Introduction to Molecular Spectra

Atomic Spectra

$$\frac{1}{\lambda} = \bar{\nu} = \bar{T}_i - \bar{T}_f \qquad \bar{T} = \frac{E}{hc}$$

Single Electron State

$n = 1, 2, \ldots \rightarrow$ energy level $E_n = -\frac{1}{n^2}\frac{Z^2 e^4 m^2}{\hbar^2}$

$l = 0, \ldots, n \rightarrow$ orbital ang. mom. $|\vec{l}| = \sqrt{l(l+1)}\,\hbar$

$m_l = -l, \ldots, +l \rightarrow l_z = m_l \hbar$

$s = \frac{1}{2} \rightarrow$ spin

$m_s = \pm\frac{1}{2} \rightarrow$ spin projection

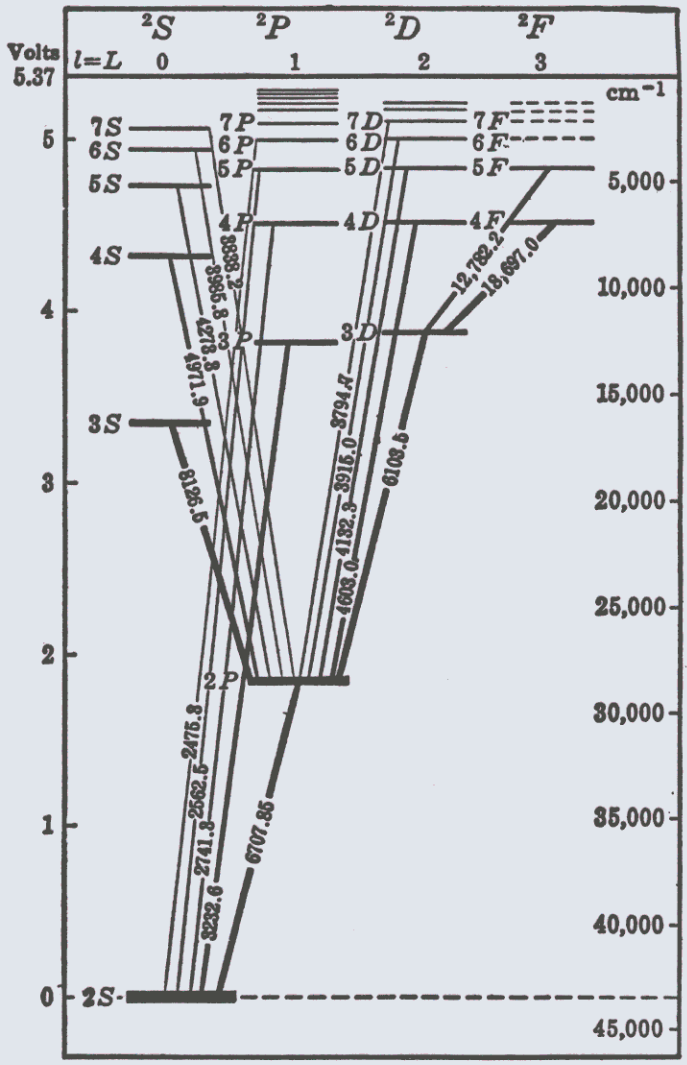


FIG. 1. **Energy Level Diagram of the Li Atom (after Grotrian).** The wave lengths of the spectral lines are written on the sloping connecting lines, which represent the transitions (see below). The symbols S, P, $\cdots$ are explained on p. 27. The numbers in front of these symbols are the principal quantum numbers n of the outer electron.

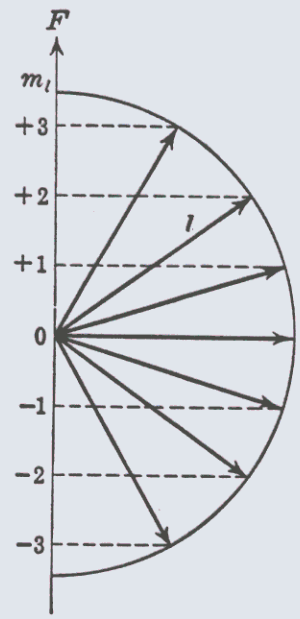


FIG. 3. **Space Quantization of l in a Field F for $l = 3$.** The figure also holds generally for other angular momentum vectors (see p. 26). The length of the vector l is $\sqrt{3 \times 4} = 3.464$ units.

Many Valence Electrons (two)

$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2$ $\quad \vec{S} = \vec{s}_1 + \vec{s}_2$ $\quad \vec{j} = \vec{\ell} + \vec{s}$

$\vec{J} = \vec{L} + \vec{S}$ $\quad \vec{J} = \vec{j}_1 + \vec{j}_2$

Fine Structure

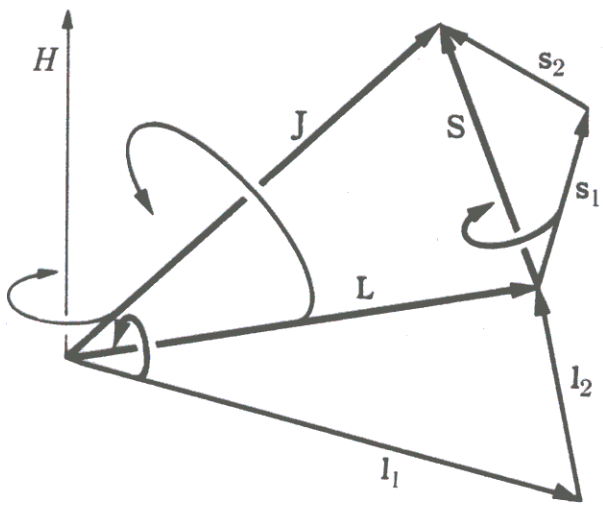
$W_{so} = A \dfrac{\vec{L}\cdot\vec{S}}{\hbar^2}$ – spin-orbit effect $\quad w_{so} = \xi \dfrac{\vec{\ell}\cdot\vec{s}}{\hbar^2}$

$W_{re} = \varepsilon_s \dfrac{\vec{s}_1\cdot\vec{s}_2}{\hbar^2} + \varepsilon_\ell \dfrac{\vec{\ell}_1\cdot\vec{\ell}_2}{\hbar^2} = \left\langle \dfrac{e^2}{r_{12}} \right\rangle$

- residual electrostatic interaction
- electron exchange

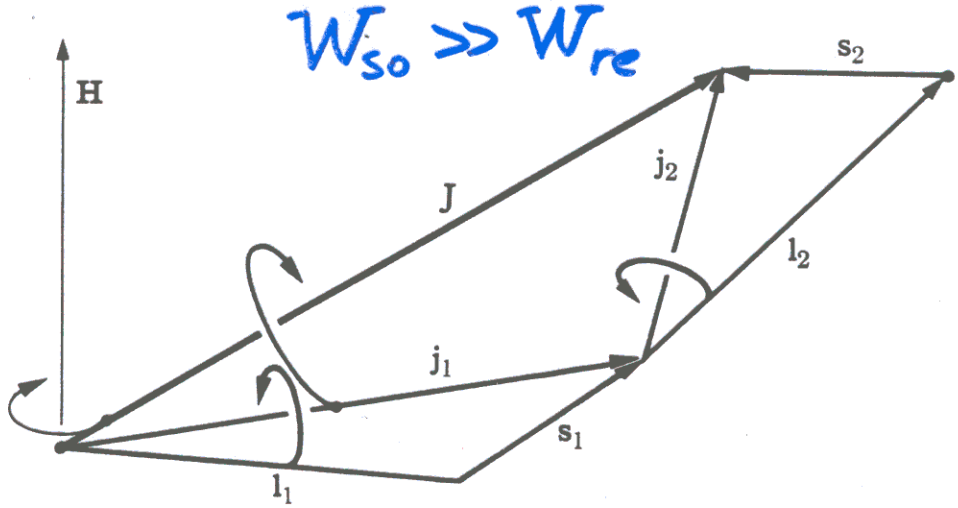
LS coupling

$W_{so} \ll W_{re}$



jj coupling (in heavy metals)

