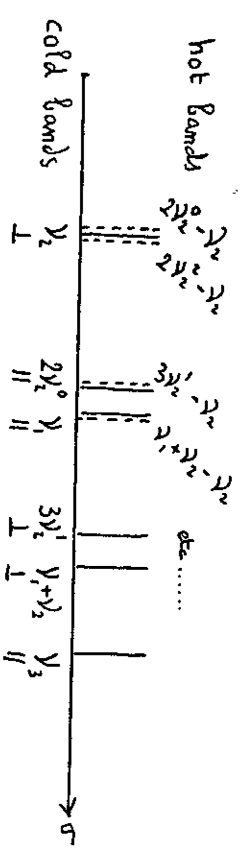


Fig. 4

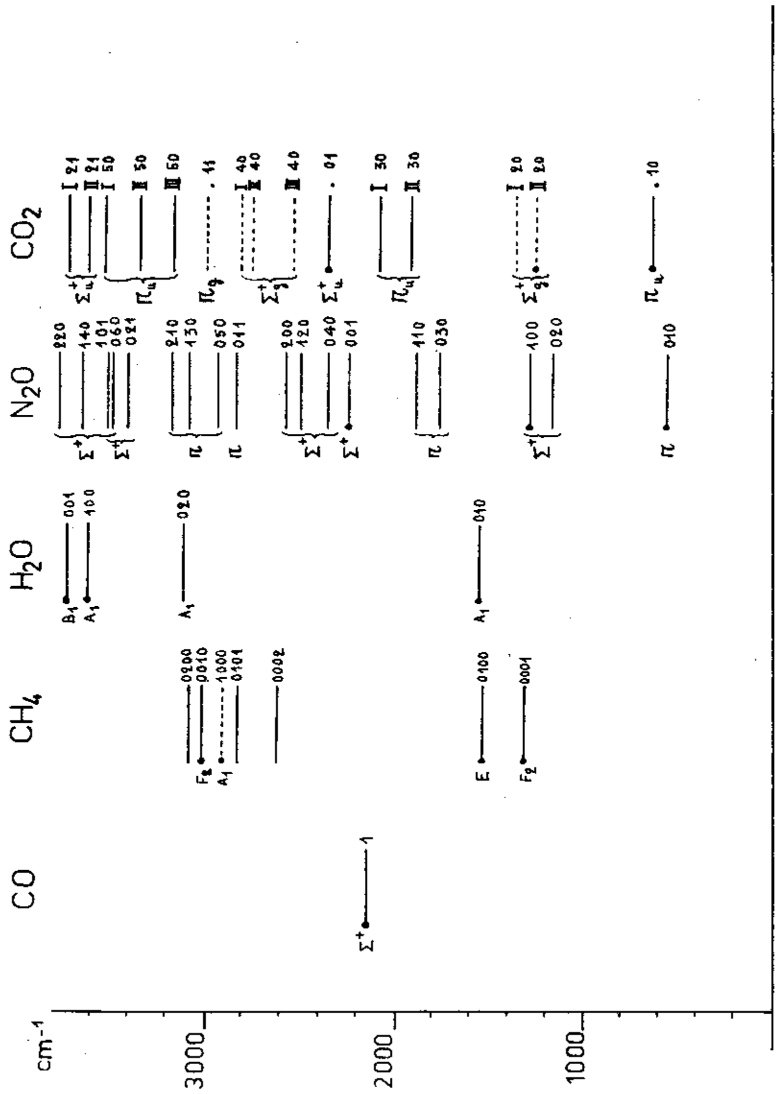


Fig 5

- fig. 4 gives, for N_2O, the diagram of the lowest vibrational energy levels, the allowed transitions between these levels in absorption (cold bands and hot bands from the lowest excited level), and a schematic picture of the spectrum showing the positions of the absorption bands [symbols $v_1 v_2^{l_2} v_3$ are used for the levels]

- fig. 5 gives diagrams of vibrational energy levels for 5 molecules (CO, CH_4, H_2O, N_2O and CO_2). In this figure, ●——— 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, l_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 ← 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)

