Group Theory in Quantum Mechanics

Based on AMOP Lecture 18-19

Lecture 29 *(5.04.17)*

Rotational eigenstates and spin-permutation symmetry

(Int.J.Mol.Sci, 14, 714(2013) p.755-774 , QTCA Unit 7 Ch. 21-25)
(PSDS - Ch. 5, 7)

Review: *SF_6 levels and nomograms for Coriolis PQR structure*
Review: *SF_6 spectral clusters of symmetry species $O \supset C_4$ and $O \supset C_3$ symmetry correlation*
Conservation (or not!) of rovibronic spin-symmetry-species
Entanglement and related issues
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$
Labeling by symmetry $O(3) \supset D_{\infty h}$
Coriolis and λ (or Λ)-doubling levels
Dipole-allowed transitions
S_n *Young Tableaus and spin-symmetry for X_n and XY_n molecules*
S_4 and spin-symmetry for XY_4 molecules (Introducing hook-length formulae)
S_6 and spin-symmetry for XY_6 molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion
C_{60} Buckminster Fullerene ("Buckyball") structure and spectra

Graphical approach to rotation-vibration-spin Hamiltonian

$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Nuclear\ Spin}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \ldots$$

OUTLINE

Example(s)

Introductory review

- *Rovibronic nomograms and PQR structure* — ν_3 and ν_4 SF_6
- *Rotational Energy Surfaces (RES) and θ_K'-cones* — ν_4 P(88) SF_6
- *Spin symmetry correlation tunneling and entanglement* — SF_6

Recent developments

- *Analogy between PE surface and RES dynamics*
- *Rotational Energy Eigenvalue Surfaces (REES)* — ν_3 SF_6

Review: *SF_6 levels and nomograms for Coriolis PQR structure*

$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$$

$$\langle H\rangle \sim \nu_{vib} + BN(N+1) + 2B(1-\zeta)\cdot \begin{cases} N+1 & \text{for : } J=N+1 \\ 0 & \text{for : } J=N \\ N & \text{for : } J=N-1 \end{cases}$$

Given: $\mathbf{J} = \ell + \mathbf{N}_{(Nuclear\ Rotor)}$

$$H^{Scalar\ Coriolis} = -B\zeta\, 2\mathbf{J}^{Total}\bullet\ell^{vibe}$$
$$= -B\zeta[\,\mathbf{J}^2-(\mathbf{J}-\ell)^2+\ell^2]$$
$$= -B\zeta[\,\mathbf{J}^2-\mathbf{N}^2+\ell^2]$$
$$= -B\zeta[\,J(J+1)-N(N+1)+\ell(\ell+1)]$$

Involves:

angular momentum ℓ of vibration "orbits"

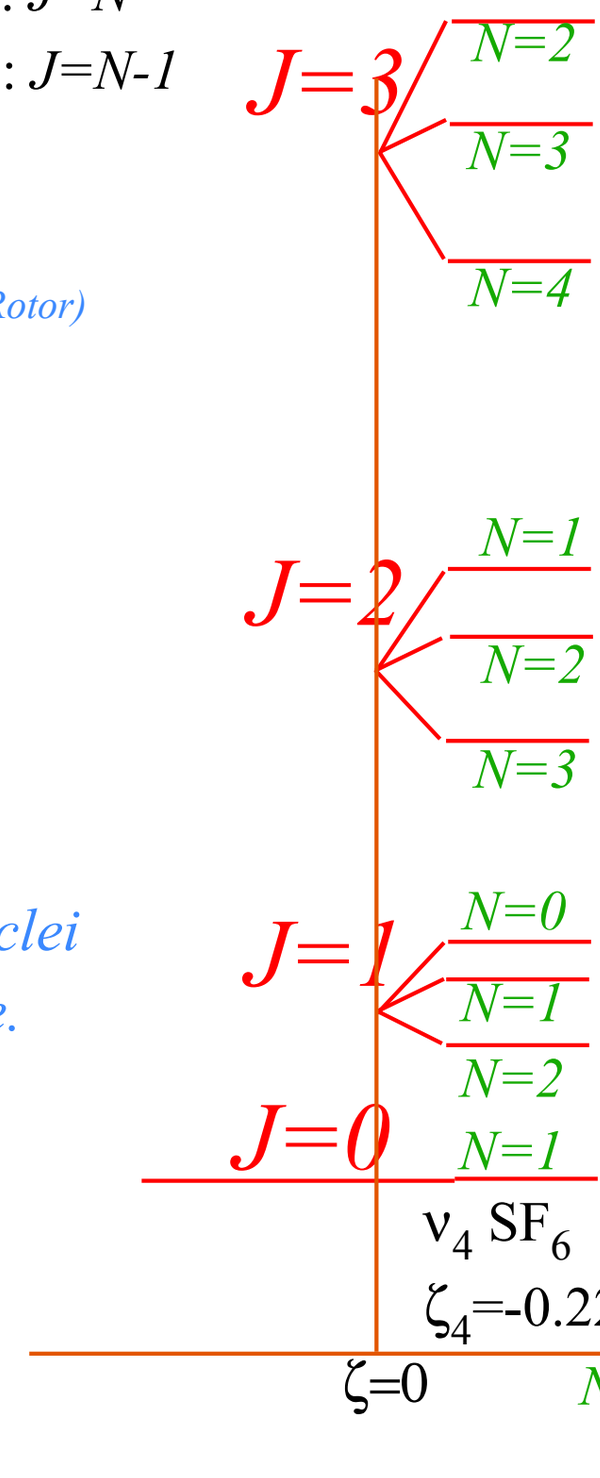
angular momentum **N** *(or* **R***) of rotating nuclei*

total momentum $\mathbf{J} = \ell + \mathbf{N}$ *of whole molecule.*

Let: $\mathbf{R}=\mathbf{N}=\mathbf{J}-\ell$, *and:* $\mathbf{N}^2 = \mathbf{J}^2 - 2\mathbf{J}\cdot\ell + \ell^2$

so: $2\mathbf{J}\cdot\ell = \mathbf{J}^2 - \mathbf{N}^2 + \ell^2$

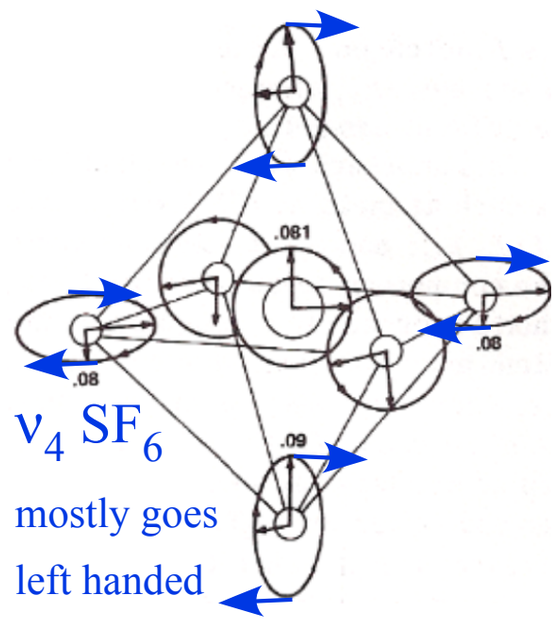
$\langle 2\mathbf{J}\cdot\ell\rangle = J(J+1) - N(N+1) + \ell(\ell+1)$



Rotation-polarized

$|x\rangle + i|y\rangle$

mode



ν_4 SF_6

mostly goes

left handed

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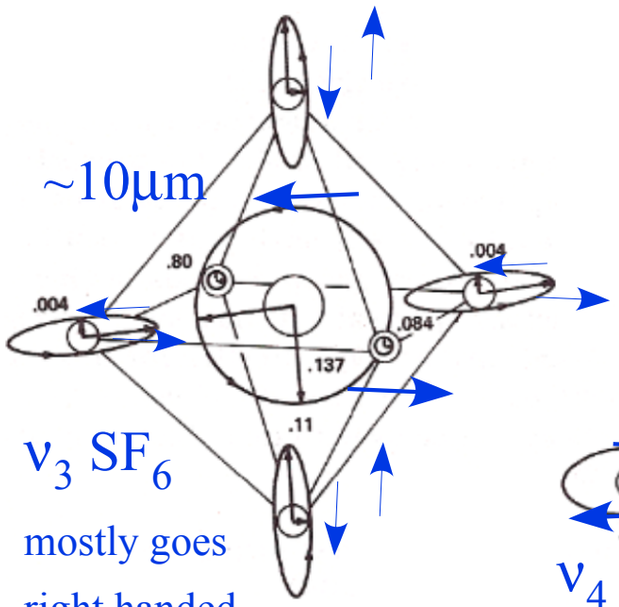

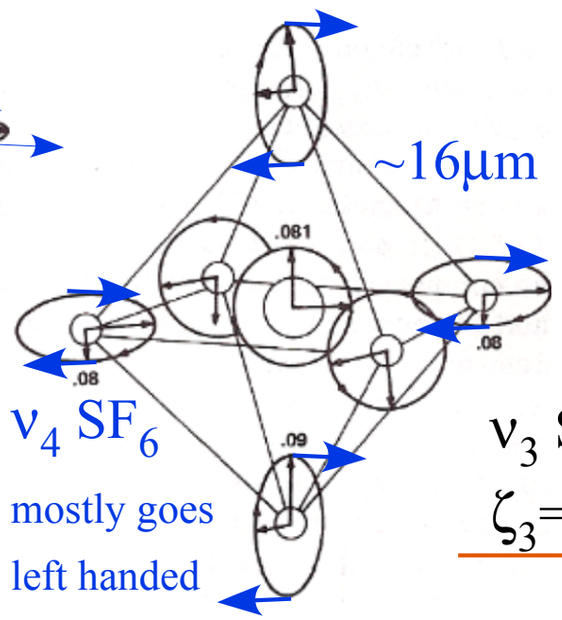

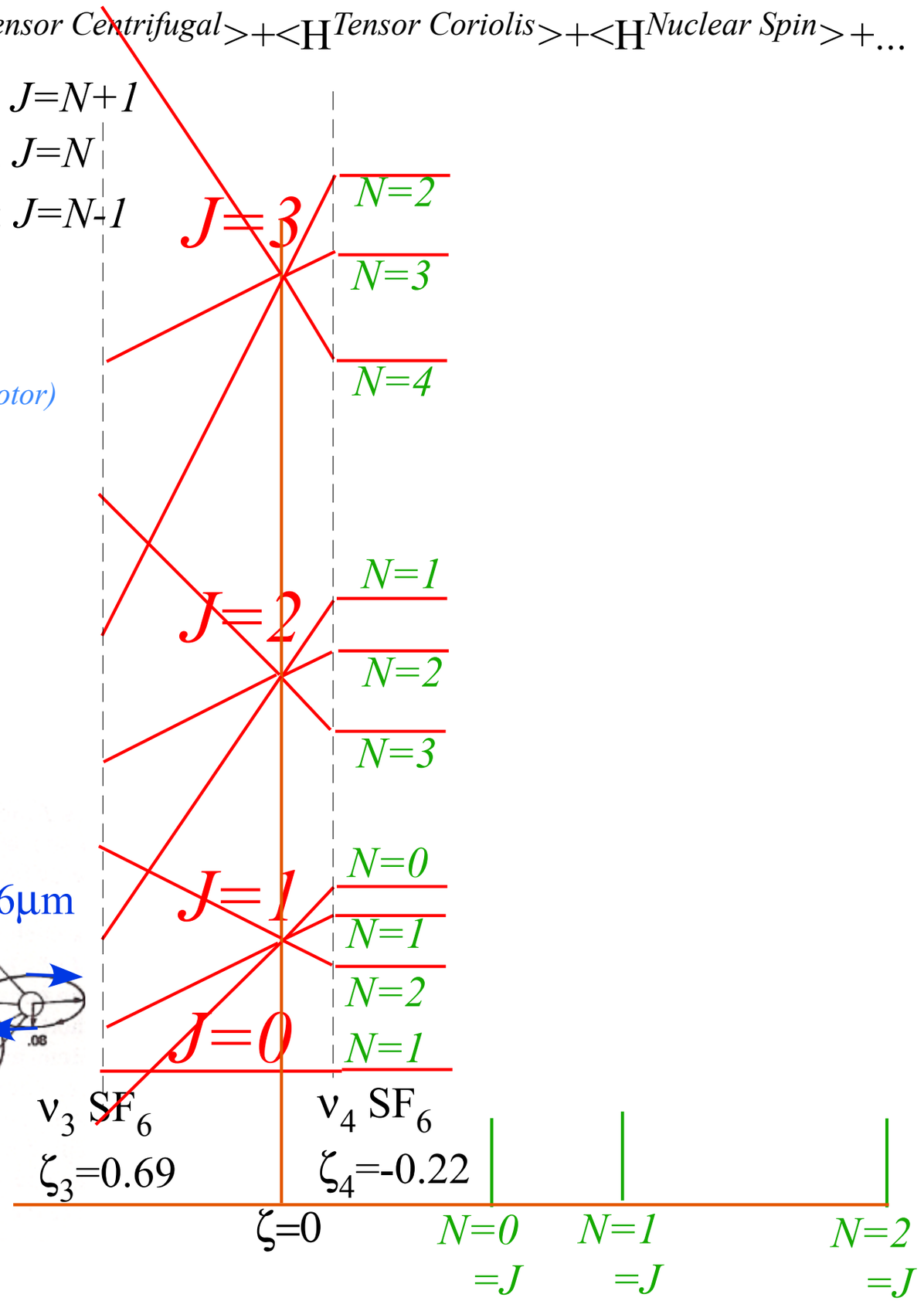

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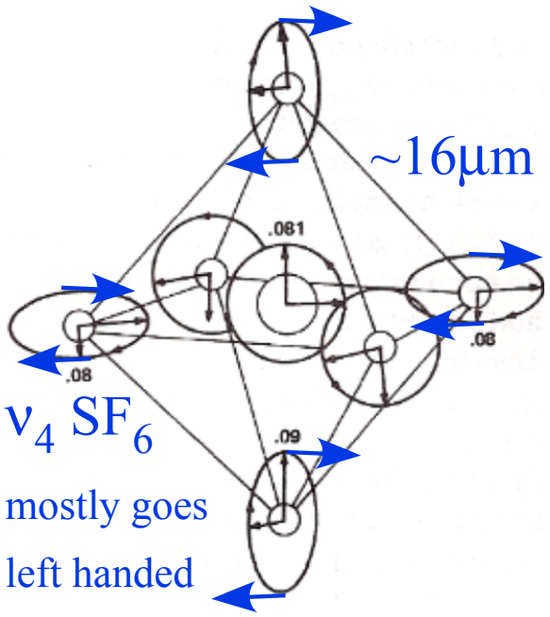

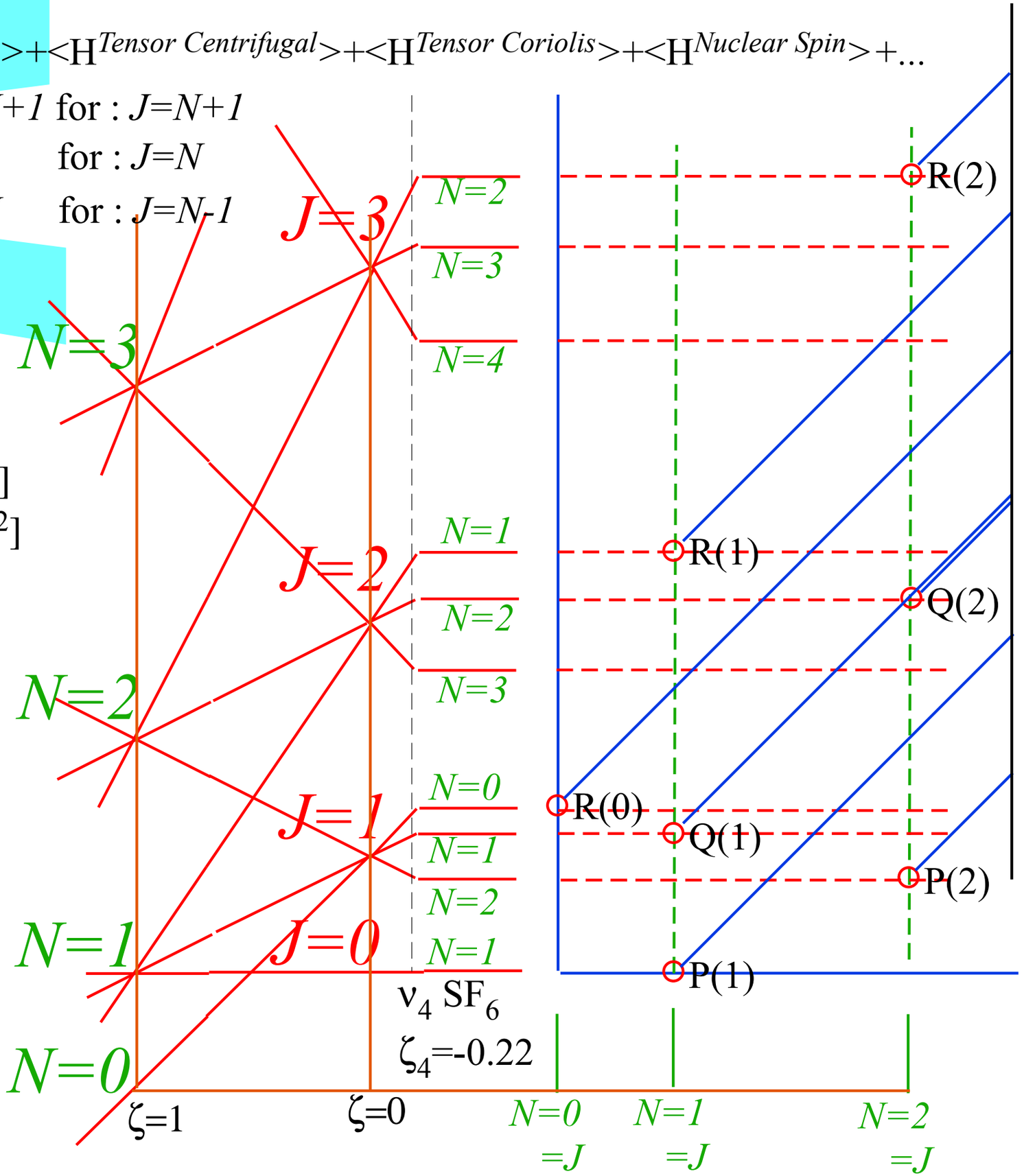

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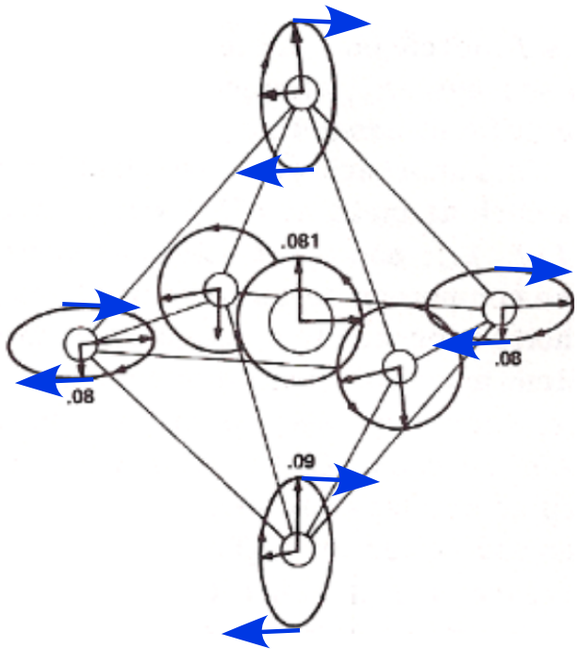
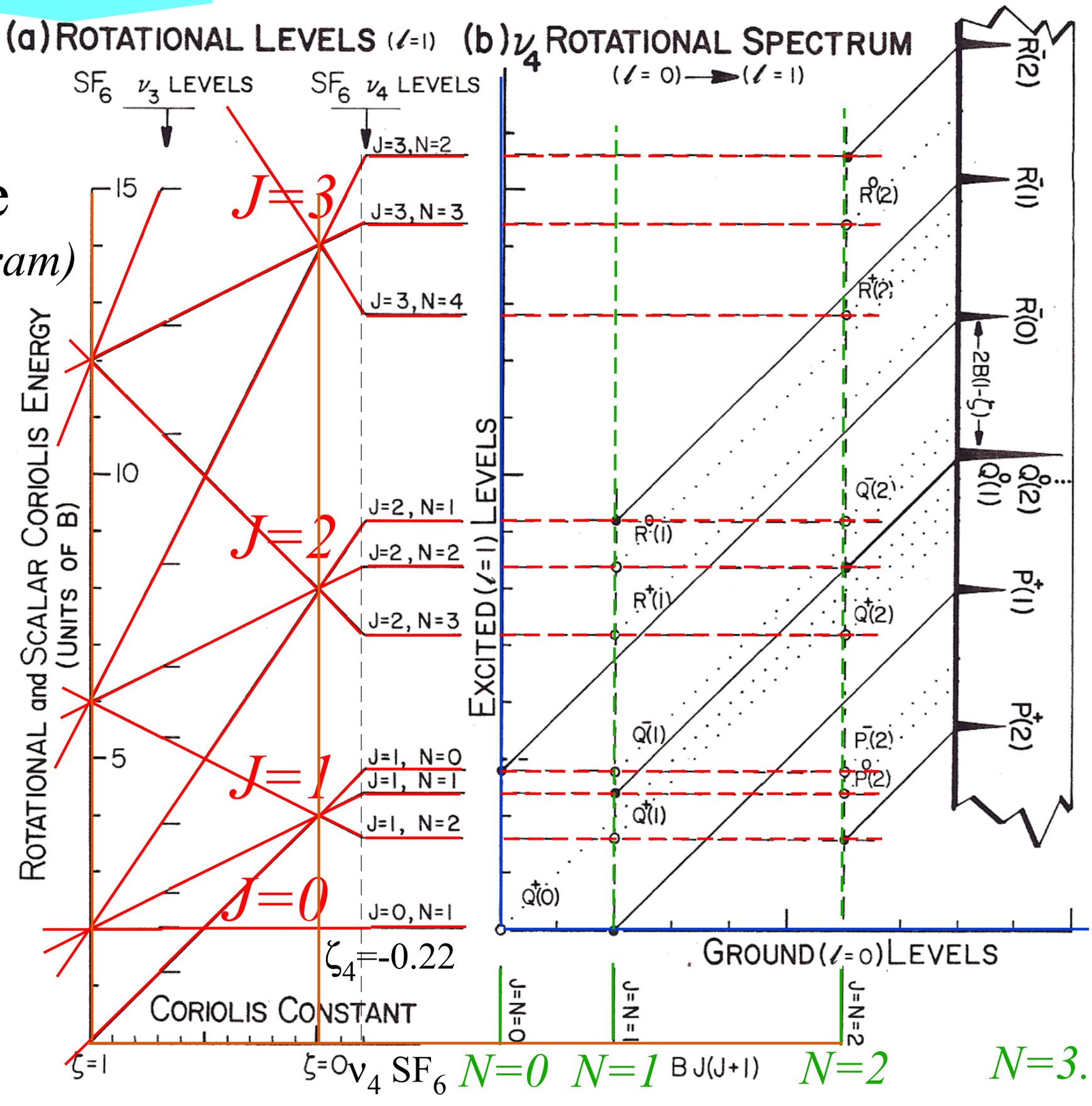
Summary of low-J (PQR) ro-vibe structure

(Using rovib. nomogram)





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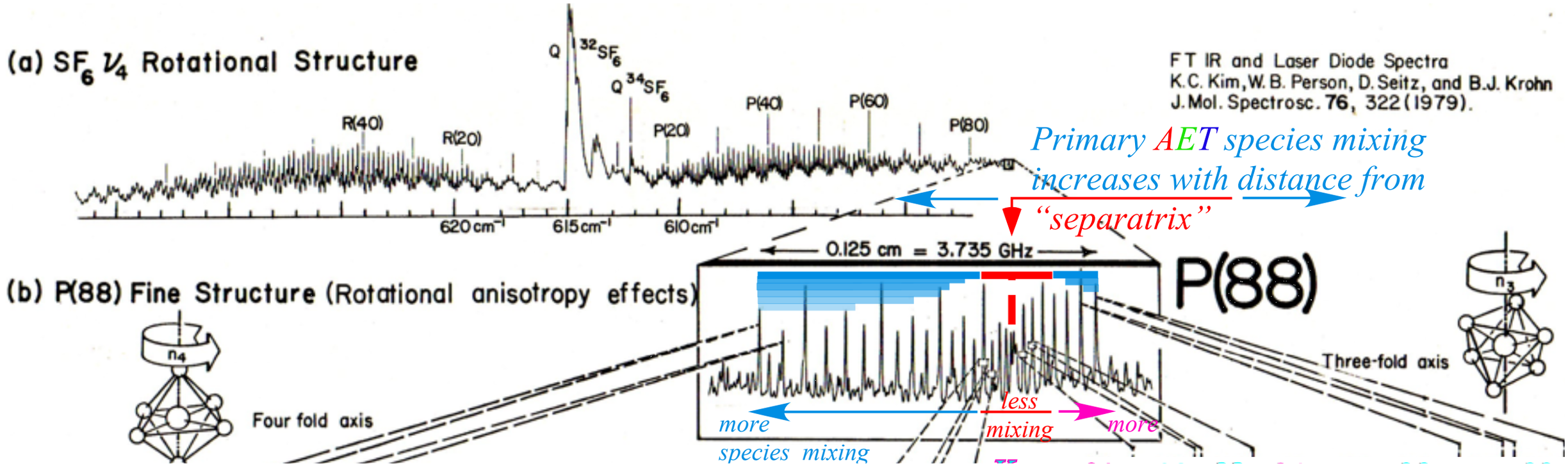

PQR structure due to Coriolis scalar interaction
between vibrational angular momentum ℓ
and total momentum $\mathbf{J} = \ell + \mathbf{N}$ *of rotating nuclei*

P(N)=P(88) structure due to tensor centrifugal/Coriolis
due to vibrational ℓ *and total momentum* $\mathbf{J} = \ell + \mathbf{N}$

Graphical approach to rotation-vibration-spin Hamiltonian

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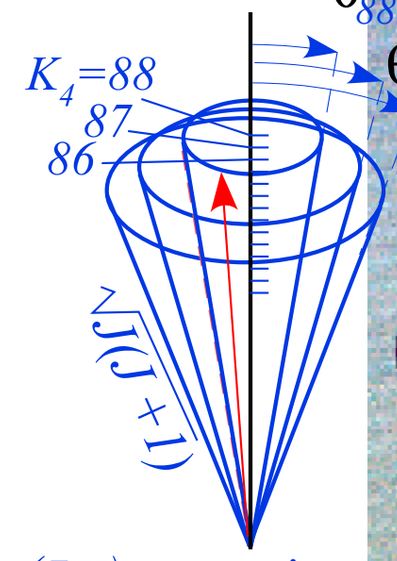
O_h or T_d Spherical Top: *(Hecht CH_4 Hamiltonian 1960)*

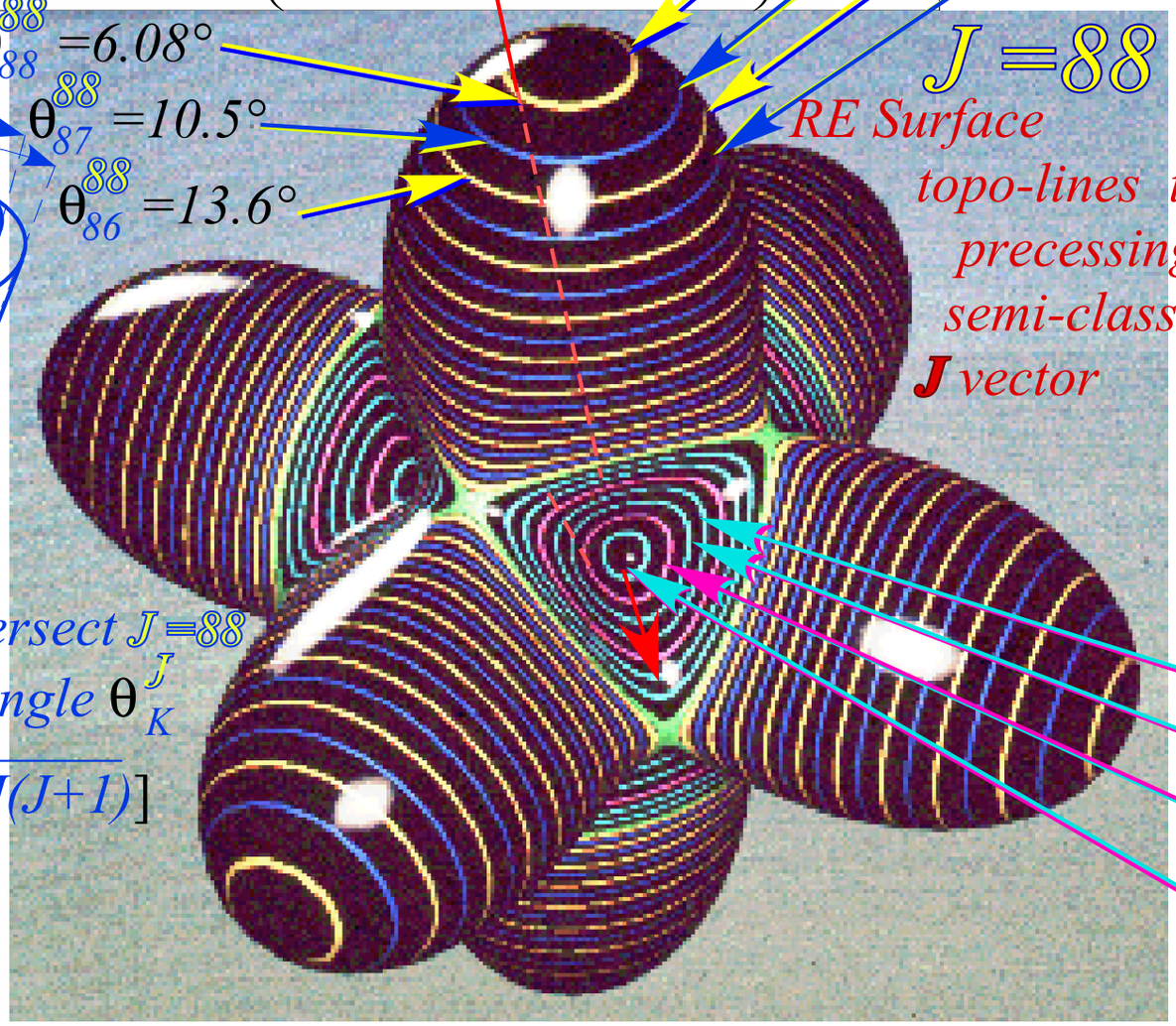
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

$$= B\mathbf{J}^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



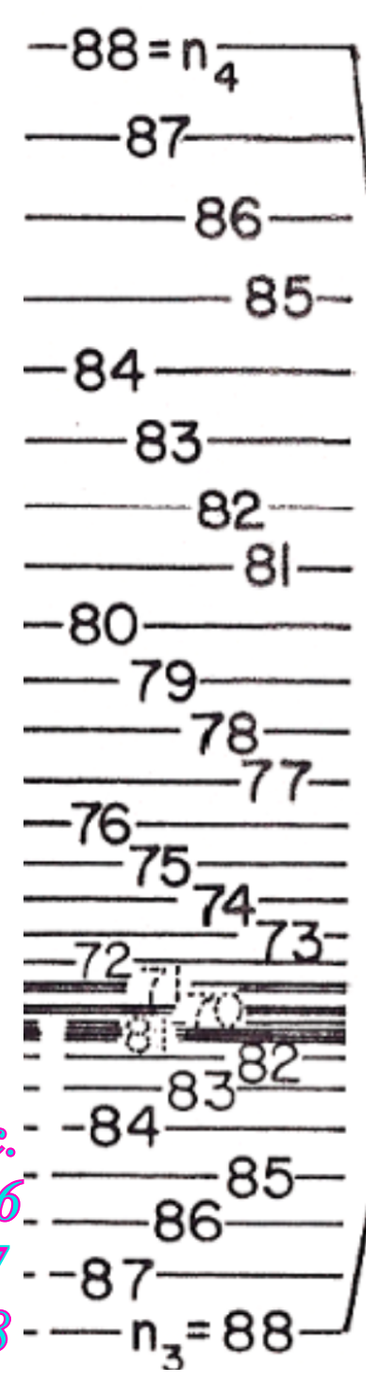
(J,K) cones intersect J =88 RE surface at angle θ_K^J

$\theta_K^J = \text{acos}[K/\sqrt{J(J+1)}]$



K_4 =88
=87
=87
etc.

etc.
=86
=87
K_3 =88



1.0GHz

vibration ground-state rotation levels

J=N
=88

SF_6 Spectra of O_h Ro-vibronic Hamiltonian described by RE Tensor Topography

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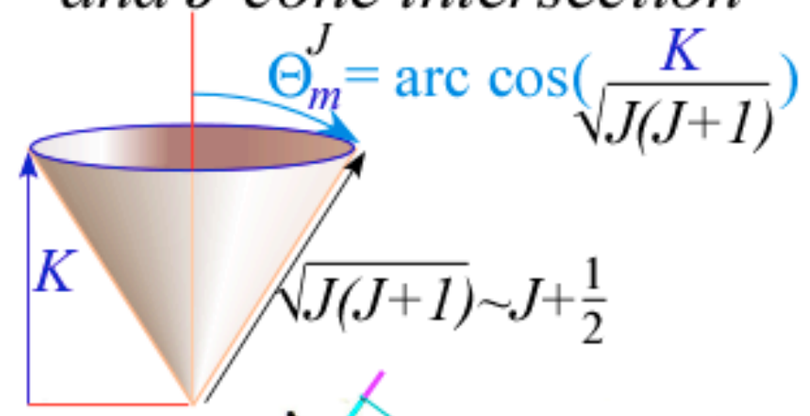
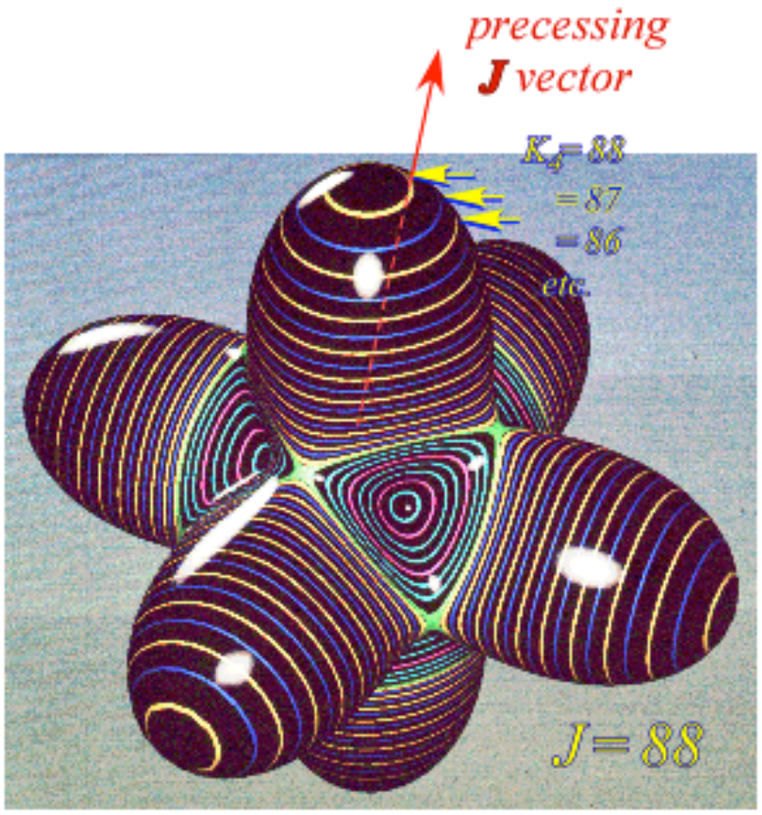
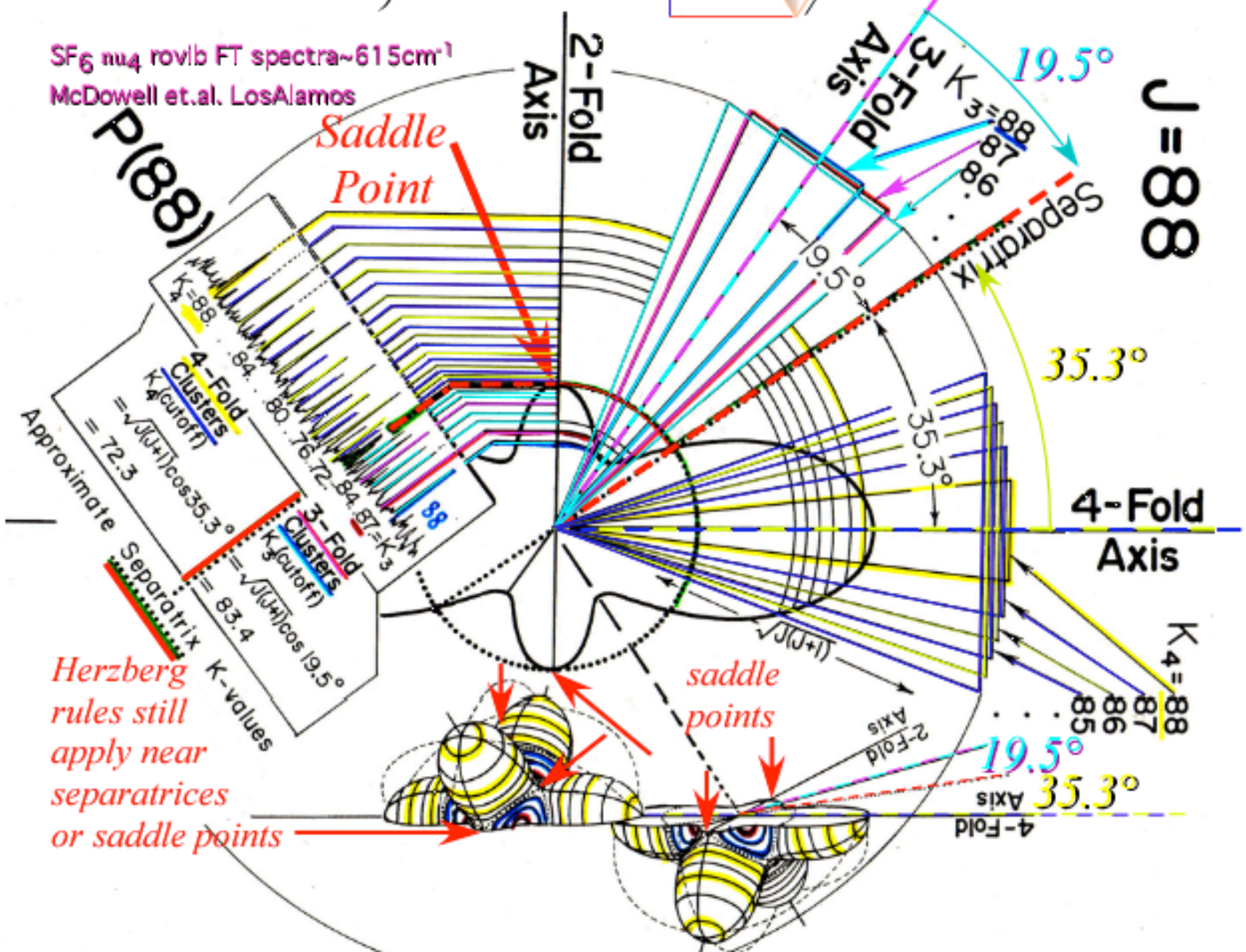
and J-cone intersection