$W_{so} \gg W_{re}$



Spectra of Diatomic Molecules

① Electronic energy $E_e \sim 13.6\,eV$

② Vibrational energy $E_v \sim 0.1\,eV$

$$E_v = h\nu_c\left(v+\tfrac{1}{2}\right) \qquad v = 0,1,2,\ldots$$

$$T_v = \omega_e\left(v+\tfrac{1}{2}\right)$$

③ Rotational energy $E_r \sim 10^{-3}\,eV$

$$E_r = |\vec{J}|^2/(2I), \quad I = \mu r_e^2, \quad |\vec{J}| = \sqrt{J(J+1)}\,\hbar$$

$$T_r = B\,J(J+1) \qquad J = 0,1,2,\ldots$$

$E_e \gg E_v \gg E_r$

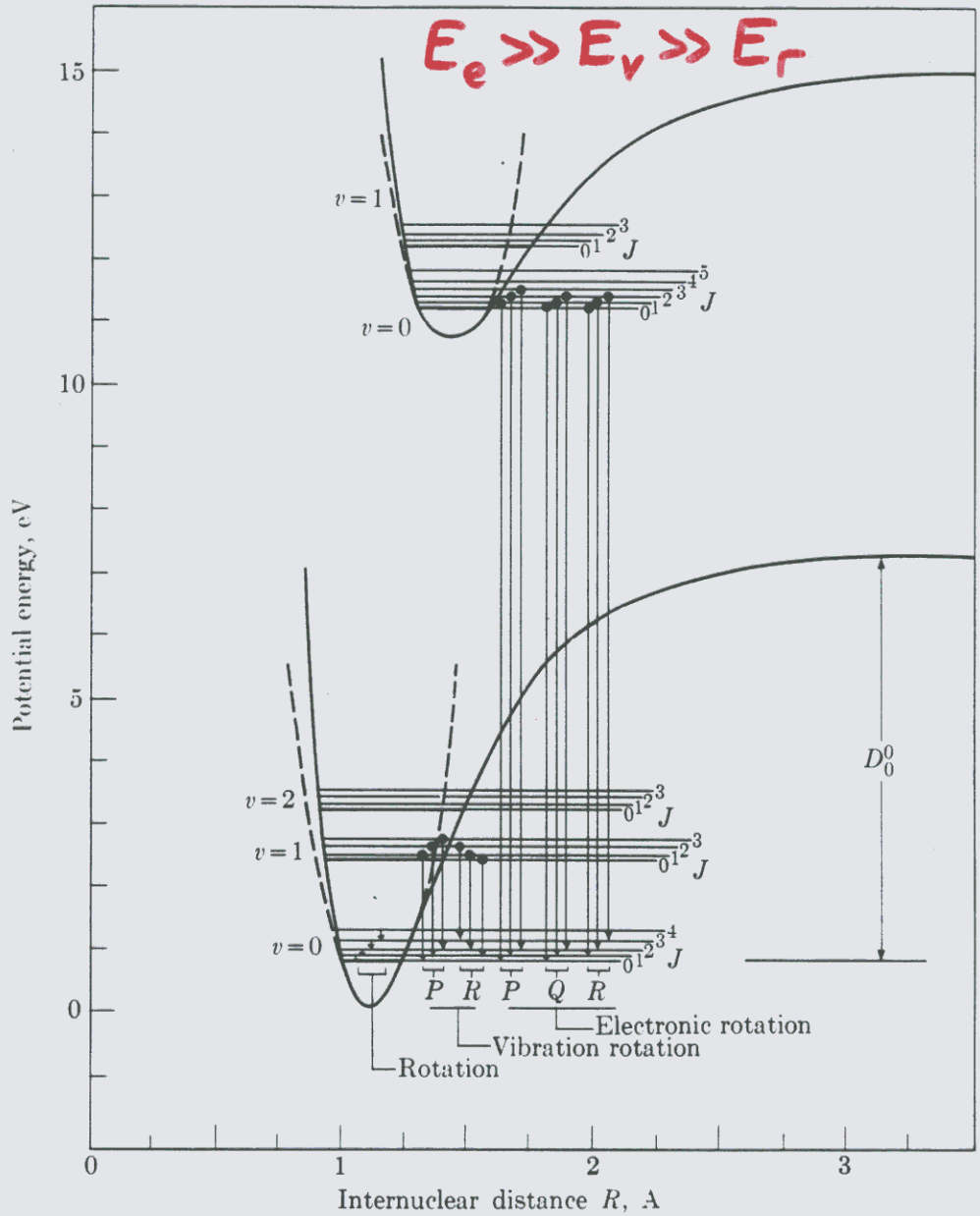


FIG. 1. Diagram illustrating electronic, vibration, and rotational energy levels and transitions of diatomic molecules. The dashed curves represent harmonic oscillator potential functions. The solid curve represents a more realistic potential energy function. (Adapted from Slater and Frank [4].)

Electronic Level Notation

Electron state

$n \rightarrow 2p \leftarrow l$

l	0	1	2	3	4 ...
state	s	p	d	f	g ...

Atomic level

multiplicity $2S+1$

n of valence electron

$6\,{}^{2}D_{3/2}$

$J = |L-S| \ldots L+S$

L	0	1	2	3	...
term	S	P	D	F	...

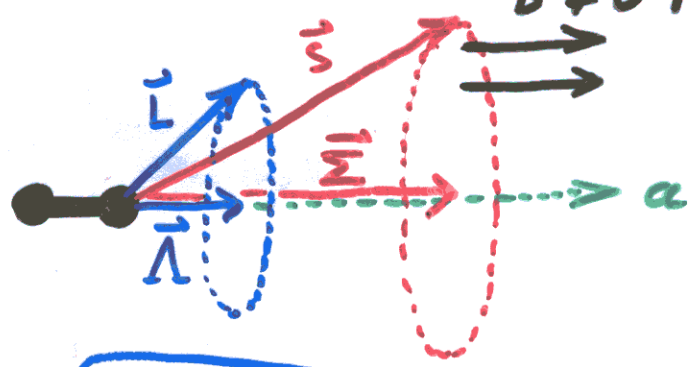
Molecular Electronic Level

$(\vec{L})_a = \Lambda\hbar$

$(\vec{S})_a = \Sigma\hbar$

$\Sigma = -S \ldots S$

$\vec{B} \neq 0$ if $\Lambda \neq 0$



X - ground state

A, B, C, .. - excited, same $2S+1$

a, b, c, ... - excited, different $2S+1$

For N_2

$A \leftrightarrow a$

$B \leftrightarrow b$

etc.

multiplicity $2S+1$

$X\,{}^{1}\Sigma^{+}_{g}$

+ or − : symmetry of ψ of reflection

$\Lambda = 0$

g - "gerade"