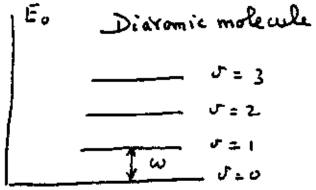
- Fermi Resonance

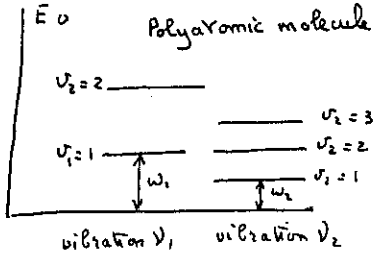
For a linear triatomic molecule, it is in principle possible, from 10 independent vibrational levels, to compute the 10 parameters ($3\ \omega_i + 6\ x_{ss'} + 1\ g_{22}^{v}$) appearing in the spectral term G (see fig. 3) and then, using G, to compute all the energy levels of the molecule. In the case 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:

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

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

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





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 $\omega_1 \simeq 2\omega_2$, then the two levels $v_1 = 1$, $v_2 = 0$ and $v_1 = 0$, $v_2 = 2$ 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 of CO_2.

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 10^00 and 02^00 are quasi-degenerate. We must consider polyads of resonating levels:

Σ diads $\begin{cases} 10^00 \\ 02^00 \end{cases}$ $\begin{cases} 10^01 \\ 02^01 \end{cases}$ ....

Π diads $\begin{cases} 11^10 \\ 03^10 \end{cases}$ $\begin{cases} 11^11 \\ 03^11 \end{cases}$ ....

Δ diads $\begin{cases} 12^20 \\ 04^20 \end{cases}$ $\begin{cases} 12^21 \\ 04^21 \end{cases}$ ....

Σ triads $\begin{cases} 20^00 \\ 12^00 \\ 04^00 \end{cases}$ $\begin{cases} 20^01 \\ 12^01 \\ 04^01 \end{cases}$ .....

Π triads $\begin{cases} 21^10 \\ 13^10 \\ 05^10 \end{cases}$ $\begin{cases} 21^11 \\ 13^11 \\ 05^11 \end{cases}$ ....

etc ....

(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

Example

$$\begin{vmatrix} E_{10^00} - X & -hc\frac{k_{122}}{\sqrt{2}} \\ -hc\frac{k_{122}}{\sqrt{2}} & E_{02^00} - X \end{vmatrix} = 0$$

$$\begin{vmatrix} E_{11^10} - X & -hck_{122} \\ -hck_{122} & E_{03^10} - X \end{vmatrix} = 0$$

$$\begin{vmatrix} E_{20^00} - X & -hck_{122} & 0 \\ -hck_{122} & E_{12^00} - X & -hc\sqrt{2}k_{122} \\ 0 & -hc\sqrt{2}k_{122} & E_{04^00} - X \end{vmatrix} = 0$$

In these equations, $E_{v_1v_2^{l_2}v_3}$ is given by the formula shown in fig 3 $\left(G(v_1 v_2 l_2 v_3) = \frac{1}{hc} E_{v_1v_2^{l_2}v_3} \right)$; the general formula for the coupling matrix element is:

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

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 than the symbols 10^00 and 02^00 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:

Σ diad
$(10^00, 02^00)_{I}$ or in short $I\,2^00$
$(10^00, 02^00)_{II}$ $II\,2^00$

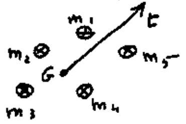
Π diad
$(11^10, 03^10)_{I}$ $I\,3^10$
$(11^10, 03^10)_{II}$ $II\,3^10$

Σ triad
$(20^00 \dots 04^00)_{I}$ or in short $I\,4^00$
$(20^00 \dots 04^00)_{II}$ $II\,4^00$
$(20^00 \dots 04^00)_{III}$ $III\,4^00$

In the shortened notation, the last numbers $2v_1+v_2{}^{l_2}\,v_3$ 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 Δ 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 Δ and consider all directions for Δ 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 xyz, 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. $I^e_{xx}, I^e_{yy}, I^e_{zz}$ will designate the principal moments of inertia of the equilibrium configuration; Table I shows the relations existing among them for the various types of molecules.

