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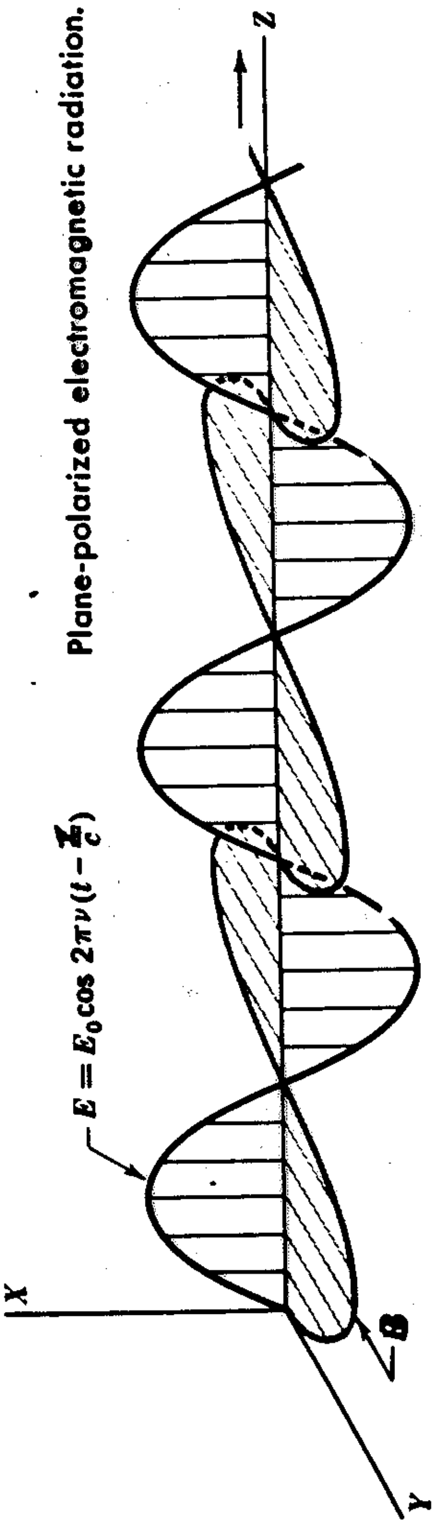
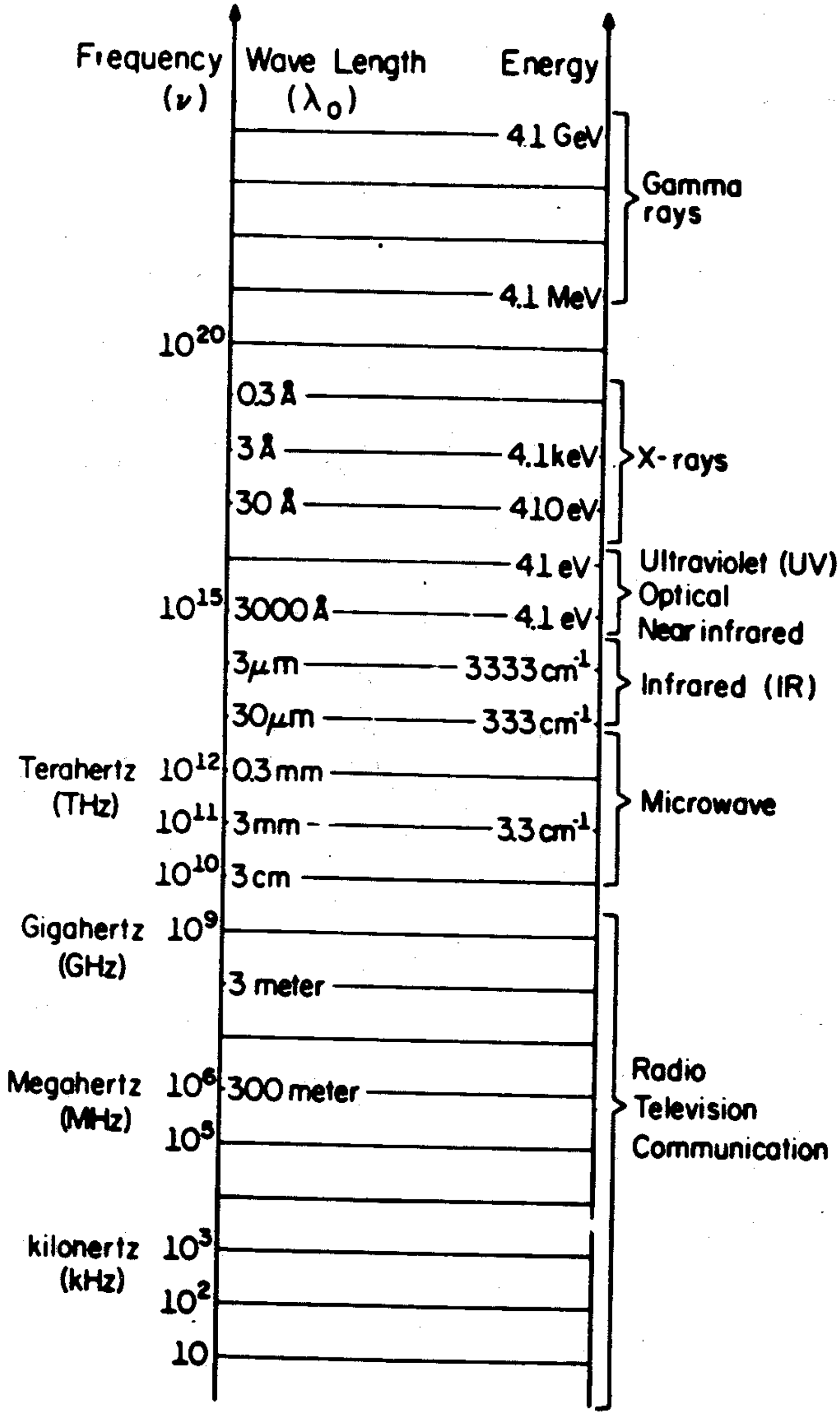


Plane-polarized electromagnetic radiation.



$c = \nu\lambda = 300 \times 10^{8} m \cdot s^{-1}$
$1 Å = 10^{-8} cm$
$1 \mu m = 10^{-4} cm = 10^{4} Å$
$1 cm^{-1} = 1.24 \times 10^{-4} eV$

The electromagnetic spectrum.

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TIME-DEPENDENT PERTURBATION THEORY

Suppose we have a system such that for $\mathcal{H}^{(0)}$ NOT EXPLICITLY dependent on time,

$\psi_n(t) = \phi_n\, exp[-iE_n t/\hbar]$ are the known solutions:

$\mathcal{H}^{(0)}\psi_n(t) = i\hbar(\partial/\partial t)\psi_n(t)$ and $\mathcal{H}^{(0)}\phi_n = E_n\phi_n$

Now consider another Hamiltonian

$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}(t)$

The solution to $\mathcal{H}$ will be a <u>linear combination</u> of the <u>complete set</u> of $\psi_n(t)$ solutions to $\mathcal{H}^{(0)}$,

$\mathcal{H}\Psi(t) = i\hbar(\partial/\partial t)\Psi(t)$ where

$$\Psi(t) = a_1(t)\,\psi_1(t) + a_2(t)\,\psi_2(t) + a_3(t)\,\psi_3(t) + ...$$

Let us illustrate with a two-level system:

Subst. $\Psi(t) = a_1(t)\phi_1\, exp[-iE_1t/\hbar] + a_2(t)\,\phi_2\, exp[-iE_2t/\hbar]$ in $\mathcal{H}\Psi(t) = i\hbar(\partial/\partial t)\Psi(t)$. The only terms left are

$$a_1(t)\mathcal{H}^{(1)}(t)\phi_1\, exp[-iE_1t/\hbar] + a_2(t)\mathcal{H}^{(1)}(t)\phi_2\, exp[-iE_2t/\hbar] = i\hbar(da_1(t)/dt)\,\phi_1\, exp[-iE_1t/\hbar] + i\hbar(da_2(t)/dt)\,\phi_2\, exp[-iE_2t/\hbar]$$

Operate on both sides with $\int\phi_1{}^*d\tau$:

$a_1(t)H^{(1)}{}_{11}\, exp[-iE_1t/\hbar] + a_2(t)H^{(1)}{}_{12}\, exp[-iE_2t/\hbar] =$

$$i\hbar(da_1(t)/dt)\ exp[-iE_1t/\hbar] \quad \&\&$$

where $H^{(1)}{}_{12} = \int\phi_1{}^*\,\mathcal{H}^{(1)}(t)\phi_2 d\tau$

Rearrange eqn &&:

$da_1(t)/dt =$

$$(1/i\hbar)\ \{\ a_1(t)H^{(1)}{}_{11} + a_2(t)H^{(1)}{}_{12}\, exp[-i(E_2 - E_1)t/\hbar]\}$$

Assume that $H^{(1)}{}_{11}(t) = 0$ at all times (i.e., no self-interaction).

Then, $da_1(t)/dt = (a_2(t)/i\hbar)\ H^{(1)}{}_{12}(t)\ exp[+i(E_1 - E_2)t/\hbar]$

Similarly,

$da_2(t)/dt = (a_1(t)/i\hbar)\ H^{(1)}{}_{21}(t)\ exp[+i(E_2 - E_1)t/\hbar]$

Generalize to more than 2 levels :

$$da_k(t)/dt = (1/i\hbar)\Sigma_n\ a_n(t)H^{(1)}{}_{kn}(t)\ exp[+i(E_k - E_n)t/\hbar] \quad **$$

Let the system be in state i, initially (t=0), then

$a_i(0) = 1$ and $a_{\text{all others}}(0) = 0$

Time integration of eq ** from t=0 to short time t_1,

$$a_f(t_1) - a_f(0) = (1/i\hbar)\int_{t=0}^{t=t1} a_i(t_1)H^{(1)}{}_{fi}(t)\ exp[+i(E_f - E_i)t/\hbar]dt$$

Note that $a_f(0) = 0$ and $a_i(t_1) \approx 1$

$a_f(t_1) = (1/i\hbar) \int_{t=0}^{t=t1} H^{(1)}_{fi}(t)\, exp[i(E_f - E_i)t/\hbar]dt$

The time-varying perturbation $\mathcal{H}^{(1)}(t)$ causes the system which was initially in state i to end up as a linear combination

$\Psi(t) = a_1(t)\phi_1\, exp[-iE_1t/\hbar] + a_2(t)\, \phi_2\, exp[-iE_2t/\hbar] + ...$

where each of the coefficients $a_f(t)$ can be found by

$a_f(t) = (1/i\hbar) \int^{t}_{t=0} H^{(1)}_{fi}(t)\, exp[i(E_f - E_i)t/\hbar]dt$

Now apply this to $\mathcal{H}^{(1)}(t) = -\mu\bullet\varepsilon(exp^{+i\omega t} + exp^{-i\omega t})$ for the electric field of the radiation of frequency $\omega = 2\pi\nu$ interacting with all charges q (nuclei and electrons) of a molecule, and write $E_f - E_i = \hbar\omega_{fi}$ to express energies in same way in:

$a_f(t) = \mu_{fi}\bullet\varepsilon\, (1/i\hbar) \int^{t}_{t=0} dt\, (exp^{+i\omega t} + exp^{-i\omega t})exp^{\,i(Ef - Ei)t/\hbar}$

$$a_f(t) = \frac{\mu_{fi}\bullet\varepsilon}{i\hbar}\left[\frac{exp^{+i(\omega fi+\omega)t} - 1}{i(\omega_{fi}+\omega)} + \frac{exp^{+i(\omega fi-\omega)t} - 1}{i(\omega_{fi}-\omega)}\right]$$

note ⇑ becomes very large when $\omega_{fi} - \omega \approx 0$ (at resonance)

$$a_f(t) \approx \frac{\mu_{fi}\bullet\varepsilon}{\hbar}\left(\frac{1-exp^{+i(\omega fi-\omega)t}}{(\omega_{fi}-\omega)}\right)$$

Take the absolute square $a_f^*(t)\, a_f(t)$:

$$|a_f(t)|^2 \approx \left|\frac{\mu_{fi}\bullet\varepsilon}{\hbar^2}\right|^2 \frac{[1-exp^{+i(\omega fi-\omega)t}][1-exp^{-i(\omega fi-\omega)t}]}{(\omega_{fi}-\omega)^2}$$

$$|a_f(t)|^2 \approx \left|\frac{\mu_{fi}\bullet\varepsilon}{\hbar^2}\right|^2 \frac{[2-2\cos(\omega_{fi}-\omega)t]}{(\omega_{fi}-\omega)^2}$$

$$|a_f(t)|^2 \approx \left|\frac{\mu_{fi}\bullet\varepsilon}{\hbar^2}\right|^2 \frac{[\sin^2 \tfrac{1}{2}(\omega_{fi}-\omega)t]}{\tfrac{1}{4}(\omega_{fi}-\omega)^2} \quad \text{now, use } \lim_{x\to 0} \frac{\sin^2 x}{x^2} = 1$$

$$|a_f(t)|^2 \approx \left|\frac{\mu_{fi}\bullet\varepsilon}{\hbar^2}\right|^2 t^2 \qquad \text{for } \omega_{fi} = \omega$$

At time t=0, system is in state ϕ_i :

$|a_i(0)|^2=1$, $|a_f(0)|^2=0$

At time t=t not too long after perturbation is turned on, the probability of finding the system (which was in state ϕ_i) in the state ϕ_f is

$$|a_f(t)|^2 \approx \left|\frac{\mu_{fi}\bullet\varepsilon}{\hbar^2}\right|^2 t^2 \quad \text{for } \omega_{fi} = \omega \qquad \text{and} \quad |a_i(t)|^2 \approx 1-\delta.$$

For the transitions into states that have energy that differ by $\hbar\omega$ from the energy of the initial state, the transition probability per unit time from state i to states f is given by

$W_{i\to f}$ per second $= 2\pi \,|\, \underline{\mu_{fi} \bullet \varepsilon} \,|^2 / \hbar \, \underline{\bullet}$ {density of final states per unit of energy}

"Fermi golden rule"

Irradiance I (time-averaged power per unit area) is related to the electric field amplitude ε by $I = \frac{1}{2} c e_0 \varepsilon^2$ where e_0 is the permittivity of free space, where $I = \int c\rho(\omega)d\omega$ where $\rho(\omega)$ is the energy density in the angular frequency interval between ω and $\omega + d\omega$ for a nearly monochromatic directional beam.

$$W_{i\to f} \text{ per second} = 2\pi \frac{|\mu_{xfi}|^2}{\hbar^2} \rho(\omega_{if}, \varepsilon_{0x})$$

where $\rho(\omega_{if}, \varepsilon_{0x})$ is the energy density at the frequency ω_{if} for x polarized light that provides a range of frequencies with the same ε_{0x} for each frequency.

For isotropic light, $\rho(\omega_{if}, \varepsilon_{0x})$ is the same for y and z and is equal to 1/3 of the total energy density so that, for isotropic light, the total transition rate is

$$W_{i\to f} \text{ per second} = \underbrace{(2\pi/3) \left|\frac{\mu_{fi}}{\hbar^2}\right|^2}_{B} \rho(\omega_{if})$$

B is Einstein's COEFFICIENT
of STIMULATED ABSORPTION ($E_f > E_i$)
or STIMULATED EMISSION ($E_f < E_i$),
<u>the same</u> since we never stipulated which was greater.

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$-\mu \bullet \mathcal{E}(t)$ (electric dipole moment) $\bullet$(electric field vector)

$-\mu_{\mathrm{induced}} \bullet \mathcal{E}(t)$ $\mu_{\mathrm{induced}} = \alpha\mathcal{E}$ $\mathcal{E}(t) = 2\,\mathcal{E}_0\cos(2\pi\nu t)$

$-\mu_{\mathrm{spin}} \bullet \mathcal{B}_1(t)$ (magnetic dip. mom.)$\bullet$(magnetic field vector)

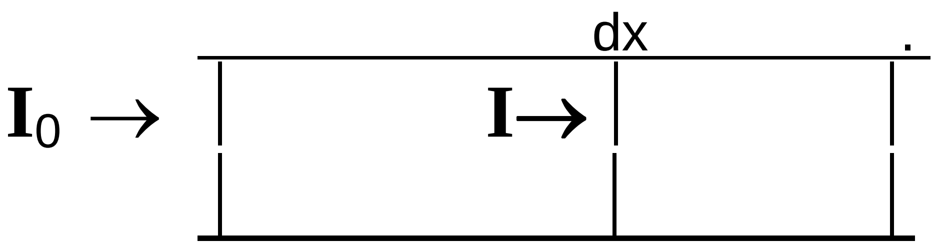
For isotropic light, the total transition rate from initial state ***i*** to final state ***f*** is given by

$W_{i\to f}$	=	$B_{i\to f}$	$\rho(\nu_{if})$
transitions per second		Einstein's coefficient for stimulated absorption or emission	radiation density at frequency ν_{if} (total radiation energy per unit volume per unit frequency)

$$B_{i\to f} = \frac{2\pi}{3\hbar^2}\left\{\int \Psi_i^{*}\boldsymbol{\mu}\Psi_f\,d\tau\right\}^2$$ for electric dipole transitions

dipole moment operator $\boldsymbol{\mu} = \mu_x\mathbf{i} + \mu_y\mathbf{j} + \mu_z\mathbf{k}$

$\mu_x = \sum_i e_i x_i$ $\mu_y = \sum_i e_i y_i$ $\mu_z = \sum_i e_i z_i$



Lambert-Beer law $\quad -d\mathbf{I} = \alpha_M(\nu)\, \mathbf{I}\, C\, dx$

concentration $\quad C \dfrac{\text{mol}}{\text{L}} = 10^3 \dfrac{\text{cm}^3}{\text{L}} \dfrac{\mathcal{N}_i}{N_{Avo}}$

radiation intensity $\quad \mathbf{I} = \dfrac{c}{n} \rho(\nu_{if})$

radiation energy
flowing through
a 1 cm^2 cross sectional area in 1 second

molar extinction coefficient $\quad \alpha_M(\nu) \quad$ L mol^{-1} cm^{-1}

loss of intensity through layer dx in 1 second with an energy absorption $h\nu_{if}$ for each transition

$$-d\mathbf{I} = \underbrace{\mathcal{N}_i\, B_{i\to f}\, \rho(\nu_{if})\, dx}_{\text{\# photons per second per unit volume}}\ \underbrace{h\nu_{if}}_{\text{energy per photon absorbed}}$$

$$\mathcal{N}_i\, B_{i\to f}\, \rho(\nu_{if})\, dx\, h\nu_{if} = \alpha_M(\nu_{if}) \frac{c}{n} \rho(\nu_{if}) \frac{10^3}{1\text{ sec}} \frac{\mathcal{N}_i}{N_{Avo}} dx$$

$$\therefore \alpha_M(\nu_{if}) = \frac{n\, N_{Avo}}{c\, 10^3} B_{i\to f}\, h\nu_{if} \quad \text{L mol}^{-1}\text{ cm}^{-1}$$

When is the integral $\int \phi_i^* \underset{\text{or } y}{\underset{\text{or } x}{z}} \phi_f \, d\tau$ NOT ZERO?

Atoms: $z = r\cos\theta$

$$\int \psi_{nlm}^* \, r\cos\theta \, \psi_{n'l'm'} \, r^2 dr \sin\theta \, d\theta \, d\phi$$

LEADS to $m = m'$ or $\Delta m = 0$

$l = l' \pm 1$ or $\Delta l = \pm 1$

since $\int_0^{2\pi} e^{-im\phi} e^{im'\phi} d\phi = \delta_{mm'}$

and $\cos\theta \, Y_{lm} = \frac{l+|m|}{2l+1} Y_{l-1,m} + \frac{l-|m|+1}{2l+1} Y_{l+1,m}$

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$$\int \psi_{nlm}^* \begin{array}{c} r\sin\theta\cos\phi \\ \text{or} \\ r\sin\theta\sin\phi \end{array} \psi_{n'l'm'} \, r^2 dr \sin\theta \, d\theta \, d\phi$$

LEADS to $m = m' \pm 1$ or $\Delta m = \pm 1$

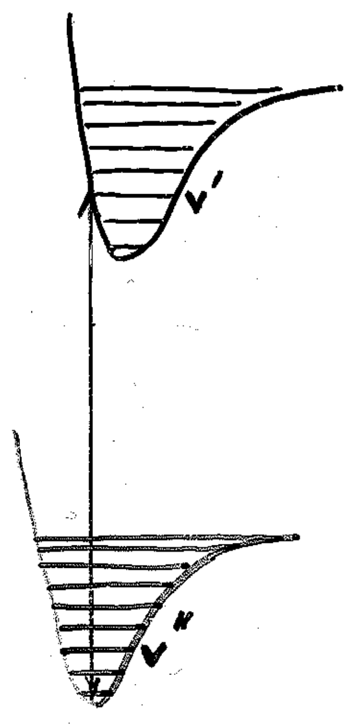
$l = l' \pm 1$ or $\Delta l = \pm 1$

since $\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2}$ $\sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i}$

and $\sin\theta \, Y_{lm} = \sim Y_{l-1,m} + \sim Y_{l+1,m}$

Also $\Delta S = 0$ since no spin in $H^{(1)}$

Molecules:



$$\Psi = \psi_{elec} \cdot \psi_{vib} \cdot \psi_{rot}$$

$$\vec{\mu} = \vec{\mu}_{electrons} + \vec{\mu}_{nuclei}$$

When is the integral

$$\int \Psi''^* \vec{\mu} \, \Psi' \, d\tau \quad \text{NOT ZERO?}$$

A) DIFFERENT ELECTRONIC STATES

$\Delta S = 0$ (no spin operator in $\vec{\mu}$)

THE ELECTRIC DIPOLE MOMENT

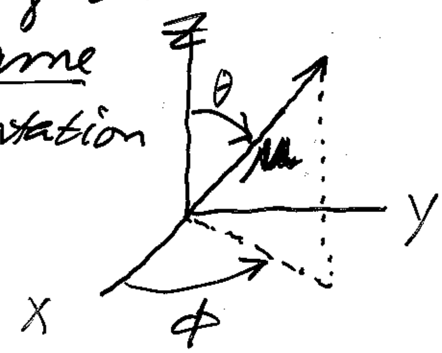
ORIENTATION IN THE LABORATORY FRAME:

$$\mu = \mu_X \hat{I} + \mu_Y \hat{J} + \mu_Z \hat{K} \quad \text{in the LAB frame}$$

where $\hat{I}$, $\hat{J}$, $\hat{K}$ are unit vectors along the laboratory X, Y, and Z axes.

$$\mu_X = \mu \sin\theta\cos\phi \quad \mu_Y = \mu \sin\theta \sin\phi \quad \mu_Z = \mu\cos\theta$$

where θ and ϕ are the angles of orientation relative to the laboratory frame



These are the angles of orientation in the molecular rotational wavefunctions

$$\Theta_{JM}(\theta) \cdot \frac{1}{\sqrt{2\pi}} e^{iM_J\phi}$$

for a diatomic molecule

DEPENDENCE ON BOND LENGTH:

$$\mu = \mu(R) = \mu(R_e) + \left(\frac{d\mu(R)}{dR}\right)_{R=R_e}(R-R_e) + \frac{1}{2!}\left(\frac{d^2\mu(R)}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \ldots$$

ELECTRONIC AND NUCLEAR CONTRIBUTIONS:

$$\mu = \mu_{elec.} + \mu_{nuclear}$$

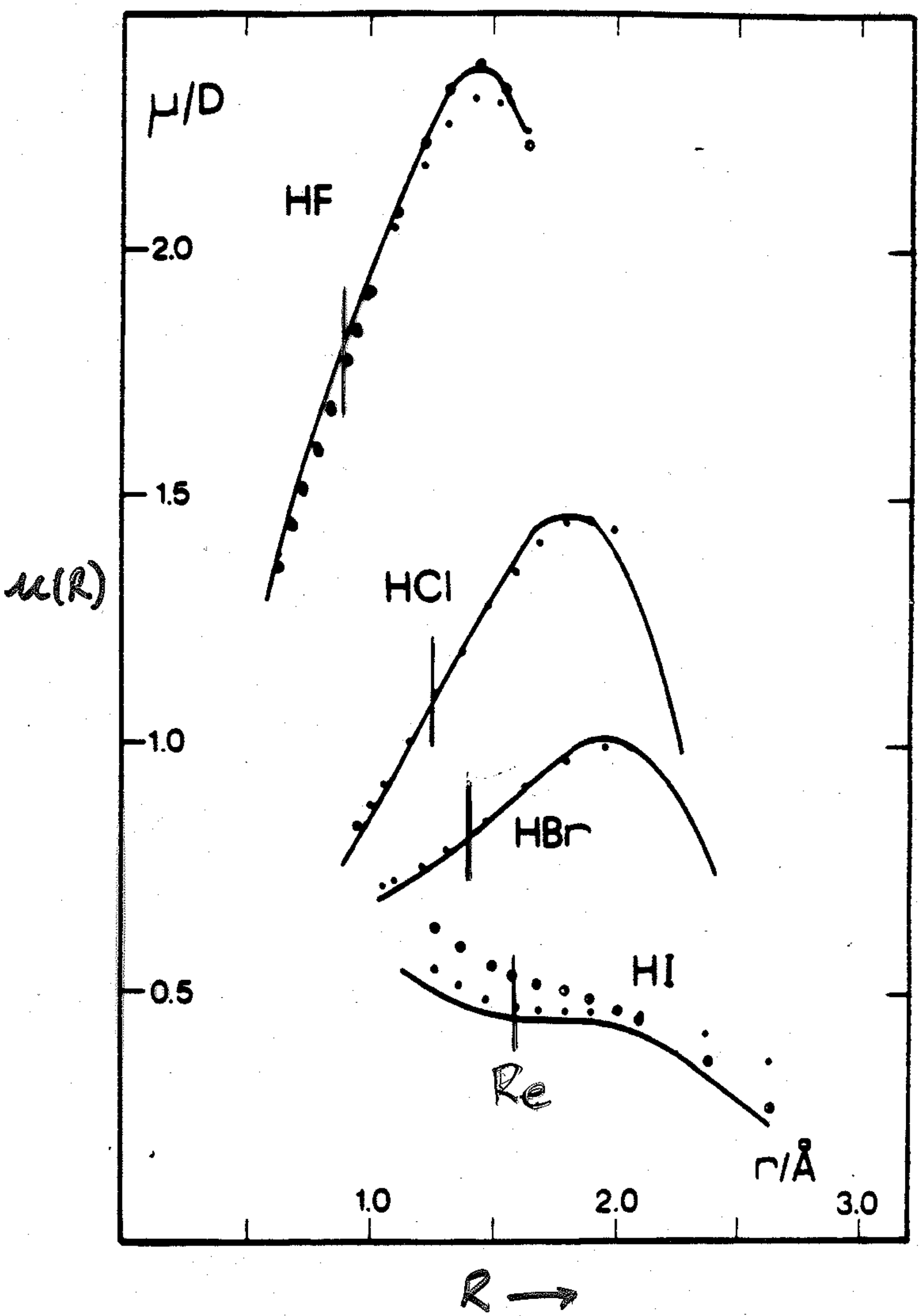
in the molecular frame

$$\mu_{x\,elec.} = \sum_i^{\text{all electrons}} e x_i$$

electronic coordinates in the molecular frame

POLYATOMIC MOLECULES:
- rotation involves 3 angles
- $\mu = \mu(Q_1, Q_2, \cdots) =$

$$\mu(\text{at equil}) + \sum_i^{\text{normal modes}} \left(\frac{\partial\mu}{\partial Q_i}\right)_{equil} Q_i + \sum_{ij} \frac{1}{2!}\frac{\partial^2\mu}{\partial Q_i \partial Q_j} Q_i Q_j + \cdots$$



Ab initio points are from Werner, Reinsch, Rosmus Chem Phys Lett. 78, 311 (1981)

THE ELECTRIC DIPOLE TRANSITION MOMENT:

$$\langle i|\mu|f\rangle = \int \psi_e''^{*} \mu_{elec} \psi_e' d\tau_e \cdot \int \psi_{v''}^{*} \psi_{rot''}^{*} \psi_{v'} \psi_{rot'} d\tau_n$$

$$+ \underbrace{\int \psi_{e''}^{*} \psi_e' d\tau_e}_{\text{ZERO for different electronic states ORTHOGONAL}} \cdot \int \psi_{v''}^{*} \psi_{rot''}^{*} \mu_n \psi_{v'} \psi_{rot'} d\tau$$

μ_{elec} belongs to symmetry species of x or y or z itself

$\Gamma_e'' \otimes \Gamma_{x \text{ or } y \text{ or } z} \otimes \Gamma_e'$ must contain A_1 or A_g or A_{1g} or A_1'
totally symmetric IRREP

That is, if Γ_e'' is totally symmetric (as most ground states are) then, can only observe electronic transitions to excited states for which Γ_e' is the same as Γ_x or Γ_y or Γ_z.
Furthermore, most intense transitions in this case are those for which $\underbrace{\int \psi_{v''}^{*} \psi_{v'} d\tau_{vib}}_{\text{"Franck-Condon factor"}}$ the OVERLAP OF VIBRL FUNCS. is large.

For a diatomic molecule:
Rotational transitions accompanying these are subject to the selection rules $\Delta M_J = 0, \pm 1$ and $\Delta J = \pm 1$ (R branch / P branch)
since the electric dipole moment in the LABORATORY frame has components

$\mu_X = \mu \sin\theta \cos\phi$ $\mu_Y = \mu \sin\theta \sin\phi$ and $\mu_Z = \mu \cos\theta$

and the rotation functions $\psi_{rot}(J'', M_J'')$ and $\psi_{rot}(J', M_J')$ are spherical harmonics $\Theta_{JM}(\theta) \cdot \frac{1}{\sqrt{2\pi}} e^{iM_J\phi}$

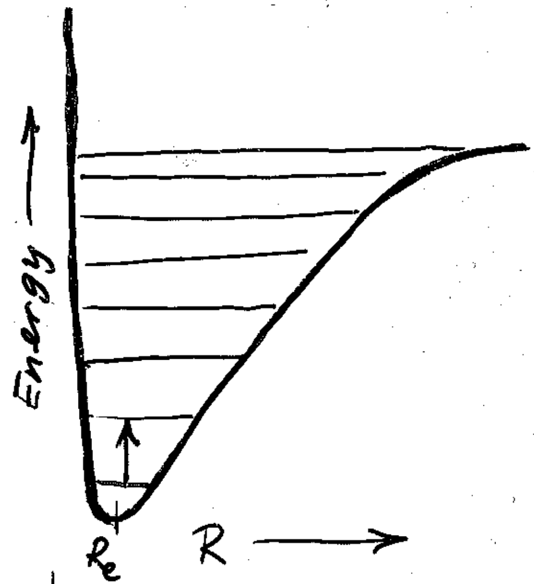
where θ and ϕ are the angles of orientation relative to the LAB frame.

IN OTHER WORDS the integrals for ROTATIONAL TRANSITIONS are the same ones as for ELECTRONIC TRANSITIONS in ATOMS !!