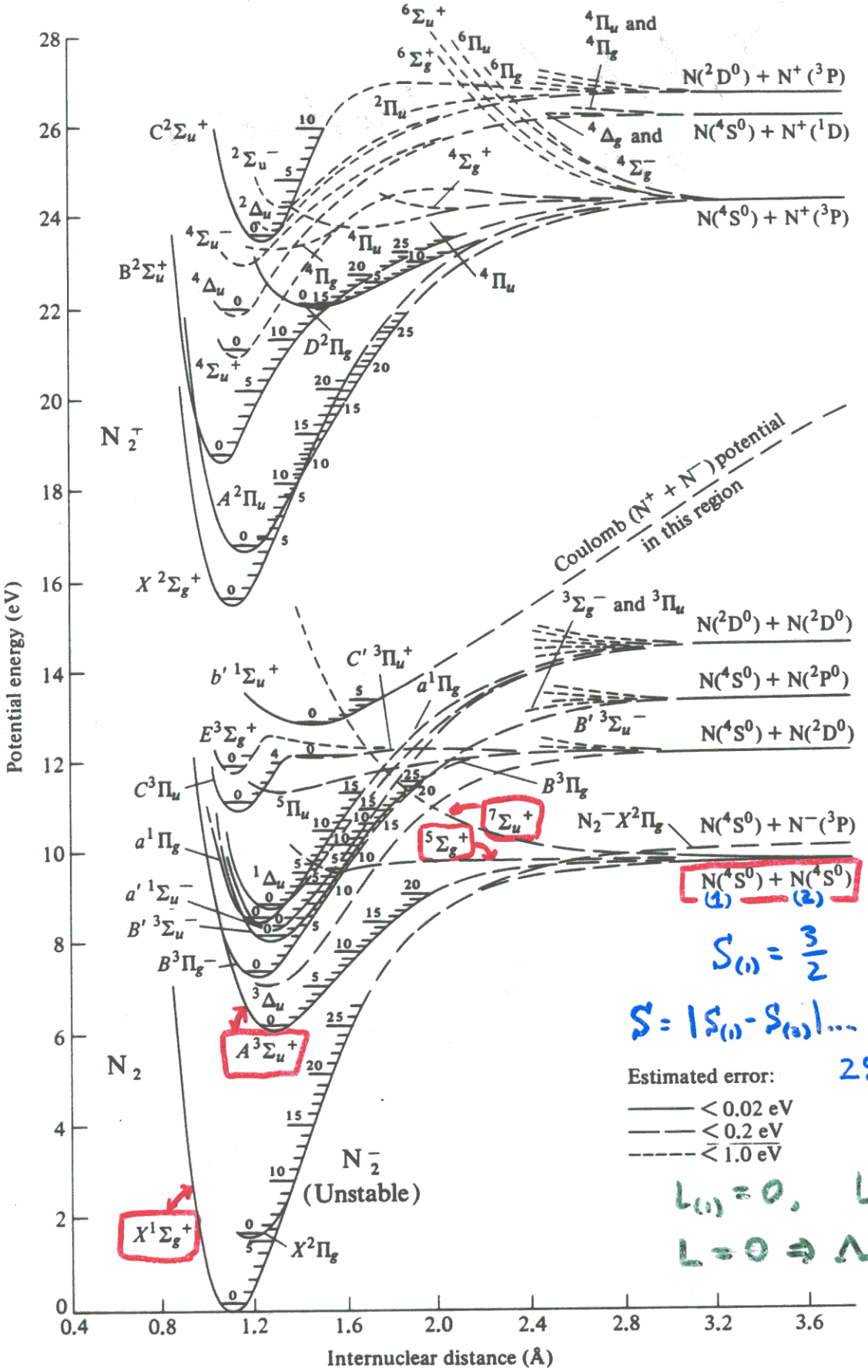
u - "ungerade"

symmetry of ψ in respect to inversion $\vec{r} \rightarrow -\vec{r}$

Λ

Λ	0	±1	±2	±3 ...
term	Σ	Π	Δ	Φ ...

N_2, N_2^+ levels



$S_{(1)} = \frac{3}{2}$ $S_{(2)} = \frac{3}{2}$

$S = |S_{(1)} - S_{(2)}| \ldots S_{(1)} + S_2 = 0, 1, 2, 3$

$2S+1 = 1, 3, 5, 7$

$L_{(1)} = 0, \quad L_{(2)} = 0$

$L = 0 \Rightarrow \Lambda = 0$

Figure 3.8 Potential energy diagram for N_2 compiled by F. R. Gilmore (Reference 7). [Reproduced with permission of F. R. Gilmore, The Rand Corporation.]