Rovibronic Energy (RE) Tensor Surface





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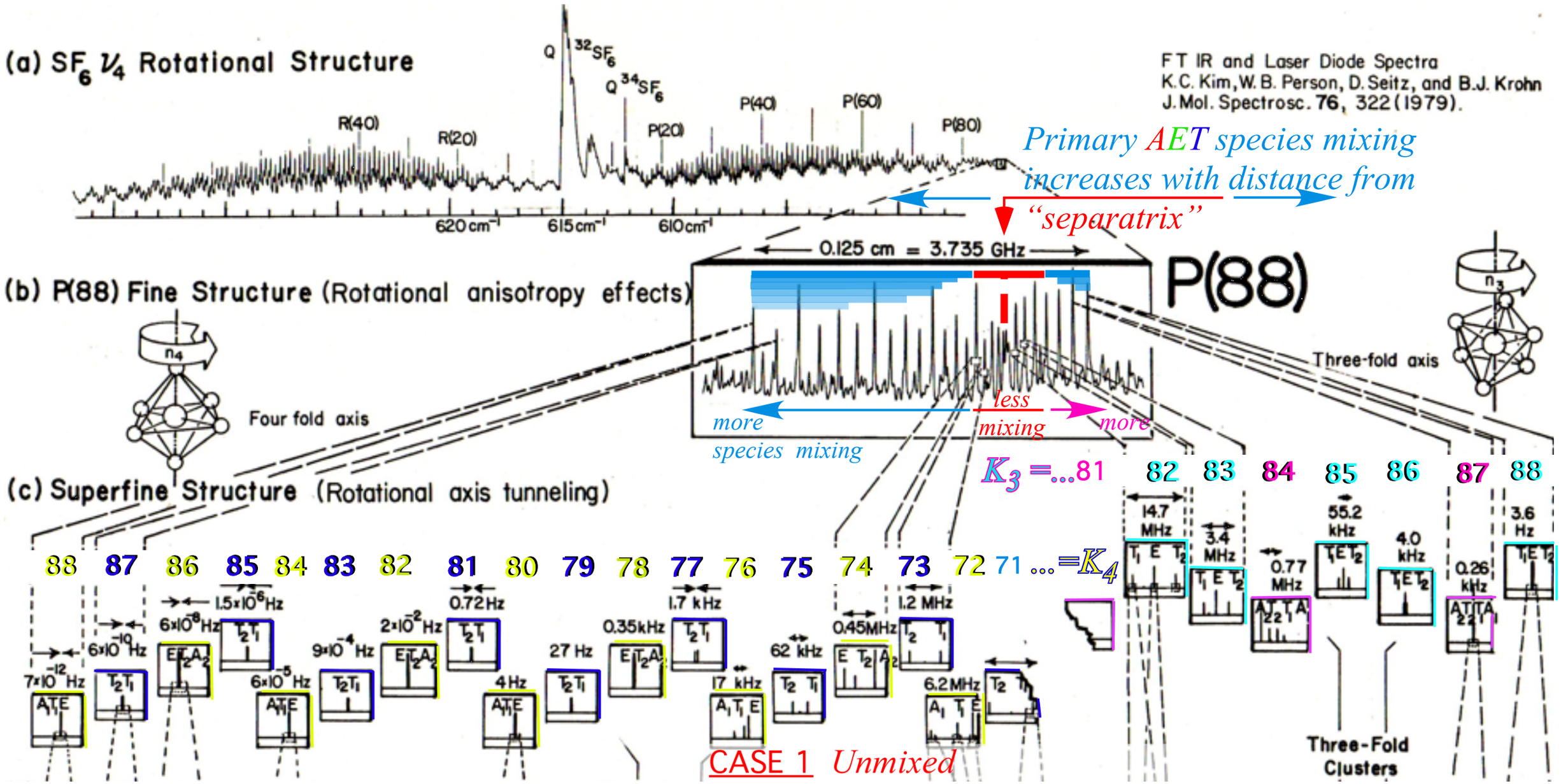

PQR structure due to Coriolis scalar interaction between vibrational angular momentum ℓ *and total momentum* $\mathbf{J} = \ell + \mathbf{N}$ *of rotating nuclei*

P(N)=P(88) structure due to tensor centrifugal/Coriolis due to vibrational ℓ *and total momentum* $\mathbf{J} = \ell + \mathbf{N}$

Superfine structure modeled by **J***-tunneling in body frame (Underlying* F*-spin-permutation symmetry is involved, too.)*

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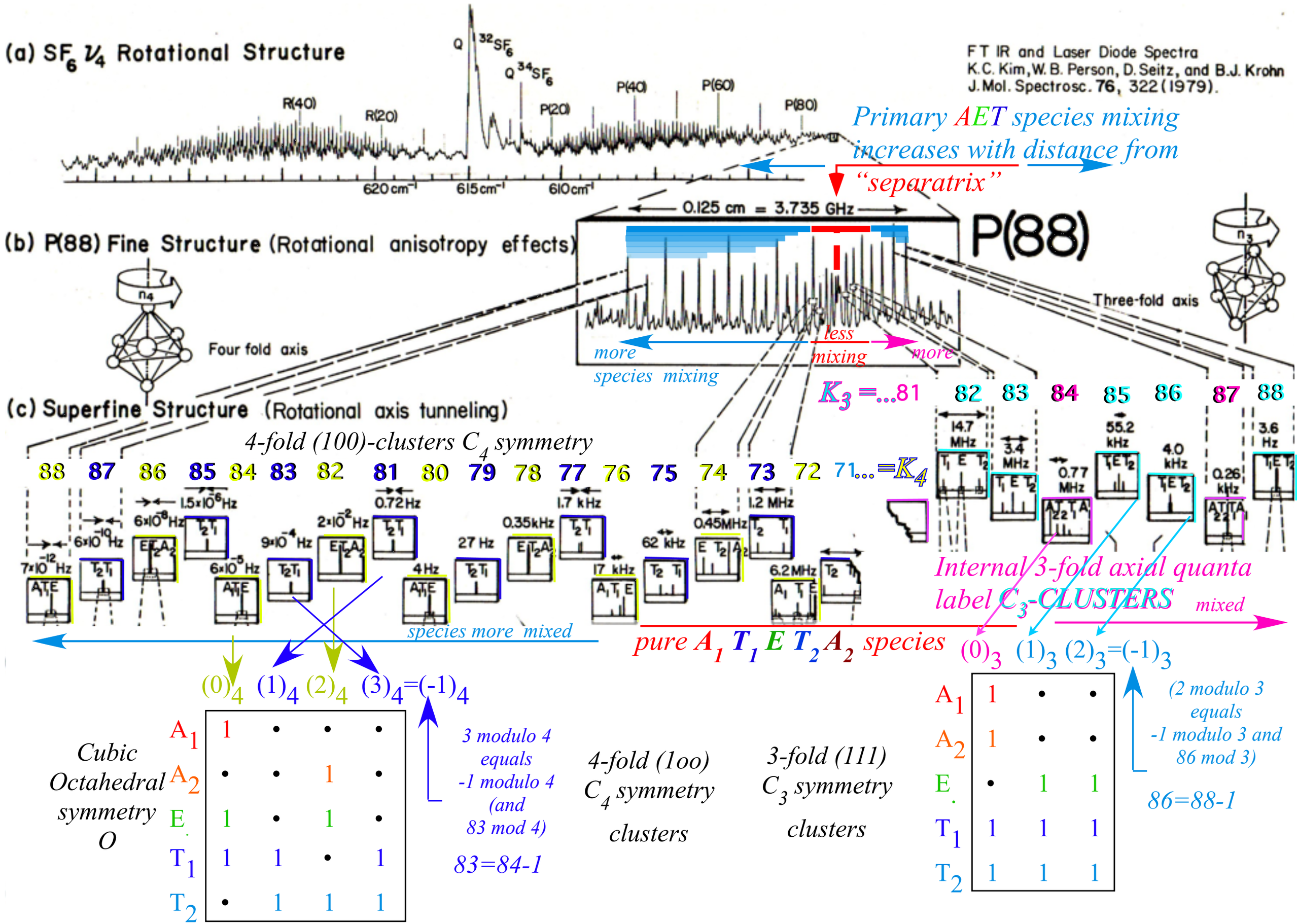

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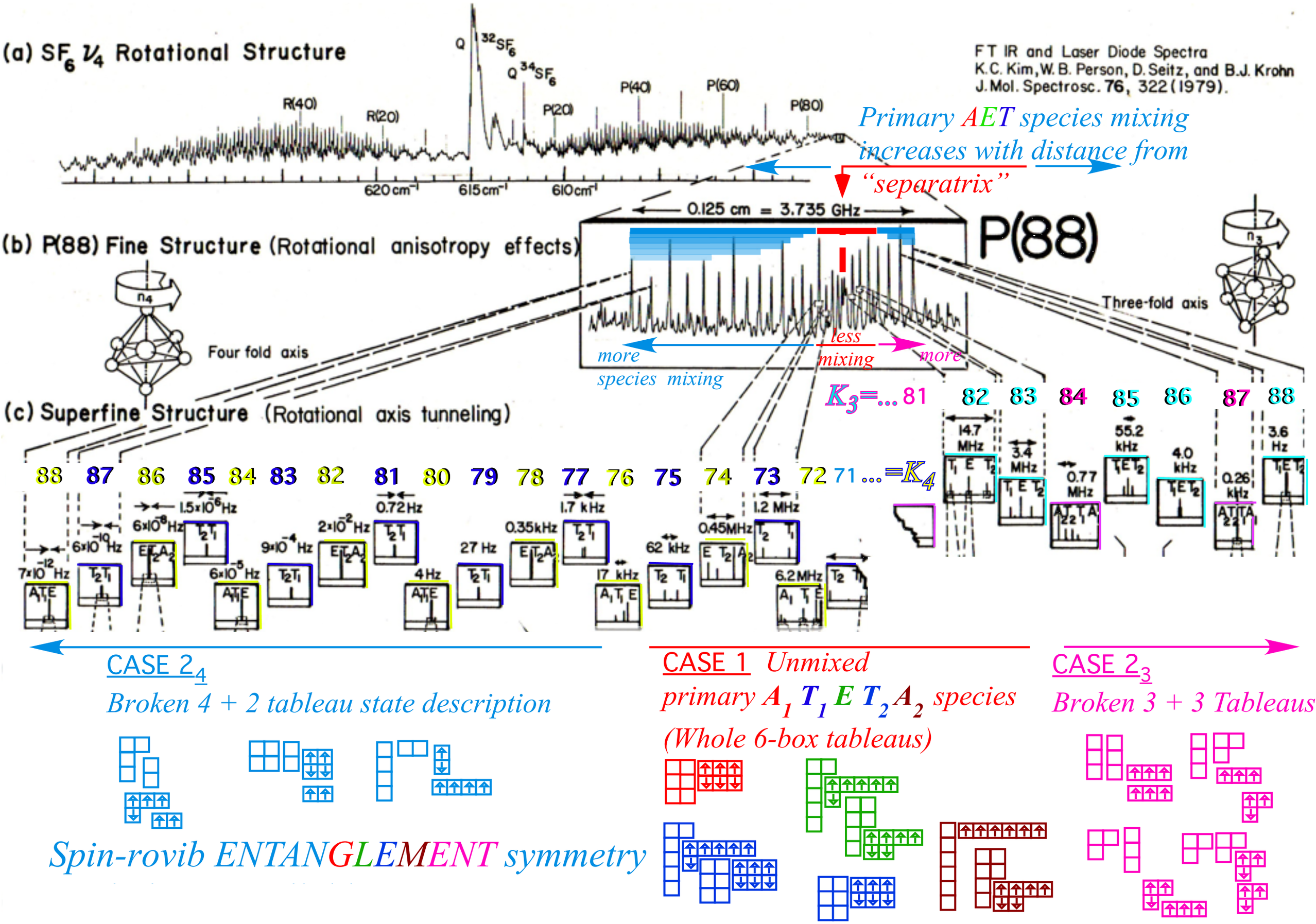

Spin-rovib ENTANGLEMENT symmetry

➔ *Conservation (or not!) of rovibronic spin-symmetry-species*

Entanglement and related issues

CONSERVATION OF ROVIBRONIC SPIN-SPECIES - Two Views:

Old

(1939, 1945, and 1966)

"...transitions between...species (A_1,..E,..T_2..)

...are **very strictly forbidden**..."

...for diatomic molecules...I p. 150

...for D_2 asymmetric tops...II p.468

...for D_n symmetric tops...II p.415

...for O-T_d spherical tops...II p.441-453

...during transitions involving...

...rotational states,...III p.246

...vibrational states,..." "

... electronic states,..." "

... collisional states..." "

versus

New (1978- 2005)

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CHEMISTRY

Nuclear Spin Conversion in Molecules

Jon T. Hougen and Takeshi Oka

Molecules with identical nuclei having nonzero spin can exist in different states called nuclear spin modifications by most researchers and nuclear spin isomers by some. Once prepared in a

as initially shown by Bonhoeffer and Harteck in 1929 (*3*). Once prepared, a *para*-H_2 sample can be preserved for mon

*[review of C_2H_4 study: Sun, Takagi, Matsushima, Science **310**, 1938(2005)]*

Strictly *versus* **NOT!**

Conservation and preservation?

No Way! *versus* **WAY!**

Conversion, perversion or transition?

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Conversion, perversion or transition?

To conserve vs. To convert

To preserve vs. To pervert

perversion

Widespread and extreme mixing of species reported in CF4, SiF_4 and SF_6:

*Ch. Borde, Phys. Rev. **A20**,254(1978)(expt.)*
*Harter, Phys. Rev. **A24**,192 (1981)(theory)*

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? *versus* ***What mixes it up?***

No Way!

WAY!

and...

What is it?

SPIN SYMMETRY correlation has a new name...

Conservation (or not!) of rovibronic spin-symmetry-species

→ ***Entanglement*** *and related issues*

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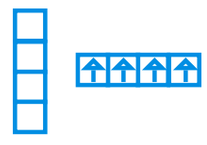
SPIN SYMMETRY *correlation* ***has a new name...***

it's now called ENTANGLEMENT!



Herzberg's terms:
"..Overall ...symmetry..."

Better terms:
..Under-all ... or internal symmetry...spin frame....."Bare" *rotor*

(From an overall "Coupled" state we SUBTRACT *vibronic "Activity" to get underlying "Bare" rotor.)*

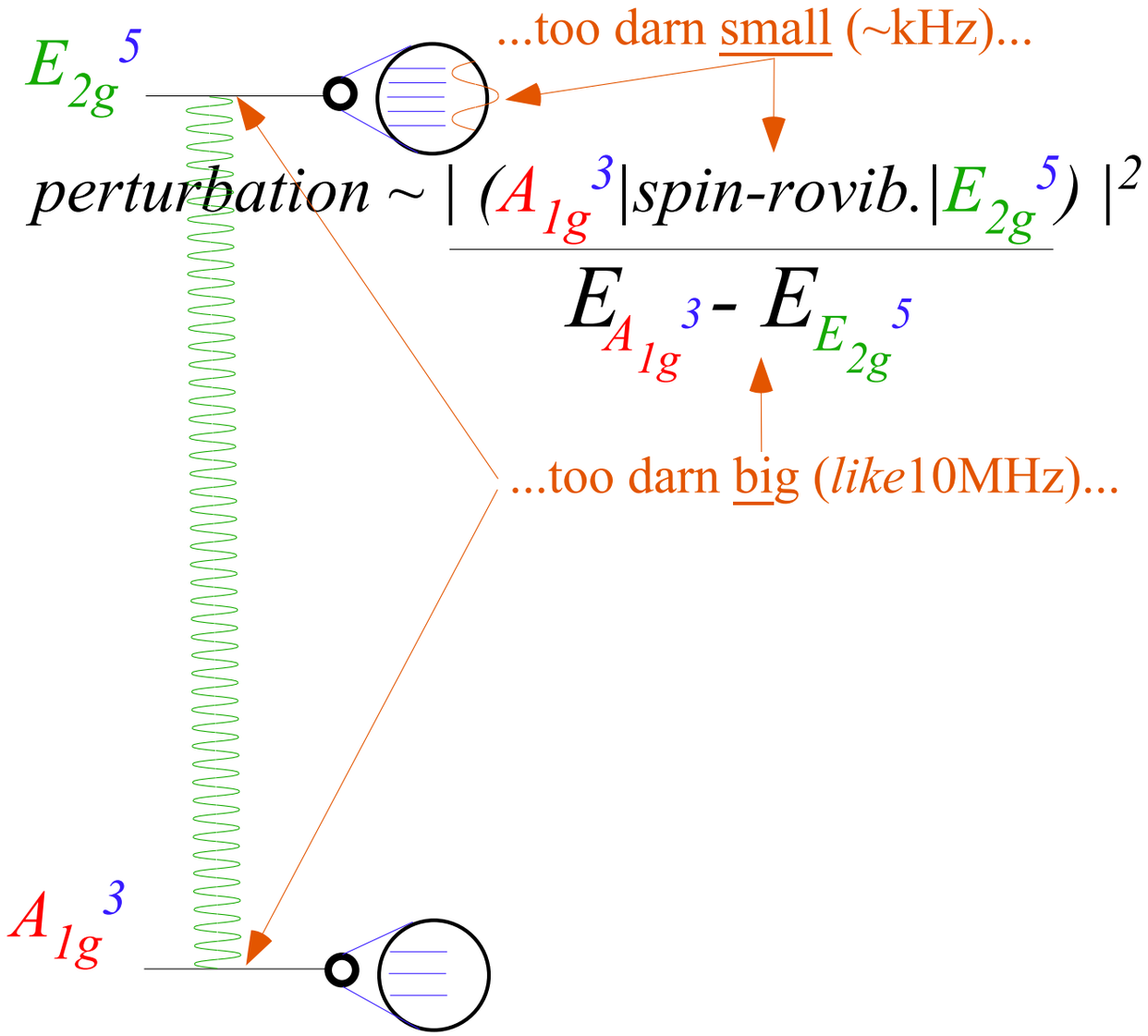
HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? *versus* ***What messes it up?***

$A_{2u}^{\ 1}$

No Way!

...because nuclear moments...
...are so very slight...”



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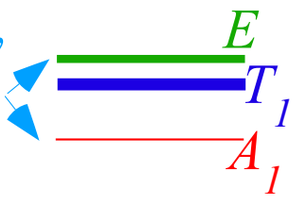
"...because nuclear moments...
...are so very slight..."

$E_{2g}{}^{5}$ ...too darn small (~kHz)...

$$perturbation \sim \left| \frac{(A_{1g}{}^{3}|spin\text{-}rovib.|E_{2g}{}^{5})}{E_{A_{1g}{}^{3}} - E_{E_{2g}{}^{5}}} \right|^2$$

...too darn big (*like*10MHz)...

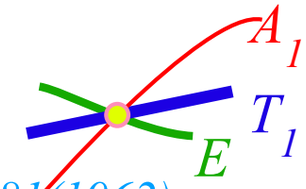
...exponentially tiny! (like 10^{-50}Hz)



$A_{1g}{}^{3}$

WAY!

...because levels of different species are forced together by angular wave localization or "level-clustering" or (rarely) by "accidental" degeneracy.



"Accidental" degeneracy
Lea, Leask & Wolf JPCSol.23,1381(1962)

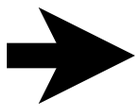
Level-clustering
Dorney and Watson JMS 42,135(1972)
Harter and Patterson PRL38,224(1977)
JCP 66,4872(1977)

RE Surface precession vs. tunneling
Harter and Patterson JMP 20,1453(1979)
JCP 80,4241(1984)

RE Superhyperfine transitions
Hyperfine effects may rule! A_1 T_1 E T_2 A_2 *get seriously mixed up.*

Harter,Patterson,and daPaixao, Rev.Mod.Phys. 50, 37(1978)
Harter and Patterson, Phys. Rev. A19,2277(1979) (CF_4)
Harter, Phys. Rev. A24,192-262(1981) (SF_6)

JPCS=Journal Phys. Chem. Solids
JMS=Journal Molecular Spectroscopy
PRL=Phys. Rev. Letters
JCP=Journal of Chemical Physics
JMP=Journal of Mathematical Physics



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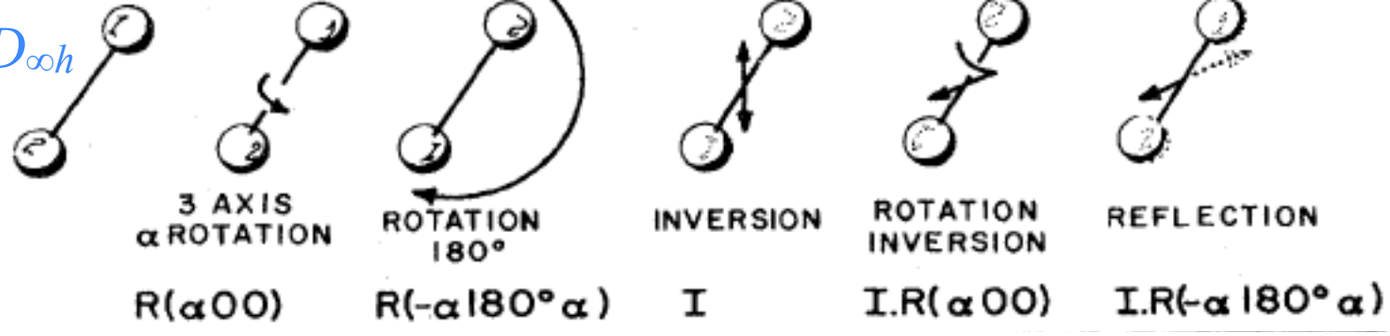
$O(3)\supset D_{\infty h}$ spin-symmetry species

3D Orthogonal group O(3) correlates with $D_{\infty h}$ symmetry

Angular momentum	*atomic label*	*molecular label*
$\ell=0$	*s or S*	σ *or* Σ
$\ell=1$	*p or P*	π *or* Π
$\ell=2$	*d or D*	δ *or* Δ
$\ell=3$	*f or F*	ϕ *or* Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	*1*	·	·	·	·	·	·	·
0^-	·	·	·	*1*	·	·	·	·
$1+$	·	·	*1*	·	*1*	·	·	·
1^-	·	*1*	·	·	·	*1*	·	·
$2+$	*1*	·	·	·	*1*	·	*1*	·
2^-	·	·	·	*1*	·	*1*	·	*1*
$3+$	·	·	*1*	·	*1*	·	*1*	·
3^-	·	*1*	·	·	·	*1*	·	*1*



$A_{1g}=\Sigma_g^+$

$A_{1u}=\Sigma_u^+$

$A_{2g}=\Sigma_g^-$

$A_{2u}=\Sigma_u^-$

$E_{1g}=\pi_g$

$E_{1u}=\pi_u$

$E_{2g}=\Delta_g$

$E_{2u}=\Delta_u$

•
•
•

Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of A⊗B

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Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

$O(3)\supset D_{\infty h}$ spin-symmetry species

3D Orthogonal group O(3) correlates with $D_{\infty h}$ symmetry

Angular momentum	*atomic label*	*molecular label*
$\ell=0$	*s or S*	σ *or* Σ
$\ell=1$	*p or P*	π *or* Π
$\ell=2$	*d or D*	δ *or* Δ
$\ell=3$	*f or F*	ϕ *or* Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	*1*	·	·	·	·	·	·	·
0^-	·	·	·	*1*	·	·	·	·
$1+$	·	·	*1*	·	*1*	·	·	·
1^-	·	*1*	·	·	·	*1*	·	·
$2+$	*1*	·	·	·	*1*	·	*1*	·
2^-	·	·	·	*1*	·	*1*	·	*1*
$3+$	·	·	*1*	·	*1*	·	*1*	·
3^-	·	*1*	·	·	·	*1*	·	*1*

	1	R(α00)	R(-α180°α)	I	I.R(α00)	I.R(-α180°α)
$A_{1g}=\Sigma_g^+$	1	1	1	1	1	1
$A_{1u}=\Sigma_u^+$	1	1	-1	-1	-1	1
$A_{2g}=\Sigma_g^-$	1	1	-1	1	1	-1
$A_{2u}=\Sigma_u^-$	1	1	1	-1	-1	-1
$E_{1g}=\pi_g$	2	2 cos α	0	2	2 cos α	0
$E_{1u}=\pi_u$	2	2 cos α	0	-2	-2 cos α	0
$E_{2g}=\Delta_g$	2	2 cos 2α	0	2	2 cos 2α	0
$E_{2u}=\Delta_u$	2	2 cos 2α	0	-2	-2 cos 2α	0
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.

FIG. 15. Characters of $D_{\infty h}=O_{2i}$ symmetry of X_2 rotor.

Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of A⊗B

Rev. Mod. Phys. 50,1,1 (1978)

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

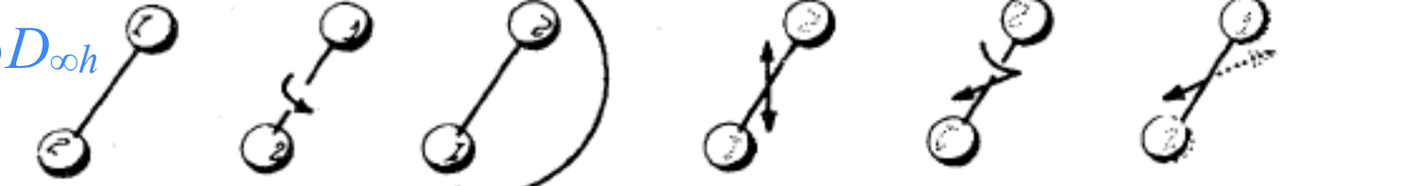
$O(3)\supset D_{\infty h}$ spin-symmetry species

3D Orthogonal group O(3) correlates with $D_{\infty h}$ symmetry

Angular momentum	*atomic label*	*molecular label*
$\ell=0$	*s or S*	σ *or* Σ
$\ell=1$	*p or P*	π *or* Π
$\ell=2$	*d or D*	δ *or* Δ
$\ell=3$	*f or F*	ϕ *or* Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	*1*	·	·	·	·	·	·	·
0^-	·	·	·	*1*	·	·	·	·
$1+$	·	·	*1*	·	*1*	·	·	·
1^-	·	*1*	·	·	·	*1*	·	·
$2+$	*1*	·	·	·	*1*	·	*1*	·
2^-	·	·	·	*1*	·	*1*	·	*1*
$3+$	·	·	*1*	·	*1*	·	*1*	·
3^-	·	*1*	·	·	·	*1*	·	*1*



	1	R(α00)	R(-α180°α)	I	I.R(α00)	I.R(-α180°α)
$A_{1g}=\Sigma_g^+$	1	1	1	1	1	1
$A_{1u}=\Sigma_u^+$	1	1	-1	-1	-1	1
$A_{2g}=\Sigma_g^-$	1	1	-1	1	1	-1
$A_{2u}=\Sigma_u^-$	1	1	1	-1	-1	-1
$E_{1g}=\pi_g$	2	2 cos α	0	2	2 cos α	0
$E_{1u}=\pi_u$	2	2 cos α	0	-2	-2 cos α	0
$E_{2g}=\Delta_g$	2	2 cos 2α	0	2	2 cos 2α	0
$E_{2u}=\Delta_u$	2	2 cos 2α	0	-2	-2 cos 2α	0
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.

TABLE VIII. $O_3\downarrow(O_{2i}=D_{\infty h})$ correlation of representations.

O_3 \ O_{2i}	$B=\Sigma_g^+$	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u	Φ_g	Φ_u	Γ_g...
$N^p=0^+$	1	···	···	···	···	···	···	···	···	···	
$=0^-$	···	···	···	1	···	···	···	···	···	···	
$=1^+$	···	···	1	···	1	···	···	···	···	···	
$=1^-$	···	1	···	···	···	1	···	···	···	···	
$=2^+$	1	···	···	···	1	···	1	···	···	···	
$=2^-$	···	···	···	1	···	1	···	1	···	···	
$=3^+$	···	···	1	···	1	···	1	···	1	···	
$=3^-$	···	1	···	···	···	1	···	1	···	1	
$=4^+$	1	···	···	···	1	···	1	···	1	···	1

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Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of A⊗B

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

➔ *Labeling by symmetry $O(3) \supset D_{\infty h}$*

Coriolis and λ-doubling levels

Dipole-allowed transitions

Diatomic or linear molecule:Labeling by symmetry $O(3)\supset D_{\infty h}$

$A=\Sigma$ symmetry $\Lambda=0$ (no e or v activity)

$A=\Pi$ symmetry $\Lambda=\pm 1$ (unit quantum of e or v activity "riding" on rotor)

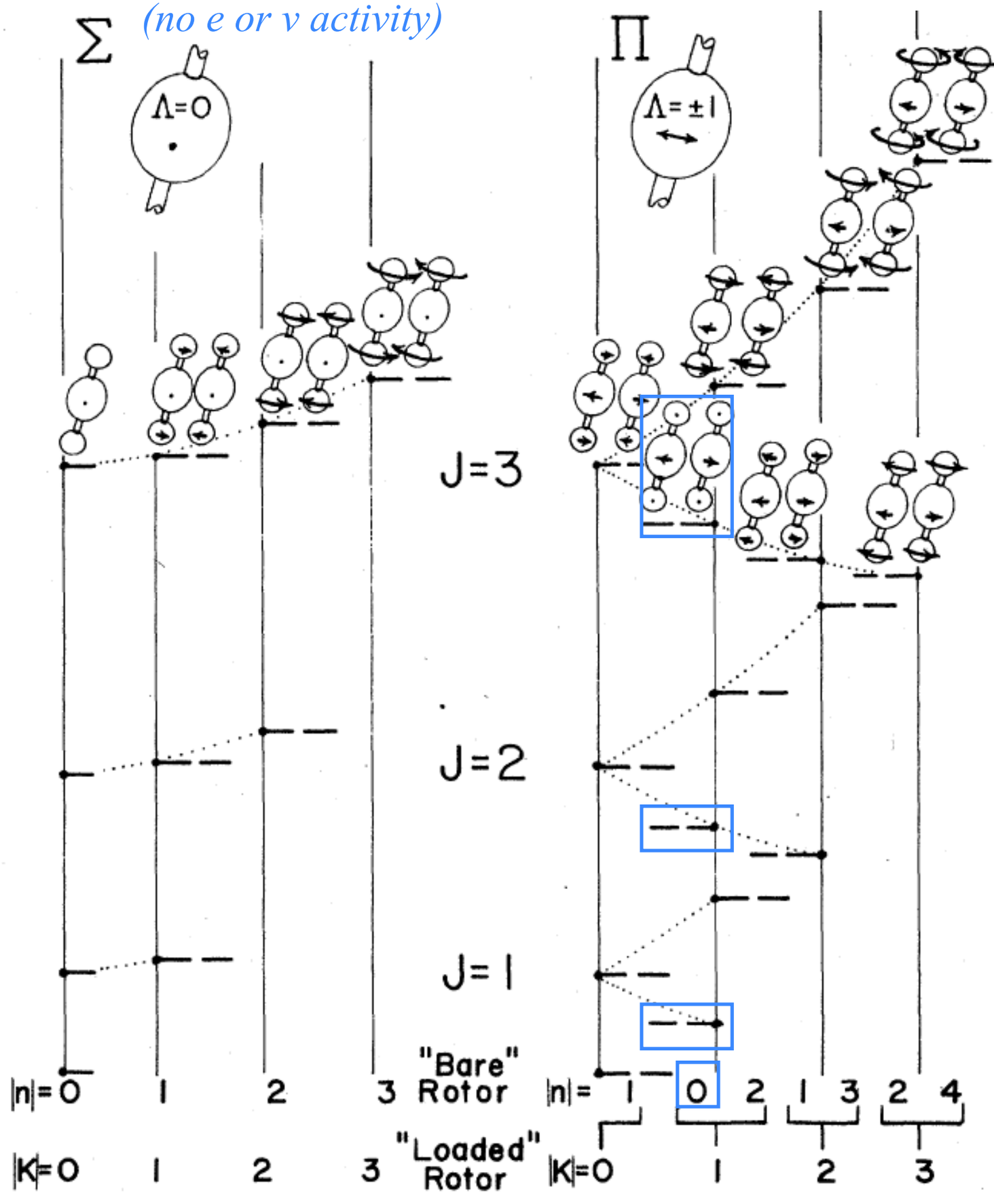

FIG. 18. Σ and Π BOA states for symmetric top molecule. The electronic or vibronic "load" is indicated by an ellipsoid surrounding a "bare" dumb-bell rotor. Arrows indicate the direction of rotation of moving wave states and relative amounts of momentum n or K. Only for the $(n=0, \Pi)$ states will it be necessary to make up standing waves to form the "Λ-doublet" states which are shown in Fig. 19.

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Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of A⊗B

Diatomic or linear molecule: Labeling by symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

$O(3) \supset D_{\infty h}$ spin-symmetry species

3D Orthogonal group O(3) correlates with $D_{\infty h}$ symmetry

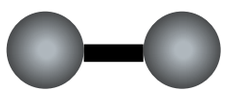
Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
$1+$	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
$2+$	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
$3+$	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

Simple diatomic examples: Hypothetical C_2 Levels (Bare rotor)

$^{12}C_2$ Levels



3^- (excluded)

2^+

1^- (excluded by no Σ_g^+ correlation)

0^+

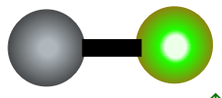
$B=\Sigma_g^+$

$(\boxed{1}\boxed{2}\ \boxed{\bullet}\boxed{\bullet}\ )$

orbit , spin-0

Ortho-Species (only)

$^{12}C^{13}C$ Levels



3^-

2^+

1^-

0^+

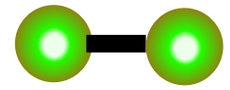
$B=\Sigma$

$(\boxed{1}\boxed{2}\ \boxed{\bullet}\boxed{\uparrow\downarrow}\ )$

orbit , spin-0 spin-$\frac{1}{2}$

$\frac{1}{2}$

$^{13}C_2$ Levels



3^- $\quad\equiv\equiv\equiv$ 3^-

2^+ $\quad$ 2^+

1^- $\quad\equiv\equiv\equiv$ 1^-

0^+ $\quad$ 0^+

$B=\Sigma_g^+$

$(\boxed{1}\boxed{2}\ \boxed{\uparrow}\boxed{\downarrow}\ )$

orbit , spin-$\frac{1}{2}$

Para-Species

$B=\Sigma_u^+$

$(\boxed{\begin{matrix}1\\2\end{matrix}}\ \boxed{\uparrow\uparrow}\boxed{\uparrow\downarrow}\boxed{\downarrow\downarrow}\ )$

orbit , spin-$\frac{1}{2}$

Ortho-Species

Pairs of Fermi (spin-$\frac{1}{2}$) nuclei required by Pauli principle to be totally antisymmetric: Either Even-Odd or Odd-Even

^{12}C has zero nuclear spin

^{13}C has nuclear spin-$\frac{1}{2}$

Diatomic or linear molecule: Labeling by symmetry $O(3)\supset D_{\infty h}\supset C_{\infty v}$

$O(3)\supset D_{\infty h}$ spin-symmetry species

3D Orthogonal group O(3) correlates with $D_{\infty h}$ symmetry

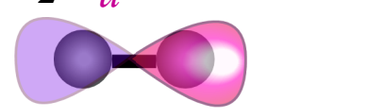
Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

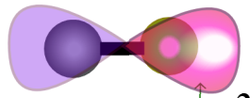
A, B, or C Correlations

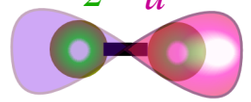
B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
$1+$	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
$2+$	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
$3+$	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

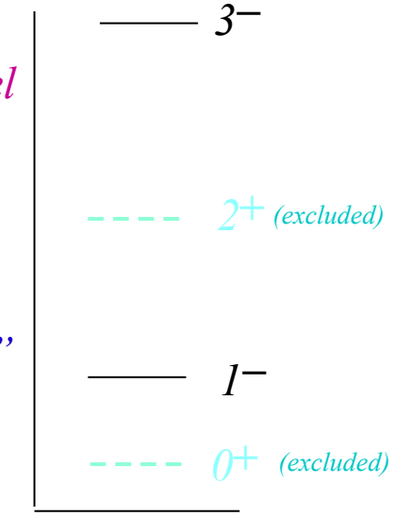
Longitudinal Dipole (1^-) Excitation "Activity" Label $A=\Sigma_u^+$

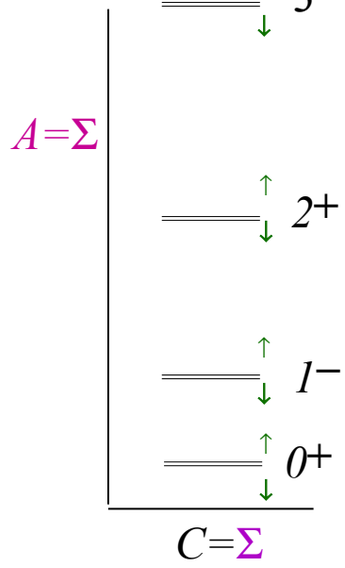
"Coupled" or "Constricted" Rotor Label C