- Hamiltonian for the rigid rotator

  We assume that the nuclei stay in their equilibrium positions, then

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

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 $I^e_{xx} = I^e_{yy}$

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

The eigenvalues of P^2 and P_z are respectively $\hbar^2 J(J+1)$ and $\hbar K$ with

$J = 0, 1, 2 \ldots$ $\qquad K = 0, \pm 1, \pm 2, \ldots \pm J$

therefore

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

with

$$B_x = \frac{h}{8\pi^2 c I^e_{xx}} \qquad B_z = \frac{h}{8\pi^2 c I^e_{zz}}$$

B_x and B_z are the "rotational constants"

  - Spherical tops $I^e_{xx} = I^e_{yy} = I^e_{zz}$

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

  - Linear molecules $I^e_{xx} = I^e_{yy}$ $\qquad I^e_{zz} = 0$

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

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

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

where $P_R^{\perp}$ and $P_R^{\parallel}$ 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 $\vec{P_R}$

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 $\overrightarrow{P_R}$ and $\overrightarrow{P_V}$. In the first order approximation, one can use for the vibrational angular momentum $\overrightarrow{P_V}$ 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 (ζ_s written in short for $\zeta^z_{n\,sz}$ 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,

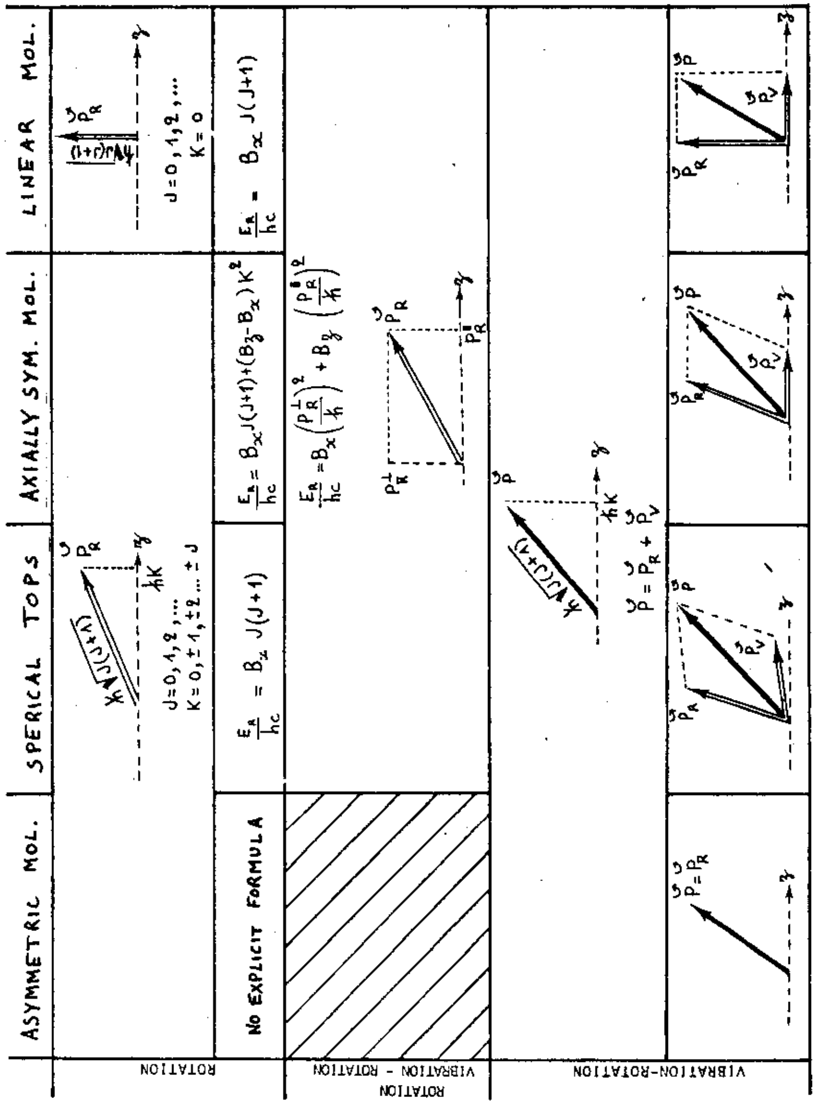


Fig. 6

Fig. 7

Axially Symmetric Molecules

$P_v = \Sigma \hbar \zeta_s l_s$

$-1 \leqslant \zeta_s \leqslant 1$

$P_v = \hbar \zeta l$ 1 degenerate vibration

Linear Molecules

$P_v = \Sigma \hbar l_s$

$P_v = \hbar l$

$K = l$

$$\frac{E_R}{hc} = B_x\left[J(J+1) - K^2\right] + B_z\left[K - \zeta l\right]^2$$

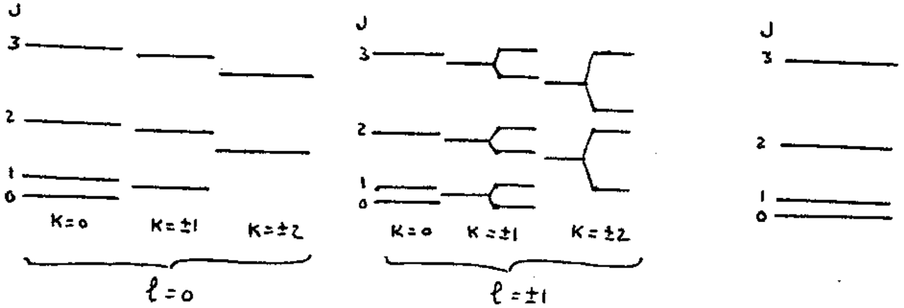
$$\frac{E_R}{hc} = \boxed{B_x J(J+1) + (B_z - B_x)K^2 - 2B_z\zeta K l}$$

$\left(-B_z\zeta^2 l^2 \text{ is written with } \frac{E_V}{hc}\right)$

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

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

$\left(-B_x l^2 \text{ is written with } \frac{E_V}{hc}\right)$



Selection Rules (threefold axis)

$\Delta l = 0, \pm3, \pm6, \ldots$

$\Delta K = 0$

$\Delta J = \begin{cases} 0, \pm1 & (\text{if } K \neq 0) \\ \pm1 & (\text{if } K = 0) \end{cases}$

$\textcircled{\parallel}$

$\Delta l = \pm1, \pm2, \pm4, \ldots$

$\Delta K = \pm1$

$\Delta J = 0, \pm1$

$\textcircled{\perp}$

$\Delta K - \Delta l = 0, \pm3, \pm6 \ldots$

Selection Rules:

$\Delta l = 0$

$\Delta J = \begin{cases} 0, \pm1 & (\text{if } l \neq 0) \\ \pm1 & (\text{if } l = 0) \end{cases}$