B) THE SAME ELECTRONIC STATE
Diatomic Molecule

$$\vec{\mu} = \mu_x \hat{\imath} + \mu_y \hat{\jmath} + \mu_z \hat{k}$$

$$\mu_x = \mu(R)\sin\theta\cos\phi$$
$$\mu_y = \mu(R)\sin\theta\sin\phi$$
$$\mu_z = \mu(R)\cos\theta$$

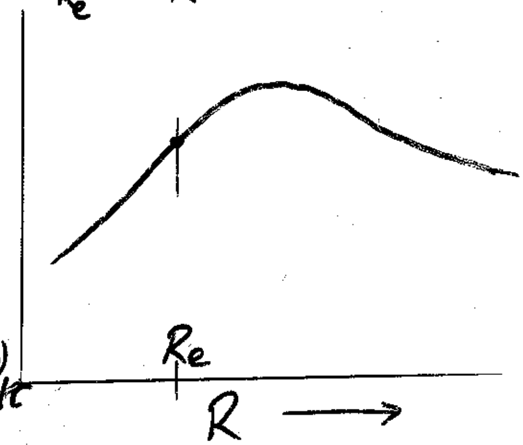


$$\mu(R) = \mu(R_e) + \left(\frac{d\mu(R)}{dR}\right)_{R=R_e}(R-R_e) + \cdots$$

When is the integral

$$\int \Psi''^{*}\vec{\mu}\,\Psi'\,d\tau \quad \text{NOT ZERO?}$$

$\mu(R)$



$$= \mu(R_e)\underline{\int \psi^{*}_{v''}\psi_{v'}\,d\tau_{vib}} \cdot \int Y^{*(\theta,\phi)}_{J''M_J''}\begin{pmatrix}\sin\theta\cos\phi\\ \text{or}\\ \sin\theta\sin\phi\\ \text{or}\\ \cos\theta\end{pmatrix} Y^{(\theta,\phi)}_{J'M_J'}\,d\tau$$

$$+\left(\frac{d\mu(R)}{dR}\right)_{R=R_e}\int \psi^{*}_{v''}(R-R_e)\psi_{v'}\,d\tau_{vib} \cdot \int Y^{*(\theta,\phi)}_{J''M_J''}\begin{pmatrix}\sin\theta\cos\phi\\ \text{or}\\ \sin\theta\sin\phi\\ \text{or}\\ \cos\theta\end{pmatrix} Y^{(\theta,\phi)}_{J'M_J'}\,d\tau$$

$+\cdots$

a) THE SAME VIBRATIONAL STATE (MICROWAVE SPECTRUM)
that $v'' = v'$

First term: $\overbrace{\text{NORMALIZATION INTEGRAL FOR } \psi_{vib}}^{1}$ $\underline{\mu(R_e)}$ $\underbrace{\int Y^{*(\theta,\phi)}_{J''M_J''}\begin{pmatrix}\sin\theta\cos\phi\\ \text{or}\\ \sin\theta\sin\phi\\ \text{or}\\ \cos\theta\end{pmatrix} Y^{(\theta,\phi)}_{J'M_J'}\,d\tau}$

NO MICROWAVE SPECTRUM
AT ALL UNLESS MOLECULE
HAS A PERMANENT ELECTRIC
DIPOLE MOMENT

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

H_2, N_2, Cl_2, etc. have no Microwave spectrum

Second and all other following terms:

Diatomic molecule $\left(\frac{d\mu}{dR}\right) = 0$ also for $H_2, N_2, Cl_2, \ldots$ homonuclear diatomics

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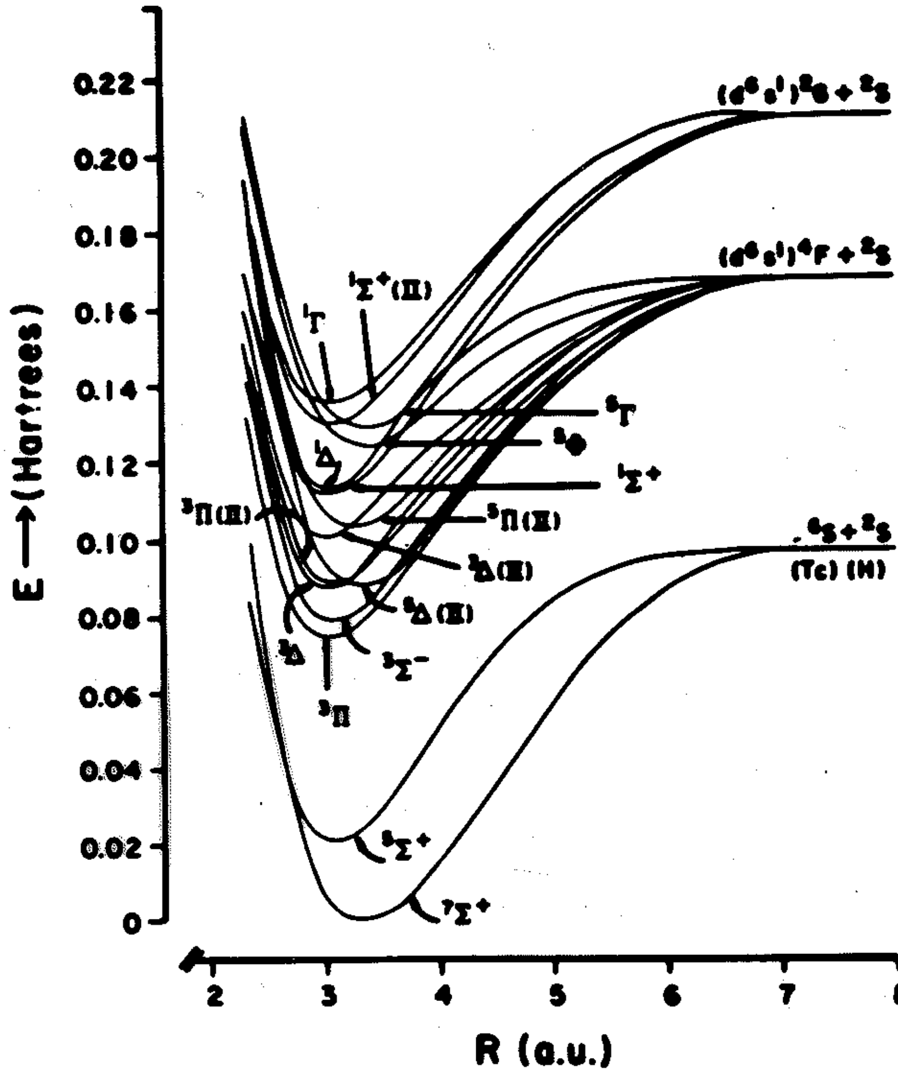
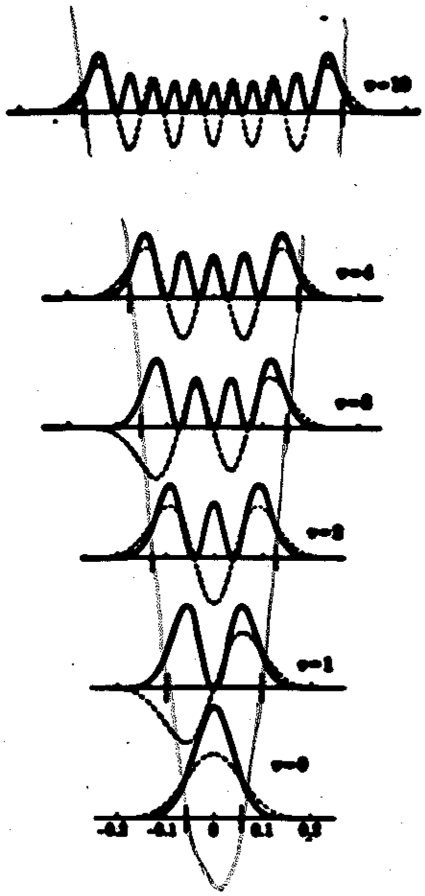

E ⟶ (Hartrees)
R (a.u.)
$(d^6s^1)^2S + {}^2S$
$(d^6s^1)^4F + {}^2S$
$^6S + {}^2S$
(Tc) (H)
$^1\Gamma$
$^1\Sigma^+(II)$
$^5\Gamma$
$^5\Phi$
$^1\Delta$
$^1\Sigma^+$
$^3\Pi(II)$
$^5\Pi(II)$
$^3\Delta(II)$
$^5\Delta(II)$
$^3\Delta$
$^3\Sigma^-$
$^3\Pi$
$^5\Sigma^+$
$^7\Sigma^+$

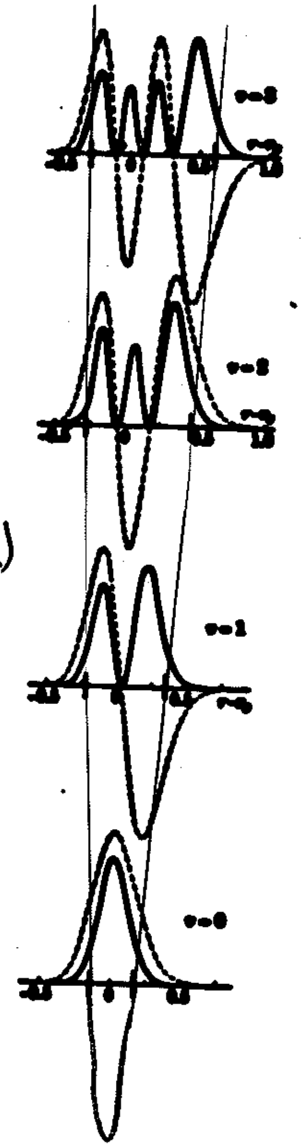
VIBRATIONAL WAVEFUNCTIONS for a HARMONIC OSCILLATOR

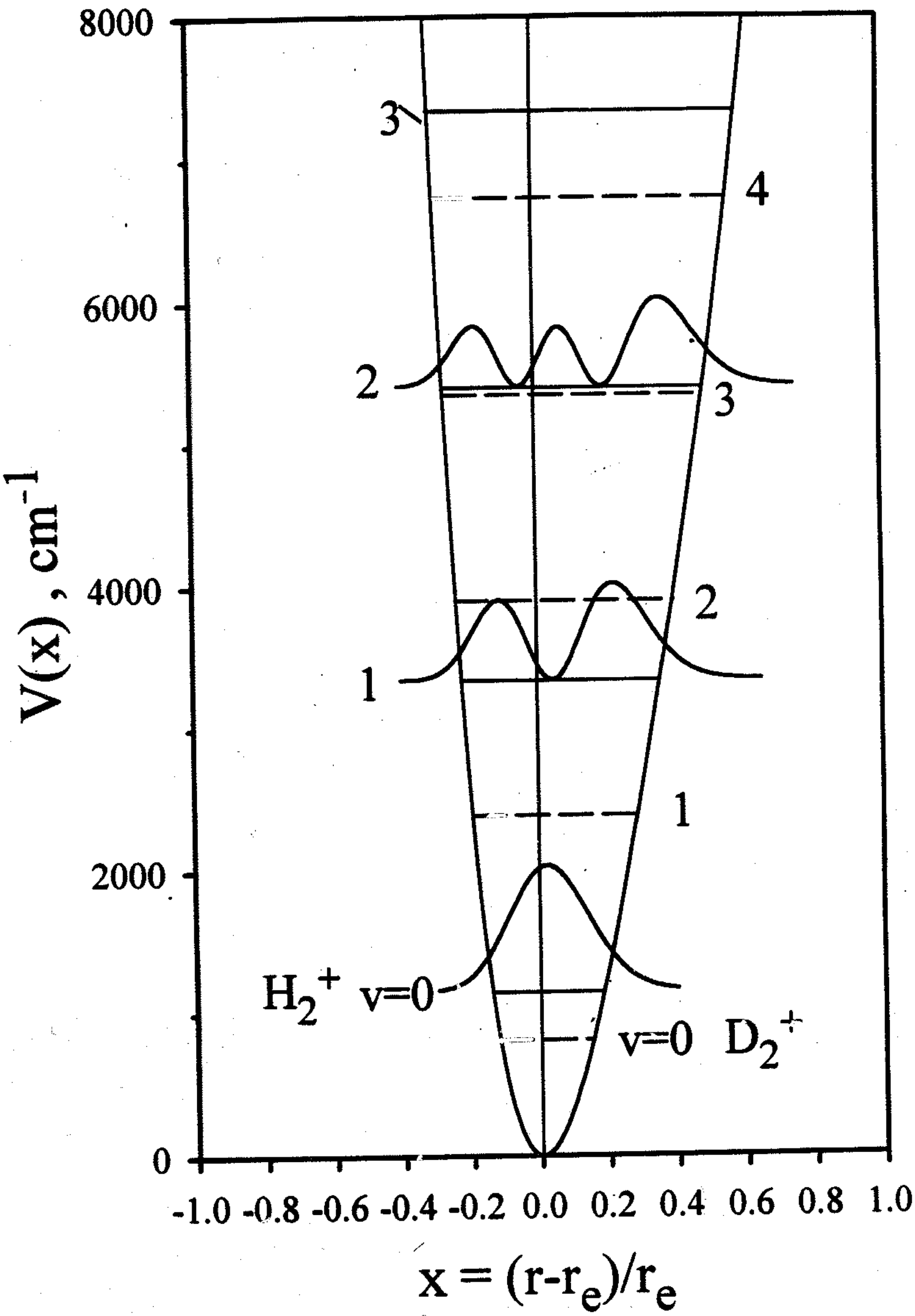
U(R)



VIBRATIONAL WAVEFUNCTIONS for a DIATOMIC MOLECULE

U(R)





8000
6000
4000
2000
0
V(x) , cm-1
3
4
2
3
2
1
1
H2+ v=0
v=0 D2+
-1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0
x = (r-re)/re

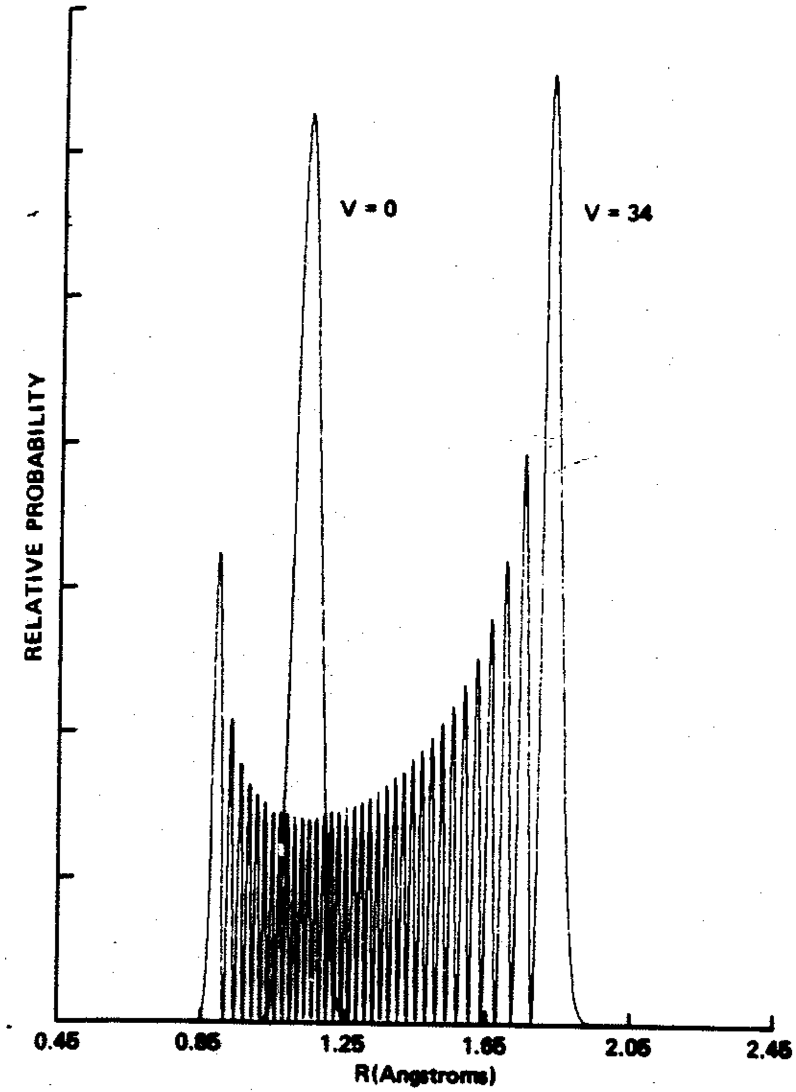


FIG. 1. Probability amplitude for nuclear position in the $V = 0$ and $V = 34$ vibrational states. For proper relative scaling multiply the vertical component of the $V = 0$ graph by 2.5.

CO molecule

from Can. J. Phys. 62, 1579 (1984)

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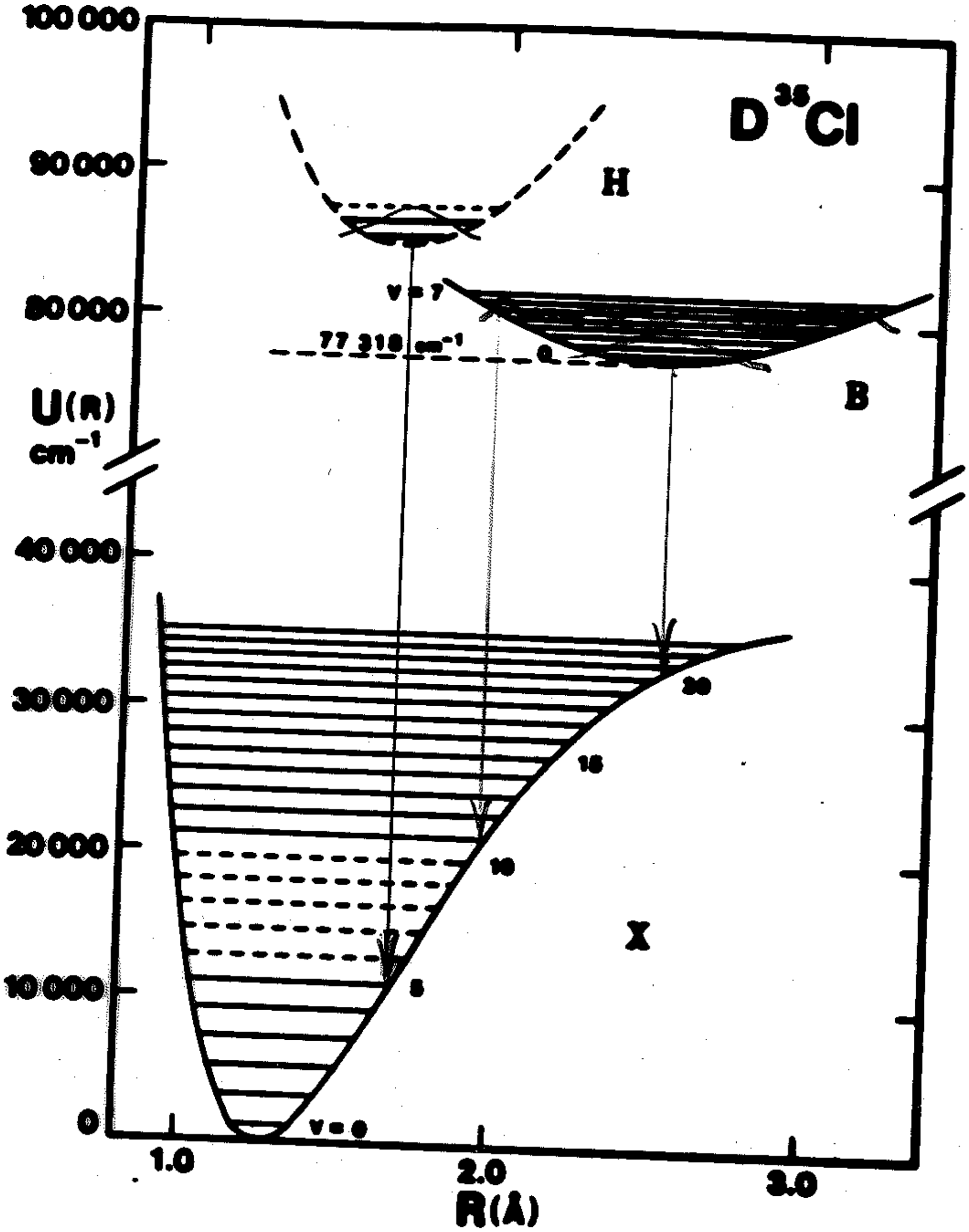
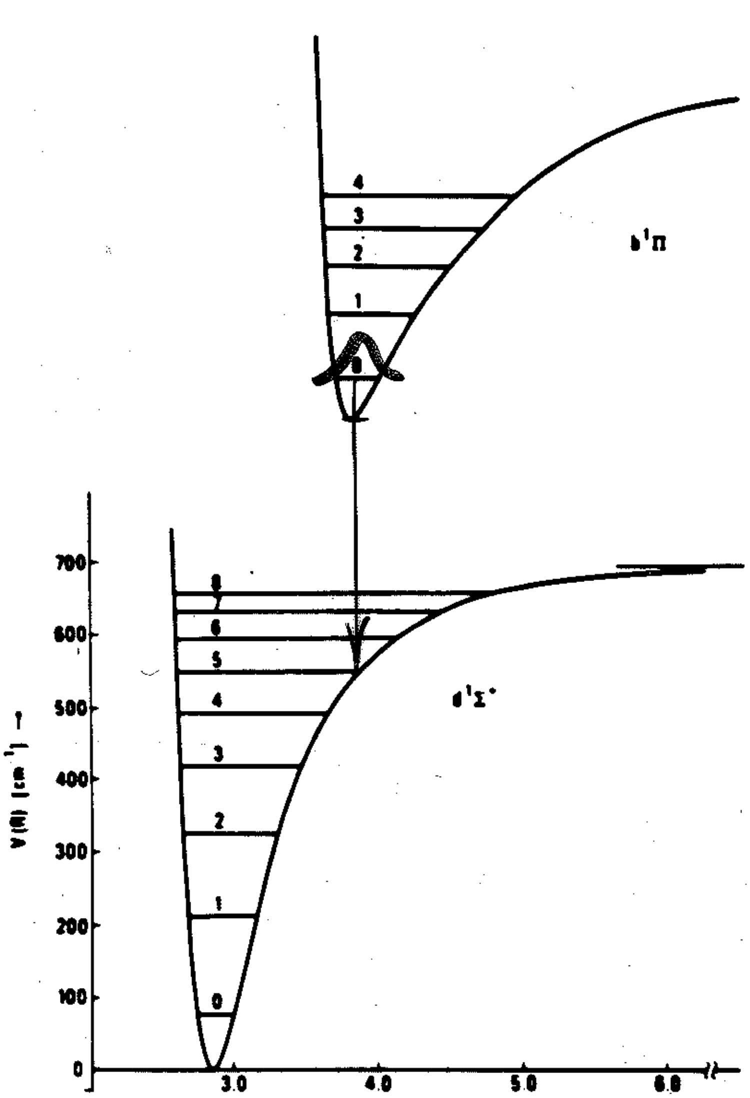
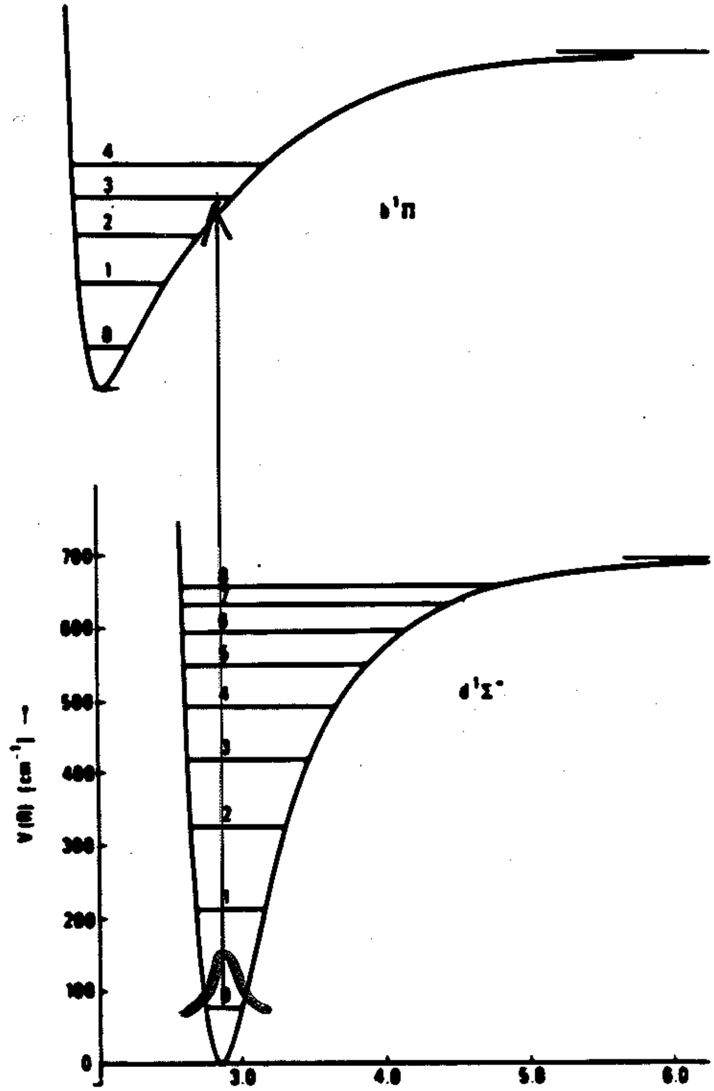
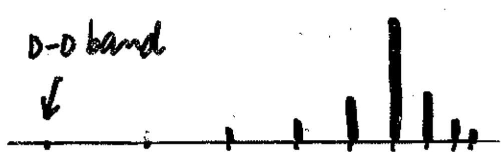

100 000
90 000
80 000
40 000
30 000
20 000
10 000
0
U(R)
cm^{-1}
D^{35}Cl
H
B
X
v = 7
77 318 cm^{-1}
0
20
15
10
5
v = 0
1.0
2.0
3.0
R(Å)

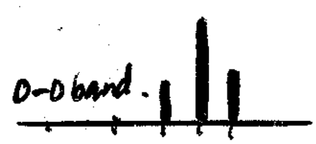




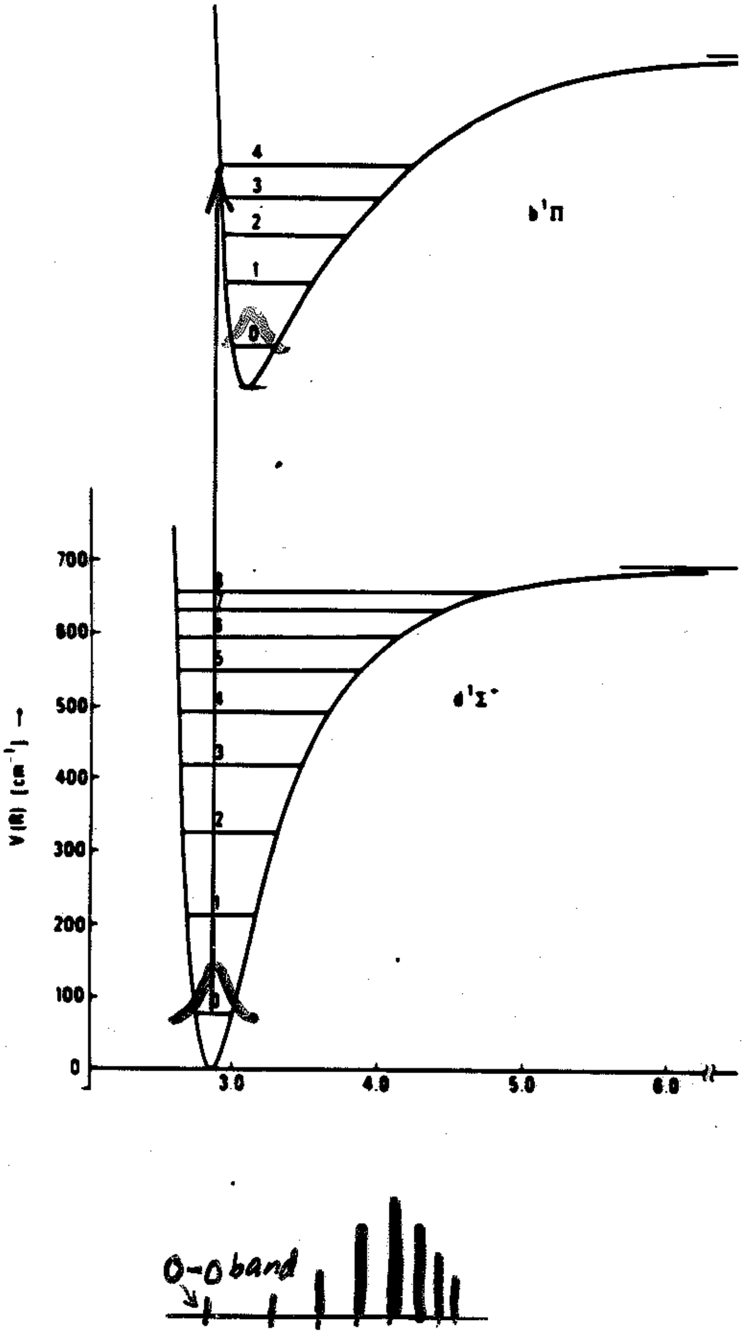


EMISSION SPECTRUM

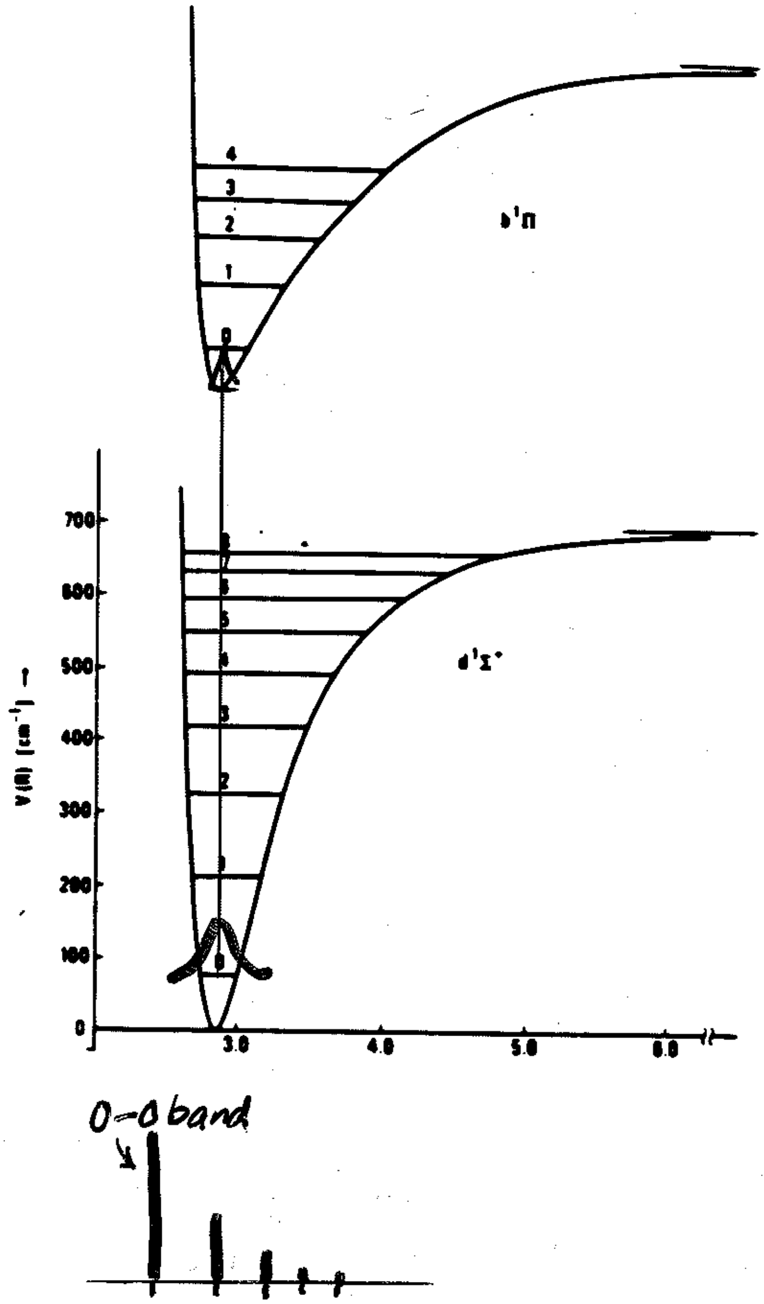
shows the vibrational spacing of the GROUND ELECTRONIC STATE