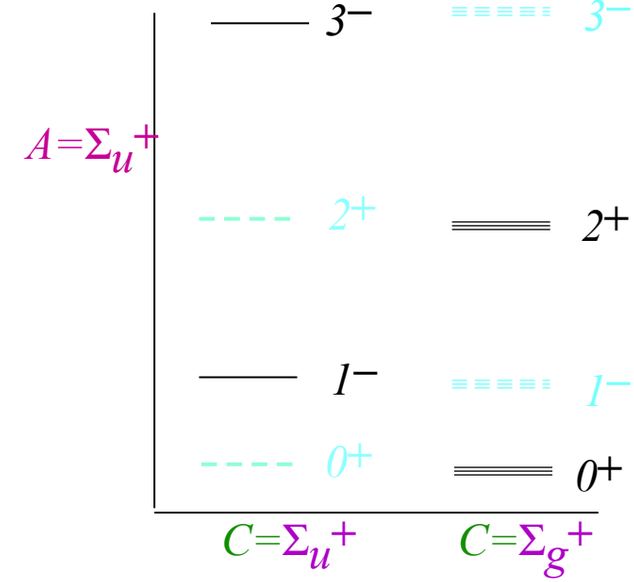


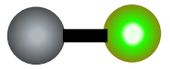


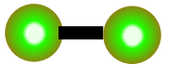


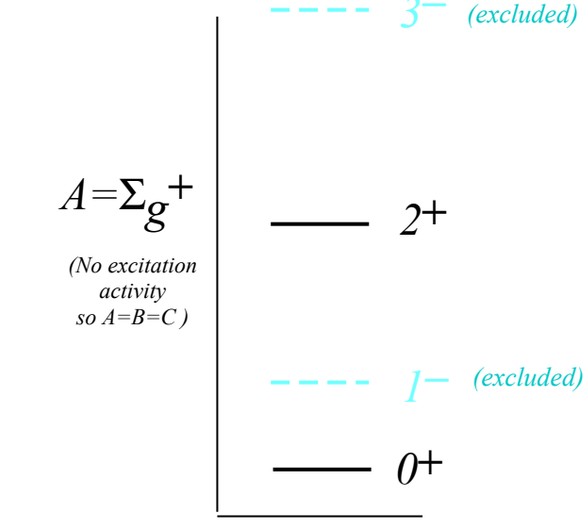


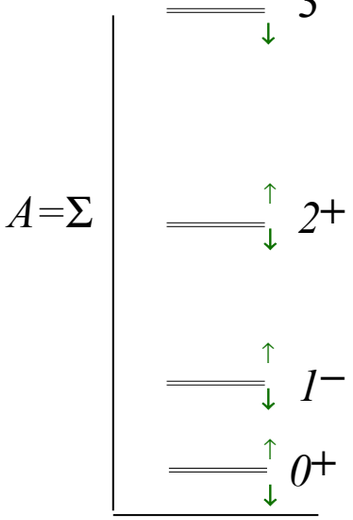


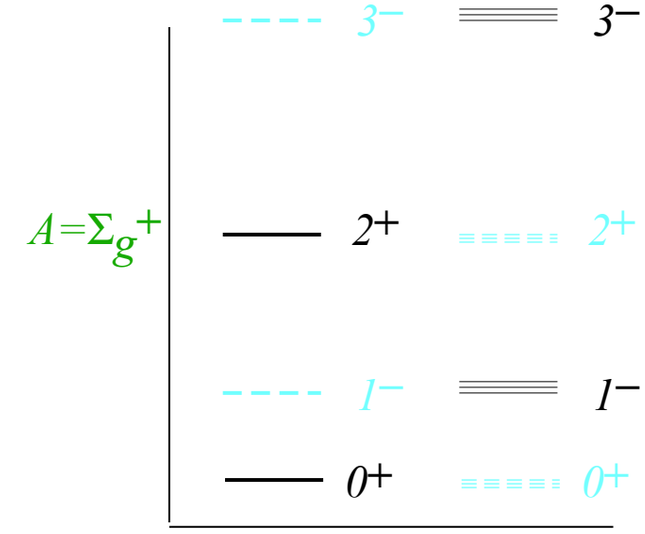












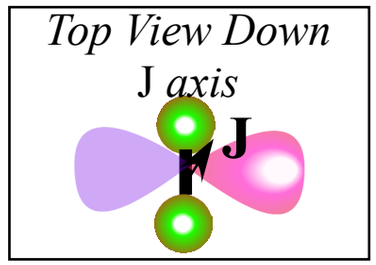
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

Labeling by symmetry $O(3) \supset D_{\infty h}$

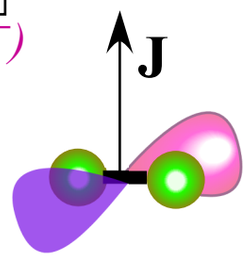
Coriolis and λ-doubling levels

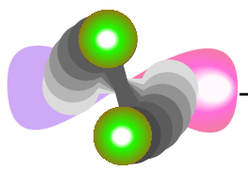
Dipole-allowed transitions

Coriolis and λ-doubling levels

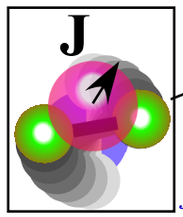


Transverse Dipole (1^-)
"Activity" Label
$A=\Pi_u(-)$ ($\perp$ to J)

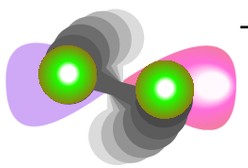


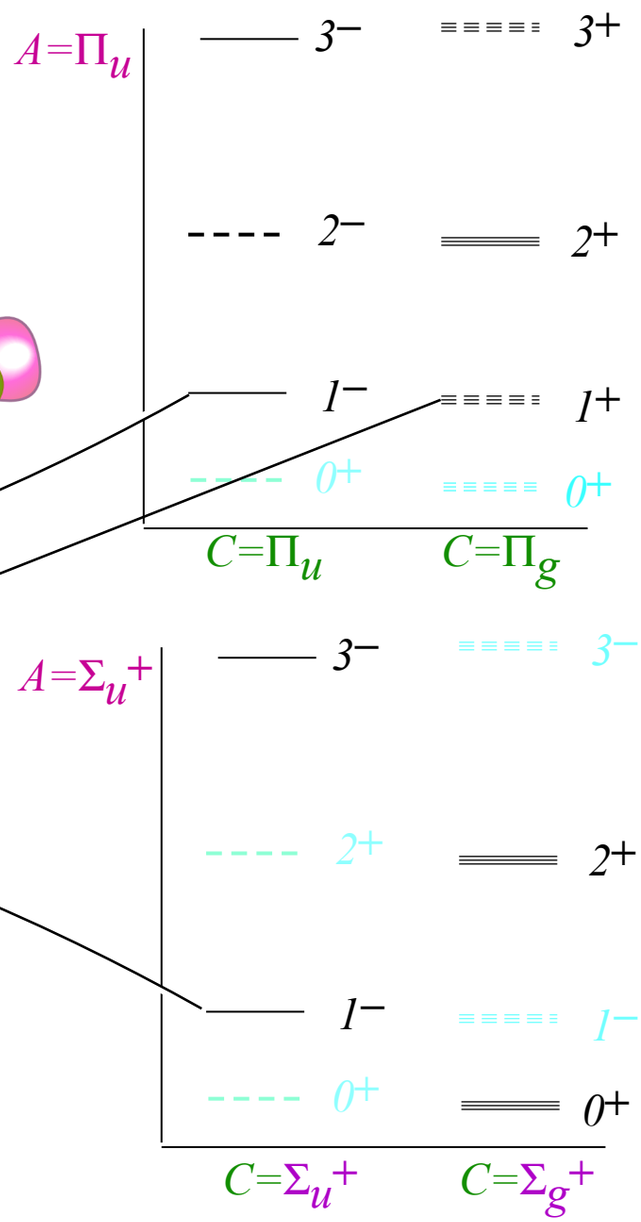


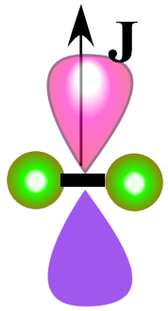
The Σ_u,Π_u waves are slipping!

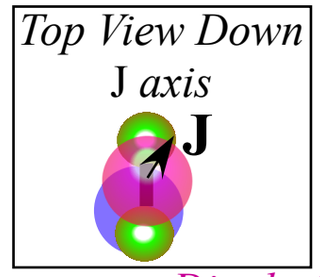


But, not a big deal for 1+



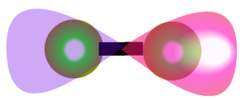


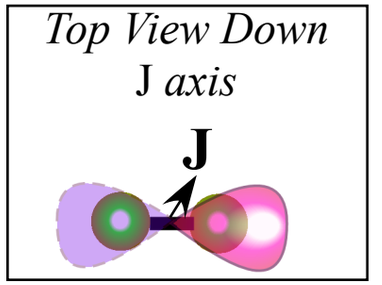




Transverse Dipole (1^-)
"Activity" Label
$A=\Pi_u(+)$ (|| to J)

$^{13}C_2$ Σ_u^+ $\Pi_u(\pm)$
Excited Levels

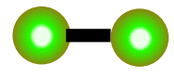




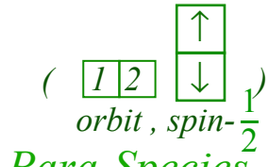
Longitudinal Dipole (1^-)
"Activity" Label
$A=\Sigma_u^+$ ($\perp$ to J)

A, B, or C Correlations

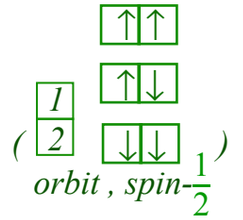
B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u ...
0^+	1	·	·	·	·	·
0^-	·	·	·	1	·	·
$1+$	·	·	1	·	1	·
1^-	·	1	·	·	·	1
$2+$	1	·	·	·	1	·
2^-	·	·	·	1	·	1
$3+$	·	·	1	·	1	·
3^-	·	1	·	·	·	1



$^{13}C_2$ Σ_g^+ Ground Levels



Para-Species



Ortho-Species

Diatomic or linear molecule: Coriolis and λ-doubling levels

$$\mathbf{H} = \mathbf{H}_e + (\mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{J}_{\bar{x}}\mathbf{L}_{\bar{x}} - 2\mathbf{J}_{\bar{y}}\mathbf{L}_{\bar{y}} - 2\mathbf{J}_{\bar{z}}\mathbf{L}_{\bar{z}})/2I_{\bar{x}\,\bar{y}}$$

$$\langle \mathbf{H} \rangle = \begin{array}{c} \begin{matrix} |\Sigma^+\rangle & |\Pi^+\rangle & |\Pi^-\rangle \end{matrix} \\ \begin{vmatrix} \epsilon_\Sigma + 4 & -2\sqrt{2} & 0 \\ -2\sqrt{2} & \epsilon_\pi + 2 & 0 \\ 0 & 0 & \epsilon_\pi + 2 \end{vmatrix} \end{array} /2I_{\bar{x}\,\bar{y}}$$

(J =1)-case

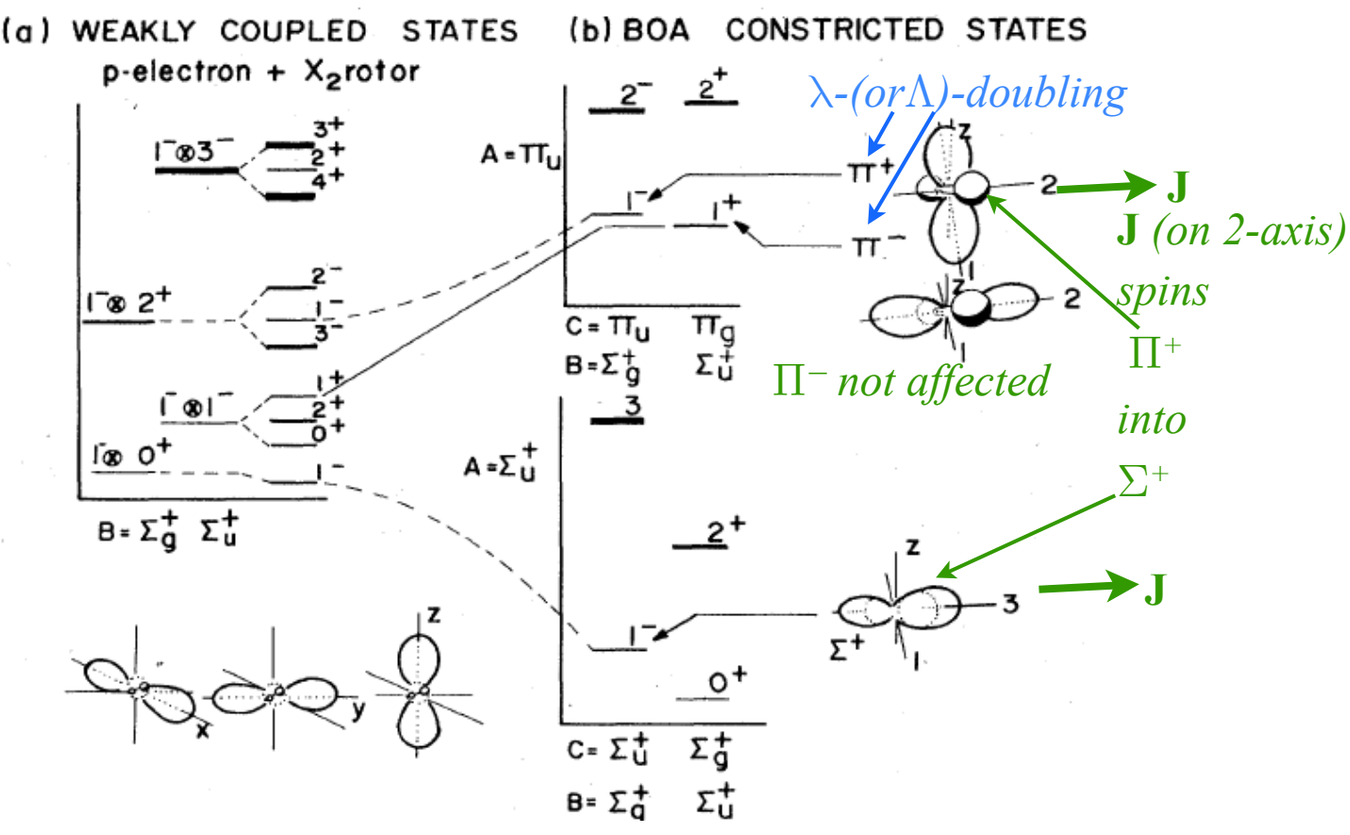


FIG. 19. Correlation diagram for $l=1$ electronic states in the presence of an X_2 rotor. (a) Weakly-coupled states. (N^P, B, and J^P are good labels.) (b) BOA-constricted states. (A, B, C, and J^P are good labels.) States with the same $B=\Sigma_g^+$ and $J^P=1^-$ are connected by dotted lines. The $B=\Sigma_u^+$ and $J^P=1^+$ state (solid line) turns out to be the same for either side as long as $l=1$ is unspoiled. Note that $A=\Pi_u$-doublets are represented by standing waves in the body system. The lower doublet is alternatively + and − parity.

Diatomic or linear molecule: Coriolis and λ-doubling levels

$$\langle \mathbf{H} \rangle = \begin{array}{c} \begin{matrix} |\Sigma^+\rangle & |\Pi^+\rangle & |\Pi^-\rangle \end{matrix} \\ \begin{bmatrix} J(J+1)+2 & -2(J(J+1))^{1/2} & 0 \\ -2(J(J+1))^{1/2} & \epsilon_\pi + J(J+1) & 0 \\ 0 & 0 & \epsilon_\pi + J(J+1) \end{bmatrix} \end{array}$$

$$\mathbf{H} = \mathbf{H}_e + (\mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{J}_{\bar{x}}\mathbf{L}_{\bar{x}} - 2\mathbf{J}_{\bar{y}}\mathbf{L}_{\bar{y}} - 2\mathbf{J}_{\bar{z}}\mathbf{L}_{\bar{z}})/2I_{\bar{x}\,\bar{y}}$$

$$\langle \mathbf{H} \rangle = \begin{array}{c} \begin{matrix} |\Sigma^+\rangle & |\Pi^+\rangle & |\Pi^-\rangle \end{matrix} \\ \begin{vmatrix} \epsilon_\Sigma + 4 & -2\sqrt{2} & 0 \\ -2\sqrt{2} & \epsilon_\pi + 2 & 0 \\ 0 & 0 & \epsilon_\pi + 2 \end{vmatrix} \end{array} /2I_{\bar{x}\,\bar{y}}$$

(J =1)-case

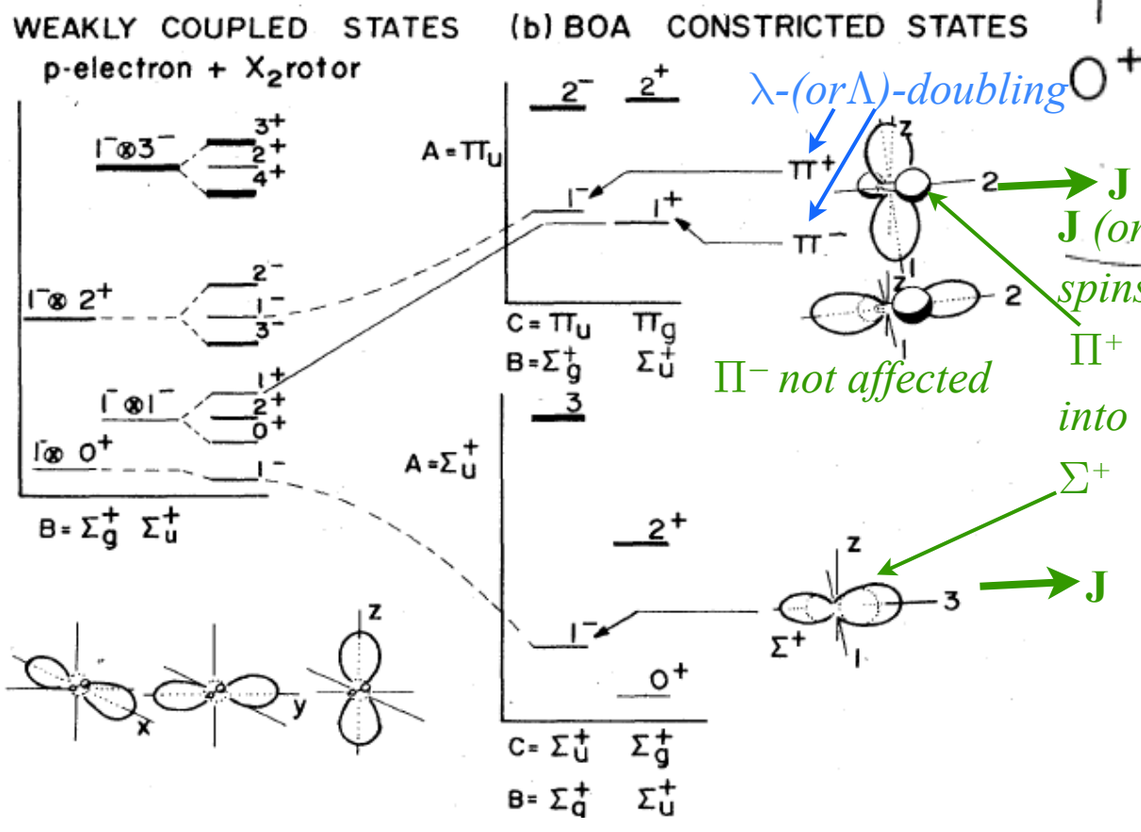


FIG. 19. Correlation diagram for $l=1$ electronic states in the presence of an X_2 rotor. (a) Weakly-coupled states. (N^P, B, and J^P are good labels.) (b) BOA-constricted states. (A, B, C, and J^P are good labels.) States with the same $B=\Sigma_g^+$ and $J^P=1^-$ are connected by dotted lines. The $B=\Sigma_u^+$ and $J^P=1^+$ state (solid line) turns out to be the same for either side as long as $l=1$ is unspoiled. Note that $A=\Pi_u$-doublets are represented by standing waves in the body system. The lower doublet is alternatively + and − parity.

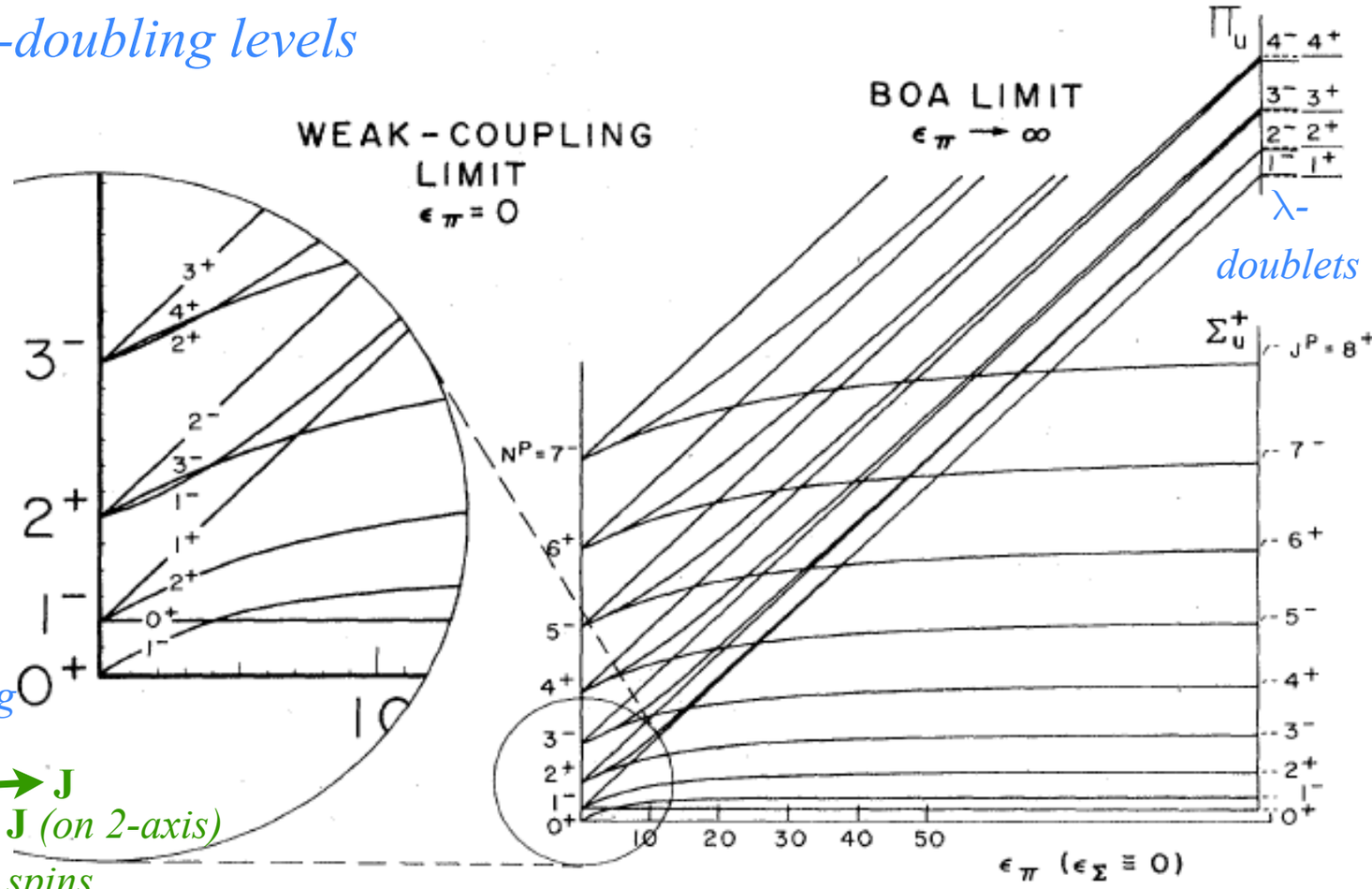
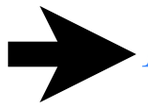


FIG. 20. ($n=0$) J-level plots ($J=0$–8) for ($l=1$: Σ, Π) as functions of electronic energy difference (ϵ_π). The right-hand side of the figure shows the separate Π and Σ manifolds that will arise in the BOA limit as $\epsilon_\pi \to \infty$. (In this figure we set $\epsilon_\Sigma = 0$, and let the rotational constant $B_v = 1/I_{\bar{x}\bar{y}}$ be unity.) Splitting or "λ doubling" is seen in the Π manifolds increasing with J. Corresponding downshifts from the pure rotational spectrum ($\sim B_v J(J+1)$ are seen in the Σ manifold. For small values of ϵ_π ($\epsilon_\pi < 5$) there is a near degeneracy between $J=N\pm1$ levels, particularly for larger values of rotor momentum N. At $\epsilon_\pi = 0$ and $\epsilon_\pi = 4$ the degeneracy is exact, while between these points the $J=N-1$ level lies slightly below the $J=N+1$ level. Pairs of $J=(N\pm1)$ weak-coupling levels are analogous to the Π pairs seen in the BOA limits, only the former are defined with respect to a *laboratory* axis. The weakly coupled $J=N$ state can be thought of as a lab analog of a Σ state.

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

Labeling by symmetry $O(3) \supset D_{\infty h}$

Coriolis and λ-doubling levels



Dipole-allowed transitions

Diatomic or linear molecule: Dipole-allowed transitions

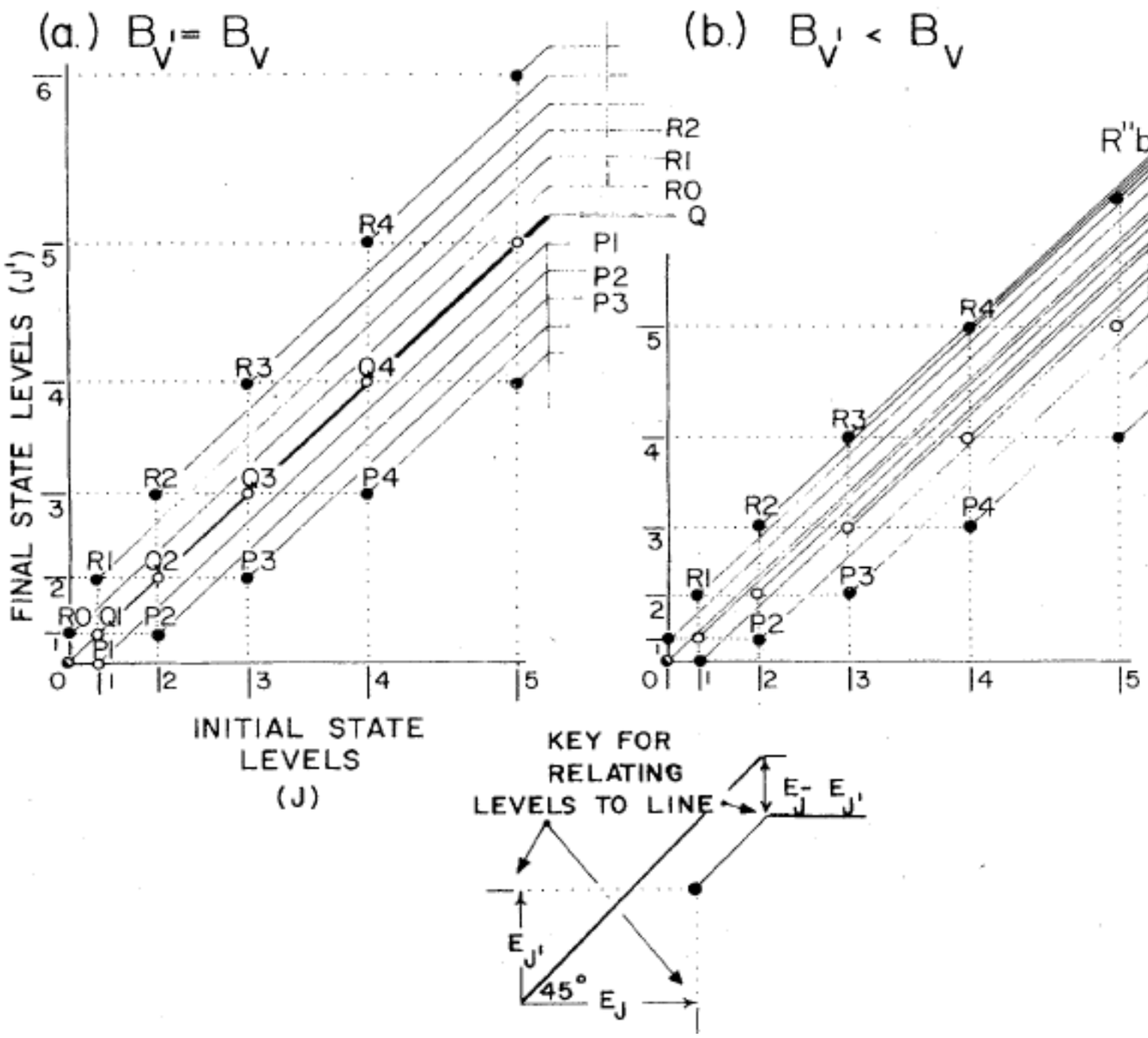


FIG. 30. Demonstrating the use of a rovibronic nomogram for the model $\Sigma \rightarrow \Sigma$ transitions by dipole excitation in a symmetric top molecule.

When excited states have lower B=1/2I (Greater inertia I)

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Diatomic or linear molecule: Dipole-allowed transitions

Transitions forbidden between states
of different Bare Rotor quantum labels
(Spin-symmetry species conserved)

Central Q-branch missing from $\Sigma \leftrightarrow \Sigma$ spectra of $D_{\infty h}$ molecules

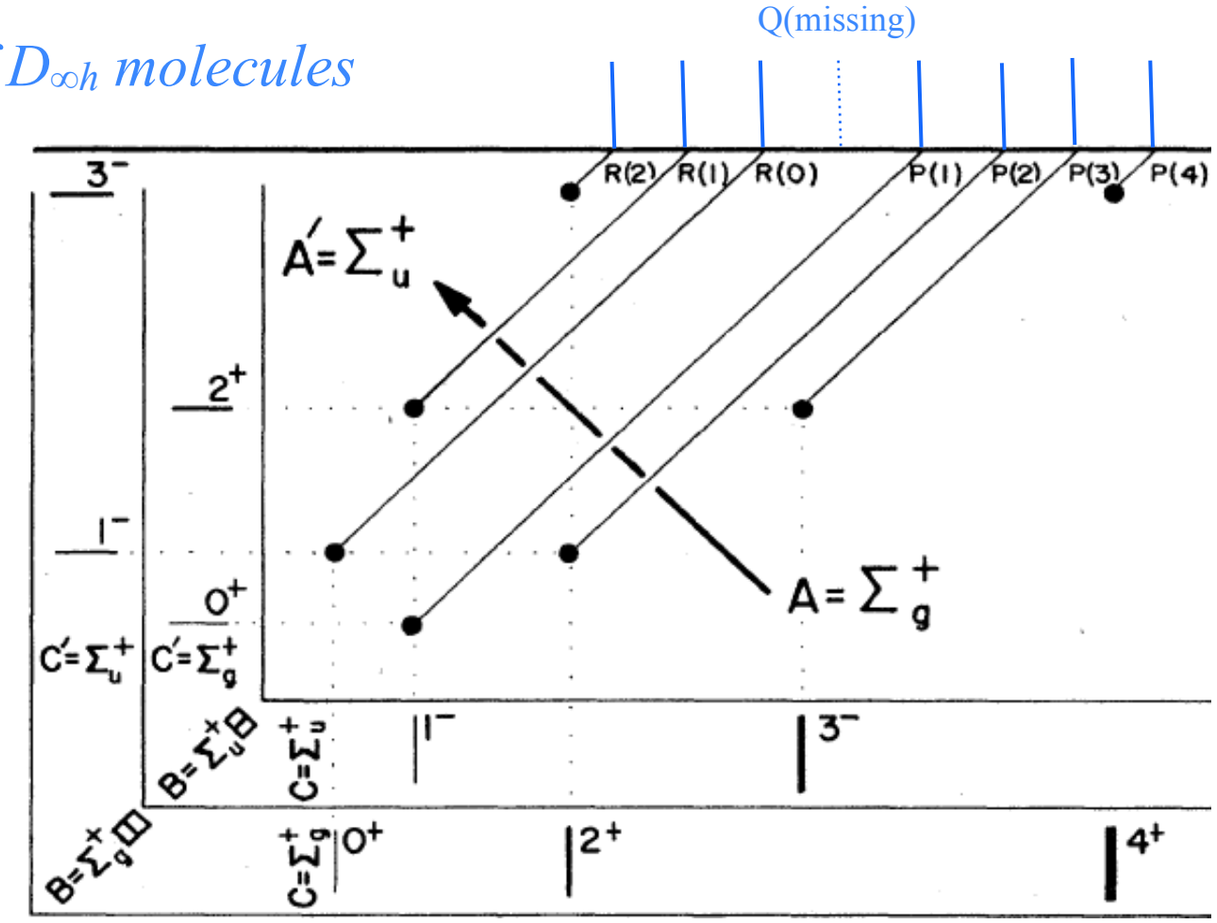

FIG. 31. Electric dipole transitions in linear symmetric (O_{2i}) molecules $X_2, XYX, \ldots$ (a) $\Sigma_g^+ \rightarrow \Sigma_u^+$. (b) $\Sigma_u^- \rightarrow \Pi_g$. Transitions are only allowed between levels lying in the same B corridor. Note that the ($\Sigma_u^- \rightarrow \Pi_g$) Q branch is not Λ doubled since the upper Π doublet is always involved in a $J \rightarrow J$ transition.

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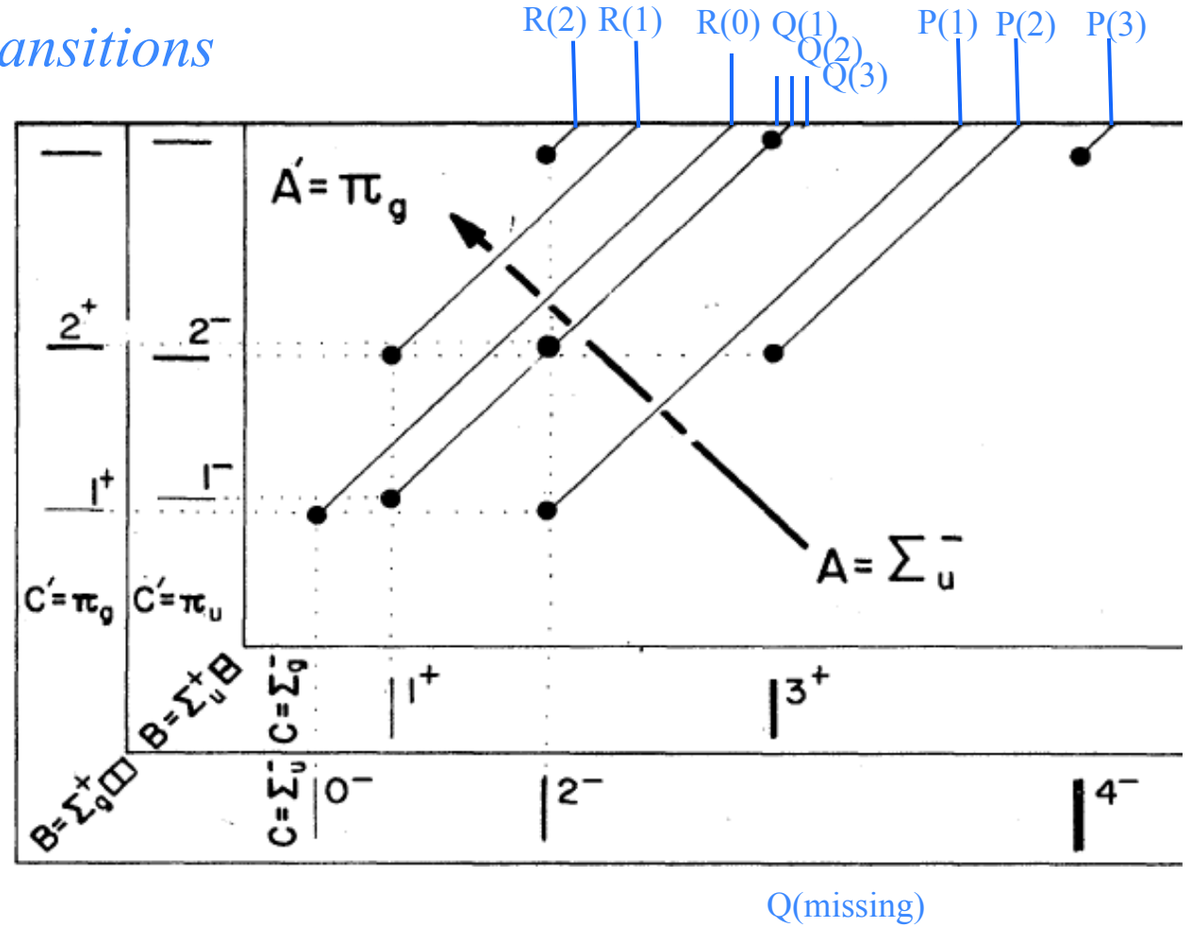
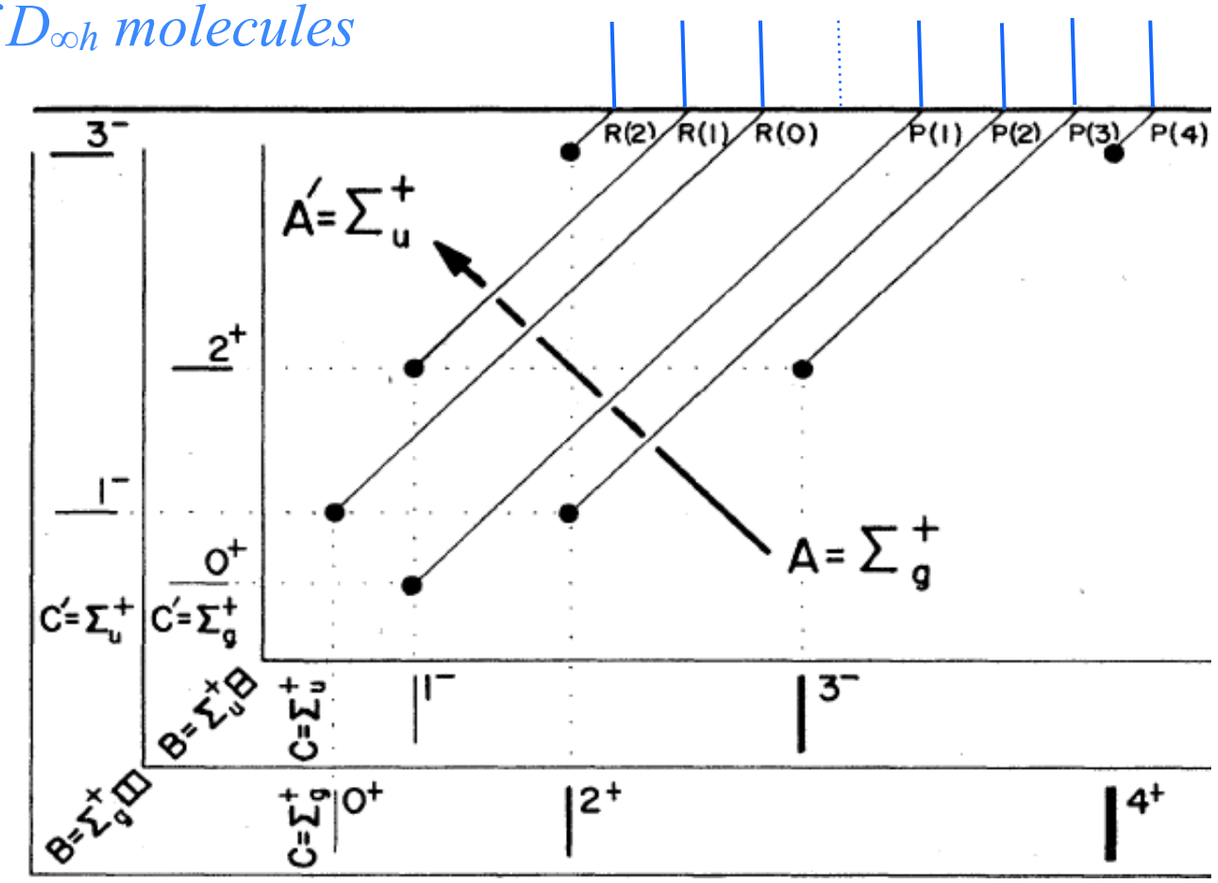
Diatomic or linear molecule: Dipole-allowed transitions

Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved)



Central Q-branch missing from $\Sigma \leftrightarrow \Sigma$ spectra of $D_{\infty h}$ molecules



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S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

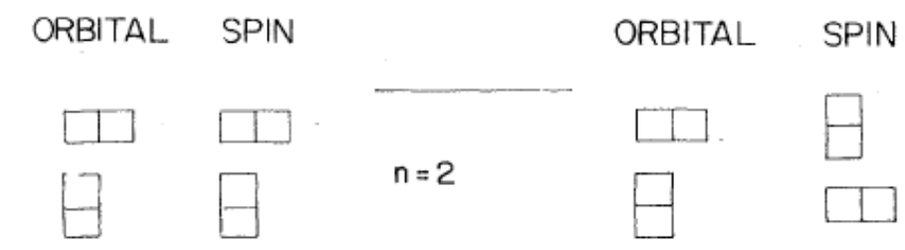
Permutation group S_n is equivalent to Point group $\mathcal{G}$

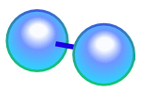
(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $\left|\begin{smallmatrix}\square\\\square\end{smallmatrix}\right\rangle = |B = \Sigma_u^+\rangle$

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n = 2, 3, 4, \ldots$).