O_2, O_2^+ levels

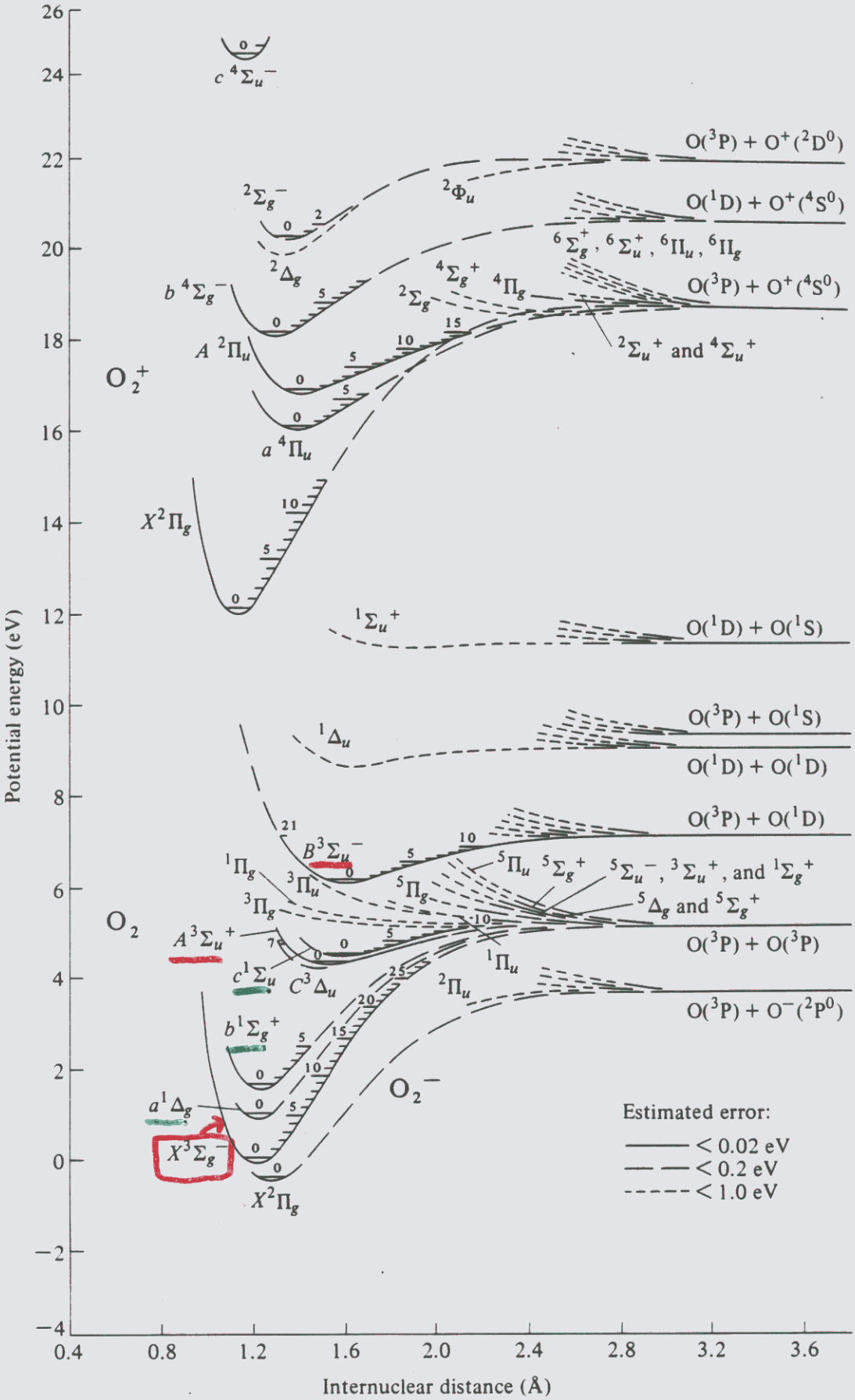


Figure 3.10 Potential energy diagram for O_2 compiled by F. R. Gilmore (Reference 7). [Reproduced with permission of F. R. Gilmore, The Rand Corporation.]

N_2, N_2^+ bands

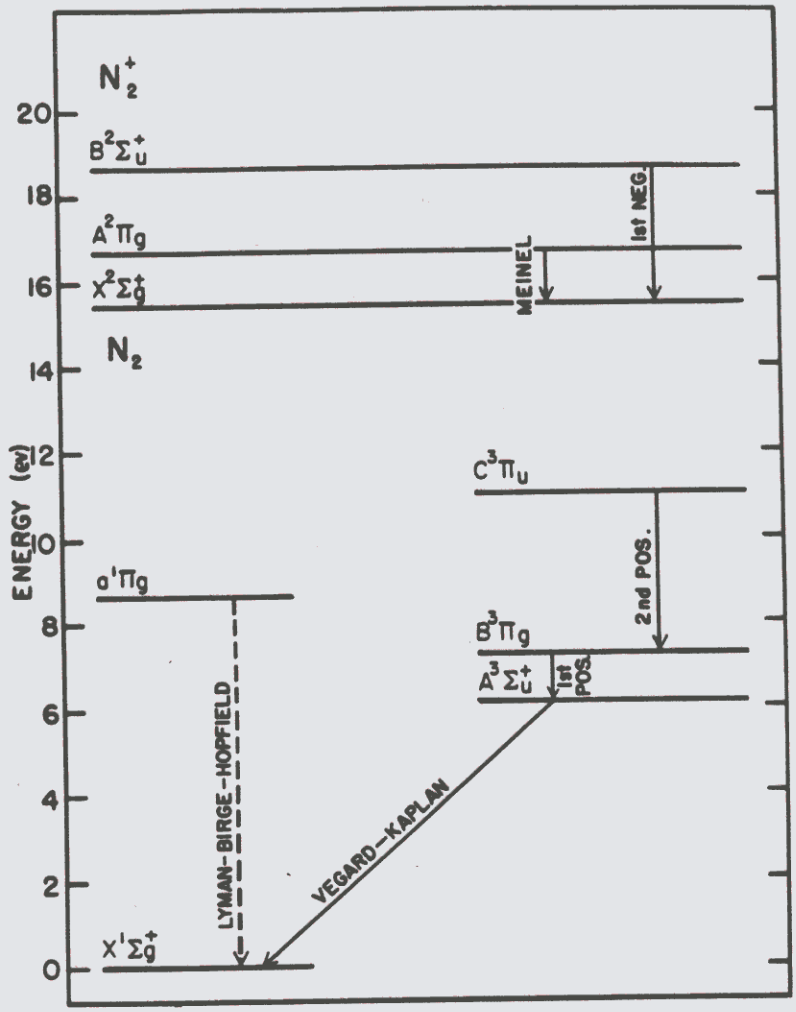


FIG. 5.32. Electronic states and band systems of N_2 and N_2^+. The dashed transition lies in the far ultraviolet and has not been detected in aurora.

O_2, O_2^+ bands

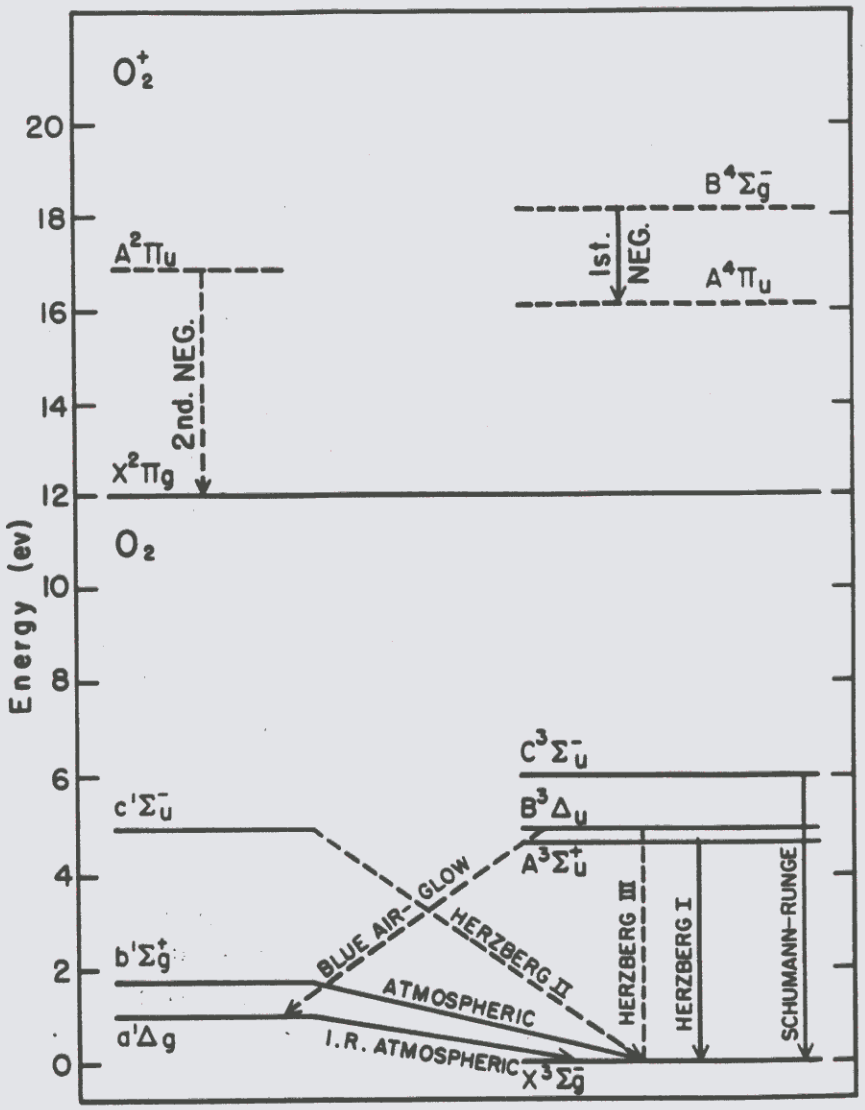


FIG. 5.33. Electronic states and band systems of O_2 and O_2^+. Only the Infrared Atmospheric, the Atmospheric, and the First Negative systems have been detected in aurora.