ABSORPTION SPECTRUM



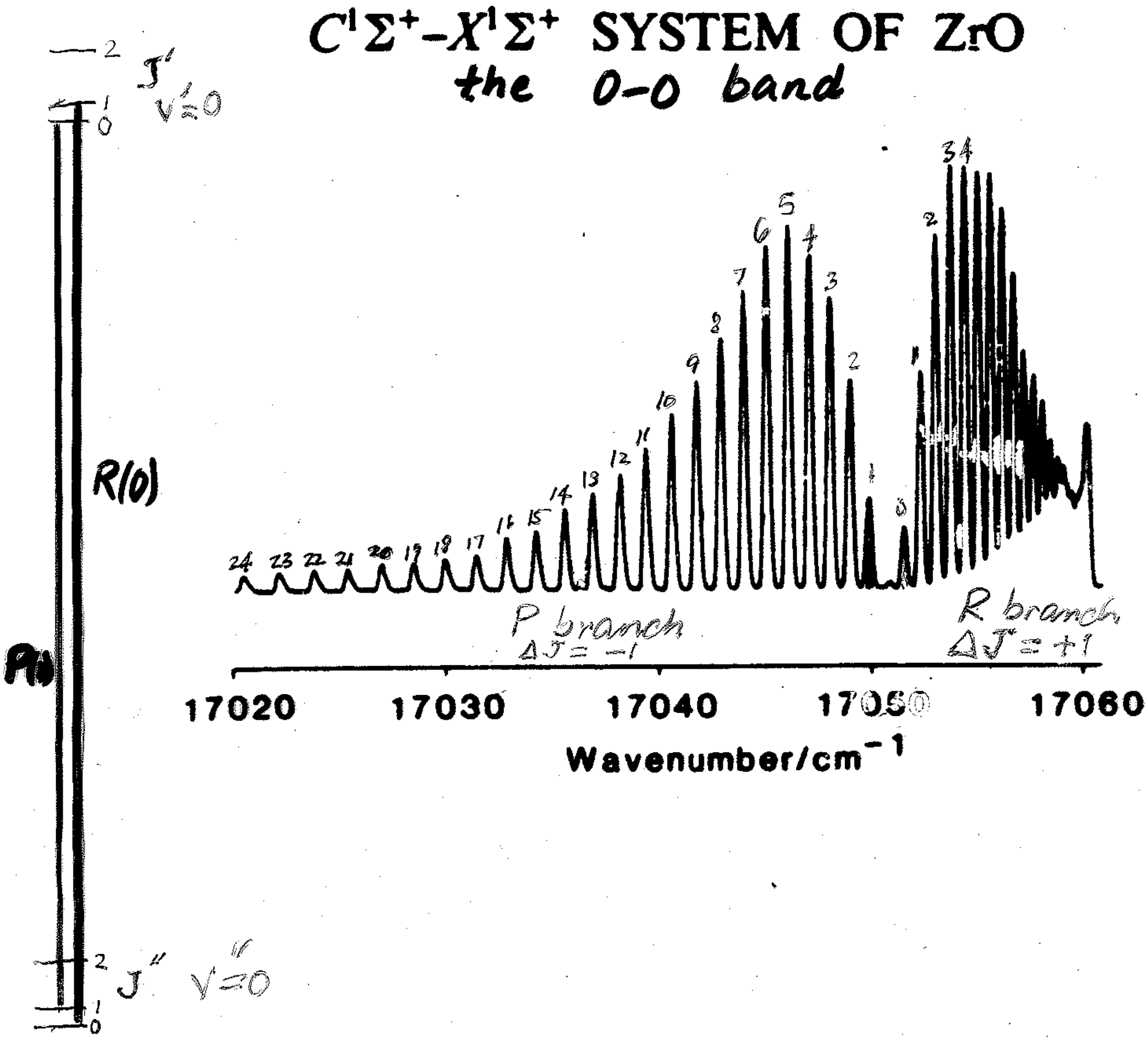
ABSORPTION SPECTRUM
shows the vibrational
spacing of the
EXCITED ELECTRONIC STATE

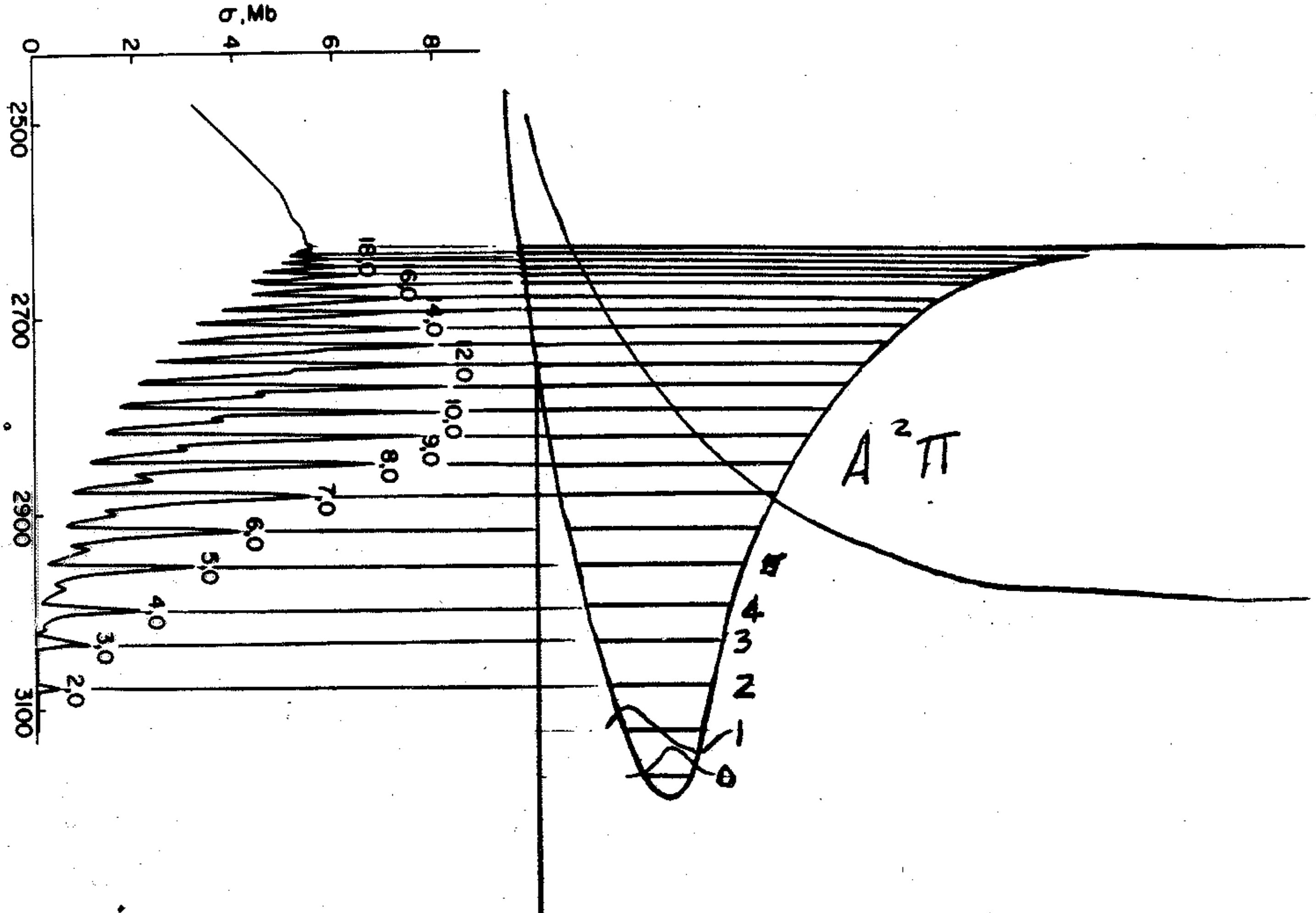


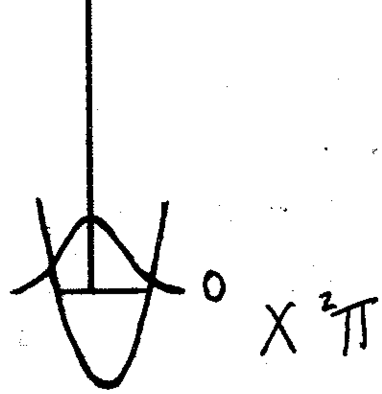
ABSORPTION SPECTRUM

RELATIVE INTENSITIES of the VIBRATIONAL BANDS CORRESPONDING TO $v' \leftarrow v''$ CHANGES ACCOMPANYING ELECTRONIC TRANSITION are determined by

$$\int \psi^*_{v''} \psi_{v'} \, d\tau$$


$C^1\Sigma^+ - X^1\Sigma^+$ SYSTEM OF ZrO
the 0-0 band
J'
v' = 0
R(0)
P(1)
J''
v'' = 0
P branch
ΔJ = -1
R branch
ΔJ = +1
17020
17030
17040
17050
17060
Wavenumber/cm⁻¹





(making use of the fact that except for $v=0$, vibrational functions have their maximum absolute values at the turning points (i.e., <u>on</u> the potential $U(R)$ curve) and <u>vertical</u> transitions.

Electronic Transitions in Diatomic Molecules

$$E = \overbrace{U_\alpha(R_e)}^{T_e} + \overbrace{\boxed{hY_{00} + h\nu_e(v+\tfrac{1}{2}) - h\nu_e x_e (v+\tfrac{1}{2})^2}}^{G(v)}$$

$$F(J) \left| \begin{array}{l} + h B_e J(J+1) - h D_e [J(J+1)]^2 \\ - h\alpha_e(v+\tfrac{1}{2}) J(J+1) + \cdots \end{array} \right.$$

usually we leave out h and use Hz or cm^{-1}

Franck-Condon determines which $v'' \rightarrow v'$ most likely to occur

For the time, ignore D_e term centrifugal stretching since it is small and consider the difference between E' and E'':

$$E' - E'' = [(T_e' - T_e'') + G'(v') - G''(v'')] \quad \text{band origins}$$
$$+ [F'(J') - F''(J'')] \quad P, Q \text{ or } R \text{ branch}$$

The frequencies of the band origins are:

$$G'(v') - G''(v'') = \nu_e'(v'+\tfrac{1}{2}) - \nu_e''(v''+\tfrac{1}{2}) + Y_{00}' - Y_{00}''$$
$$- (\nu_e x_e)'(v'+\tfrac{1}{2})^2 + (\nu_e x_e)''(v''+\tfrac{1}{2})^2$$

The frequencies of the rotational lines relative to the band origins are: where $B_v \equiv B_e - \alpha_e(v+\tfrac{1}{2})$, J is lower level rotational quantum number.

$$R(J) \quad F'(J+1) - F''(J) = (B'_{v'} + B''_{v''})(J+1) + (B'_{v'} - B''_{v''})(J+1)^2$$

$$Q(J) \quad F'(J) - F''(J) = (B'_{v'} - B''_{v''})J + (B'_{v'} - B''_{v''})J^2$$

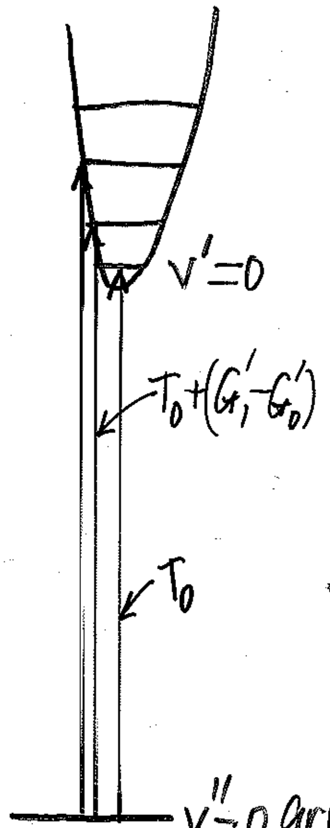
if present

$$P(J) \quad F'(J-1) - F''(J) = -(B'_{v'} + B''_{v''})J + (B'_{v'} - B''_{v''})J^2$$

Usual case: If $r_e' > r_e''$ $B'_{v'} < B''_{v''} \longrightarrow$ get band head in R branch

Unusual: If $r_e' < r_e''$ $B'_{v'} > B''_{v''} \longrightarrow$ band head in P branch

In absorption: CAN FIND OUT DISSOCIATION ENERGY OF UPPER STATE



observed absorption frequencies $\longrightarrow$

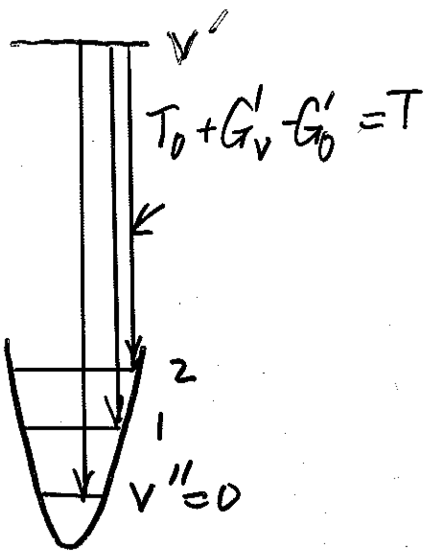
$\Delta G_1'$

$0 \leftarrow 0$	$1 \leftarrow 0$	$2 \leftarrow 0$	$3 \leftarrow 0$	...
T_0	$T_0+(G_1'-G_0')$	$T_0+(G_2'-G_0')$	$T_0+(G_3'-G_0')$	

$$\Delta G_1' = T_0+(G_1'-G_0') - T_0 = G_1'-G_0'$$

$$\Delta G_2' = [T_0+(G_2'-G_0')] - [T_0+G_1'-G_0'] = G_2'-G_1' \quad \ldots etc.$$

In emission:



emitted frequencies: $\longrightarrow$

$v'\to 3$	$v'\to 2$	$v'\to 1$	$v'\to 0$
	$T-(G_2''-G_0'')$	$T-(G_1''-G_0'')$	T

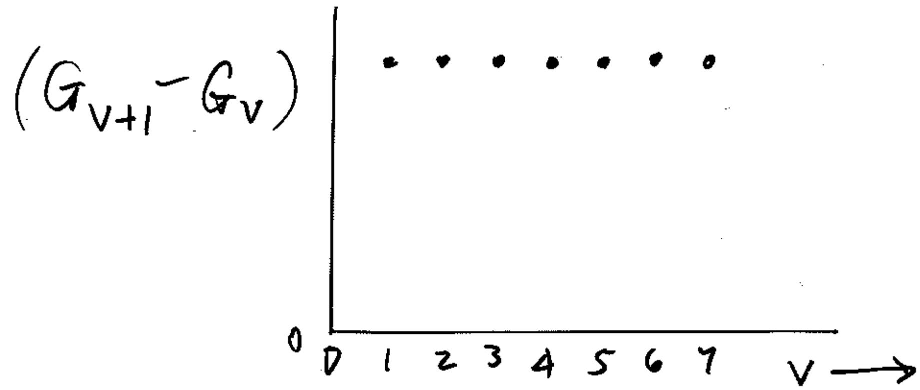
CAN FIND OUT DISSOCIATION ENERGY OF LOWER STATE

$$\Delta G_1'' = T-(G_1''-G_0'') - T = -(G_1''-G_0'')$$

$$\Delta G_2'' = T-(G_2''-G_0'')-[T-(G_1''-G_0'')] = -(G_2''-G_1'')$$

HARMONIC OSCILLATOR:

$$G_{v+1} - G_v = \Delta G_v = h\nu_e \quad \text{for any } v$$

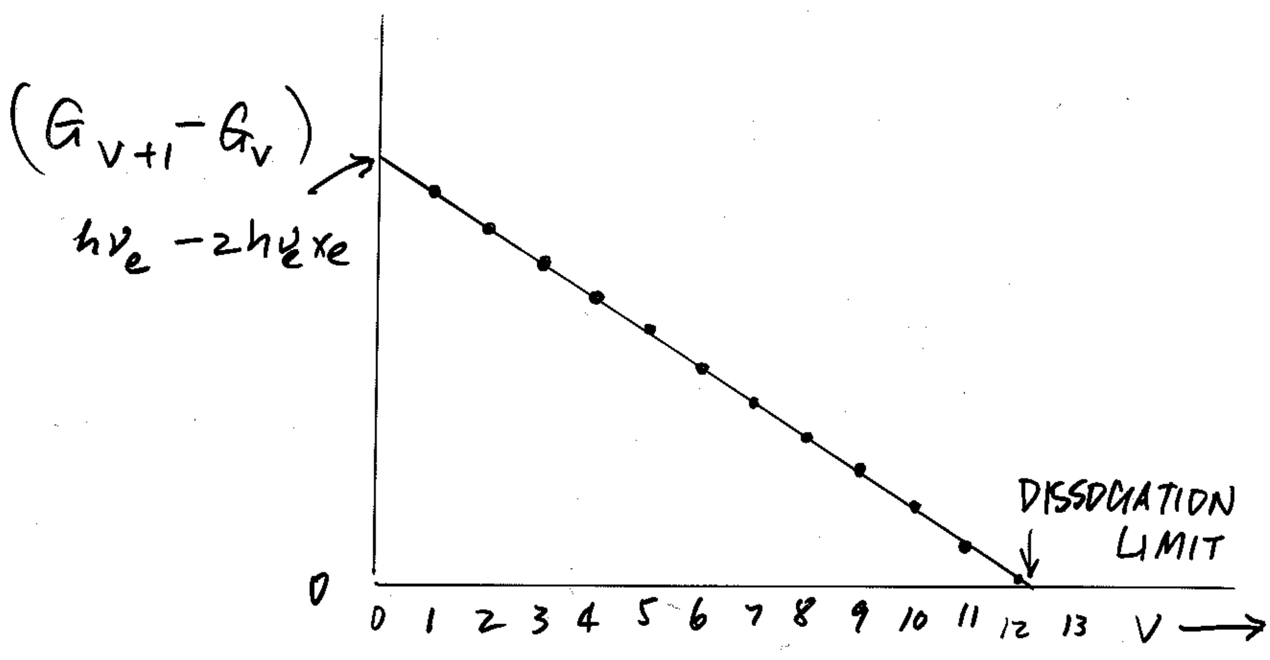


ANHARMONIC OSCILLATOR:

$$G_v = h\nu_e (v + \tfrac{1}{2}) - h\nu_e x_e (v + \tfrac{1}{2})^2$$

$$G_{v+1} - G_v = h\nu_e + - h\nu_e x_e \left[\begin{array}{l} v^2 + 3v + \frac{9}{4} \\ -v^2 - v - \frac{1}{4} \end{array} \right]$$

$$= h\nu_e - 2h\nu_e x_e (v+1)$$

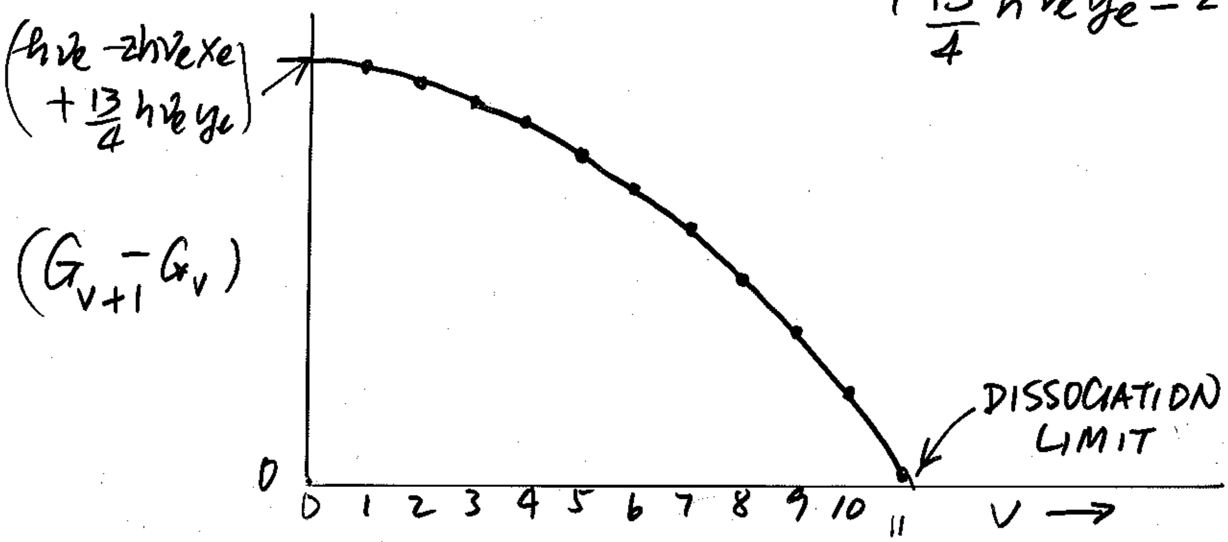


TYPICAL DIATOMIC MOLECULE

$$G_v = h\nu_e(v+\tfrac{1}{2}) - h\nu_e x_e (v+\tfrac{1}{2})^2 + h\nu_e y_e (v+\tfrac{1}{2})^3$$

$$G_{v+1} - G_v = h\nu_e - 2h\nu_e x_e (v+1) + h\nu_e y_e \underbrace{\left[v^3 + \tfrac{9}{2}v^2 + \tfrac{27}{4}v + \tfrac{27}{8} - (v^3 + \tfrac{3}{2}v^2 + \tfrac{3}{4}v + \tfrac{1}{8}) \right]}_{3v^2 + 6v + \frac{13}{4}}$$

$$= h\nu_e + \begin{pmatrix} 6h\nu_e y_e \\ -2h\nu_e x_e \end{pmatrix} v + 3h\nu_e y_e v^2 + \tfrac{13}{4} h\nu_e y_e - 2h\nu_e x_e$$



Birge - Sponer plots for determination of Dissociation energies of ground or excited electronic states

Example: an excited state

THE SCHUMANN-RUNGE BANDS OF $^{18}O_2$

JOURNAL OF MOLECULAR SPECTROSCOPY **131,** 96–112 (1988)

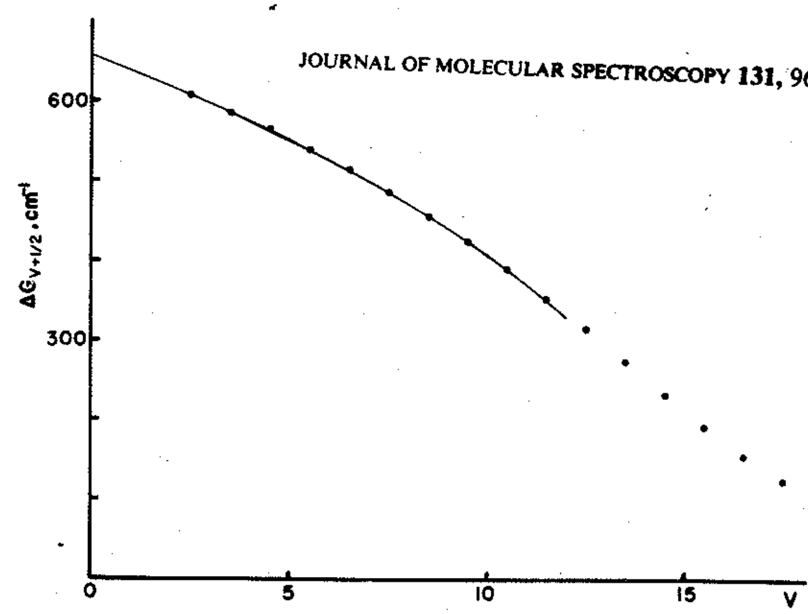


FIG. 3. Plot of vibrational spacings $\Delta G_{v+1/2}$ versus v for the $B^3\Sigma_u^-$ state of $^{18}O_2$. The curve is calculated from the vibrational constants of $^{16}O_2$ and reduced mass ratio.

Another example (next 3 pages) is that of ^7LiH molecule from J. Mol. Spectrosc. 76, 17 (1979).

TABLE II

Band Origins of the $A^1\Sigma^+ - X^1\Sigma^+$ System of ^7LiH

v' \ v''	2		3		4		5		6		7		8		9	
0			21997.81	1227.77	20770.04	1185.45	19584.59	1143.90	18440.69	1102.59	17338.10	1061.71	16276.39	1021.16	15255.23	980.24
			280.72		280.81		280.75		280.91		280.93		280.87			
1	23549.46	1270.93	22278.53	1227.68	21050.85	1185.51	19865.34	1143.74	18721.60	1102.57	17619.03	1061.77	16557.26			
	312.98		313.04		312.85		312.96						313.00			
2	23862.44	1270.87	2259[illegible].57	1227.87	21363.70	1185.40	20178.30						16870.26	1021.16	15849.10	
	335.69		335.69		335.62		335.91						335.55			
3	24198.13	1270.87	22927.26	1227.94	21699.32	1185.11[a]	20514.21	1143.64[a]	19370.57	1102.73	18267.84	1062.03[a]	17205.81			
	352.82		352.90				352.73		352.52							
4	24550.95	1270.79	23280.16				20866.94	1143.85	19723.09						16537.59	980.59
	366.14						365.70									
5	24917.09				22417.88	1185.24	21232.64						17924.83			
					375.72											
6					22793.60				20464.45							
									382.94							
7									20847.39							

v' \ v''		10[b]		11		12
0	980.24	14274.99	939.97	13335.02		
				280.86		
1				13615.88	897.97	12717.91

[a]These values were not used in the averaging due to the poor quality of associated bands.

Note. The upper entry for each band is the band origin (in cm^{-1}). Underlined numbers between bands are $\Delta G'$ or $\Delta G''$ values.

V'' V' $\Delta G'$ $\Delta G''$

average these

$$\begin{array}{r} 23549.46 \\ -\ 22278.53 \\ \hline 1270.93 \end{array}$$

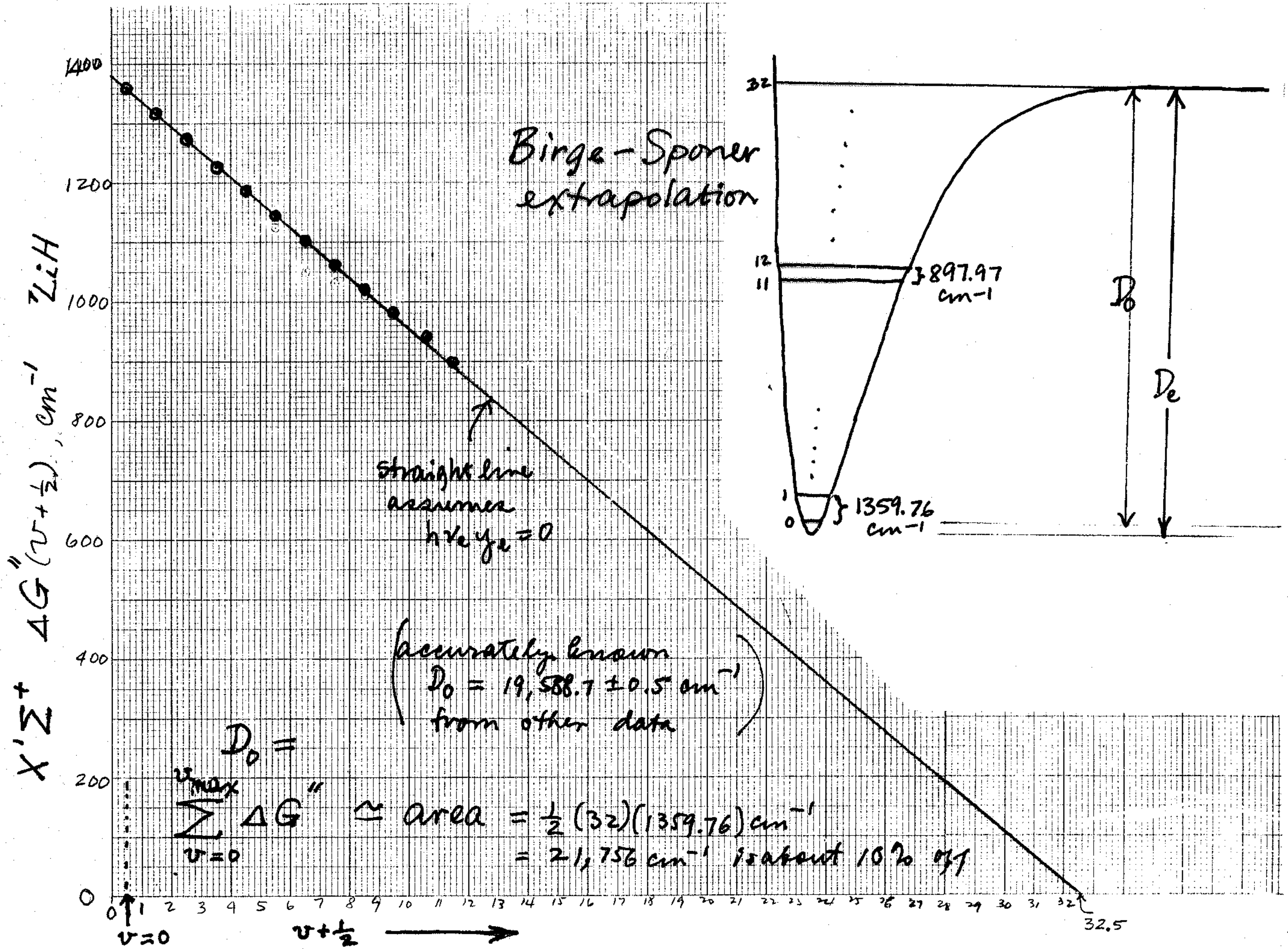
TABLE III

Average Experimental Vibrational Spacings $\Delta G'$ and $\Delta G''$ (in cm^{-1}) in the $A^1\Sigma^+$ and $X^1\Sigma^+$ States of ^7LiH

$v + \frac{1}{2}$	$\Delta G'(v+\frac{1}{2})$ in $A\ ^1\Sigma^+$ Table II	$\Delta G'(v+\frac{1}{2})$ in $A\ ^1\Sigma^+$ Ref. 4	$\Delta G''(v+\frac{1}{2})$ in $X\ ^1\Sigma^+$ Table II	$\Delta G''(v+\frac{1}{2})$ in $X\ ^1\Sigma^+$ Ref. 4
1/2	<u>280.84</u>	280.81		<u>1359.76</u>
3/2	<u>312.97</u>	312.81		<u>1314.85</u>
5/2	<u>335.69</u>	335.45	1270.87	1270.91
7/2	352.74	<u>352.79</u>	<u>1227.82</u>	1228.92
9/2	365.92	<u>365.85</u>	<u>1185.40</u>	1185.33
11/2	375.72	<u>375.60</u>	<u>1143.83</u>	
13/2	382.94	<u>382.68</u>	<u>1102.63</u>	
15/2		<u>387.55</u>	<u>1061.74</u>	
17/2		<u>390.37</u>	<u>1021.16</u>	
19/2		<u>391.59</u>	<u>980.42</u>	
21/2		<u>391.05</u>	<u>939.97</u>	
23/2		<u>389.19</u>	<u>897.97</u>	
25/2		<u>385.94</u>		
27/2		<u>381.32</u>		
29/2		<u>375.21</u>		

Note. Recommended values are underlined.