$\Delta l = \pm1$

$\Delta J = 0, \pm1$

$\Delta J = -1$ P branch $\Delta J = 0$ Q branch $\Delta J = +1$ R branch

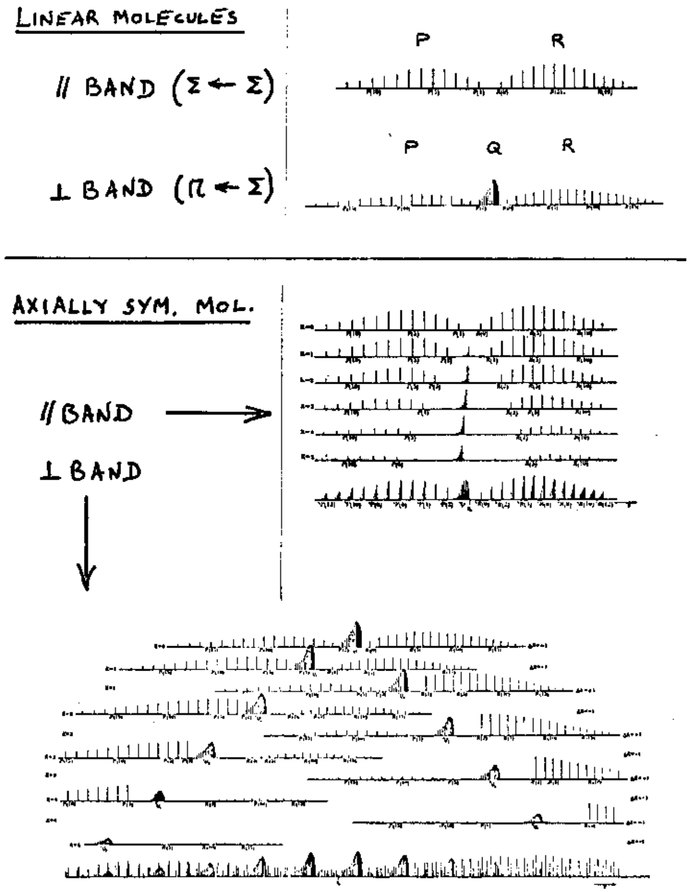


Fig. 8

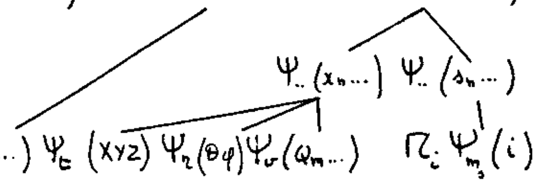
- Missing rotational levels

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.

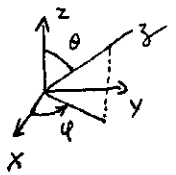
$$\Phi_{a\ldots\ldots}(x_N \ldots s_N \ldots x_e \ldots s_e)$$

it is a function of all position coordinates $x_N \ldots\ldots x_e \ldots\ldots$ and spin coordinates $s_N \ldots\ldots s_e \ldots\ldots$ of nuclei and electrons. The quantum numbers $a \ldots\ldots$ 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)

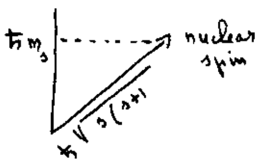
$$\Phi_{a\ldots}(x_N \ldots s_N \ldots x_e \ldots s_e \ldots) \simeq \Psi_e(x_e \ldots\ldots s_e \ldots)\, \Psi_n(x_n \ldots s_n \ldots)$$



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, $\theta\ \varphi$ are the angles defining the orientation of the molecular axis z, Q_m is a normal coordinate; m_s is the spin projection quantum number.



(XYZ space fixed axes)



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 $\frac{1}{2}$, $\frac{3}{2}$ ...), 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, ...), this is the case for the two nuclei of ^{16}O (spin zero).

When we permute the two oxygen nuclei,

- Φ is symmetric
- Ψ_t 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 $\Psi_0(O_2)\Psi_0(C)\Psi_0(O_1) \equiv \Psi_0(O_1)\Psi_0(C)\Psi_0(O_2)$
- Ψ_e 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 y perpendicular

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

$C_y(\pi) = i \cdot \sigma_{xz}$ (product of a reflexion 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 $C_y(\pi)$

(let us recall that + − are respectively symmetric and antisymmetric with respect to σ_{xz} 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 00^01

- From all what has been said, it results that Ψ_r 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

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

Ψ_r 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

In this section the following symbols are used

- P_α component of the total angular momentum on axes xyz linked to the equilibrium configuration
- $Q_{s\sigma}$ normal coordinate $\quad Q_{s\sigma} = \sum_i l_{is\sigma}^{\alpha} \, m_i^{1/2} \Delta \alpha_i$
- $p_{s\sigma}^{\circledast}$ conjugate momentum of $Q_{s\sigma}$
- $\Delta\alpha_i = \alpha_i - \alpha_i^\circ$ cartesian displacement of nucleus i ($\alpha = x, y, z$)
- α_i ($= x_i, y_i, z_i$) instantaneous coordinate of nucleus i
- α_i° (or β_i° or γ_i°) equilibrium coordinate of nucleus i
- p_α component of the internal angular momentum

$$p_\alpha = \sum_{s\sigma} \mathcal{A}_{s\sigma}^{\alpha} \, p_{s\sigma}^{\circledast}$$