(a) BOSE NUCLEI I=0,1,2,... (b) FERMI NUCLEI $I=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots$





$S_2 \sim C_2$

S_2

	(1)(2)	(12)
A_1 (1 2)	1	1
A_2 (1 / 2)	1	-1

C_2	**1**	**σ**
A_1	1	1
A_2	1	-1

Rev. Mod. Phys. 50,1,1 (1978)

S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

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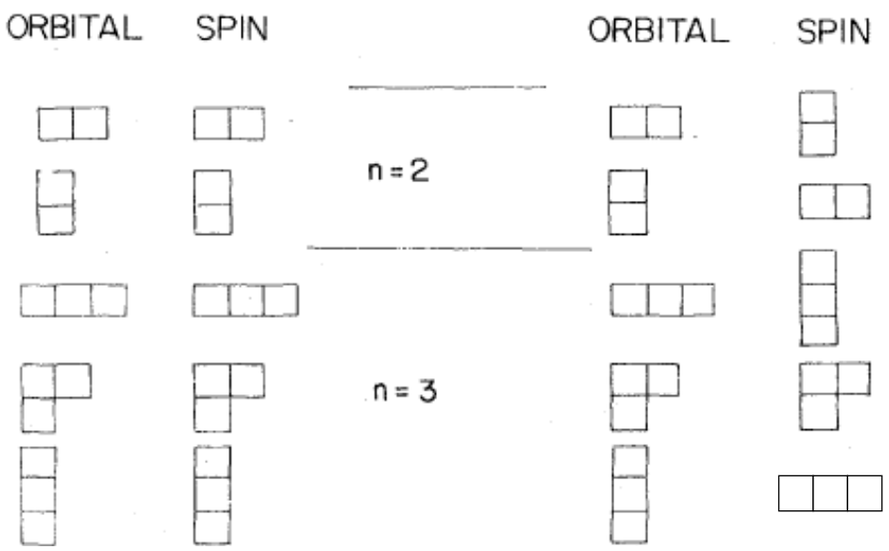
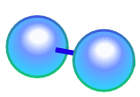
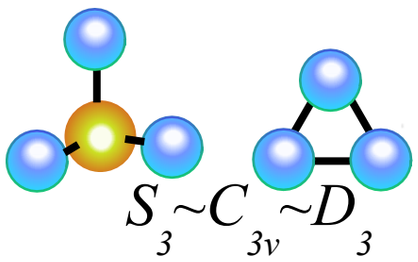




$S_2 \sim C_2$



$S_3 \sim C_{3v} \sim D_3$

S_2

	(1)(2)	(12)
A_1 (1 2)	1	1
A_2 (1 / 2)	1	-1

C_2	**1**	**σ**
A_1	1	1
A_2	1	-1

S_3

	(1)(2)(3)	(123) (132)	(12) (13) (23)
A_1 (1 2 3)	1	1	1
A_2 (1 / 2 / 3)	1	1	-1
E (1 2 / 3 ; 1 3 / 2)	2	-1	0

C_{3v}	**1**	$\mathbf{r}^1$ $\mathbf{r}^2$	$\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$ $\boldsymbol{\sigma}_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Rev. Mod. Phys. 50,1,1 (1978)

S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

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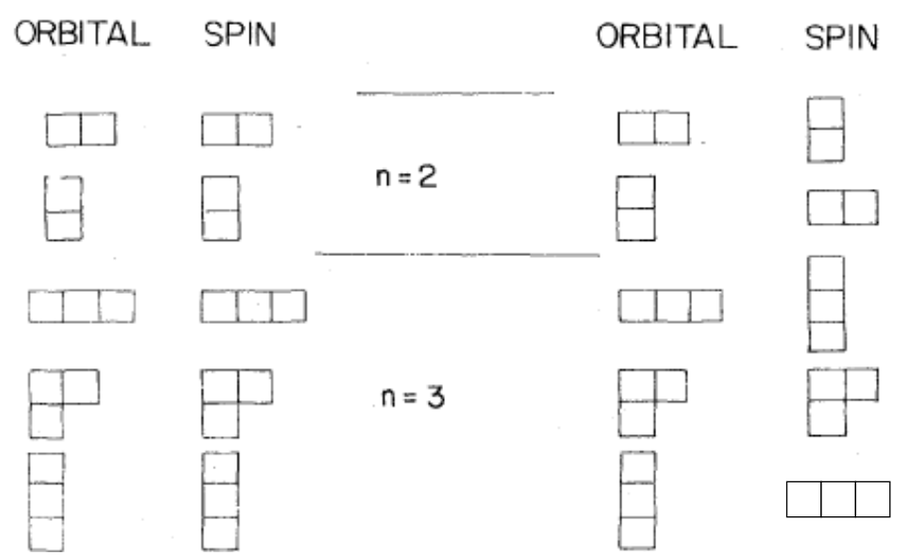
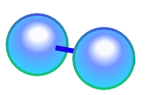
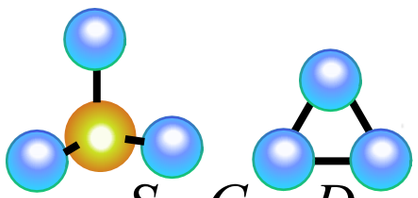
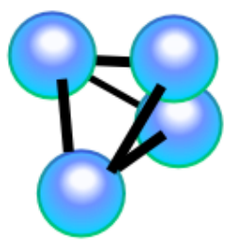




$S_2 \sim C_2$



$S_3 \sim C_{3v} \sim D_3$



$S_4 \sim T_d$

Permutation group S_n is equivalent to Point group $\mathcal{G}$

S_2

	(1)(2)	(12)
A_1	1	1
A_2	1	-1

C_2	**1**	**σ**
A_1	1	1
A_2	1	-1

S_3

	(1)(2)(3)	(123) (132)	(12) (13) (23)
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

C_{3v}	**1**	$\mathbf{r}^1$ $\mathbf{r}^2$	$\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$ $\boldsymbol{\sigma}_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

S_4

	(1)(2)(3)(4)	(123)(4)	(12)(34)	(1234)	(12)(3)(4)
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_2	3	0	-1	1	-1
T_1	3	0	-1	-1	1

Tetrahedral: $\mathcal{G} = T_d$

T_d	**1**	$\mathbf{r}_{1\ldots4}$	180° $\boldsymbol{\rho}_{xyz}$	**I**·90° $\mathbf{R}_{xyz}$	**I**·180° $\boldsymbol{\sigma}_{1\ldots6}$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_2	3	0	-1	-1	1
T_1	3	0	-1	1	-1

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S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

Permutation group S_n is equivalent to Point group $\mathscr{G}$

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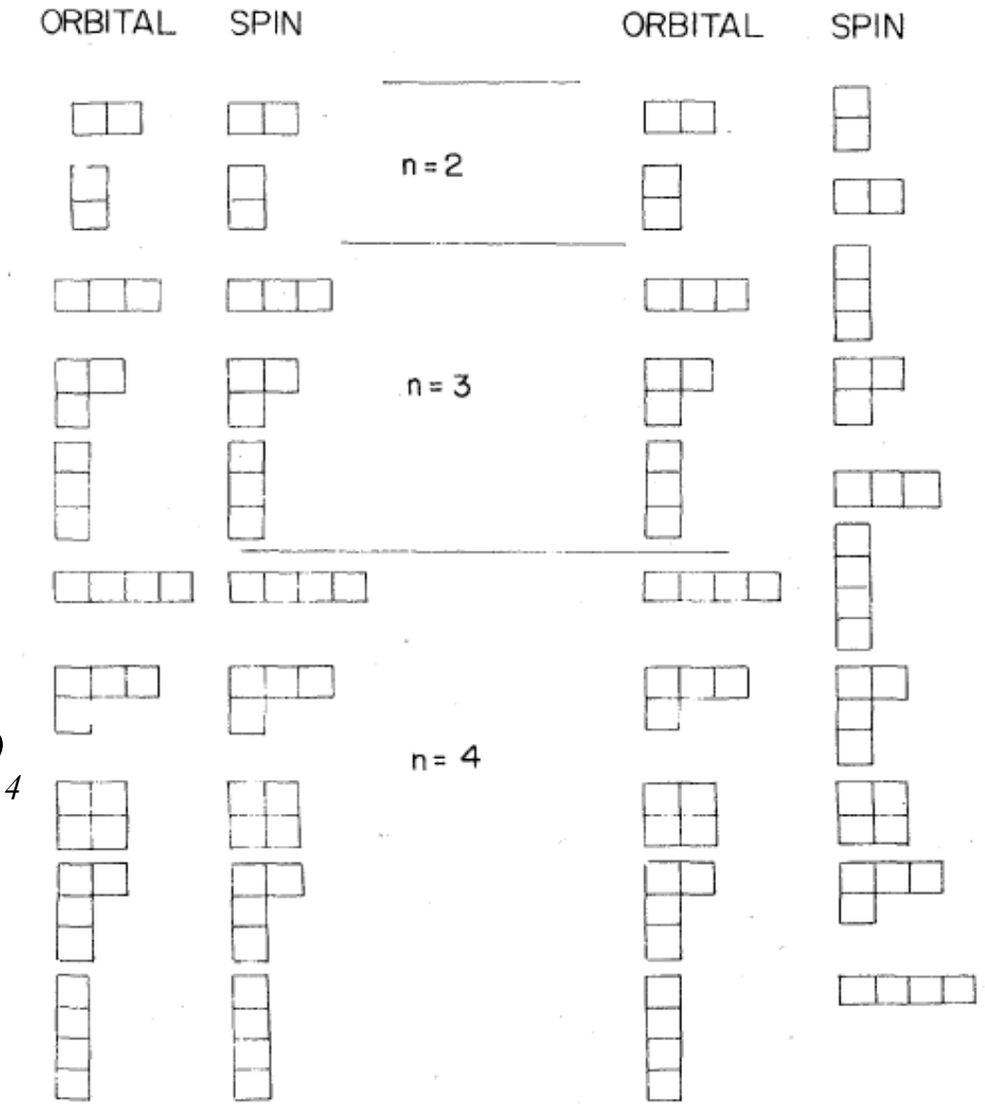
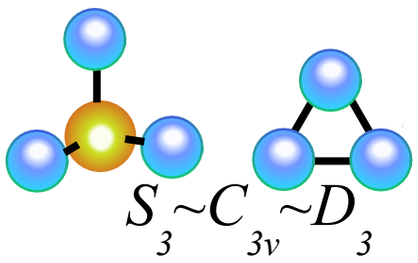
FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n = 2, 3, 4, \ldots$).

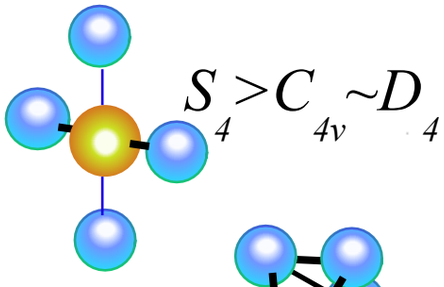
(a) BOSE NUCLEI I=0,1,2,... (b) FERMI NUCLEI $I=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots$



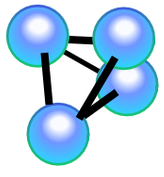
$S_2 \sim C_2$



$S_3 \sim C_{3v} \sim D_3$



$S_4 > C_{4v} \sim D_4$



$S_4 \sim T_d$

S_2

	(1)(2)	(12)
A_1	1	1
A_2	1	-1

C_2	**1**	**σ**
A_1	1	1
A_2	1	-1

S_3

	(1)(2)(3)	(123) (132)	(12) (13) (23)
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

C_{3v}	**1**	$\mathbf{r}^1$ $\mathbf{r}^2$	$\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$ $\boldsymbol{\sigma}_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

S_4

	(1)(2)(3)(4)	(123)(4)	(12)(34)	(1234)	(12)(3)(4)
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_2	3	0	-1	1	-1
T_1	3	0	-1	-1	1

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S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\begin{smallmatrix}\square\\\square\end{smallmatrix}\rangle = |B = \Sigma_u^+\rangle$

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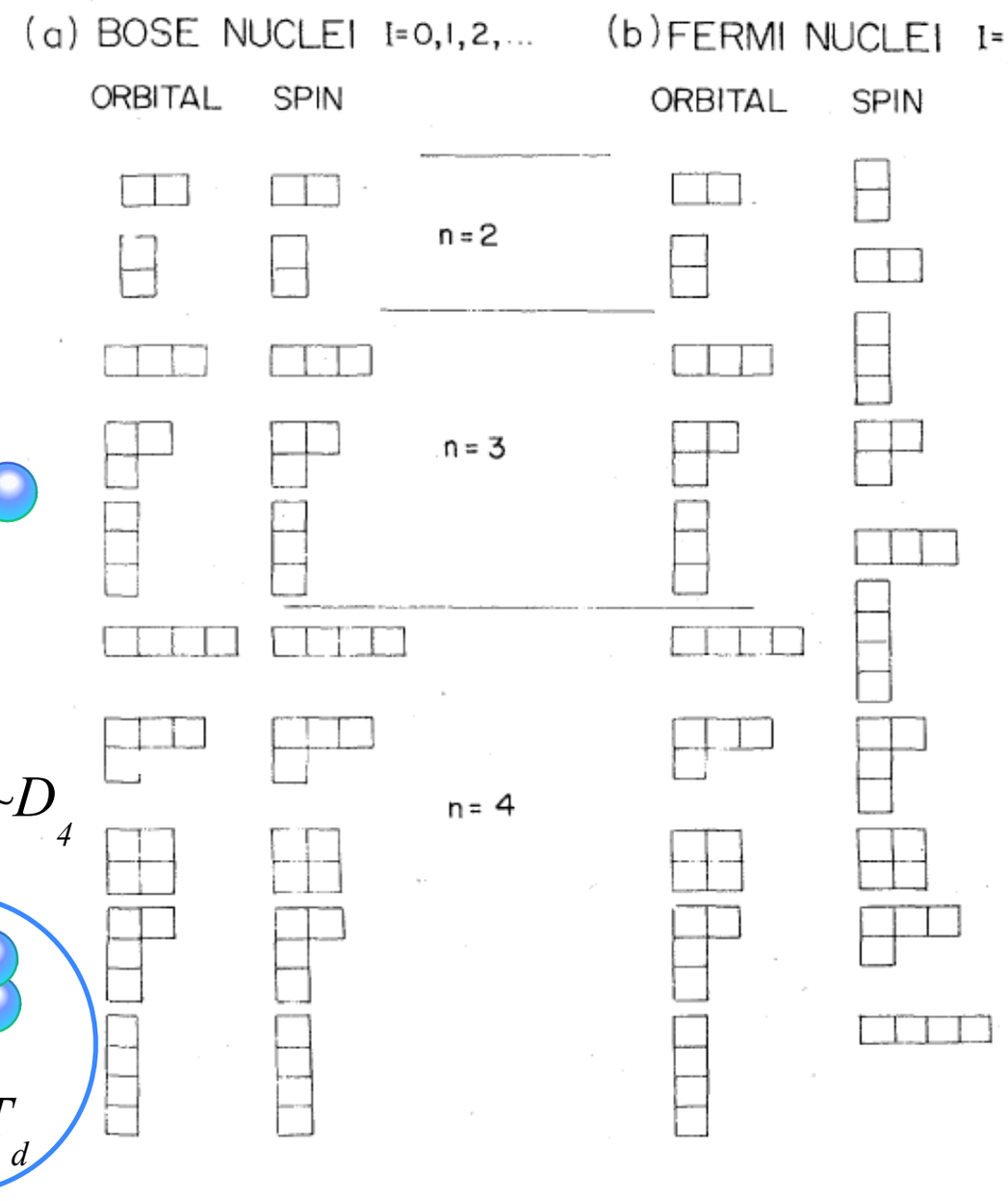
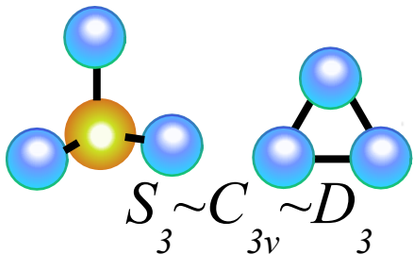
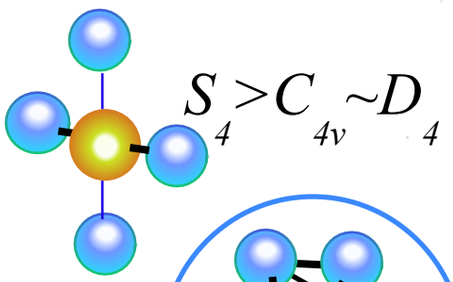
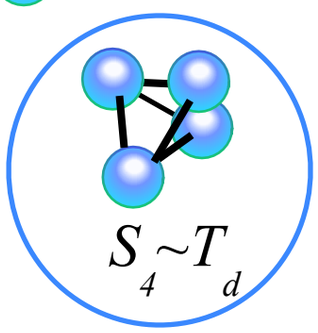








Methane-like:XY_4

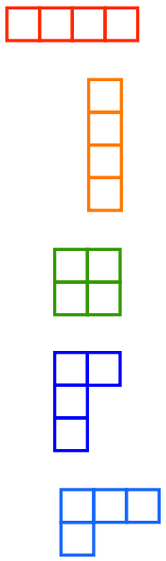


TABLE XIII. T_d characters and symmetry.

	T_d	1	$R(\frac{2\pi}{3})$	$R(\pi 00)$	$IR(\frac{\pi}{2}00)$	$IR(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2})$	Boson $\{\mu_s\}$	Fermion $\{\mu_s\}$
	A_1	1	1	1	1	1	{4}	{1}{1}{1}{1}
	A_2	1	1	1	−1	−1	{1}{1}{1}{1}	{4}
	E	2	−1	2	0	0	{2}{2}	{2}{2}
$(L_xL_yL_z)$	F_1	3	0	−1	1	−1	{2}{1}{1}	{3}{1}
(xyz)	F_2	3	0	−1	−1	1	{3}{1}	{2}{1}{1}{1}

TABLE XIV. $O_3 \downarrow T_d$ correlation.

	A_1	A_2	E	F_1	F_2		A_2	A_1	E	F_2	F_1
$J^p = 0^+$	1	···	···	···	···	0^-	1	···	···	···	···
1^+	···	···	···	1	···	1^-	···	···	···	1	···
2^+	···	···	1	···	1	2^-	···	···	1	···	1
3^+	···	1	···	1	1	3^-	···	1	···	1	1
4^+	1	···	1	1	1	4^-	1	···	1	1	1
5^+	···	···	1	2	1	5^-	···	···	1	2	1
6^+	1	1	1	1	2	6^-	1	1	1	1	2
7^+	···	1	1	2	2	7^-	···	1	1	2	2

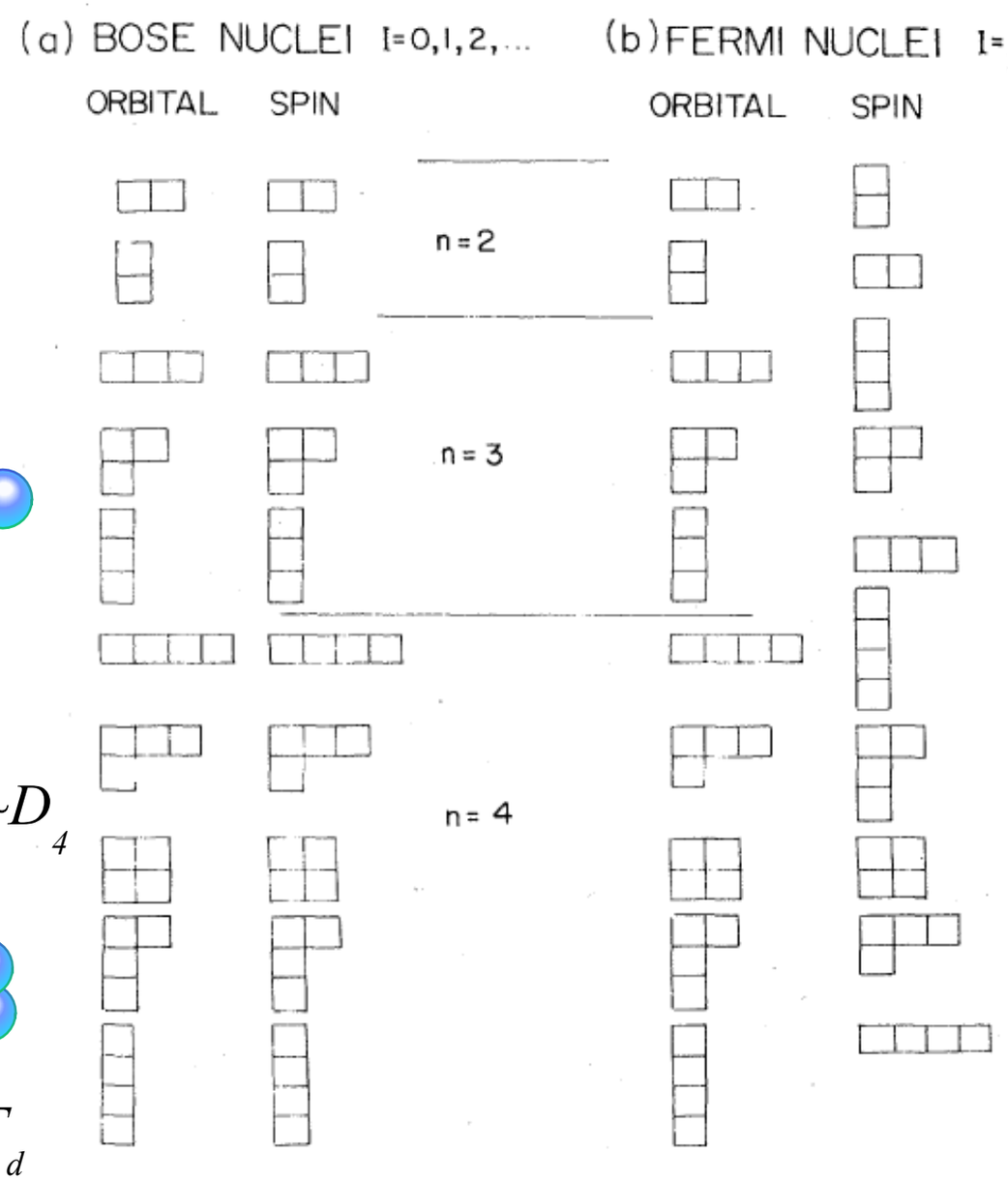
Rev. Mod. Phys. 50,1,1 (1978)

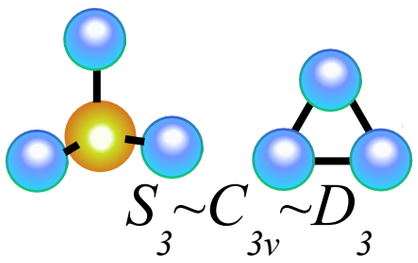
S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

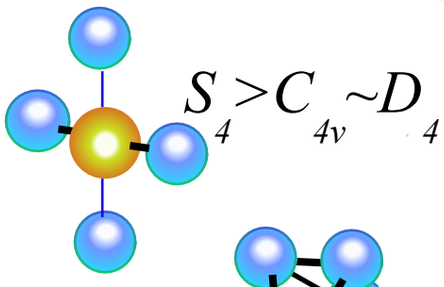
(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\begin{smallmatrix}\square\\\square\end{smallmatrix}\rangle = |B = \Sigma_u^+\rangle$

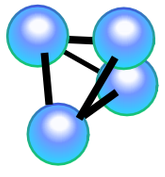
FIG. 25. Orbital tableau labeling of a homonuclear diatomic

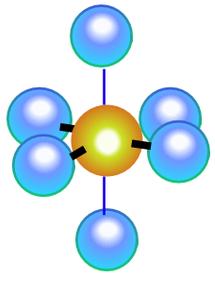
FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n = 2, 3, 4, \ldots$).





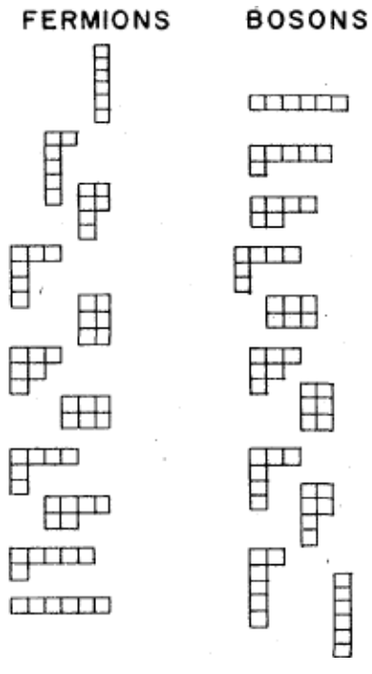


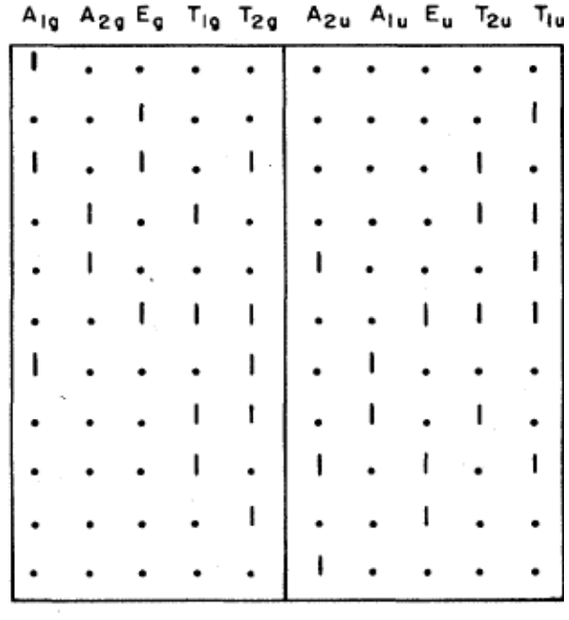




Hexa-flouride-like:XY_6

FIG. 27. Spin tableau-(B) correlation for octahedral XY_6 molecule (see Appendix D).





Rev. Mod. Phys. 50,1,1 (1978)

S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

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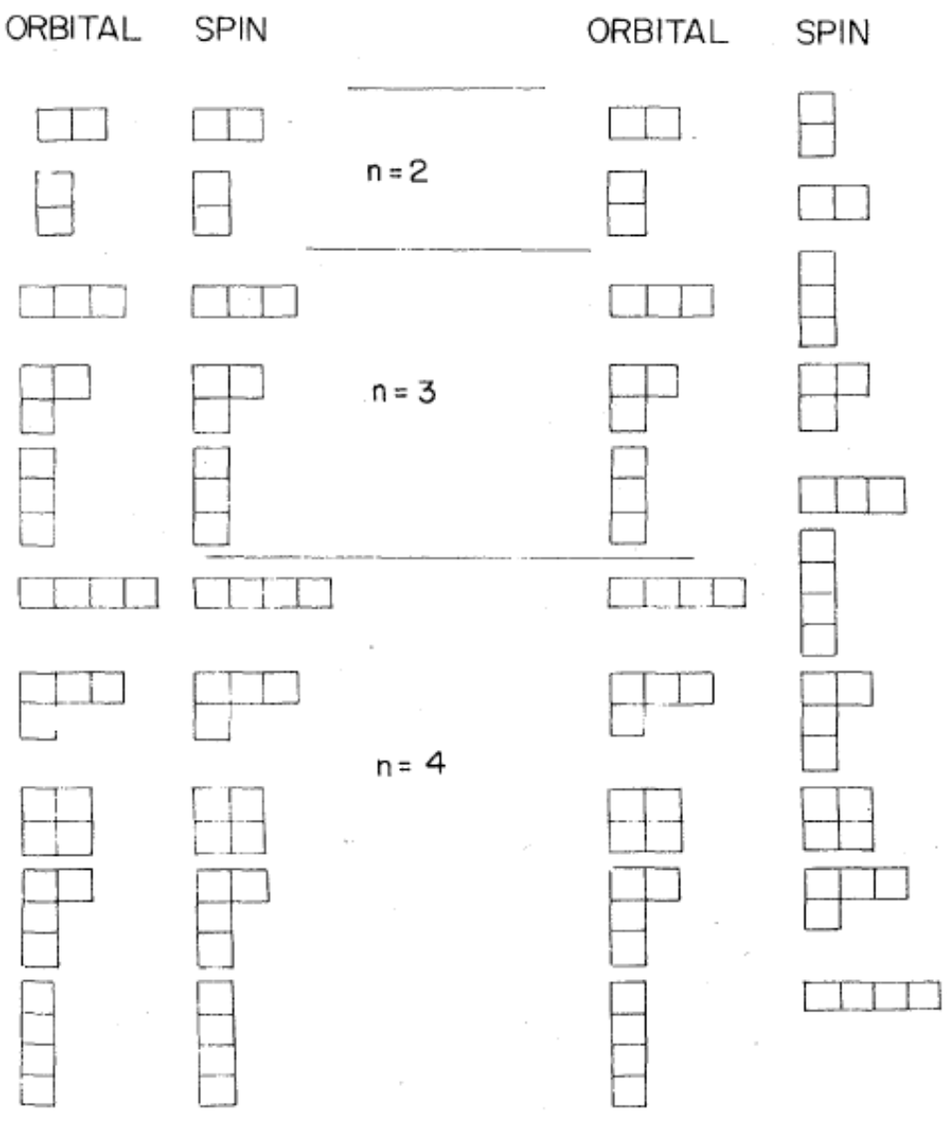
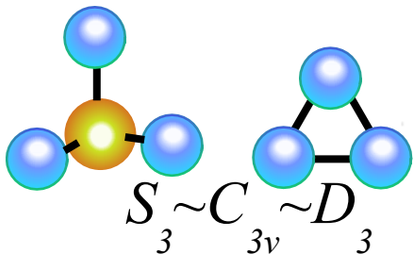
FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n = 2, 3, 4, \ldots$).

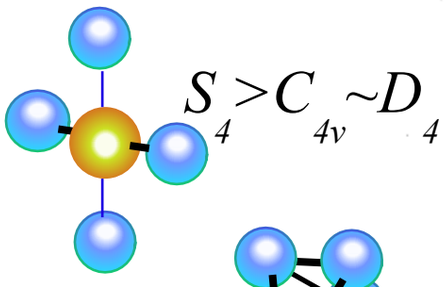
(a) BOSE NUCLEI $I = 0, 1, 2, \ldots$ (b) FERMI NUCLEI $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$



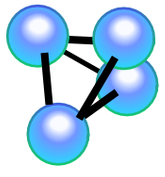
$S_2 \sim C_2$



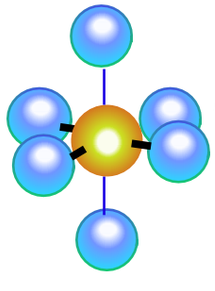
$S_3 \sim C_{3v} \sim D_3$



$S_4 > C_{4v} \sim D_4$



$S_4 \sim T_d$

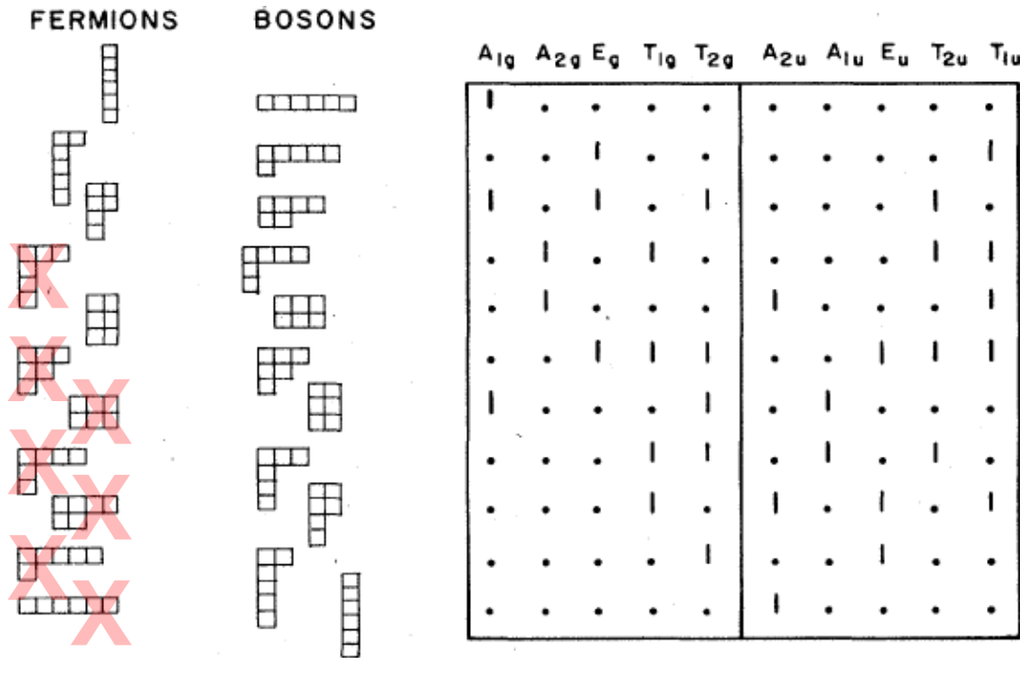


$S_6 > O_h$

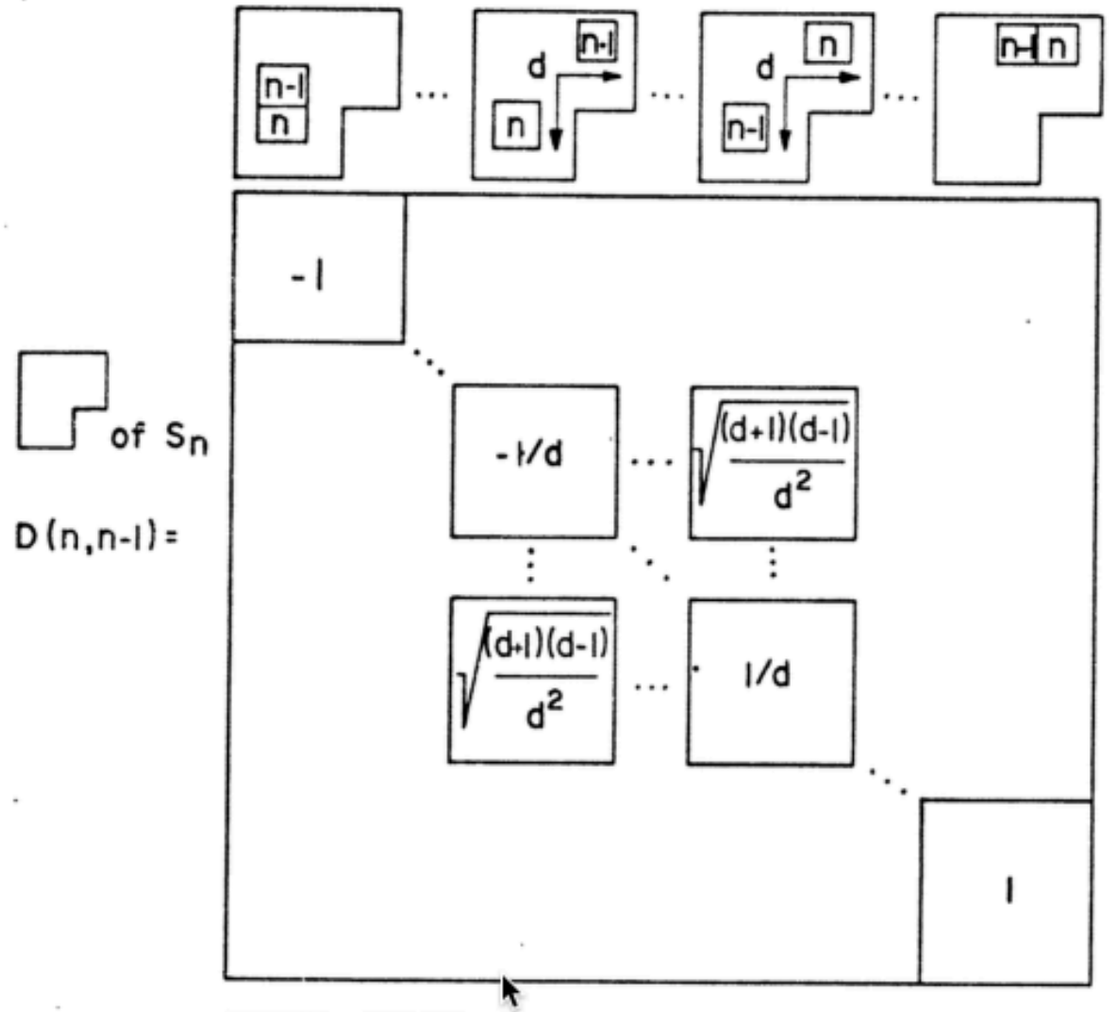
Compare to spin-½ case of $S_6 > O_h$ table on p.57 where orbit-tableau with more than 2 columns are *forbidden*

Hexa-flouride-like:XY_6

FIG. 27. Spin tableau–(B) correlation for octahedral XY_6 molecule (see Appendix D).