See graph (Birge-Sponer plot) on next page for the $X\ ^1\Sigma^+$ state only.
Can of course do the same for the excited electronic state $A\ ^1\Sigma^+$ as well.


Birge-Sponer extrapolation
$X^1\Sigma^+ \quad \Delta G''(v+\frac{1}{2})$, cm^{-1} ^7LiH
1400
1200
1000
800
600
400
200
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32
32.5
$v=0$
$v+\frac{1}{2}$
straight line assumes $h\nu_e y_e = 0$
(accurately known $D_0 = 19{,}588.7 \pm 0.5\ cm^{-1}$ from other data)
$D_0 = \sum_{v=0}^{v_{max}} \Delta G'' \simeq \text{area} = \frac{1}{2}(32)(1359.76)\ cm^{-1}$
$= 21{,}756\ cm^{-1}$ is about 10% off
32
12
11
1
0
897.97 cm-1
1359.76 cm-1
D_0
D_e

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b) DIFFERENT VIBRATIONAL STATES (INFRARED SPECTRUM)

First term is ZERO since $\int \psi^*_{v''} \psi_{v'} d\tau_{vib}$ functions are ORTHOGONAL

Second term :

$$\left(\frac{d\mu(R)}{dR}\right)_{R=R_e} = 0 \text{ also for } H_2, N_2, Cl_2, \dots \text{ homonuclear diatomics}$$

HO: For a harmonic oscillator with eigenfunction $\psi_v(\underbrace{R-R_e}_{\text{call it } q})$

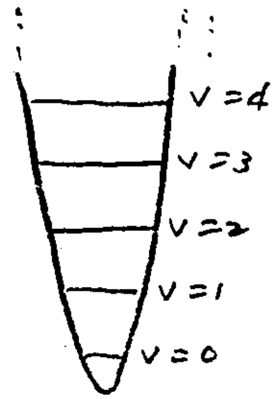


Table of integrals:

$$\int \psi^*_{v''}(R-R_e)\psi_{v'}\, d\tau \qquad \left(\frac{h}{4\pi \nu \mu}\right)^{1/2} \begin{bmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & 0 & 0 \\ \sqrt{1} & 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 & \sqrt{4} & 0 & 0 \\ & & \ddots & & & \ddots & \end{bmatrix}$$

$$\Delta V = \pm 1$$

$$q_{mn} = \left[\sqrt{n}\,\delta_{m,n-1} + \sqrt{n+1}\,\delta_{m,n+1}\right]\left(\frac{h}{4\pi \nu \mu}\right)^{\frac{1}{2}}$$

Other HO integrals

$$q^2_{mn} = \left\{\sqrt{n(n-1)}\,\delta_{m,n-2} + (2n+1)\delta_{mn} + \sqrt{(n+1)(n+2)}\,\delta_{m,n+2}\right\}\left(\frac{h}{4\pi \nu \mu}\right)$$

$$q^3_{mn} = \left\{\sqrt{n(n-1)(n-2)}\,\delta_{m,n-3} + 3n^{3/2}\delta_{m,n-1} + 3(n+1)^{3/2}\delta_{m,n+1} + \sqrt{(n+1)(n+2)(n+3)}\,\delta_{m,n+3}\right\}\left(\frac{h}{4\pi \nu \mu}\right)^{3/2}$$

IN OTHER WORDS, for a HARMONIC OSCILLATOR the following integrals are NOT ZERO!

$\langle q \rangle_{v,v\pm1}$ $\quad \langle q^2 \rangle_{v,v;\ v,v\pm2}$ $\quad \langle q^3 \rangle_{v,v\pm1;\ v,v\pm3}$ $\quad \langle q^4 \rangle_{v,v;\ v,v\pm2;\ v,v\pm4}$

similarly for the linear momentum

$\langle p \rangle_{v,v\pm1}$, $\{\langle qp \rangle \text{ or } \langle pq \rangle \text{ or } \langle p^2 \rangle\}_{v,v;\ v,v\pm2}$, etc...

For the <u>true</u> VIBRATIONAL <u>WAVEFUNCTIONS</u>: $\langle v''|\mu(R)|v'\rangle$

$\langle v''|\ \mu(R_e) + \left(\frac{d\mu}{dR}\right)_{Re} q + \frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{Re} q^2 + \cdots |v'\rangle$ integral

can be TRANSFORMED INTO the **HO integral**

$$\begin{aligned}\langle HO|\ & \mu(R_e) + \left(\frac{d\mu}{dR}\right)_{Re} q + \frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{Re} q^2 + \frac{1}{3!}\left(\frac{d^3\mu}{dR^3}\right)_{Re} q^3 \\ & + \left(\frac{d\mu}{dR}\right)_{Re}(k q^2 + k p^2) \\ & + \left(\frac{d\mu}{dR}\right)_{Re}\left[(f+k^2)p^2 q + (f+k^2)q^3\right] \\ & + \frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{Re}(k p^2 q + k q^3) + \cdots\ |HO\rangle\end{aligned}$$

where k stands for a quantity proportional to the quadratic force constant $\left(\frac{d^2U}{dR^2}\right)_{Re}$

and f stands for a quantity proportional to the cubic force constant $\left(\frac{d^3U}{dR^3}\right)_{Re}$

Therefore, for a diatomic molecule, the most probable transitcon

$v = 0$ to $v = 1$

has a probability which is proportional to $\left(\frac{d\mu}{dR}\right)_{Re}$

Less probable but observable also are the transitions

$v = 0$ to $v = 2$ and others ($v=0$ to $v=3$, etc)

which has a probabilty which is proportional to

$$\left\{\frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{Re} + \left(\frac{d\mu}{dR}\right)_{Re} k\right\}$$

or $\left\{\frac{1}{3!}\left(\frac{d^3\mu}{dR^3}\right)_{Re} + \left(\frac{d\mu}{dR}\right)_{Re}(f+k^2) + \frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{Re} k\right\}$ etc...

$$E = U_\alpha(R_e) + (v+\tfrac{1}{2})\nu_e - x_e\nu_e\,(v+\tfrac{1}{2})^2 + y_e\nu_e\,(v+\tfrac{1}{2})^3 + B_eJ(J+1) - D_e[J(J+1)]^2 - \alpha_e(v+\tfrac{1}{2})J(J+1) + Y_{00}$$

where all spectroscopic quantities are expressed in energy units (or the corresponding frequency or wavenumbers). In energy units, the following are positive quantities:

$B_e \equiv \hbar^2 / 2\mu\, R_e^2$ — B_e rotational constant

$h x_e\nu_e \equiv \frac{1}{4} B_e^2/(h\nu_e)^2 \cdot \{ (^{10}/_3)B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 - U^{iv}(R_e)R_e^4 \}$

$x_e\nu_e$ anharmonicity constant

$D_e \equiv 4\, B_e^3/(h\nu_e)^2$

D_e centrifugal distortion constant

$\alpha_e \equiv -\,2\, B_e^2/h\nu_e \cdot \{3 + 2\, B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 \}$

α_e vibrational rotational coupling constant

$Y_{00} \equiv B_e^2/16(h\nu_e)^2 \cdot \{ U^{iv}(R_e)R_e^4 - (^{14}/_9)B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 \}$

$h\nu_e \equiv (h/2\pi)[\, U''(R_e)/\mu\,]^{1/2}$ — ν_e harmonic frequency

μ reduced mass $\quad 1/\mu = 1/m_A + 1/m_B$

R_e equilibrium bond length

Rotational constant for the v<u>th</u> vibrational state is B_v

$B_v = B_e - \alpha_e\,(v+\tfrac{1}{2})$

Y_{00} same anharmonic correction to <u>every</u> vibrational level

Since Y_{00} is a constant for the electronic state, it is usually put together with $U(R_e)$.

PEAK POSITIONS in MOLECULAR SPECTRA

are given by

$$h\nu = E_{v'J'} - E_{v''J''}$$

Example: For a diatomic molecule, the transitions within the same electronic state appear at the following frequencies:

$$\nu = \left[\left(v'+\tfrac{1}{2}\right) - \left(v''+\tfrac{1}{2}\right)\right]\nu_e - \nu_e x_e\left[\left(v'+\tfrac{1}{2}\right)^2 - \left(v''+\tfrac{1}{2}\right)^2\right]$$

$$+ B_e\left[J'(J'+1) - J''(J''+1)\right] - \alpha_e\left\{\begin{array}{l}(v'+\tfrac{1}{2})J'(J'+1) \\ -(v''+\tfrac{1}{2})J''(J''+1)\end{array}\right\}$$

$$- D_e\left\{\left[J'(J'+1)\right]^2 - \left[J''(J''+1)\right]^2\right\}$$

For $v'=1$ $v''=0$:

P Branch $J' = J''-1$

$$\nu_{P(J'')} = \nu_e - 2\nu_e x_e - 2B_e J'' - \alpha_e(J''-2)J'' + 4D_e(J'')^3$$

$$\approx \text{roughly } \nu_{center} - 2B_e J''$$

R Branch $J' = J''+1$

$$\nu_{R(J'')} = \nu_e - 2\nu_e x_e + 2B_e(J''+1) - \alpha_e(J''+1)(J''+3) - 4D_e(J''+1)^3$$

$$\approx \text{roughly } \nu_{center} + 2B_e(J''+1)$$

Adjacent peaks:

$$\nu_{P(1)} - \nu_{P(2)} = 2B_e + \alpha_e - 28D_e,$$

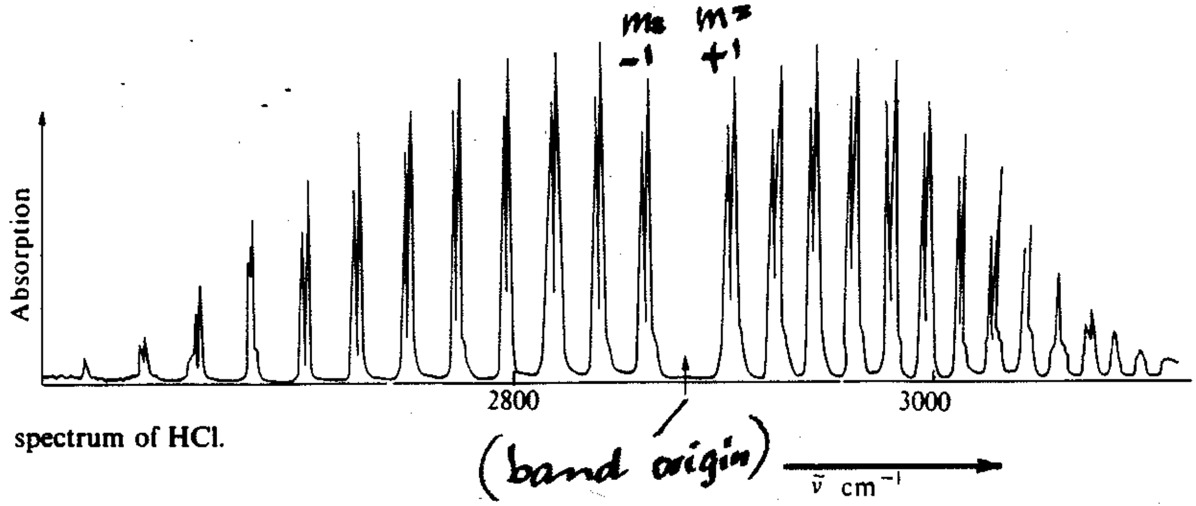
Note: further apart than just $2B_e$

$$\nu_{R(1)} - \nu_{R(0)} = 2B_e - 5\alpha_e - 28D_e$$

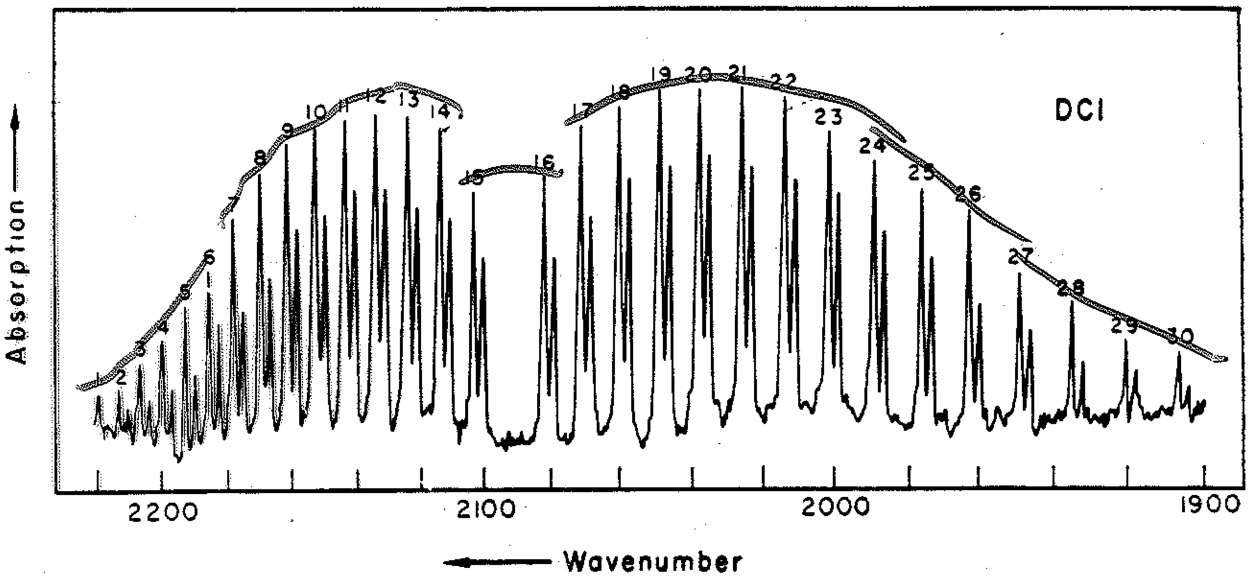
Note: closer together than just $2B_e$.

INFRARED

1. HCl and DCl spectra are compared below:



spectrum of HCl.



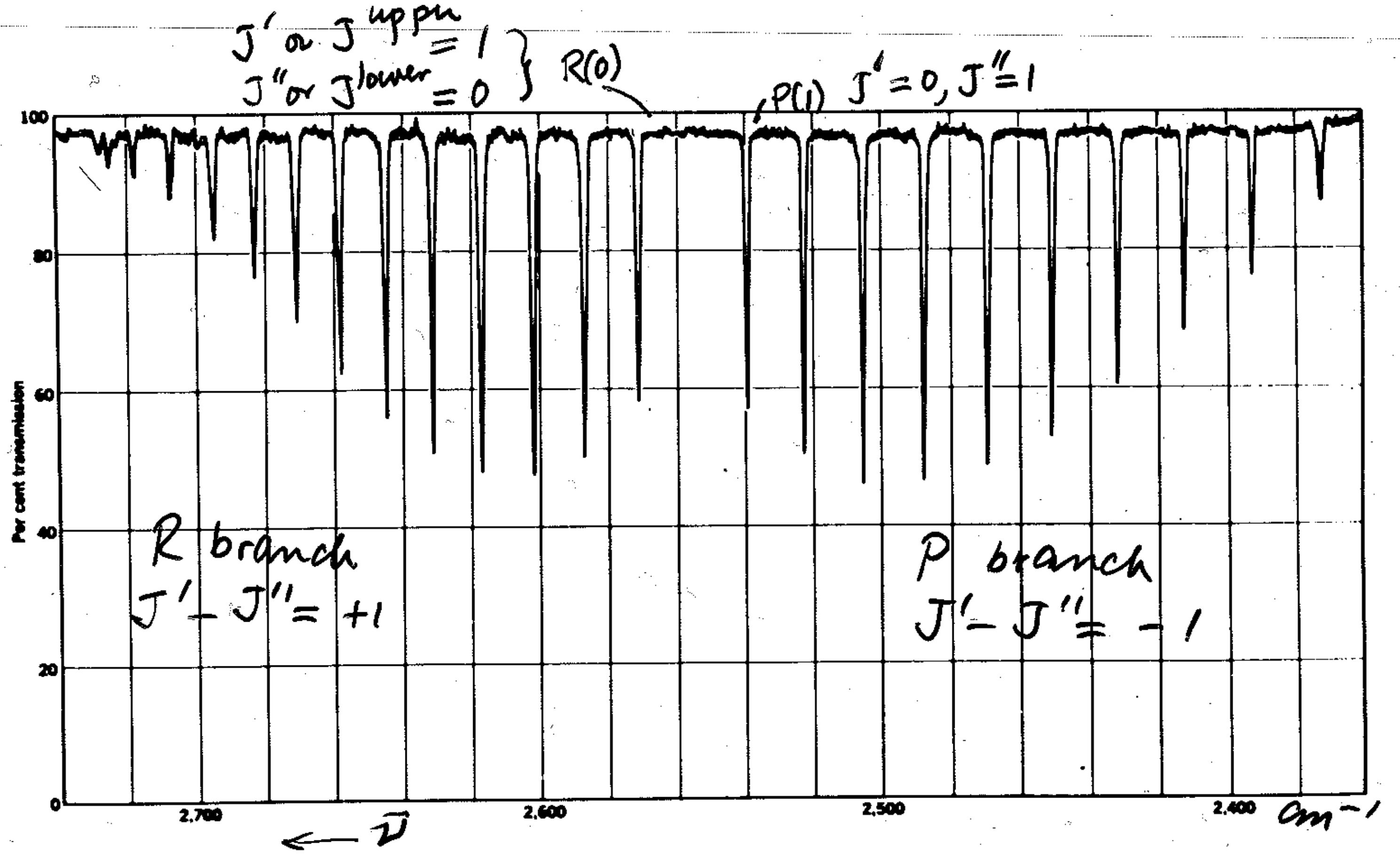
The deuterium chloride fundamental rotation-vibration band at 2224–1905 cm^{-1}.
The numbers on the lines refer to the IUPAC standard lines.

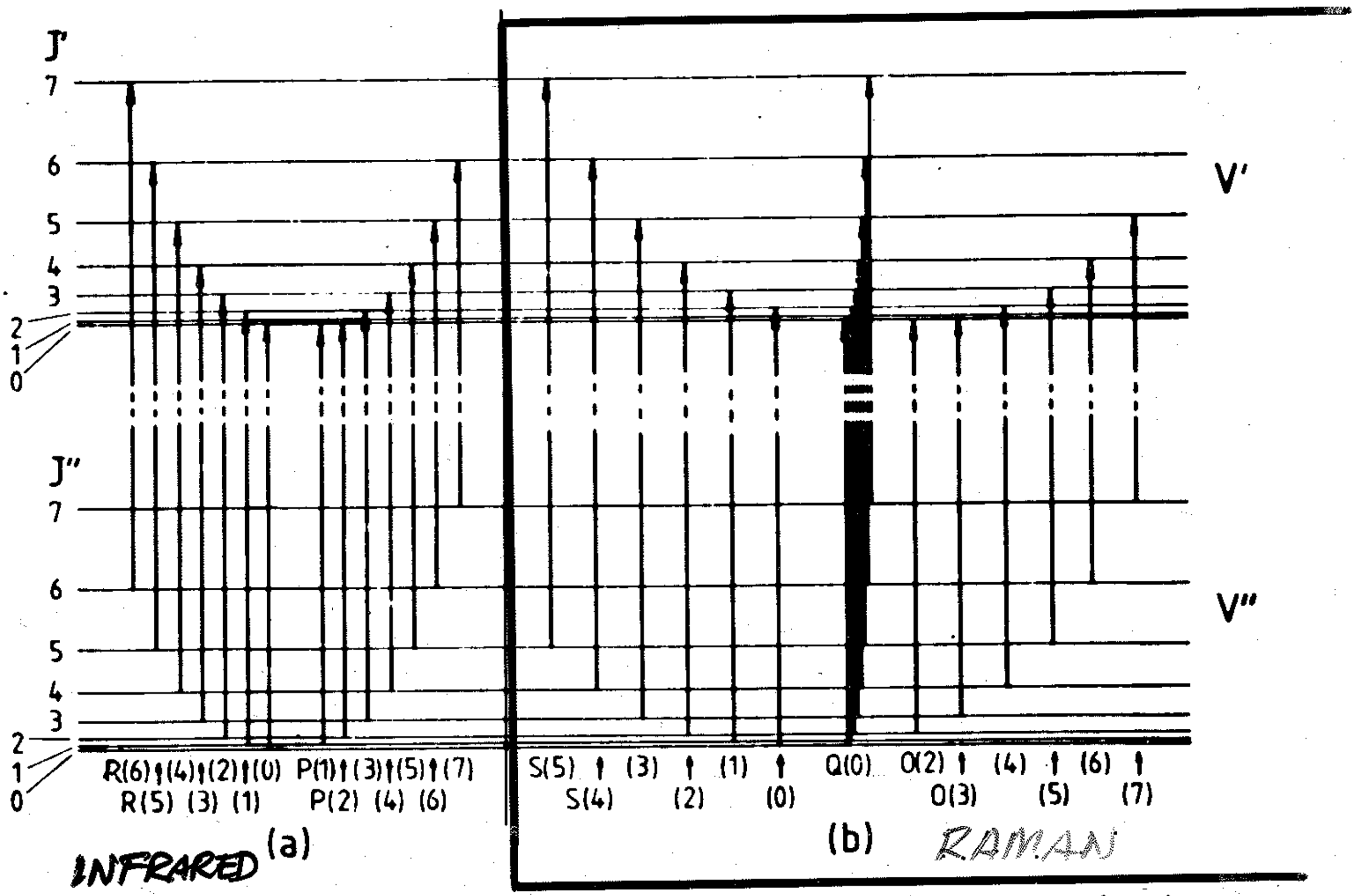
Peak positions given by: $m = \pm 1, \pm 2, \ldots$ (a running no.)

$$\underbrace{h\nu_e(v'-v'') - h\nu_e x_e\left[(v'+\tfrac{1}{2})^2 - (v''+\tfrac{1}{2})^2\right]}_{\text{position of band origin}} + \left[2B_e - \alpha_e(v'+v''+1)\right]m - \alpha_e(v'-v'')m^2 - 4\bar{D}_e m^3$$

can see a band head if α_e large enough

$^1H^{35}Cl$ has $\nu_e = 2989.74$ cm^{-1} $x_e\nu_e = 52.05$ cm^{-1} $B_e = 10.594$ cm^{-1}





Rotational transitions accompanying a vibrational transition in (a) an infrared spectrum and (b) a Raman spectrum of a diatomic molecule.

(1) $R(0)$ means $J_{lower} = 0 \longrightarrow J_{upper} = 1$ for $J'' = 0 \rightarrow J' = 1$

$P(1)$ means $J_{lower} = 1 \longrightarrow J_{upper} = 0$

double prime stands for lower
prime stands for upper

that is, the number given is the J value for the lower vibrational level, and $J_{upper} = J_{lower} - 1$ for P branch, $J_{upper} = J_{lower} + 1$ for R branch

Using the given formula:

$$E_{upper} = U(R_e) + h\nu_e(1+\tfrac{1}{2}) + [hB_e - h\alpha_e(1+\tfrac{1}{2})]J'(J'+1) + hY_{00} - h\nu_e x_e(1+\tfrac{1}{2})^2 - h\bar{D}_e[J'(J'+1)]^2$$

$$E_{lower} = U(R_e) + h\nu_e(0+\tfrac{1}{2}) + [hB_e - h\alpha_e(0+\tfrac{1}{2})]J''(J''+1) + hY_{00} - h\nu_e x_e(0+\tfrac{1}{2})^2 - h\bar{D}_e[J''(J''+1)]^2.$$

P Branch: $J' = J'' - 1$

$$h\nu_{observed} = (h\nu_e - 2h\nu_e x_e) - h[B_e - \alpha_e]2J'' - h\alpha_e(J'')^2 + 4h\bar{D}_e(J'')^3$$

$$J'' = 1, 2, 3, \ldots$$

R Branch: $J' = J'' + 1$

$$h\nu_{observed} = (h\nu_e - 2h\nu_e x_e) + h[B_e - \alpha_e]2(J''+1) - h\alpha_e(J''+1)^2 - 4\bar{D}_e(J''+1)^3$$

$$J'' = 0, 1, 2, 3, \ldots$$

Neglecting α_e and $\bar{D}_e$, spacing would be equal between P lines and R lines. $\alpha_e > \bar{D}_e$ (see given formulas and remember that $B_e/\nu_e \sim 10/3000$ for example.) ~~Including~~ the effect of α_e, the quadratic dependence on J'' gives an <u>increase</u> in the spacing between P branch lines as J'' increases since the term in J'' and in $(J'')^2$ are the <u>same</u> sign. On the other hand they are <u>opposite</u> in sign in the R branch so there will be a <u>decrease</u> in the spacing between R branch lines as J'' increases.

Since $\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ and $\frac{1}{\mu} = \frac{1}{m_H} + \frac{1}{m_{Cl}}$ for HCl

$\frac{1}{\mu} = \frac{1}{m_D} + \frac{1}{m_{Cl}}$ for DCl

$\frac{1}{\mu} = \frac{1}{1} + \frac{1}{35}$ or $\mu = \frac{35}{36}$ for ${}^1H^{35}Cl$

$\mu = \frac{37}{38}$ for ${}^1H^{37}Cl$

$\mu = \frac{70}{37}$ for $D^{35}Cl$

$\mu = \frac{74}{39}$ for $D^{37}Cl$

$$\nu_e({}^1H^{37}Cl) = \frac{\nu_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)^{1/2}}{\left(\frac{37}{38}\right)^{1/2}}$$

$$= .9992\,\nu_e({}^1H^{35}Cl)$$

$$\nu_e(D^{35}Cl) = \frac{\nu_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)^{1/2}}{\left(\frac{70}{37}\right)^{1/2}}$$

$$= 0.7168\,\nu_e({}^1H^{35}Cl)$$

$$\nu_e(D^{37}Cl) = \frac{\nu_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)^{1/2}}{\left(\frac{74}{39}\right)^{1/2}}$$

$$= 0.7158\,\nu_e({}^1H^{35}Cl)$$

Looking at the given formula for $\nu_e x_e$ we see that $\nu_e x_e \propto \frac{1}{\mu}$. Thus

$$\nu_e x_e({}^1H^{37}Cl) = \frac{\nu_e x_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)}{\left(\frac{37}{38}\right)} = 0.9985\,\nu_e x_e({}^1H^{35}Cl)$$

$$\nu_e x_e(D^{35}Cl) = \frac{\nu_e x_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)}{\left(\frac{70}{37}\right)} = 0.51389\,\nu_e x_e({}^1H^{35}Cl)$$

$$\nu_e x_e(D^{37}Cl) = \frac{\nu_e x_e({}^1H^{35}Cl)\cdot\left(\frac{35}{36}\right)}{\left(\frac{74}{39}\right)} = 0.5124\,\nu_e x_e({}^1H^{35}Cl)$$

and $B_e \propto \frac{1}{\mu}$ also so the same factors hold for B_e

$$B_e({}^1H^{37}Cl) = 0.9985\,B_e({}^1H^{35}Cl)$$
$$B_e(D^{35}Cl) = 0.51389\,B_e({}^1H^{35}Cl)$$

$\alpha_e \propto \mu^{-3/2}$ from the given formula

$$\alpha_e(D^{35}Cl) = (0.51389)^{3/2}\alpha_e({}^1H^{35}Cl) = .3684\,\alpha_e({}^1H^{35}Cl)$$

α_e can be estimated (neglecting $\bar{D}_e$) from $D^{35}Cl$ lines at $1920\ cm^{-1}$: P(14) and $2200\ cm^{-1}$: R(11), using $\nu_e = .7168\,(2989.74)$ $\nu_e x_e = .5139(52.05)$, $B_e = .5139(10.59)$ all in cm^{-1} or 2143.0, 26.75 and $5.444\,cm^{-1}$

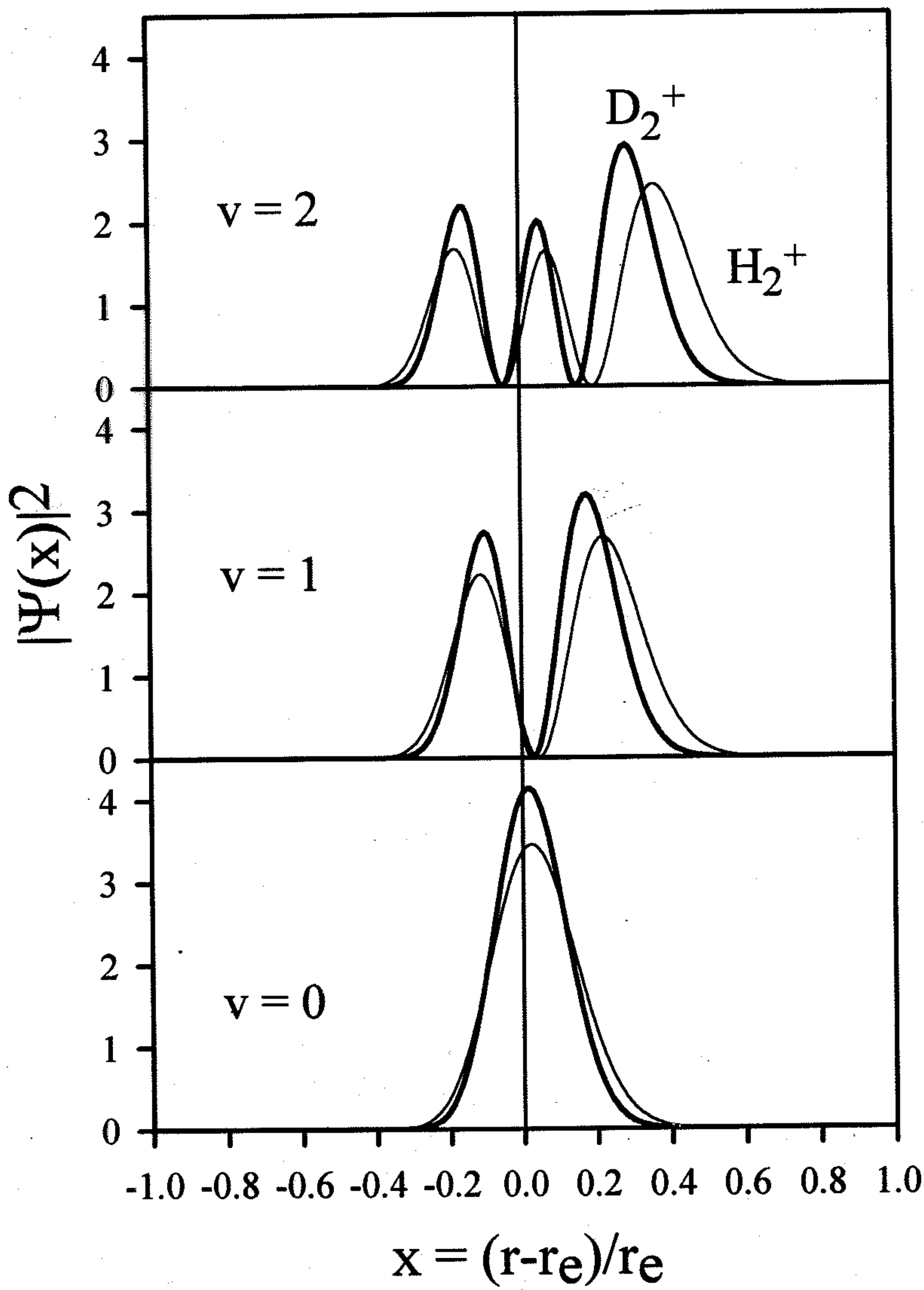
$$P(14) = 1920\ cm^{-1} = 2143.0 - 2(26.75) - [5.444 - \alpha_e]\,2\,(14) - \alpha_e (14)^2$$

$$R(11) = 2200\ cm^{-1} = 2143.0 - 2(26.75 + [5.444 - \alpha_e]\,2\,(12) - \alpha_e\,(12)^2$$

$$\text{spacing} = 2200 - 1920 = 280\ cm^{-1} = 5.444(52) - \alpha_e(52) - \alpha_e[(14)^2 - (12)^2]$$