Fine Structure of Rotational Levels

Spin-axis interaction

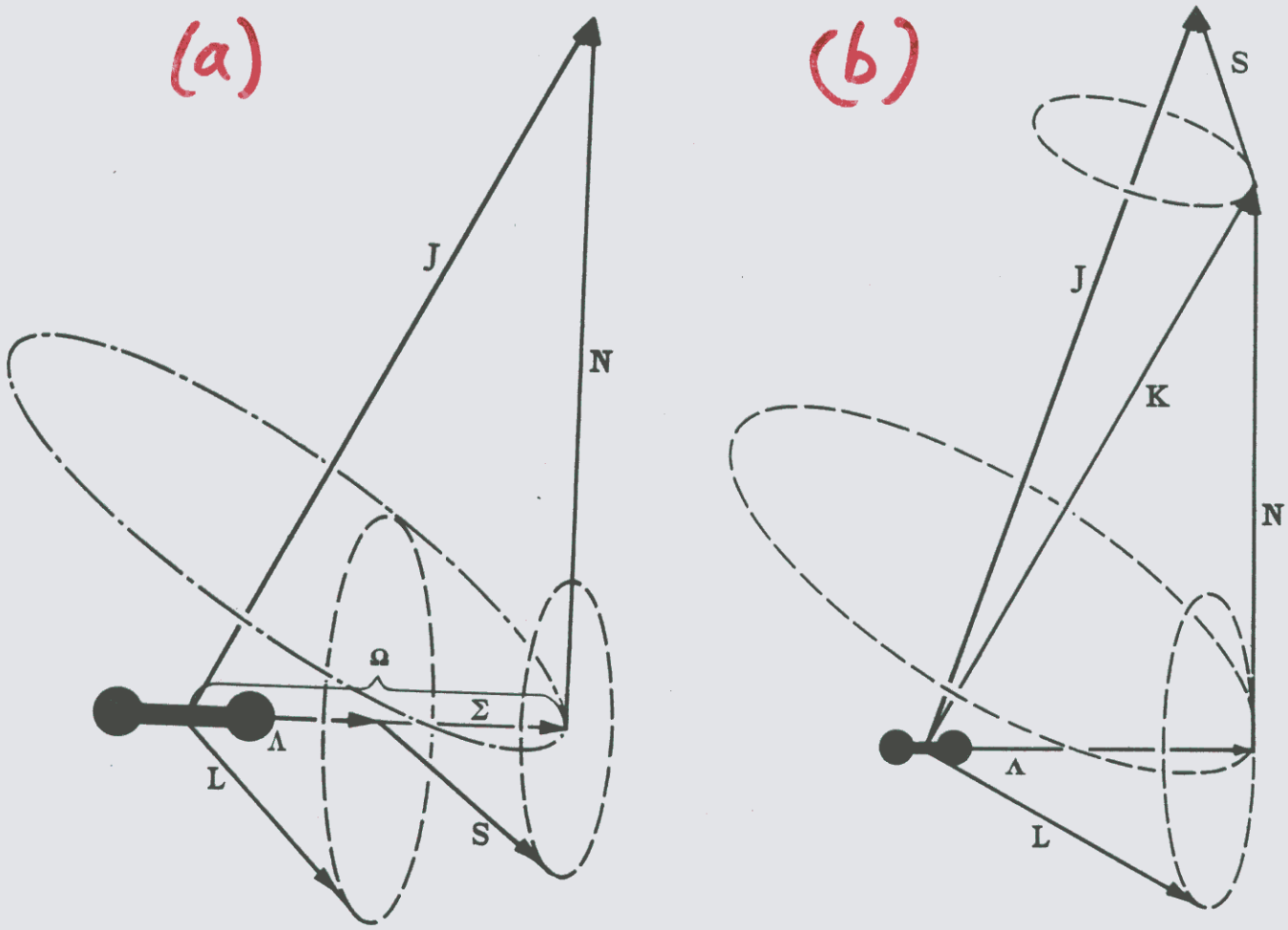
2 cases (Hund) - (a) and (b)

(a) $W_{SA} \gg E_r$

$\Omega = \Lambda + \Sigma$ (analogous to $\vec{J} = \vec{L} + \vec{S}$)

(b) $W_{SA} \ll E_r$

-usually for $\Lambda = 0$



Rotation-vibration transitions and their infrared spectra

$E', \bar{T}'$ - upper

$E'', \bar{T}''$ - lower

$\bar{T}' \rightarrow \bar{T}''$

$$\frac{1}{\lambda} = \bar{\nu} = \underbrace{\frac{E'}{hc}}_{\bar{T}'} - \underbrace{\frac{E''}{hc}}_{\bar{T}''}$$

$\Delta v = \pm 1$

$\Delta J = \pm 1$

$\Delta J = +1$ P branch

$\Delta J = -1$ R branch

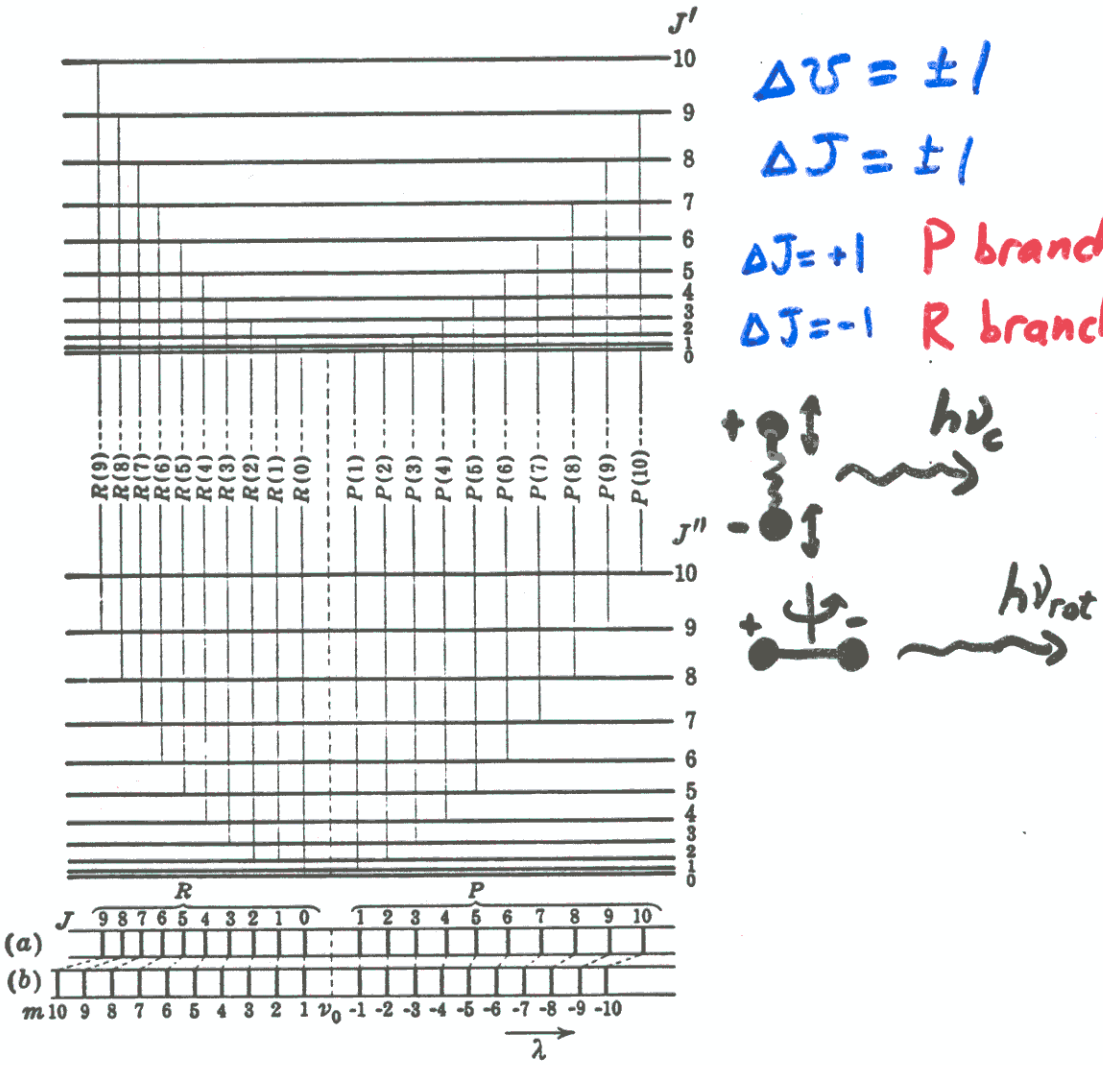
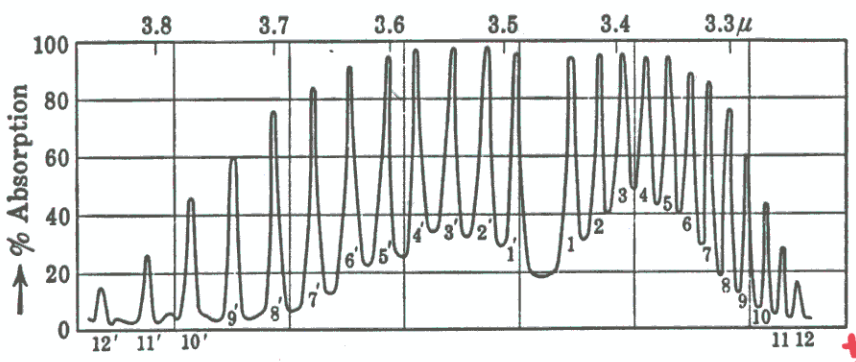