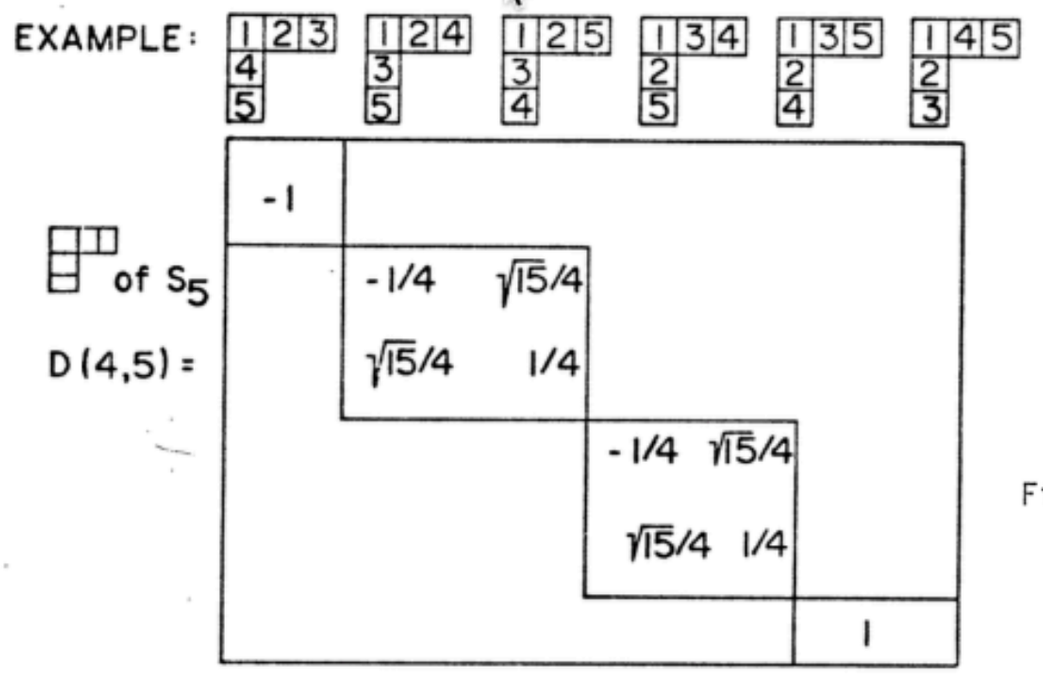


Rev. Mod. Phys. 50,1,1 (1978)



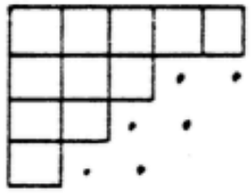
$$D^{E}_{(\sigma_2)} = D^{[2,1]}_{(bc)} = \begin{array}{|c|c|}\hline a & b \\ \hline c \\ \cline{1-1}\end{array} \quad \begin{array}{|c|c|}\hline a & c \\ \hline b \\ \cline{1-1}\end{array} \quad \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$$

$$D^{[2,1]}_{(ab)} = \begin{array}{|c|c|}\hline a & b \\ \hline c \\ \cline{1-1}\end{array} \quad \begin{array}{|c|c|}\hline a & c \\ \hline b \\ \cline{1-1}\end{array} \quad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$



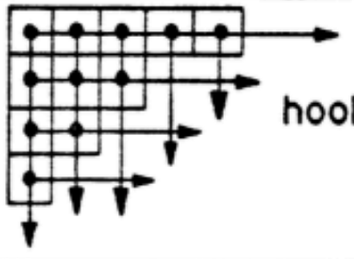
From unpublished Ch.10 for
Principles of Symmetry, Dynamics & Spectroscopy

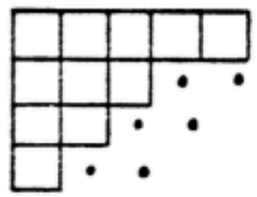
Fig. 10.1.2 Yamanouchi formulas for permutation operators.
Integer d is the "city block" distance between (n) and (n-1) blocks, i.e., the minimum number of streets to be crossed when traveling from one to the other. Note that when numbers (n) and (n-1) are ordered smaller above larger, the permutation is negative (anti-symmetric if d=1), and positive (symmetric if d=1) when the smaller number is left of the larger number. [The (n-1) will never be above and left of (n) since that arrangement would be "non-standard."]

Dimension of  =

representation of S_n

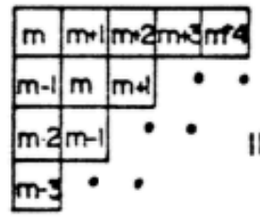
$$= \frac{n!}{\text{product of hooklengths}}$$

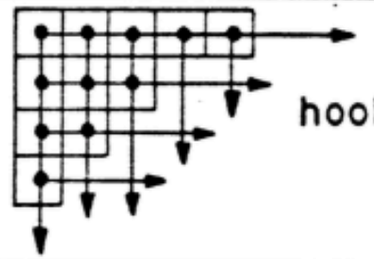


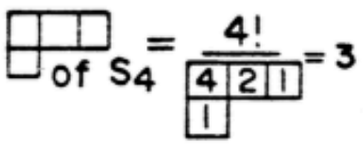
(b) Dimension of  =

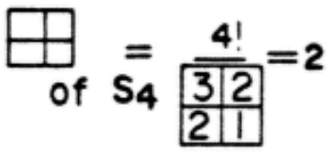
representation of U_m

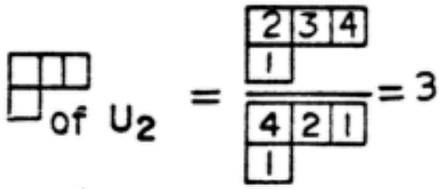
$$= \frac{\text{product of integers}}{\text{product of hooklengths}}$$

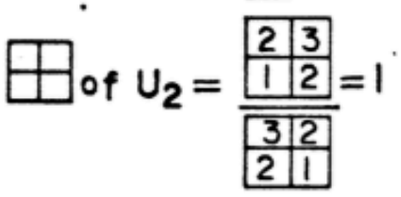


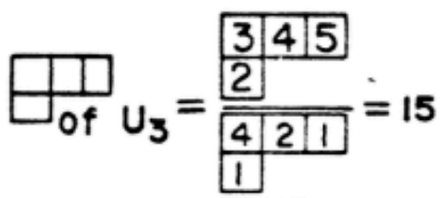


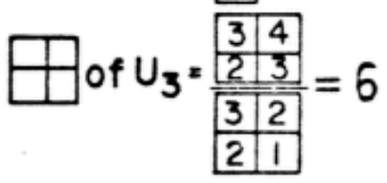












From unpublished Ch.10 for
Principles of Symmetry, Dynamics & Spectroscopy

Fig. 10.1.5 Hall - Robinson Hooklength Formulas
Dimension of representations of (a) S_n and (b) U_m labeled by a single tableau are given by the formulas. A hooklength of a tableau box is simply the number of boxes in a "hook" consisting of all the boxes below it, to the right of it, and itself.

S_n Young Tableaus and spin-symmetry for X_n and XY_n molecules

S_n Young Tableau irrep dimension formula

$$\ell^{[\mu_s]}(S_n) = \frac{\text{Dimension of } S_n \text{ Tableau } [\mu_1][\mu_2]\cdots[\mu_n]}{\text{hook-length product}} = \frac{n! = n\cdot(n-1)\cdot(n-2)\cdots 3\cdot 2\cdot 1}{\text{hook-length product}}$$

•8	•6	•4	•2	•1
•5	•3	•1		
•3	•1			
•1				

Examples:

$$\ell^{A_1} = \ell^{[3,0,0]}(S_3) = \frac{3\cdot 2\cdot 1}{3\ 2\ 1} = 1$$

$$\ell^{A_2} = \ell^{[1,1,1]}(S_3) = \frac{3\cdot 2\cdot 1}{\begin{array}{|c|}\hline 3\\\hline 2\\\hline 1\\\hline\end{array}} = 1$$

$$\ell^{E} = \ell^{[2,1,0]}(S_3) = \frac{3\cdot 2\cdot 1}{\begin{array}{|c|c|}\hline 3 & 1\\\hline 1\\\cline{1-1}\end{array}} = 2$$

S_3

A_1 1 2 3

A_2 1 / 2 / 3

E 1 2 / 3 and 1 3 / 2

(1)(2)(3) (

1 / 1 / 2

FIG. 28. Robinson formula for statistical weights. The "hook-length" of a box in the tableau is the number of boxes in a "hook" which includes that box and all boxes in the line to the right and in the column below it.

$$\ell^{[\mu_s]}(U_m) = \frac{\text{Dimension of } S_n * U_m \text{ Tableau } [\mu_1][\mu_2]\cdots[\mu_m]}{\text{hook-length product}} = \frac{\text{m-dimension product}}{\text{hook-length product}}$$

m	*m*+1	*m*+2	*m*+3	*m*+4
m-1	*m*	*m*+1		
m-2	*m*-1			
m-3				

•8	•6	•4	•2	•1
•5	•3	•1		
•3	•1			
•1				

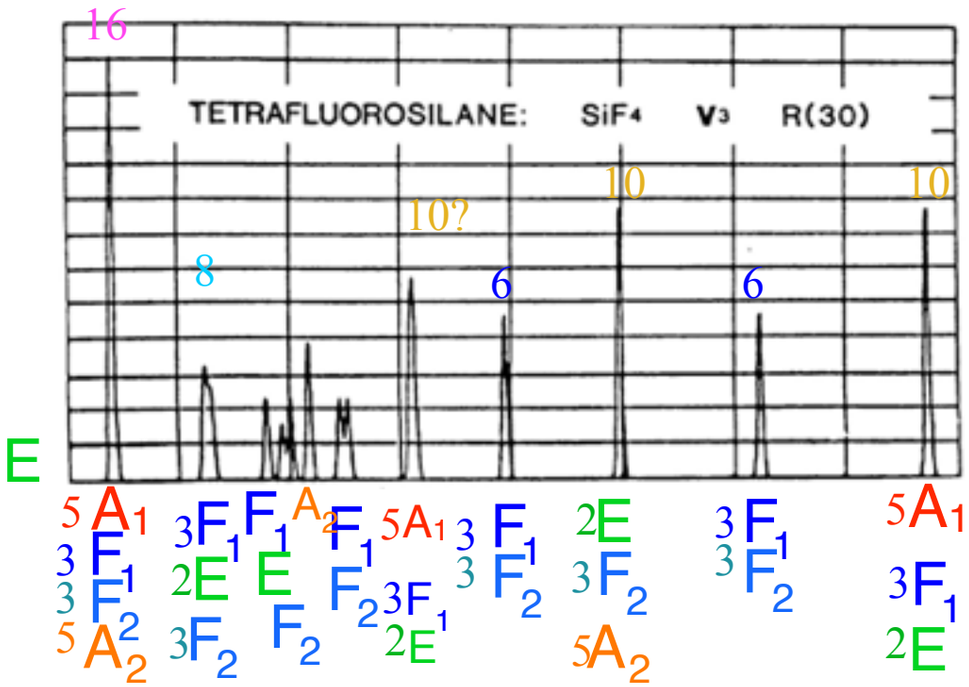
Examples:

$$\ell^{[2,1,0]}(S_3 * U(3)) = \frac{\begin{array}{|c|c|}\hline 3 & 4\\\hline 2\\\cline{1-1}\end{array}}{\begin{array}{|c|c|}\hline 3 & 1\\\hline 1\\\cline{1-1}\end{array}} = 8$$

$$\ell^{[3,0,0]}(S_3 * U(3)) = \frac{\begin{array}{|c|c|c|}\hline 3 & 4 & 5\\\hline\end{array}}{3\ 2\ 1} = 10$$

For applications of Tableaus and Tensors to Atomic physics
Go to Lect. 30 p. 16

S_4 and spin-symmetry for XY_4 molecules (Introducing hook-length formulae)



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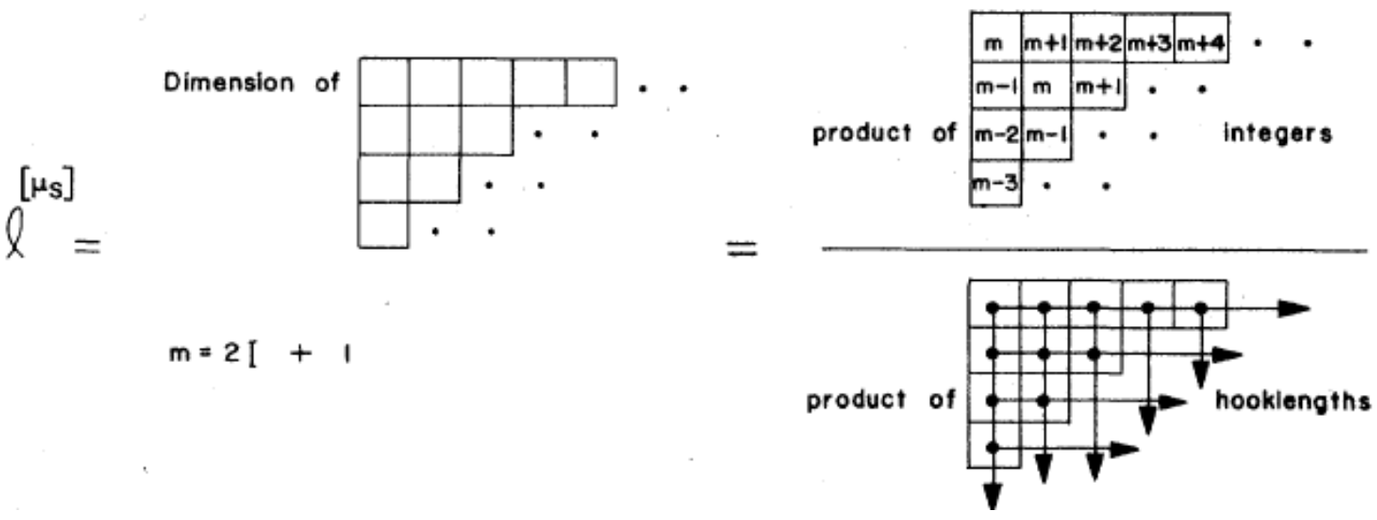
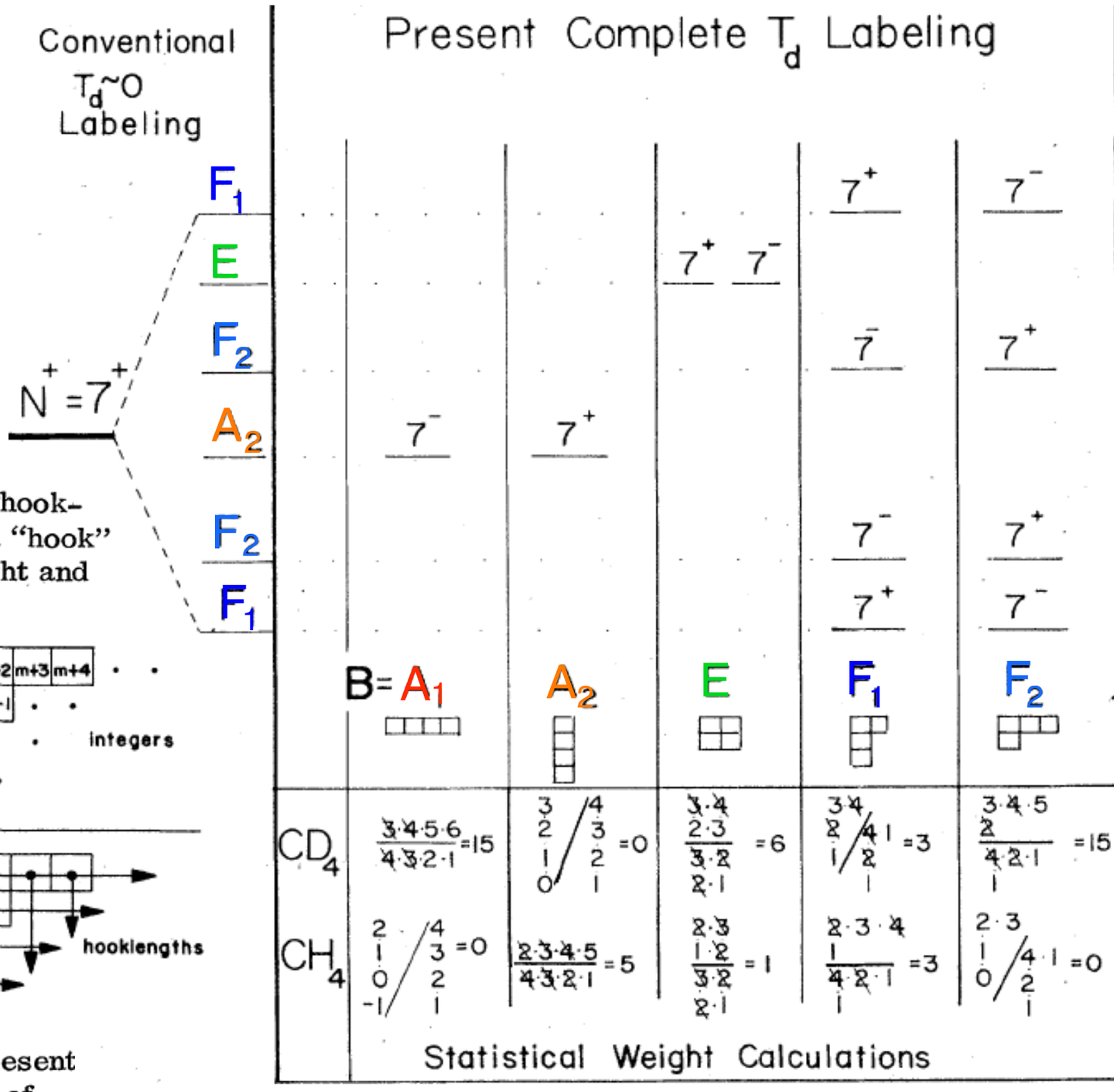


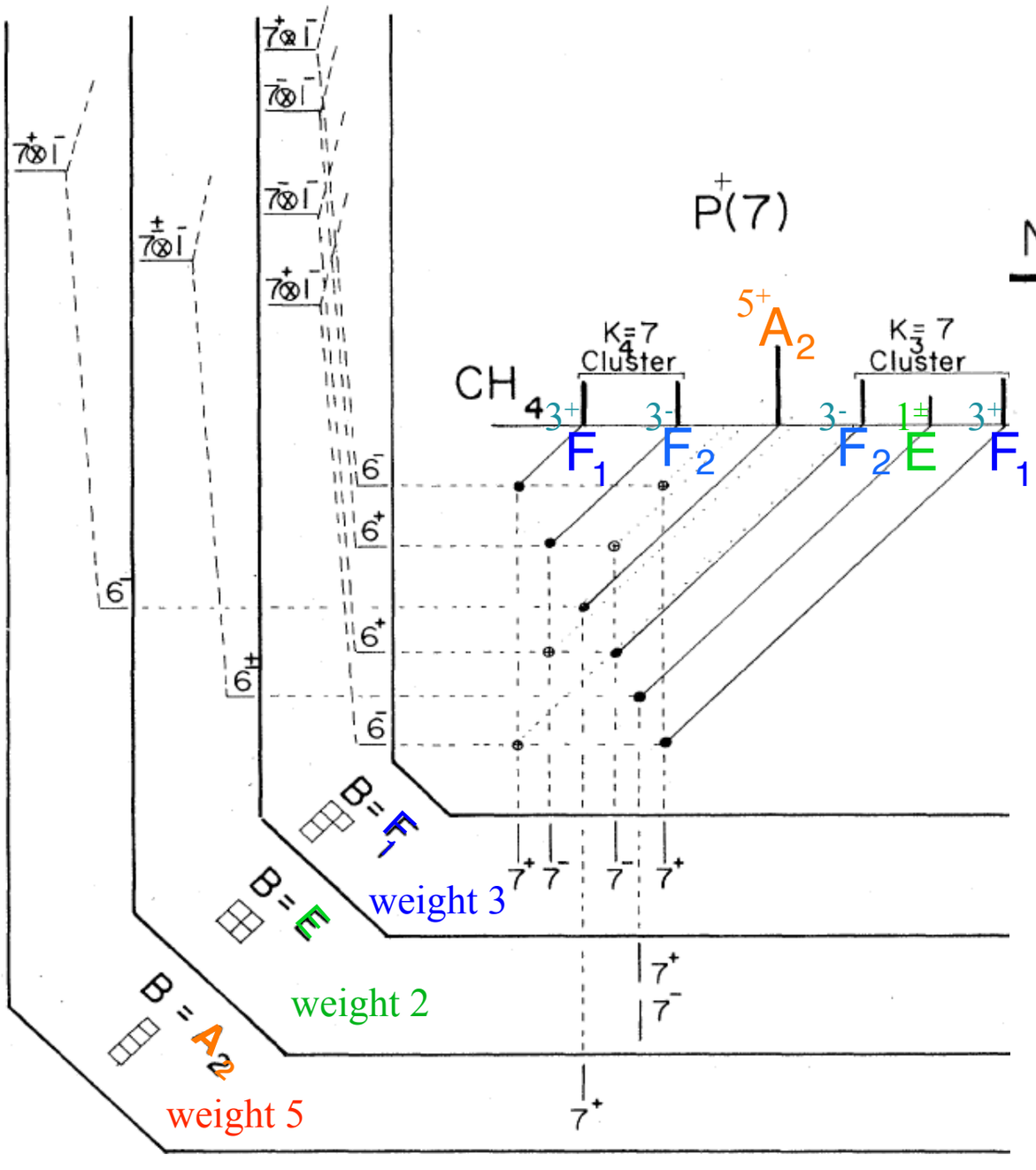
FIG. 36. Comparison of conventional CH_4 labeling with present labeling. The latter shows clearly the "hidden" structure of inversion doublets which has a structure very much like that of NH_3. For CH_4, however, only the E levels are actually double according to the statistical weight calculations.

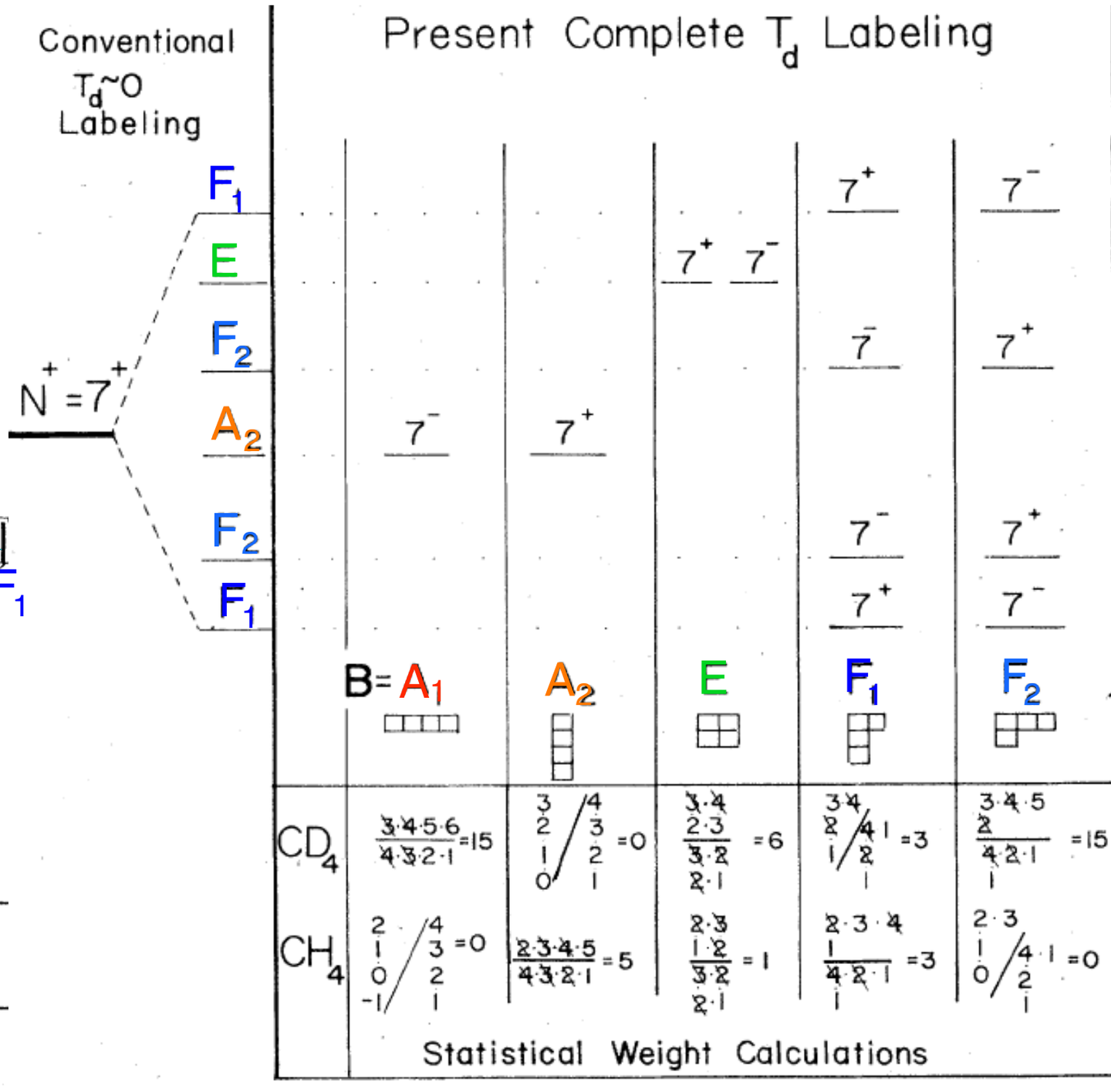


Rev. Mod. Phys. 50,1,1 (1978)

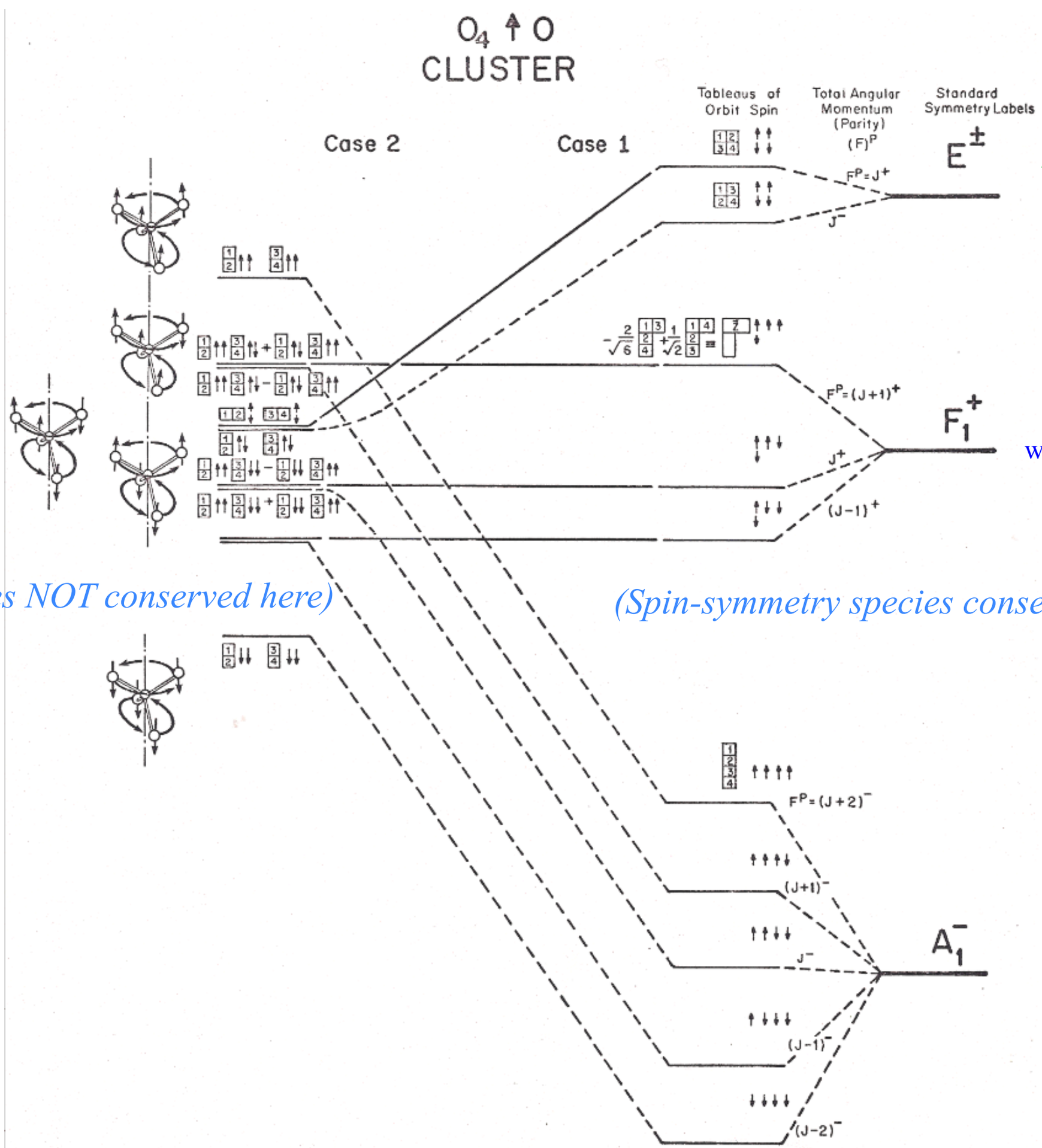
S_4 and spin-symmetry for XY_4 molecules (Introducing hook-length formulae)

Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved here)





Rev. Mod. Phys. 50,1,1 (1978)



weight 2

weight 3

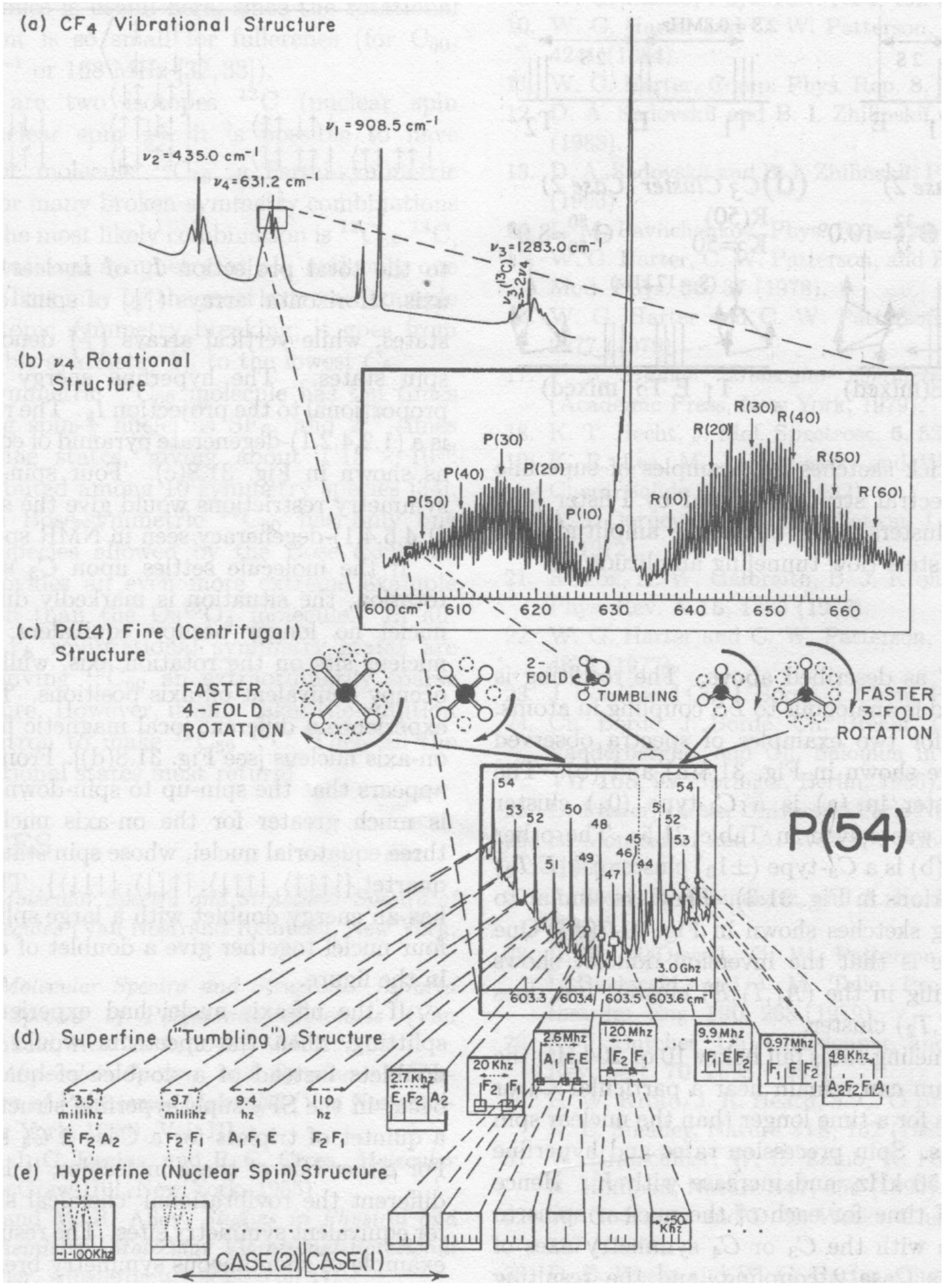
weight 5

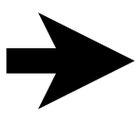
(Spin-symmetry species NOT conserved here)

(Spin-symmetry species conserved here)

Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

W.G.Harter
Ch. 31
Atomic, Molecular, & Optical Physics Handbook
Am. Int. of Physics
Gordon Drake Editor
(1996)





S_6 and spin-symmetry for XY_6 molecules

Entanglement and Disentanglement

Resulting hyperfine spectra

Superhyperfine spectra

Spin-0 nuclei give Bose Exclusion

S_6 and XY_6 molecules

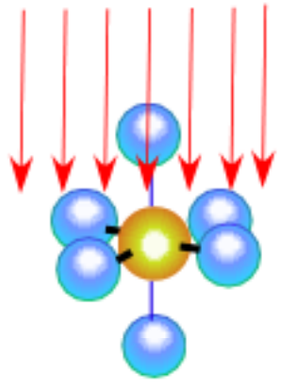
Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, *STATE versus PARTICLE,*

boils down to :

OUTSIDE versus INSIDE

OUTSIDE or LAB
Symmetry reduction
results in
Level or Spectral
SPLITTING
External B-field
does Zeeman splitting

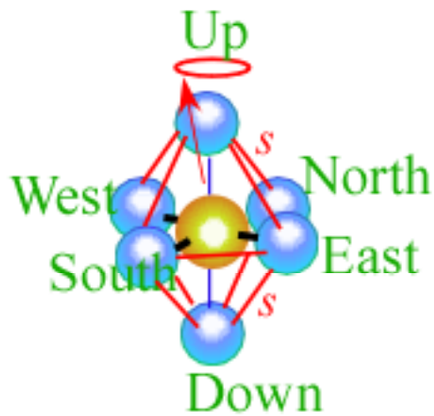


INSIDE or BODY
Symmetry reduction
results in
Level or Spectral
UN-SPLITTING
("clustering")

Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

*Internal **J** gets "stuck" on RES axes*
Must "tunnel" axis-to-axis at rate s



|U>|D>|E>|W>|N>|S>

H	0	s	s	s	s
0	H	s	s	s	s
s	s	H	0	s	s
s	s	0	H	s	s
s	s	s	s	H	0
s	s	s	s	0	H

Review $O \supset C_4$ correlations:

S_6 and XY_6 molecules

Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, STATE versus PARTICLE,

boils down to :

OUTSIDE versus INSIDE

OUTSIDE or LAB
Symmetry reduction
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External B-field
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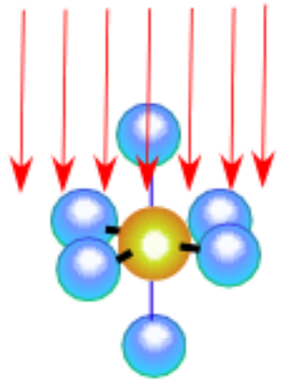

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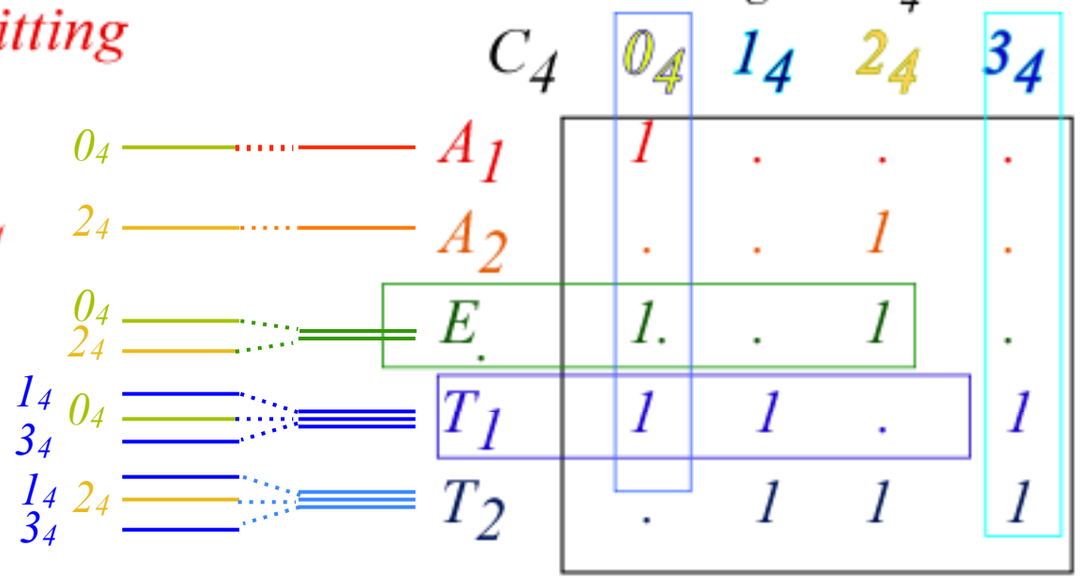
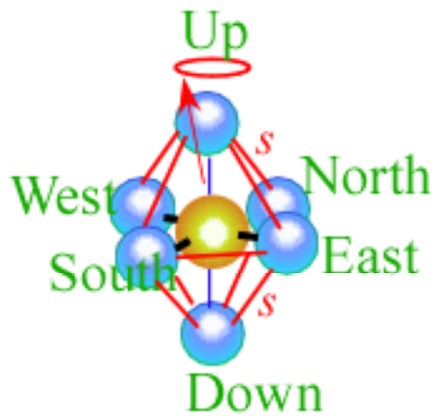


INSIDE or BODY
Symmetry reduction
results in
Level or Spectral
UN-SPLITTING
("clustering")

Internal **J** gets "stuck" on RES axes
Must "tunnel" axis-to-axis at rate s



|U>|D>|E>|W>|N>|S>

H	0	s	s	s	s
0	H	s	s	s	s
s	s	H	0	s	s
s	s	0	H	s	s
s	s	s	s	H	0
s	s	s	s	0	H

Review O⊃C_4 correlations:

Duality: The "Flip Side" of Symmetry Analysis.