$$\mathcal{A}_{s\sigma}^{\alpha} = \sum_i \sum_{s'\sigma'} \left(l_{is'\sigma'}^{\beta} \, l_{is\sigma}^{\gamma} - l_{is\sigma}^{\beta} \, l_{is'\sigma'}^{\gamma} \right) Q_{s'\sigma'} \qquad \alpha \neq \beta \neq \gamma$$

$$p_\alpha = \sum_{s\sigma s'\sigma'} \zeta_{s\sigma s'\sigma'}^{\alpha} \, Q_{s\sigma} \, p_{s'\sigma'}^{\circledast}$$

$$\zeta_{s\sigma s'\sigma'}^{\alpha} = \sum_i \left(l_{is\sigma}^{\beta} \, l_{is'\sigma'}^{\gamma} - l_{is'\sigma'}^{\beta} \, l_{is\sigma}^{\gamma} \right)$$

$$\downarrow$$

"Coriolis coupling coefficient" $\left\} \begin{array}{l} \zeta_{s\sigma s\sigma}^{\alpha} = 0 \\ \zeta_{s'\sigma' s\sigma}^{\alpha} = -\zeta_{s\sigma s'\sigma'}^{\alpha} \end{array} \right.$ $\qquad -1 \leqslant \zeta_{s\sigma s'\sigma'}^{\alpha} \leqslant 1$

- V potential function

Hamiltonians

$$\text{Hamiltonians}\begin{cases}\text{classical} & H_0\ H_{I}\ H_{II}\ \text{(approximate)}\ H_{III}\ \text{(exact)}\\ \text{quantic} & H_{WH}\ H_{DD}\ \text{(both exact and equivalent)}\end{cases}$$

"Rigid rotator - Harmonic oscillators" Approximation

$$H_0 = H_{0R} + H_{0V} = \frac{1}{2}\sum_{\alpha}\frac{P_\alpha^2}{I^e_{\alpha\alpha}} + \frac{1}{2}\sum_{s\sigma} p_{s\sigma}^{\circledast\,2} + \frac{1}{2}\sum_{s\sigma}\lambda_s Q_{s\sigma}^2$$

Influence of anharmonicity

$$H_I = \frac{1}{2}\sum_{\alpha}\frac{P_\alpha^2}{I^e_{\alpha\alpha}} + \frac{1}{2}\sum_{s\sigma} p_{s\sigma}^{\circledast\,2} + V$$

$$V = \frac{1}{2}\sum_{s\sigma}\lambda_s Q_{s\sigma}^2 + hc\sum_{s\sigma s'\sigma' s''\sigma''} k_{s\sigma s'\sigma' s''\sigma''}\, Q_{s\sigma} Q_{s'\sigma'} Q_{s''\sigma''} + \dots$$

Influence of non-rigidity

$$H_{II} = \frac{1}{2}\sum_{\alpha\beta}\mu'_{\alpha\beta} P_\alpha P_\beta + \frac{1}{2}\sum_{s\sigma} p_{s\sigma}^{\circledast\,2} + V$$

$$\{\mu'_{\alpha\beta}\} = \{I_{\alpha\beta}\}^{-1}$$

$$I_{\alpha\alpha} = I^e_{\alpha\alpha} + \sum_{s\sigma} a^{\alpha\alpha}_{s\sigma} Q_{s\sigma} + \sum_{s\sigma s'\sigma'} A^{\alpha\alpha}_{s\sigma s'\sigma'} Q_{s\sigma} Q_{s'\sigma'}$$

$$(\alpha \neq \beta) \qquad I_{\alpha\beta} = \sum_{s\sigma} a^{\alpha\beta}_{s\sigma} Q_{s\sigma} + \sum_{s\sigma s'\sigma'} A^{\alpha\beta}_{s\sigma s'\sigma'} Q_{s\sigma} Q_{s'\sigma'}$$

$$(\alpha \neq \beta \neq \gamma) \quad \begin{cases} a^{\alpha\alpha}_{s\sigma} = 2\sum_i m_i^{\frac{1}{2}}\left(\beta_i^0\, l^{\beta}_{is\sigma} + \gamma_i^0\, l^{\gamma}_{is\sigma}\right)\\ a^{\alpha\beta}_{s\sigma} = -\sum_i m_i^{\frac{1}{2}}\left(\alpha_i^0\, l^{\beta}_{is\sigma} + \beta_i^0\, l^{\alpha}_{is\sigma}\right)\end{cases}$$