FIG. 54. **Energy Level Diagram explaining the Fine Structure of a Rotation-Vibration Band.** In general, the separation of the two vibrational levels is considerably larger compared to the spacing of the rotational levels than shown in the figure (indicated by the broken parts of the vertical lines representing the transitions). The schematic spectrograms (*a*) and (*b*) give the resulting spectrum with and without allowance for the interaction between rotation and vibration. In these spectrograms, unlike most of the others, short wave lengths are at the left.



has dipole moment

FIG. 32. **Fine Structure of the Principal Absorption Band (Fundamental) of HCl in the Near Infrared [after Imes (354)].** The ordinates give the percentage absorption, calculated from the galvanometer deflections. The numbers below the individual lines are the *m* values. The *P* branch is to the left, and the *R* branch is to the right. With still higher resolution [see Meyer and Levin (491) and Smith (1428)] each line is found to consist of two components on account of isotope effect (see Fig. 33 and p. 142).

Electronic Transitions

- picture complicates due to rotation-vibration interaction and unharmonicity of the molecule

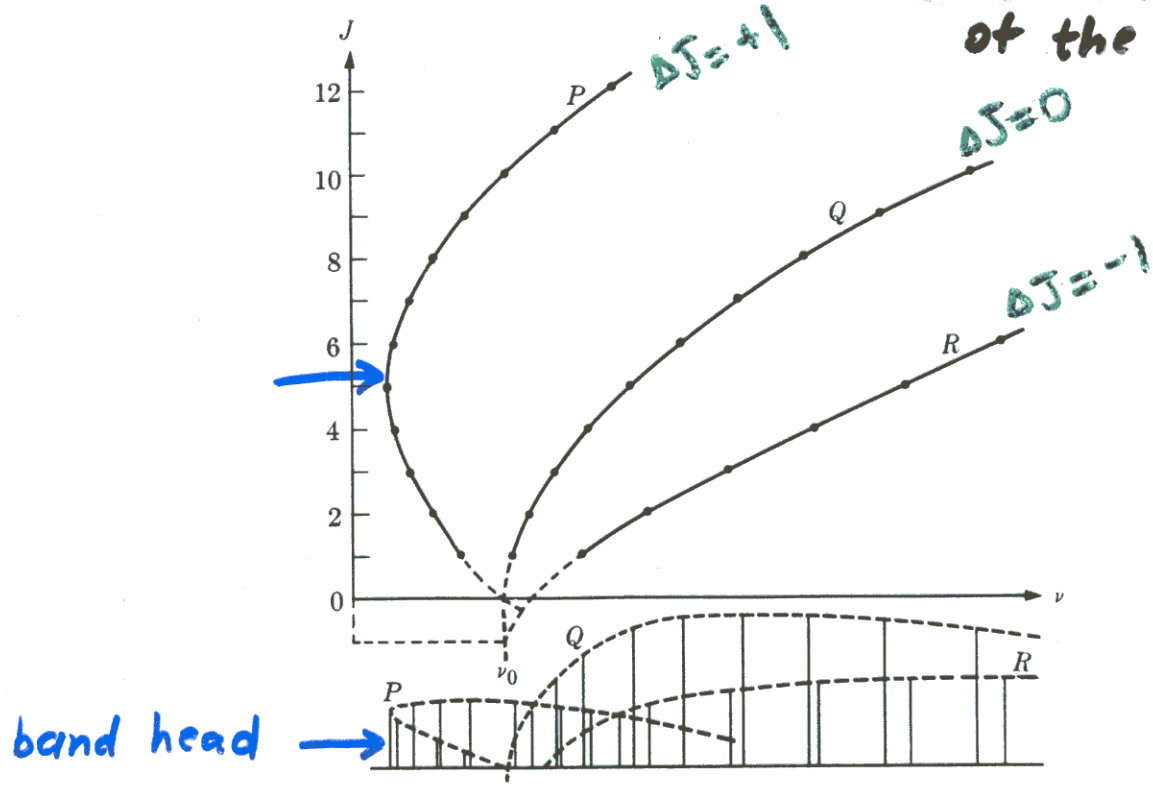


FIG. 2. Fortrat diagram of the $^1\Sigma \rightarrow {}^1\Pi$ band of CO. P values correspond to electron shifts from nJ levels in Σ to $n + 1$ levels in Π or a change of $+1$ in J. Q values correspond to a zero change in J and R to a -1 change in J. All P, Q, and R values in this diagram originate in the same v level in Π and terminate in the same v level in Σ. If the v level in Σ is 0 and in Π is 0, the band is known as the 0-0 band, and correspondingly, if the electron shifts are from $v = 1$ in Σ to $v = 0$ in Π, it will be known as the 1-0 band. (From Brode [1.16].)