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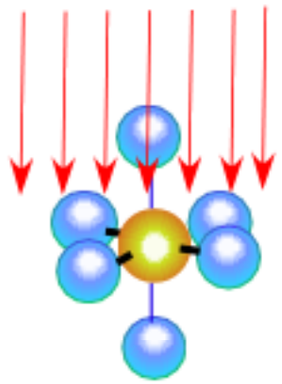
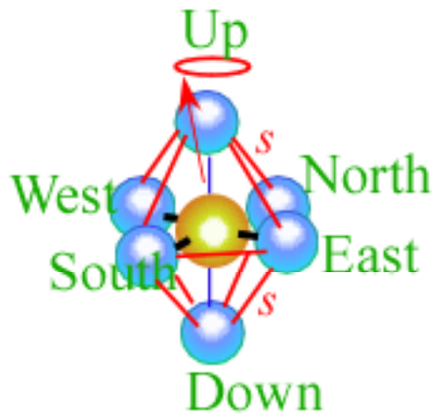
OUTSIDE versus INSIDE

OUTSIDE or LAB Symmetry reduction results in Level or Spectral SPLITTING External B-field does Zeeman splitting



INSIDE or BODY Symmetry reduction results in Level or Spectral UN-SPLITTING ("clustering")

*Internal **J** gets "stuck" on RES axes*
Must "tunnel" axis-to-axis at rate s



|U>|D>|E>|W>|N>|S>

H	0	s	s	s	s
0	H	s	s	s	s
s	s	H	0	s	s
s	s	0	H	s	s
s	s	s	s	H	0
s	s	s	s	0	H

Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

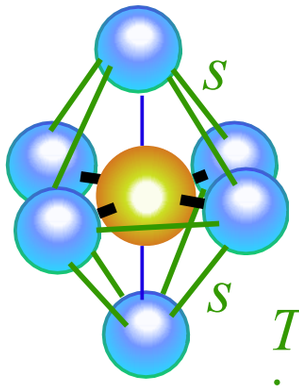
Review $O \supset C_4$ correlations:

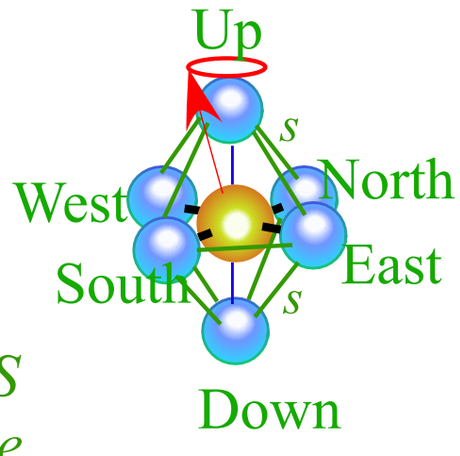
*Tunneling (s) between axes splits the **0_4** cluster as shown on following pages*

***0_4** cluster splitting (derived on following page)*

S_6 and XY_6 molecules

*Internal **J** gets "stuck" on RES axes*
Must "tunnel" axis-to-axis at rate s





|U>|D>|E>|W>|N>|S>

H	*0*	*s*	*s*	*s*	*s*
0	*H*	*s*	*s*	*s*	*s*
s	*s*	*H*	*0*	*s*	*s*
s	*s*	*0*	*H*	*s*	*s*
s	*s*	*s*	*s*	*H*	*0*
s	*s*	*s*	*s*	*0*	*H*

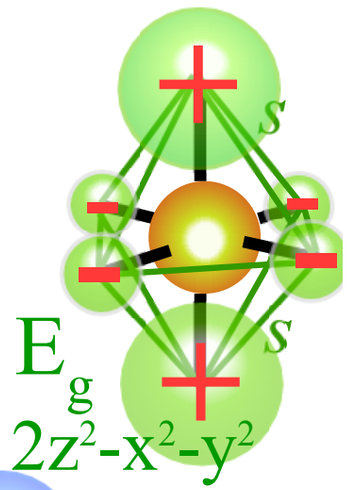
Tunneling s=-S is negative here

Review $O(0_4) \supset C_4$ cluster:

0_4 *cluster splitting*

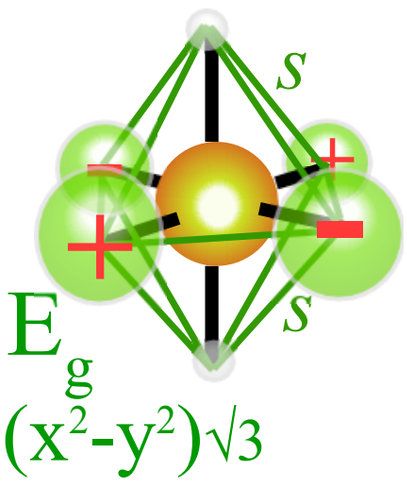
$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}} = (H-2s) \begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}}$$

E_{1g} $+2S$



E_g $2z^2-x^2-y^2$

$$\begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}}$$

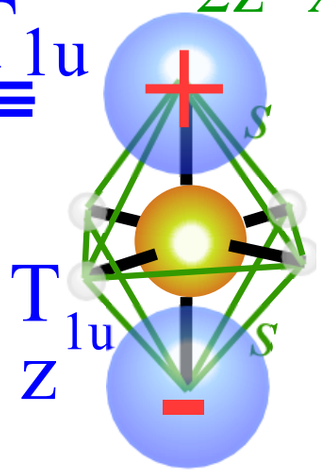


E_g $(x^2-y^2)\sqrt{3}$

$$\begin{vmatrix} 0 \\ 0 \\ -1 \\ -1 \\ +1 \\ +1 \end{vmatrix} \frac{1}{2}$$

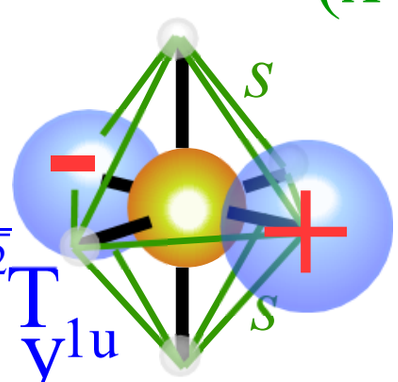
$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} +1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}} = (H+0) \begin{vmatrix} +1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}}$$

T_{1u}

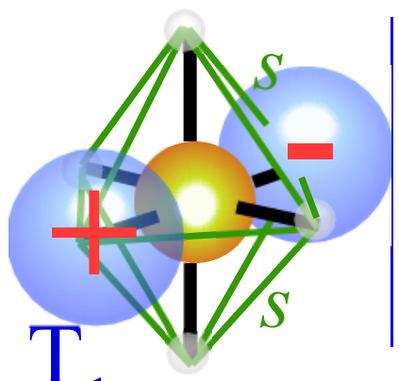


T_{1u} z

$$\begin{vmatrix} 0 \\ 0 \\ +1 \\ -1 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}}$$



T_{1u} y

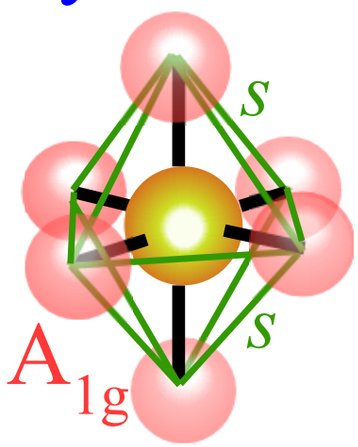


T_{1u} x

$$\begin{vmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ +1 \end{vmatrix} \frac{1}{\sqrt{2}}$$

$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}} = (H+4s) \begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}}$$

$-4S$



A_{1g}

$$\begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}}$$

S_6 and XY_6 molecules

Duality: The "Flip Side" of Symmetry Analysis.

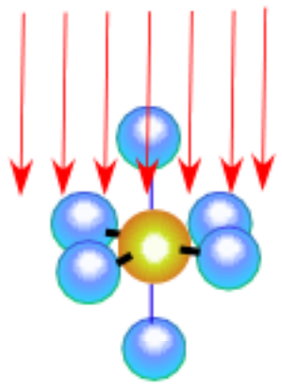
LAB versus BODY, STATE versus PARTICLE,

boils down to :

OUTSIDE versus INSIDE

OUTSIDE or LAB Symmetry reduction results in Level or Spectral SPLITTING

External B-field does Zeeman splitting



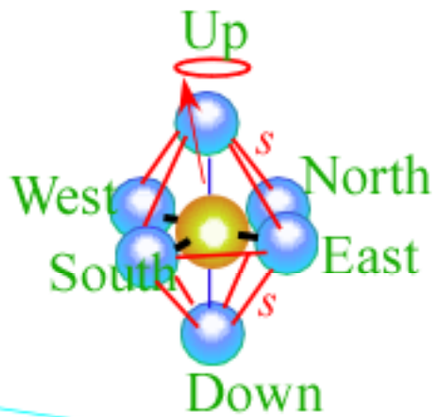
Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

INSIDE or BODY Symmetry reduction results in Level or Spectral UN-SPLITTING ("clustering")

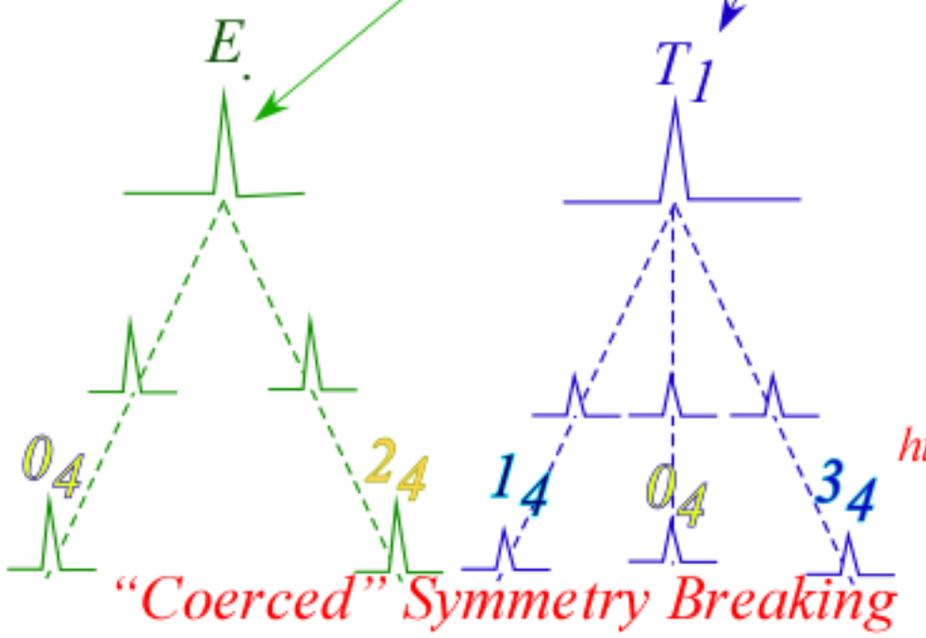
Internal **J** gets "stuck" on RES axes

Must "tunnel" axis-to-axis at rate s



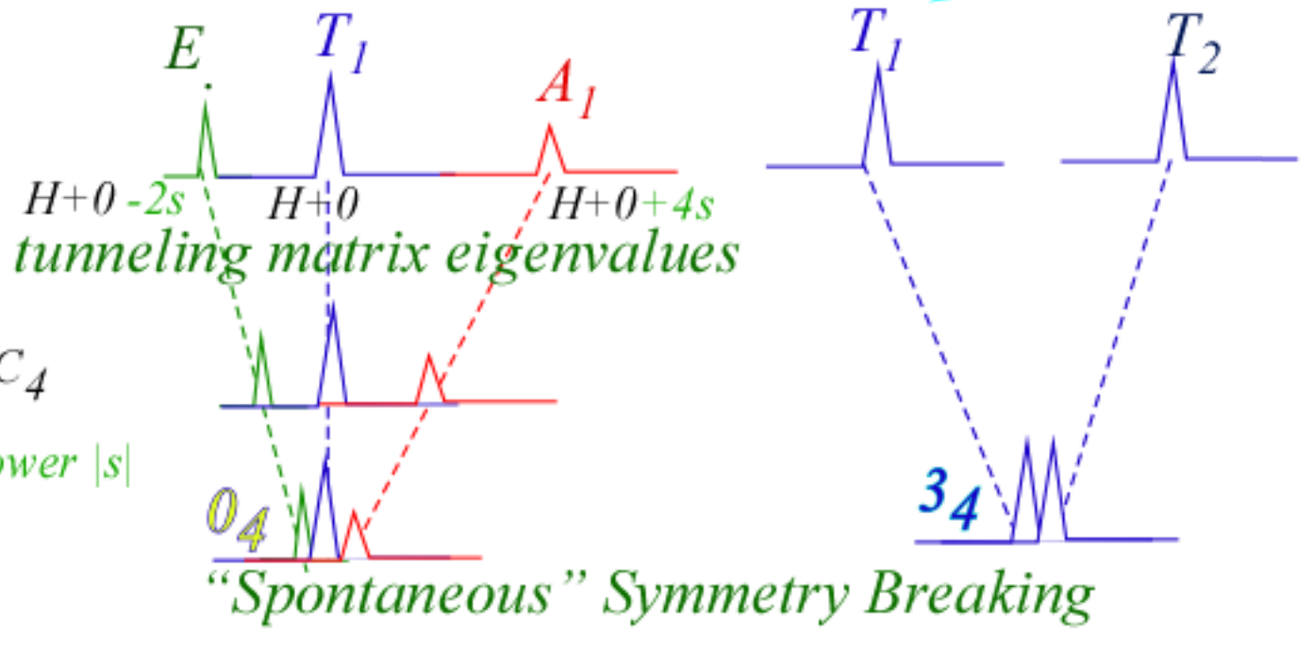
|U>|D>|E>|W>|N>|S>

H	0	s	s	s	s
0	H	s	s	s	s
s	s	H	0	s	s
s	s	0	H	s	s
s	s	s	s	H	0
s	s	s	s	0	H



Stronger C_4

higher |**B**| lower |s|



S_6 and spin-symmetry for XY_6 molecules

Entanglement and Disentanglement

Resulting hyperfine spectra

Superhyperfine spectra

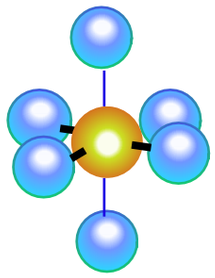
Spin-0 nuclei give Bose Exclusion

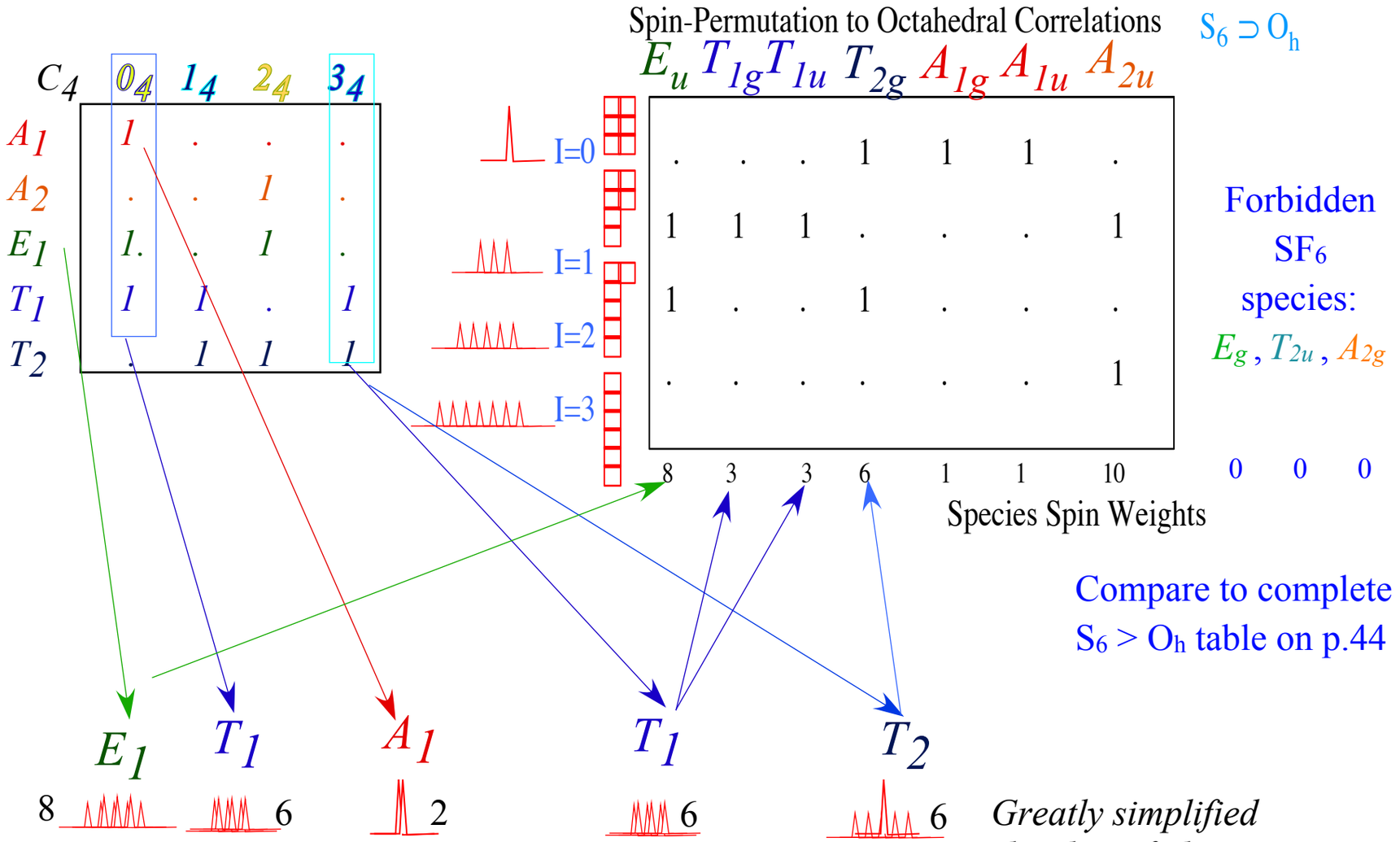
Entanglement!

How F-nuclei become entangled

total-spin-I-symmetry O_h species in SF_6.

With rotation all six  *nuclei are equivalent*





Forbidden SF_6 species: E_g , T_{2u} , A_{2g}

0 0 0

Compare to complete $S_6 > O_h$ table on p.44

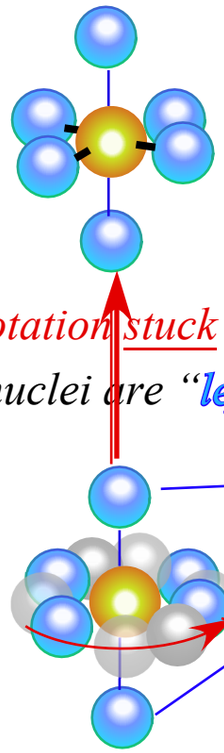
Greatly simplified sketches of ultra high resolution IR SF_6 spectroscopy of Christian Borde′, C. Saloman, and Oliver Pfister (Pfister did SiF_4, too.)

See SF_6 spectra with A_2 T_2 E level cluster on pages 66-67

DISentanglement!

How F-nuclei become distinguished
(but not distinguishable)
in SF_6.

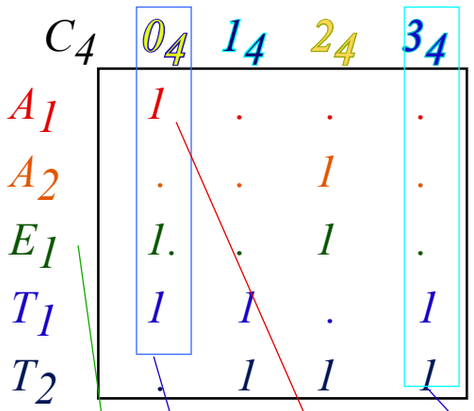
Without rotation being stuck on C_4 *axis all six*  *nuclei are equivalent*

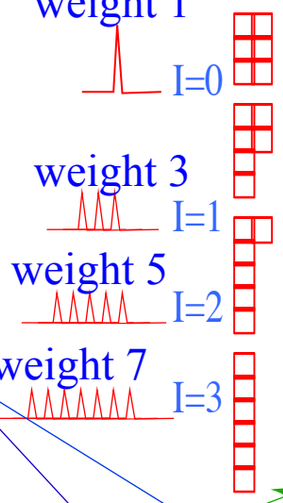


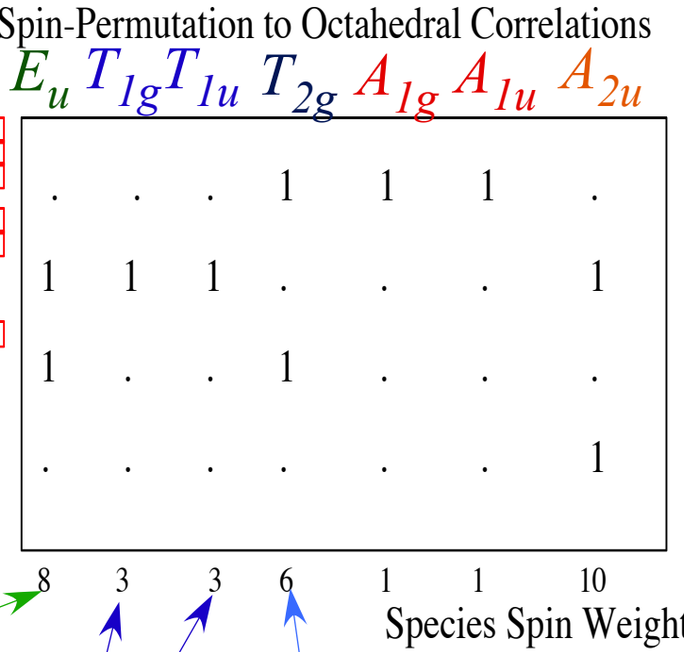
With rotation stuck on C_4 *axis polar nuclei are "**left out in the cold**"*

"Brrr-rr it's cold!"

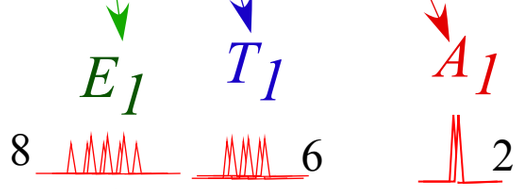
"WE like it HOT!"

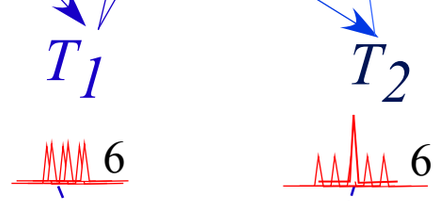


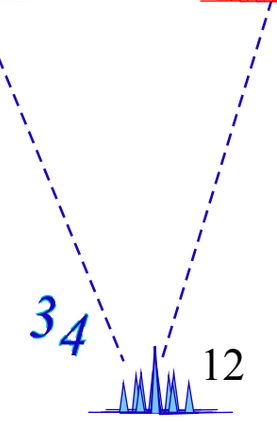




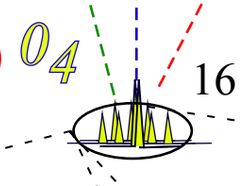
Forbidden SF_6 species: E_g , T_{2u} , A_{2g}



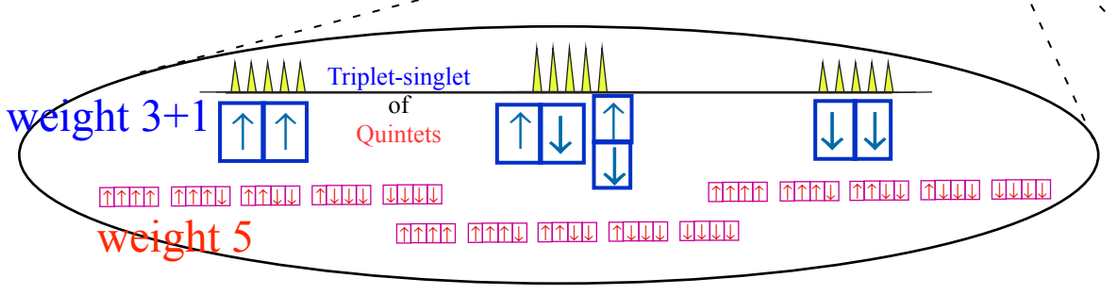




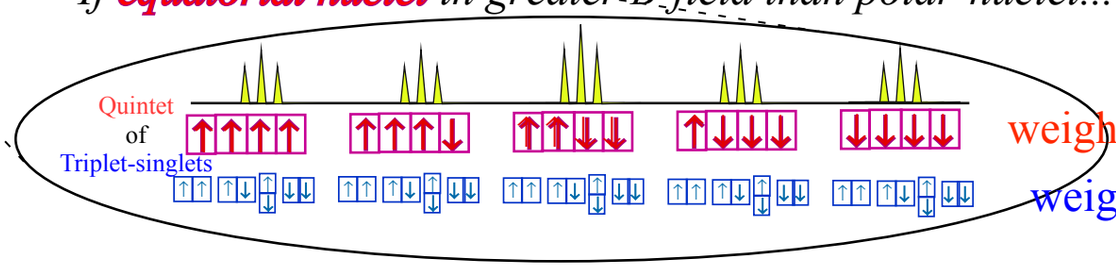
Greatly simplified sketches of ultra high resolution IR SF_6 *spectroscopy of Christian Borde', C. Saloman, and Oliver Pfister (Pfister did* SiF_4*, too.)*



*If **polar nuclei** in greater B-field than equatorial-nuclei...*



*If **equatorial nuclei** in greater B-field than polar-nuclei...*



S_6 and spin-symmetry for XY_6 molecules

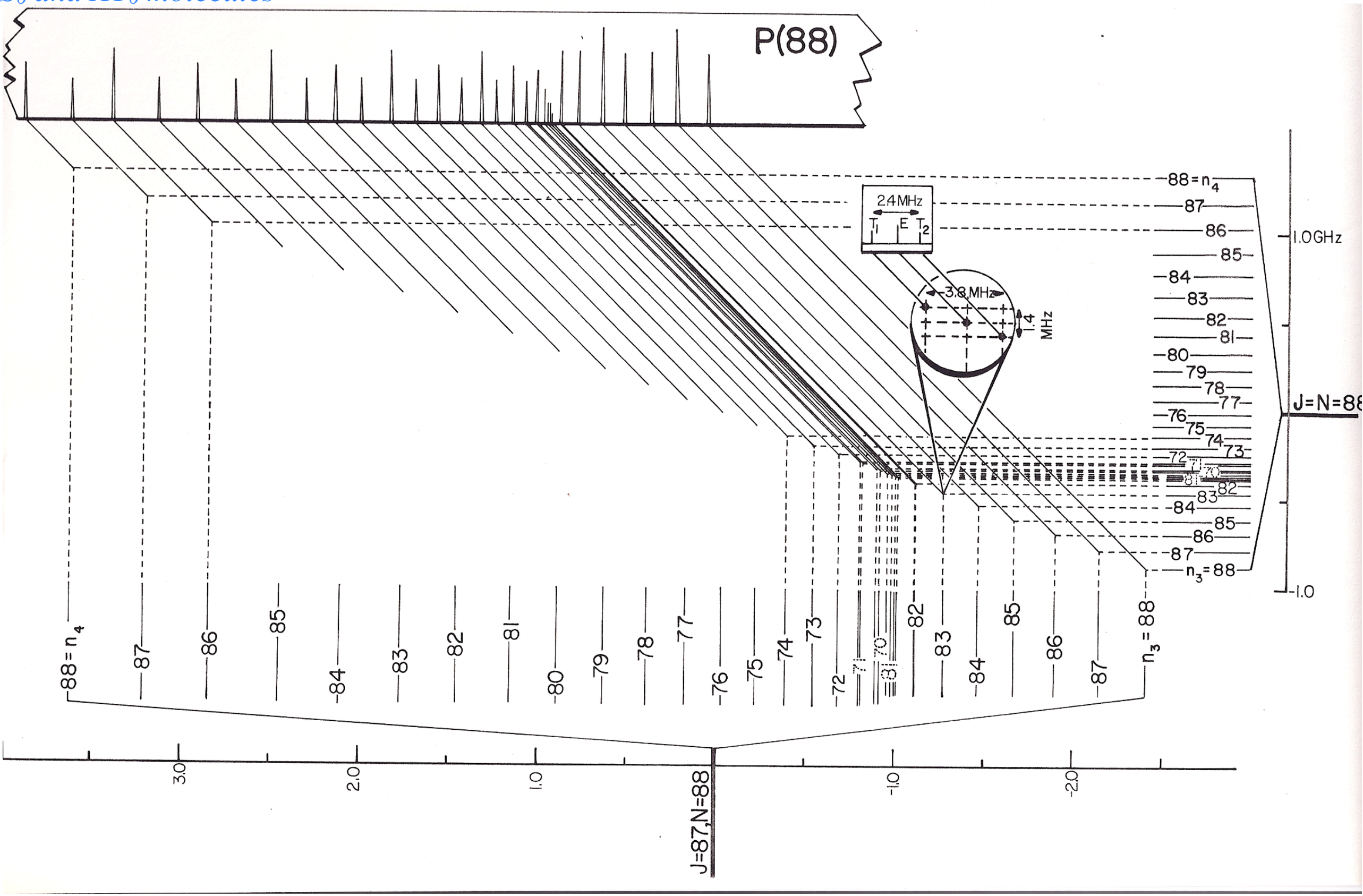
Entanglement and Disentanglement

Resulting hyperfine spectra

Superhyperfine spectra

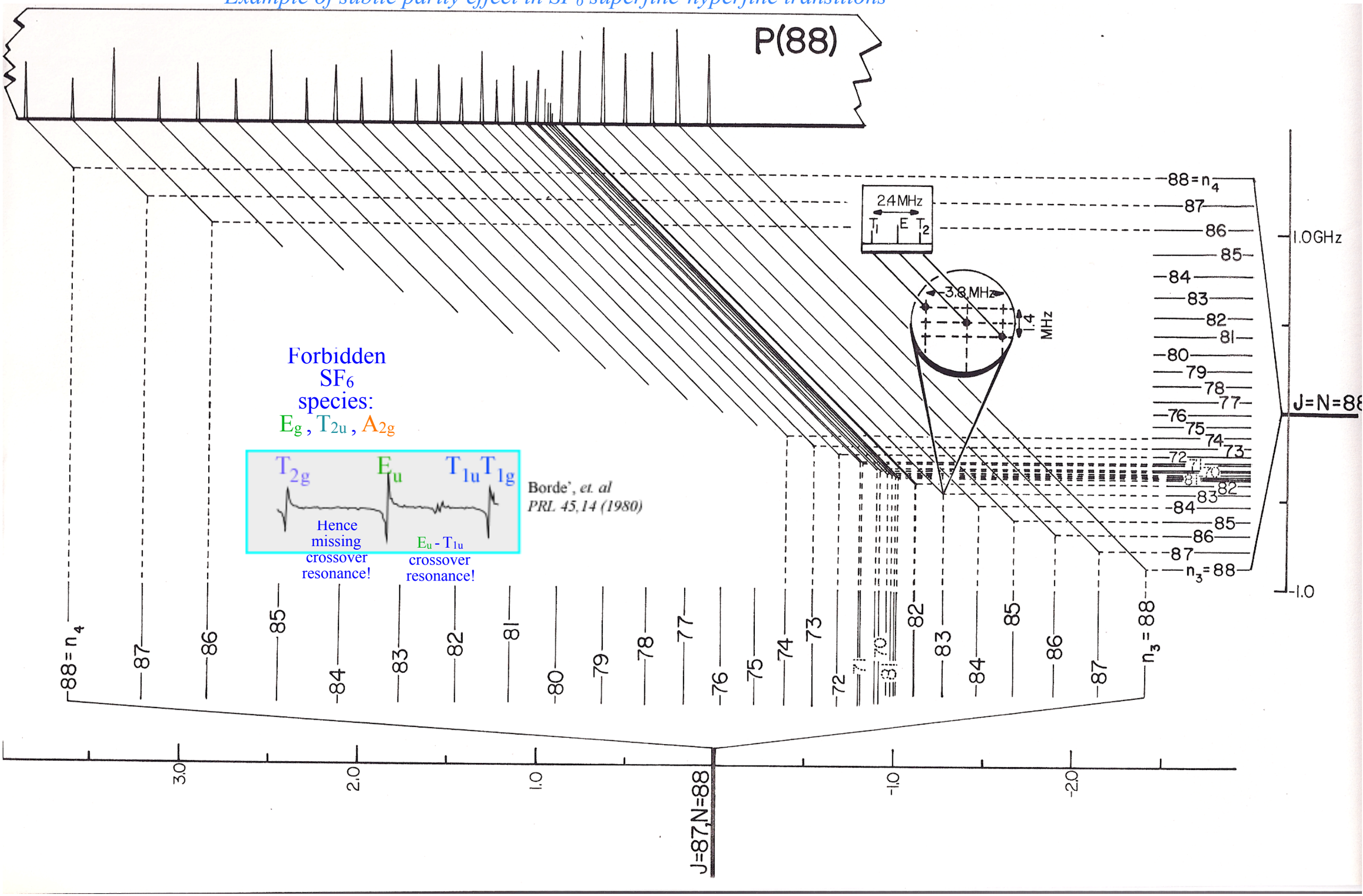
Spin-0 nuclei give Bose Exclusion

S_6 and XY_6 molecules



Harter, Phys. Rev. A 24, 192-263 (1981)

Example of subtle parity effect in SF_6 superfine-hyperfine transitions



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S_6 and spin-symmetry for XY_6 molecules

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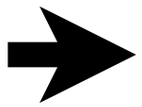
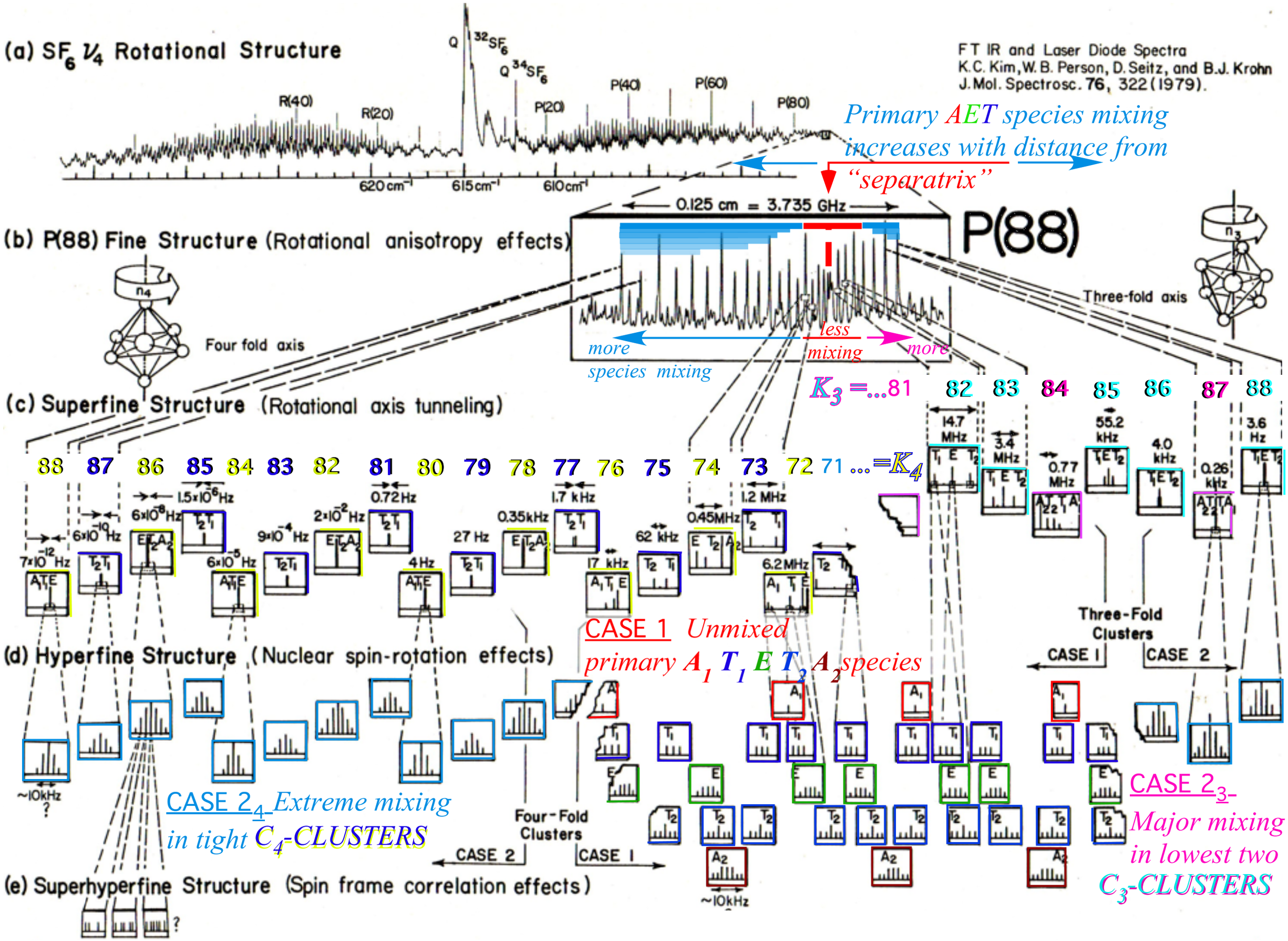
Resulting hyperfine spectra



Superhyperfine spectra

Spin-0 nuclei give Bose Exclusion



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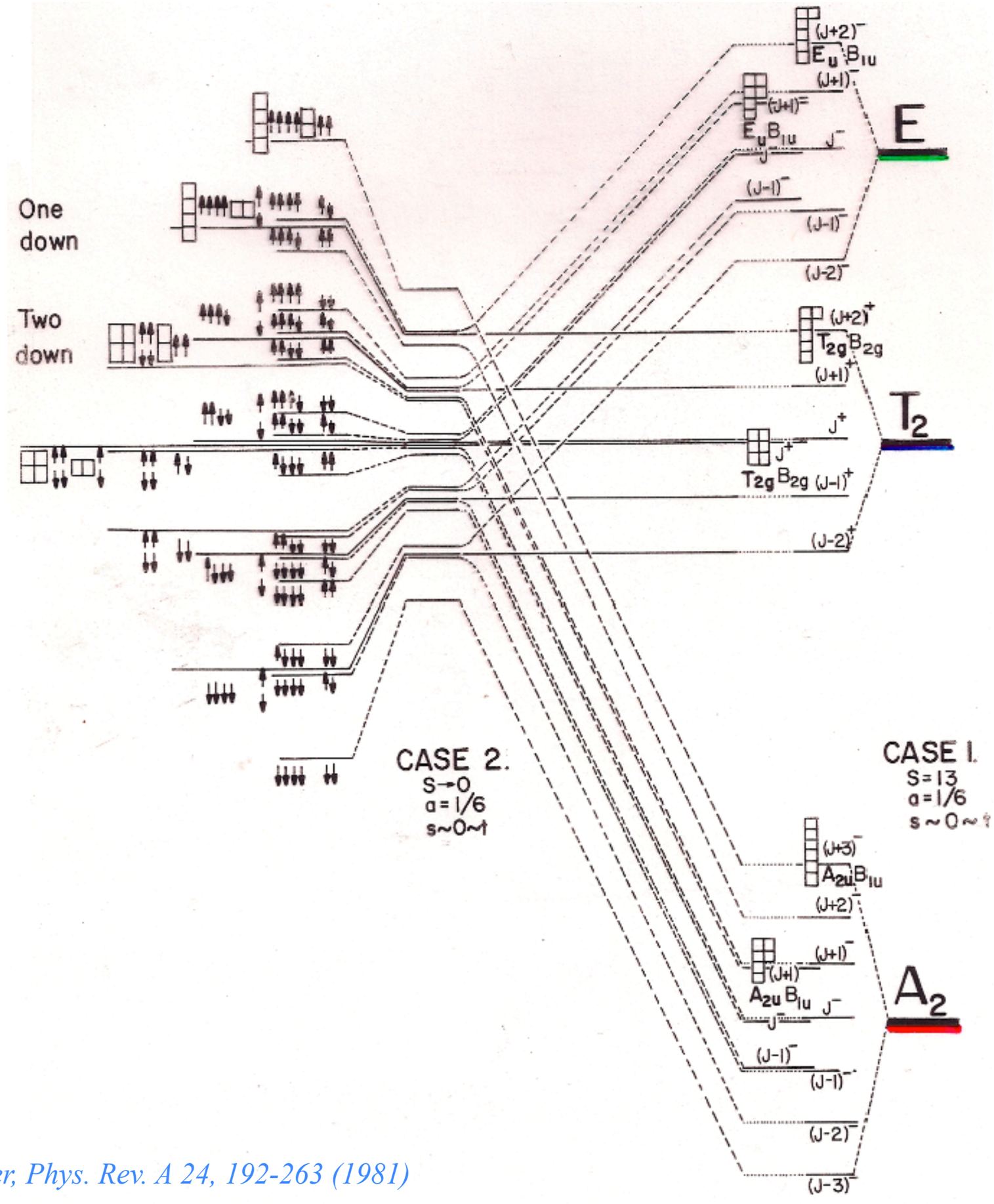