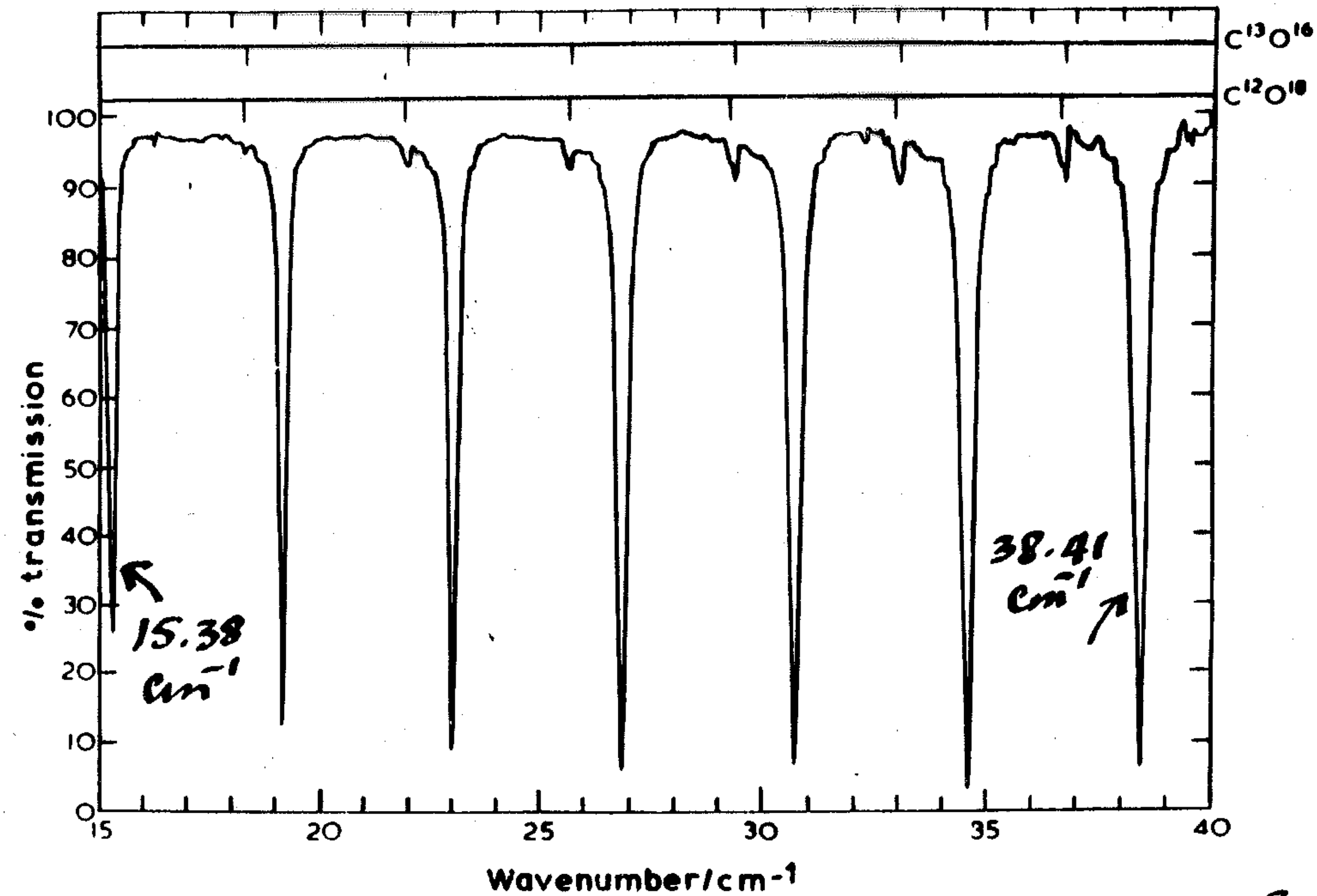
$$= 5.444\,(52) - 104\,\alpha_e$$

$\therefore\ \alpha_e = .029\,cm^{-1}$ which is a little off since we neglected $\bar{D}_e$ and eye-balled the P(14) and R(11) frequencies.



v = 2
v = 1
v = 0
D_2^+
H_2^+
$|\Psi(x)|^2$
$x = (r-r_e)/r_e$
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
0
1
2
3
4

MICROWAVE



$$\nu_{J+1 \leftarrow J} = 2(J+1)\underbrace{\left[B_e - (v''+\tfrac{1}{2})\alpha_e\right]}_{B_{v''}} - 4\bar{D}_e (J+1)^3$$

hardly ever get a "head" because $\bar{D}_e$ is so small

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
6. APPROXIMATION METHODS
7. DIATOMIC MOLECULES
8. MOLECULAR SPECTROSCOPY
    - 8.1 Nature of electromagnetic radiation, the time dependent E and B fields
    - 8.2 Quantum theory of absorption/emission of radiation: Fermi's golden rule
    - 8.3 Einstein's coefficients for stimulated absorption/emission and Lambert-Beer law
    - 8.4 Selection rules and transition moments for electric dipole transitions
    - 8.5 Molecular energy levels and states
    - 8.6 Transitions between different electronic states
    - 8.7 Transitions within the same electronic state: vibration-rotation spectroscopy
    - **8.8 Symmetry of states of polyatomic molecules**
    - 8.9 Vibration-rotation spectroscopy of polyatomics

GROUP THEORY and APPLICATIONS of SYMMETRY

GROUP THEORY is a mathematical tool for treating SYMMETRY

What is a **GROUP**?

A group is a SET made up of entities called **ELEMENTS** with a system of relations between elements of the set:

The GROUP POSTULATES

1. CLOSURE relation – The **PRODUCT** of any two elements of the group is an element of the group. The group is said to be CLOSED UNDER MULTIPLICATION

2. ASSOCIATION relation – the associative law holds, that is,

$$a(bc) = (ab)c$$

so that the product of any number of elements is determined uniquely by the order in which they are multiplied

3. **IDENTITY** – The group contains an identity element. There is only one possible, that is, an element which COMMUTES with all the others and leave them unchanged.

$$aE = a \qquad Ea = a$$

4. INVERSE – The **INVERSE** of any element of the group is also contained in the group.

$$a^{-1}a = E \qquad aa^{-1} = E$$

For each element there is only one inverse

In general, the elements of a group do NOT COMMUTE, that is,

ab is not in general the same as ba

ORDER of a group = number of group elements

GROUPTHEORY – is the collection of theorems concerning groups which can be derived from the group postulates and the specific nature of the combining laws.

The group structure is completely determined if we know the products of any two elements of the group — can be displayed in a

MULTIPLICATION TABLE

For a group of order 4, having elements E, a, b, and c

	E	a	b	c
E	E	a	b	c
a	a	a^2	ab	ac
b	b	ba	b^2	bc
c	c	ca	cb	c^2

(0 1 2 3) under addition modulo 4

	0 1	1 i	2 -1	3 $-i$
0 1	1_0	i_1	-1_2	$-i_3$
1 i	i_1	-1_2	$-i_3$	1_0
2 -1	-1_2	$-i_3$	1_0	i_1
3 $-i$	$-i_3$	1_0	i_1	-1_2

identity element 1

inverses: 1 1

-1 -1

i $-i$

How to check if multiplication table is correct:

IN EACH ROW each element appears once and only once

IN EACH COLUMN each element appears once and only once

SUBGROUPS - Within a GROUP there are smaller groups. The order of a SUBGROUP must be an INTEGRAL FACTOR of the ORDER of the group. A group of order 6 can only have subgroups of order 1, 2, or 3.

CLASSES - A class is a complete set of elements which are CONJUGATE to one another, which means they are related by SIMILARITY TRANSFORMATIONS

$A = Y^{-1} B Y \quad B = X^{-1} A X$ where X and Y do not necessarily belong to the same class as A or B.

If A is CONJUGATE to B and C, then B and C are conjugate with each other.

The ORDER of a CLASS must be an integral factor of the order of the group. A group of order 6 can only have classes of order 1, 2, or 3.

SYMMETRY ELEMENTS and SYMMETRY OPERATIONS

A set of SYMMETRY OPERATIONS (complete but non-redundant) constitutes a group.

EQUIVALENT points or atoms are INDISTINGUISHABLE

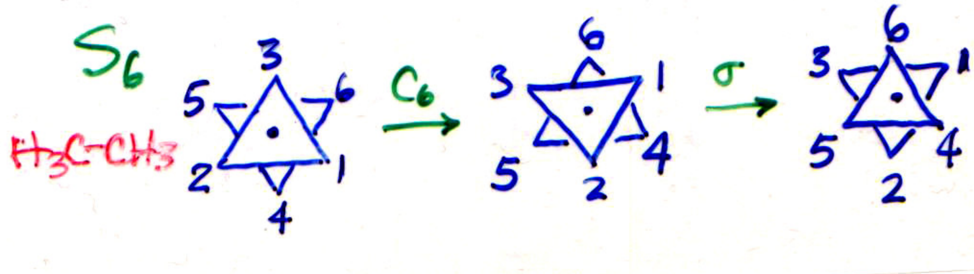
SYMMETRY OPERATION - a movement of a body such that after the movement has been carried out EVERY POINT OF THE BODY IS COINCIDENT WITH AN EQUIVALENT POINT OF THE BODY IN ITS ORIGINAL ORIENTATION or THE POSITION AND ORIENTATION OF THE BODY AFTER PERFORMING THE OPERATION IS INDISTINGUISHABLE though not necessarily identical TO THE ORIGINAL.

SYMMETRY ELEMENTS — geometrical entities: line, plane, point with respect to which SYMMETRY OPERATIONS may be carried out.

SYMMETRY ELEMENT		SYMMETRY OPERATION	
σ	plane	σ	reflection through the plane
i	center of symmetry, center of inversion	i	inversion through the center
C_n	proper axis	C_n	proper rotation (counterclockwise) by $2\pi/n$ about the axis
S_n	improper axis	S_n	improper rotation that is, the sequence σC_n rotation followed by reflection

POINT GROUP as opposed to SPACE GROUP or LINE GROUP

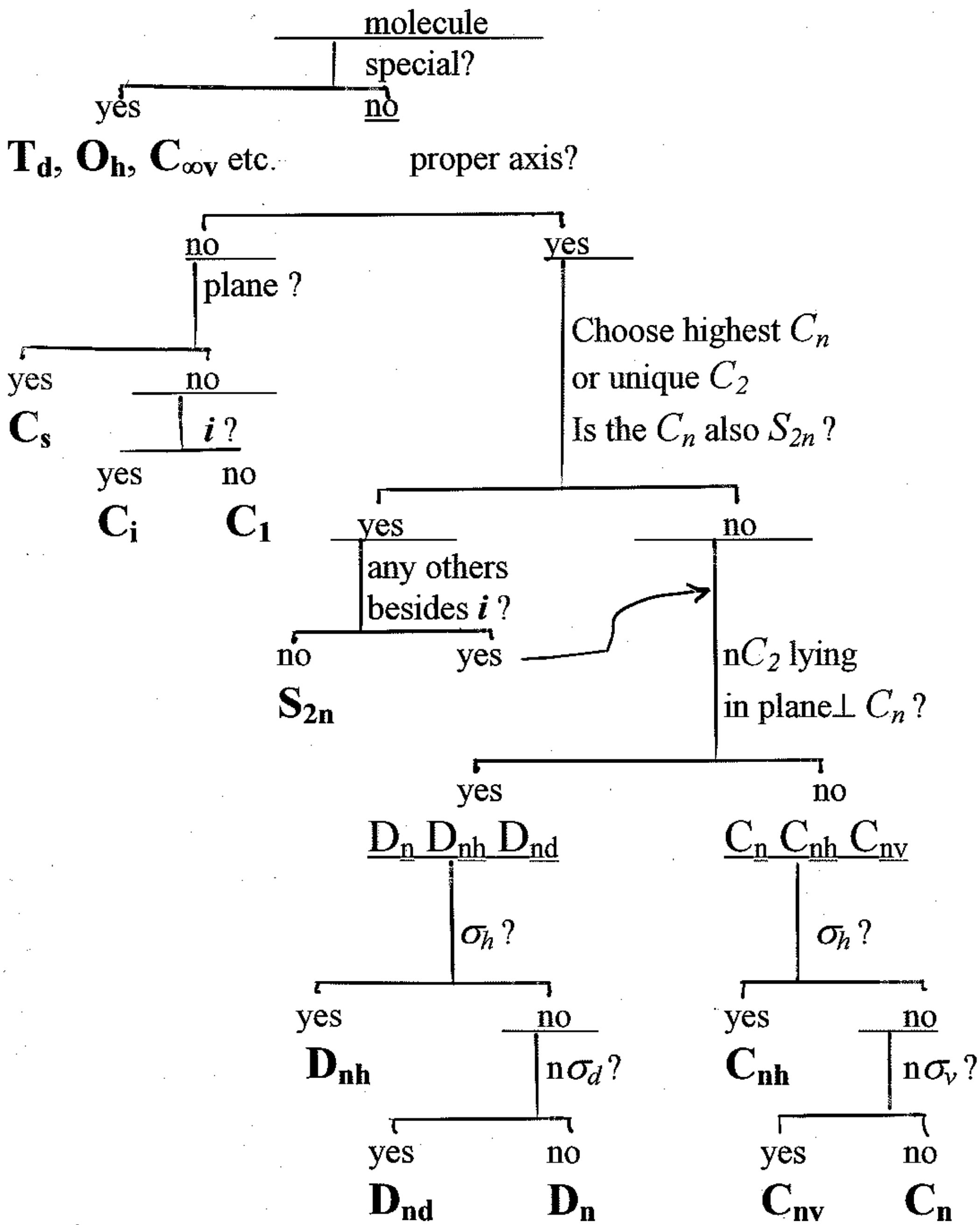
All these operations leave one point (the center) unchanged



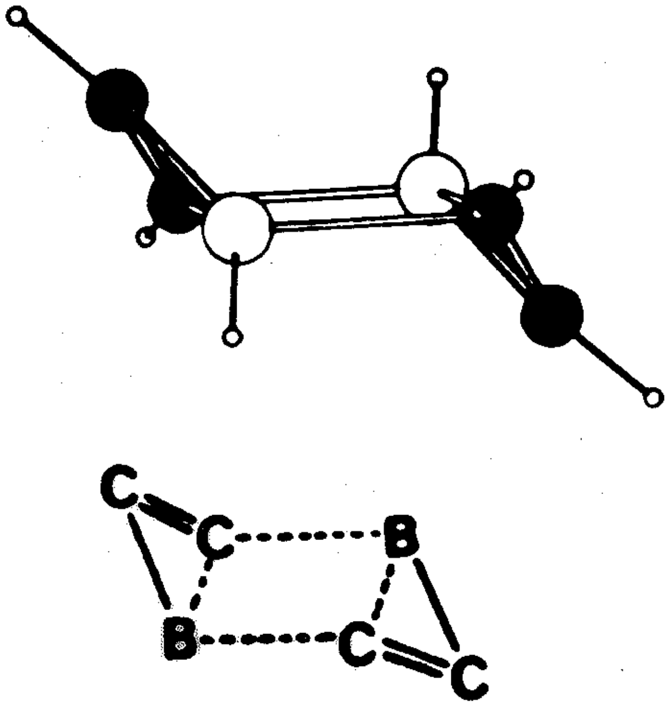
SYMMETRY POINT GROUPS

SYMMETRY ELEMENT	SYMMETRY OPERATIONS (ELEMENTS of the GROUP)	ORDER	GROUP
none	E	1	C_1
σ	$\sigma,\ \sigma^2 = E$	2	C_s
i	$i,\ i^2 = E$	2	C_i
C_n	$C_n,\ C_n^2,\ C_n^3, \cdots C_n^n = E$	n	C_n
S_n (n even)	$S_n,\ S_n^2 = C_{n/2},\ S_n^3, \cdots S_n^n = E$	n	S_n
S_n (n odd or $C_n + \sigma_h$	n odd means that σ_h and C_n must also exist $S_n, S_n^2 = C_n^2, S_n^3, S_n^4 = C_n^4, \ldots S_n^n = \sigma, S_n^{n+1} = C_n, S_n^{n+2} = S_n^{n+3} C_n^3, \cdots S_n^{2n} = C_n^n = E$	$2n$	C_{nh}
$C_n + nC_2\ (\perp C_n)$	$C_n,\ C_n^2, \cdots, C_n^n = E\ + nC_2$	$2n$	D_n
$C_n + n\sigma_v$	$C_n,\ C_n^2, \cdots, C_n^n = E\ + n\sigma_v$	$2n$	C_{nv}
$C_n + n\sigma_v + \sigma_h$	$C_n,\ C_n^2 \cdots, C_n^n = E + n\sigma_v + nC_2$ $+ S_n, S_n^2, \cdots S_n^n = \sigma_h$ ($\sigma_v + \sigma_h$ create C_2 operations)	$4n$	D_{nh}
$C_n + nC_2\ (\perp C_n) + n\sigma_d$ σ_d bisects angles between adjacent pairs of C_2 axes	$C_n, \cdots C_n^n = E\ + nC_2 + n\sigma_d$ $+ S_{2n}, S_{2n}^3, S_{2n}^5, \cdots S_{2n}^{2n-1}$ (only odd powers since even ones are $S_{2n}^2 = C_n$ etc)	$4n$	D_{nd}
special groups $C_\infty + \infty\sigma_v$		∞	$C_{\infty v}$
$C_\infty + \infty\sigma_v + \sigma_h$		∞	$D_{\infty h}$
	operations on a tetrahedron	24	T_d
	operations on an octahedron	48	O_h

Systematic symmetry classification of molecules:

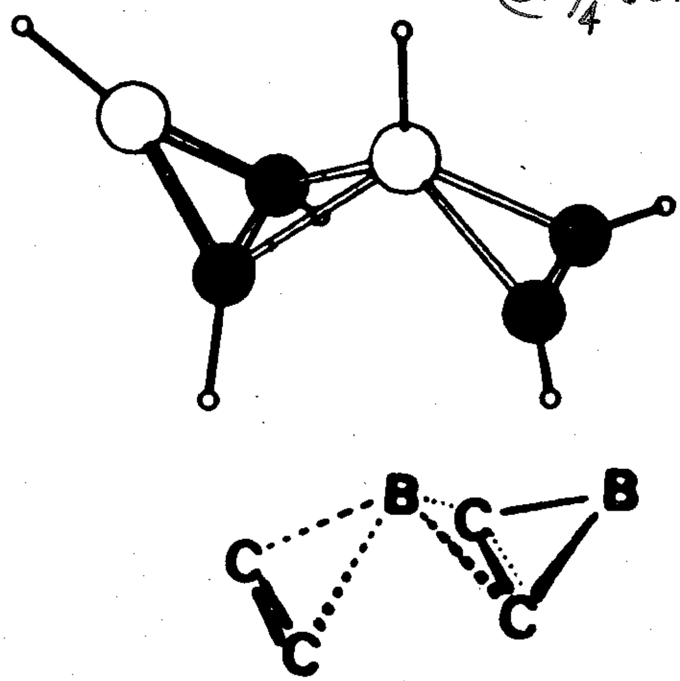


$(CH)_4(BH)_2$ T.S.



C_i

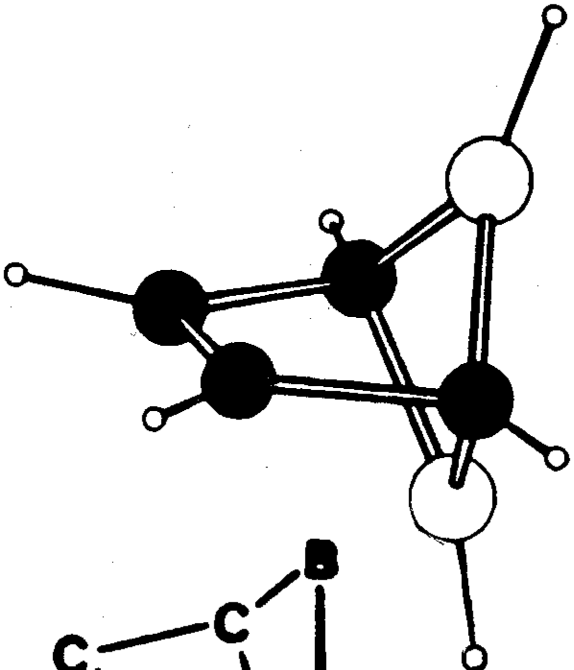
$(CH)_4(BH)_2$ T.S.

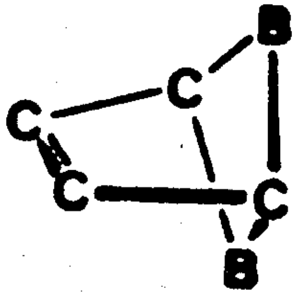


C_s

$(CH)_4(BH)_2$

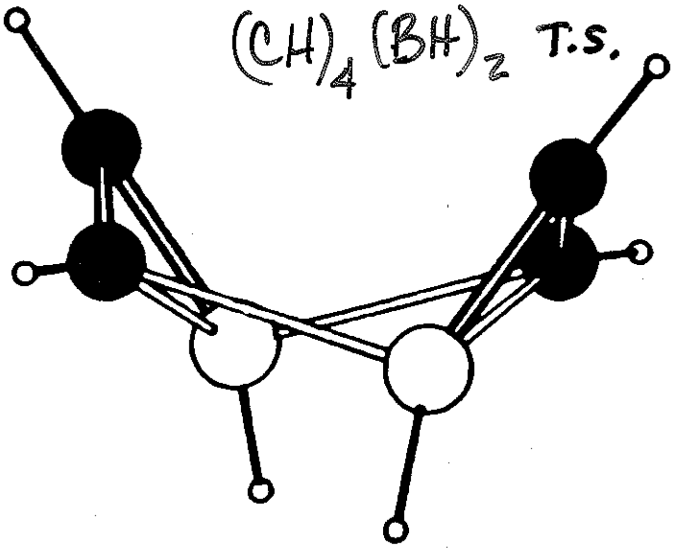
5,6-diborabicyclo[2.1.1] hexene

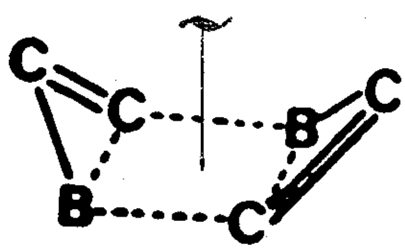




C_{2v}

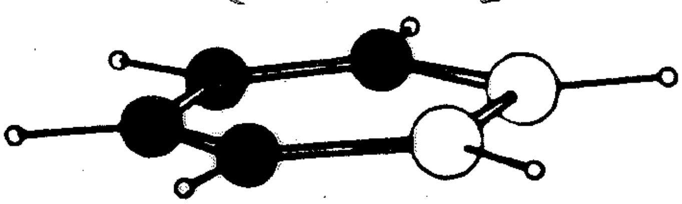
$(CH)_4(BH)_2$ T.S.



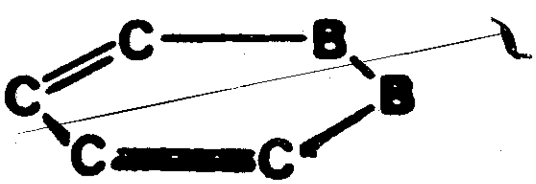


C_2

$(CH)_4(BH)_2$ T.S.

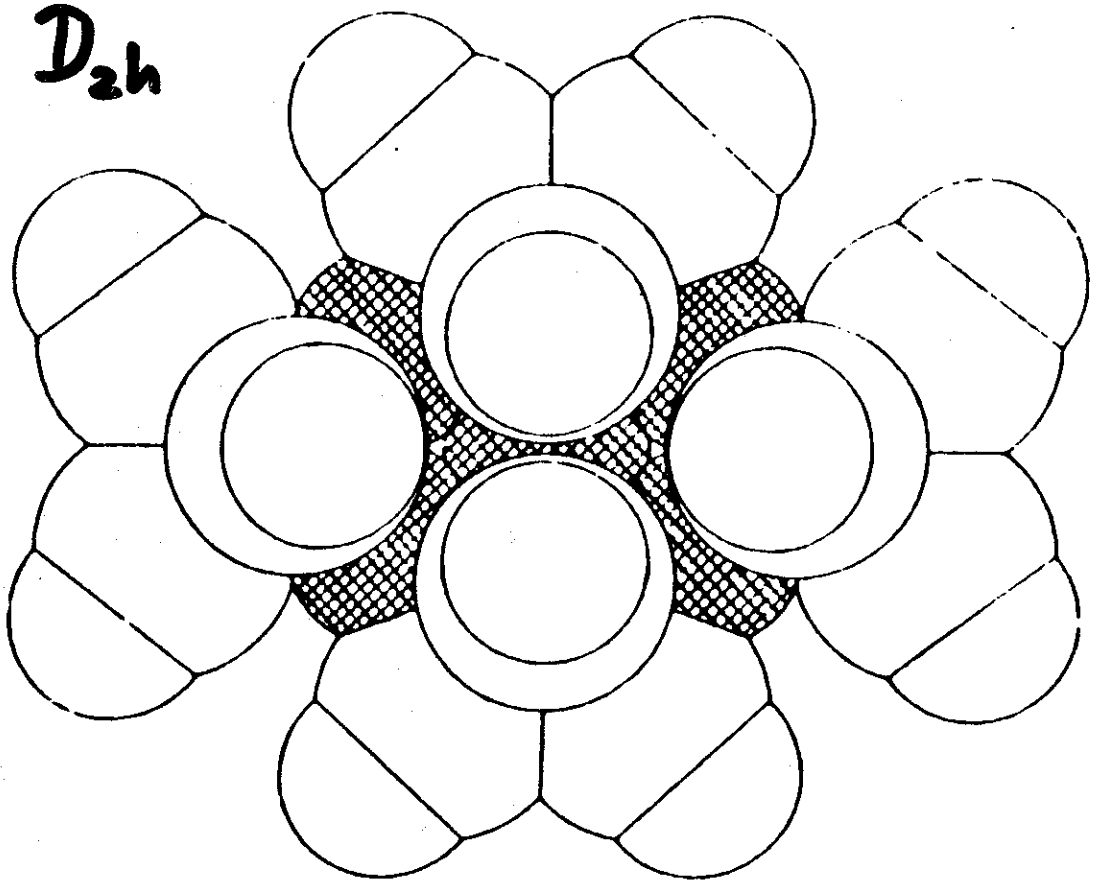


1,2-diboracyclohexa-3,5-diene

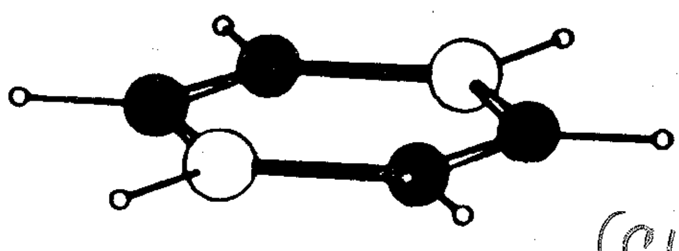


C_{2v}

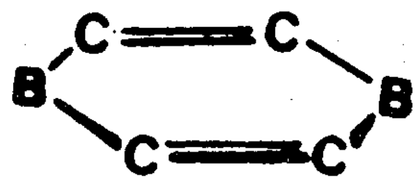
D_{2h}



$Cu_5Fe_4(CO)_{16}^{3-}$ cluster anion viewed ⊥ to the plane of the metal atoms (Cu atoms are shaded)



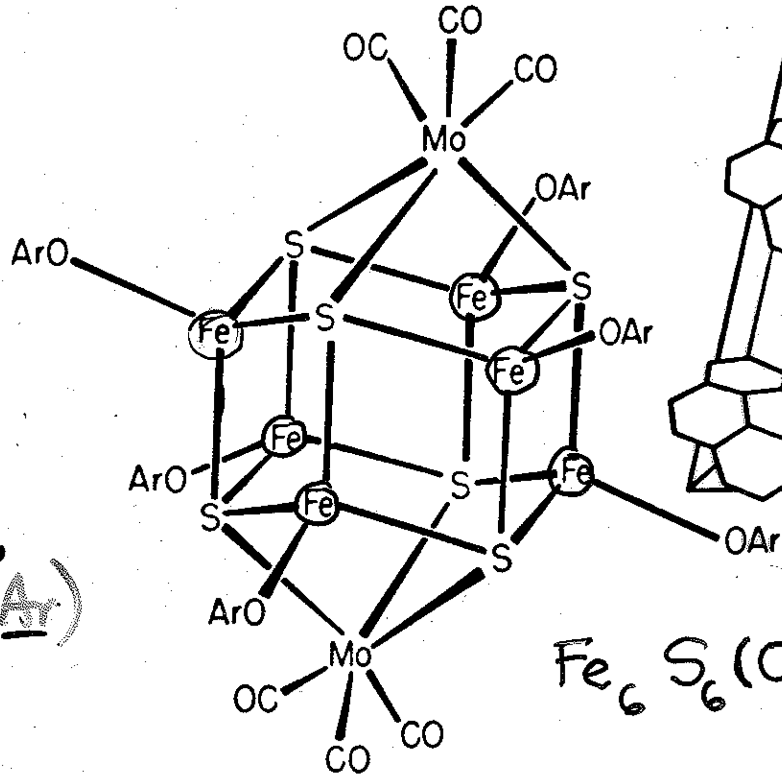
$(CH)_4(BH)_2$
1,4-diboracyclohexa-2,5-diene

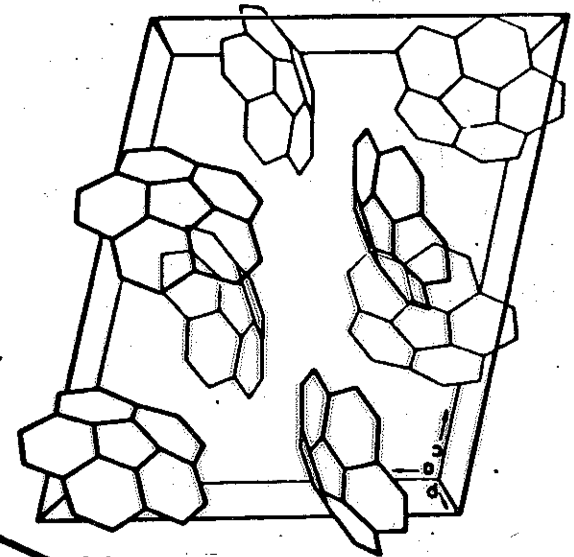


D_{2h}

S_6

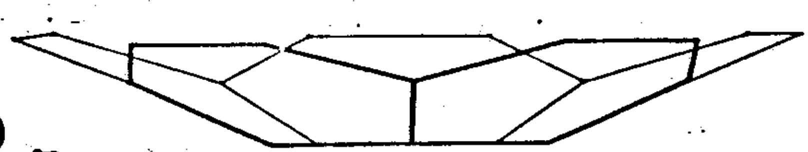
D_{3d} (neglect Ar)