Influence of interaction between rotation and vibration

$$H_{III} = \frac{1}{2}\sum_{\alpha\beta}\underbrace{(P_\alpha - p_\alpha)\,\mu_{\alpha\beta}\,(P_\beta - p_\beta)} + \frac{1}{2}\sum_{s\sigma} p_{s\sigma}^{\circledast\,2} + V$$

the order of the three factors is not important in classical mechanics; it is important in quantum mechanics because $\mu_{\alpha\beta}$ does not commute with p_α and p_β (see next page)

$$p_\alpha = \sum_{s\sigma s'\sigma'} \zeta^{\alpha}_{s\sigma s'\sigma'}\, Q_{s\sigma}\, p^{\circledast}_{s'\sigma'} \qquad \text{internal angular momentum}$$

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

$$\left.\begin{matrix}\alpha=\beta\\ \alpha\neq\beta\end{matrix}\right\} \quad I'_{\alpha\beta} = \underset{\substack{/\\ \text{nonvanishing only if } \alpha=\beta}}{I^e_{\alpha\beta}} + \sum_{s\sigma} a^{\alpha\beta}_{s\sigma} Q_{s\sigma} + \sum_{s\sigma s'\sigma'} A'^{\alpha\beta}_{s\sigma s'\sigma'} Q_{s\sigma} Q_{s'\sigma'}$$

$$A'^{\alpha\beta}_{s\sigma s'\sigma'} + A'^{\alpha\beta}_{s'\sigma' s\sigma} = \sum_{\delta}\frac{a^{\alpha\delta}_{s\sigma}\, a^{\beta\delta}_{s'\sigma'} + a^{\alpha\delta}_{s'\sigma'}\, a^{\beta\delta}_{s\sigma}}{4 I^e_{\delta\delta}} \quad \begin{cases}\alpha=\beta\\ \alpha\neq\beta\end{cases}$$

Influence of quantum-mechanical effects

- non commutativity of operators:

$$H_{WH} = \frac{1}{2}\sum_{\alpha\beta}(P_\alpha - p_\alpha)\,\mu^{-\frac{1}{2}}\mu_{\alpha\beta}\,(P_\beta - p_\beta)\,\mu^{\frac{1}{2}} + \frac{1}{2}\sum_{s\sigma} p^{\circledast}_{s\sigma}\,\mu^{-\frac{1}{2}}\,p^{\circledast}_{s\sigma}\,\mu^{\frac{1}{2}} + V$$

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

- choice of a convenient volume element in the configuration space

$$H_{DD} = \frac{1}{2}\mu^{\frac{1}{4}}\sum_{\alpha\beta}(P_\alpha - p_\alpha)\,\mu^{-\frac{1}{2}}\mu_{\alpha\beta}\,(P_\beta - p_\beta)\,\mu^{\frac{1}{4}} + \frac{1}{2}\mu^{\frac{1}{4}}\sum_{s\sigma} p^{\circledast}_{s\sigma}\,\mu^{-\frac{1}{2}}\,p^{\circledast}_{s\sigma}\,\mu^{\frac{1}{4}} + V$$

(Darling - Dennison Hamiltonian)

$$H_{DD} = H_{III} + \Lambda(\dots Q_{s\sigma} \dots)$$

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

Remarks:

1) Molecular parameters $\lambda_s\ k_{s\sigma s'\sigma' s''\sigma''}\ k_{s\sigma s'\sigma' s''\sigma'' s'''\sigma'''} \dots$

$I^e_{\alpha\alpha}\quad a^{\alpha\beta}_{s\sigma}\quad \zeta^{\alpha}_{s\sigma s'\sigma'}$

2) Particular case of linear molecules:

$\vec{P}_R\ (= \vec{P} - \vec{P}_v)$ is perpendicular to z → $P_z - p_z = 0$ (Sayvetz relation)

in $\sum_{\alpha\beta}$, α or $\beta = x, y$ no terms with subscript z in the Hamiltonian