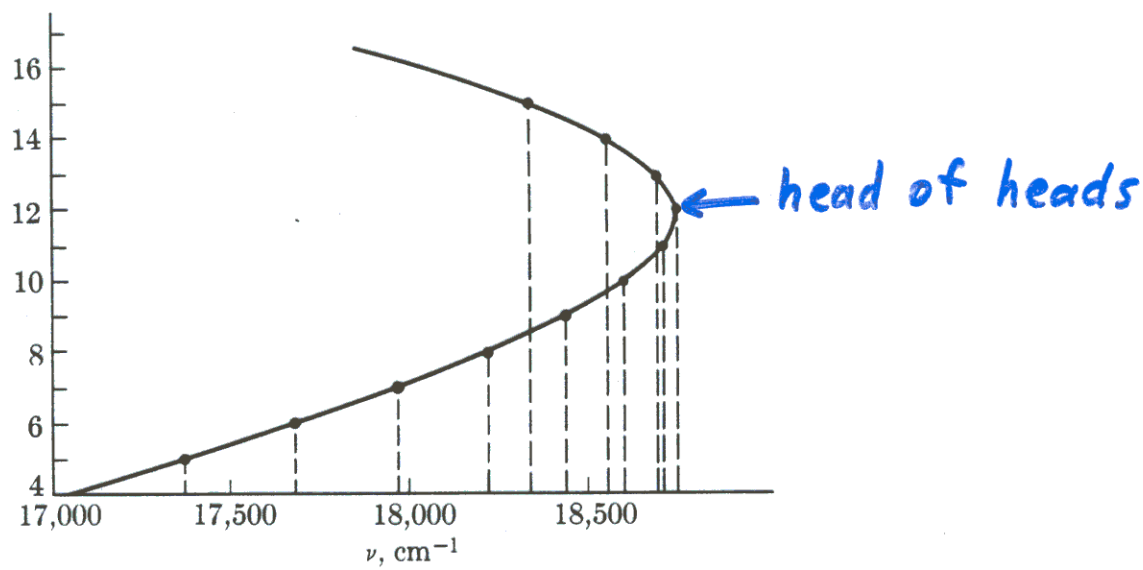


FIG. 1. Graphical representation of the sequence $\Delta v = -4$ of the N_2^+ bands. The abscissas of the small circles give the positions of the bands in the spectrum. (After Herzberg, [1.1].)

Transition probability and line intensity

Electron transition is so fast that r_e doesn't change

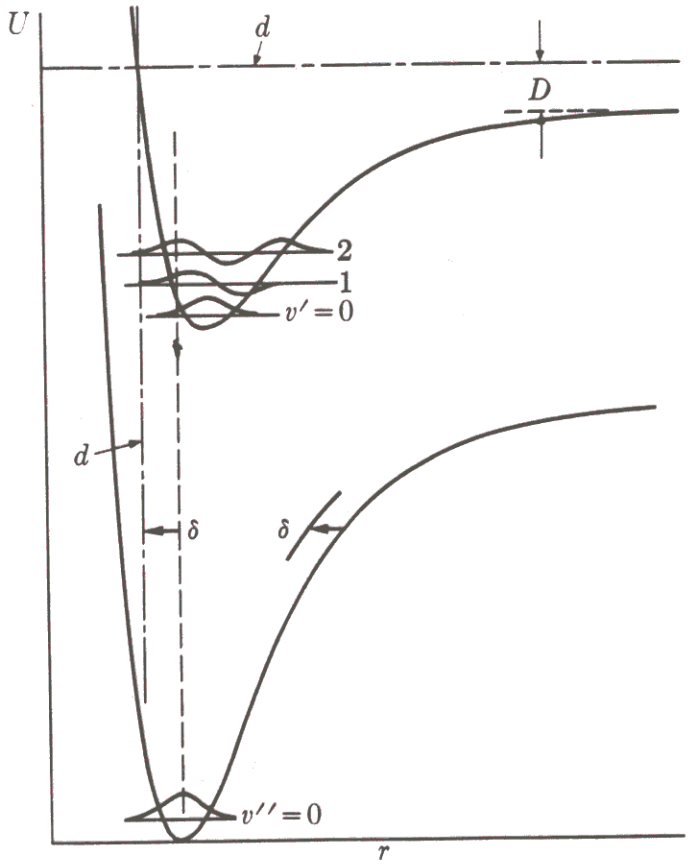


FIG. 2. Franck-Condon principle according to wave mechanics. The potential curves are so drawn that the "best" overlapping of the eigenfunctions occurs for $v' = 2$, $v'' = 0$ (see the dashed vertical line). The lines labeled d indicate the preferred transition if the lower potential curve were displaced to the left by δ. Then D represents the energy of the dissociation products. (After Herzberg [1.1].)

TABLE 1

Selection Rules for Molecular Transitions

	Electric Dipole (E1)	Magnetic Dipole (M1)	Electric Quadrupole (E2)
Total inversion	$+ \leftrightarrow -$	$+ \leftrightarrow +$ $- \leftrightarrow -$	$+ \leftrightarrow +$ $- \leftrightarrow -$
Electronic inversion	$g \leftrightarrow u$	$g \leftrightarrow g$ $u \leftrightarrow u$	$g \leftrightarrow g$ $u \leftrightarrow u$
ΔJ	$0, \pm 1$	$0^*, \pm 1$ $(0 \nleftrightarrow 0)$	$0, \pm 1, \pm 2^\dagger$
ΔS (a), (b)	0	0	0
$\Delta \Sigma$ (a)	0	See $\Delta \Lambda$	0
$\Delta \Lambda$ (a)	$0, \pm 1$	± 1 if $\Delta \Sigma = 0$; 0 if $\Delta \Sigma = \pm 1$	$0, \pm 1, \pm 2$
$\Delta \Omega$ (a)	$0^\ddagger, \pm 1$	± 1	$0, \pm 1, \pm 2$
$\Delta \Lambda$ (b)	$0^*, \pm 1$	$0, \pm 1$	$0, \pm 1, \pm 2$
ΔK (b)	$0^\S, \pm 1$	$0, \pm 1^\S$	$0, \pm 1^\S, \pm 2$

* Not $0 - 0$. † Not $0 - 0$, $0 - 1$, $\frac{1}{2} - \frac{1}{2}$.
‡ If $0 - 0$ then $\Delta J = 0$. § Not for $\Sigma - \Sigma$ transitions.

Raman effect

Light scattered at slightly displaced frequencies due to modulation of molecular dipole moment by vibration and rotation

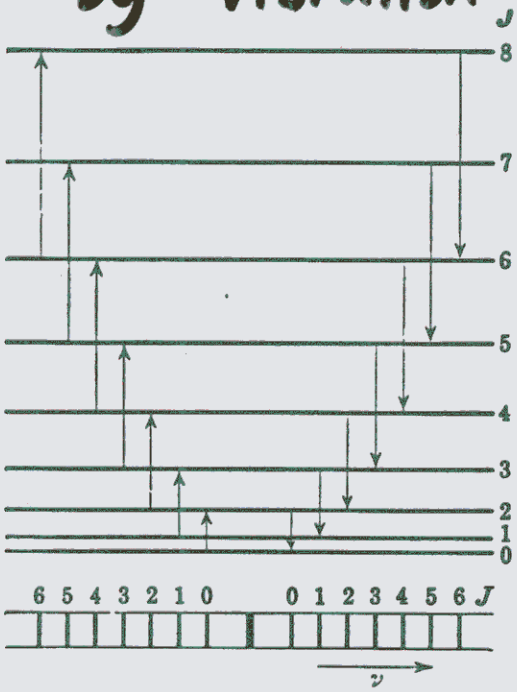


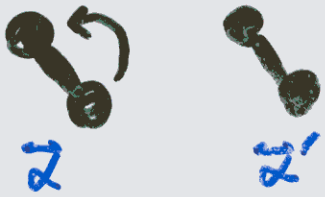
FIG. 45. **Energy Level Diagram for the Rotational Raman Spectrum.** In the schematic spectrogram below, the heavy line in the middle gives the position of the undisplaced line. To the left are the Stokes Raman lines, and to the right are the anti-Stokes lines. The numbers added to the Raman lines are the J values of the lower state.