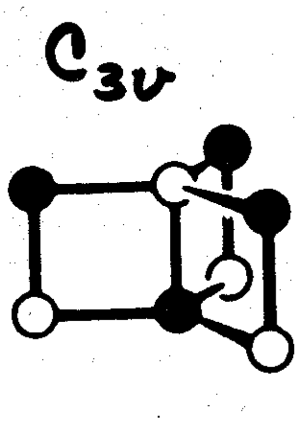
$Fe_6S_6(OAr)_6(Mo(CO)_3)_2^{=}$

C_{5v}

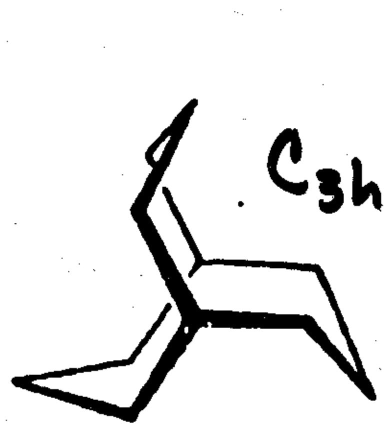


CORANNULENE

C_{3v}

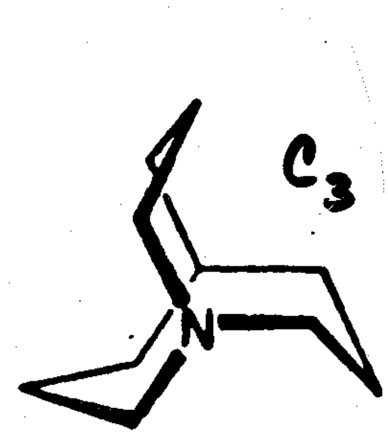


C_{3h}

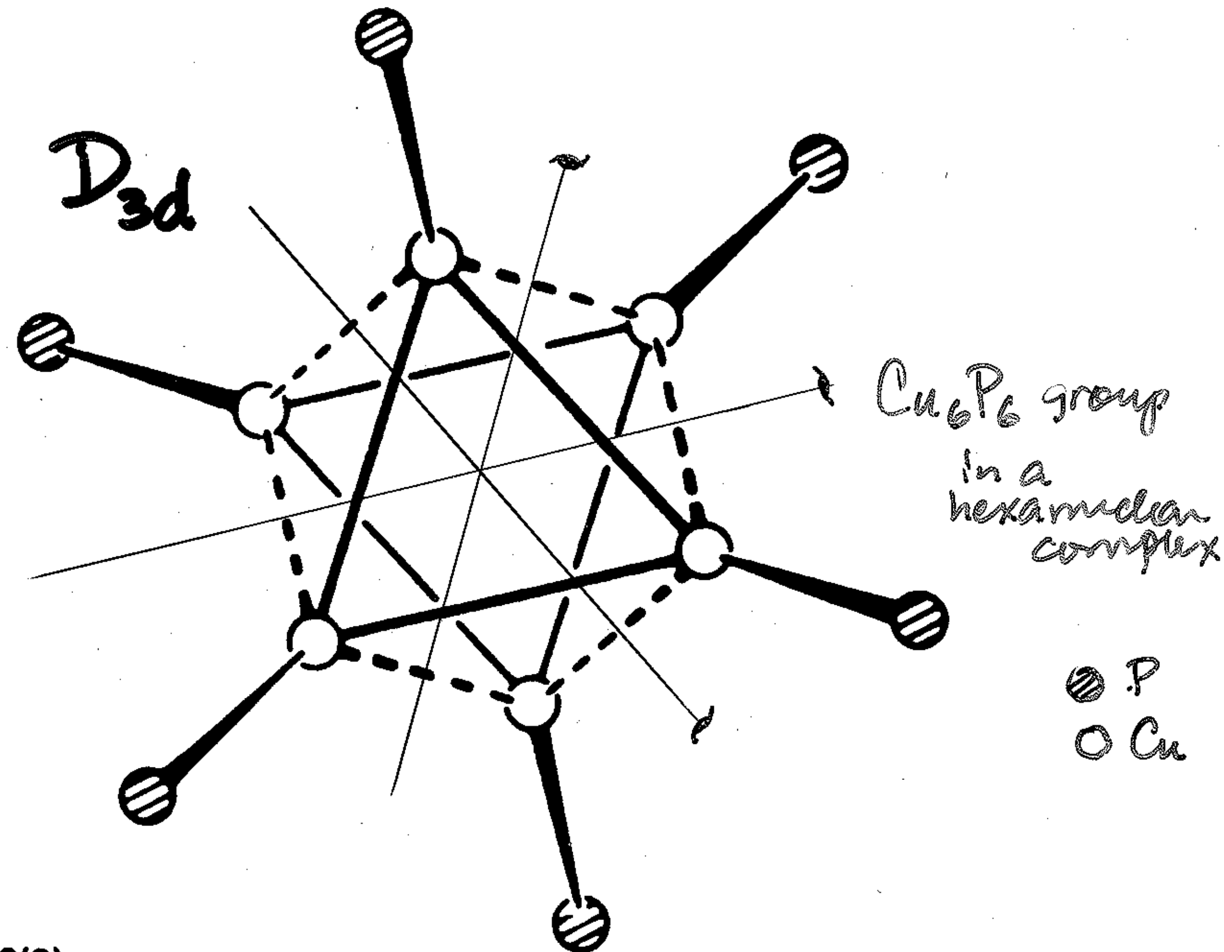


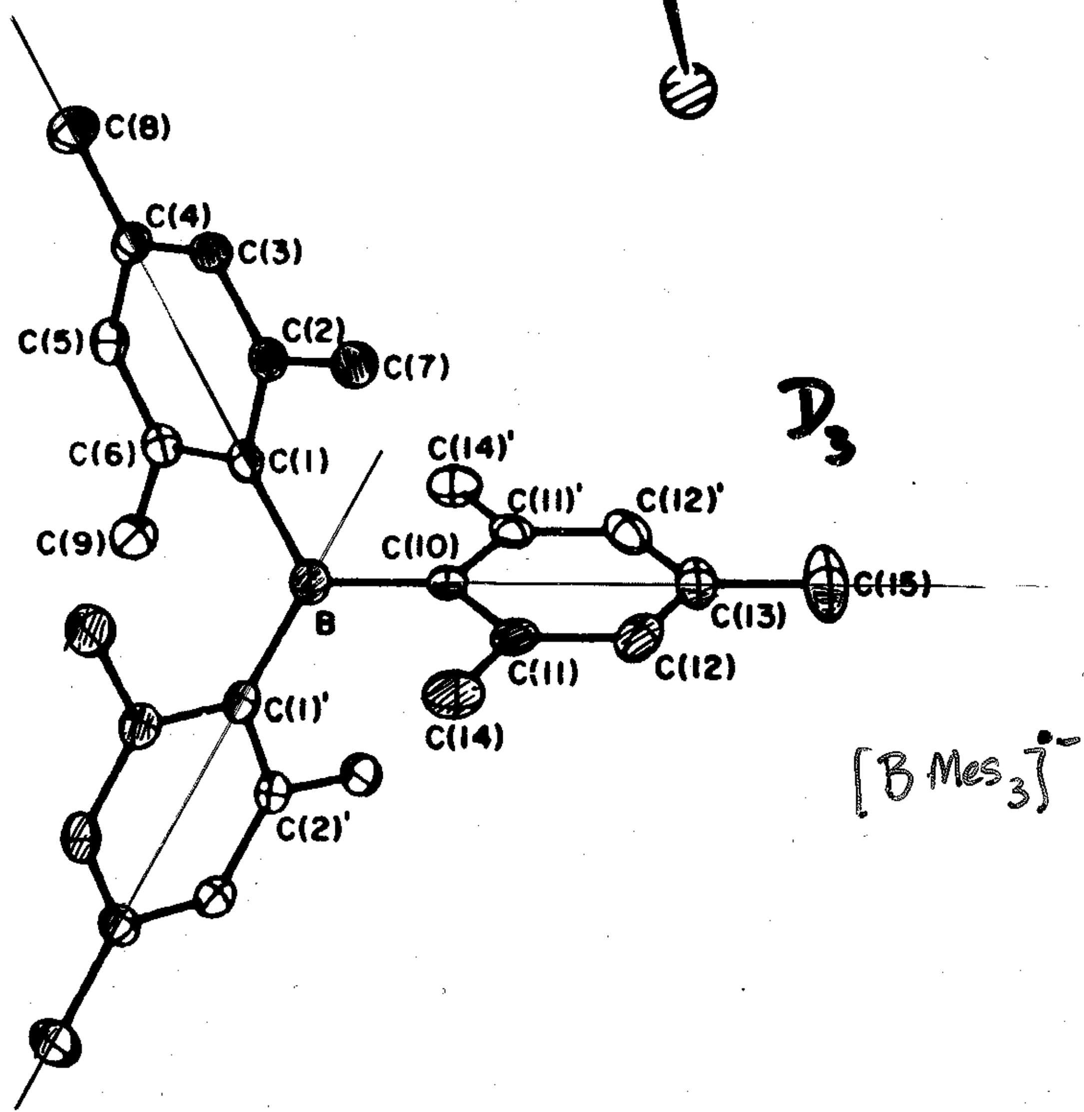
Bicyclo[3.3.3]undecane

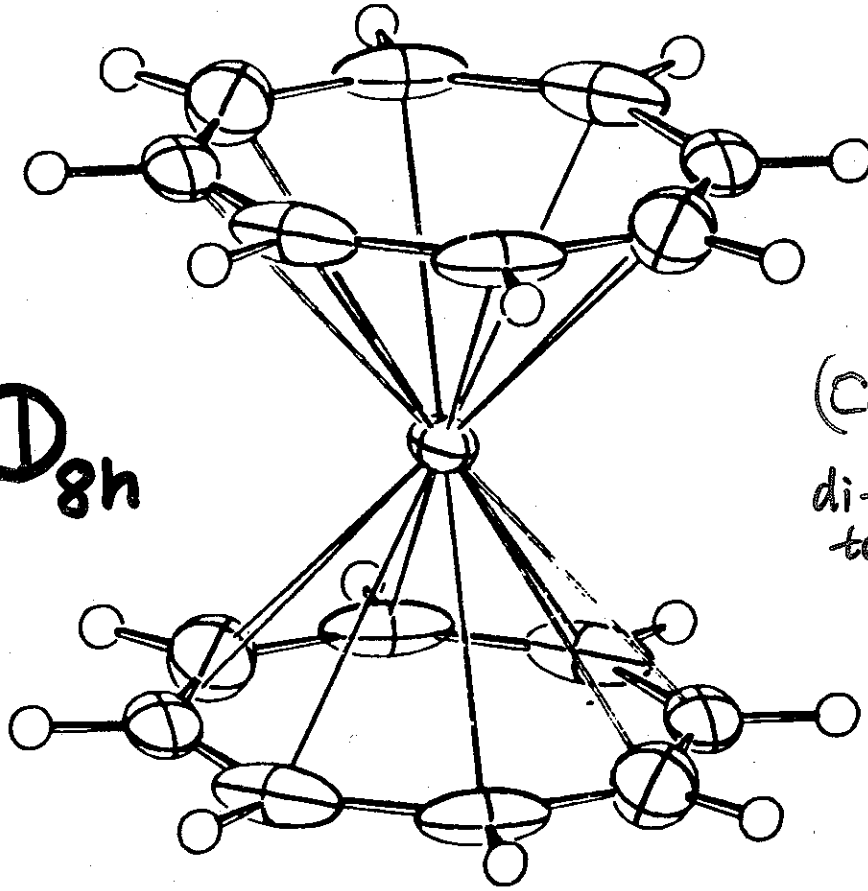
C_3



1-azabicyclo [3.3.3] undecane


D3d
Cu6P6 group
in a
hexanuclear
complex
P
Cu

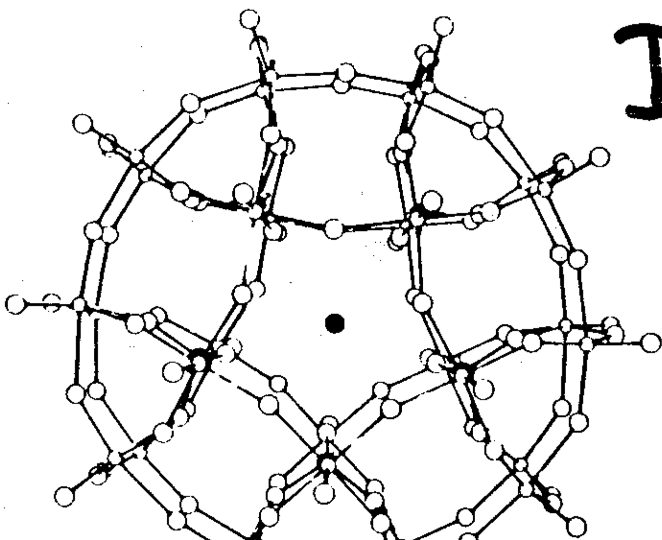

D3
C(8)
C(4)
C(3)
C(5)
C(2)
C(7)
C(6)
C(1)
C(9)
C(14)'
C(11)'
C(12)'
C(10)
B
C(13)
C(15)
C(11)
C(12)
C(14)
C(1)'
C(2)'
[B Mes3]•−



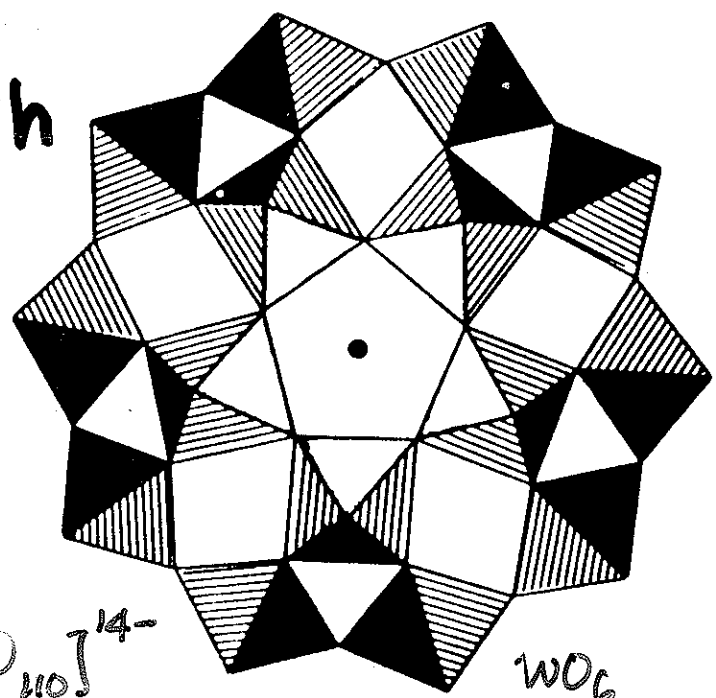
D_{8h}

$(C_8H_8)_2U$

di-π-cyclooctatetraene uranium



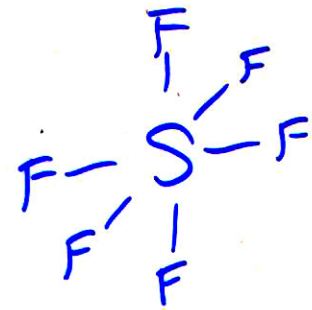
D_{5h}

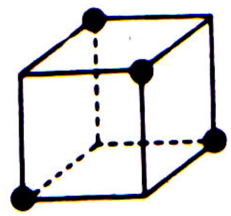


• W
○ O

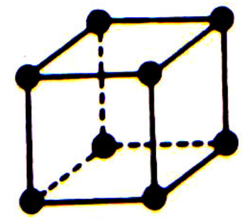
$[NaP_5W_{30}O_{110}]^{14-}$

WO_6 octahedra

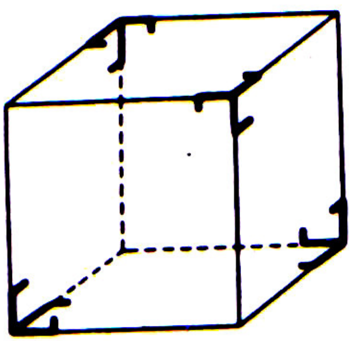




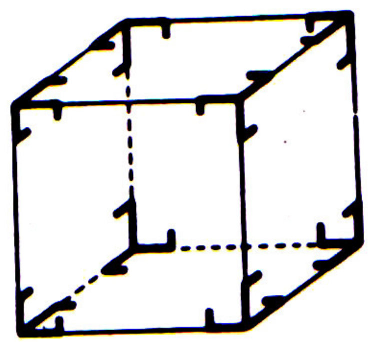
T_d



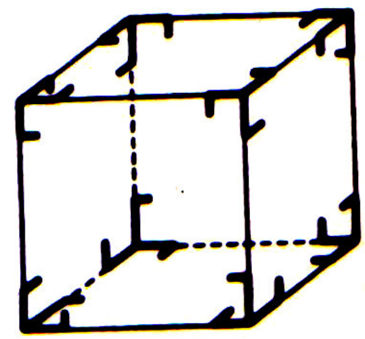
O_h



T



T_h



O

MATRIX REPRESENTATIONS

REPRESENTATION - a set of SQUARE MATRICES each corresponding to a single operation in the group which can be combined among themselves in a manner parallel to the way in which the group elements combine.

For example, the C_{3v} group has the following 6 SYMMETRY OPERATIONS:

$$E \qquad C_3 \qquad C_3^2 \qquad \sigma_v \qquad \sigma_v' \qquad \sigma_v''$$

A possible matrix representation of C_{3v} is the set of matrices; a one-dimensional representation

$$[1] \qquad [1] \qquad [1] \qquad [1] \qquad [1] \qquad [1] \qquad 1\times 1 \text{ matrices}$$

or the set of matrices: a 3-dimensional representation

$$\underset{D(E)}{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}} \quad \underset{D(C_3)}{\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}} \quad \underset{D(C_3^2)}{\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}} \quad \underset{D(\sigma_v)}{\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}} \quad \underset{D(\sigma_v')}{\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}} \quad \underset{D(\sigma_v'')}{\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}} \quad 3\times 3 \text{ matrices}$$

Multiplication of the matrices follow the rules of multiplication of the symmetry operations themselves. For example:

$$C_3\, C_3^2 = E \qquad\qquad C_3\sigma_v' = \sigma_v''$$

$$[1]\,[1] = [1] \qquad\qquad [1][1] = [1]$$

or

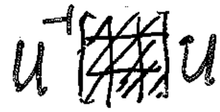
$$\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix} = \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} \qquad \begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix} = \begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}$$

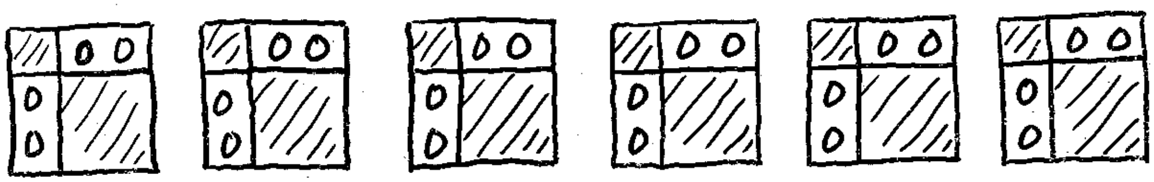
In this way, the square matrices REPRESENT the elements of the group.

Some representations are **REDUCIBLE**. This means that it is possible, using some matrix U to TRANSFORM <u>EACH</u> MATRIX in the set into a BLOCKED-OUT MATRIX, which can be taken apart in IDENTICAL MANNER, to give 2 or more representations of smaller dimension.

For example

$$\begin{array}{cccccc} E & C_3 & C_3^2 & \sigma_v & \sigma_v' & \sigma_v'' \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \end{array}$$





after the transformation

CHARACTER

χ	3	0	0	1	1	1

THE character OF THE IDENTITY OPERATION IS 3

IRREDUCIBLE REPRESENTATION – a representation made up of matrices such that it is impossible to reduce <u>ALL</u> by the same similarity transformation.

BEFORE and AFTER the SIMILARITY TRANSFORMATION the SUM OF THE DIAGONAL ELEMENTS (called the TRACE of the matrix, or the CHARACTER) of each matrix remains the same.

In a given REPRESENTATION (reducible or not) the CHARACTERS of all matrices BELONGING to SYMMETRY OPERATIONS in the SAME CLASS are IDENTICAL

For example, in C_{3v} the 3 classes are

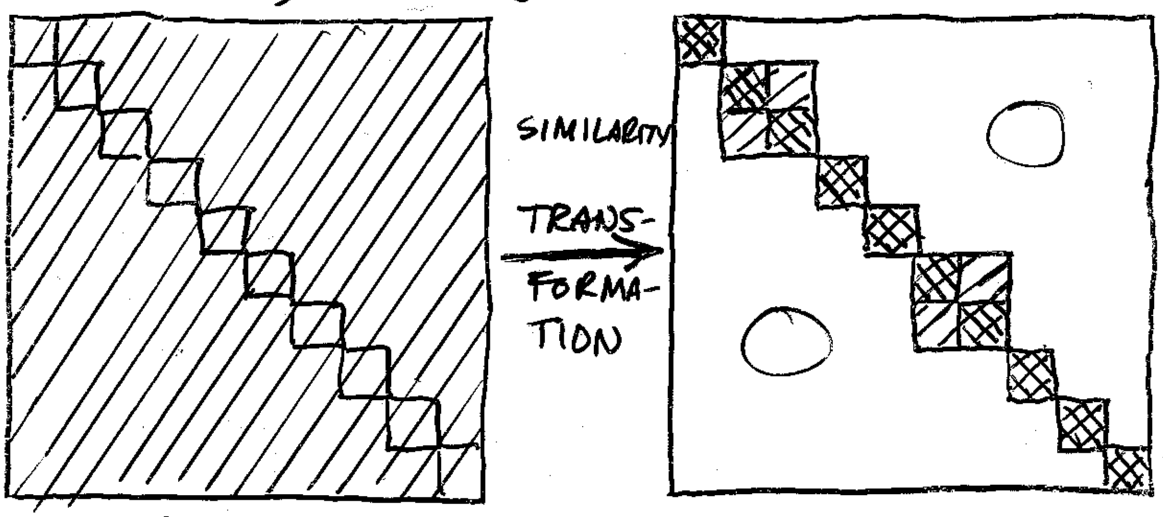
	(E)	$(C_3$ and $C_3^2)$	(all σ_v)
χ	3	0	1

Since the TRACE (sum of diagonal elements) of a matrix is not changed by any similarity transformation, then, for each operation R_{op}:

$$\chi^{red}(R_{op}) = \sum_i \underbrace{a_i}_{} \chi^{(i)}(R_{op})$$

The number of times that the block constituting the $i^{\underline{th}}$ IRREP will appear along the diagonal after the reducible representation is completely reduced.

GROUP C_{3V}, operation C_3



$\chi^{red}(C_3) = 4$ $\qquad$ $2\chi^{A_1}(C_3) + 4\chi^{A_2}(C_3) + 2\chi^{E}(C_3) = 4$

ALL 6 matrices BLOCK OUT IN THIS WAY.
(for 6 symmetry operations)

From the above we can prove the THEOREMS (by using LOT)

A VERY USEFUL RELATION $\Longrightarrow$ $$a_i = \frac{1}{h} \sum_{R_{op}} \chi^{red}(R_{op})\, \chi^{(i)*}(R_{op})$$

THIS ALLOWS US TO FIND HOW MANY TIMES an IRREP is contained in a reducible REPRESENTATION

RECALL that $\Psi = \sum_j c_j \phi_j$ where ϕ_j are functions in a complete orthonormal set

To find c_i

Operate on both sides with $\int \phi_i^* d\tau$

$$\int \phi_i^* \Psi \, d\tau = \sum_j c_j \underbrace{\int \phi_i^* \phi_j \, d\tau}_{\delta_{ij}} = \sum_j c_j \delta_{ij} = c_i$$

ORTHOGONALITY

In other words:

$$c_i = \int \phi_i^* \Psi \, d\tau$$

$$\chi^{red}(R_{op}) = \sum_j a_j \chi^{(j)}(R_{op})$$

To find a_i

Multiply both sides by $\chi^{(i)*}(R_{op})$ and integrate (i.e., sum over all R_{op})

$$\sum_{R_{op}}^{h} \chi^{(i)*}(R_{op}) \chi^{red}(R_{op}) = \sum_j a_j \underbrace{\sum_{R_{op}}^{h} \chi^{(i)*}(R_{op}) \chi^{(j)}(R_{op})}_{h\,\delta_{ij}} = h a_i$$

LOT

In other words:

$$a_i = \frac{1}{h} \sum_{R_{op}}^{h} \chi^{(i)*}(R_{op}) \chi^{red}(R_{op})$$

WHAT is SO SPECIAL about IRREDUCIBLE REPS?

1. THE GREAT ORTHOGONALITY THEOREM (GOT)

For a group of order h (=6 for C_{3v}), and any two IRREDUCIBLE REPRESENTATIONS

$\mathbb{D}^{l}(R_{op})$ and $\mathbb{D}^{l'}(R_{op})$ $\quad R_{op} = E, C_3,$ etc...

belonging to symmetry species Γ_l and $\Gamma_{l'}$ the GOT states that

$$\sum_{R_{op}} \mathbb{D}^{l}_{ij}(R_{op})\, \mathbb{D}^{l'}_{i'j'}(R_{op}) = \frac{h}{d_l}\, \delta_{ll'}\, \delta_{ii'}\, \delta_{jj'}$$

where d_l is the size of the matrix

In words:

If you select any position in a matrix of one irreducible rep and any position in a matrix of a second irreducible rep, multiply together the numbers you find there and then sum the product over all elements of the group, the answer is ZERO unless you choose not only THE SAME SYMMETRY SPECIES in the two cases, but also THE SAME LOCATION to take the numbers from in both sets of matrices, in which case the answer is the number $\frac{h}{d_l}$.

Example, C_{3v} again:

	R_{op}: E	C_3	C_3^2	σ_v	σ_v'	σ_v''	
IRREP Γ_1	$[1]$	$[1]$	$[1]$	$[1]$	$[1]$	$[1]$	$d_1 = 1$
IRREP Γ_2	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2} \\ \frac{3}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2} \\ -\frac{3}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2} \\ \frac{3}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2} \\ -\frac{3}{2} & \frac{1}{2} \end{bmatrix}$	$d_2 = 2$

Γ_1 and Γ_1: $1^2 + 1^2 + 1^2 + 1^2 + 1^2 + 1^2 = 6$

1,1 of Γ_2 and 1,2 of Γ_2:

$$1\cdot 0 + (-\tfrac{1}{2})(-\tfrac{1}{2}) + (-\tfrac{1}{2})(\tfrac{1}{2}) + 1\cdot 0 + (-\tfrac{1}{2})(\tfrac{1}{2}) + (-\tfrac{1}{2})(-\tfrac{1}{2}) = 0$$

1,1 of Γ_2 and Γ_1:

$$(1)(1) + (-\tfrac{1}{2})(1) + (-\tfrac{1}{2})(1) + (1)(1) + (-\tfrac{1}{2})(1) + (-\tfrac{1}{2})(1) = 0$$

2. THE LITTLE ORTHOGONALITY THEOREM (LOT)

(If we start with GOT, set $i=j$, $i'=j'$ and sum over these diagonal elements we get LOT)

$$\sum_{R_{op}} \chi^{(\ell)}(R_{op})^{*} \chi^{(\ell')}(R_{op}) = h\,\delta_{\ell\ell'}$$

Think of **GOT** in the following way:

Any set of corresponding matrix elements (say the 1,1 element) one from each matrix, behave as the components of a vector in h-dimensional space such that all these vectors are mutually orthogonal and each is normalized so that the square of its length equals h/d_ℓ (h = no. of symmetry ops R_{op}; d_ℓ = size of matrix in the ℓ^{th} IRREP)

Think of LOT in the following way:

The characters (sum of diagonal elements) of each matrix representation behave as the components of a vector in h-dimensional space such that all these vectors are mutually orthogonal.

In 3-dimensional cartesian space the mathematical STATEMENT of ORTHOGONALITY is

$$U \cdot V = 0 \quad \text{or} \quad U_x V_x + U_y V_y + U_z V_z = 0$$

The statement in LOT for C_{3v} group is:

$$\chi^{(1)}(E)^{*} \cdot \chi^{(2)}(E) + \chi^{(1)}(C_3)^{*} \cdot \chi^{(2)}(C_3) + \chi^{(1)}(C_3^{2})^{*} \cdot \chi^{(2)}(C_3^{2}) + \chi^{(1)}(\sigma_v)^{*} \cdot \chi^{(2)}(\sigma_v) + \chi^{(1)}(\sigma_v')^{*} \cdot \chi^{(2)}(\sigma_v') + \chi^{(1)}(\sigma_v'')^{*} \cdot \chi^{(2)}(\sigma_v'') = 0$$

3. The sum of the SQUARES of the characters in any IRREP equals h

$$\sum_{R_{op}} |\chi^{(\ell)}(R_{op})|^2 = h$$

4. The sum of the SQUARES of the dimensions of the IRREPS of a group is equal to the order of the group.

$$d_1^2 + d_2^2 + \cdots = h$$

5. The NUMBER OF IRREPS (and since each SYMMETRY SPECIES has its own IRREP), the NUMBER OF SYMMETRY SPECIES is equal to the number of CLASSES in the group.

6. The character of the IDENTITY OPERATION is equal to the size (dimension of the representation).
of the matrix

EXAMPLE:

Group C_{2v} has the symmetry operations

$$E \quad C_2 \quad \sigma_v \quad \sigma_v'$$

Each one is in a separate class because there is no symmetry operation that can be used to transform a rotation about an axis into a reflection, and also the symmetry operation C_2 cannot be used to transform σ_v into σ_v'.

Using 5. The number of SYMMETRY SPECIES each one represented by an IRREP is 4 (same as number of classes).