Expansion of the Hamiltonian

$$H_{\underline{\mathrm{III}}} = \frac{1}{2}\sum_{\alpha\beta} \mu_{\alpha\beta} P_\alpha P_\beta - \frac{1}{2}\sum_{\alpha\beta}\left(p_\alpha \mu_{\alpha\beta} P_\beta + \mu_{\alpha\beta} p_\beta P_\alpha\right)$$

$$+ \frac{1}{2}\sum_{\alpha\beta} p_\alpha \mu_{\alpha\beta} p_\beta + \frac{1}{2}\sum_{s\sigma} p_{s\sigma}^{\circledast\,2} + V$$

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

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

$$\mu_{\alpha\beta} = \left(I'_{\alpha\gamma} I'_{\beta\gamma} - I'_{\alpha\beta} I'_{\gamma\gamma}\right) / \Delta \qquad \alpha \neq \beta \neq \gamma \qquad \Delta = \left|I'_{\alpha\beta}\right|$$

$$\mu_{\alpha\alpha} = \frac{1}{I^e_{\alpha\alpha}} - \sum_{s\sigma} \frac{a^{\alpha\alpha}_{s\sigma}}{\left(I^e_{\alpha\alpha}\right)^2} Q_{s\sigma} + \cdots\cdots$$

$$\mu_{\alpha\beta} = - \sum_{s\sigma} \frac{a^{\alpha\beta}_{s\sigma}}{I^e_{\alpha\alpha} I^e_{\beta\beta}} Q_{s\sigma} + \cdots\cdots$$

$$H_{\underline{\mathrm{III}}} = H_0 + H_1 + \cdots\cdots$$

$$H_0 = \frac{1}{2}\sum_\alpha \frac{P_\alpha^2}{I^e_{\alpha\alpha}} + \frac{1}{2}\sum_{s\sigma} p_{s\sigma}^{\circledast\,2} + \frac{1}{2}\sum_{s\sigma} \lambda_s Q_{s\sigma}^2$$

$$H_1 = -\frac{1}{2}\sum_{\alpha\beta}\sum_{s\sigma} \frac{a^{\alpha\beta}_{s\sigma}}{I^e_{\alpha\alpha} I^e_{\beta\beta}} Q_{s\sigma} P_\alpha P_\beta$$

$$- \sum_\alpha \frac{1}{I^e_{\alpha\alpha}} p_\alpha P_\alpha$$

$$+ hc \sum_{s\sigma s'\sigma' s''\sigma''} K_{s\sigma s'\sigma' s''\sigma''} Q_{s\sigma} Q_{s'\sigma'} Q_{s''\sigma''}$$

Remark : we use $H_{\underline{\mathrm{III}}}$ because $\Lambda(\ldots . Q_{s\sigma} \ldots .)$ does not contribute in the lowest orders

First order corrections to the rotation - vibration energy

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 ($Q_{s\sigma}, \ldots\; p^{\circledast}_{s\sigma} \ldots$) 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) :

$$\left\langle n \left| \frac{H_1}{hc} \right| n \right\rangle = \left\langle n \left| - \sum_\alpha \frac{1}{hc I^e_{\alpha\alpha}} p_\alpha P_\alpha \right| n \right\rangle = -2 B_z \zeta K \ell$$

(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 $\omega_1 \simeq \omega_2$; 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 $\left\langle 1\; 0 \left| - \sum_\alpha \frac{p_\alpha P_\alpha}{hc I^e_{\alpha\alpha}} \right| 0\; 1 \right\rangle$ 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 ν_1 and ν_3 of H_2O (i.e. between states 100 and 001) ; Coriolis resonance occurs between ν_2 and ν_4 of CH_4 (i.e. between states 0100 and 0001).

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

$$\langle v_1\ v_2\ v_3 \,|\, hc\, k_{1\sigma 2\sigma 3\sigma}\, Q_{1\sigma}\, Q_{2\sigma}\, Q_{3\sigma} \,|\, v_1-1\,,\ v_2+1\,,\ v_3+1 \rangle$$

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

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)