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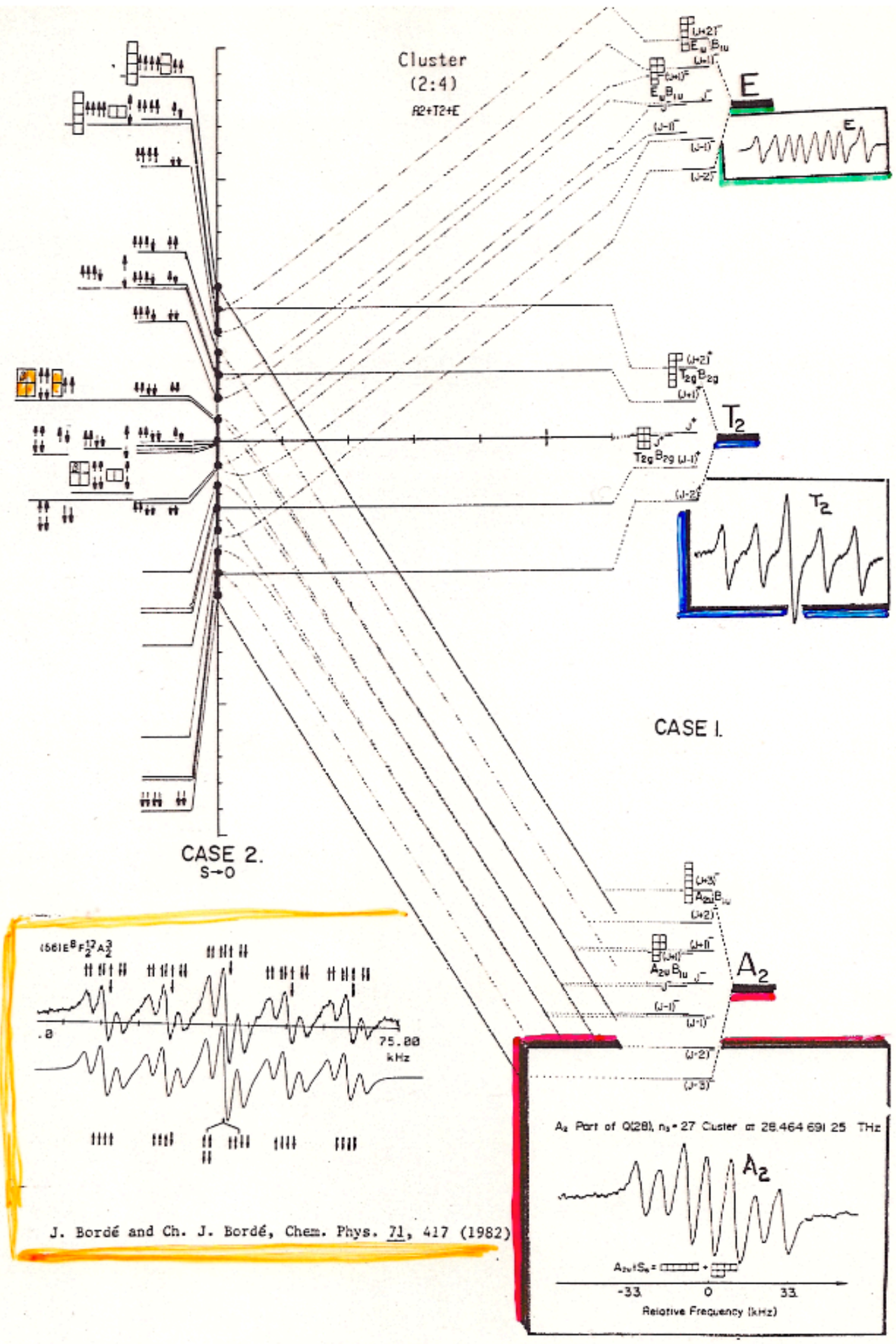
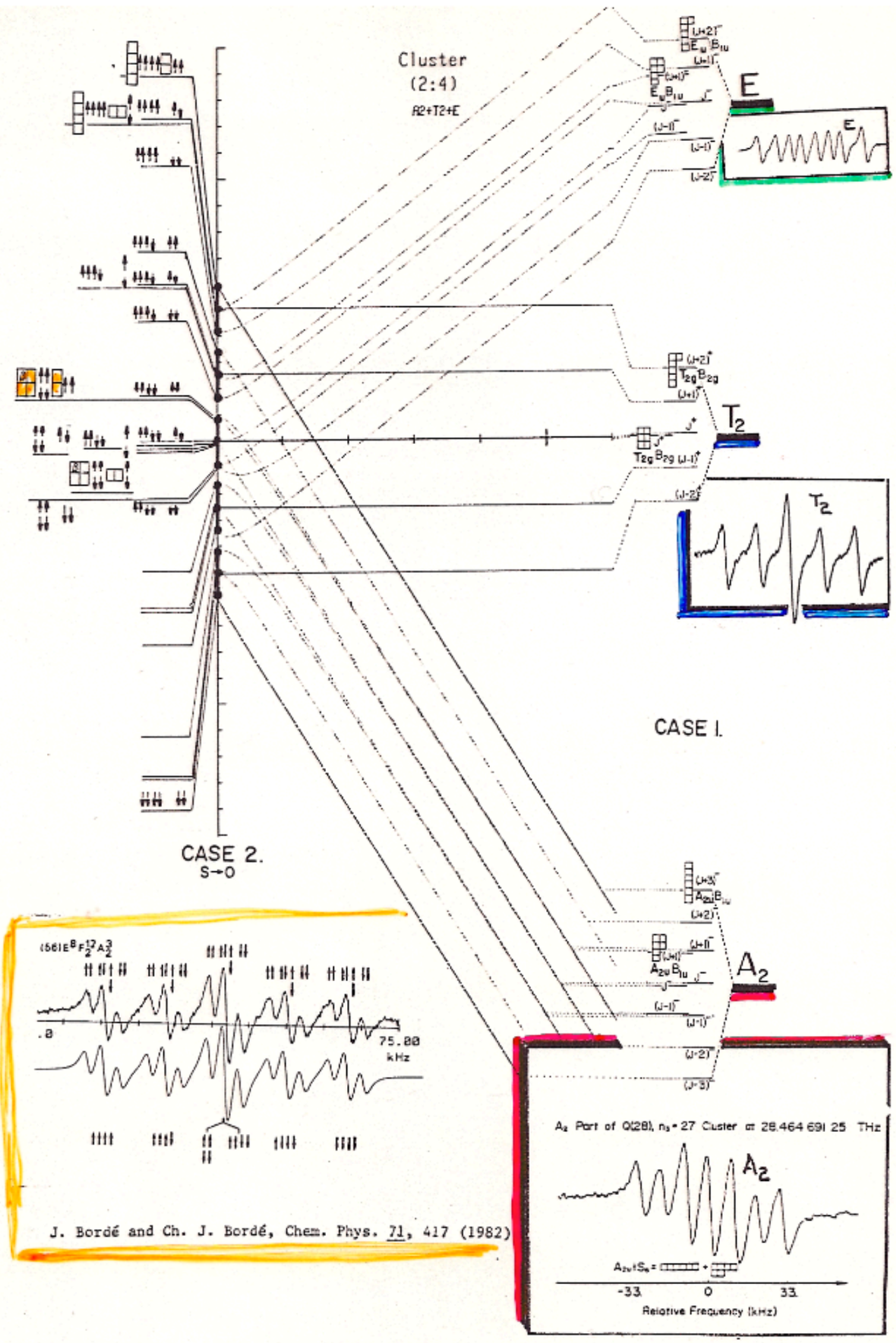


weight 8=5+3

weight 6=5+1

weight 10=7+3



Forbidden species: E_g T_{2u} A_{2g}

$S_6 \supset O_h$ Spin-Permutation to Octahedral Correlations

C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E_1	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

Spin weight 1 I=0; weight 3 I=1; weight 5 I=2; weight 7 I=3

E_u	T_{1g}	T_{1u}	T_{2g}	A_{1g}	A_{1u}	A_{2u}
.	.	.	1	1	1	.
1	1	1	.	.	.	1
1	.	.	1	.	.	.
.	.	.	.	.	.	1

8 3 3 6 1 1 10

Species Spin Weights

E_1 8 T_1 6 A_1 2 — T_1 6 T_2 6

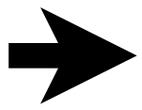
0_4 16 3_4 12

S_6 and spin-symmetry for XY_6 molecules

Entanglement and Disentanglement

Resulting hyperfine spectra

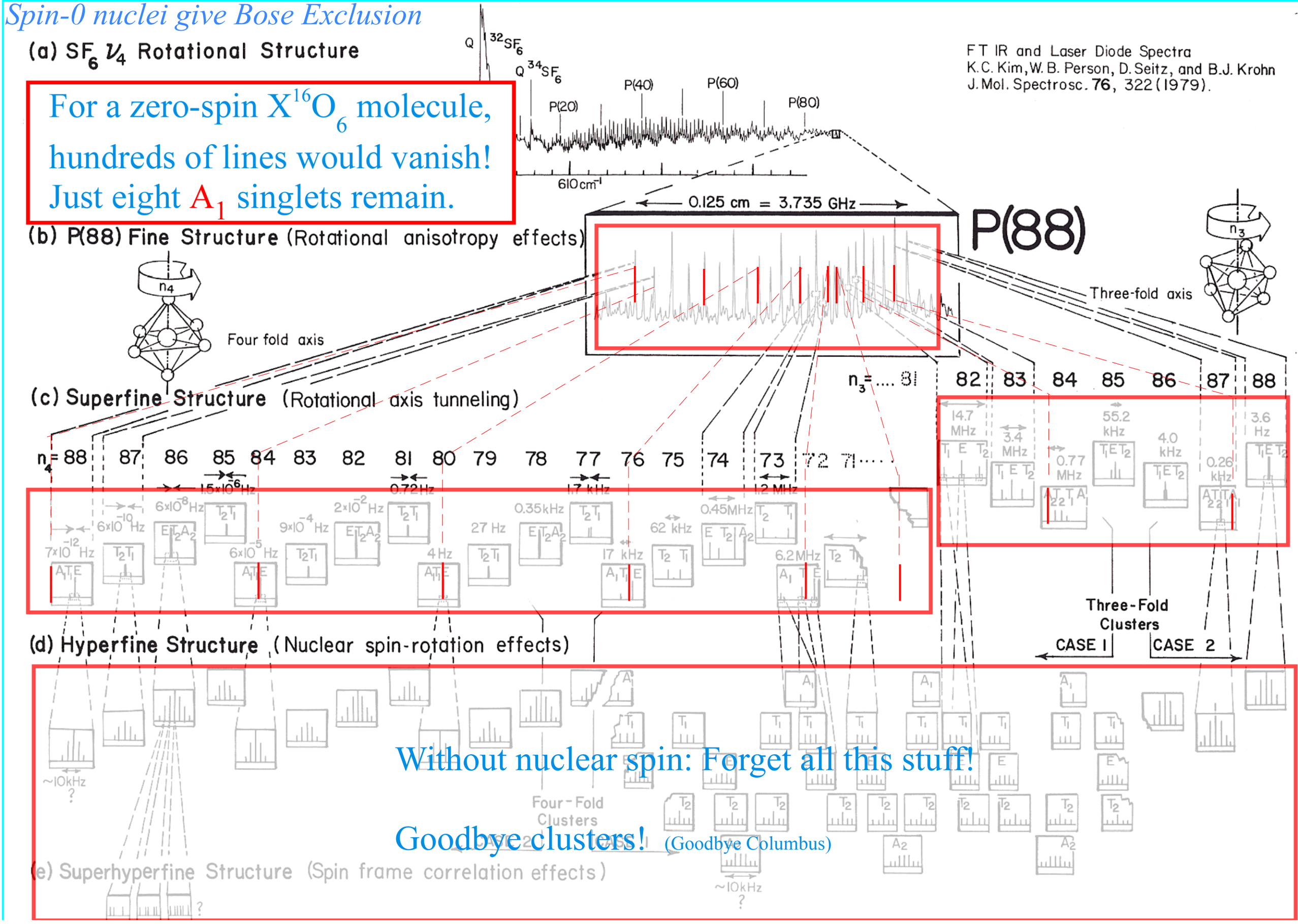
Superhyperfine spectra



Spin-0 nuclei give Bose Exclusion

Spin-0 nuclei give Bose Exclusion

For a zero-spin $X^{16}O_6$ molecule, hundreds of lines would vanish! Just eight A_1 singlets remain.



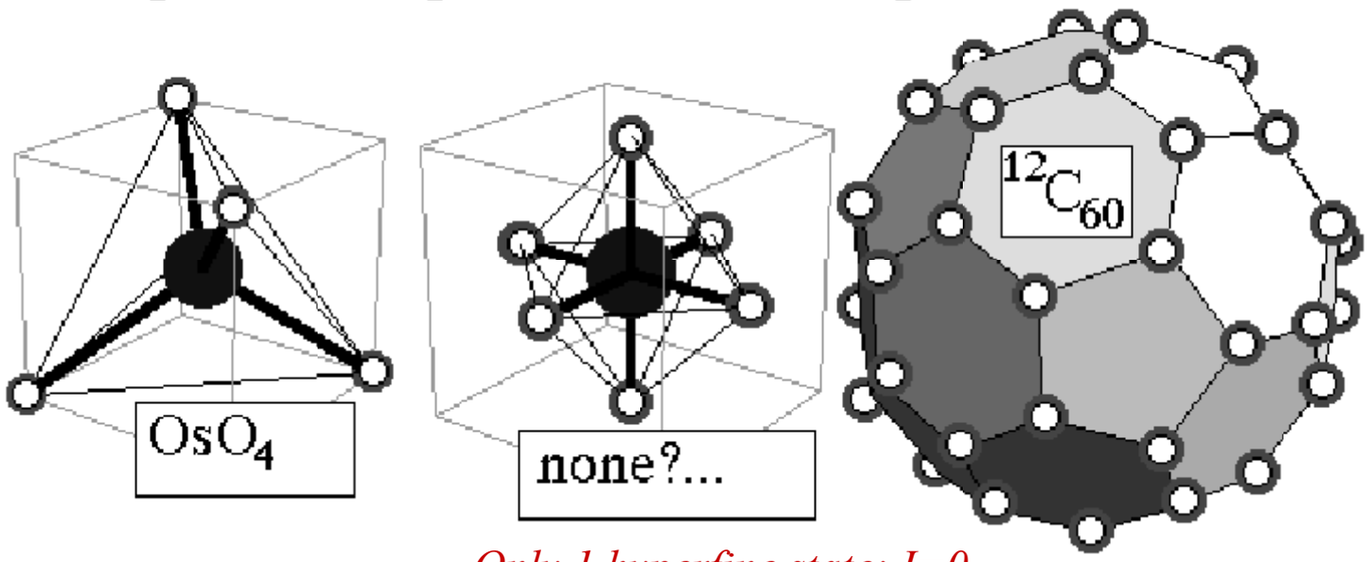
Without nuclear spin: Forget all this stuff!

Goodbye clusters! (Goodbye Columbus)

Spin-0 nuclei give Bose Exclusion

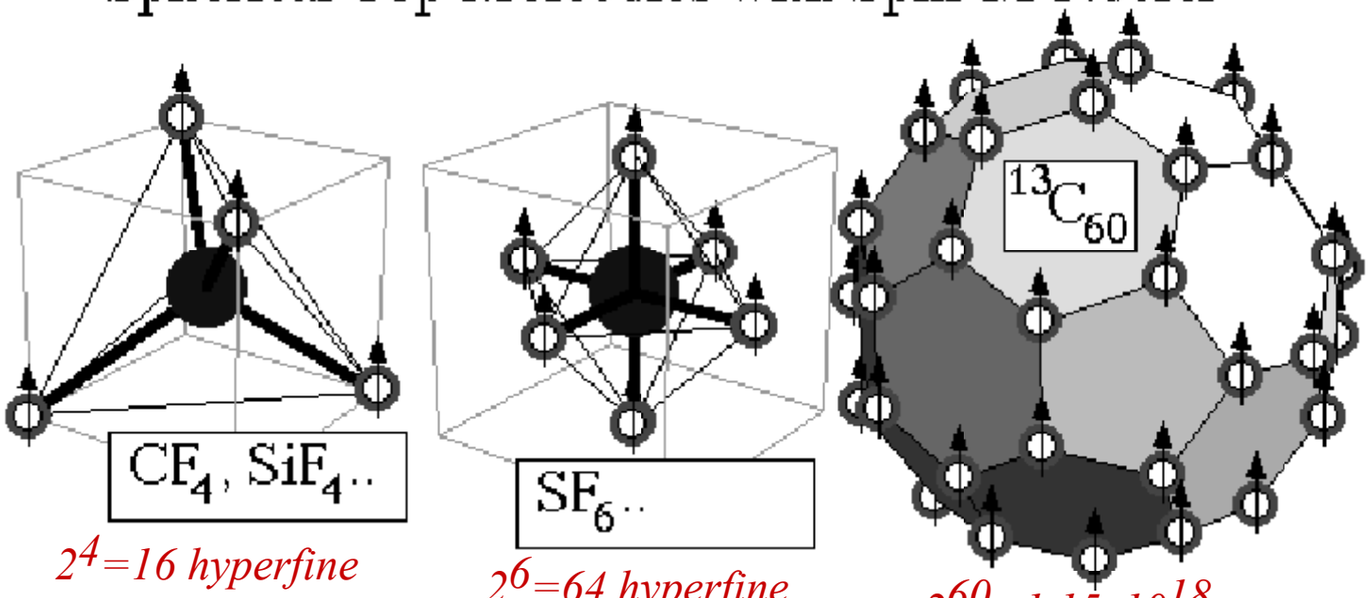
Some examples of Bose Exclusion

Spherical Top Molecules with Spin-0 Nuclei



Only 1 hyperfine state: I=0

Spherical Top Molecules with Spin-1/2 Nuclei



2^4=16 hyperfine states: I=0-2

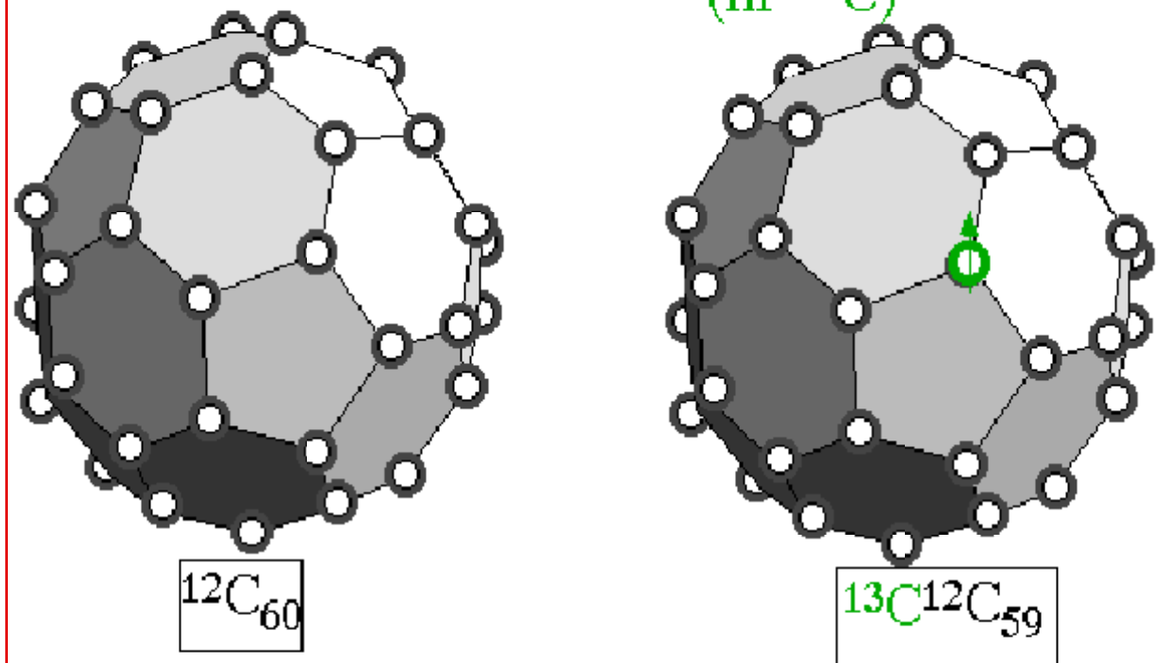
2^6=64 hyperfine states: I=0-3

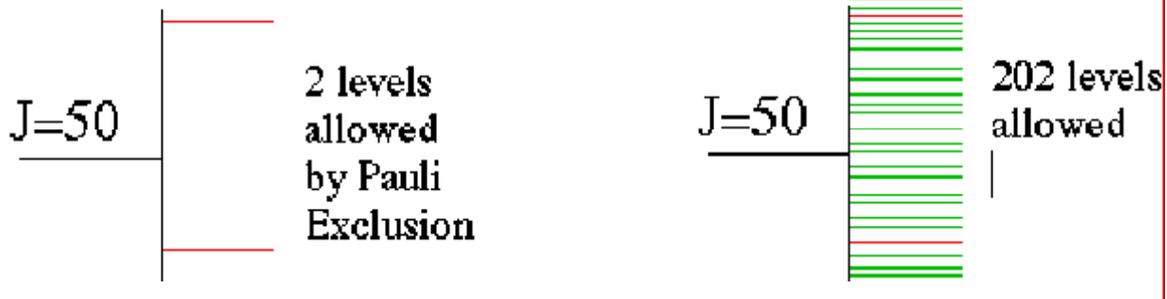
2^{60}=1.15x10^{18} hyperfine states: I=0-30

Example of extreme symmetry exclusion

... (and partial recovery)

Y_h Symmetry reduced to C_v by a single neutron (in ^{13}C)





Question: Where did those 200 levels go?

Better Question: Where did those 1.15 octillion levels go?

Some examples of Fermi (non) Exclusion

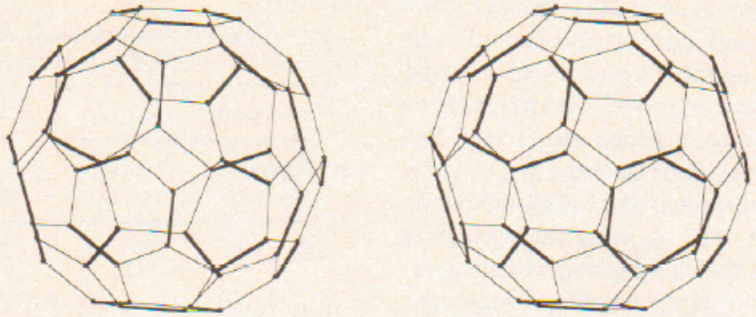


Fig. 1. Stereoscopic view of Buckyball. "Double bonds" lie along the darker lines and "single bonds" lie along the lighter lines. Carbon atoms are located at the vertices.

are more like a single bond and those along an edge bordered by two hexagons are more like a double bond. This is illustrated in the stereoscopic drawing in fig. 1.

The position of each carbon atom is determined by 60 symmetrically placed orthogonal coordinate triads whose origins are located at the vertices of the Buckyball structure. These are shown in stereo in fig. 2a. This 180-dimensional coordinate system is used to form a harmonic approximation to the classical equations of motion,

$$\ddot{X}_i = -f_{ij} X_j \,.$$

The elements f_{ij} are components of a force matrix

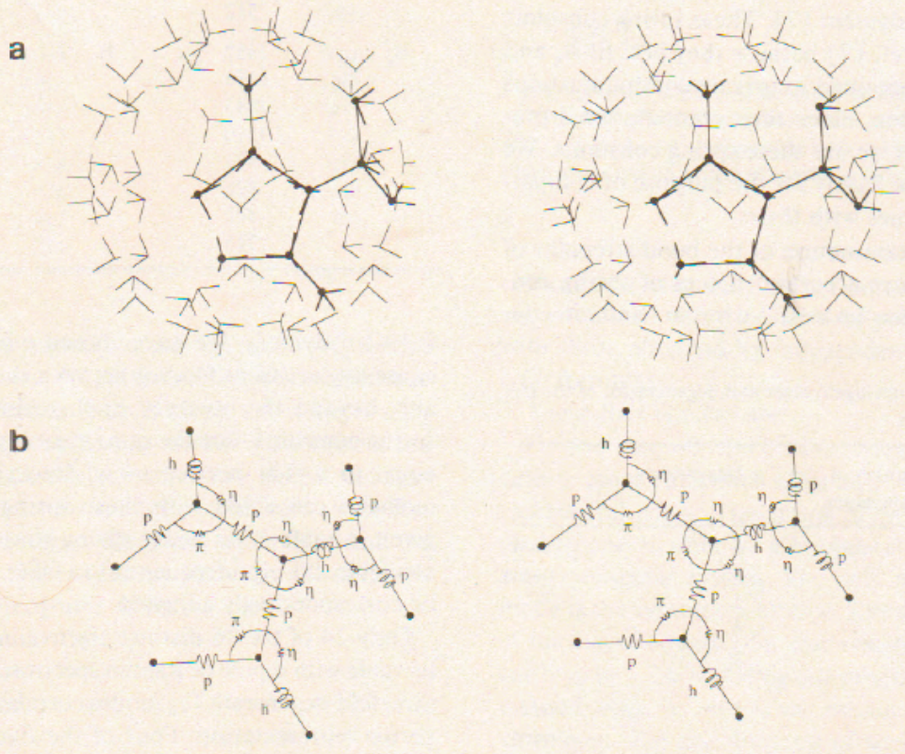
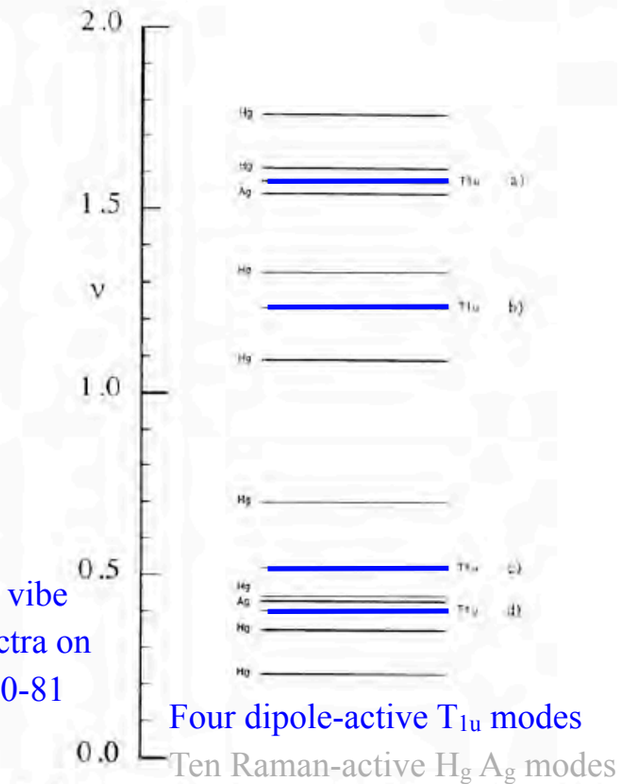


Fig. 2. (a) Stereoscopic view of the 60 orthogonal coordinate triads used in the initial formulation of the force matrix. The unit cell is highlighted. (b) Stereoscopic view of the unit cell required for the calculation of the force matrix. Single bond parameters are p and π. Double bond parameters are h and η.

Table 3
Symmetry-labeled eigenfrequencies of Buckyball for $p=\pi=7.6\times10^5$ dyn/cm, $\pi=\eta=0.7\times10^5$ dyn/cm

Even parity		Odd parity	
I_h group label	frequency (cm^{-1})	I_h group label	frequency (cm^{-1})
A_g	1830	A_u	1243
	510		
T_{1g}	1662	T_{1u}	1868
	1045		1462
	513		618
			478
T_{2g}	1900	T_{2u}	1954
	951		1543
	724		1122
	615		526
			358
G_g	2006	G_u	2004
	1813		1845
	1327		1086
	657		876
	593		663
	433		360
H_g	2068	H_u	2086
	1910		1797
	1575		1464
	1292		849
	828		569
	526		470
	413		405
	274		



See vibe spectra on p. 80-81

Four dipole-active T_{1u} modes

Ten Raman-active H_g A_g modes

Fig. 3. Spectrum of the possibly dipole and Raman active modes of Buckyball. The spring constants are $p=h=7.6\times10^5$ dyn/cm and $\pi=\eta=0.7\times10^5$ dyn/cm. The scale is in units of 1185 cm^{-1}. Lines a–d correlate with eigenmodes in fig. 4.

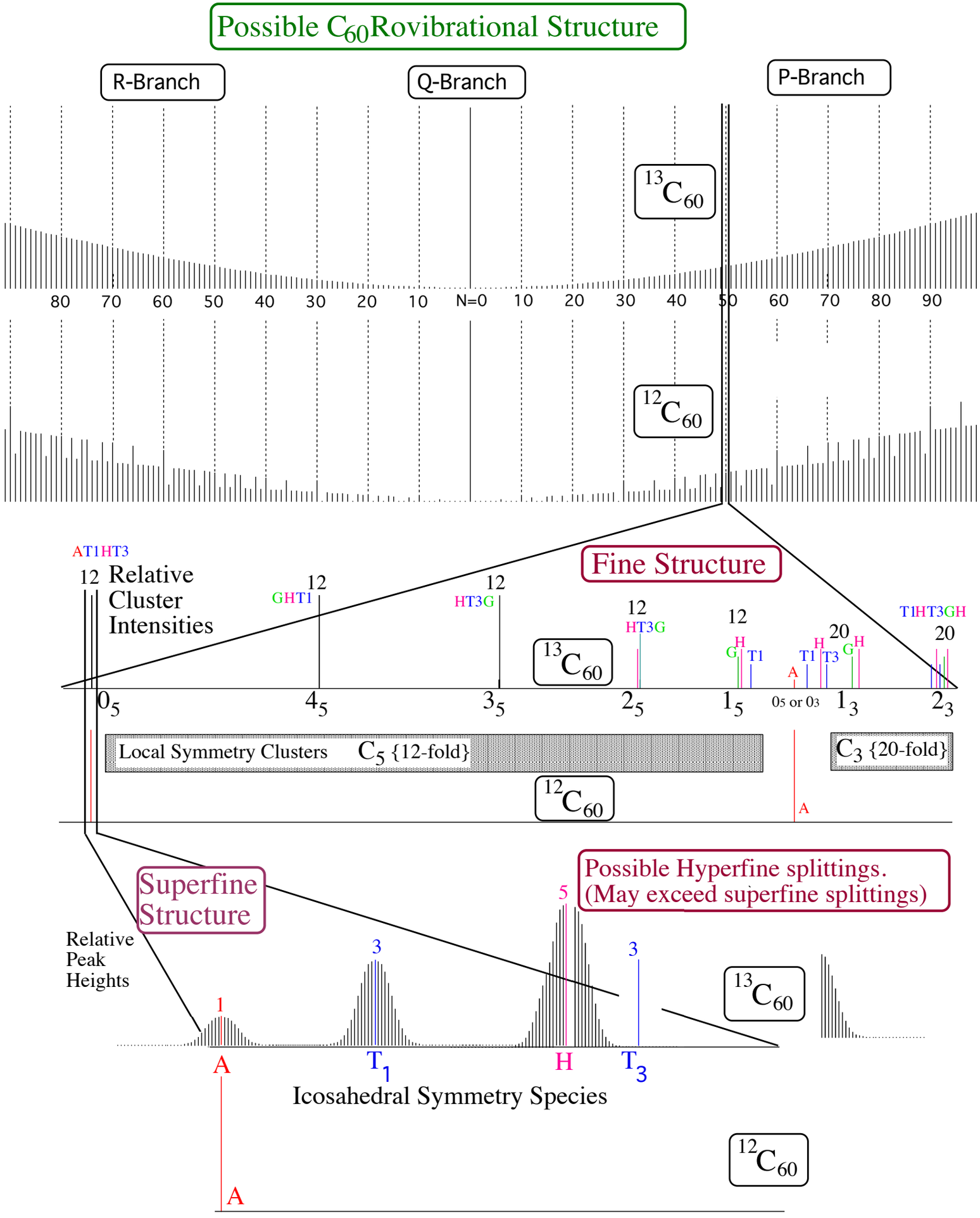
eigenvalues. The eight fivefold degenerate H_g modes correlate with the R_3 quadrupole representation and are possibly Raman active. In addition the two A_g modes may also be Raman active. Hence there are a total of ten possibly Raman active modes and four possibly dipole active modes. A spectrum of the Raman and dipole eigenvalues is given in fig. 3 and the four dipole active modes are shown in the three-dimensional stereograms of fig. 4.

3. Special cases

By a judicious choice of spring constants it is possible to check the validity of the general computational procedure. Here we discuss four different choices of spring constants. Comparison of the results obtained using icosahedral projection is made with those obtained by independently derived analytic formulas.