Using 4. $d_1^2 + d_2^2 + d_3^2 + d_4^2 = h = 4$ (the order of the group)
↳ only one possible solution:
$d_1 = d_2 = d_3 = d_4 = 1$ (all IRREPS of C_{2v} are 1-dimension matrices)

Using 6. The character of the identity operation is 1

Using 3. The squares of the characters are all the same, all are equal to 1 since this is the only solution to the equation:

$$|\chi(E)|^2 + |\chi(C_2)|^2 + |\chi(\sigma_v)|^2 + |\chi(\sigma_v')|^2 = 4 \quad \text{for each IRREP}$$

This would mean that $\chi^{(i)}(R_{op}) = +1$ or -1. We find all the possible combinations of +1 and −1 values such that they are ORTHOGONAL (using 2.):

Group C_{2v}

	Symmetry Operations				
	E	C_2	σ_v	σ_v'	SYMMETRY SPECIES Name
IRREP 1 for SYMMETRY SPECIES 1	[1]	[1]	[1]	[1]	A_1
IRREP 2 for SYMMETRY SPECIES 2	[1]	[−1]	[−1]	[1]	B_2
IRREP 3 for SYMMETRY SPECIES 3	[1]	[−1]	[1]	[−1]	B_1
IRREP 4 for SYMMETRY SPECIES 4	[1]	[1]	[−1]	[−1]	A_2

$\chi(E)$ is the dimension of the IRREP

Choices of +1 or −1 such as to ensure ORTHOGONALITY

HOW TO NAME THE SYMMETRY SPECIES or IRREP

1. Based on the dimension of the IRREP (based on $\chi(C_n)$)
   - 1 — A or B
   - 2 — E
   - 3 — T (or F in other books)
2. Subscript (NOT ALWAYS subscript 3 also)
   - 1 if SYMMETRIC with respect to $C_2 \perp C_n$ or with respect to $\sigma \parallel C_n$
   - 2 if ANTISYMMETRIC (character is negative)
3. prime ′ if SYMMETRIC with respect to σ_h
   or double prime ″ if ANTISYMMETRIC
4. g if SYMMETRIC with respect to i
   or u if ANTISYMMETRIC

Notation for the Irreducible Representations of Point Groups

Property represented	Symbol	Meaning
Degeneracy of representation	A, B	Non degenerate
	E	Double degenerate
	T	Triple degenerate
	G	Fourfold degenerate
	H	Fivefold degenerate
Symmetry with respect to the principal axis	A	Symmetrical
	B	Antisymmetrical
Symmetry with respect to inversion	Suffix g	Symmetrical (in German: *gerade*)
	Suffix u	Antisymmetrical (in German: *ungerade*)
	Used with any of the above symbols	
Symmetry with respect to σ_h	Prime ′	Symmetrical
	Double prime ″	Antisymmetrical
	Used with any of the above symbols	
Symmetry with respect to the secondary binary axes	Suffix 1	The most symmetrical of the A or B representations
	Suffixes 2,3	Other A or B representations
	Used with symbols A or B	
Transformation properties of the spherical harmonics (see § 6.5)	Suffix 1	Representation to which there belongs the spherical harmonic with $m = 1$
	Suffix 2	Representation to which there belongs the spherical harmonic with $m = 2$
	Used with symbol E	

EXAMPLES: A CHARACTER TABLE SHOWS THE character χ for each symmetry operation R_{op} (in classes) for the various IRREDUCIBLE REPRESENTATIONS labeled by their SYMMETRY SPECIES

These R_{op} each in a class by itself

GROUP of order 8

SYMMETRY SPECIES Γ

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
A_g	1	1	1	1	1	1	1	1
B_{1g}	1	1	−1	−1	1	1	−1	−1
B_{2g}	1	−1	1	−1	1	−1	1	−1
B_{3g}	1	−1	−1	1	1	−1	−1	1
A_u	1	1	1	1	$\boxed{-1}$	−1	−1	−1
B_{1u}	1	1	−1	−1	$\boxed{-1}$	−1	1	1
B_{2u}	1	−1	1	−1	$\boxed{-1}$	1	−1	1
B_{3u}	1	−1	−1	1	$\boxed{-1}$	1	1	−1

χ

u

THESE ARE ALSO THE IRREPS THEMSELVES SINCE all are 1X1 MATRICES for group D_{2h}

GROUP of order 12

all in one class σ_v, σ_v', σ_v''

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
E'	$\boxed{2}$	−1	0	2	−1	0
A_1''	1	1	1	$\boxed{-1}$	−1	−1
A_2''	1	1	−1	$\boxed{-1}$	−1	1
E''	$\boxed{2}$	−1	0	$\boxed{-2}$	1	0

SYMMETRY OPERATIONS

subscript 2

″

2 dimensional IRREPS

6 classes
6 SYMMETRY SPECIES (IRREPS)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
T_{2g}	$\boxed{3}$	0	1	−1	−1	3	−1	0	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
T_{2u}	$\boxed{3}$	0	1	−1	−1	−3	1	0	1	−1
⋮										

3-dimensional IRREPS

$\chi(E)$ gives the dimension of the IRREP

there are a total of 10 SYMMETRY SPECIES for O_h

HOW TO GENERATE A MATRIX REPRESENTATION (usually a REDUCIBLE one) BY USING A BASIS

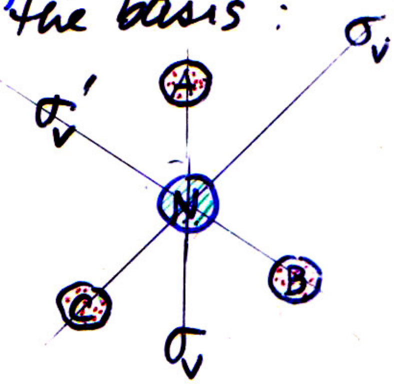
Step ① Choose the basis (orbitals, arrows, objects, cartesian displacements, etc.)

For example: for C_{3v} one could use as a basis for a 4x4 representation the following

$$\begin{bmatrix} s_N \\ s_A \\ s_B \\ s_C \end{bmatrix}$$

- s_N 2s orbital on N of NH_3 molecule
- s_A 1s orbital on H_A
- s_B 1s orbital on H_B
- s_C 1s orbital on H_C

Step ② To find the matrix representation of each symmetry operation R_{op}, CARRY OUT THAT SYMMETRY OPERATION on the basis:



SYMMETRY OPERATION, BASIS ↓

$$\sigma_v\, s_N = s_N$$
$$\sigma_v\, s_A = s_A$$
$$\sigma_v\, s_B = s_C$$
$$\sigma_v\, s_C = s_B$$

Put these in matrix form of equations.

$$\sigma_v \begin{bmatrix} s_N \\ s_A \\ s_B \\ s_C \end{bmatrix} = \underbrace{\begin{array}{c|cccc} & s_N & s_A & s_B & s_C \\ \hline s_N & 1 & 0 & 0 & 0 \\ s_A & 0 & 1 & 0 & 0 \\ s_B & 0 & 0 & 0 & 1 \\ s_C & 0 & 0 & 1 & 0 \end{array}}_{} \begin{bmatrix} s_N \\ s_A \\ s_B \\ s_C \end{bmatrix} \xrightarrow{\text{after matrix multiplication}} \begin{bmatrix} s_N \\ s_A \\ s_C \\ s_B \end{bmatrix}$$

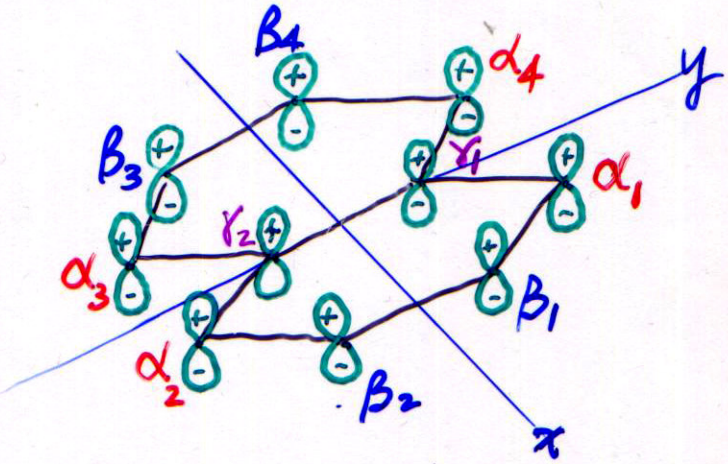
This matrix $\mathbb{D}(\sigma_v)$ is the matrix representation of σ_v in this basis

Equivalent but less commonly used form is to use a row vector (Atkins does it this way):

$$\sigma_v [s_N \; s_A \; s_B \; s_C] = [s_N \; s_A \; s_B \; s_C] \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \xrightarrow{\text{after matrix multiplication}} [s_N \; s_A \; s_C \; s_B]$$

Another **EXAMPLE**:

Choose the basis of ten $2p_z$ orbitals of naphthalene for the group D_{2h}. This gives a reducible 10x10 matrix representation.



D_{2h} $R_{op} =$	E	σ_{xy}	σ_{xz}	σ_{yz}	i	$C_2^{(z)}$	$C_2^{(y)}$	$C_2^{(x)}$
$R_{op}\alpha_1 =$	α_1	$-\alpha_1$	α_2	α_4	$-\alpha_3$	α_3	$-\alpha_4$	$-\alpha_2$
$R_{op}\alpha_2 =$	α_2	$-\alpha_2$	α_1	α_3	$-\alpha_4$	α_4	$-\alpha_3$	$-\alpha_1$
$R_{op}\alpha_3 =$	α_3	$-\alpha_3$	α_4	α_2	$-\alpha_1$	α_1	$-\alpha_2$	$-\alpha_4$
$R_{op}\alpha_4 =$	α_4	$-\alpha_4$	α_3	α_1	$-\alpha_2$	α_2	$-\alpha_1$	$-\alpha_3$
$R_{op}\beta_1 =$	β_1	$-\beta_1$	β_2	β_4	$-\beta_3$	β_3	$-\beta_4$	$-\beta_2$
$R_{op}\beta_2 =$	β_2	$-\beta_2$	β_1	β_3	$-\beta_4$	β_4	$-\beta_3$	$-\beta_1$
$R_{op}\beta_3 =$	β_3	$-\beta_3$	β_4	β_2	$-\beta_1$	β_1	$-\beta_2$	$-\beta_4$
$R_{op}\beta_4 =$	β_4	$-\beta_4$	β_3	β_1	$-\beta_2$	β_2	$-\beta_1$	$-\beta_3$
$R_{op}\gamma_1 =$	γ_1	$-\gamma_1$	γ_2	γ_1	$-\gamma_2$	γ_2	$-\gamma_1$	$-\gamma_2$
$R_{op}\gamma_2 =$	γ_2	$-\gamma_2$	γ_1	γ_2	$-\gamma_1$	γ_1	$-\gamma_2$	$-\gamma_1$

$$\sigma_{xz}\begin{bmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\\ \alpha_4\\ \beta_1\\ \beta_2\\ \beta_3\\ \beta_4\\ \gamma_1\\ \gamma_2\end{bmatrix} = \begin{bmatrix} 0&1&0&0&&&&&&\\ 1&0&0&0&&&&&&\\ 0&0&0&1&&&&&&\\ 0&0&1&0&&&&&&\\ &&&&0&1&0&0&&\\ &&&&1&0&0&0&&\\ &&&&0&0&0&1&&\\ &&&&0&0&1&0&&\\ &&&&&&&&0&1\\ &&&&&&&&1&0 \end{bmatrix}\begin{bmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\\ \alpha_4\\ \beta_1\\ \beta_2\\ \beta_3\\ \beta_4\\ \gamma_1\\ \gamma_2\end{bmatrix} \xRightarrow[\text{mult.}]{\text{after matrix}} \begin{bmatrix}\alpha_2\\ \alpha_1\\ \alpha_4\\ \alpha_3\\ \beta_2\\ \beta_1\\ \beta_4\\ \beta_3\\ \gamma_2\\ \gamma_1\end{bmatrix}$$

$$\chi^{red}(\sigma_{xz}) = 0$$

$$\sigma_{xy}\begin{bmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\\ \alpha_4\\ \beta_1\\ \beta_2\\ \beta_3\\ \beta_4\\ \gamma_1\\ \gamma_2\end{bmatrix} = \begin{bmatrix} -1&0&0&0&&&&&&\\ 0&-1&0&0&&&&&&\\ 0&0&-1&0&&&&&&\\ 0&0&0&-1&&&&&&\\ &&&&-1&0&0&0&&\\ &&&&0&-1&0&0&&\\ &&&&0&0&-1&0&&\\ &&&&0&0&0&-1&&\\ &&&&&&&&-1&0\\ &&&&&&&&0&-1 \end{bmatrix}\begin{bmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\\ \alpha_4\\ \beta_1\\ \beta_2\\ \beta_3\\ \beta_4\\ \gamma_1\\ \gamma_2\end{bmatrix} \xRightarrow[\text{mult.}]{\text{after matrix}} \begin{bmatrix}-\alpha_1\\ -\alpha_2\\ -\alpha_3\\ -\alpha_4\\ -\beta_1\\ -\beta_2\\ -\beta_3\\ -\beta_4\\ -\gamma_1\\ -\gamma_2\end{bmatrix}$$

$$\chi^{red}(\sigma_{xy}) = -10$$

NOTE! only the "UNSHIFTED" ORBITALS give NON-ZERO DIAGONAL MATRIX ELEMENTS

Since α positions can not be converted into β or γ positions by symmetry operations the α, β, and γ blocks do not ever mix for any R_{op}. This matrix representation is already partially blocked out into 4x4, 4x4, and 2x2

The characters of the these smaller matrix representations are easily obtained by

a) looking at the $R_{op}\alpha_i$ etc. table

b) (even without having that table) merely counting the unshifted orbitals and getting the sign right. Those orbitals that are centered on the symmetry element (i.e., on a symmetry axis for rotation, on the center for inversion, on a symmetry plane for reflection) do not become interchanged with others in the set.

Characters		E	σ_{xy}	σ_{xz}	σ_{yz}	i	$C_2(z)$	$C_2(y)$	$C_2(x)$
Γ_α	4x4	4	-4	0	0	0	0	0	0
Γ_β	4x4	4	-4	0	0	0	0	0	0
Γ_γ	2x2	2	-2	0	2	0	0	-2	0

Now, can we find the IRREDUCIBLE REPRESENTATIONS contained in the 4x4, 4x4, and 2x2 reps?

Use $a_i = \frac{1}{h} \sum_{R_{op}} \chi^{(i)*}(R_{op}) \, \chi^{red}(R_{op})$

Given the character table for D_{2h}:

symmetry species	same R_{op} as above							
A_g	1	1	1	1	1	1	1	1
B_{1g}	1	1	-1	-1	1	1	-1	-1
B_{2g}	1	-1	1	-1	1	-1	1	-1
B_{3g}	1	-1	-1	1	1	-1	-1	1
A_u	1	-1	-1	-1	-1	1	1	1
B_{1u}	1	-1	1	1	-1	1	-1	-1
B_{2u}	1	1	-1	1	-1	-1	1	-1
B_{3u}	1	1	1	-1	-1	-1	-1	1

We find:

$\Gamma_\alpha = B_{2g} \oplus B_{3g} \oplus A_u \oplus B_{1u}$

$\Gamma_\beta = B_{2g} \oplus B_{3g} \oplus A_u \oplus B_{1u}$

$\Gamma_\gamma = B_{3g} \oplus B_{1u}$

PROJECTION OPERATORS:

$$R\,\psi_{\alpha k} = \sum_{j=1}^{l_\alpha} \psi_{\alpha j}\,\Gamma_\alpha(R)_{jk}$$

where $\psi_{\alpha k}$ has l_α partner functions

Multiply by $\Gamma_\beta^*(R)_{j'k'}$ and sum over all R

$$\sum_R \Gamma_\beta(R)^*_{j'k'}\,R\,\psi_{\alpha k} = \sum_R \Gamma_\beta(R)^*_{j'k'} \sum_{j=1}^{l_\alpha} \psi_{\alpha j}\,\Gamma_\alpha(R)_{jk}$$

$$= \sum_{j=1}^{l_\alpha} \underbrace{\sum_R \Gamma_\beta(R)^*_{j'k'}\,\Gamma_\alpha(R)_{jk}}_{\frac{h}{l_\alpha}\delta_{\alpha\beta}\delta_{jj'}\delta_{kk'}}\,\psi_{\alpha j}$$

GOT

$$\underbrace{\left(\frac{l_\alpha}{h}\sum_R \Gamma_\beta(R)^*_{j'k'}\,R\right)}\psi_{\alpha k} = \delta_{\alpha\beta}\,\delta_{jj'}\,\delta_{kk'}\,\psi_{\alpha j}$$

This generates from the function in the k^{th} position of the set of partner functions

the function in the jth position

Therefore, if we know one function we can get the other $l_\alpha - 1$ functions by means of this operator - called a "projection operator"

Special case is the character operator

Let $\alpha = \beta \quad j' = k' = \mu$

$$\left(\frac{l_\alpha}{h}\sum_R \Gamma_\alpha(R)^*_{\mu\mu}\,R\right)\psi_{\alpha k} = \psi_{\alpha\mu}\,\delta_{\mu k}$$

If we apply the projection operator to an arbitrary function ψ and then sum over all $\mu = 1$ up to l_α both sides

$$\Big(\frac{l_\alpha}{h} \sum_R \underbrace{\sum_\mu \Gamma_\alpha(R)^*_{\mu\mu}}_{\text{character}} R \Big) \underset{\uparrow}{\psi} = \sum_{\mu=1}^{l_\alpha} \psi_{\alpha\mu} \underbrace{\delta_{\mu k}}_{\substack{\text{for each } k \\ \text{we got this}}}$$

$$\sum_{k=1}^{l_\alpha} \psi_{\alpha k}$$

$$\underbrace{\Big(\frac{l_\alpha}{h} \sum_R^h \chi^*_\alpha(R) \cdot R \Big)}_{\text{character operator}} \psi = \sum_{\mu=1}^{l_\alpha} \psi_{\alpha\mu}$$

It projects out of a <u>general</u> function a sum of basis functions spanning the representation Γ_α

APPLICATION:

A linear combination of $2p_z$ orbitals on the 4 alpha carbons of napthalene and the $2p_z$ orbitals on the 4 beta carbons are needed to form a MOLECULAR ORBITAL THAT BELONGS TO THE SYMMETRY SPECIES B_{2g}. Ditto to form a molecular orbital that belongs to the symmetry species A_u

How do we find these symmetry adapted linear combinations that belong to a particular symmetry species (IRREP)?

Project out of the $2p_z$ orbital α_1 a linear combination belonging to B_{2g} by

$$P_{B_{2g}} = \frac{d_{B_{2g}}}{h} \sum_{R_{op}} \underbrace{\chi^{B_{2g}*}(R_{op})}_{\text{from the character table}} R_{op}$$

$$= \frac{1}{8}\left[E - \sigma_{xy} + \sigma_{xz} - \sigma_{yz} + i - C_2(z) + C_2(y) - C_2(x) \right]$$

$$P_{B_{2g}}\alpha_1 = \frac{1}{8}\left[\alpha_1 - (-\alpha_1) + \alpha_2 - \alpha_4 + (-\alpha_3) - \alpha_3 + (-\alpha_4) - (-\alpha_2) \right]$$

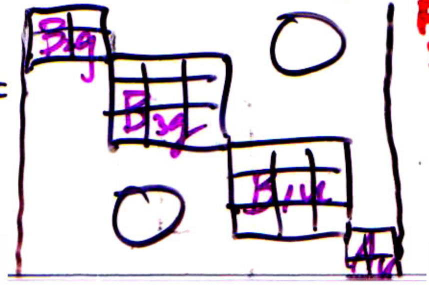
$$= \frac{1}{8}\left[2\alpha_1 + 2\alpha_2 - 2\alpha_3 - 2\alpha_4 \right] \quad \text{not yet normalized}$$

$$\phi^{\alpha}_{B_{2g}} = N\{\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4\} \quad \text{THIS is a SALC}$$

We can find all the 10 SALCs:

$$\phi^{\alpha}_{B_{2g}} \quad \phi^{\beta}_{B_{2g}} \quad \phi^{\alpha}_{B_{3g}} \quad \phi^{\beta}_{B_{3g}} \quad \phi^{\gamma}_{B_{3g}} \quad \phi^{\alpha}_{A_u} \quad \phi^{\beta}_{A_u} \quad \phi^{\alpha}_{B_{1u}} \quad \phi^{\beta}_{B_{1u}} \quad \phi^{\gamma}_{B_{1u}}$$

If we use these 10 functions as the complete set of basis functions with which to set up the Hamiltonian for the pi electrons of napthalene, we get

$\mathbb{H} =$ 

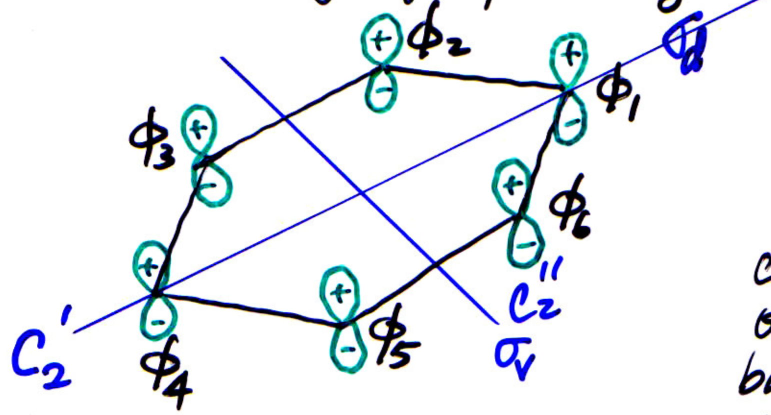
FUNCTIONS BELONGING TO DIFFERENT SYMMETRY SPECIES DO NOT MIX

Now we need only to solve 2X2 or 3X3 blocks rather than 10X10.

EXAMPLE:

Sometimes the MOLECULAR ORBITALS are determined entirely by symmetry:

D_{6h}



Use the 6 carbon $2p_z$ orbitals a a basis for a representation Γ

As we have seen in the naphthalene example, we can find the character of each symmetry operation in the reducible representation that can be generated from the basis ϕ_1, ϕ_2 ϕ_3 $\cdots$ ϕ_6 by looking only at the ϕ_i that are NOT SHIFTED by the symmetry operation, i.e. they must lie on the axis, or plane of symmetry. See if they turn into themselves with or without a change in SIGN.

D_{6h}	E	$2C_6$	$2C_3^{(z)}$	$C_2^{(z)}$	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ	6	0	0	0	−2	0	0	0	0	−6	2	0

Decompose this into the IRREPS contained in Γ by using

$$a_i = \frac{1}{24} \sum_{R_{op}} \chi^{(i)*}(R_{op})\, \chi^{\Gamma}(R_{op})$$

$$\Gamma = A_{2u} \oplus B_{1g} \oplus E_{1g} \oplus E_{1u}$$

In this case we can actually use a SUBGROUP C_6 of group D_{6h} since it provides the same results and we can identify directly which SYMMETRY SPECIES in C_6 group correspond to the A_{2u} B_{1g} E_{1g} and E_{1u} of the D_{6h} group

Group C_6	E	C_6	C_3	C_2	C_3^2	C_6^5	SYMMETRY SPECIES: subgroup C_6	group D_{6h}
$R_{op}\phi_1 =$	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6		
CHARACTERS A	1	1	1	1	1	1	A	A_{2u}
B	1	-1	1	-1	1	-1	B	B_{1g}
TOGETHER is a PSEUDO E: $1a$	1	ϵ	$-\epsilon^*$	-1	$-\epsilon$	ϵ^*	E $1a$	E_{1g}
$1b$	1	ϵ^*	$-\epsilon$	-1	$-\epsilon^*$	ϵ	$1b$	
E also: $2a$	1	$-\epsilon^*$	$-\epsilon$	1	$-\epsilon^*$	$-\epsilon$	E $2a$	E_{2u}
$2b$	1	$-\epsilon$	$-\epsilon^*$	1	$-\epsilon$	$-\epsilon^*$	$2b$	

CHARACTER TABLE

The IRREPS contained in Γ

$$\epsilon \equiv e^{i\,2\pi/6} = \cos\left(\tfrac{2\pi}{6}\right) + i\sin\left(\tfrac{2\pi}{6}\right)$$

Create the projection operators

$$\mathcal{P}_A = \underbrace{\frac{d_A}{h}}_{\text{forget about this, need to normalize the SALCs later.}} \sum_{R_{op}} \underbrace{\chi^{A*}(R_{op})}_{\text{from the character table}}\, R_{op}$$

$\psi_{A_{2u}}$ comes from $\mathcal{P}_A\phi_1 = (1E\phi_1 + 1C_6\phi_1 + 1C_3\phi_1 + 1C_2\phi_1 + 1C_3^2\phi_1 + 1C_6^5\phi_1)$

all characters are 1 for symmetry species A

Can get SALCs by inspection of above table:

$$\psi_{A_{2u}} = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_{B_{1g}} = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

$$\psi_{E_{1ga}} = (\phi_1 + \epsilon\phi_2 - \epsilon^*\phi_3 - \phi_4 - \epsilon\phi_5 + \epsilon^*\phi_6)$$

$$\psi_{E_{1gb}} = (\phi_1 + \epsilon^*\phi_2 - \epsilon\phi_3 - \phi_4 - \epsilon^*\phi_5 + \epsilon\phi_6)$$

Can form 2 REAL functions instead of using these 2 COMPLEX functions

$$\psi_{E_{2ua}} = (\phi_1 - \epsilon^*\phi_2 - \epsilon\phi_3 + \phi_4 - \epsilon^*\phi_5 - \epsilon\phi_6)$$

$$\psi_{E_{2ub}} = (\phi_1 - \epsilon\phi_2 - \epsilon^*\phi_3 + \phi_4 - \epsilon\phi_5 - \epsilon^*\phi_6)$$

Ditto!

since

$$\frac{\epsilon + \epsilon^*}{2} = \cos\left(\tfrac{2\pi}{6}\right) = \tfrac{1}{2}$$

$$\frac{\epsilon - \epsilon^*}{2i} = \sin\tfrac{2\pi}{6} = \tfrac{\sqrt{3}}{2}$$

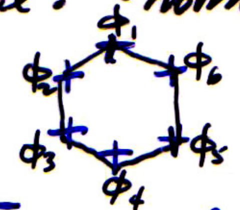
So take

$$\left(\psi_{E_{1g}}^{+}\right)_{real} = \tfrac{1}{2}\left(\psi_{E_{1ga}} + \psi_{E_{1gb}}\right)$$ normalize later

and $$\psi_{E_{1g}}^{-} = \tfrac{1}{2i}\left(\psi_{E_{1ga}} - \psi_{E_{1gb}}\right)$$

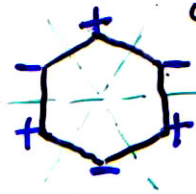
The final SALCs (all REAL functions) are: (not normalized)

$$\psi_{A_{2u}} = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$



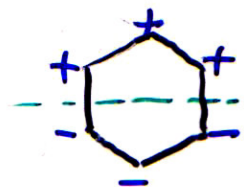
zero nodes

$$\psi_{B_{1g}} = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$



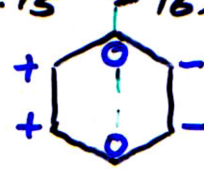
3 nodes

$$\psi_{E_{1g}^{+}} = (\phi_1 + \tfrac{1}{2}\phi_2 - \tfrac{1}{2}\phi_3 - \phi_4 - \tfrac{1}{2}\phi_5 + \tfrac{1}{2}\phi_6)$$



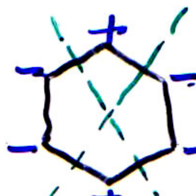
one node

$$\psi_{E_{1g}^{-}} = (\phi_2 + \phi_3 - \phi_5 - \phi_6)\frac{\sqrt{3}}{2}$$



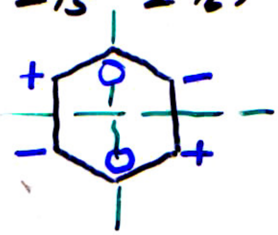
one node

$$\psi_{E_{2u}^{+}} = (\phi_1 - \tfrac{1}{2}\phi_2 - \tfrac{1}{2}\phi_3 + \phi_4 - \tfrac{1}{2}\phi_5 - \tfrac{1}{2}\phi_6)$$



two nodes

$$\psi_{E_{2u}^{-}} = (\phi_2 - \phi_3 + \phi_5 - \phi_6)\frac{\sqrt{3}}{2}$$



two nodes

Energies are in the order:

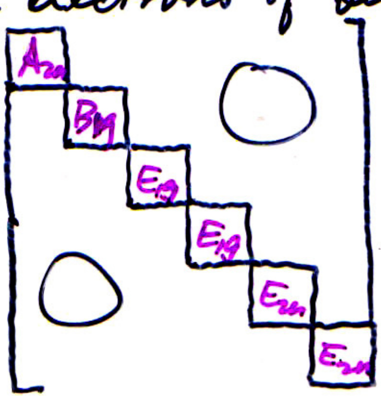
B_{1g} — 3 nodes (highest energy)

E_{2u} — 2 nodes

E_{1g} — 1 node

A_{2u} — 0 nodes (lowest energy)

If we use these functions (SALCs) as the complete set of basis functions with which to set up the Hamiltonian of the pi electrons of benzene, we get

$\mathbb{H} =$ 

Therefore these SALCS $\psi_{A_{2u}}$ $\psi_{B_{1g}}$ $\psi_{E_{1g}^{+}}$ $\psi_{E_{1g}^{-}}$ $\psi_{E_{2u}^{+}}$ $\psi_{E_{2u}^{-}}$ are the MOLECULAR ORBITALS of the pi electrons of benzene

SYMMETRY OPERATIONS on FUNCTIONS:

Consider some set of linearly independent functions $\{F_1 \;\; F_2 \cdots F_j \cdots F_n\}$

Let the symmetry operations of some particular point group be $\{R \;\; S \;\; W \cdots\}$

In particular, let $RS = W$

Let the effect of R on any F_j is to transform F_j into some linear combination of the functions $F_1, F_2, \cdots, F_n$

$$R F_j = \sum_{i=1}^{n} F_i r_{ij}$$

r_{ij} are constants

There are $j = 1, 2, \cdots n$ such relations for R

$$S F_j = \sum_{i=1}^{n} F_i s_{ij}$$

$$W F_j = \sum_{i=1}^{n} F_i w_{ij}$$

Let the square matrices $\mathbb{R}, \mathbb{S}, \mathbb{W}, \cdots$ be made up from coefficients $r_{ij}, s_{ij}, w_{ij}, \cdots$

Then: The matrices $\{\mathbb{R} \;\; \mathbb{S} \;\; \mathbb{W} \cdots\}$ form a REPRESENTATION (generally reducible) of the point group

Proof: $WF_j = \sum_i^n F_i w_{ij} = RSF_j = R\sum_i^n F_i s_{ij} = \sum_i^n (RF_i) s_{ij}$

$$= \sum_{i=1}^n \left(\sum_{k=1}^n F_k r_{ki}\right) s_{ij} = \sum_{k=1}^n \sum_{i=1}^n F_k r_{ki} s_{ij}$$

interchange dummy indices i, k

$$= \sum_i^n F_i \sum_k r_{ik} s_{kj}$$

$\therefore \; w_{ij} = \sum_k r_{ik} s_{kj}$ since the F_i are linearly independent

$$\mathbb{W} = \mathbb{R}\,\mathbb{S}$$

Theorem: Any set of n linearly independent functions that are transformed into linear combinations of one another by the symmetry operations of a group forms a basis for an **n-dimensional** representation of the group.

ELECTRONIC or VIBRATIONAL EIGENFUNCTIONS are BASES for IRREDUCIBLE REPRESENTATIONS:

- The Hamiltonian $\mathcal{H}$ commutes with any symmetry operation R since a symmetry operation of the point group to which the molecule belongs sends the molecular framework into a configuration physically INDISTINGUISHABLE from the original one, it does not affect either the electronic or the vibrational hamiltonian which is defined relative to the molecular framework

Non-degenerate case:

$$R\mathcal{H}\Psi_i = RE_i\Psi_i$$

$$\mathcal{H}\underbrace{R\Psi_i} = E_i\underbrace{R\Psi_i} \quad \mathcal{H} \text{ commutes with } R$$

$\therefore R\Psi_i$ is also a solution to the Schrödinger eqn

Since $R\Psi_i$ has to be normalized, given that Ψ_i is itself already normalized, then

$$R\Psi_i = \pm\Psi_i$$

$\therefore$ For each non-degenerate eigenvalue we can generate a representation of the group with 1-dimensional matrices having matrix elements 1 or -1, that is, a one-dimensional IRREDUCIBLE REPRESENTATION of the point group of the molecule.