$\Delta J = \pm 2$

Why?

$\vec{p} = \overleftrightarrow{\alpha} \vec{E}$

rotate by 180° $\overleftrightarrow{\alpha}' = \overleftrightarrow{\alpha}$



Frequency of modulation is twice the frequency of rotation

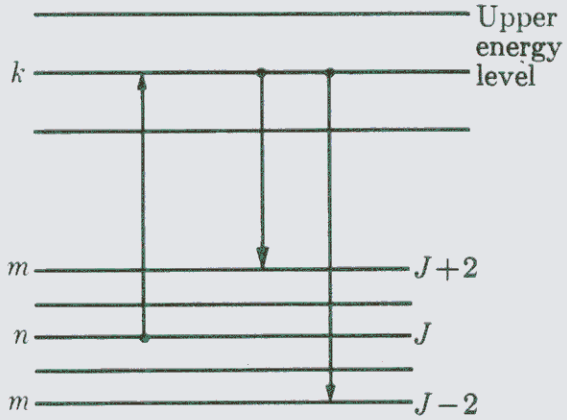


FIG. 1. Schematic of Raman transition. (From Harnwell and Stephens [1.10].)

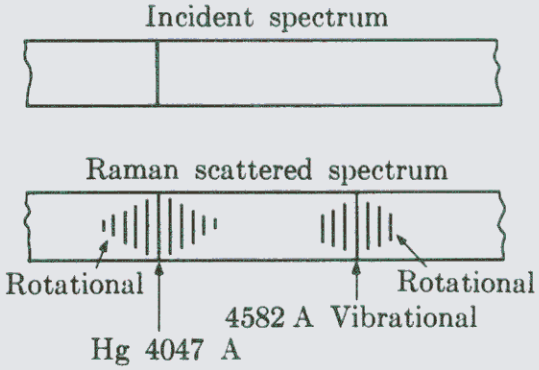


FIG. 2. Raman scattering from HCl. (From Harnwell and Stephens [1.10].)

Spectra of Polyatomic Molecules

H_2O, CO_2

1) $I \longrightarrow \overleftrightarrow{I}$ – inertia tensor $\begin{pmatrix} I_A & 0 & 0 \\ 0 & I_B & 0 \\ 0 & 0 & I_C \end{pmatrix}$

$I_A = I_B \neq I_C \rightarrow$ "symmetric top"

$I_A = I_B = I_C \rightarrow$ "spherical top"

$I_A \neq I_B \neq I_C \rightarrow$ "asymmetric top"

2) Several normal modes of oscillations

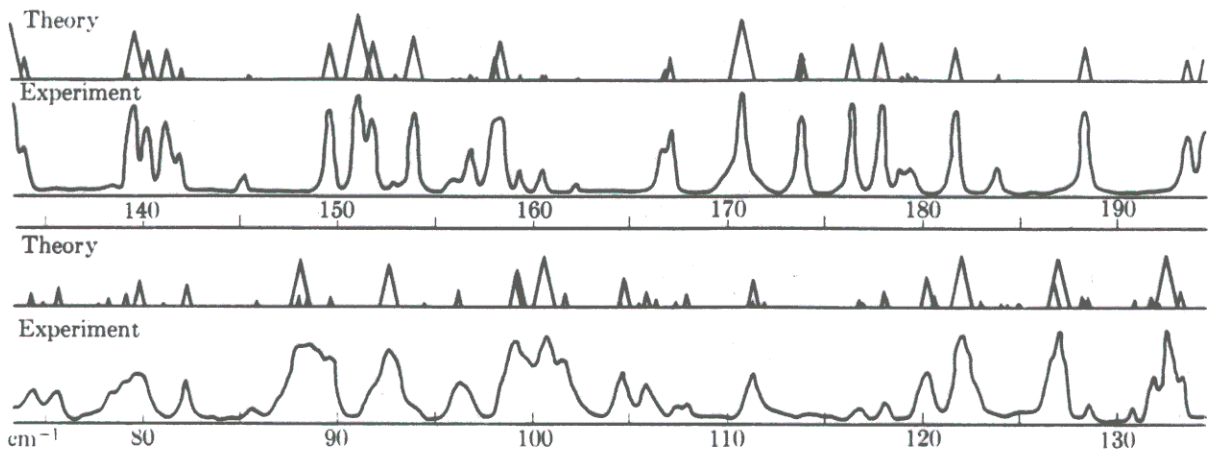


FIG. 3. Comparison of part of the H_2O rotational spectrum with the theoretical spectrum. (From Randall, Dennison, Ginsberg, and Weber [6].)

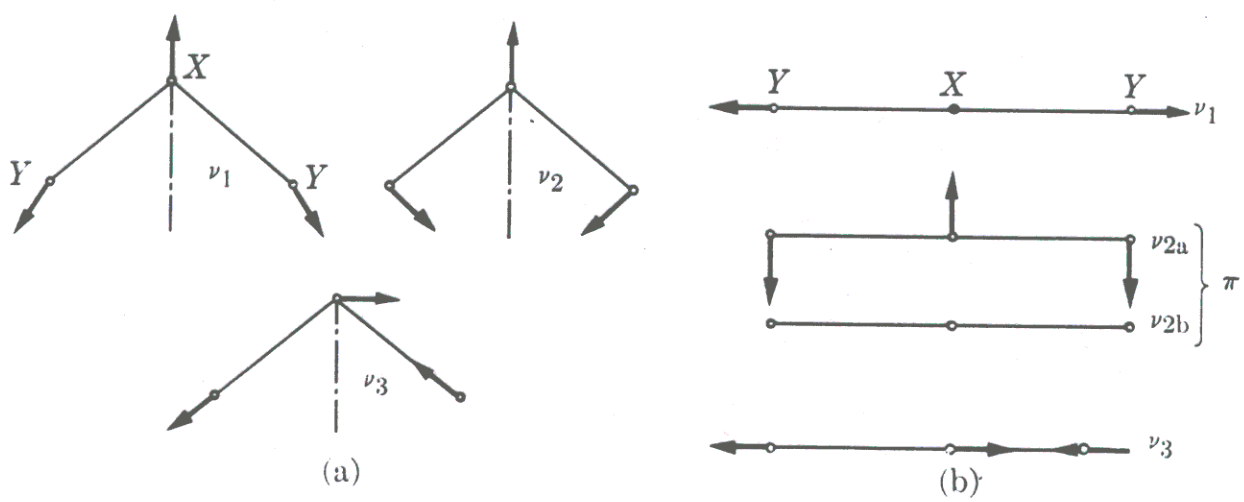


FIG. 4. Schematic normal vibrations of bent and linear XY_2 molecule.

Literature used:

1. A. Green and P. Wyatt
"Atomic and Space Physics" (1965)

2. G. Herzberg
"Spectra of Diatomic Molecules" (1950)

3. J. Chamberlain
"Physics of the Aurora and Airglow" (1961)

4. J. Steinfeld
"Molecules and Radiation" (1974)