These four choices are:

(i) $p=\pi=\eta=0$, $h=1$. Here we have isolated 30 carbon atom pairs each alligned with one of the 30 icosahedral edges. The atoms in each pair are coupled to one another by a hexagonal bond and form a C_2 symmetric system. The only non-zero normal mode is the symmetric stretch. The analytic solution of the eigenfrequency for this system is found quite easily to be $\sqrt{2h/m}$. Using our programed projection method with $h=m=1$ we obtain $\sqrt{2}$ in perfect agreement. For the same set of spring constants in ref. [7] they report a symmetric stretch eigenfrequency of 1, clearly in disagreement with analytic results. In addition to calculating the eigenfrequency



J=50

Fine structure comparing

$^{13}C_{60}$ (2^{60} Hyperfine levels) with

$^{12}C_{60}$ (1^{60} Hyperfine level)

W.G.Harter, D.E.Weeks,
Chem. Phys. Letters 194,3(1992)

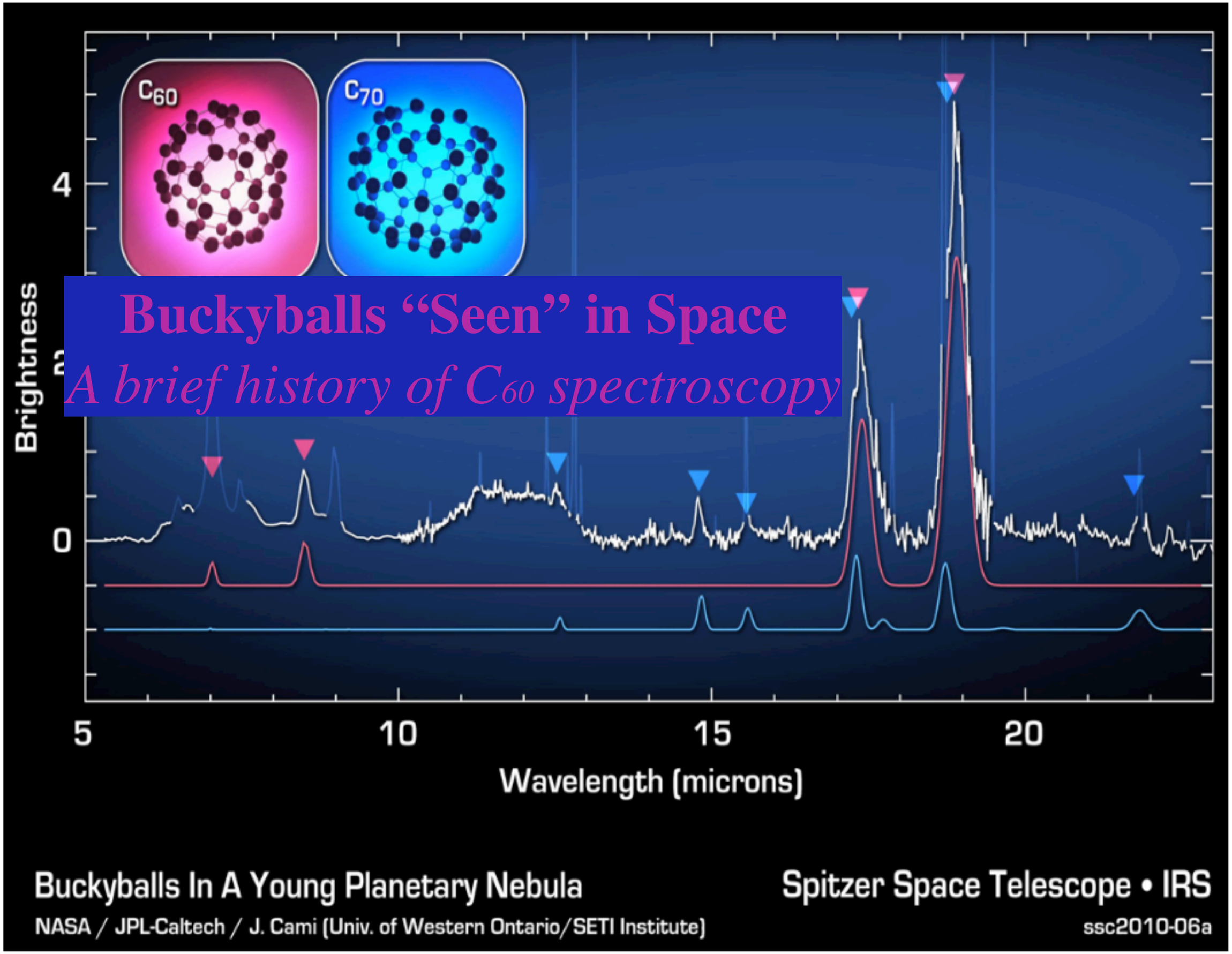
Buckyballs "Seen" in Space

A brief history of C_{60} spectroscopy

Bill Harter
UAF - Physics

Buckyballs "Seen" in Space

A brief history of C_{60} spectroscopy



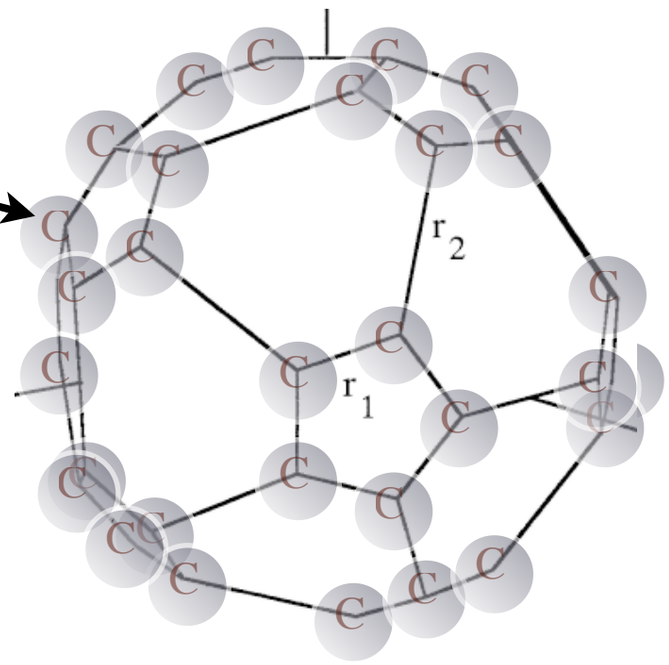
1st Try at "Seeing" in Lab

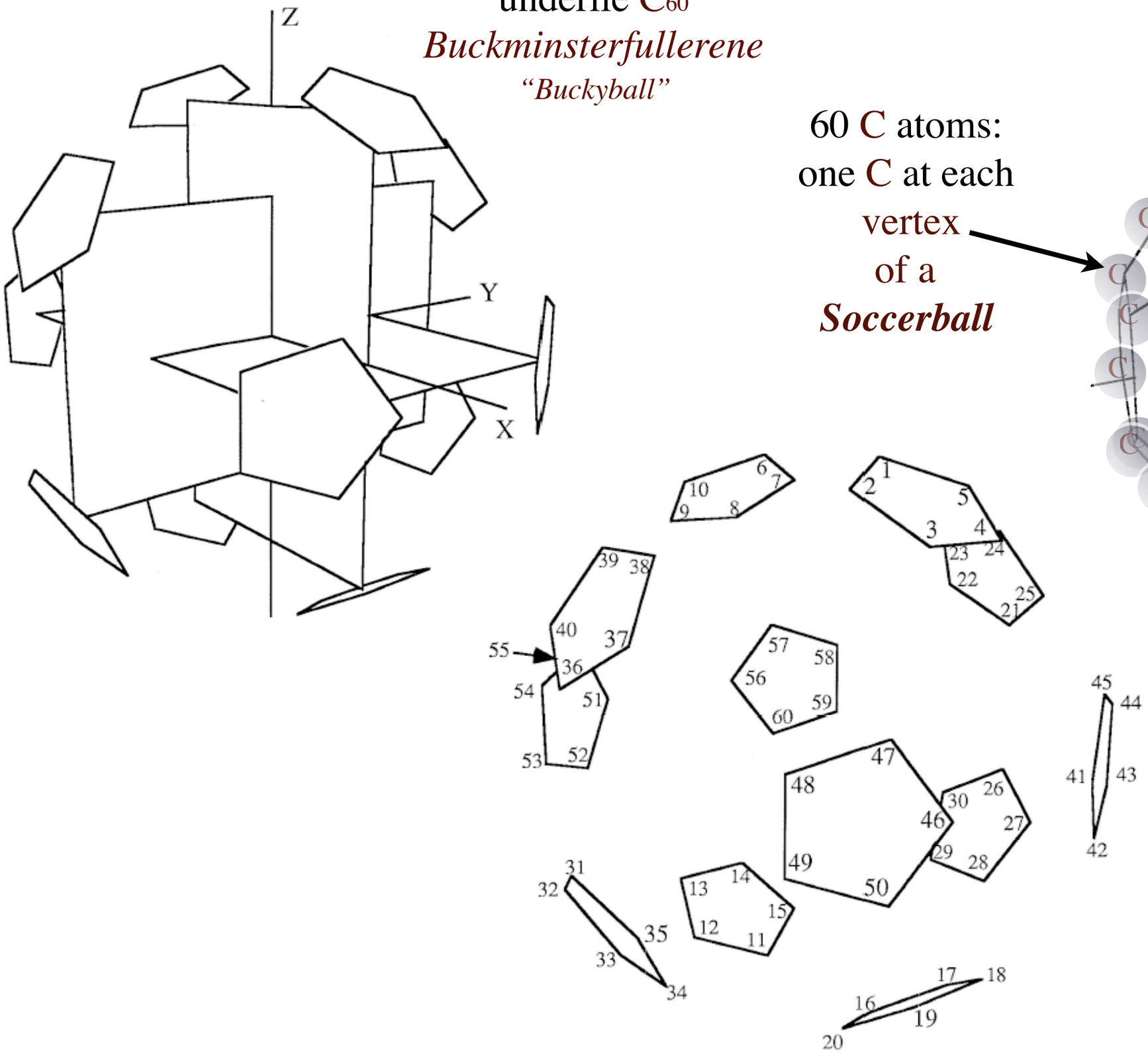
Mass spectroscopy gives something with atomic weight 720

Richard Smalley, Bob Curl, and Harry Kroto (1985)
Guess structure is C_{60} "soccer ball"

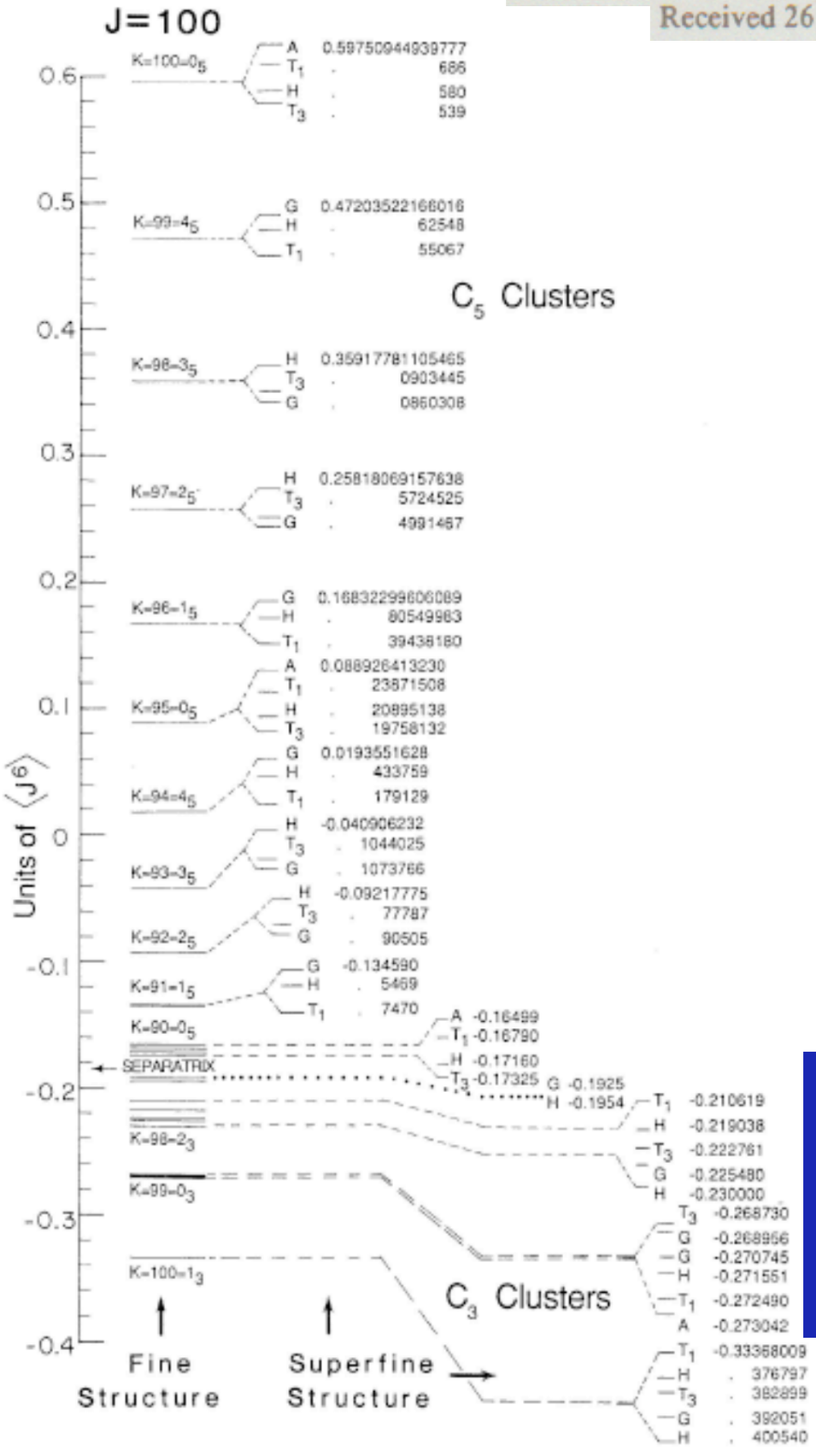
Three *Golden* rectangles
(Ratio: *(√5+1)/2 : 1=1.618...)*
underlie C_{60}
Buckminsterfullerene
"Buckyball"

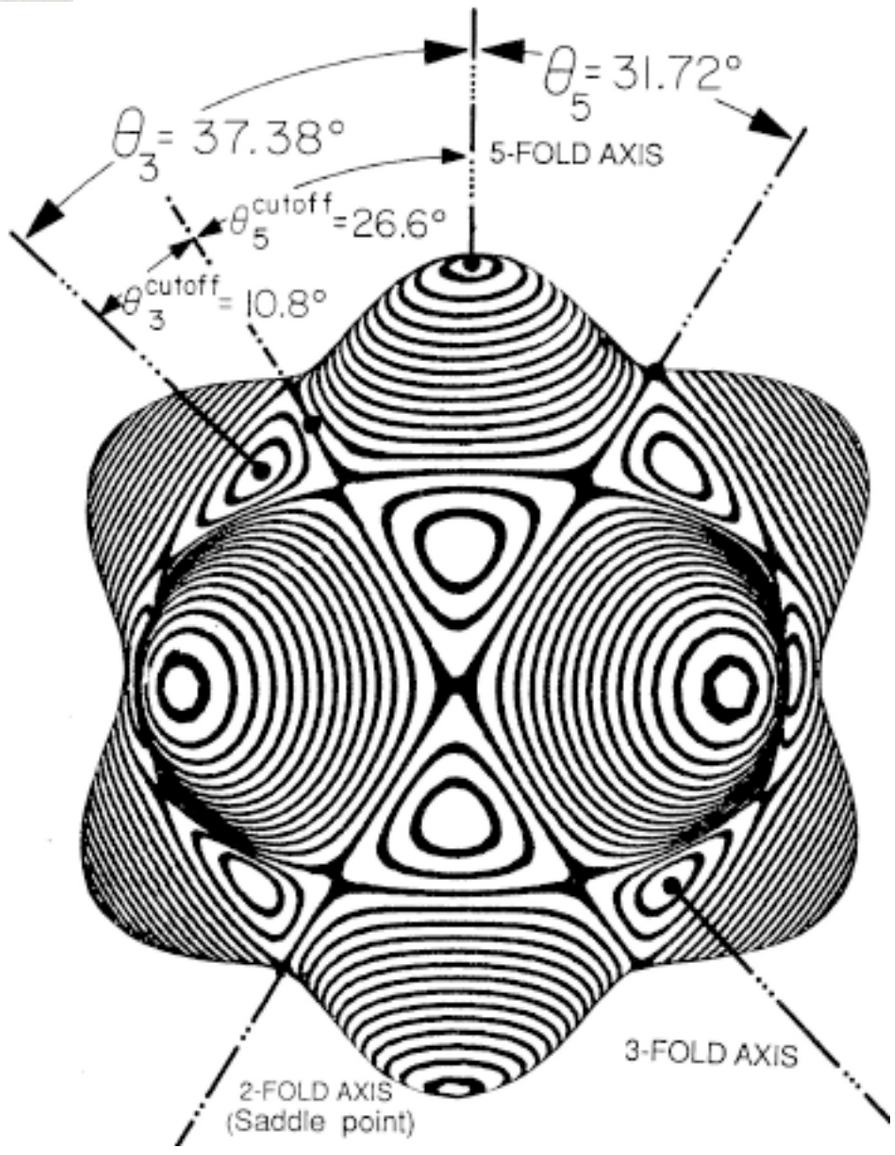
60 C atoms:
one C at each
vertex
of a
Soccerball





William G. HARTER and David E. WEEKS
Department of Physics, J. William Fulbright College, University of Arkansas, Fayetteville, AR 72701, USA
Received 26 August 1986





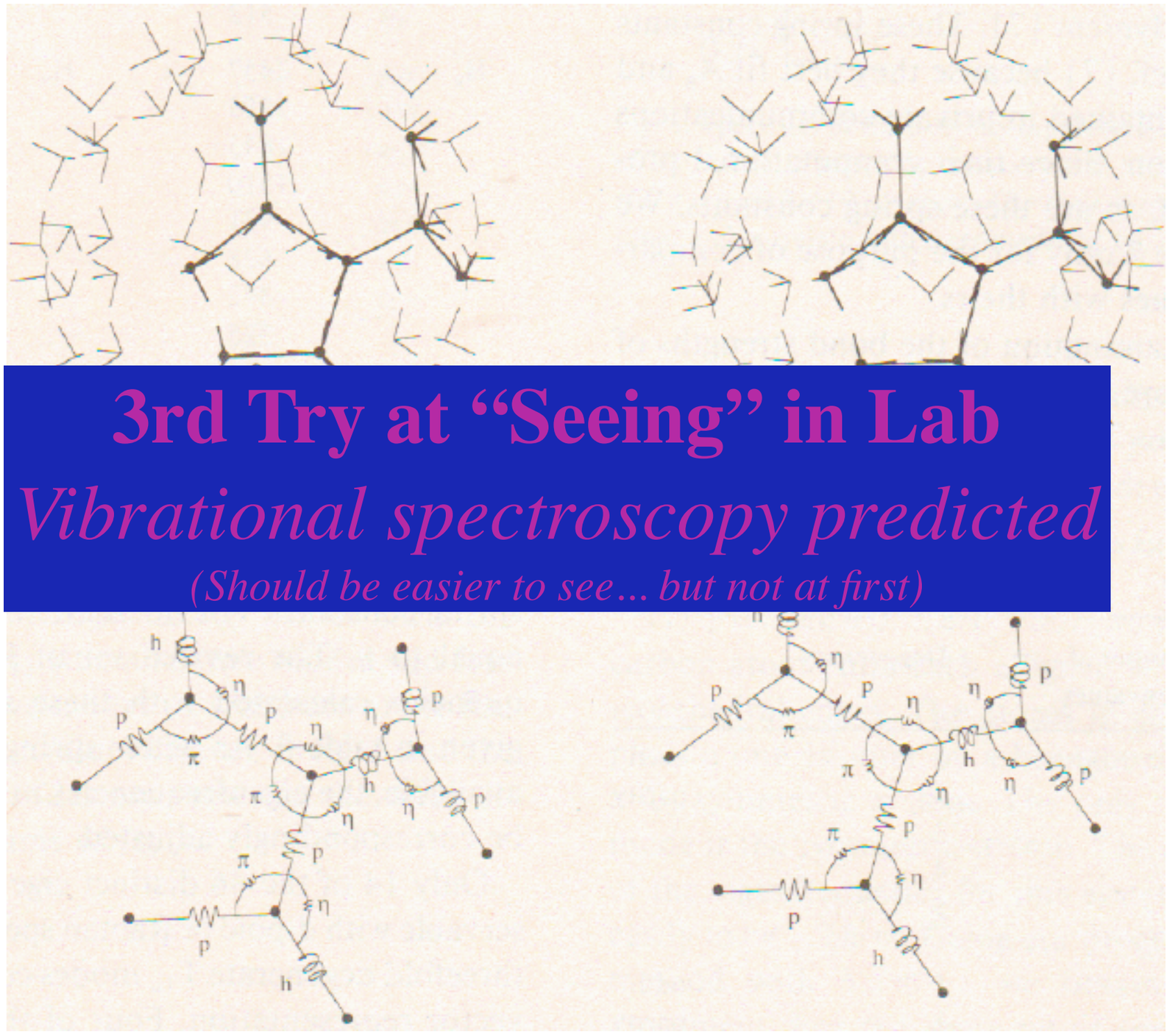
2nd Try at "Seeing" in Lab

Rotational spectroscopy predicted

(but still too hard to see)

3·60=180 coordinates of C_{60}

"Buckyball" vibrational coordinates



3rd Try at "Seeing" in Lab

Vibrational spectroscopy predicted

(Should be easier to see… but not at first)

Volume 144, number 4 CHEMICAL PHYSICS LETTERS 4 March 1988

VIBRATIONAL FREQUENCIES AND NORMAL MODES OF BUCKMINSTERFULLERENE

David E. WEEKS and William G. HARTER

3rd Try(contd)

Vibration spectra predicted (Easy to see... just 2 pairs of lines)

Table 3
Symmetry-labeled eigenfrequencies of Buckyball for $p=h=7.6\times10^5$ dyn/cm, $\pi=\eta=0.7\times10^5$ dyn/cm

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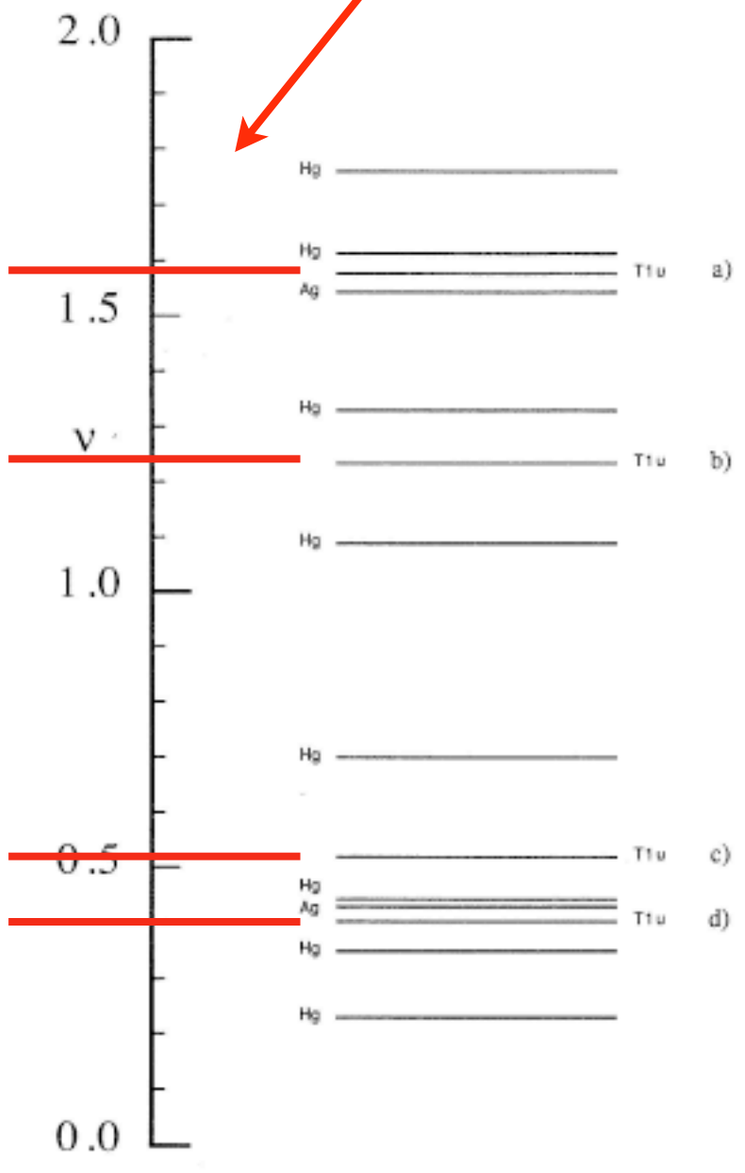
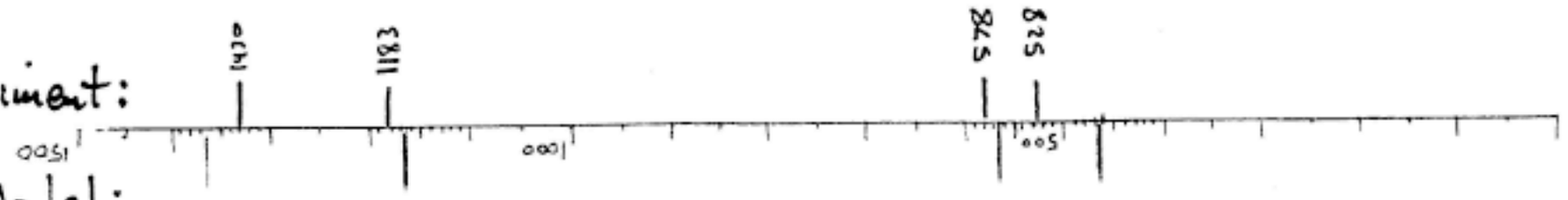


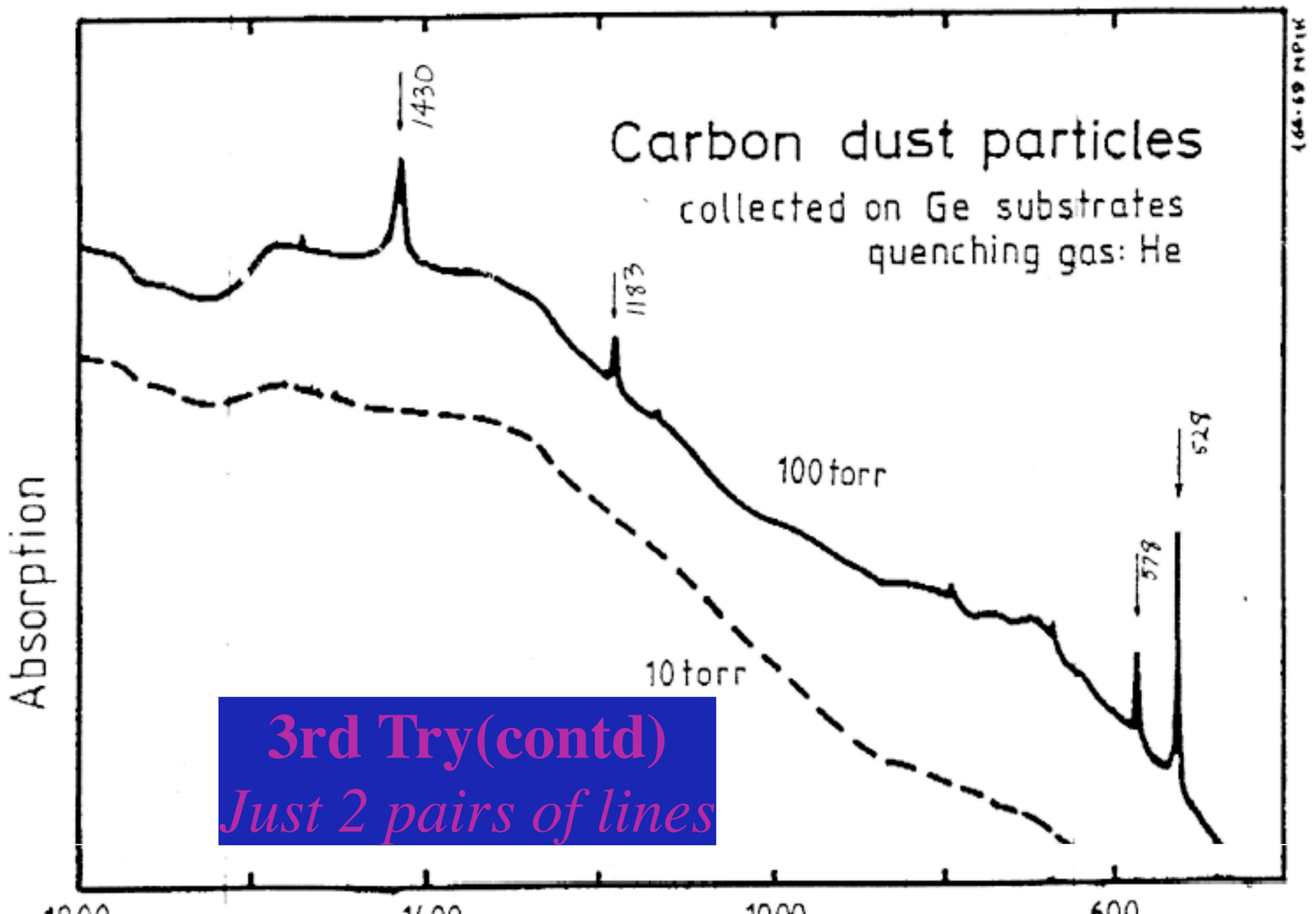
Fig. 3. Spectrum of the possibly dipole and Raman active modes of Buckyball. The spring constants are $p=h=7.6\times10^5$ dyn/cm and $\pi=\eta=0.7\times10^5$ dyn/cm. The scale is in units of 1185 cm^{-1}. Lines a–d correlate with eigenmodes in fig. 4.

Experiment:

p=h - Spring Model:

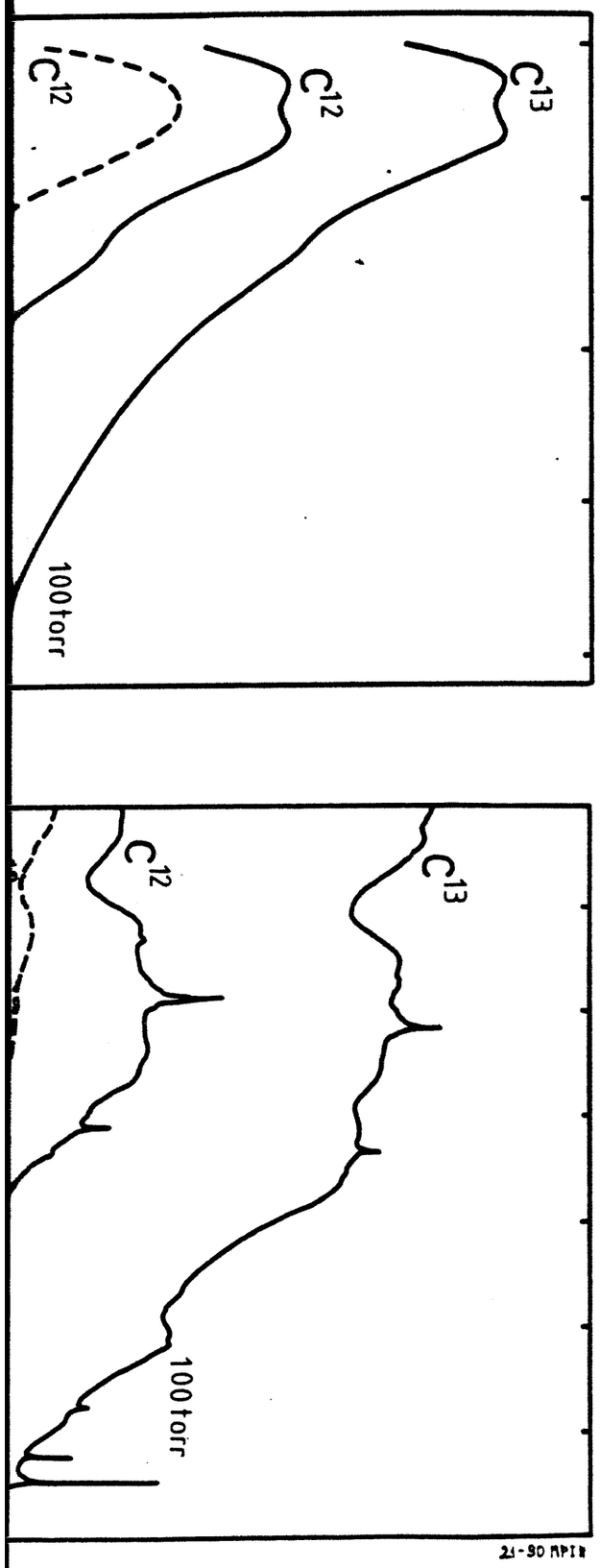


Data: W. Kratschmer, K. Fostiropoulos Max Planck
Don R. Huffman U of Arizona



3rd Try(contd)

Just 2 pairs of lines



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TUCSON, ARIZONA 85721 USA

COLLEGE OF ARTS AND SCIENCES
FACULTY OF SCIENCE
DEPARTMENT OF PHYSICS
BUILDING #81
(602) 621-6820

May 23, 1990

Dr. William G. Harter
Dept. of Physics
The University of Arkansas
Fayetteville, Arkansas 72701

Dear Bill,

Here is a copy of the first paper on C_{60} which has just been accepted for publication in Chem. Phys. Letters.

We have had much fun with your program. It is delightful.

Things are moving very fast in the Buckyball arena. We now think we can concentrate the material and produce it in sufficient quantity for many experiments.

Thanks again for the discussions we have had and for your program.

Sincerely,

Don

Donald R. Huffman
Professor of physics

DRH
Incl.

Fig 12.4.2

a tunable laser and discovered that molecular rotation resembles just what its name implies—the rotation of a planet on its axis. As molecules spin around their center of gravity, they wobble in a conical pattern or "precess" as they rotate around a multitude of axes. Also, molecules execute a generally slower "tunneling" or tumbling motion that would be forbidden in a world

Former Georgia Tech physics professor Dr. William Harter proposed a molecular rotational dynamics theory he used to make the first predictions on the rotational-vibrational spectra of the soccer ball-shaped molecule Buckminsterfullerene (C60), nicknamed "buckyball."

Physicist William Harter has come up with innovative teaching solutions to help reduce the 'physics anxiety' of students faced with galloping light waves, quantum mechanics, and the paradoxes of the physical universe. (Photo by Marc Francoeur)

spectra of the soccer ball-shaped molecule Buckminsterfullerene (C60), nicknamed "buckyball."

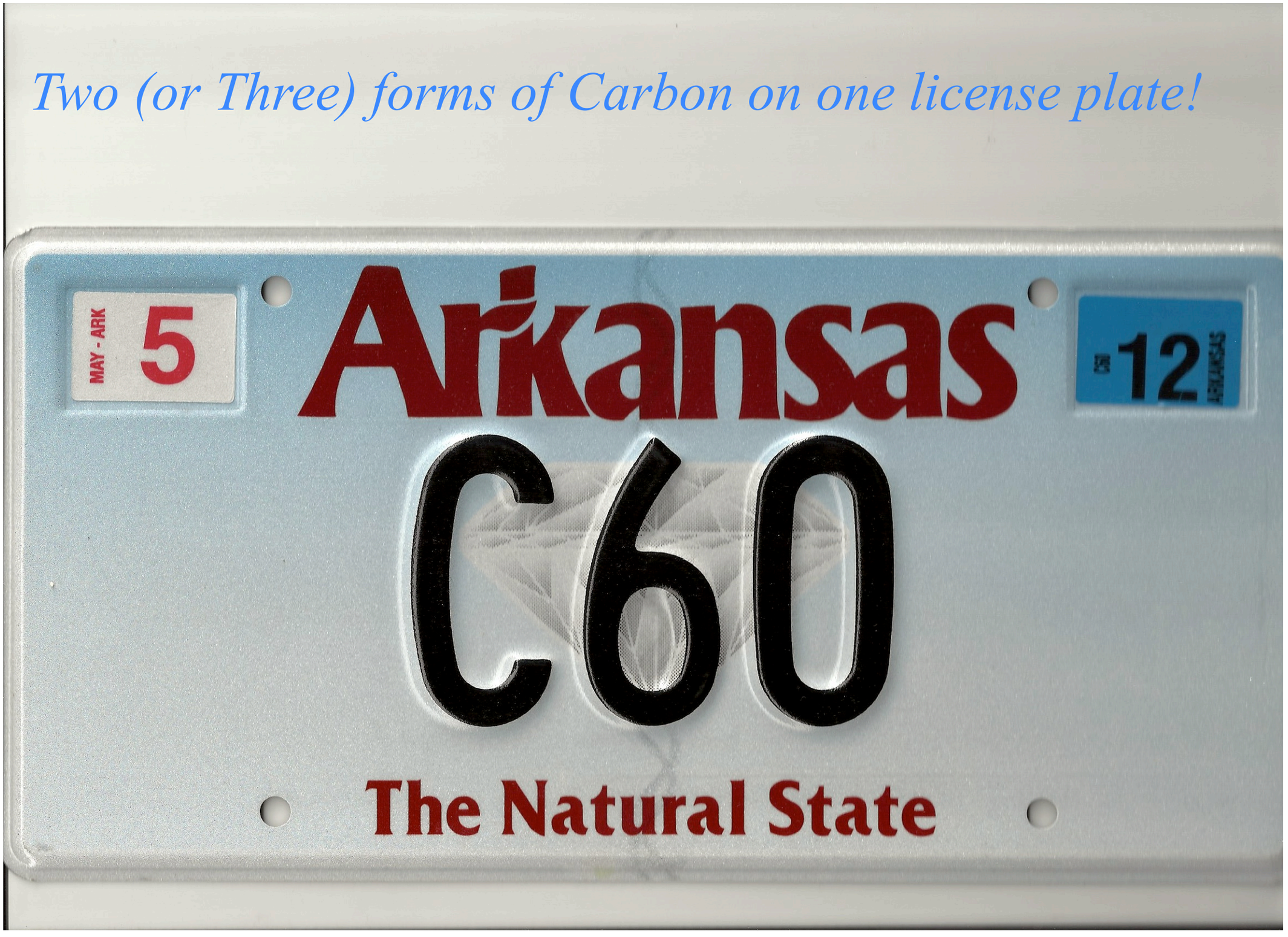
This structure had been proposed in 1985 by a group of Rice University researchers, who had seen a mass-spectra peak of atomic mass 720. Subsequently, researchers from the University of Arizona and the Max Planck Institute used Harter and Weeks' findings and their Macintosh software program to further analyze C60.

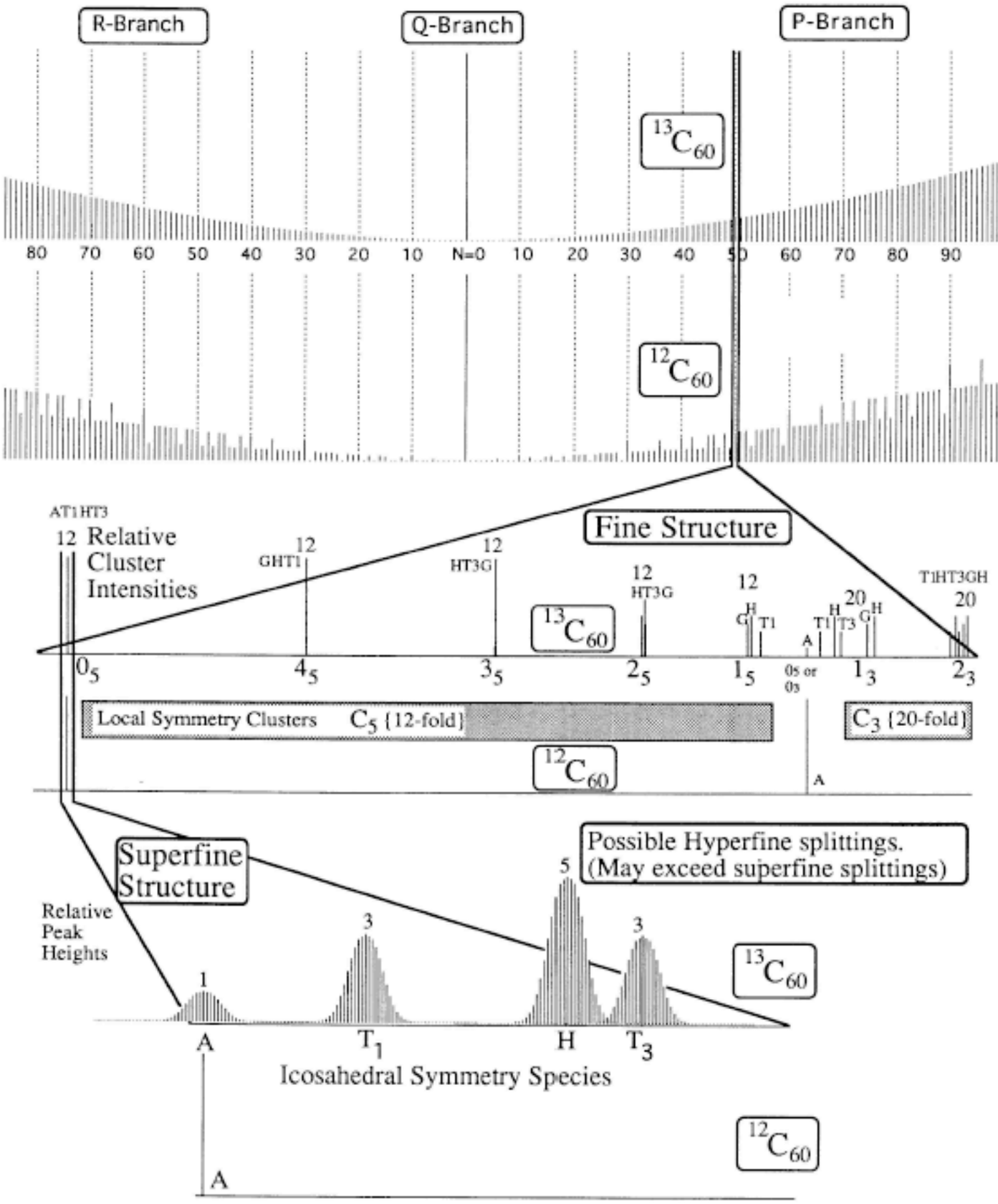
In 1989, those researchers realized from Harter and Weeks' vibrational spectral predictions that they had been making C60 since the early 1970s. Other experts were skeptical, but IBM labs at San Jose, Calif. verified the University of Arizona's results in 1990. Just two years later, *Science* named C60 "Molecule of the Year," and the Rice University-led research team received a Nobel Prize in chemistry in 1996 for its work with the molecule.

Harter is now a professor of physics at the University of Arkansas, where he studies optimal control theory for quantum systems. In 1995, he was elected a fellow of the American Physical Society. Weeks is a professor at the U.S. Air Force Postgraduate School near Wright Patterson AFB in Dayton, Ohio.

■ For more information, contact Dr. William Harter at: wharter@comp.uark.edu.

Two (or Three) forms of Carbon on one license plate!




R-Branch
Q-Branch
P-Branch
$^{13}C_{60}$
80 70 60 50 40 30 20 10 N=0 10 20 30 40 50 60 70 80 90
$^{12}C_{60}$
AT1HT3
12 Relative Cluster Intensities
Fine Structure
12 GHT1
12 HT3G
$^{13}C_{60}$
12 HT3G
12 G H T1
A T1 H T3 20 G H
T1HT3GH 20
0_5 4_5 3_5 2_5 1_5 0_5 or 0_3 1_3 2_3
Local Symmetry Clusters C_5 {12-fold}
C_3 {20-fold}
$^{12}C_{60}$
A
Superfine Structure
Possible Hyperfine splittings.
(May exceed superfine splittings)
Relative Peak Heights
1 3 5 3
$^{13}C_{60}$
A T_1 H T_3
Icosahedral Symmetry Species
$^{12}C_{60}$
A