Degenerate case: l_α-fold degenerate with energy eigenvalue E_α

$$\mathcal{H}\Psi_{\alpha j} = E_\alpha\Psi_{\alpha j} \qquad j = 1, 2, 3, \cdots l_\alpha \text{ partner functions}$$

Any linear combinations of $\Psi_{\alpha j}$ are also solutions of $\mathcal{H}$ with the same energy eigenvalue E_α

Apply a symmetry operation R on one of the functions $\Psi_{\alpha j}$

$$\mathcal{H}\underbrace{R\Psi_{\alpha j}}_{\sum_{i=1}^{l_\alpha}\Psi_{\alpha i}\, r_{ij}} = E_\alpha R\Psi_{\alpha j}$$

For some other symmetry operation $\mathbf{S}$

$$\mathbf{S}\Psi_{\alpha j} = \sum_{i}^{l_\alpha} \Psi_{\alpha i} s_{ij}$$

$$\mathbf{W}\Psi_{\alpha j} = \sum_{i}^{l_\alpha} \Psi_{\alpha i} w_{ij} = \mathbf{RS}\Psi_{\alpha j}$$

As before, we find $w_{ij} = \sum_k r_{ik} s_{kj}$ or $\mathbb{W} = \mathbb{R}\mathbb{S}$

Thus, the functions $\Psi_{\alpha j}$ $j = 1, 2, \ldots l_\alpha$ together form a basis for the reducible or irreducible l_α-dimensional representation of the point group of the molecule. That is, we can write

$$\mathbf{R}\Psi_{\alpha j} = \sum_{i=1}^{l_\alpha} \Psi_{\alpha i} \Gamma_\alpha(\mathbf{R})_{ij}$$

If reducible then can always reduce to block-diagonal form by a similarity transformation which converts all of $\{\mathbb{R}, \mathbb{S}, \mathbb{W}, \ldots\}$ into the same block diagonal form by

$\mathbb{C}^{-1}\mathbb{R}\mathbb{C}$, $\quad \mathbb{C}^{-1}\mathbb{S}\mathbb{C}$, $\quad$ etc.

The new set of functions divide up into subsets whose members transform among themselves under the action of the symmetry operations $\{\mathbf{R}, \mathbf{S}, \mathbf{W}, \text{etc.}\}$

SUMMARY:

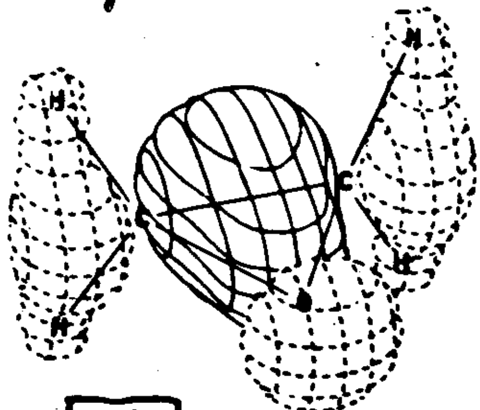
- The NONDEGENERATE electronic or vibrational eigenfunctions of a molecule are BASES for one-dimensional IRREPS of the molecular point group
- The l_α-fold DEGENERATE functions are BASES for l_α-dimensional IRREPS of the molecular point group

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

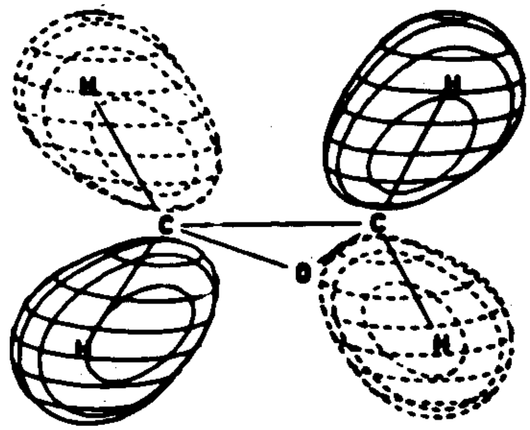
C_{2h}	E	$C_2(z)$	i	σ_h xy plane		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

ethylene oxide

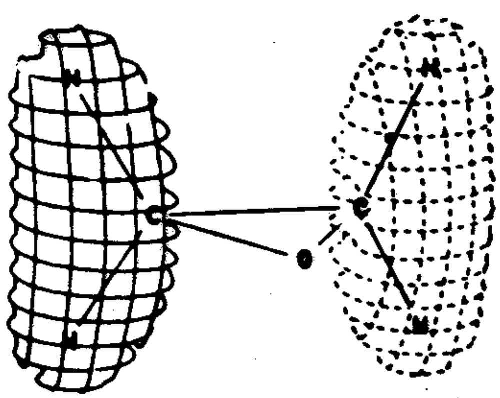
C–C yz plane
 O



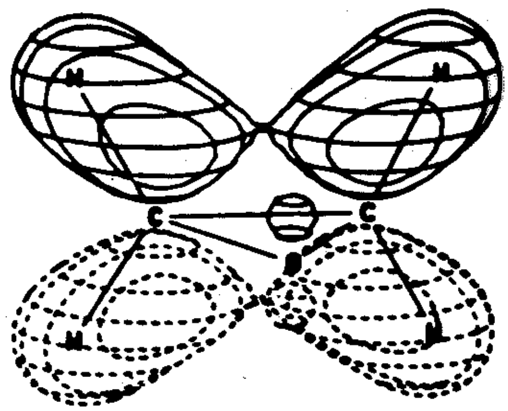
A_1 E=-0.6551 σ



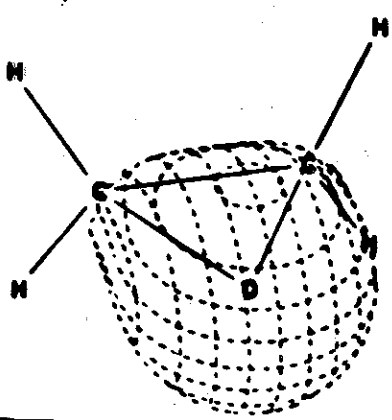
A_2 E=-0.5531 π_{CH_2}



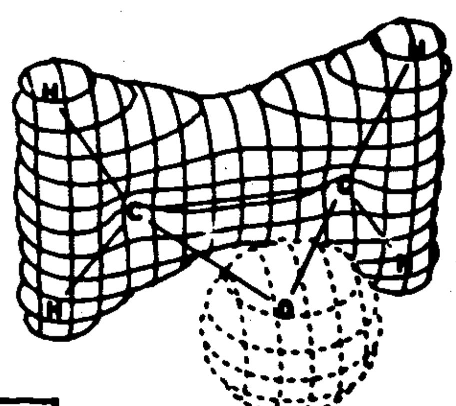
B_2 E=-0.8718 σ_{CH_2}



B_1 E=-0.7182 π_{CH_2}



A_1 E=-1.4284 σ_{CO}, σ_{CC}



A_1 E=-0.9389 σ_{CC}, σ_{CH_2}, n

16 electrons

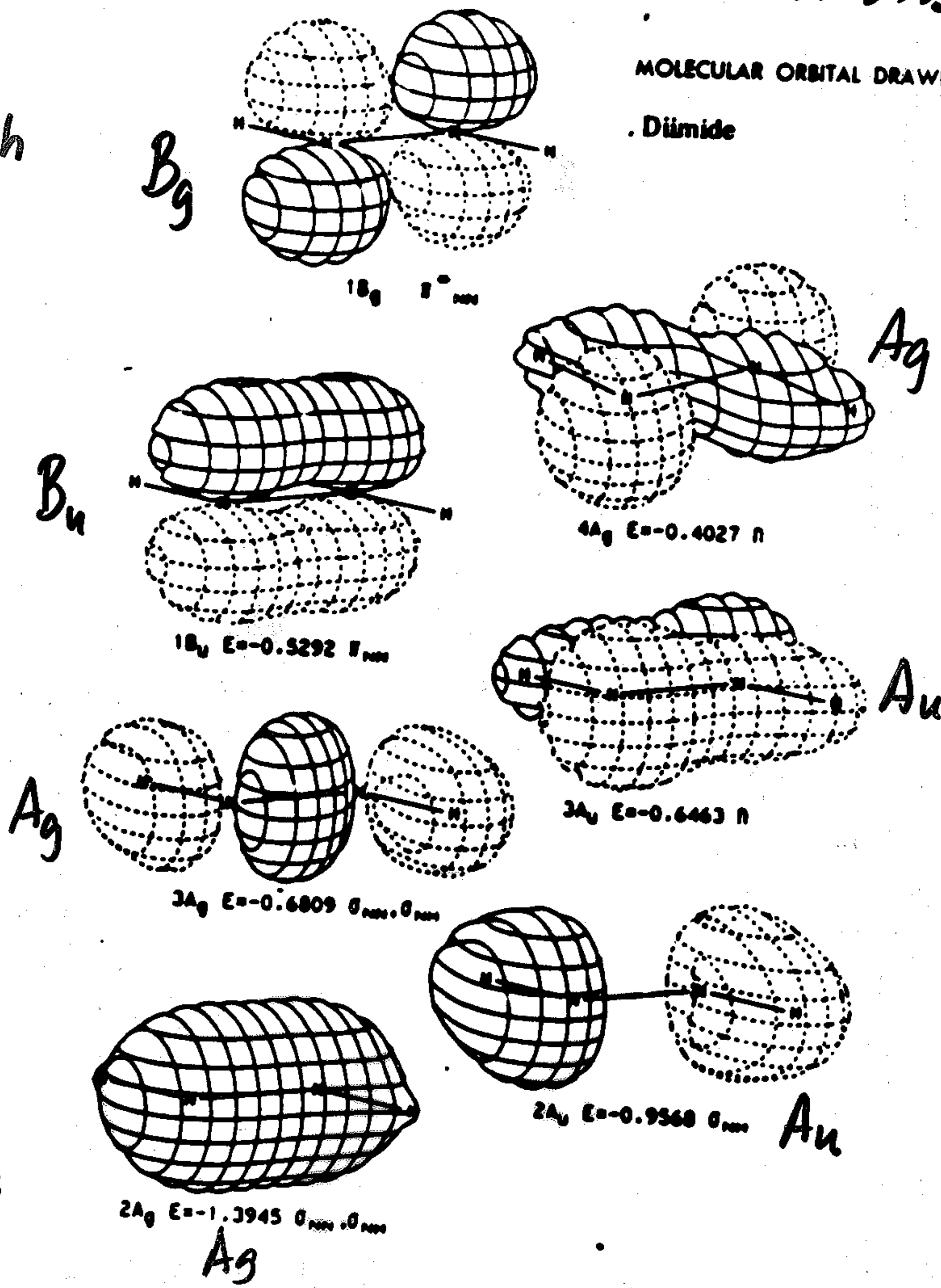
MOLECULAR ORBITAL DRAWINGS

. Diimide

C_{2h}

$1B_g$	
$4A_g$	−.4027
$1B_u$	−.5292
$3A_u$	−.6463
$3A_g$	−.6809
$2A_u$	−.9568
$2A_g$	−1.3945

$\left.\begin{array}{l} 1A_u \\ 1A_g \end{array}\right\}$ 4 electrons in 1s shells of N atoms



DIRECT PRODUCTS -

Can form direct products of groups
" " " functions
" " " matrices
" " " representations

The direct product of 2 square matrices $\mathbf{a}$ and $\mathbf{b}$ of dimension m and n respectively is a matrix $\mathbf{C}$ of dimension mn such that

$$\mathbf{C}_{ik;jl} = \mathbf{a}_{ij}\,\mathbf{b}_{kl}$$

row ik

Example :

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{array}{c} \begin{array}{cccc} \text{col } 11 & \text{col } 12 & \text{col } 21 & \text{col } 22 \end{array} \\ \left(\begin{array}{cc|cc} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ \hline a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{array}\right) \end{array}$$

trace of $a = a_{11} + a_{22}$

trace of $b = b_{11} + b_{22}$

$\text{Trace} = (a_{11}+a_{22})(b_{11}+b_{22})$

columns or rows of the direct product matrix are numbered as

11 12 13 14 ... 21 22 23 24 ....

row 11 of direct product matrix = row 1 × row 1

- Theorem :

The characters of the direct product representation are equal to the products of the characters of the representations based on the individual sets of functions.

$$R F_i = \sum_{j=1}^{m} F_j x_{ji} \qquad R G_k = \sum_{l=1}^{n} G_l y_{lk}$$

Then
$$R(F_i G_k) = (RF_i)(RG_k) = \sum_{j=1}^{m} \sum_{l=1}^{n} \underbrace{F_j G_l}_{\text{basis}} \underbrace{x_{ji} y_{lk}}_{\text{elements of the direct product of matrices } x \text{ and } y}$$

The product functions $F_i G_k$ then form a basis for a $m \times n$ representation of the group, since the product functions are transformed into linear combinations of one another by the symmetry operations of the group.

Can form direct products of two groups

$$C_{nh} = C_n \otimes C_s \quad \text{for odd } n$$
$$C_{nh} = C_n \otimes C_i \quad \text{for even } n$$
$$D_{nh} = D_n \otimes C_i$$

The operations $R_i S_j$ form a group
The direct products of the matrices which are the I.R.REP. of the groups form a representation of the direct product group

The direct product enables one to find the rep of a wfn when the reps of its factors are known.

Examples

$$\Psi_{vib} = \underbrace{\psi_{HO}(Q_1)}\cdot\underbrace{\psi_{HO}(Q_2)}\cdot\ldots$$

different IRREPS   Take the direct product to find sym. species of Ψ_{vib}

$\Psi_{electronic}$ =

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)(4a_1)$$

Take the direct products to find sym. species of electronic states.

Theorem: The direct product of two irreducible reps Γ_α and Γ_β contains the totally symmetric IRREP if and only if Γ_α is the complex conjugate of Γ_β.

(By complex conjugate rep. we mean the rep whose matrices are the complex conjugates of the original rep)

Proof: The characters of the totally symmetric IRREP are all 1 $(A, A_1, A_{1g}, A_g, A_1')$

Find the no. of times the totally sym. irrep. occurs in $\Gamma_\alpha \otimes \Gamma_\beta$:

$$a_{A_{1g}} = \frac{1}{h} \sum_R^h \chi_{\alpha\otimes\beta}(R) \cdot \chi^*_{A_{1g}}(R) = \frac{1}{h} \sum_R^h \chi_{\alpha\otimes\beta}(R)$$

But $\chi_{\alpha\otimes\beta}(R) = \chi_\alpha(R) \cdot \chi_\beta(R)$

can be written as $\left[\chi_{\alpha^*}(R)\right]^* \cdot \chi_\beta(R)$

in terms of characters of Γ_{α^*}

However, LOT says

$$\sum_R^h \chi_i(R)^* \chi_j(R) = h\,\delta_{ij}$$

Therefore

$$a_{A_{1g}} = \frac{1}{h} \sum_R^h \left(\chi_{\alpha^*}(R)\right)^* \chi_\beta(R) = \delta_{\alpha^*\beta}$$

which says that the totally symmetric irrep is contained in the direct product of two IRREPs iff they are complex conjugates of each other.

What about the direct product of several IRREPs?

$$\Gamma_\alpha \otimes \Gamma_\beta \otimes \Gamma_\phi = \underbrace{(\Gamma_\alpha \otimes \Gamma_\beta)}_{\text{maybe reducible}} \otimes \underset{\text{IRreducible}}{\Gamma_\phi}$$

Thus, the product contains the totally symmetric IRREP if

a) Γ_ϕ^* is contained in the $\Gamma_\alpha \otimes \Gamma_\beta$ product. That is, if $\Gamma_\alpha \otimes \Gamma_\beta$ is reducible, one of the IRREPs which can be blocked out of it must be Γ_ϕ^*

b) Alternatively, Γ_α^* is contained in the direct product $\Gamma_\beta \otimes \Gamma_\phi$ or Γ_β^* is contained in the direct product $\Gamma_\alpha \otimes \Gamma_\phi$.

Consider the integral

$$\int f_A^* f_B \, d\tau$$

An integral should be invariant (even in sign) to all symmetry operations. This means that an integral forms a basis for the totally symmetric irrep of the group, that is A, A_1, A_g, A_{1g}, ...
The integral must be zero unless the integrand is totally symmetric or contains the totally symmetric IRREP.
Thus, the integral is zero unless $\Gamma_A^* \otimes \Gamma_B$ contains the totally symmetric IRREP.

DIRECT PRODUCTS of REPS

The over-all molecular wavefunction is the PRODUCT

$$\Psi = \psi_{vib} \cdot \psi_{rot} \cdot \psi_{electronic} \cdot \psi_{\substack{nuclear \\ spin}}$$

which can be classified according to the IRREPS (Symmetry Species) of the molecular point group. To find out WHICH ONE? we need to form **DIRECT PRODUCTS** of REPRESENTATIONS.

Theorem: THE CHARACTERS of the DIRECT PRODUCT REPRESENTATION are equal to the products of the characters of the representations based on the individual sets of functions

Example: $E_{1u} \otimes E_{1u}$ in group D_{6h} order = 24

$R_{op}=$	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
$\chi(E_{1u})=$	2	1	-1	-2	0	0	-2	-1	1	2	0	0
$\chi(\underbrace{E_{1u}\otimes E_{1u}})=$	4	1	1	4	0	0	4	1	1	4	0	0

This is obviously a REDUCIBLE rep. so we apply the recipe:

$$a_i = \frac{1}{h} \sum_{R_{op}} \chi^{(i)*}(R_{op}) \chi(R_{op})$$

and we will get

$$a_{A_{1g}} = \frac{1}{24}\left[4\cdot 1 + 2(1\cdot 1) + 2(1\cdot 1) + 4\cdot 1 + 0 + 0 + 4\cdot 1 + 1\cdot 1 + 1\cdot 1 + 4\cdot 1 + 0 + 0\right] = 1 \text{ etc}$$

In fact we get

$$\underbrace{E_{1u} \otimes E_{1u}}_{\text{order } 4} = A_{1g} \oplus A_{2g} \oplus E_{2g}$$

We can take direct products of more than two representations in the same way:

$$\chi(E_{1u} \otimes A_{2g} \otimes E_{2g}) \text{ for } R_{op} = \chi_{E_{1u}}(R_{op}) \cdot \chi_{A_{2g}}(R_{op}) \cdot \chi_{E_{2g}}(R_{op})$$

Generally, the DIRECT products of representations are reducible reps of dimension = products of dimensions of the individual ones.

$A \otimes A$ or $B \otimes B \rightarrow A$

$A \otimes B \rightarrow B$

$\Gamma_g \otimes \Gamma_g$ or $\Gamma_u \otimes \Gamma_u \rightarrow \Gamma_g$

$\Gamma_g \otimes \Gamma_u \rightarrow \Gamma_u$

$\Gamma_1 \otimes \Gamma_1$ or $\Gamma_2 \otimes \Gamma_2 \rightarrow \Gamma_1$ similarly for Γ' and Γ''

$\Gamma_1 \otimes \Gamma_2 \rightarrow \Gamma_2$

THEOREM: **THE DIRECT PRODUCT of two IRREPS $\Gamma_\alpha \otimes \Gamma_\beta$ CONTAINS the TOTALLY SYMMETRIC IRREP** (A, A_{1g}, A_1, A_g etc) **IF and ONLY IF Γ_α is the COMPLEX CONJUGATE of Γ_β**, that is $\Gamma_\alpha^* = \Gamma_\beta$ or if REAL, **IF and ONLY IF** $\Gamma_\alpha = \Gamma_\beta$.

For direct product of several IRREPS:

$\underbrace{\Gamma_\alpha \otimes \Gamma_\beta}_{\text{may be reducible}} \otimes \Gamma_\phi$ contains the **TOTALLY SYMMETRIC IRREP** if when $\Gamma_\alpha \otimes \Gamma_\beta$ Blocks out into IRREPS one of which is Γ_ϕ^*

Consider the integral:

$\int f_A^* \, f_B \, d\tau$ → SHOULD BE INVARIANT even in SIGN to ALL symmetry operations, since symmetry operations do nothing more than change the defined orientation of the Cartesian axes.

THIS means the INTEGRAL must BE ZERO unless the integrand is TOTALLY SYMMETRIC or contains the IRREPS A A_1 A_{1g} A_1' or A_g !!!

Application of direct products:

1. $\int \psi_i^* \mathcal{H} \psi_j \, d\tau = ?$

$\mathcal{H}$ belongs to the TOTALLY SYMMETRIC IRREP since the energy can not change in either sign or magnitude as a result of a symmetry operation. Thus, the symmetry of the integrand depends on the representations to which ψ_i^* and ψ_j belong. Thus, $\int \psi_i^* \mathcal{H} \psi_j \, d\tau \neq 0$ only if ψ_i^* and ψ_j belong to the same IRREP.

2. $\int \psi_i^* x \, \psi_j \, d\tau \neq 0$ only if $\Gamma_i^* \otimes \Gamma_j \otimes \Gamma_x$ contains the totally symmetric IRREP

that is, $\Gamma_x \otimes \Gamma_j$ contains Γ_i
or $(\Gamma_i^* \otimes \Gamma_j)$ contains the IRREP Γ_x^*

3. Expectation values

$$\int \psi_i^* \begin{pmatrix} \mu_x \\ \mu_y \\ \text{or } \mu_z \end{pmatrix} \psi_i \, d\tau \neq 0 \text{ only if } \Gamma_x \text{ belongs to } A, A_1, A_g, A_{1g} \text{ etc.}$$

since $\psi_i^* \psi_i$ belongs to the totally symmetric IRREP

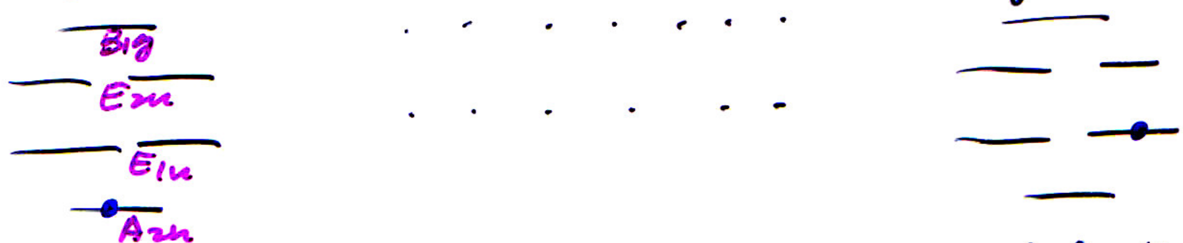
IF the pi electrons are NON-INTERACTING with each other and other electrons (sigma) of benzene, then: we can write a simple sum

$$H = H(1) + H(2) + H(3) + H(4) + H(5) + H(6) + H\left(\substack{\text{sigma}\\ \text{others}}\right)$$

of one-electron hamiltonians $H(1)$ etc.

This is the basis of MOLECULAR ORBITAL THEORY.

Electron 1 eigenvalues . . . . Electron 6 eigenvalues



Put them (all 6) on the same picture, for example for the ground state:

Total energy = simple sum of these energies

Wavefunction is a product

$$\Psi(1,2,3,4,5,6) = \psi_{A_{2u}}(1)\cdot\psi_{A_{2u}}(2)\cdot\psi_{E_{1u}^{+}}(3)\cdot\psi_{E_{1u}}(4)\cdot\psi_{E_{1u}}(5)\cdot\psi_{E_{1u}}(6)$$

multiplied by spin functions

$$\alpha(1)\cdot\beta(2)\cdot\alpha(3)\cdot\beta(4)\cdot\alpha(5)\cdot\beta(6)$$

Question: What then is the SYMMETRY SPECIES for the ground state of benzene?

Answer: We need to take DIRECT PRODUCTS of the IRREPS to find the correct SYMMETRY SPECIES

$$A_{2u}\otimes A_{2u}\otimes E_{1u}\otimes E_{1u}\otimes E_{1u}\otimes E_{1u} = ?\quad \overset{\text{answer}}{A_{1g}}$$

From these

How to find the result

D_{6h}	E	$2C_6$	$2C_3$	$\overset{z}{C_2}$	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		$\boxed{x^2+y^2, z^2}$ A_{1g}
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	$\boxed{(xz, yz)}$ E_{1g}
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		$\boxed{(x^2-y^2, xy)}$ E_{2g}
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
Γ_z A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
$\Gamma_{x,y}$ E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

For example, benzene has a ground electronic state A_{1g} (as we have seen already). Then the UV-visible spectra of benzene (electronic transitions) will depend on the transition probability integral

$$\int \Psi^*_{A_{1g}} (x \text{ or } y \text{ or } z)\, \Psi_{?\,\text{excited}}\, d\tau$$

This integral will be NON-ZERO IF AND ONLY IF

$\Gamma_{\text{excited state}} = \Gamma_x$ or Γ_y or Γ_z which in this case (D_{6h}) happens to be A_{2u} and E_{1u}

This means that the UV-Vis spectra of benzene will consist of transitions from the ground state to those excited states that are of the SYMMETRY SPECIES A_{2u} and E_{1u}. Furthermore, the ground vibrational state of benzene being also A_{1g}, the INFRARED spectra of benzene will include only those bands corresponding to upper vibrational states that are A_{2u} and E_{1u}.

RAMAN SPECTRA

3. Raman spectra depend on electric dipole polarizabilities which are expressed in terms of the operators x^2, xy, xz, y^2, yz, z^2. Again, the ground vibrational state of benzene being A_{1g}, the RAMAN spectra of benzene will include only those bands corresponding to excitation to vibrational states that are Γ_{x^2} or Γ_{xy} or .... that is, A_{1g}, E_{1g}, E_{2g} only.

EXAMPLES:

1. HAMILTONIAN MATRIX $\int \psi_i^* \mathcal{H} \psi_j \, d\tau = ?$

The Hamiltonian $\mathcal{H}$ belongs to A, A_1, A_g, A_1', or A_{1g} since the ENERGY cannot change in either SIGN or MAGNITUDE as a result of a symmetry operation. Thus, the symmetry of the integrand, in this example, depends on the IRREPS to which ψ_i^* and ψ_j belong. Thus,

$$\int \psi_i^* \mathcal{H} \psi_j \, d\tau \neq 0 \text{ IF AND ONLY IF } \psi_i \text{ and } \psi_j$$

belong to the SAME IRREP, i.e. if $\Gamma_i^* = \Gamma_j$

Therefore the $\mathbb{H}$ matrix in the basis of SALCs belonging to the different IRREPS will always BLOCK OUT:

$$\mathbb{H} = \begin{pmatrix} A_u & & & 0 \\ & B_{2g} & & \\ & & B_{1u} & \\ 0 & & & B_{3g} \end{pmatrix}$$

GROUP THEORY CAN TELL US WHEN MATRIX ELEMENTS ARE NECESSARILY ZERO.

(provided the SALCs that belong to the same IRREP are arranged next to each other, the blocking out will be as obvious as shown above)

2. ELECTRIC DIPOLE TRANSITIONS $\int \psi_i^* x \, \psi_j \, d\tau = ?$ or $\int \psi_i^* y \, \psi_j \, d\tau = ?$ or $\int \psi_i^* z \, \psi_j \, d\tau = ?$

are the integrals related to electronic transition probabilities. The first is NON-ZERO IF AND ONLY IF

$$\Gamma_i^* \otimes \Gamma_x \otimes \Gamma_j \text{ contains } A, A_1, A_g, A_1', \text{ or } A_{1g}$$

that is, IF AND ONLY IF $\Gamma_i^* \otimes \Gamma_j$ contains the IRREP Γ_x

THE SAME ARGUMENTS CAN BE USED FOR THE y and z integrals

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
6. APPROXIMATION METHODS
7. DIATOMIC MOLECULES
8. MOLECULAR SPECTROSCOPY
    8.1 Nature of electromagnetic radiation, the time dependent E and B fields
    8.2 Quantum theory of absorption/emission of radiation: Fermi's golden rule
    8.3 Einstein's coefficients for stimulated absorption/emission and Lambert-Beer law
    8.4 Selection rules and transition moments for electric dipole transitions
    8.5 Molecular energy levels and states
    8.6 Transitions between different electronic states
    8.7 Transitions within the same electronic state: vibration-rotation spectroscopy
    8.8 Symmetry of states of polyatomic molecules
    8.9 Vibration-rotation spectroscopy of polyatomics

continuing B. SAME ELECTRONIC STATE

b) DIFFERENT VIBRATIONAL STATES (INFRARED SPECTRUM)

POLYATOMIC MOLECULES

Replace $\mu(R) = \mu(R_e) + \left(\frac{d\mu}{dR}\right)_{R_e}(R-R_e) + \cdots$

by (for the x component):

$$\mu_x = \mu_x(\text{at equil. geometry}) + \sum_k \left(\frac{\partial \mu_x}{\partial Q_k}\right)_{eq} Q_k + \cdots$$

where

Q_k is the SIMULTANEOUS DISPLACEMENTS of ALL NUCLEI in the molecule FROM THEIR EQUILIBRIUM POSITIONS

EACH Q_k BELONGS to an IRREP of the point group of the molecule.

μ_x itself belongs to the same IRREP (call it Γ_x) as the coordinate x

$$\left(\frac{\partial \mu_x}{\partial Q_k}\right)_{eq} = 0 \text{ unless } Q_k \text{ BELONGS to } \Gamma_x$$

Thus, instead of the term $\left(\frac{d\mu}{dR}\right)_{R_e} \int \psi_{v''}(R-R_e)\psi_{v'}\, d\tau_{vib}$

we will have for polyatomic molecules the term:

$$\sum_k \underbrace{\left(\frac{\partial \mu_x}{\partial Q_k}\right)_{eq}}_{\substack{\text{NON-ZERO ONLY IF} \\ Q_k \text{ BELONGS TO } \Gamma_x \text{ IRREP.}}} \int \psi_{v_k''} \underbrace{Q_k}_{\text{BELONGS TO } \Gamma_x} \psi_{v_k'}\, d\tau$$

which is NON-ZERO ONLY IF

$\Gamma_{v_k''} \otimes \Gamma_x \otimes \Gamma_{v_k'}$

yields the TOTALLY SYMMETRIC IRREP (A, A_1, A_{1g}, A_g, $\cdots$) of the point group of the molecule, that is, if

$$\Gamma_{v_k''} \otimes \Gamma_{v_k'} = \Gamma_x$$

...similarly for ~~y~~ and z dipole moment components.

For a molecule in its ground (lowest energy) state
$$\Gamma_{v_K''} = A \text{ or } A_1 \text{ or } A_{1g} \text{ or } A_1' \text{ or } A_g \qquad (v_K''=0)$$
$$\Gamma_{v_K'} = \Gamma_{Q_K} \text{ if } v_K'=1$$
$$\text{or } = \underbrace{\Gamma_{Q_K} \otimes \Gamma_{Q_K} \otimes \Gamma_{Q_K} \otimes \cdots}_{v_K' \text{ times}}$$

For $v_K''=0$ to $v_K'=1$ (that is, for a "FUNDAMENTAL" vibrational band to be observed in the INFRARED),
$A_{1g} \otimes \Gamma_{x \text{ or } y \text{ or } z} \otimes \Gamma_{Q_K}$ must belong to A_{1g},
that is, $\Gamma_{Q_K} = \Gamma_x$ or Γ_y or Γ_z

Just as for diatomic molecules, other transitions can be observed, corresponding to
$\Delta v = \pm 2$ "FIRST OVERTONE"
$\Delta v = \pm 3$ "SECOND OVERTONE" etc
but in every case it must be true that
$$\underset{\substack{\text{initial}\\\text{vibrational}\\\text{state}}}{\Gamma''} \otimes \underset{\substack{\text{final}\\\text{vibrational}\\\text{state}}}{\Gamma'} = \Gamma_x \text{ or } \Gamma_y \text{ or } \Gamma_z$$